



# **UNDERSTANDING THE EFFECTS OF DIFFERENT GRASSLAND MANAGEMENT PRACTICES ON THE SOIL-TO-WATER TRANSFER CONTINUUM**

**Submitted by Sabine Peukert, to the University of Exeter as a thesis for the degree of Doctor of Philosophy in Geography, November 2014**



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## **Abstract**

One of the major challenges for agriculture today is to manage soil properties and their spatial distribution to optimize productivity and minimize environmental impacts, such as diffuse pollution. To identify best management practices, the effects of different agricultural management practices on pollutant sources, mobilization, transfer and delivery to water bodies need to be understood. Grasslands managed for dairy and meat production, despite being widespread, have received less research attention than other agricultural land uses. Therefore, this thesis studies the effects of different grassland management practices on soil properties and their spatial distribution and the mobilization and delivery of multiple diffuse pollutants.

As a grassland case study, monitoring for this thesis was conducted across three fields (6.5 – 7.5 ha) on the North Wyke Farm Platform, a grassland experimental farm in the UK. First, the effects of permanent grassland management (permanent for at least 6 years, but different grassland management > 6 years ago) were characterized as a baseline, followed by quantifying the short-term effects of ploughing and reseeded of permanent grassland fields. Throughout those management periods, i) a range of soil physical (bulk density [BD]) and chemical (soil organic matter [SOM], total N [TN], total phosphorus [TP], total carbon [TC]) soil properties and their spatial distribution were sampled and analysed by geostatistics, and ii) hydrological characteristics and multiple pollutant fluxes (suspended sediment [SS] and the macronutrients: total oxidized nitrogen-N [TON<sub>N</sub>], total phosphorus [TP], and total carbon [TC]) were monitored at high temporal resolution (monitoring up to every 15 minutes).

The permanent grassland fields (or areas within fields) can be considered to be functioning differently. Past management legacy (more than 6 years ago) has affected soil properties and their distribution with subsequent effects on sediment and macronutrient delivery from the fields to surface waters. Overall, permanent grasslands were found to contribute significantly to agricultural diffuse pollution. The estimated erosion and macronutrient losses were similar to or exceeded the losses reported for other grasslands, mixed land use and

even arable sites, and sediment and TP concentrations exceeded those recommended by EU / UK water quality guidelines.

Ploughing and reseeded did not homogenize spatial variation and did not override past management effects. Long-term management differences affected soil properties and altered soil processes, so that the fields subsequently responded differently to ploughing and reseeded. All nutrient concentrations were significantly reduced in the older grassland field (no ploughing for 20 years), but not in the younger grassland field (no ploughing for 6 years). Ploughing and reseeded significantly accelerated the losses of sediment and macronutrients and sediment, TP and TON<sub>N</sub> exceedance frequencies of EU / UK water quality guidelines increased. Additionally, ploughing and reseeded caused a shift in the relative importance of nutrients, by increasing the relative importance of N.

Such large sediment and nutrient losses from intensively managed grasslands should be acknowledged in land management guidelines and advice for future compliance with surface water quality standards. The between-field and within-field variation highlights the importance of baseline characterization and paired catchment studies. The long-term effects of management still acting on soil properties and subsequently water quality indicates how long it may take to see soil and water quality improvements after implementing mitigation measures. Therefore, long-term management history always has to be included when interpreting soil and water quality data.

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## Abbreviations

ADAS	Agricultural and environmental consultancy
ATP	Adenosine triphosphate
BD	Bulk density
BfN	Bundesamt für Naturschutz (Ministry of the Environment, Germany)
BMEL	Bundesministerium für Ernährung und Landwirtschaft (Ministry of Food and Farming, Germany)
BMP	Best management practice
BPS	Basic Payment Scheme
C	Carbon
CAP	Common agricultural Policy
CO <sub>2</sub>	Carbon dioxide
DAFM	Department of Agriculture, Food & the Marine, Ireland
DEFRA	Department for Environment, Food & Rural Affairs, UK
DEM	Digital elevation model
DIC	Dissolved inorganic carbon
DNA	Deoxyribonucleic acid
DOC	Dissolved organic carbon
DOI	Digital Object Identifier System
DRP	Dissolved reactive phosphorus
EC	European Community
EEA	European Environment agency
EEC	European Economic Area
EFA	Ecological Focus Area
ELS	Entry Level Stewardship
EPA	Environmental Protection Agency, USA
EU	European Union
EU FFD	EU Freshwater Fisheries Directive
FAO	Food and Agriculture Organization of the United Nations
FYM	Farm yard manure
GAEC	Good agricultural and environmental condition
GEC	Good ecological status

HLS	Higher Level Stewardship
LOI	Loss on Ignition
MEA	Millennium Ecosystem Assessment
N <sub>2</sub> O	Nitrous oxide
NEA	National Ecosystem Assessment
NH <sub>4</sub> <sup>+</sup>	Ammonium
NO <sub>2</sub> <sup>-</sup>	Nitrite
NO <sub>3</sub> <sup>-</sup>	Nitrate
NTU	Nephelometric turbidity units
NVC	National Vegetation Classification
NVZ	Nitrate Vulnerable Zone
OC	Organic carbon
OECD	Organisation for Economic Co-operation and Development
P	Phosphorus
POC	Particulate organic carbon
PP	Particulate Phosphorus
PSD	Particle size distribution
REPS	Rural Environmental Protection Scheme, Ireland
SFP	Single Farm Payment
SOC	Soil organic carbon
SOM	Soil organic matter
SRP	Soluble reactive phosphorus
SS	Suspended sediment
Stdev	Standard deviation
TAG	Technical Advisory Group on the Water Framework Directive, UK
TC	Total carbon
TIC	Total inorganic carbon
TOC	Total organic carbon
TON <sub>N</sub>	Total oxidized nitrogen-N
TP	Total phosphorus
TPC	Total particulate carbon
USDA	U.S. Department of Agriculture
USEPA	U.S. Environmental Protection Agency
UV	Ultraviolet

WFD	Water Framework Directive
$\delta^{15}\text{N}$	Nitrogen 15 isotope value
$\delta^{13}\text{C}$	Carbon 13 isotope value (relative to international standard)

## **Chapter 1**

### **Introduction**

This thesis aims to study the effect of agricultural management on the environment, its health and functioning; and more specifically, the impacts of agricultural grassland management practices on the degradation of soil and water quality. Over the past 50 years, intensification of agricultural management has resulted in greater and more rapid changes in ecosystems than ever before in human history (Matson *et al.*, 1997; Bennett & Balvanera, 2007). Sixty percent of ecosystems are now classed as degraded (MEA, 2005), via loss of topsoil, disruption of nutrient cycles, diffuse water pollution, flooding and greenhouse gas emissions. Such ecosystem degradation affects human health, well-being, security and economic systems (MEA, 2005; Bennett & Balvanera, 2007). For example, soil degradation threatens future food security and agricultural diffuse pollution of water has effects on human well-being in terms of health (polluted drinking and bathing water), security (muddy floods, future resources of clean water) and incurs high economic costs (Parris, 2011). Finally, environmental degradation has been linked to the collapse of early human civilizations (Balmford & Bond, 2005). In total, good environmental functioning has been estimated to be worth \$ 125 - 145 trillion a year globally (2011 prices) (Constanza *et al.*, 1997; 2014; Balmford & Bond, 2005; Daily *et al.*, 1997).

Agricultural yields have doubled in Europe and the United States over the past 50 years (Foley *et al.*, 2011; McGonigle *et al.*, 2012; Howden *et al.*, 2013). Such increases in yield were achieved by developing new crop varieties as well as altering the environment in which the crops grow by adding nutrients that are required for crop growth, improving soil physical conditions (via tillage), and altering soil moisture conditions, via artificial drainage or irrigation in areas where it is required (Foley *et al.*, 2005; Foley *et al.*, 2011; Wall *et al.*, 2012; Howden *et al.*, 2013). As a consequence, agricultural food production was effectively decoupled from the natural environmental conditions and ecosystem

functions by which food production had always been limited in the past (Foley *et al.*, 2005; Dungait *et al.*, 2012).

Today, the human population is facing the challenge of continuously needing to increase food production, whilst minimizing the environmental impact (Foley *et al.*, 2011; Foresight, 2011; McGonigle *et al.*, 2012). Agricultural land covers a greater land area than any other individual land use globally (40 %), in OECD countries (50 %) and in the United Kingdom (70 %) and is likely to expand and intensify further to meet the increasing demand of a growing human population (Foley *et al.*, 2005; Bennett & Balvanera, 2007; Gordon *et al.*, 2010; Power, 2010; Foley *et al.*, 2011; NEA, 2011; 2014). The way in which humans decide to meet future food needs, will control the health and functioning of the environment as well as human health and wealth (Bennett & Balvanera, 2007). Therefore, a sustainable intensification of land use on the land already designated to agricultural land use is required; to increase food production whilst minimizing the degradation of the environment (Carpenter *et al.*, 2009; Foresight, 2011; McGonigle *et al.*, 2012).

To achieve sustainable intensification of agriculture, best management practices need to be identified that combine maximum food production with minimum environmental impacts (McGonigle *et al.*, 2012). Therefore, the environmental impacts of different agricultural management practices need to be understood in detail. In terms of agricultural diffuse pollution, the influences of management practices on pollutant sources, their mobilization, transfer and delivery to water bodies must be understood (Haygarth *et al.*, 2005). Once best management practices have been identified, such knowledge needs to be incorporated in decision making and policy regulations; so that good management practices become widely implemented over time (McGonigle *et al.*, 2012).

To date, extensive research has been conducted on the relationship between agricultural management and diffuse water pollution, and a complex policy infrastructure has been put in place to regulate and reduce the environmental impacts of agriculture. An example of this is the EU Water Framework Directive (WFD), which provides the overarching framework for

water protection in the EU and requires Member States to restore water courses to 'Good Ecological Status' by 2015. However, despite these efforts, the problem of agricultural diffuse pollution has not been solved. The detailed influence of agricultural management on diffuse pollution is still not fully understood and more than half of all water courses in the EU failed to reach good ecological status in 2012 (EEA, 2012), despite the EU-wide implementation of mitigation measures. Whilst a lot of mechanistic understanding has been generated, the scientific evidence mostly emphasizes the importance of variability and shows the high level of complexity in the research field (Harris & Heathwaite, 2012). There is often a mismatch between real-world farm management settings and those required to provide reliable scientific evidence from controlled experiments. Consequently, the ability of research to highlight clear recommendations is limited, and the direct translation of research findings into policies is complicated. Additionally, there is a mismatch between the time when regulation is required and the time it takes to provide sound and reliable scientific evidence to do so (Schroeder, 2004; Blackstock *et al.*, 2010).

Therefore, there is an ongoing need for targeted and improved research (Brown *et al.*, 2010; Foresight, 2011; McGonigle *et al.*, 2012; Sutherland *et al.*, 2006; 2010). Some of the questions that need to be answered include:

- What do we need to do to enhance our detection of water quality improvements and the effectiveness of mitigation measures?
- How inherently variable are agricultural systems in space and time?
- How can water quality monitoring become more ecologically relevant?
- Have wrong assumptions been made in the past? For example, do wide-spread grassland systems contribute as little to diffuse pollution as they have been assumed to?
- How can research bridge the gap between the demands for providing robust, reliable scientific evidence, and the demands to be relevant to policy making?

## Chapter 2

### Context of Research

#### **I. Introduction: the importance of understanding the effects of agricultural management on soil and water quality**

Agricultural land use inevitably alters soil properties to maximize crop production in the short term (Powlson *et al.*, 2011). These practices include a) the alteration of soil physical conditions by tillage, livestock trampling or use of heavy machinery, b) the addition of nutrients in the form of fertilizers and manures, c) the modification of vegetation cover by cultivating different varieties, planting a uniform vegetation cover, reducing overall vegetation cover by regular harvesting, by livestock grazing or by removing vegetation cover completely by ploughing, d) changing of natural soil moisture regimes by either draining soils or irrigating soils where required (Foley *et al.*, 2005; Foley *et al.*, 2011). Such alterations affect soil quality on-site with subsequent short and long-term effects on soil physical processes and nutrient cycling and cause off-site diffuse water pollution (Bilotta *et al.*, 2007a; Pilgrim *et al.*, 2010; Dick *et al.*, 2011b).

Soil quality refers to the soil's physical and chemical properties which determine its capacity to function, sustain plant and animal production, support human health, and regulate nutrient cycles in a way which minimises the environmental impact of surrounding ecosystems, such as the losses of key nutrients and sediment particles to freshwater and eventually oceans (Haygarth & Ritz, 2009; Creamer *et al.*, 2010). Agricultural management causes threats to soil quality by causing soil compaction, soil loss, decline of organic matter and soil organic carbon and contamination by over-application of nutrients, pesticides and herbicides (Creamer *et al.*, 2010).

Soils are connected to ground and surface water by rainfall infiltrating into the soil profile and leaching either through to the groundwater or reaching surface waters via surface runoff or sub-lateral flow. Agricultural diffuse pollutants, such as suspended sediment (SS) and the macronutrients carbon

(C), nitrogen (N) and phosphorus (P), are mobilized, transported and delivered to freshwater ecosystems, where they may cause a deterioration of water quality (Haygarth *et al.*, 2005; McGonigle *et al.*, 2012). Water quality refers to properties of water in terms of its physical (turbidity, suspended sediment, temperature, flow dynamics), chemical (nutrient status, contamination) and ecological status (microbes, macroinvertebrates, macrophytes, species richness) (Brauman *et al.*, 2007; Bilotta *et al.*, 2008).

Agriculture is considered to be responsible for 55 % of the non-point water pollution in the EU (Buckley & Carney, 2013a) (Figure 2.1). Today, more than half of all European water courses (EEA, 2012), 40 % of water courses in the USA (Evans-White *et al.*, 2013) and two thirds of all surface waters in the UK (McGonigle *et al.*, 2012) do not reach good ecological status (Figure 2.2). In the UK alone, diffuse agricultural pollution contributes to water quality failures by being the source for 72 % of sediments and high proportions of macronutrients: 81 % of N and 31 % of P (Zhang *et al.*, 2014). Carbon is not yet included in water quality guidelines in terms of freshwater ecosystem health, but rising C concentrations in surface waters are known to have an impact on water quality (Edwards *et al.*, 2008). These pollutants have effects on human well-being in terms of health (polluted drinking and bathing water), security (flooding) and incur high economic costs (Pretty *et al.*, 2003; Parris, 2011). Also, they have impacts on aquatic biota ranging from direct toxic effects to ecological deterioration due to eutrophication. The increased occurrence of algal blooms associated with eutrophication (Smith *et al.*, 2006) causes subsequent dissolved oxygen depletion, reduced light availability, cascading through the entire aquatic food web, perturbing the balance of organisms and is generally reducing invertebrate and fish abundance and diversity (Smith & Schindler, 2009).



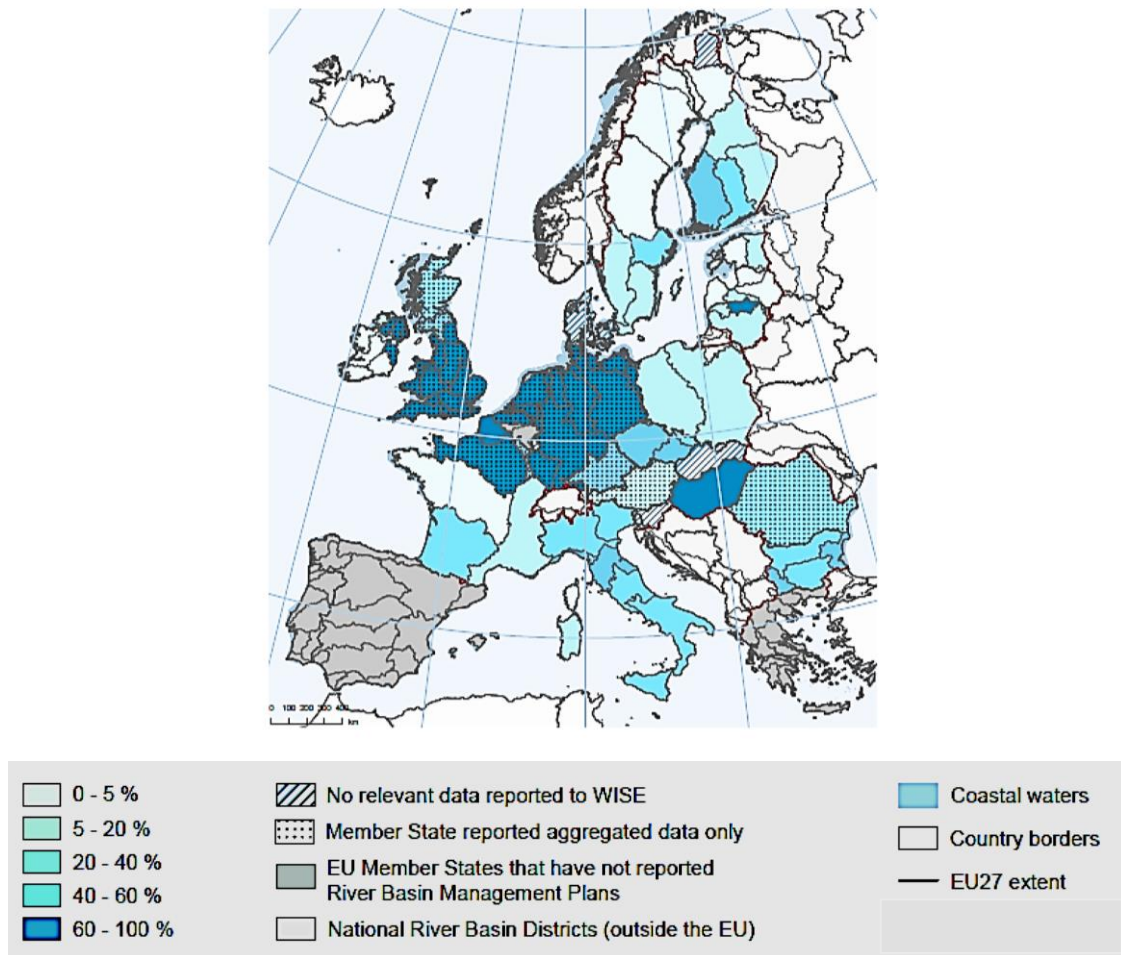


Figure 2.1. Proportion of surface water bodies in the EU member states affected by pollution pressures associated with agriculture. Source: EC, 2012a.

a) Rivers and Lakes

b) Coastal Waters

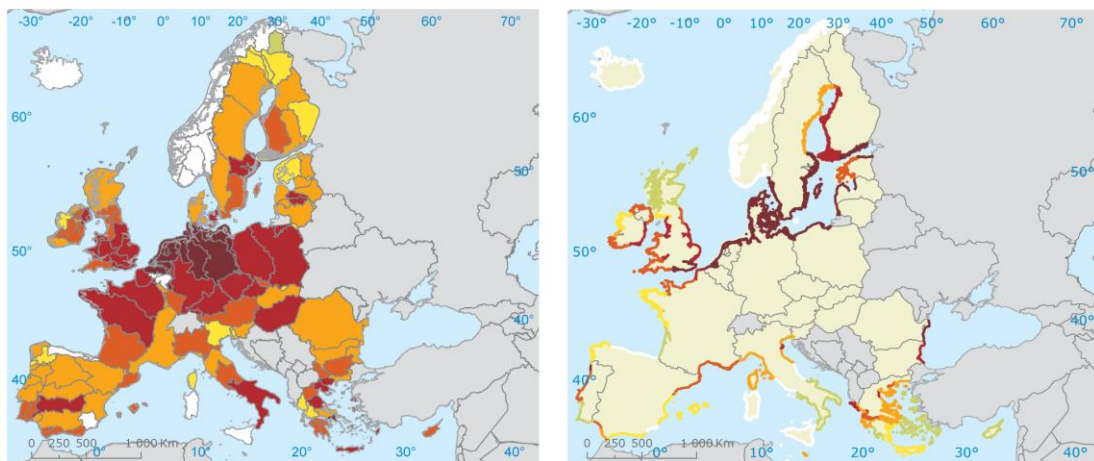


Figure 2.2. Proportion of classified surface water bodies in EU member states that were classified as less than good ecological status a) in rivers and lakes, and b) in coastal and transitional waters. Source: EEA, 2012

This literature review follows the conceptual framework of the problem-solving machinery that is laid out in figure 2.3: A synthesis of scientific research findings forms the scientific evidence base, on which decisions are made towards policy implementation with the aim of mitigating, in this case, the issues of soil degradation and agricultural diffuse pollution. Once policies are implemented, their effectiveness is monitored which feeds back to scientific research. It raises new questions that need to be addressed in scientific research to be incorporated into a new, more advanced scientific evidence base, on which more informed decisions are made which lead to a policy reform.

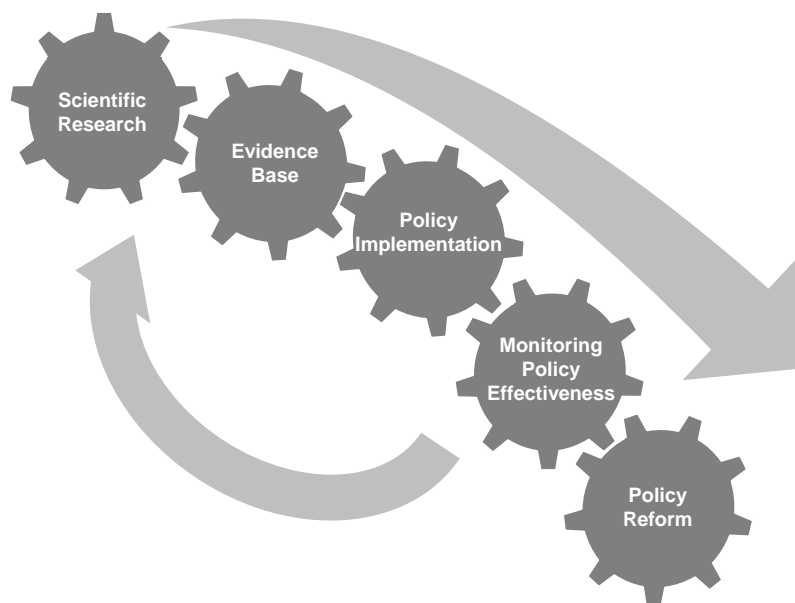


Figure 2.3. Conceptual framework of the problem-solving machinery. A synthesis of scientific research findings forms the scientific evidence base, on which decisions are made towards policy implementation with the aim of mitigating the issues of soil degradation and agricultural diffuse pollution. Once policies are implemented, their effectiveness is monitored which feeds back to scientific research. It raises new questions that need to be addressed in scientific research to be incorporated into a new, more advanced scientific evidence base, on which more informed decisions are made which lead to a policy reform.

Following this framework, this literature review provides an overview of the scientific evidence available on the effects of agricultural management on the soil-to-water continuum. Following this, the current policy approaches to mitigate soil degradation and agricultural diffuse pollution that are in place in the

EU and more specifically the UK are discussed, followed by an evaluation of the effectiveness of those policies. The last section identifies issues that may be limiting the effectiveness of policies and that have to be incorporated and addressed in scientific research; some of which were addressed in this thesis.

## **II. Overview: The effects of agricultural management on the soil to water continuum**

### **A. Effects of agricultural management on soil structure, soil physical properties and soil erosion**

The soil is the most important growing medium for agricultural crops. It provides nutrients to plants and an environment for microorganisms and fauna, which in return cycle key nutrients (Powlson *et al.*, 2011). Soils therefore provide the basis of food production. Soils are a porous medium, made up of inorganic particles (derived from the underlying geology) and organic particles (derived from past and present vegetation cover) (Bilotta *et al.*, 2007a). The proportion of inorganic to organic particles, the sizes of inorganic particles and their arrangement (as well as many other factors) determine soil type and structure and the way in which rainwater infiltrates through soils (in combination with a wide range of other factors, such as rainfall intensity, topography and vegetation cover) (Ward & Robinson, 2000; Bilotta *et al.*, 2007a; Haygarth & Ritz, 2009). If rainwater moves rapidly through or over the soil surface down slopes rather than being infiltrated and retained by soils, soil particles can be mobilized by physical detachment and transported to surface waters. This loss of topsoil due to erosion impacts soil structure, soil fertility and water quality (Lal, 2001; Creamer *et al.*, 2010). As soil losses by erosion are in general greater than soil formation rates (typically 30 – 40 times higher), soils are now considered as non-renewable resources (Creamer *et al.*, 2010; Hancock *et al.*, 2015).

Erosion rates have been accelerated 10-1000 times by human activities, compared to natural erosion rates, mostly by agricultural land management (Montgomery, 2007). The use of heavy machinery or livestock trampling causes

deterioration of soil structure via soil compaction. Soil compaction refers to the compression of soils resulting in reduced air spaces in the soil, a higher density of soil per volume of soil (bulk density). Compaction reduces infiltration capacity of soils and therefore promotes surface runoff generation and reduces resilience to erosion (Bilotta *et al.*, 2007a; Creamer *et al.*, 2010; Matthews *et al.*, 2010). If soil structure is already impacted, for example if soils are waterlogged or frozen, further reductions in soil quality are more likely (Creamer *et al.*, 2010). A healthy and dense vegetation cover is key to a good soil structure and provides protection from soil erosion (Ward & Robinson, 2000). Vegetation cover intercepts raindrops and thereby reduces their kinetic energy, enhances infiltration and provides additional surface roughness above ground. Below-ground, high root density increase aggregate stability, increase water-holding capacity and reduce rill and interill formation (Gyssels, 2003; 2005; DeBeats, 2006; Powlson *et al.*, 2011). Therefore, reducing vegetation cover reduces soil quality and increases soil erosion rates.

Ploughing is known to increase soil erosion and deterioration in soil structure long-term, because it breaks up soil aggregates, thereby reducing the stability of the soil to detachment (Six *et al.*, 2000; Soussana *et al.*, 2004; Grandy & Robertson, 2006). Additionally, ploughing (lifting soil and re-placing it) causes a downslope movement of soil; therefore, ploughing *per se* is a soil degradation process (Govers *et al.*, 1994).

The accelerated delivery of sediment particles to surface waters has several impacts. Rivers with high sedimentation rates may have reduced water holding capacities, leading to increased risk of flooding (Bilotta *et al.*, 2008). Additionally, suspended sediments have direct effects on aquatic biota, such as the clogging of respiratory organs with subsequent effects on biodiversity (Bilotta & Brazier, 2008; Jones *et al.*, 2012). Suspended sediments are also responsible for the transport of a range of other contaminants, such as organic pollutants and nutrients (Bilotta & Brazier, 2008).

## **B. Effects of agricultural management on soil organic matter, soil carbon and carbon export to surface waters**

After soil physical structure (and acidity and salinity), soil organic matter (SOM) is the soil property with the greatest impact on soil quality and functioning (Kristensen *et al.*, 2003; Haygarth & Ritz, 2009; Powlson *et al.*, 2011). Soil organic matter is crucial for food production (Dungait *et al.*, 2012). The cycling of SOM determines the cycling of the macronutrients C, N and P (Silveira, 2005). SOM improves soil structure as it is an essential component of soil aggregates, it improves water holding capacity (Franzluebbers, 2002) and microbiological activity, and it is a major source of energy for soil biota (Haygarth & Ritz, 2009). Organic matter or organic C (OC) inputs to soils occur naturally by root deposition or by decomposing plant matter or any other living cells and tissue (Soussana *et al.*, 2004; Haygarth & Ritz, 2009). In soils, SOM or soil organic carbon (SOC) occur either as dissolved, bioavailable forms in the soil solution, or as non-bioavailable forms in micro or macroaggregates (Silveira, 2005; Creamer *et al.*, 2010). The main component of SOM is SOC (48 - 60 %) (Rossel *et al.*, 2001), but SOM is also an important source of other nutrients, such as N and P (Foth & Turk, 1972). Soil organic matter or C is mobilized from the soil and delivered to surface waters either as dissolved or as particulate C, which is either sorbed to sediment particles, mobilized as part of microaggregates, or mobilized directly as excreted manures or Farm Yard Manure (FYM) particles immediately after applications (Hope *et al.*, 1997a; Hope *et al.*, 1997b; Quinton *et al.*, 2006; Quinton *et al.*, 2010; Glendell & Brazier, 2014).

Agricultural soils store less SOM than natural soils (Creamer *et al.*, 2010), with SOM either lost as greenhouse gas emissions (Foley *et al.*, 2011) or via water (Quinton *et al.*, 2006; Quinton *et al.*, 2010; Glendell & Brazier, 2014). The reduced vegetation cover in agricultural land causes the reduced SOM inputs below and above-ground (Powlson *et al.*, 2011). Ploughing also causes a reduction in SOM in agricultural soils by increasing SOM / SOC degradation (Soussana *et al.*, 2004; Grandy & Robertson, 2006; Acharya *et al.*, 2012; Beniston *et al.*, 2014). Soil organic matter that was previously stored in deeper soil horizons becomes exposed to air and microbes. Soil aggregates which

previously protected SOM from degradation, are broken up and expose SOM to mineralization (Paustein *et al.*, 2000; Six *et al.*, 2000; Soussana *et al.*, 2004; Kalbitz *et al.*, 2005; Grandy & Robertson, 2006). This reduced protection of SOM / SOC within the soil accelerates its mobilization from the soils and delivery to surface waters (Franzluebbers, 2002; Lal, 2005; Glendell & Brazier, 2014). Manure applications and inputs by grazing animals causes an increase in soil dissolved organic matter (DON) or addition of OM to the soil surface, which can be easily mobilized and transported to surface waters (Chantigny, 2003).

Large C concentrations in water reduce dissolved oxygen contents and therefore affect aquatic fauna and flora indirectly (Edwards *et al.*, 2008; Sandford *et al.*, 2013). Additionally, C in drinking water is thought to be carcinogenic and the discolouration caused by dissolved organic C (DOC) in water incurs high costs for the water treatment industry (Worall & Burt, 2007).

### **C. Effects of agricultural management on soil nitrogen and its export to surface waters**

Nitrogen is contained in proteins and is therefore essential for all organisms, and is a key limiting nutrient for agricultural crops (Dungait *et al.*, 2012; Marschner, 2012). Nitrogen occurs in the soils either as inorganic forms (Nitrate  $\text{NO}_3^-$ , Nitrite  $\text{NO}_2^-$ , Ammonium  $\text{NH}_4^+$ ), mostly stored in dissolved form in the soil solution, or as organic N in organic matter particles, locked up in soil aggregates or applied as organic manures (Chadwick, 2000). Most forms of organic N need to mineralize to become available for plant uptake (Chadwick, 2000). Naturally, N inputs into soils occur by SOM inputs from the overlying vegetation cover or biological N fixation (Dungait *et al.*, 2012). The forms of N that are typically mobilized and delivered to surface waters are dissolved inorganic or organic N, mobilized by diffusion from the soil water to rainwater during low flow periods (Webb & Walling, 1985; Gächter *et al.*, 2004; Granger *et al.*, 2010; Graeber *et al.*, 2012) or N sorbed to sediment / SOM, mobilized by physical detachment.

Agriculture has increased the global N cycle by ca. 100 % (Whitehead & Crossman, 2012). Agricultural N inputs either in inorganic form (manufactured

inorganic fertilisers) or in organic form (manures / slurries / faeces) have raised soil N levels and have increased the soil pool available for N mobilization to surface waters (Burt *et al.*, 2011). Furthermore, natural N cycling processes are disrupted by agricultural N inputs. Biological N fixation is reduced, rates of N mineralization are decreased and crops use N less efficiently, so that crop production becomes increasingly dependent on further nutrient additions rather than utilizing the already high soil N sources (Dungait *et al.*, 2012). Ploughing causes mineralization of organic matter and therefore organic N sources in the soil become available to following season's crop, but may also be increasingly lost to water (Eriksen, 2001; Sharpley, 2003; Eriksen *et al.*, 2004; Hansen *et al.*, 2005; Burt *et al.*, 2011).

Elevated N in drinking water is associated with human health issues, such as being carcinogenic and causing reproductive and developmental problems (Kay *et al.*, 2012). Nitrogen impacts in water courses range from direct toxic effects of  $\text{NO}_2^-$ , which is potentially toxic to aquatic fauna even in low concentrations (Lewis & Morris, 1986), to causing eutrophication, mostly reported in coastal areas (Maier *et al.*, 2012), but also likely in freshwater systems. Eutrophication refers to an accelerated aquatic primary productivity, which is generally associated with excessive growth of algae with subsequent effects on light availability and dissolved oxygen. Consequently, such changes alter aquatic species abundance and composition, generally associated with a decline in invertebrate and fish species (Bilotta *et al.*, 2008). Water treatment costs for N are estimated to be approximately £ 15 million per year in the UK (2001 prices) (Pretty *et al.*, 2003).

#### **D. Effects of agricultural management on soil phosphorus and its export to surface waters**

Phosphorus is an essential element for all organisms, as it is a constituent of cytoplasmic membranes, bones and teeth, deoxyribonucleic acid (DNA) and adenosine triphosphate (ATP), and an essential nutrient for agricultural crops (Hart *et al.*, 2004; Cordell *et al.*, 2009; Marschner, 2012; Darch *et al.*, 2013). Soil P is naturally derived from the weathering of sedimentary deposits with long residence times (Cordell *et al.*, 2009; Darch *et al.*, 2013) and from plant and

microbial residues (Darch *et al.*, 2013). Soils are naturally low in P. Soil P occurs as either inorganic P, which is considered as being readily available to plants, or as organic P, which needs to be hydrolyzed to inorganic P to become available (Darch *et al.*, 2013). Both forms of P can be either dissolved in the soil solution or sorbed to sediment particles or occur as part of plant material or microbial cells (Darch *et al.*, 2013). Soil P is mobilized by different processes, by solubilization in the water (chemical mobilization) or by detachment of particulate P sorbed to sediment particles (physical mobilization) (Darch *et al.*, 2013). Soil particle detachment generally occurs during high energy flows (during storm events), whereas solubilization may occur in lower flows (Turner & Haygarth, 2000; McDowell *et al.*, 2001; Hart *et al.*, 2004; Jordan *et al.*, 2005; Darch *et al.*, 2013).

The global P cycle has been increased by ca. 400 % due to agricultural practices (Whitehead & Crossman, 2012). Additions of P, either by mineral manufactured inorganic P fertilizer or organic P in manures or slurry, have led to an accumulation of P in agricultural soils (Eghball, 2002; Sharpley, 2003). For example, the P surplus in grasslands in the UK is estimated to be up to 24 kg P ha<sup>-1</sup> year (Haygarth *et al.*, 1998). Phosphorus fertilization is known to disrupt the natural P cycle in soils resulting in less organic P to inorganic P conversion than in natural soils and crop P use efficiency has reduced in high P environments because the innate mechanisms of P acquisition by natural plants are not found in many agricultural crops (Dungait *et al.*, 2012). Such reduced P use efficiency in crops causes an increased dependency on P inputs. However, global rock phosphate reserves are predicted to soon get exhausted and the reserves are owned by only a few, politically instable countries (Power, 2010; Darch *et al.*, 2013). Additionally, amendments of P can cause incidental losses to surface waters, when fertilizer / manure applications occur before rainfall events or higher P losses in general occur due to the increased P stores in agricultural soils (Preedy *et al.*, 2001; Eghball, 2002; Sharpley, 2003). Reduced vegetation cover increases the losses of particulate P by increased rates of soil erosion. Ploughing causes P mineralization as well as accelerates erosion rates, thereby increasing P losses after ploughing (Addiscott, 1988; Sharpley, 2003; Butler & Haygarth, 2007).



A rise in P, even to concentrations as low as 10s of micrograms L<sup>-1</sup> in freshwater systems can cause eutrophication (Ulen *et al.*, 2007; Bilotta *et al.*, 2008). Water treatment costs of P (and soil) removal are estimated to be \$ 55 million year<sup>-1</sup> in the USA (2000 prices) (Pretty *et al.*, 2000).

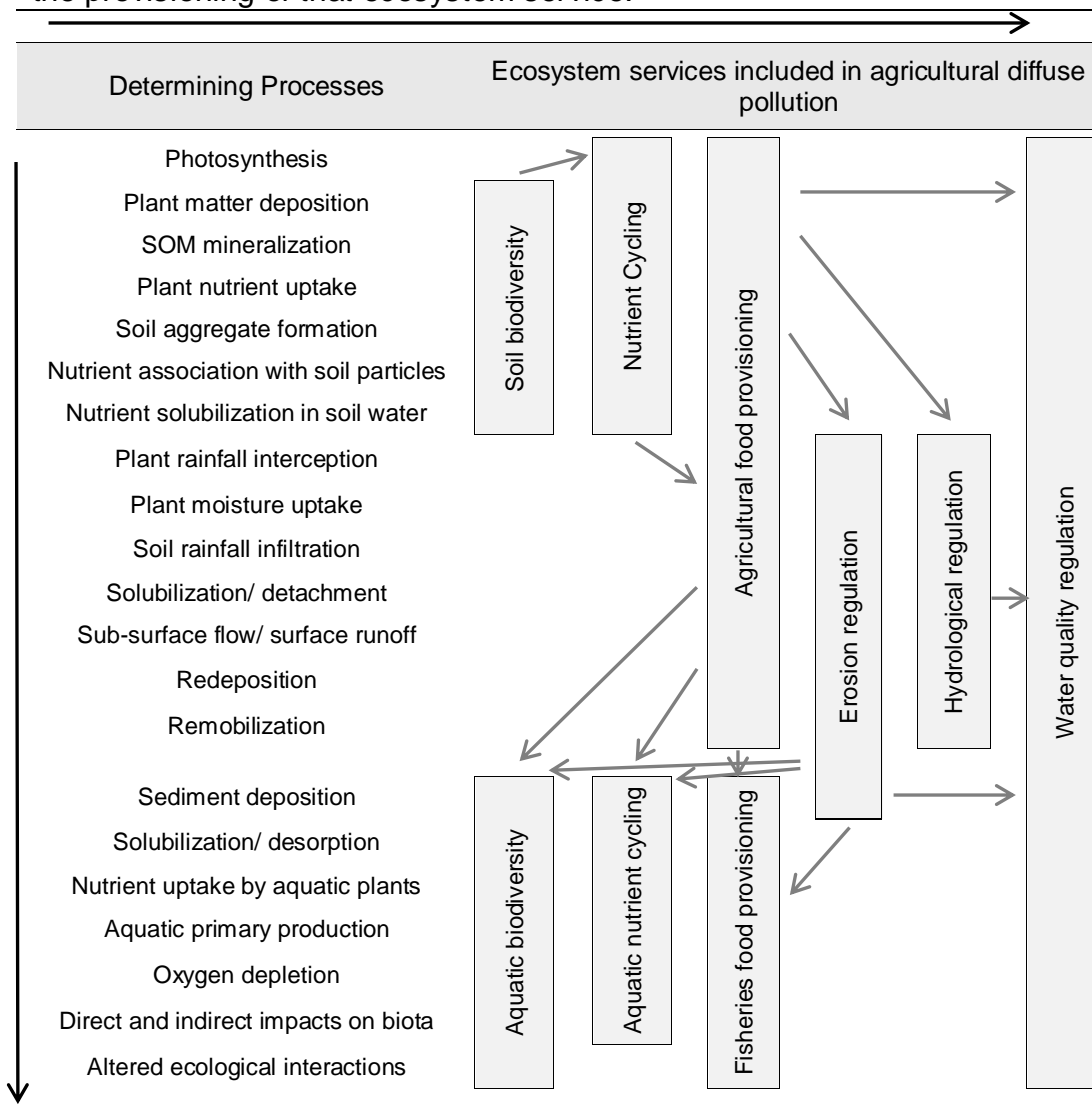
The above review illustrates the many processes involved throughout the soil-to-water continuum, most of which are profoundly altered by agricultural management. These processes and how they are altered are summarized in table 2.1, organized as source, mobilization, transport and delivery to the impacts in surface waters.

These processes do not only affect water quality, but are interlinked with a range of other ecosystem services, and many trade-offs occur between these different services (Table 2.2) (Swinton *et al.*, 2007; Carpenter *et al.*, 2009). Soil structure, nutrient cycling and soil biodiversity are considered as supporting services, affecting the regulating services, like hydrological regulation, erosion regulation and water quality regulation. Also, nutrient cycling and biodiversity in the water support water quality regulation. The provisioning of supporting and regulating services are generally positively correlated, whereas provisioning services, such as agricultural food production have negative trade-offs with the provisioning of supporting and regulating ecosystem services (Pilgrim *et al.*, 2010; Smart *et al.*, 2010; Dick *et al.*, 2011a; NEA, 2011).

Table 2.1. Summary of the soil-to-water continuum in agricultural landscapes. Ecosystem structure (first column) affects the processes (second column), that determine the individual continuum components source, mobilization, transport, delivery and impact (fourth column). These determining processes are altered by agricultural management (third columns).

→			
Ecosystem Structure	Determining Processes	Alteration by Agricultural Management	Continuum component
Sunlight, Soil formation, Temperature	Photosynthesis	Nutrient additions, Reduction of Vegetation cover	Source
	Plant matter deposition SOM mineralization Plant nutrient uptake Soil aggregate formation		
Rainfall, Topography, Soil texture, Soil type, Porosity, Vegetation cover, Temperature	Nutrient association with soil particles	Reduction of vegetation cover, Alteration of soil structure and stability	Mobilization, Transport & Delivery
	Nutrient solubilization in soil water		
	Plant rainfall interception		
	Plant moisture uptake		
	Soil rainfall infiltration		
Water, Hydrological dynamics, Light penetration, Temperature	Solubilization/ detachment	Increased input of sediment and nutrient inputs	Impact
	Sub-surface flow-/ surface runoff		
	Redeposition		
	Remobilization		
	Sediment deposition		
Water, Hydrological dynamics, Light penetration, Temperature	Solubilization/ desorption	Increased input of sediment and nutrient inputs	Impact
	Nutrient uptake by aquatic plants		
	Aquatic primary production		
	Oxygen depletion		
	Direct and indirect impacts on biota		
	Altered ecological interactions		

Table 2.2. Determining processes (first column) affect ecosystem services and their interactions. The size and position of the ecosystem service boxes depend on the processes that they are determined by, all processes that are parallel to the ecosystem service box are determining the provisioning of that ecosystem service.



### **III. Approaches to mitigate soil degradation and agricultural diffuse pollution**

The EU Common Agricultural Policy (CAP) and the EU Water Framework Directive (WFD) (2000/60/EC) provide the overall framework for regulating, defining and mitigating agricultural diffuse pollution. These overarching regulations contain several sub-regulations, such as the Nitrates Directive (91/787/EEC). Currently, the EU Soil Thematic Strategy (COM (2006)231) sets the thematic framework for soil protection and what kind of measures must be taken. A Soil Framework Directive had been debated in the EU, but never came into action (EC, 2014a). Therefore, soil protection measures are included in other regulations that are targeting water quality or general agricultural management (Creamer *et al.*, 2010). These EU regulations lay out the overarching aims and timeframes in which targets should be met, but each EU member state decides on the ways in which these regulations are implemented and how their effectiveness is monitored. Similar regulations are in place elsewhere, for example the Clean Water Act in the USA (EPA, 2014).

The CAP is currently under reform (EU, 2013), but decisions on how individual member states are implementing the reform have not been released, yet (due in January 2015). Therefore, the mitigation efforts in the UK up until now are reviewed in the next section.

#### **A. Mitigation efforts in the UK**

A catalogue of mitigation measures to reduce diffuse pollution from agriculture has been compiled and reviewed in the UK, most of which are included in regulations (Newell-Price *et al.*, 2011).

Mitigation measures to reduce soil degradation and diffuse pollution in the UK, as part of EU policies, are implemented by a mixture of different methods. These methods include command and control measures, which are regulations that farmers have to comply with, and incentive-based regulation as well as locally targeted incentive schemes, which aim to provide a financial incentive to

farmers to change their behaviour towards more environmentally beneficial management. Farmers can receive payments / subsidies for voluntarily joining schemes that promote beneficial agricultural management (Blackstock *et al.*, 2010) (Figure 2.4).

Nitrate Vulnerable Zones (NVZs) are command and control regulations and were designated in the UK under the EU Nitrates Directive (1991/7787/EEC, COM/91/676/EEC) (Figure 2.5a). These NVZs were designated in catchments which were identified to have high surface and groundwater N concentrations. Farms located in such NVZs have to comply with all regulatory demands set for NVZs (DEFRA, 2008). In total, 50 NVZs were designated in England, covering 70 % of the UK land area and containing 69 % of the arable land and 57 % of the grasslands in the UK (Cardenas *et al.*, 2011; Johnson & Lord, 2011). Elsewhere, for example in Ireland and Germany, the whole country has been designated as an NVZ (Figure 2.5b).

The Single Farm Payment (SFP) scheme is a major subsidy scheme in the EU, as part of the EU CAP. Farmers who are receiving single farm payments have to comply with certain regulatory requirements (Cross Compliance: (DEFRA, 2006; 2007a; 2007b; 2007c), such as maintaining land in 'good agricultural and environmental condition' (GAEC) and statutory management requirements (DEFRA, 2007c; 2009; 2010; 2006). The same scheme exists all across the EU member states, for example in Ireland (DAFM, 2014a) and in Germany (BMEL, 2014).

Environmental stewardship schemes are also part of the EU CAP. The schemes aim to encourage farmers to deliver environmental management that goes beyond the requirements under the Single Farm Payment scheme. Participating farmers can choose between a range of options, some of which target soil and water quality improvements (DEFRA, 2005a), but also include other aims, such as protecting and enhancing biodiversity. Agri-environmental schemes were until now divided into Entry Level Stewardship (ELS), containing a catalogue of management options which can be chosen (Natural England, 2008) and a Higher Level Stewardship scheme (HLS), which has more specific management prescriptions decided on a case-by-case basis. Similar schemes have been established in other EU member states, such as the Rural Environment Protection Scheme in Ireland (REPS) (DAFM, 2014b) and "agri-

environment and nature conservation programs” in each federal state in Germany (BfN, 2009).

The ‘Catchment Sensitive Farming Initiative’ (Natural England, 2014) or local river improvement projects are examples of locally targeted incentive schemes. Priority catchments are identified for such schemes, and one-to-one advice is provided to individual farms to implement specific mitigation measures and funding is often available.

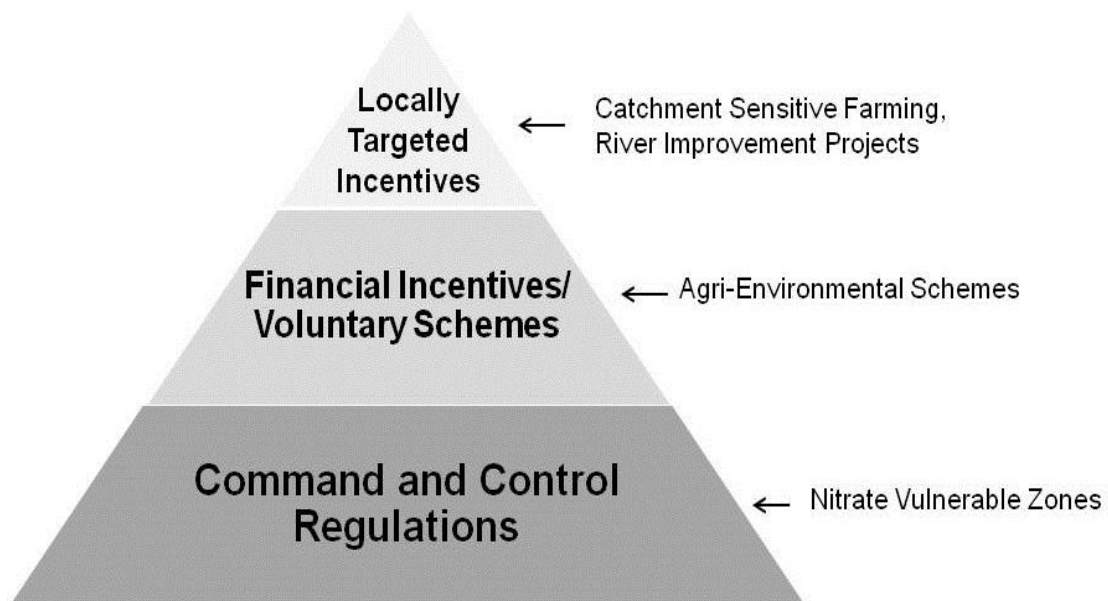


Figure 2.4. Mechanisms of policy delivery for mitigation measures to reduce agricultural diffuse pollution and soil degradation in the UK (after McGonigle *et al.*, 2012).

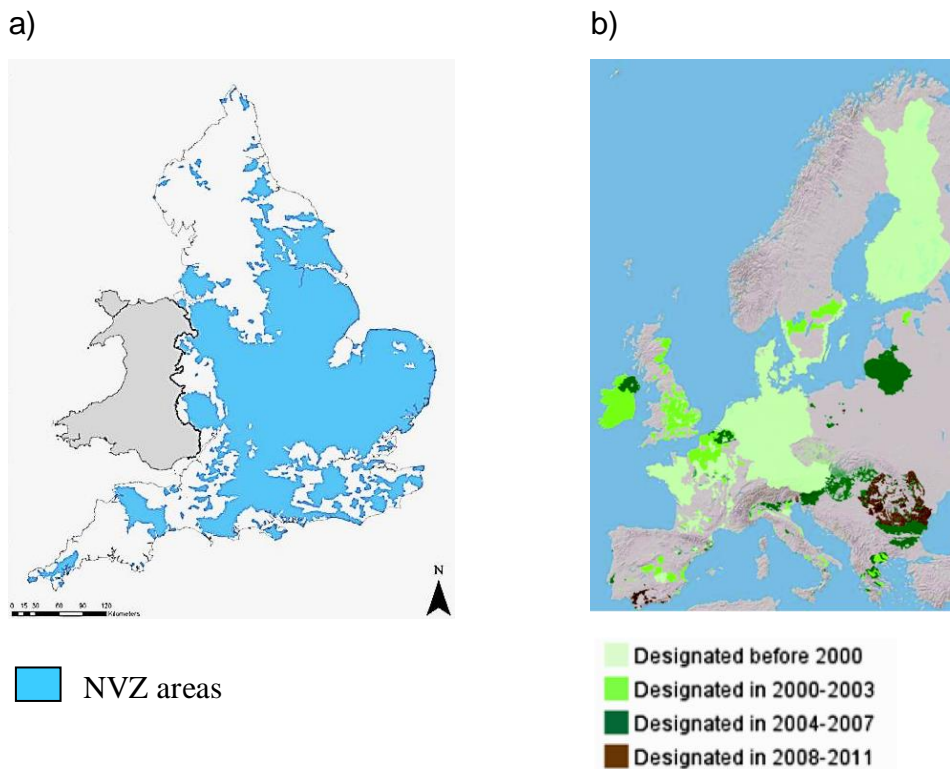


Figure 2.5. Areas designated as Nitrate Vulnerable Zones (NVZ) in a) England and b) in the EU member states. Sources: a) (DEFRA, 2013) b) (EC, 2014b).

The specific management demands (SFP, NVZ) or options given (ELS) in existing regulations can be grouped into three major thematic groups.

a) Regulations aim to reduce nutrient inputs into agricultural land and thereby reduce the nutrient surpluses in the soil and potential pollutant sources. Input reductions are targeted by setting standards on maximum nutrient usage (NVZ), reducing the time when nutrients / fertilizers / manures can be applied (closed periods, NVZ) and demanding / encouraging the development of nutrient management plans wherein the farmer is required to calculate the exact amount of nutrients that need to be spread, taking into account crop nutrient requirements, soil available nutrients, nutrients comprised in manure and fertilizers (NVZ, ELS, SFP). Additionally, no fertilizer / manure is allowed to be spread in proximity to surface waters, ditches, hedges or on buffer strips (NVZ, SFP, ELS).

b) Regulations specify certain times / conditions and locations where farming operations / applications should be avoided to reduce the impact of operations on soil conditions so that infiltration is enhanced and the generation of surface

runoff minimized. Driving heavy vehicles is discouraged / banned under certain soil and weather conditions, such as when the soil is moist, waterlogged, poached, frozen, snow covered or compacted and when rainfall is due in the days following operations and applications (ELS, SFP). Closed periods (NVZ) are set in the winter season, where most of the above described conditions coincide. Furthermore, ploughing or spreading is discouraged in areas identified as high risk, such as steep slopes (SFP, ELS).

c) Regulations encourage / demand the maintenance and establishment of vegetation cover. This comprises a range of management practices. Choosing crops with high vegetation cover and which do not leave soil bare over winter is advised (ELS, SFP). However, if rotation leaves soil bare over winter, planting cover crops is encouraged (ELS, SFP). Furthermore, undersowing crops with vegetation cover (for example maize) is advised. Converting agricultural and or leys to grassland, specifically to permanent grassland, is recommended (ELS). In addition to this, increasing vegetation at field bottoms or in proximity to surface waters in form of vegetative buffer strips, as wide as possible / feasible, and allowing vegetation cover to build up is promoted by regulations (ELS, SFP). Regulatory demands or recommendations are not always solely targeting soil and water protection, but also a range of other important environmental aspects, such as greenhouse gas emissions and biodiversity.

Future reforms of the EU CAP are going to further emphasize the importance of vegetation cover by including 'greening rules' in the new single farm payment schemes (Basic Payment Scheme [BPS]). Greening rules include the encouragement for reinstating permanent grasslands and keeping a set percentage of arable land as ecological focus areas (EFA), which include measures to increase vegetation cover, such as buffer strips, hedges, fallow land, catch crops and cover crops (DEFRA, 2014). Also, a new guideline on soils will be included in the standards of good agricultural and environmental condition (GAECs) under cross compliance (DEFRA, 2014).



## **B. Water quality standards: Which surface waters are impaired and need mitigation measures?**

The water framework directive provides a holistic framework for defining and classifying water quality. Its aim was for all surface waters to reach 'good ecological status' in the EU by 2015 with a possible extension for another 12 years (Kallis & Butler, 2001; Hering *et al.*, 2010). 'Good ecological status' is defined in terms of biological, chemical and physical quality (Kallis & Butler, 2001). The categories for classification of watercourses that have not been heavily modified are bad, poor, moderate, good and high ecological status. The status of a watercourse is decided by a one-out-all-out principle, a watercourse is classified as its lowest classed element (Hering *et al.*, 2010). The elements monitored for ecological status are macroinvertebrates, macrophytes, diatoms and fish. Properties monitored for chemical status include  $\text{NO}_3^-$ ,  $\text{NO}_2^-$ ,  $\text{NH}_4^+$ , suspended solids, P, pH and dissolved oxygen, but also include chemicals classed as priority substances and dangerous substances. Hydromorphological elements include, for example, river depth, structure and substrate of the river bed and the structure of the riparian zone (TAG, 2008).

The WFD takes a catchment approach (Hering *et al.*, 2010). Water quality in each catchment is classified (Figure 2.6, 2.7) and catchment management plans are developed to improve the water quality status of the entire catchment, thereby including all stakeholders within catchments, such as farmers and land-owners, industry and local communities (Kallis & Butler, 2001; Hering *et al.*, 2010).

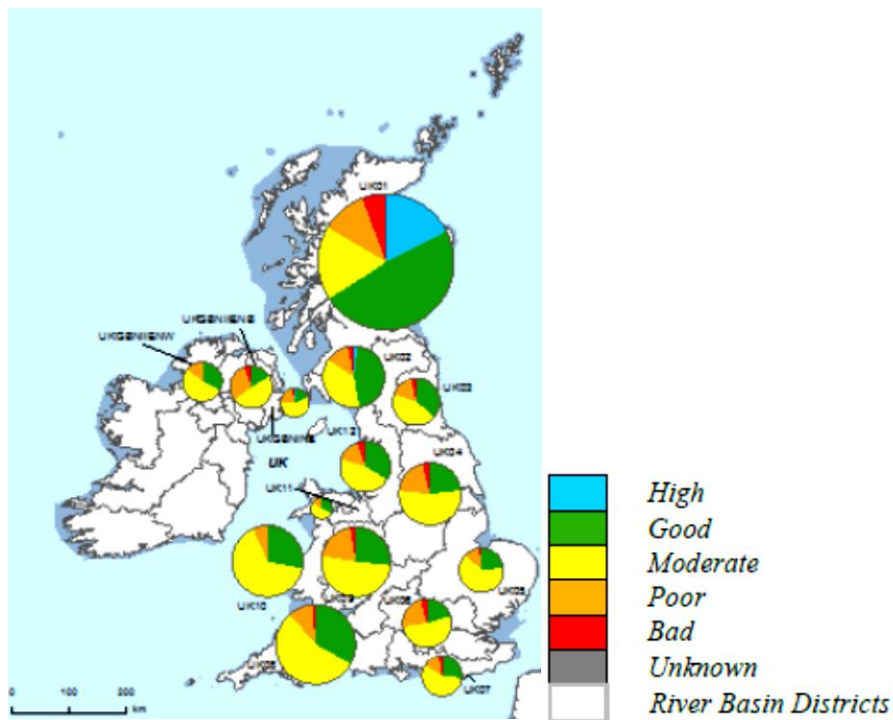
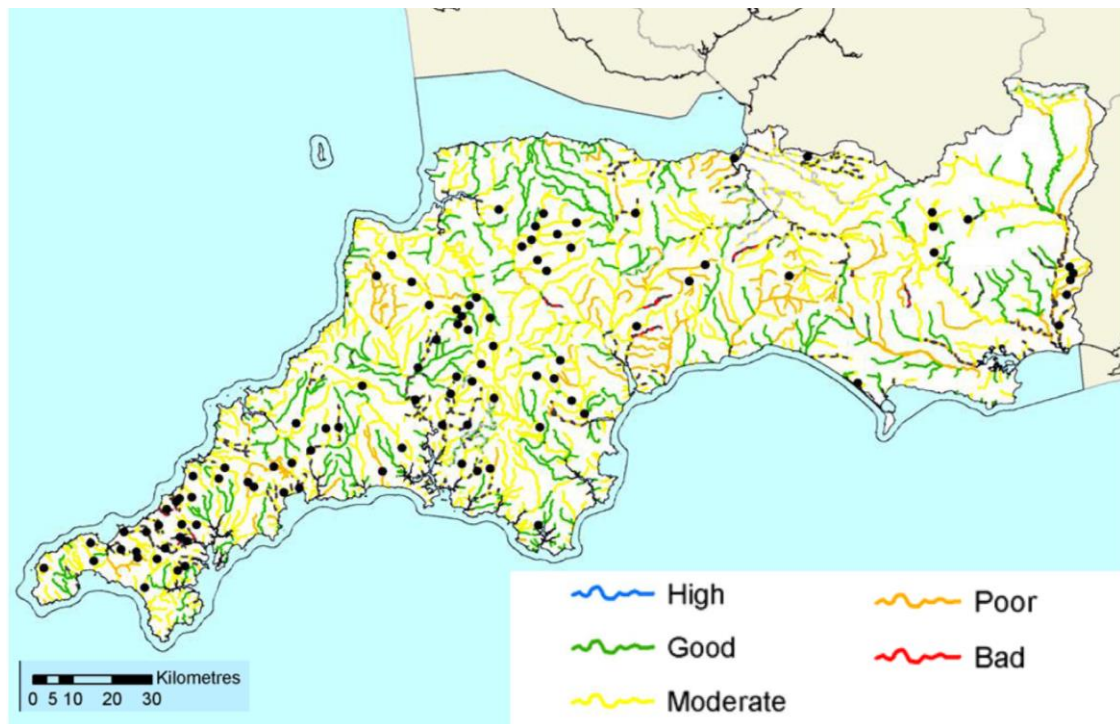


Figure 2.6. Ecological status classification of surface waters (excluding heavily modified water bodies) in the UK under the WFD classification system, divided by river basin district. Source: (EC, 2012b).



Ecological status classification of surface waters in the South West River Basin District. Here, 33 % of surface waters meet good ecological status. Source: (EA, 2009).

#### **IV. Have these mitigation measures been effective?**

The overall effectiveness of the above mitigation measures has not (yet) become evident (ADAS, 2011; Johnson & Lord, 2011; van Grinsven *et al.*, 2012; Kay *et al.*, 2009). In 2012, more than half of all European water courses (EEA, 2012) and two thirds of all surface waters in the UK (McGonigle *et al.*, 2012) did not meet good ecological status. Nitrate concentrations have only moderately decreased in Europe (van Grinsven *et al.*, 2012) and have even continued to increase in many rivers in the UK by  $0.02 \text{ mg L}^{-1} \text{ year}^{-1}$  (Worall *et al.*, 2009; Burt *et al.*, 2011). Additionally, the overall impact of the NVZ mitigation measures in the UK was found to be small. Only 29 % of the NVZ areas showed a reduction of  $\text{NO}_3^-$  concentrations, but 31 % showed a worsening in comparison to control catchments and 69 % showed no significant improvement at all, 12 - 15 years after the first designation of NVZs (Worall *et al.*, 2009). Water quality has not significantly improved, despite significant decreases in soil N and P surpluses (van Grinsven *et al.*, 2012). In the UK, the soil N surplus has decreased mostly in the grassland sector (Johnson & Lord, 2011), but the P surplus has decreased more in the arable sector and is now approaching 0, whilst the P surplus in grassland systems is still significant (Johnson & Lord, 2011).

Interestingly, individual mitigation measures have been shown to be very effective at controlling diffuse pollution at smaller scales (reduced nutrient inputs (Lord, 2007), for example buffer strips (Zhang, 2010), conversion from arable land use to grassland (Fullen, 2006; Hodkinson, 2007), use of cover crops (Strock, 2004), minimal tillage and contour cultivation (Stevens *et al.*, 2009). However, those small-scale improvements do not necessarily upscale to larger catchment-scale, national-scale or EU-wide studies (Verstraeten *et al.*, 2006; Worall *et al.*, 2009; van Grinsven *et al.*, 2012). Therefore, it seems very unlikely that the goals of the WFD will be met by 2015 (Hering *et al.*, 2010).

## **V. Overview of the issues that are limiting the problem-solving capacity of water quality science**

There may be several explanations for why mitigation measures do not seem effective in reducing diffuse pollution. This section identifies some of the issues that are limiting the problem-solving capacity of water quality science and discusses how these issues could be addressed in scientific research. Once these issues are addressed, an improved scientific evidence base may be formed, which may eventually lead to effective policy making and mitigation of soil degradation and agricultural diffuse pollution. Figure 2.8 summarizes the identified issues on the feedback arrow within the conceptual framework of the problem-solving machinery that was developed to structure this literature review. Effectiveness may not be detected, because of the ways in which water quality is monitored, which aspects of water quality are monitored and at what spatial and temporal scales experiments are designed. There are also several knowledge gaps, which may have led to wrong decision-making on choosing mitigation measures. These issues are reviewed in the following section. Following each discussion of individual issues, short paragraphs in *italic* explain how these issues were incorporated into the research in this thesis.

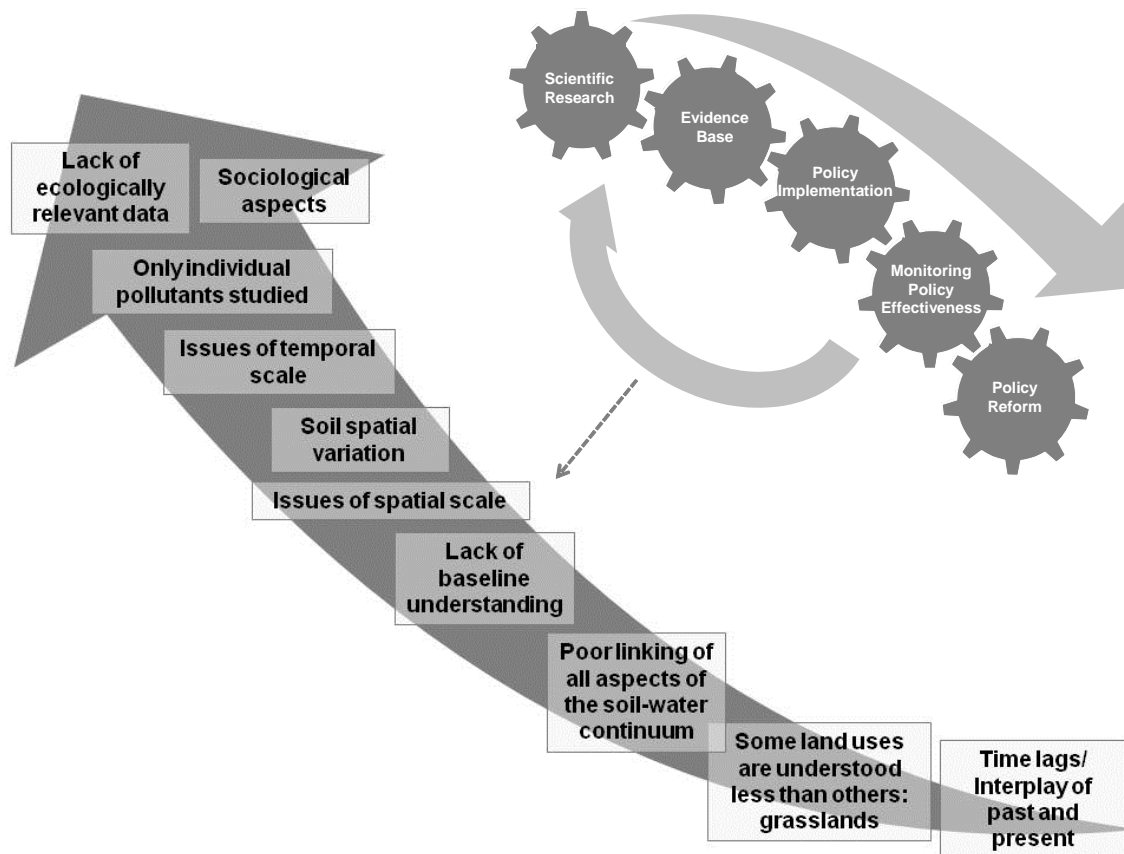


Figure 2.8. The issues that are identified and discussed in this literature review, which should feed back into scientific research to form a new, improved scientific evidence base.

#### **A. Time lags between management and responses / The interplay of current and past management**

The effects of mitigation management may not yet be evident, because there are time lags between implementing beneficial management and its effects. Time lags are estimated to act over months up to years, decades and even centuries (Stalnacke *et al.*, 2003; Carstensen *et al.*, 2006; Burt *et al.*, 2011; Wall *et al.*, 2012; Buckley & Carney, 2013; Sharpley *et al.*, 2013; Wang *et al.*, 2013; Burt *et al.*, 2014). Soil nutrient reserves and water quality today may reflect past management, meaning that we may have not yet experienced peak pollutant concentrations, as found in areas of the Eden catchment, UK, and that mitigation measures may prove to be effective only over the next decades (Wang *et al.*, 2013).

It takes time to reduce nutrient reserves that have accumulated over 50 years of intensive management. Organic matter turnover times in south-western France have been estimated to take ca. 36 years (Balesdent *et al.*, 1987). Soil fertility rates persisted up to 80 years after intensively managed land had been abandoned (Horrocks *et al.*, 2014). Reductions in N and P surpluses have already been seen in Europe (van Grinsven *et al.*, 2012) and the UK (Johnson & Lord, 2011). However, short-term management can exacerbate the severity of the influence of past management. For example, if fields with high legacy nutrient contents are ploughed shortly before heavy rainfall, nutrient losses can be exacerbated.

Pollutant reductions in surface waters may lag behind changes to soil stores because of accumulated sediment in-channel, with associated nutrients being recycled within fluvial systems, recycling dissolved nutrients in aquifers, and the time it takes to flush out the accumulated sediment (Stalnacke *et al.*, 2003; Carstensen *et al.*, 2006; Hamilton, 2012). Furthermore, once pollutant concentrations are reduced in surface waters, it still takes considerable time (estimated to be between 10 - 20 years) for the biology and ecology of the system to return to equilibrium (Jepperson, 2005; Hering *et al.*, 2010).

Such long response times imply that any soil or water condition monitored today has to be interpreted with respect to both short-term management as well as long-term management. Long-term management records, however, are often not available. Additionally, long-term monitoring campaigns are required to evaluate the effects of mitigation measures (Wall *et al.*, 2011). There is a temporal mismatch between the time it takes for scientific research to reliably identify the most effective mitigation measures and the time when regulations need to be implemented (Schroeder, 2004). Finally, expectations for compliance with the water framework directive have to be adjusted; even the next target of meeting good ecological status in 2027 is not likely to be met (Hering *et al.*, 2010).

*This thesis studied the effects of management practices on soil and water quality. Current and past management records were consulted when interpreting results.*

## **B. Some land uses are studied less than others: intensively managed grasslands are relatively poorly understood**

Some agricultural land uses are less studied, and therefore less well understood than others, for example intensively managed temperate grasslands. Temperate grasslands are generally managed for dairy and meat production and cover 40 % of the agricultural land in western Europe and the United States and more than half (65 %) of the agricultural land in the UK (Bilotta *et al.*, 2007a; Bilotta *et al.*, 2008). Grasslands have previously been assumed to contribute little to total agricultural diffuse pollution in comparison to their arable counterparts (Evans, 2005; Brazier *et al.*, 2007). However, this assumption has been challenged by several recent studies demonstrating significant sediment and macronutrient losses from grasslands with pollutant concentrations exceeding EU water quality guidelines and with pollution rates comparable to those reported for arable sites (Preedy *et al.*, 2001; Bilotta *et al.*, 2008; Bilotta *et al.*, 2010; Granger *et al.*, 2010; Sandford *et al.*, 2013; Thompson *et al.*, 2014). The diffuse pollution from grasslands is also underestimated in EU regulations. Such misunderstandings of management practices leads to incorrect agricultural decision-making, such as policies encouraging conversion from cultivated land to grassland (Agri-environmental Schemes, NVZs (Lord, 2007)), which may eventually reduce the effectiveness of mitigation measures.

The impacts of grassland management on diffuse pollution were underestimated for several reasons. a) The vegetation cover in grasslands is not as uniform and dense as previously assumed (Bilotta *et al.*, 2007b). Livestock grazing, trampling, poaching and pugging reduce vegetation cover and destroy soil structure (Bilotta *et al.*, 2007a; Cournane, 2011). Vegetation cover is also often temporarily removed, as ploughing and reseeded is part of a normal rotation cycle in grassland systems (Butler & Haygarth, 2007). Additionally, grasslands are often located on steeply sloping land and heavy, often waterlogged soils, which exacerbate surface runoff down-slope despite the vegetation cover (Bilotta *et al.*, 2007b; Bilotta *et al.*, 2008).

b) Grassland soils accumulate large amounts of organic matter and nutrients at the soil surface, the layer that interacts mostly with runoff (Schärer *et al.*, 2007). Nutrients added to grasslands by fertilizer and manure additions, but

also by direct excretion by grazing animals, are not frequently mixed into the soil profile. Such surface accumulation increases the available nutrient pool for mobilization to surface waters, even once nutrient additions are reduced, due to the legacy of past management (Sharpley *et al.*, 2013; Haygarth *et al.*, 2014). Organic material was originally not included in the definition of soil erosion and was removed during conventional laboratory analysis by drying sediment particles at too high temperatures (Bilotta *et al.*, 2007b). Total erosion may be underestimated by up to 34 % in grasslands if organic matter is not included (Bilotta *et al.*, 2008; Bilotta *et al.*, 2010).

c) Fine sediment material (both organic and mineral) is preferentially transported in grasslands, which was not included in the original definition of suspended sediment and was, therefore, not included in erosion monitoring (Bilotta *et al.*, 2007b). Sediment particles were typically defined by researchers as anything larger than 0.45  $\mu\text{m}$ , detected by filtering, and anything below that size was defined as solutes (Bilotta *et al.*, 2007b). Fine soil material, colloids, comprise particularly fine soil particles, occurring in animal faeces, organic matter and fertilizers (1 nm - 1  $\mu\text{m}$ ) (Bilotta *et al.*, 2007b). These have large surface areas and surface charges which lead to high sorption capacity for nutrients. Therefore it is important that they are understood and monitored as an important part of particulate loss from landscapes.

The diffuse pollution losses from grasslands need to be evaluated and compared to other land uses, so that grassland management effects can be better acknowledged in management guidelines for future compliance with water quality standards. The global demand for meat production is expected to rise rapidly as per capita income increases in developing countries and grasslands are, therefore, to become an even more important land use in the future (Bennett & Balvanera, 2007).

*The research conducted for this PhD thesis focused on intensively managed temperate grasslands.*



### **C. Poor linking of all aspects of the soil to water continuum**

Improvements in soil quality (reduction in excess soil nutrients) and improvements in water quality (reductions of nutrient concentrations) are often evaluated separately, even though both operate on a continuum from soil to water (Haygarth *et al.*, 2005). The relationships between soil conditions, site characteristics such as topography and resultant water quality have to be quantified to evaluate the effectiveness of mitigation measures and understand the mechanisms by which they affect water quality (Wall *et al.*, 2011). For example, Johnson & Lord (2011) found a reduction in soil nutrient surpluses in grasslands, but no overall reduction in surface water nutrient concentrations, showing that potential nutrient sources may have reduced, but their mobilization rates need further mitigation efforts.

The links between soil content and delivery to surface waters is more researched and better understood for P, than for N and C. All relationships between soil nutrient and water nutrient content are complex and obscured by the influence of many other factors, such as topography, hydrological connectivity and of course land management. Soil P is generally only viewed as an indicator of potential P source and has to be considered in combination with other influences (Heckrath *et al.*, 1995; Jordan *et al.*, 2000; Quinton *et al.*, 2003; Djodjic *et al.*, 2004). Rates of N mobilization and delivery to surface waters are generally only linked with fertilizer inputs or the balance between N inputs and N uptake by crops rather than with total soil N content. Such studies show poor correlations (Stalnacke *et al.*, 2003; Siegling & Kage, 2006; Buczko & Kuchenbuch, 2010). Total soil N content, including organic and inorganic soil N in addition to agricultural inputs, should be included in such studies. In terms of carbon, negative relationships have been established when comparing natural landscapes with high soil C contents and low C losses and agricultural soils low in C with high C losses (Quinton *et al.*, 2006; Glendell & Brazier, 2014; Glendell *et al.*, 2014), but such studies have not been conducted between agricultural fields / catchments. Linking soil nutrient content and water nutrient content can also provide insight into the time it takes for mitigation measures to reduce legacy soil nutrients and for those reductions to take full effect on water courses.

*This PhD thesis used the nutrient / pollutant transfer continuum concept to evaluate the effects of grassland management, thereby linking the effects of management practices on both soil status and water quality in terms of the macronutrients P, N and C.*

#### **D. Lack of baseline understanding**

Detecting an improvement to soil and water quality by mitigation management is often limited by poor understanding of the effects of the conventional management, to which post-mitigation data can be compared. Before any new management practice can be quantified, a baseline understanding or characterization of the '*status quo*' of the conventional management in both soil properties and resulting water quality is therefore essential (McGrath & Zhang, 2003; Tan & Lal, 2005; Breuer *et al.*, 2006). Many water quality studies use paired catchment studies involving a baseline characterization, so that the effects of management change can be identified as relative change from the baseline period (Schilling *et al.*, 2013). However, soil studies often compare soil properties between sites with different management histories without baseline characterization and rely on the fundamental assumption that the sites were similar in terms of soil properties prior to land-use change (Boerner *et al.*, 1998; Breuer *et al.*, 2006; Matlack, 2009). Wrong inferences may be made about management effects without analyzing management effects relative to baseline conditions. Additionally, monitoring before the change in management and long-term monitoring afterwards should enable us to judge how long it takes for the new management to take effect and how long the legacy of past management lasts (Wall *et al.*, 2011).

*This thesis first characterized soil status and the rates of diffuse pollution in conventionally managed grasslands as a baseline. Then, the effects of altered management practices were compared back to the baseline, using both a before-after and a controlled-perturbed experimental design.*

## **E. Issues of spatial scale**

Small-scale (plot-scale, field-scale) experiments have demonstrated the effectiveness of mitigation measures, but those effective reductions could not be detected in larger-scale studies (catchment or national-scale studies). Such discrepancies occur, because the scale of study determines the processes that are captured and therefore determine the value of information that the research can provide (Wall *et al.*, 2012). Different processes are acting on different scales. For example, small-scale experiments capture processes such as nutrient uptake by individual plants, larger plot / hillslope / field-scale studies capture more processes including nutrient cycling, mobilization / transport and potential re-deposition of pollutants, while catchment-scale studies capture the mixture of numerous pollutant sources and land uses as well as additional processes such as the cycling of pollutants within and delivery of pollutants to surface waters. Therefore, smaller-scale studies on mitigation measures capture the isolated effectiveness of individual mitigation measures, but this effectiveness does not translate to reduced pollutant concentrations / loads / yields at larger scales for several reasons. a) Other pollutant sources or pollutant transport mechanisms within the catchment may have obscured the mitigation management that was effective in isolation (Wall *et al.*, 2012). For example, small-scale buffer strip studies demonstrate the effectiveness of buffer strips in reducing diffuse pollution, but buffer strips are not as effective at the catchment-scale, because runoff is channelled by roads to surface waters and thereby by-passed buffer strips (Verstraeten *et al.*, 2006). b) Pollutant delivery may have been reduced, but processes such as the recycling of legacy sediment and nutrient reserves within streams or aquifers were responsible for maintaining high pollutant concentrations. Therefore, smaller-scale experiments reduce the complexity of the wider landscape, and processes cannot be up-scaled in a linear fashion (Harris & Heathwaite, 2012).

While lab- to plot-scale studies have provided much of the essential mechanistic understanding, larger-scale understanding is now required to solve the issue of agricultural diffuse pollution (McGonigle *et al.*, 2012). Such larger-scale research is more policy-relevant, but challenges scientific methodologies and the capacity to provide clear results (Haygarth *et al.*, 2005a; Doody *et al.*,

2012; Wall *et al.*, 2012). While large-scale studies show the effects of realistic agricultural management nested within the realistic set of multiple pollutant sources, they cannot be replicated (every field / catchment is influenced by a unique set of factors), and such inherent variation limits the use of conventional statistical tests, reduces statistical power and increases uncertainty (Harris & Heathwaite, 2012). In contrast, small-scale experiments allow the precise control of conditions, which often do not reflect either natural conditions (natural rainfall; Dunkerley *et al.*, 2008) or realistic management, but therefore comply with the requirements for conventional statistics and inferences can be made with high certainty.

It could be argued that the catchment scale is the policy-relevant scale under the WFD. However, any effort towards reducing pollution is generally targeted towards individual pollutant sources within catchments, because they are managed separately by different stakeholders (for example farmers, land owners or rural industry) (Wall *et al.*, 2012). Therefore, the scale of management decisions and policy implementation is not the catchment scale, but in the case of agricultural diffuse pollution, it is the farm scale. Herein, field-to farm-scale research is suggested as a logical scale to guide agricultural diffuse pollution research. The farm-scale is the scale of agricultural decision making but individual fields are generally treated as individual management units (Wall *et al.*, 2012). Additionally, working farms are managed under realistic farm management practices, generally in line with local farming practices, while short-term and long-term management are often known by the farmer (Wall *et al.*, 2012). Field to farm-scale research within a catchment may provide insight into a) the likely contribution a single type of agricultural land use has on overall water pollution and therefore improve pollution source apportionment within catchments, b) the isolated effects of individual soil and nutrient (mitigation) management practices (Melland *et al.*, 2012). If such field- to farm-scale experiments are nested within catchment studies, the isolated effects of mitigation measures can then be seen in context with the multiple processes that occur in catchments. Wall *et al.* (2012) demonstrated the usefulness of such nested field- to farm- to catchment studies. The usefulness of farm-scale experiments has been reviewed before (Garcia *et al.*, 2008; Pilgrim *et al.*, 2010), and evaluation of mitigation measures is often conducted at the farm-

scale in Ireland (Wall *et al.*, 2012), but there are few comprehensive field to farm-scale monitoring experiments underway, especially in intensively managed grasslands.

*The research for this PhD thesis was conducted at the field- to farm-scale, on an experimental grassland farm under management that is representative of the wider area of intensively-farmed grasslands in the UK.*

## **F. Soil spatial variation**

The effects of management practices on soil quality or the effectiveness of mitigation management may not be reliably detected by simply taking soil samples and averaging their values for a site of interest. Changes in soil properties following management change may not be detectable by comparing overall means. It is not just the average soil condition in a field that may change due to management, but also the spatial distribution of soil properties. Averaging does not account for the specific locations where the deviations from the mean occur or the distances over which soil properties vary (Glendell *et al.*, 2014). Spatial variation exists in agricultural landscapes (Mariott *et al.*, 1997; McCormick *et al.*, 2009), despite the homogenization effect of agricultural management via uniform fertilizer applications, uniform vegetation cover and uniform soil physical management (Robertson *et al.*, 1993; Chiba *et al.*, 2010; Glendell *et al.*, 2014). Therefore, any soil sampling should quantify spatial variation and map the distribution of soil properties (Goovaerts, 1998; 1999). Alterations in the distribution of soil properties or changes in certain areas of fields can then be reliably identified as actual changes, which may not have been detected by conventional soil sampling methods.

Geostatistical analysis is a useful tool to quantify spatial variation and visualize the distribution of soil properties (Oliver *et al.*, 1989a; 1991; Goovaerts, 1999; Oliver & Webster, 2014). The spatial location of samples is incorporated into analysis by first calculating the distances between sampling points and then calculating the squared differences between sampling points that are separated by certain distances. An experimental variogram is then plotted that shows the variance between sampled points as a function of

separation distance. Variogram models are then fitted to the experimental variograms, describing the continuous function and ignoring point-to-point fluctuations (Oliver & Webster, 2014). These variogram models can then be used to visualize the distribution of soil properties across the site of interest, by predicting values at unsampled locations using a method called kriging (Oliver & Webster, 1990).

Additional benefits can be gained from accounting for spatial variability, such as optimizing sampling designs, understanding underlying soil processes and optimizing land management. Characterizing the distances over which properties vary can provide insight into optimal sampling distances to sufficiently capture the existing variation, whilst keeping sampling effort and costs to a minimum (Oliver & Webster, 1991). Comparing the patterns of spatial variability between different soil properties may provide insight into underlying processes. The patterns or scales of spatial variability may differ between different soil properties, because the processes that cause the variability may occur at different scales (Goovaerts, 1998). Maps that visualize the distribution of soil properties can be utilized for decision making. The spatial distribution of soil properties can be used in precision farming to inform site specific management (Stafford, 2000). For example, areas of soil nutrient surpluses can be identified and avoided when spreading fertilizers, thereby reducing over-fertilization, fertilizer costs and potentially environmental impacts (Stafford, 2000).

*This thesis used a geostatistical sampling strategy to quantify the distribution of soil properties.*

## **G. Issues of temporal scale**

The degree of diffuse pollution reductions that can be detected depends on the temporal resolution of the available data. a) The effectiveness of mitigation measures may not be evident, because the data resolution used by regulatory bodies is low, and varies highly between EU member states (Wall *et al.*, 2011; Kay *et al.*, 2012; van Grinsven *et al.*, 2012). Generally, studies that employed high temporal resolution monitoring have a higher capacity to detect diffuse

pollution reductions than those with low resolution monitoring (Wall *et al.*, 2011; Kay *et al.*, 2012; Mellander *et al.*, 2012; van Grinsven *et al.*, 2012; Wall *et al.*, 2012). Temporally intensive monitoring can detect fine-scale dynamics, which coarser monitoring would miss, for example the importance of non-storm P transfers (Jordan *et al.*, 2012; Melland *et al.*, 2012) or reductions of N concentrations in high winter flows (Kay *et al.*, 2012). The recent development of near continuous, automatic monitoring equipment allows relatively low effort and low cost high-resolution monitoring, compared to manual sampling and lab analysis (Kirchner *et al.*, 2004; Jordan *et al.*, 2007). High-resolution monitoring also allows for more accurate and precise calculation of pollutant loads and yields (Cassidy & Jordan, 2011).

b) The effectiveness of mitigation measures may not be detected, because longer datasets and overall means of pollutant concentrations may be influenced by seasonal and inter-annual climatic variation rather than just mitigation management. Disentangling whether changes in surface water quality are driven by mitigation measures or inter-annual variability is a major challenge, which can only be tackled once long-term datasets exist (Burt *et al.*, 2014).

c) External, unrelated influences, such as altered rainfall patterns due to climate change, may alter the relationships between agricultural management and diffuse pollution. For example, lower frequency but higher intensity rainfalls have already been noted to occur and have been predicted to become more likely in the future (Hering *et al.*, 2010; Jordan *et al.*, 2012).

Therefore, long-term and high resolution monitoring is required. Long-term studies can evaluate response times and disentangle the effects of management and climatic variability, whilst high temporal resolution monitoring can provide mechanistic understanding. Datasets with high temporal resolution are also important when classifying rivers. Regulatory monitoring is mostly conducted at low temporal resolution, which may lead to incorrect classification of surface waters as well as potentially identifying wrong reasons for failure, which may then subsequently lead to the implementation of inappropriate mitigation measures (Kay *et al.*, 2012).

Analyzing datasets with high temporal resolution is challenging. High-resolution datasets capture fine-scale variability and have therefore lower statistical power (Harris & Heathwaite, 2012). Traditional methods would have averaged or normalized the data to reduce 'noise', which now has to be considered as important fine-scale processes rather than removed (Harris & Heathwaite, 2012). Additionally, correlations are obscured by delays between one driving factor and another responding property (e.g. flow and sediment hysteresis), which may not be detected with lower resolution monitoring (Harris & Heathwaite, 2012).

*The monitoring conducted for this thesis took a high-resolution approach of sampling continuously up to every 15 minutes throughout 2 years.*

#### **H. Total diffuse pollution is rarely monitored**

Multiple pollutants are rarely studied together, nor are all fractions of nutrients considered in the same study; causing issues in detecting the effectiveness of mitigation measures on each pollutant.

Mostly inorganic, dissolved fractions of nutrients are measured as they are / were considered as the bio-available forms. Not accounting for all fractions of nutrients causes several issues. a) The total nutrient input is underestimated and therefore the likely impact is underestimated. Recent studies have shown that both inorganic and organic, particulate and dissolved forms of N and P can become bioavailable. Organic N can become bioavailable by assimilation by bacteria (See *et al.*, 2006) and organic P by hydrolysis (Darch *et al.*, 2013), particulate N and P by desorption. b) Mitigation measures may be considered as effective when they reduce the delivery of dissolved inorganic nutrients to surface waters, whilst it is not actually quantified whether particulate or organic forms of the same pollutant have been reduced as well. Therefore, mitigation measures may be wrongly identified as being effective, but may actually cause undesired effects. c) While mitigation measures may have reduced the delivery of dissolved inorganic nutrients, this reduction may not be detectable further down-stream, because legacy organic nutrients or particulate forms of nutrients



may have been recycled. The water quality classification under the WFD and the Nitrates Directive has been criticized, because only inorganic forms of N and P are considered. Water quality guidelines in the USA for example are set for total N and total P (USEPA, 2000).

Multiple pollutants are rarely studied together. Mitigation measures are often introduced to reduce the delivery of individual pollutants to surface waters rather than the whole suite of pollutants and their effectiveness is generally assessed only on the pollutant of interest. However, 'pollution swapping' can occur, when a mitigation measure that was introduced for one pollutant actually increases the delivery of another pollutant (Stevens, 2009; Stevens & Quinton, 2009). For example, vegetative buffer strips are often introduced to reduce soil erosion, but have been demonstrated to increase losses of dissolved organic carbon and potentially recycle particulate nutrients within and release them at a later date (Stevens & Quinton, 2009; Roberts *et al.*, 2011). Additionally, compiling understanding on multiple pollutants from studies that investigated individual pollutants is highly limited, because of slightly different experimental designs, soil types, land management or rainfall patterns. Therefore, the effect of mitigation measures on the mixture of all pollutants needs to be understood.

*This thesis took a multi-pollutant approach to assess the effects of grassland management practices on overall diffuse pollution.*

## **I. Lack of ecologically relevant data**

Water quality research is often only concerned with the continuum from soils to the delivery of pollutants to surface waters, and is often not linked with the ecological effects that those pollutant concentrations have in the water. Therefore, water quality research often does not present its data in ecologically relevant ways. Studying multiple pollutants together is one step in the right direction. It is widely acknowledged that it is not the availability of single nutrients, but the relative availability of multiple nutrients that are important both and it is recognized that biota respond differently to multiple stressors than to individual stressors (Harpole *et al.*, 2011). The acknowledgement of the relative importance of nutrients has challenged the general consensus that freshwater

systems are always P limited (Elser *et al.*, 2007; Conley *et al.*, 2009) and marine systems are always N limited (Elser *et al.*, 2007; Sylvan *et al.*, 2007; Pearl, 2009). Aquatic organisms have different elemental requirements (Elser & Urabe, 1999) and the C:N:P ratios therefore have effects on growth rates and reproduction (Sardanas *et al.*, 2012). For example, high availability of P in relation to C and N fits to the requirements of faster-growing biota, leading to higher abundances of fast-growing biota compared to slow-growing biota, which are adapted to utilize lower quality food resources (Elser *et al.*, 2000).

Additionally, research often reports average concentrations over the monitoring period, but aquatic biota experience the rapidly changing relative concentrations of multiple stressors (Bilotta *et al.*, 2010; Collins *et al.*, 2011; Thompson *et al.*, 2014). Therefore, the durations and frequencies of exposure should be reported. The timing of high and low concentrations relative to life stages is especially important (Bilotta *et al.*, 2010; Collins *et al.*, 2011). Blanket water quality guidelines fail to recognise such duration and timing of exposure relative to life stages (Bilotta *et al.*, 2012). High resolution research combined with multi-pollutant research can provide important information for receptor response studies, so that realistic concentrations and exposure times can be studied (Thompson *et al.*, 2014), and so that eventually more appropriate water quality standards can be set (Bilotta *et al.*, 2010; Collins *et al.*, 2011).

*This research took a multi-pollutant approach. Sediment and the total nutrients carbon, nitrogen and phosphorus and their ratios were studied through flow conditions and time.*

## **J. Sociological aspects**

It has been suggested that NVZ measures in the UK may not be effective, because the regulatory demands may have not changed farmer behaviour (Kay *et al.*, 2012). Farmers may have already managed their land within the restrictions of the NVZ regulations or did not comply due to the lack of rigorous policing (Kay *et al.*, 2012). Additionally, reductions in N inputs in the UK could generally be linked with price fluctuations in fertilizer costs rather than with the

designation of the NVZs (ADAS, 2011). Therefore, farmers' decision making and current land management has to be understood in detail.

Farmer decision making is mostly driven by economics and farmer participation in incentive schemes are mostly driven by the provided level of financial compensation (Wilson & Hart, 2000; Wilson, 2001; Nimmo-Smith *et al.*, 2007). Incentive-based schemes can only be effective if they have high levels of participation. Therefore, incentive schemes have to be set up to provide attractive levels of compensatory payments and to do so, the cost-effectiveness of mitigation management needs to be studied. Bailey *et al.* (2007) and Cardenas *et al.* (2011) are examples of such cost-effectiveness studies. Cost-effectiveness studies can be easily combined with diffuse pollution studies at the farm-scale, as this is the scale of decision making and the scale of socio-economic drivers (deGroot *et al.*, 2010). Results of such studies would be ideal tools to educate farmers. Farmers can relate to the scale of research and they may be encouraged by examples of how diffuse pollution can be reduced on single farms.

Based upon the issues reviewed herein, the following chapter outlines the aims and research questions of this study and details how they further the understanding of the effects of management practices on soil and water quality in intensively managed grasslands.

## **Chapter 3**

### **Thesis Structure, Aims and Specific Research Questions**

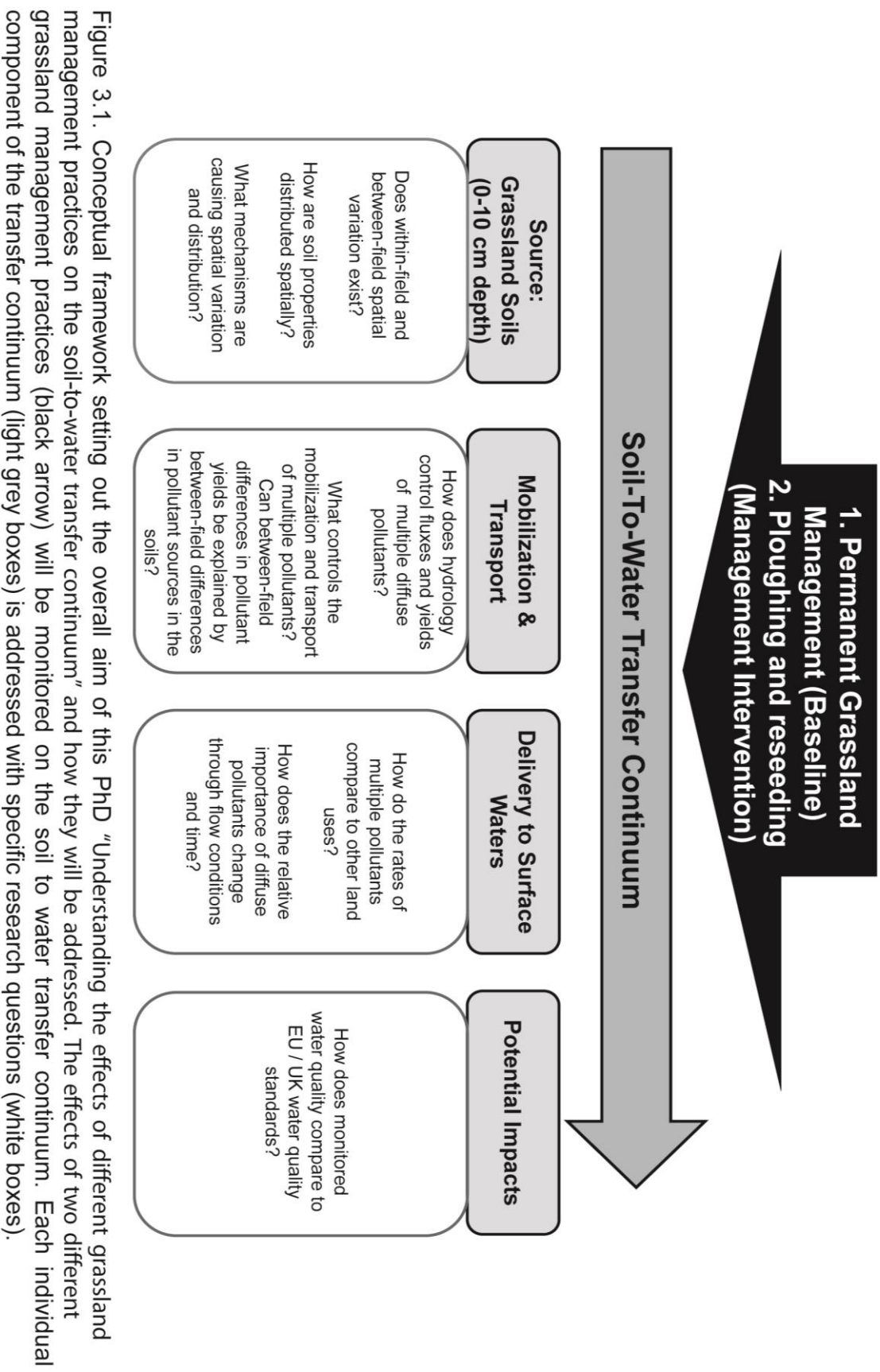
The overall aim of this thesis was to understand the effect of different grassland management practices on the soil to water transfer continuum. To address this aim, research was conducted on the newly established field- to farm-scale grassland experiment, the North Wyke Farm Platform in the south west of the UK, as a grassland case study. The North Wyke Farm Platform was established in 2010 as a grassland research platform managed as a realistic mixed beef and lamb production system ([www.rothamsted.ac.uk/farmplatform](http://www.rothamsted.ac.uk/farmplatform)). The Farm Platform is divided into three farmlets, on which the effects of different grassland management practices are contrasted. Each farmlet consists of five component fields, all of which are hydrologically isolated, so that water leaving the fields by sub-surface lateral or surface flow is channelled via French drains into flumes, where water quality and quantity is monitored with a range of automated or semi-automated monitoring equipment, monitoring continuously and at high temporal resolution (up to every 15 minutes) (Griffith *et al.*, 2013; Murray *et al.*, 2013).

The conceptual framework in figure 3.1 sets out the aims of this PhD research and how they were assessed. More specifically, this thesis first gained an understanding of the effects of conventional grassland management as a baseline, whilst the Farm Platform farmlets were all managed as conventional grasslands (Chapter 4, 5, and 6) (black arrow in figure 3.1). This period of baseline characterization was followed by a period of management intervention on the three farmlets; whereby one farmlet remained under conventional permanent grassland management as a control field, whilst the other two farmlets were ploughed and reseeded with different mixtures, a ryegrass-clover mixture and a new ryegrass variety (black arrow in figure 3.1). Chapters 7 and 8 contrasted the effects of management change on soil and water quality with respect to the baseline and the control farmlet. The effects of those grassland management practices on the soil-to-water continuum (dark grey arrow in figure 3.1) were quantified by measuring multiple grassland soil properties (bulk

density [BD], soil organic matter [SOM]), carbon [C], nitrogen [N] and phosphorus [P]) and monitoring hydrology and multiple agricultural diffuse pollutants (suspended sediment [SS], C, N and P) from grassland fields at high resolution. More specifically, the individual soil to water transfer continuum components (light grey boxes in figure 3.1) were addressed by specific research questions (white boxes in figure 3.1). The following paragraphs discuss the individual chapters of this thesis in more detail.

The spatial variation and the distribution of soil properties are poorly understood. Disregarding spatial variation increases uncertainty and therefore optimal sampling designs that capture spatial variation need to be identified prior to soil sampling campaigns. Additionally, management effects do not only alter mean soil properties but also their distribution. **Chapter 4** 'Understanding spatial variability of soil properties: a key step in establishing field- to farm-scale agro-ecosystem experiments' explored spatial variation and the distribution of soil properties in one field on the Farm Platform as a preparation for work conducted in further chapters, using geostatistical approaches. Additionally, multiple soil physical and chemical soil parameters are included, all of which are important for processes occurring throughout the soil to water continuum. This paper was published in the journal *Rapid Communications in Mass Spectrometry* in 2012 (**26**, 2413-2421, DOI: 10.1002/rcm.6336). This paper addressed the following specific research questions:

- **Question 4.1** Does spatial variation exist in an example intensively managed grassland field?
- **Question 4.2** How should future soil sampling be conducted on Farm Platform fields?
- **Question 4.3** How are soil properties distributed across this field?
- **Question 4.4** What could be controlling the spatial variation?



Grasslands have previously been understudied compared to other agricultural land use, multiple pollutants are rarely monitored together and the temporal resolution of measurements has been highly discontinuous. **Chapter 5** 'Intensive management in grassland causes diffuse water pollution' was written to address all of the above points by monitoring multiple pollutants at high temporal resolution (up to every 15 minutes). Additionally, focusing on the surface water quality at the field- or farm-scale provides advantages over interpreting water quality at the outflow of larger catchments. This paper was published in the *Journal of Environmental Quality* in 2014 (43, 2009-2023, DOI: 10.2134/jeq2014.04.0193). The specific research questions were:

- **Question 5.1** How do rates of sediment and macronutrient delivery from intensively managed grasslands compare to other agricultural land uses?
- **Question 5.2** What are the controlling factors on hydrology and how does hydrology affect fluxes and yields of sediment and macronutrients in intensively managed grasslands?
- **Question 5.3** How does the relative importance of diffuse pollutants from intensively managed grasslands change through flow conditions and time?
- **Question 5.4** How does water quality from intensively managed grasslands compare to EU and UK recommended water quality standards at the farm-scale?

Soil properties and water quality are often studied in isolation, even though they occur on the same soil to water continuum. Additionally, conventional management of a site has to be understood before the effects of management change can be reliably detected. **Chapter 6** 'Quantifying the field-scale variation of ecosystem structure and function within an intensively managed grassland' established within and between-field differences in soil properties as well as between-field differences in water quality in three conventional intensively managed grassland fields with the same short-term management (< 6 years ago), but different long-term management (management records going back 30 years). The overarching aim of this paper was to establish a robust baseline

understanding to which future work within this thesis and on the Farm Platform can be compared. The following specific research questions were addressed:

- **Question 6.1** Does within and between-field variation of soil properties exist in intensively managed grassland fields with the same short term management, but contrasting long-term management?
- **Question 6.2** Can between-field differences in water quality be explained by between-field differences in soil properties and between-field differences in site characteristics?
- **Question 6.3** Are those fields suitable for paired catchment / control / treatment field comparisons?

The implementation of the management scenarios followed the baseline period, keeping one farmlet as a conventional grassland control and ploughing and reseeded the treatment farmlets with different mixtures. The implementation of most sustainable intensification measures on grasslands includes ploughing and reseeded with for example innovative varieties of grass / legumes. Detailed monitoring of the effects of ploughing is required, because ploughing and reseeded is known to degrade soil quality and increase the losses of diffuse pollutants, which may compromise the long-term effectiveness of such intensification measures. Chapters 7 and 8 therefore quantify the effects of ploughing on the Farm Platform grassland fields. **Chapter 7** quantified ‘the effects of ploughing and reseeded grasslands on soil properties and spatial variation’. A novel aspect of this research was not only to quantify the effect of ploughing on soil properties in fields with different long-term management histories, but also on their spatial distribution. Additionally, post-ploughing effects can be more reliably identified because they can be seen in relation to the pre-characterized baseline soil properties and their distribution in earlier chapters. Chapter 7 addressed these specific questions:



- **Question 7.1** Can fields subjected to no management change act as controls, or is annual scale (year-on-year) variability in soil characteristics significant?
- **Question 7.2** Does ploughing and reseeded impose a significant change on soil physical properties and soil nutrient contents?
- **Question 7.3** Does ploughing and reseeded affect spatial variability and the spatial distribution of soil properties, which in turn may affect herbage yield and therefore productivity?

**Chapter 8** ‘The effects of ploughing and reseeded grasslands on sediment and macronutrient delivery to surface waters’ monitored multiple diffuse pollutants at high temporal resolution after ploughing. The post-ploughing time series were compared with those time-series monitored during the baseline and in the control field. The following specific questions were addressed:

- **Question 8.1** Can changes be detected between baseline water quality from permanent grasslands the previous year and post-ploughing and reseeded water quality?
- **Question 8.2** How do pollutant losses after ploughing and reseeded compare to a permanent grassland control and the permanent grassland baseline period?
- **Question 8.3** Have controls on fluxes and yields of sediment and macronutrients changed with respect to the baseline and what may be controlling pollutant losses after ploughing and reseeded?
- **Question 8.4** How does the relative importance of diffuse pollutants from ploughed and reseeded intensively managed grassland change through flow conditions and time?
- **Question 8.5** How does water quality from ploughed and reseeded grassland fields compare to EU / UK recommended water quality standards?

Each results chapter / paper is followed by short sections in *italics*, which connect the individual results chapters / papers. These sections identify questions that were raised by the results of the current chapter and lead the reader to the appropriate following chapters which addressed these questions. Additionally, these sections discuss how questions that were raised by previous chapters were answered in the current chapter / paper. To conclude this thesis, **chapter 9** summarises the key findings and their implications and proposes areas of further research.

## Chapter 4

### Understanding Spatial Variability of Soil Properties: a Key Step in Establishing Field to Farm-Scale Agro-Ecosystem

#### Experiments

This chapter was published as a stand-alone paper as: Peukert, S., Bol, R., Roberts, W., Macleod, C.J.A., Murray, P.J., Dixon, E.R., Brazier, R.E. 2012. *Rapid Communications in Mass Spectrometry*, **26**, 2413-2421.

#### **I. Abstract**

**RATIONALE.** Spatial variability of soil properties is poorly understood, despite its importance in designing appropriate experimental sampling strategies. As preparation for a farm-scale agro-ecosystem services monitoring project, the North Wyke Farm Platform, there was a need to assess the spatial variability of key soil chemical and physical properties.

**METHODS.** The field-scale spatial variability of soil chemical (total N, total C, soil organic matter), soil physical properties (bulk density and particle size distribution) and stable isotopes ( $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$ ) was described using geostatistical approaches in an intensively managed grassland.

**RESULTS.** The scales over which stable isotopes vary (ranges: 212 – 258 m) were larger than those of the total nutrients, soil organic matter and bulk density (ranges: 84 – 170 m). Two visually and statistically distinct areas of Great Field (north and south) were identified in terms of co-occurring high / low values of several soil properties.

**CONCLUSION.** The resulting patterns of spatial variability suggest lower spatial variability of stable isotopes than that of total nutrients, soil organic matter and bulk density. Future sampling regimes should be conducted in a grid with < 85 m distance between sampling locations to sufficiently capture spatial variability of the measured soil properties on the Farm Platform. Consultation of management histories of the sampled field revealed that it previously comprised

two fields with contrasting management histories, suggesting an effect of management legacy (> 5 years) on the patterns of spatial variability.

## II. Introduction

The spatial variability of soil properties is poorly understood (Bilotta *et al.*, 2007b). However, understanding spatial variability is very important prior to conducting any experimental sampling. Soil spatial variability is present over short distances not only in natural ecosystems, but also in agricultural systems with presumed uniform management and vegetation cover (Mariott *et al.*, 1997; Goovaerts, 1998). Spatial variability of soil properties may be related to the combined action of physical, chemical and biological processes as well as anthropogenic land use patterns, which vary in space and time across the landscape (Goovaerts, 1998). The scales of spatial variation may differ between different soil properties, because the processes that cause variability may occur at different scales, e.g. from the single plant scale to larger topographical scales (Goovaerts, 1998).

Understanding the patterns and processes of soil spatial variability is key to land based experiments from the plot to the landscape scale. Disregarding spatial variability may negatively affect the reliability of results in monitoring experiments and increase scientific uncertainty (Goovaerts, 1998). Therefore, exploring spatial variability and identifying appropriate sampling regimes that capture spatial variability sufficiently is required prior to planning and conducting experimental sampling (Webster *et al.*, 2006). Geostatistical analysis is a useful tool to describe the scales of spatial variability of different soil properties and suggest optimal sampling distances that sufficiently capture spatial variability.

This study is a preparation for a long-term agro-ecosystem monitoring experiment in intensively managed grassland: North Wyke Farm Platform. The soil properties of interest here were stable isotopes ( $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$ ) and a range of related soil chemical and physical properties that support the delivery of multiple ecosystem services. Spatial variability of  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  and their related soil chemical and physical properties has been described by several researchers across different scales, but not in intensively managed grasslands

(Bol *et al.*, 2008). Spatial isotopic variability can be explained by the spatial variability of plant matter inputs, the spatial variability of plant matter decomposition and agricultural management (Table 4.1).

Table 4.1. Factors affecting the spatial variability of stable isotopes ( $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$ ). Spatial isotopic variability can be explained by the spatial variability of both plant matter inputs into the soil and plant matter decomposition (first column), which are affected by several factors (second column) and altered by agricultural management (third column).

Causes of $^{13}\text{C}$ and $^{15}\text{N}$ spatial variability	Factors affecting the causes of $^{13}\text{C}$ and $^{15}\text{N}$ spatial variability	Alteration by agricultural land use
Spatial variability of plant matter input into the soil *	Amount of plant matter input Isotopic signature of plant tissue	Reduction of plant residue Alteration of crop cover/ fertiliser/manure application Alteration of crop cover over time
	Past and present inputs	
Spatial variability of plant matter decomposition	<u>Environmental factors: *<sup>1</sup></u>	
	Soil temperature	Altered by tillage
	Soil moisture	
	Topography (water movement altering soil moisture and nutrient distribution)	Artificial drainage
$\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ spatial variability	<u>Soil structure: *<sup>2</sup></u>	
	Clay content (protects organic matter from decomposition)	
	Bulk density (high bulk density causes anaerobic conditions and slows decomposition)	Soil compaction

\* (Bernoux *et al.*, 1998; Boutton *et al.*, 1998; Webster *et al.*, 2006; Bol *et al.*, 2008).

\*<sup>1</sup> (Sutherland *et al.*, 1991; van Kessel *et al.*, 1993; Amundson *et al.*, 2003; Biswas *et al.*, 2008).

\*<sup>2</sup> (Tiessen & Stewart, 1982; Selles *et al.*, 1986; Golchin *et al.*, 1995).

This study characterizes existing field-scale (6.7 ha) spatial isotopic variability in combination with a range of other chemical and physical soil surface (0 - 7.5 cm soil depth) properties in intensively managed temperate grassland. This study addressed the following specific research questions:

**Question 4.1** Does spatial variation exist in the following soil variables in an example intensively managed grassland field:  $\delta^{13}\text{C}$ ,  $\delta^{15}\text{N}$ , total N (TN), total C (TC), soil organic matter (SOM), bulk density (BD), soil particle size distribution (PSD)?

**Question 4.2** How should future soil sampling be conducted on the Farm Platform?

**Question 4.3** How are soil properties distributed across the field?

**Question 4.4** What is controlling spatial variation?

### III. Methods

#### A. Study Site

To characterize spatial variability, a series of soil chemical and soil physical properties were quantified on one field (Great Field) of the Rothamsted Research North Wyke Farm Platform, in south-west England (50.8 °N, 3.0 °W), Figure 4.1, 4.2a. The North Wyke Farm Platform (67 ha) is managed as a conventional intensive beef and sheep production system.

The sampling field, Great Field, is located on a south-east facing hillslope, which slopes down towards the centre-west of the field (Figure 4.2b). The North Wyke soils are a clay loam overlying shales of the Crackington formation with thin subsidiary sandstone bands (Bilotta *et al.*, 2008; Harrod & Hogan, 2008). There are three main soil types on Great Field, Hallsworth (USDA Aeric haplaquept, FAO Stagni-vertic cambisol), Halstow (USDA typic haplaquept, FAO dystic gleysol), and Denbigh (USDA Dystic eutrochrept, FAO Stagni-eutric cambisol), Figure 4.2b (Harrod & Hogan, 2008). These soil types represent the most common hydrological soil types in England and Wales, covering 13.9 % of the land area (Bilotta *et al.*, 2008). The long-term annual temperature and rainfall are 9.6 °C and 1056 mm, respectively, with a high proportion of rainfall occurring between October and March resulting in water logged soils and a large proportion of rainfall response occurring as saturation-excess overland flow (mean of 40 years) (Harrod & Hogan, 2008; Dixon *et al.*, 2010). The rainfall and annual temperature at North Wyke have

been described as typical of much of the intensively managed grassland areas in the UK (Smith & Trafford, 1976).

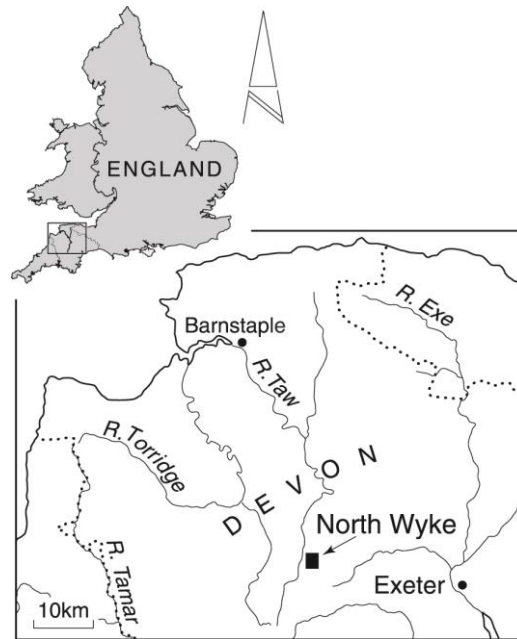


Figure 4.1. Location map of the sampling site, Rothamsted Research North Wyke, in south-west England.

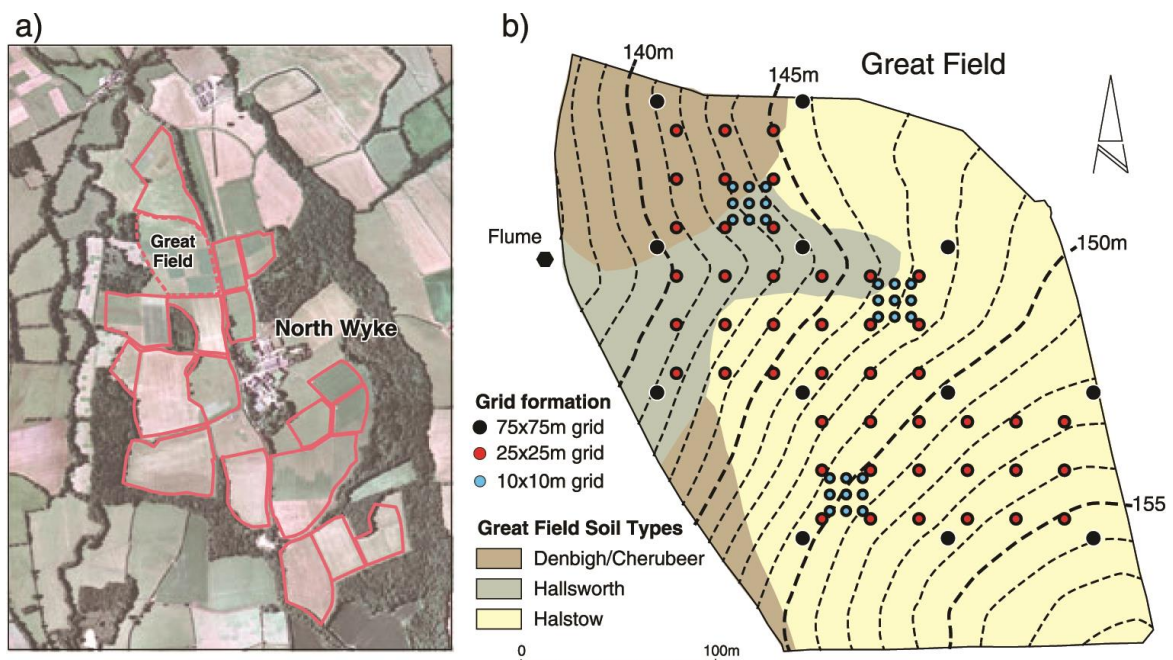


Figure 4.2. Description of the sampling site and the chosen sampling field: Great Field. a) Location of Great Field within the Farm Platform, Rothamsted Research, UK; b) Great Field topography, sloping towards the flume in the centre-west of the field, distribution of the three different soil types occurring on Great Field, and the nested sampling design.

## **B. Geostatistical sampling design**

To quantify spatial variability of soil characteristics, a nested geostatistical sampling pattern was chosen (Figure 4.2b). Determining the spatial structure of soil characteristics depends on the spatial scale at which they are quantified. Small scale measurements will only characterize small scale variability and large scale measurements large scale variability (Webster *et al.*, 2006; Turnbull *et al.*, 2010). Therefore, a nested sampling scheme allows the estimation of the contribution from all distances to the overall variability (Oliver & Webster, 1986; Oliver & Webster, 1991; Webster *et al.*, 2006).

To compare spatial variability across three different scales, 84 samples in total were taken: 12 samples at broad scale (75 x 75 m grid), 45 samples at intermediate scale (25 x 25 m grid), 27 samples at small scale (10 x 10 m grid) (Figure 4.2b). A hand-held GPS (Nomad Trimble, Sunnyvale, USA) was used to map and mark the sampling points.

## **C. Sample collection, preparation and analysis**

All measurements were taken in May 2011 from 0 - 7.5 cm soil depth, the soil layer which comprises the soil-plant-water processes of interest for the long-term monitoring project, such as organic matter dynamics, biological activity, surface runoff and erosion (Turnbull *et al.*, 2010). The topsoil layer is particularly important in grasslands, as this is the main rooting zone and therefore the area of intense biological activity. In some situations applied manure / fertilizers can accumulate on the surface without mixing down through the soil profile and may then be susceptible to run off (Schärer *et al.*, 2007).

With exception of bulk density (BD) samples, samples taken from each location were oven dried at 105 °C for 24 hours. Dried soils were then sieved through a 2 mm mesh and subsamples were taken for individual analyses. Soil organic matter (SOM) analysis was conducted by loss on ignition (LOI) by heating at 400 °C for 16 h (Davies, 1974). Particle size distribution (PSD) was determined by first treating the samples with H<sub>2</sub>O<sub>2</sub> to remove fine organic matter and then analyzing them on a Saturn DigiSizer™5200 (Micromeritics,



Dunstable, UK). For  $\delta^{13}\text{C}$ ,  $\delta^{15}\text{N}$ , total carbon (TC) and total nitrogen (TN) analysis, soil was finely ground and then analysed using an elemental analyser (NA2000, Carlo Erba Instruments, Milan, Italy) linked to a SerCon 20 - 22 isotope ratio mass spectrometer (SerCon Ltd, Crewe, UK). For bulk density (BD), a known volume of soil ( $249.54 \text{ cm}^3$ ) was taken using metal rings with 75 mm diameter and 55 mm depth. Soil samples were then weighed and the volume of stones and roots ( $> 2 \text{ mm}$ ) determined and subtracted from the total volume of the metal ring. Soil was then oven dried at  $85 \text{ }^\circ\text{C}$  until constant mass was reached. Bulk density ( $D_b$ ) was then calculated using the formula:

$$D_b = \frac{M_d}{V}$$

where,  $M_d$  is the mass (g) of oven-dried soil and  $V(\text{cm}^3)$  is the volume of soil. Nutrient and SOM storages ( $\text{g cm}^{-2}$ ) were calculated by multiplying the total nutrient and SOM values with BD for 7.5 cm soil depth. Elevation (m) for each sampling point was derived from a photogrammetrical 5m Bluesky digital elevation model (DEM), as a proxy for water movement and resulting soil moisture (Armstrong & Garwood, 1991).

#### **D. Statistical analysis**

To investigate the spatial structure of the measured soil properties (**Question 4.1**), geostatistical analysis was carried out by measuring the average dissimilarity between data separated by a given vector ( $h$ ). The scale of spatial dependence was calculated by computing semi-variograms  $\gamma(h)$ , half the average of squared differences between data separated by the lag distance vector  $h$ , with  $r$  as the number of pairs of samples points separated by distance  $h$  for the property  $z$  (Oliver *et al.*, 1989b; Oliver & Webster, 1991; Goovaerts, 1998; 1999; Turnbull *et al.*, 2010). Before carrying out geostatistical analysis, exploratory data analysis was carried out to test for normal distribution and outliers in the dataset. All data were standardized by log and normal score transformation to enable a comparison between variables with differing units (Turnbull *et al.*, 2010). Omnidirectional experimental variograms were

computed using Variowin2.21 (Pantier, Springer, New York), using regular lag distances of 5 m up to the maximum distance of 300 m.

To identify optimal future sampling distances (**Question 4.2**), the ranges of the computed semi-variograms were used. The range described the distance between sampling points at which maximum variability is captured (Oliver *et al.*, 1989a).

Ordinary kriging was conducted with ArcGIS 10 (ESRI, Redlands, California) to visualise variability and predict soil characteristics at unsampled locations in the form of surface prediction maps (**Question 4.3**) (Oliver & Webster, 1990; Goovaerts, 1999). Ordinary kriging is a form of spatial interpolation, whereby mathematical models are first fitted to the values on the experimental semi-variograms (e.g. spherical, gaussian) and the model is then used to predict values of the continuous soil attributes at unsampled locations. By using these models, kriging takes into account the spatial arrangement of the sampling points by assigning different weighting to sample points. Points that are nearer to the location to be predicted are assigned larger weights than points that are further away (Oliver & Webster, 1990).

To understand the underlying mechanisms of spatial variability (**Question 4.4**), Pearson's correlation coefficient ( $r$ ) (GenStat 14<sup>th</sup> edition, VSN International, Hemel Hempstead, UK) was used to test the strength of correlation between individual soil properties. Correlations were considered as significant at the  $p < 0.05$  level.

## **IV. RESULTS & DISCUSSION**

### **A. General information on measured soil variables**

The mean and standard deviation values for all measured soil variables are summarized in table 4.2. The stable isotope values are in line with previous stable isotope experiments (Dixon *et al.*, 2010).

Table 4.2. Summary of the mean and standard deviation (StDev) values of the measured soil properties.

Measured Soil Property	Measured values: Mean $\pm$ StDev
$\delta^{13}\text{C}$ (‰)	-27.18 $\pm$ 0.99
$\delta^{15}\text{N}$ (‰)	5.31 $\pm$ 0.47
Total Carbon (g kg <sup>-1</sup> )	52.8 $\pm$ 16.7
Total Nitrogen (g kg <sup>-1</sup> )	5.3 $\pm$ 1.4
Soil Organic Matter (g kg <sup>-1</sup> )	110.1 $\pm$ 31.4
Bulk density (g cm <sup>3</sup> )	0.95 $\pm$ 0.16
Total Carbon Storage (mg cm <sup>-2</sup> )*	364 $\pm$ 77.6
Total Nitrogen Storage (mg cm <sup>-2</sup> )*	36.8 $\pm$ 6.7
Organic matter storage (mg cm <sup>-2</sup> )*	762 $\pm$ 24.0
% soil < 2 $\mu\text{m}$	20.0 $\pm$ 3.6
% soil 2 - 63 $\mu\text{m}$	72.7 $\pm$ 2.5
% soil > 63 $\mu\text{m}$	7.1 $\pm$ 2.5

\* for 7.5 cm soil depth

## B. Spatial variability of soil characteristics

The first aim of this study was to describe the spatial variability of the measured soil properties. The range of autocorrelation indicates the distance (m) below which most variability occurs and above which variability remains the same (Oliver *et al.*, 1989b; a; Oliver & Webster, 1991; Goovaerts, 1998; 1999). The semivariograms showed that the ranges of autocorrelation varied between soil properties (Table 4.3). The range of autocorrelation of  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  was 212 m and 258 m, respectively. These ranges were similar with the ranges at which C and N storage were autocorrelated, at 235 m and 278 m, respectively. However, other soil properties show smaller ranges than those of stable isotopes. BD, SOM, TC and TN were autocorrelated at 84 m, 113 m, 119 m and 170 m, respectively. Additionally, PSD showed varied ranges of autocorrelation, 44m for soil < 2  $\mu\text{m}$ , 71 m for soil 2 - 63  $\mu\text{m}$  and 142 m for soil > 63  $\mu\text{m}$ .

The lower the range distance, the higher is the spatial variability, because the distance between two sampling points over which all variability in the

dataset occurs is small. Therefore, BD (range = 84 m) and SOM (range = 113 m) have higher spatial variability compared to the stable isotopes  $\delta^{13}\text{C}$  (range = 212 m) and  $\delta^{15}\text{N}$  (range = 258 m).

Overall, spatial variability for stable isotopes was smaller than that of their associated total nutrients in Great Field. This has been reported before for the case of  $\delta^{15}\text{N}$  in relation to total N and organic C (Selles *et al.*, 1986). Variability of BD and SOM occur at similar spatial scales, up to 84 m, larger spatial variability than that of stable isotopes in Great Field.

Here, spatial variability of the measured soil properties was lower than that reported by other studies in different environments: in a Scottish upland grassland (range = 13.5 m) (Mariott *et al.*, 1997) and a natural semi-arid region (range = 1.73 m) (Turnbull *et al.*, 2010). The lower spatial variability in Great Field compared to these other studies may be explained by the long history of intensively managed agriculture, which homogenized soil characteristics in contrast to a shorter and less intensive agricultural influence in the Scottish upland grassland and no homogenization in the natural semi-arid region.

Table 4.3. Summary of geostatistical analysis.

	Nugget values	Range values (m)	Partial Sill values
$\delta^{13}\text{C}$ (‰)	0.72	212	1.40
$\delta^{15}\text{N}$ (‰)	0.60	258	1.60
Total Carbon ( $\text{g kg}^{-1}$ )	0.17	119	1.20
Total Nitrogen ( $\text{g kg}^{-1}$ )	0.33	170	1.30
Soil Organic Matter ( $\text{g kg}^{-1}$ )	0.18	113	1.20
Bulk density ( $\text{g cm}^3$ )	0.27	84	1.10
Total Carbon Storage ( $\text{mg cm}^{-2}$ )*	0.54	235	1.50
Total Nitrogen Storage ( $\text{mg cm}^{-2}$ )*	0.65	278	1.60
Organic matter storage ( $\text{mg cm}^{-2}$ )*	0.43	95	1.20
% soil < 2 $\mu\text{m}$	0.92	44	1.10
% soil 2 - 63 $\mu\text{m}$	0.58	71	1.00
% soil > 63 $\mu\text{m}$	0.43	142	1.30

\* for 7.5 cm soil depth

### **C. Future sampling resolution**

Our second aim was to inform future optimal sampling distances at the farm-scale. The range of autocorrelation is the distance (m) between any two locations at which further increase in distance does not result in further increases in variability (Oliver *et al.*, 1989b; a; Oliver & Webster, 1991; Goovaerts, 1998; 1999). The ranges of autocorrelation provide the basis for designing optimal sampling schemes, because the ranges describe the largest sampling distance that can be chosen between sampling points, while the maximum variability is still sufficiently captured. In case of a regular sampling grid, the larger the cell sizes are that can be chosen, the smaller is the number of required samples, reducing sampling effort and cost (Oliver *et al.*, 1989a; Oliver & Webster, 1991). The varying scales of spatial variability found here for the measured soil properties mean that the number of samples varies, which are required to capture spatial variability sufficiently for these properties in future sampling regimes.

For the farm-scale Farm Platform and other sampling sites in similar soil, climatic and management conditions, a 210 m grid would describe spatial variability sufficiently both for the stable isotopes and for nutrient storage. In contrast, an optimal sampling regime for SOM and BD would require a smaller scale of approximately, 84 m grid, to capture spatial variability sufficiently. When establishing a sampling grid for all soil properties, the smallest range in the dataset determines the cell sizes, in the case of this study it is BD with 84 m.

### **D. Visualization of spatial variability: prediction of soil characteristics at unsampled locations**

The third aim of this study was to extrapolate spatial variability at the field-scale by predicting values of soil characteristics at unsampled locations. A selection of kriged surfaces are shown in figure 4.3. Note that the predictions made by kriging are more certain the closer the predicted location is to the sampled locations (Oliver *et al.*, 1989a). In locations where SOM, total nutrients, nutrient storages and  $\delta^{15}\text{N}$  values are high, BD and  $\delta^{13}\text{C}$  values are low. Two visually

distinct areas of co-occurring high / low values of several soil properties can be identified: in the north of the field: SOM, total nutrients, nutrient storages and  $\delta^{15}\text{N}$  values are high and BD and  $\delta^{13}\text{C}$  values are low, whereas the opposite pattern occurs in the south of the field. Figure 4.3 shows a dotted line dividing these two visibly different parts of the field. The kriged surfaces for PSD show no different patterns of variability between north and south. The kriged surface for % soil < 2  $\mu\text{m}$  is shown in Figure 4.3i.

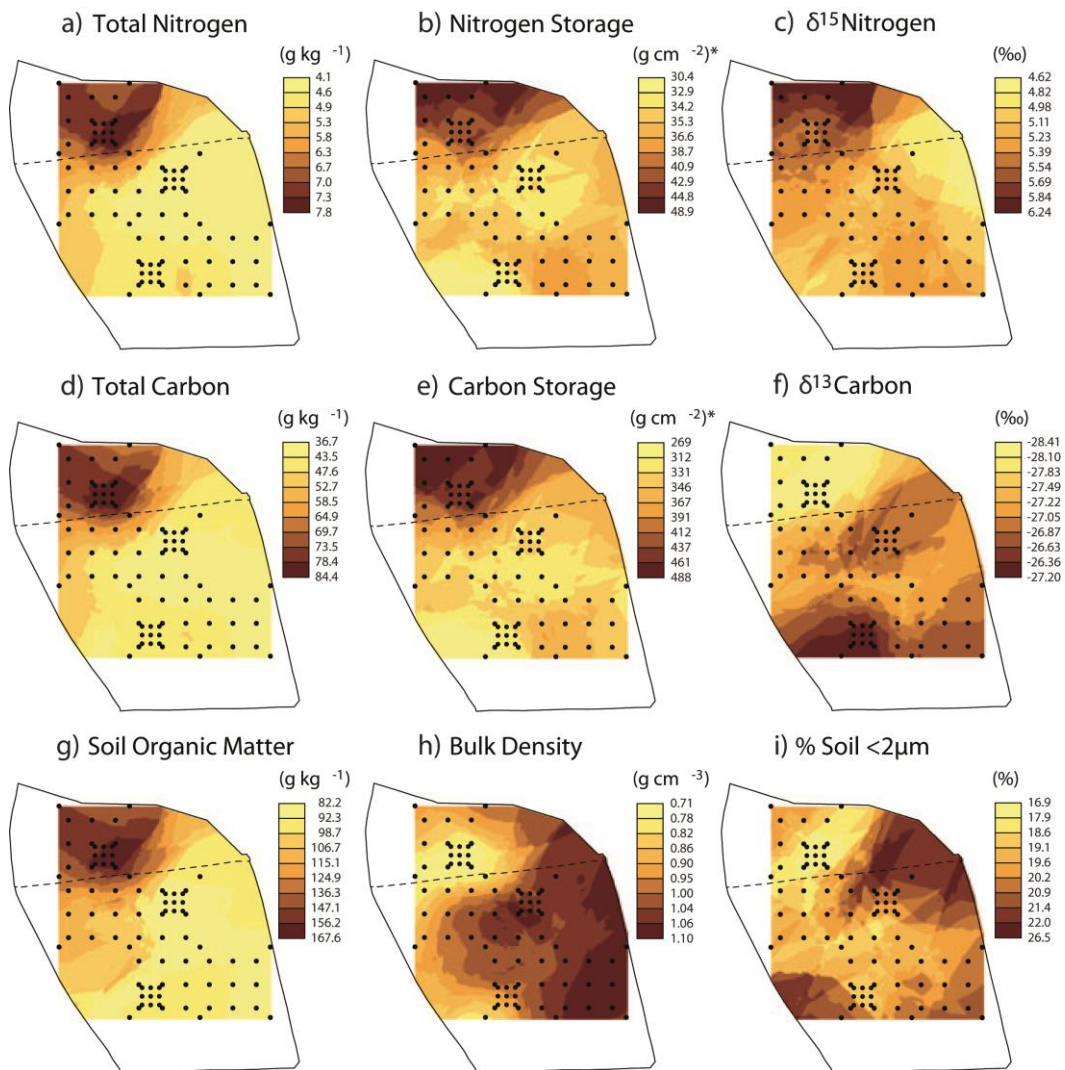


Figure 4.3. Kriged surfaces for a selection of soil properties a - i (0 - 7.5 cm soil depth). The colour contours refer to value categories for each soil property. Dots illustrate the nested geostatistical sampling design. The horizontal dotted line through the field shows the line dividing the two visibly different parts of the field.

\* for 7.5 cm soil depth

## E. What controls spatial variability?

The fourth aim was to discuss possible underlying mechanisms controlling the spatial variation of the measured soil properties. This initial study can only point out processes that may be responsible for the spatial variability found.

Pearson's correlations were used to indicate which soil properties are related, or may be affected by common underlying processes, a summary is given in table 4.4. The correlation results confirm the similar / opposing patterns that are visualized in the kriged surfaces, as well as the different patterns of PSD in relation to the other soil properties (Figure 4.3). Soil organic matter, total nutrients, nutrient storages and  $\delta^{15}\text{N}$  values were positively correlated with each other, but negatively correlated with BD and  $\delta^{13}\text{C}$ . Bulk density and  $\delta^{13}\text{C}$  were positively correlated. There was no significant correlation between PSD and any other soil variable despite the % of soil < 2  $\mu\text{m}$  being reported to protect SOM and total nutrients from microbial decomposition by several studies (Tiessen & Stewart, 1982; Golchin *et al.*, 1995). Furthermore, elevation was negatively correlated with SOM, total nutrients, nutrient storages and  $\delta^{15}\text{N}$ , but positively correlated with BD and  $\delta^{13}\text{C}$ .

Table 4.4. Summary of Pearson's correlations between measured soil properties\*. R values are only given for significant ( $P < 0.05$ ) correlations ( $n = 84$ ). Particle size distribution measurements (% soil < 2  $\mu\text{m}$ , % soil 2 - 63  $\mu\text{m}$ , % soil > 63  $\mu\text{m}$ ) were not significantly correlated with any other soil property, except each other and % soil 2 - 63  $\mu\text{m}$  and % soil > 63  $\mu\text{m}$  with BD (0.24, -0.33, respectively), % soil 2 - 63  $\mu\text{m}$  with SOM (0.33).

	BD	SOM	SOM Storage	TC	TC Storage	$\delta^{13}\text{C}$	TN	TN Storage	$\delta^{15}\text{N}$
SOM	-0.64								
SOM Storage		0.74							
TC	-0.67	0.94	0.62						
TC Storage		0.73	0.86	0.79					
$\delta^{13}\text{C}$	0.29	-0.63	-0.55	-0.61	-0.59				
TN	-0.64	0.91	0.62	0.52	0.7848	-0.61			
TN Storage		0.56	0.83	0.61	0.87	-0.53	0.68		
$\delta^{15}\text{N}$	-0.30	0.47	0.47	0.51	0.48	-0.48	0.47	0.47	
Elevation	0.51	-0.57	-0.32	-0.57	-0.38	0.4	-0.54	-0.23	-0.3

\* BD, Bulk density; SOM, Soil organic matter; TC, Total carbon; TN, Total nitrogen

Soil organic matter can be considered as the key factor driving most other soil properties (Foth & Turk, 1972; Blume *et al.*, 2010). Soil organic matter affects soil TC and TN content of the soil as they are the main constituents of SOM (Foth & Turk, 1972). SOM also affects soil structure, particularly BD, which subsequently influences nutrient storages (Foth & Turk, 1972; Blume *et al.*, 2010). The turnover of SOM then affects stable isotope values. However, the spatial variability of decomposition rates may not explain the stable isotope values here. Unlike in this study,  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  are known to be generally positively correlated due to similar discrimination against  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  throughout SOM turnover (van Kessel *et al.*, 1993; Hogberg, 1997; Gerzebeck *et al.*, 2001; Bol *et al.*, 2005). Furthermore, elevation may influence SOM distribution and subsequently the distribution of the other soil properties. Elevation can be considered as a proxy for water movement through the field: rain falling in higher elevations will move as throughflow or overland flow to lower elevations (Armstrong & Garwood, 1991). This water may then transport SOM and total nutrients and deposit these in lower elevation areas, leading to SOM and nutrient enrichment in these areas. In addition, downslope water movement may result in differing moisture contents (wetter areas at lower elevations in the field). Soil moisture conditions alter the decomposition processes of the C and N cycle differently, which may explain the negative correlation between the stable isotopes found here (Sutherland *et al.*, 1991; Amundson *et al.*, 2003; Biswas *et al.*, 2008).

To statistically test for differences between the two visually distinctive areas of co-occurring high / low values of several soil properties shown in the kriging maps (Figure 4.3), two sided t-tests were conducted (GenStat 14<sup>th</sup> edition, VSN International, Hemel Hempstead, UK). The t-tests confirmed the visual difference between the soil properties measured in the northern and the southern part of Great Field as well as a difference in elevation: significantly higher elevations in the southern than the northern part of the field (Table 4.5).



Table 4.5. Descriptive statistics of the measured soil properties for the whole of Great Field (n = 84), mean and standard deviation (Stdev) values of the southern (n = 63) and the northern part (n = 21) and the difference between those (n = 84). Significant differences are underlined.

Measured Soil Property	Southern Part: Mean $\pm$ Stdev values	Northern Part: Mean $\pm$ Stdev values	Sig. difference between north and south
$\delta^{13}\text{C}$ (‰)	-26.86 $\pm$ 0.88	-28.13 $\pm$ 0.64	<u>P &lt; 0.001</u>
$\delta^{15}\text{N}$ (‰)	5.18 $\pm$ 0.42	5.72 $\pm$ 0.38	<u>P &lt; 0.001</u>
Total Carbon (g kg <sup>-1</sup> )	44.4 $\pm$ 7.0	78.1 $\pm$ 10.4	<u>P &lt; 0.001</u>
Total Nitrogen (g kg <sup>-1</sup> )	4.5 $\pm$ 0.6	7.4 $\pm$ 0.4	<u>P &lt; 0.001</u>
Soil Organic Matter (g kg <sup>-1</sup> )	95.2 $\pm$ 17.8	154.0 $\pm$ 17.2	<u>P &lt; 0.001</u>
Bulk density (g cm <sup>3</sup> )	1.0 $\pm$ 0.13	0.8 $\pm$ 0.13	<u>P &lt; 0.001</u>
Total Carbon Storage (mg cm <sup>-2</sup> )*	331 $\pm$ 52.4	461 $\pm$ 56.7	<u>P &lt; 0.001</u>
Total Nitrogen Storage (mg cm <sup>-2</sup> )*	34.5 $\pm$ 4.8	43.7 $\pm$ 6.9	<u>P &lt; 0.001</u>
Organic matter storage (mg cm <sup>-2</sup> )*	710 $\pm$ 133.2	917 $\pm$ 106.4	<u>P &lt; 0.001</u>
% soil < 2 $\mu\text{m}$	20.4 $\pm$ 3.8	18.9 $\pm$ 2.7	P = 0.108
% soil 2 - 63 $\mu\text{m}$	72.7 $\pm$ 2.8	72.5 $\pm$ 1.3	P = 0.668
% soil > 63 $\mu\text{m}$	6.6 $\pm$ 2.4	8.4 $\pm$ 2.3	<u>P = 0.003</u>
Elevation (m)	147 $\pm$ 3.8	141 $\pm$ 1.4	<u>P &lt; 0.001</u>

\* for 7.5 cm soil depth

A consultation of the past farm management records revealed that the area, which is now Great Field, previously comprised two fields (north 1.5 ha and south 5.55 ha) with contrasting management histories. The dividing line drawn in figure 4.3 corresponds to the past dividing field boundary. The northern part has been managed as permanent grassland for 25 years, whereas the southern part has been ploughed approximately three times in the last 25 years and was cropped with winter-barley in 2007 followed by plough-reseed with a ryegrass / clover mixture. In terms of vegetation cover, both parts of the field are classified as the same National Vegetation Classification (NVC) category: 'MG7 *Lolium perenne* *Poa trivialis* and related grasslands', but the southern part has a higher clover content (*Trifolium repens*), less dense vegetation cover and approximately double the sward height compared to the northern part. These management histories are representative of normal management cycles of intensive grassland management (Bilotta *et al.*, 2007a; Butler & Haygarth, 2007).

Different past management in combination with differing soil moisture conditions as a result of water movement to lower elevations may have affected SOM, BD, total nutrient content similarly while affecting stable isotope contents differently. Management legacy may go back at least 5 years as the major difference in land management in the two parts of Great Field occurred 5 years ago. There may be one or a combination of the following mechanisms responsible for the differences in the measured soil properties in the two parts of Great field: elevation and resulting water movement (Armstrong & Garwood, 1991; Liu *et al.*, 2007), different nutrient management (Bruck *et al.*, 2001; Choi *et al.*, 2003a; Choi *et al.*, 2003b; Bol *et al.*, 2005; Watzka *et al.*, 2006; Senbayram *et al.*, 2008; Kriszan *et al.*, 2009), different soil physical management (Haynes & Naidu, 1998; Paustein *et al.*, 2000; Freibauer *et al.*, 2004; Koch & Stockfisch, 2006; Liu *et al.*, 2006; Biswas *et al.*, 2008), different rates of N<sub>2</sub> fixation (Shearer & Kohl, 1986) and differences in the isotopic signature of the past vegetation cover (Bol *et al.*, 2005). The mechanisms by which these factors may have affected soil property values in the two parts of the field are shown in table 4.6.

Further work is required to gain more understanding of the underlying processes, which is one of the main aims of the long-term Farm Platform project. Studying spatial variability has shown to be very useful: patterns of spatial variability were found that had not been anticipated before, like the previously divided parts of Great Field and the importance of past management legacy in contributing to soil chemical and physical status. Similar time lags between agricultural management and soil status and have previously been reported by several authors (Addiscott, 1988; Stalnacke *et al.*, 2003; Burt *et al.*, 2008). These time lags mean that short-term studies (less than at least 5 years) analyzing the effects of agricultural management change on soil properties have to be interpreted very carefully and past management has to be taken into account. For the Farm Platform, the time lag of at least 5 years indicates how long it may take to see effects of the new management that is planned in 2013. Furthermore, the results here emphasize the importance of detailed spatial characterization of baseline soil status and of understanding the underlying processes contributing to the observed spatial patterns and functions when establishing field to farm-scale experiments.

## V. CONCLUSIONS

Soil spatial variability in one of the large North Wyke Farm Platform grassland fields revealed a lower spatial variability in stable isotopes ( $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$ ) than their respective total nutrients, SOM and BD (**Question 4.1**). The patterns of spatial variability suggests that for BD a minimum sampling distance of 85 m is sufficient to capture spatial variability. The minimum sampling distance can be increased to 110 m when sampling soil chemical properties. These suggested sampling distances allow researchers to optimize future sampling effort on the Farm Platform (**Question 4.2**). This study has underlined the importance of characterizing spatial variability and discussing possible mechanisms that may be controlling key soil chemical and physical properties: Field-scale prediction maps (**Question 4.3**) have uncovered information that was not anticipated: the differences between the northern and the southern part of the field being potentially caused by differing management history going back at least 5 years (**Question 4.4**). These findings have important implications, not only for future sampling on the Farm Platform and comparable sites but also in showing that recent and historical management must be taken into consideration when establishing field to farm-scale agro-ecosystem experiments.

Table 4.6. Summary of the mechanisms that may be responsible for the differences in the measured soil properties in the two parts of Great field. Mechanisms (first column) and processes by which the opposing values in the southern (second column) and the northern (third column) part of the field may be caused.

<b>Potential mechanisms responsible</b>	<b><u>South: barley-plough-reseed</u></b>	<b><u>North: permanent grassland</u></b>
Elevation-water movement	High BD, $\delta^{13}\text{C}$ values Low SOM, TC, TN, $\delta^{15}\text{N}$ High elevation	High SOM, TN, TC, $\delta^{15}\text{N}$ values Low BD, $\delta^{13}\text{C}$ values Lower elevation
Nutrient management	<u>Water movement away from the southern part:</u> SOM, TC, TN washed away* lower soil moisture content → reduced denitrification (low $\delta^{15}\text{N}$ )* <sup>1</sup>	<u>Water movement into the northern part:</u> transport and deposition of SOM, TC, TN* higher soil moisture → increases denitrification → $\delta^{15}\text{N}$ enrichment* <sup>1</sup>
Soil physical management	<u>Fertilised field: inorganic N inputs</u> fertiliser contains no SOM, TC* <sup>2</sup> increased plant photosynthetic activity- $\delta^{13}\text{C}$ enrichment* <sup>4</sup>	<u>Grazed field: manure inputs</u> manure contains high SOM, TC, $\delta^{15}\text{N}$ * <sup>2 *3</sup>
$\text{N}_2$ fixation	<u>Ploughed in 2007</u> breaks soil aggregates, increases soil aeration- exposes SOM → increased C decomposition → $\delta^{13}\text{C}$ enrichment lower soil moisture * <sup>6</sup>	<u>Permanent grassland</u> SOM protection and no soil mixing → surface accumulation of nutrients* <sup>5</sup> higher soil moisture content → increased denitrification → $\delta^{15}\text{N}$ enrichment
Isotopic signature of past vegetation	<u>More clover → more <math>\text{N}_2</math> fixation</u> $\text{N}_2$ fixed by clover ( $\delta^{15}\text{N}$ signatures= 0)* <sup>7</sup>	<u>Less clover cover → less <math>\text{N}_2</math> fixation</u> higher $\delta^{15}\text{N}$ signatures of overlying vegetation
	<u>Past vegetation: barley</u> higher $\delta^{13}\text{C}$ signature and lower $\delta^{15}\text{N}$ signature of barley* <sup>8</sup>	<u>Past vegetation: grass</u> lower $\delta^{13}\text{C}$ and higher $\delta^{15}\text{N}$ signature of grass* <sup>8</sup>

\* Bol *et al.*, 2005; Senbayram *et al.*, 2008

\*<sup>1</sup> Choi *et al.*, 2003; Choi *et al.*, 2003a; Watzka *et al.*, 2006; Kriszan *et al.*, 2009

\*<sup>2</sup> Bruck *et al.*, 2001; Senbayram *et al.*, 2008

\*<sup>3</sup> Schaerer *et al.*, 2007; Liu *et al.*, 2006; Koch & Stockfish, 2006; Freibauer *et al.*, 2004; Paustein *et al.*, 2000

\*<sup>4</sup> Biswas *et al.*, 1991; Liu *et al.*, 2006; Freibauer *et al.*, 2004; Haynes & Naidu, 1998

\*<sup>5</sup> Shearer *et al.*, 1986

\*<sup>6</sup> Bol *et al.*, 2005

*This chapter showed that there is significant spatial variation in this example intensively managed grassland field (Great Field) and that this variation has to be accounted for when sampling soils. When exploring possible underlying mechanisms that are causing the spatial distribution of soil properties, significant differences between two parts of the field, it was revealed that Great Field was previously comprised of two fields, with contrasting past management (up to 5 years ago). The different past management was identified as the driver for spatial variation in this field. Whilst this is an important finding, which could not have been detected without such high resolution spatial sampling and without consultation of current as well as past farm management records, it raises the question whether Great Field is an appropriate example of intensively managed grassland fields in terms of a) ranges of spatial variation and therefore optimal sampling strategies and b) possible underlying mechanisms controlling spatial variation. Therefore, to address these issues, chapter 6 employs the same nested sampling design in the following summer on Great Field again as well as on two other intensively managed grassland fields on the Farm Platform.*

*Semivariogram models in this chapter were fitted by eye with some limited help of statistics within the Variowin program and kriging was conducted in ArcGIS. Whilst the method of model fitting has proven to work relatively reliably (Oliver & Webster, 2014), and many papers use ArcGIS for kriging (e.g. Glendell et al., 2014), there are more reliable methods available (Oliver and Webster, 2014). Uncertainty as to whether the methods that were used in this chapter were reliable arose during this PhD. Because this chapter had already been published, it was kept as it was published, but the following chapters that employ geostatistics (Chapter 6 and 7) use improved methods. Uncertainty about the methods used in this chapter raise the following questions, a) whether the north-south pattern that was found in this chapter is in fact an underlying trend in the data, b) whether the possible underlying trend in the datasets may subsequently compromise the ranges of spatial variation that were presented in this chapter and c) whether the surface prediction maps that were created by using default settings in ArcGIS are reliable. Therefore, chapter 6 and 7 use improved geostatistical methods and address these issues by using a statistical package in GenStat specifically developed for fitting semivariogram models reliably by testing the model of best fit. The identified semivariogram model of*

*best fit is then used for kriging and provides statistical cross-validation of the kriging (Oliver & Webster, 2014). The kriged values are then exported into ArcGIS for mapping.*

*Additionally, results in this chapter also raised the question of how long the effects of the past management differences will remain or what sort of management intervention would homogenize the field. Therefore, Great Field is firstly sampled in the same way again in the following year when the current management was still the same (Chapter 6) and secondly sampled again two years after this sampling period, when the entire field had been ploughed and reseeded (Chapter 7).*

*The next chapter (Chapter 5) quantified hydrological characteristics and the fluvial fluxes of suspended sediment and macronutrients in three intensively managed grassland fields.*

## Chapter 5

### Intensive Management in Grasslands Causes Diffuse Water Pollution at the Farm-Scale

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#### **I. Abstract**

Arable land-use is generally assumed to be the largest contributor to agricultural diffuse pollution. This study adds to the growing evidence that conventional temperate intensively managed lowland grasslands contribute significantly to soil erosion and diffuse pollution rates.

This is the first grassland study to monitor hydrological characteristics and multiple pollutant fluxes (suspended sediment [SS] and the macronutrients: total oxidized nitrogen-N [TON<sub>N</sub>], total phosphorus [TP] and total carbon [TC]) at high temporal resolution (monitoring up to every 15 minutes) over one year. Monitoring was conducted across three fields (6.5 - 7.5 ha) on the North Wyke Farm Platform, UK. The estimated annual erosion rates (up to 527.4 kg ha<sup>-1</sup>), TP losses (up to 0.9 kg ha<sup>-1</sup>) and TC losses (up to 179 kg ha<sup>-1</sup>) were similar to or exceeded the losses reported for other grassland, mixed land-use and arable sites. TON<sub>N</sub> annual yields (up to 3 kg ha<sup>-1</sup>) were less than arable land use fluxes and earlier grassland N studies; an important result as the study site is situated within a Nitrate Vulnerable Zone. The high-resolution monitoring allowed detailed 'system's functioning' understanding of hydrological processes, mobilization-transport pathways of individual pollutants and the changes of the relative importance of diffuse pollutants through flow conditions and time. SS and TP concentrations frequently exceeded water quality guidelines recommended by the European Freshwater Fisheries Directive (25 mg L<sup>-1</sup>) and the European Water Framework Directive (0.04 mg soluble reactive P L<sup>-1</sup>),

suggesting that intensively managed grasslands pose a significant threat to receiving surface waters.

Such sediment and nutrient losses from intensively managed grasslands should be acknowledged in land management guidelines and advice for future compliance with surface water quality standards.

## **II. Introduction**

Approximately 40 % of water courses in the USA (Evans-White *et al.*, 2013), more than half of all European water courses (EEA, 2012) and two thirds of all surface waters in the UK do not reach drinking water status or good ecological status (McGonigle *et al.*, 2012). In the UK alone, diffuse agricultural pollution contributes to water quality failures as the source for 72 % of sediment and high proportions of macronutrients: 81 % of nitrogen and 31 % of phosphorus (Zhang *et al.*, 2014). Carbon is not yet included in water quality guidelines in terms of freshwater ecosystem health, but rising carbon concentrations in surface waters are known to have an impact on water quality (Edwards *et al.*, 2008). These pollutants cause human health problems (polluted drinking and bathing water) and high economic costs (Parris, 2011). Ecological deterioration of water courses, due to eutrophication, is also a problem: increased occurrence of algal blooms with subsequent dissolved oxygen depletion, reduced light availability and perturbation of the balance of organisms, generally associated with a decline in invertebrate and fish species (Bilotta *et al.*, 2008).

The effects of different agricultural land uses on pollutant sources, mobilization, transfer and delivery to water bodies need to be understood in detail (Haygarth *et al.*, 2005), to support the need for sustainable intensification of agriculture, whilst minimizing diffuse pollution, and eventually to identify best management practices (BMPs). However, gaining such knowledge has been constrained for several reasons, discussed below.

First, grasslands managed for dairy and meat production, despite covering more than half (65 %) of the agricultural land in the UK and extensive areas of western Europe, Australia and New Zealand and the United States (40 %) (Brazier *et al.*, 2007; Bilotta *et al.*, 2008) have received less research attention than other land uses in terms of water quality research. Only recently has the



general assumption been challenged that grasslands contribute little to total agricultural diffuse pollution in comparison to their arable counterparts (Brazier *et al.*, 2007). Several studies have since demonstrated sediment and macronutrient losses from grasslands to be comparable with those of arable fields / catchments and to exceed EU water quality guidelines (Preedy *et al.*, 2001; Bilotta *et al.*, 2008; Granger *et al.*, 2010).

Second, multiple diffuse agricultural pollutants are rarely considered in the same study. However, it is widely acknowledged that it is not the availability of single nutrients, but the relative availability of multiple nutrients that impact aquatic ecosystems. The impacts range from direct toxic effects on aquatic biota to effects on primary productivity, cascading through the entire aquatic food web (Elser & Urabe, 1999; Dungait *et al.*, 2012). The acknowledgment of the relative importance of nutrients has challenged the general consensus that freshwater systems are always P limited (Elser *et al.*, 2007; Conley *et al.*, 2009). Additionally, most studies focus on inorganic forms of N and P as they were considered as the bioavailable forms and EU / UK water quality regulations focus on those forms. Such studies fail to capture the total nutrient delivery of both directly bioavailable (inorganic forms) and organic forms that can become available by assimilation by bacteria (organic N, (See *et al.*, 2006)) or hydrolysis (organic P, (Darch *et al.*, 2013)). Water quality guidelines in the USA for example are set as total N and total P (USEPA, 2000).

Third, the depth of scientific understanding has often been limited by the temporal resolution of the data. The recent development and increased use of near-continuous water quality sampling equipment promises great advances in hydrochemical process understanding (Kirchner *et al.*, 2004). Generally, the higher the data resolution and the longer the time series, the more revealing are the results. Estimating accurate pollutant loads and yields (Cassidy & Jordan, 2011), understanding fine temporal variability of sediment and nutrient fluxes (Jordan *et al.*, 2012; Melland *et al.*, 2012) and calculating accurate and precise water quality guideline exceedance frequencies (Bilotta *et al.*, 2010; Thompson *et al.*, 2014) are examples of what is possible with high-resolution monitoring.

Finally, catchment scale water quality research, whilst conducted at a pragmatic 'hydrological' scale is often limited in providing information on pollutant sources within catchments, process information on the contribution of

individual units of land use or information on the effectiveness of policy efforts towards reducing water pollution. Each catchment has numerous pollutant sources and land uses, which are managed separately by different stakeholders (e.g. farmers, landowners or rural industry). Any effort towards reducing pollution is generally targeted towards individual pollutant sources and their managers. Therefore, the scale of management decisions and policy implementation is not the catchment scale, but in the case of agricultural diffuse sources, it is the individual farm scale. Here, we suggest that field- to farm-scale research is a logical scale to guide agricultural diffuse pollution research. Field to farm-scale research within a catchment might give insight into a) the likely contribution a single type of agricultural land use has on overall water pollution and therefore improve pollution source apportionment within catchments, b) the effects of individual soil and nutrient management practices, and c) the effectiveness of mitigation measures. The usefulness of farm-scale experiments has been reviewed before (Pilgrim *et al.*, 2010), but there are few, comprehensive field to farm-scale monitoring experiments underway, especially in intensively managed grasslands.

Addressing the above limitations in water quality research, this study quantifies the hydrological characteristics and the fluvial fluxes of suspended sediment and the macronutrients TC, TON<sub>N</sub> (total oxidised nitrogen) and TP at high resolution (up to 15 minute sampling intervals) over one year in intensively managed grasslands. Thus, this study provides novel information to answer the following key questions:

**Question 5.1** How do rates of sediment and macronutrient delivery from intensively managed grasslands compare to other agricultural land uses?

**Question 5.2** What are the controlling factors on hydrology and how does hydrology affect fluxes and yields of sediment and macronutrients in intensively managed grasslands?

**Question 5.3** How does the relative importance of diffuse pollutants from intensively managed grasslands change through flow conditions and time?

**Question 5.4** How does water quality from intensively managed grasslands compare to EU and UK recommended water quality standards at the farm-scale?

### III. Methods

#### A. Field Site

This study was undertaken at the North Wyke Farm Platform in south-west England, UK (50°046'10"N, 30°54'05"W) (Figure 5.1a - b), described in more detail by Griffith *et al.* (2013). Three large fields (6.6 - 7.6 ha) were chosen for sampling: Great Field (Field 2), Orchard Dean (Field 5), and Middle and Higher Wyke Moor (Field 8), as they represented the same scale of interest (Figure 5.1c - e). The total area of the farm is 68.4 ha.

During the sampling period for this study, the Farm Platform was managed as a conventional beef and sheep production system. Application of fertilizers on the Farm Platform is in accordance with the Code of Good Agricultural Practice (DEFRA, 2009; 2010) and the Nitrate Vulnerable Zone guidelines (DEFRA, 2008) and is therefore considered to represent standard management practices for grassland systems. The grasslands of the Farm Platform are classified as intensively managed grassland. The three sampling fields were mainly used for cattle grazing (~30 cattle per field for ~ 75 - 95 days in all three fields) and sheep grazing (90 weaned lambs for 20 days in Field 8) during the summer of 2012. Additionally, the fertilizer N inputs during the sampling period were: field 2: 522 kg (6.71 ha catchment size), field 5: 503 kg (6.59 ha catchment size), field 8: 495 kg (7.59 ha catchment size). No mineral P and K or Farmyard manure (FYM) were applied to the sampling fields during the monitoring period.

Each field is hydrologically isolated (to a depth of 0.8 m) so that water leaving the field by sub-surface lateral flow or surface runoff is channelled via French drains into flumes, which are outfitted with water quality and quantity monitoring equipment. The hydrological soil types common on the North Wyke Farm Platform are representative of the most common hydrological soil types in England and Wales, covering approximately 13.9 % of the land area, (Boorman *et al.*, 1995) and are typical for many areas under grassland management (Bilotta *et al.*, 2008). The North Wyke soils are clay loams overlying shales of the Crackington formation with thin subsidiary sandstone bands (Bilotta *et al.*,

2008; Harrod & Hogan, 2008) (soil series classifications according to different systems in Figure 5.1c - e). The soil series vary in their hydrological characteristics, but all have low water storage capacity and are slowly permeable up to 30 cm soil depth, where they have a clay-rich layer with very low hydraulic conductivities, allowing the (near to) hydrological isolation of the fields (Harrod & Hogan, 2008). The rainfall and annual temperature (1056 mm and 9.5 °C, respectively, mean of 40 years) at North Wyke are typical of much of the intensively managed grassland areas in the western UK (Harrod & Hogan, 2008).

## **B. Site Instrumentation**

The Farm Platform instrumentation set-up is described in detail by Griffith *et al.* (2013). In short, every field is equipped with a rainfall and soil moisture monitoring station and the water leaving each field drains to a flume with a range of automated or semi-automated water quantity and quality monitoring equipment (locations shown in Figure 5.1c - e). All data are collected at 15-minute time intervals and transmitted by a remote telemetry unit (RTU) ([www.adcon.at](http://www.adcon.at)) via UHF radio telemetry to a centrally located base-station (a850 Gateway). The base station sends the raw data into the AddVantagePro software ([www.adcon.at](http://www.adcon.at)), which stores, processes and visualises these data (Griffith *et al.*, 2013).

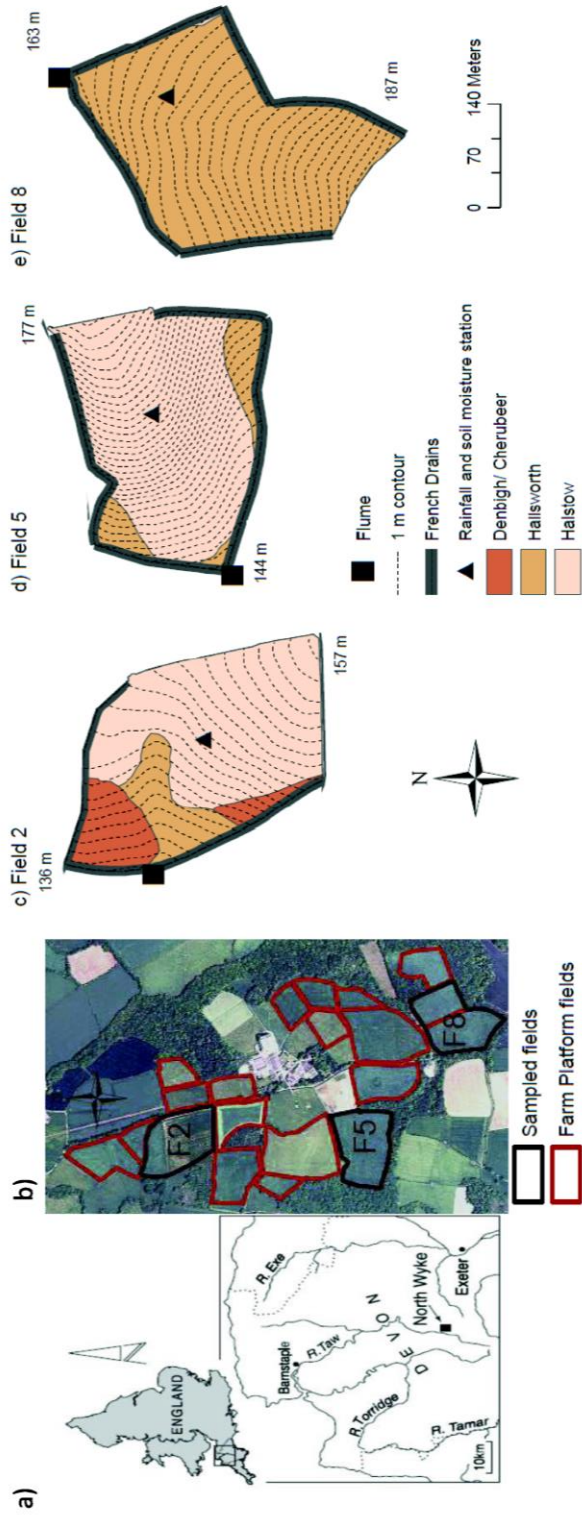


Figure 5.1. Description of the sampling site: the North Wyke Farm Platform. a) Location of the Farm Platform and b) the three sampling fields within the Farm Platform. c) - e) individual sampling field topography, soil types\*, location of flumes, rain gauges and soil moisture probes for field 2 (6.71 ha), field 5 (6.59 ha) and field 8 (7.59 ha), respectively.

\*Names for soil types under international classifications: Denbigh / Cherubier (Avery, 1980): FAO Stagni-eutric cambisol, USDA: Dystric eutrochrept; Halstow (Avery, 1980): FAO Stagni-vertic cambisol, USDA Aeric haplaquept; Halsworth (Avery, 1980): FAO Stagni-vertic cambisol, USDA Typic haplaquept (in Harrod and Hogan, 2008).

### C. Hydrology and water quality monitoring

Hydrology data presented here were continuously monitored from April 2012 - April 2013. Each field is equipped with a tipping bucket rain gauge, with a 0.2 mm resolution (ADCON RG1, ADCON, Davis, USA). The discharge in each flume was measured by a 4230 Bubbler Flow Meter (Teledyne Isco, Lincoln, USA). The flow meter measures the flow height (h) in the flumes ([www.tracomfrp.com](http://www.tracomfrp.com)), where the relationship between water height and flow rate is derived. Adcon SM1 soil moisture probes were used to measure soil moisture content (expressed as % soil moisture) through the soil profile: at 10, 20 and 30 cm soil depths (Griffith *et al.*, 2013).

Hydrological data presented here were monitored from 1<sup>st</sup> April 2012 to 1<sup>st</sup> April 2013. Suspended sediment (SS) and the macronutrients carbon (total C), phosphorus (total P) and nitrogen (total oxidized nitrogen-N: TON<sub>N</sub>) were monitored by a combination of different approaches, from making use of recent advances in continuous sampling equipment to manual sampling and laboratory analysis. Manual TC samples were taken from 1<sup>st</sup> April 2012 to 1<sup>st</sup> April 2013. Automatic and semi-automatic water quality data (SS, TON<sub>N</sub>, TP) were used for the hydrological season, from 1<sup>st</sup> October 2012 - 1<sup>st</sup> April 2013, from when the sensors were fully installed, operational, and quality assured.

Total oxidized N and SS were monitored continuously (flow permitting) by automated sensors located in a stainless-steel by-pass cell. The runoff water was automatically pumped into a by-pass cell every 15 minutes if flow was > 0.2 L s<sup>-1</sup> and the last sample was held in the by-pass cell when flow dropped < 0.2 L s<sup>-1</sup> (Griffith *et al.*, 2013). The by-pass cell was required to keep sensors constantly submerged. TON<sub>N</sub> was measured by an optical UV absorption sensor, NITRATAX plus SC (Hach Lange, Germany, Düsseldorf, [www.hach-lange.co.uk](http://www.hach-lange.co.uk)) by passing UV light using a two-beam turbidity compensated photometer through the water and measuring the absorption. The absorption was then converted to TON<sub>N</sub> concentrations, using the known UV light absorption rates of nitrate dissolved in water below the wavelength of 250 nm (Griffith *et al.*, 2013).

As a proxy for SS, turbidity was continuously monitored using a YSI multiparameter sonde (6600V2, YSI, Yellow Springs, USA; [www.ysi.com](http://www.ysi.com)). To

convert turbidity measurements (Nephelometric Turbidity Units, NTU) into SS ( $\text{mg L}^{-1}$ ), the relationship between NTU and SS measured on the same samples was established (Table 5.1). Flow-proportional samples were taken via auto-sampler (ISCO 3700, Teledyne Isco, Lincoln, USA) and then analyzed in the laboratory for SS by filtering a known volume of sample through a pre-weighed, dry, glass fibre filter paper (1.2  $\mu\text{m}$  pore size, Whatman GFC) followed by drying at 105 °C for 60 min and re-weighing to determine SS (Bilotta *et al.*, 2008).

Total P was measured by a Dr. Lange Sigmatax-Phosphax suite (Hach Lange, Hach Lange, Germany, Düsseldorf, Germany; [www.hach-lange.co.uk](http://www.hach-lange.co.uk)). The Phosphaxes are installed by the flumes and were manually switched on and off according to flow conditions. The Sigmatax-Phosphax suite extracts the water directly from the flume with the Sigmatax unit and homogenises a 100 mL sub-sample with a 3-minute ultra-sound homogenization. The sample is then digested with sulphuric acid-persulphate before addition of molybdate antimony and ascorbic acid (Jordan *et al.*, 2007).

Total C was measured by taking flow-proportional grab-samples via auto-sampler, and then analyzed in the laboratory for TC. The sample bottles were collected and transferred to the laboratory within 24 hours, immediately refrigerated and analyzed within 48 hours of the event. A Scalar Formacs analyzer was used (Formacs<sup>HT</sup> TOC / TN Analyzer, Scalar, Breda, Netherlands). The samples were not filtered and stirred before needle injection into the analytical instrument in order to provide a measurement as close to the total amount of carbon as possible (both dissolved organic and inorganic and particulate organic and inorganic C), here simply called total C. Within the Scalar Formacs, samples were heated to 850 °C and all forms of carbon were oxidised to carbon dioxide with cobalt oxide. Carbon dioxide was then determined by infrared detection. Total inorganic carbon (TIC) and total organic carbon (TOC) was automatically measured/ calculated in this procedure. The average % of TIC and TOC in all TC samples was calculated.

The quality of the data were assured by a) regular equipment calibration and drift checks, b) running a quality assurance programme, which incorporates sensor drifts, as well as filters out values that are above and below the known limits of detection by the sensors and c) using the established relationship by cross-validation between automated measurements and laboratory analysis

from samples taken within the same 15-minute slots during hydrological events to correct the data (Table 5.1).

Table 5.1. Correlation functions between automated measurements and laboratory measurements (event-based samples taken in the same 15-minute slot).

	$\text{TON}_N^*$ probe <sup>*1</sup> - $\text{TON}_N$ lab <sup>*2</sup>	$\text{TON}_N^*$ probe <sup>*1</sup> - $\text{TON}_N$ lab <sup>*3</sup>	TP* probe <sup>*4</sup> - TP lab <sup>*5</sup>	TP* probe <sup>*4</sup> - TP lab <sup>*6</sup>	Turbidity probe <sup>*7</sup> - SS lab
Flume 2	$y=1.07x-0.51$ ( $R^2=0.77$ , N=12)	$y=0.53x+0.06$ ( $R^2=0.4$ , N=24)	$y=1.53x-0.04$ ( $R^2=0.89$ , N=16)	$y=1.29x-0.005$ ( $R^2=0.82$ , N=11)	
Flume 5	$y=0.62x-0.32$ ( $R^2=0.76$ , N=17)	$y=0.53x+0.002$ ( $R^2=0.47$ , N=70)	$y=0.78x+0.03$ ( $R^2=0.69$ , N=16)	$y=0.91x+0.02$ ( $R^2=0.86$ , N=16)	$y=1.18x+0.05$ ( $R^2=0.75$ , N=256)
Flume 8	$y=0.7x-0.01$ ( $R^2=0.7$ , N=17)	$y=0.83x-0.01$ ( $R^2=0.68$ , N=27)	$y=1.26x-0.02$ ( $R^2=0.72$ , N=19)	$y=1.08x-0.004$ ( $R^2=0.72$ , N=17)	

\*  $\text{TON}_N$ , total oxidised nitrogen-N; TP, total phosphorus; SS, suspended sediment

\*<sup>1</sup>  $\text{TON}_N$  probe, Nitratax

\*<sup>2</sup> the Nitratax was factory calibrated in Jan 2013, this calibration is pre- factory calibration

\*<sup>3</sup> the Nitratax was factory calibrated in Jan 2013, this calibration is post factory calibration

\*<sup>4</sup> TP probe, Phosphatax

\*<sup>5</sup> 1<sup>st</sup> Phosphax deployment: 14/12/2012-20/12/2012,

\*<sup>6</sup> 2<sup>nd</sup> Phosphax deployment: 25/01/2013-12/02/2013.

\*<sup>7</sup> Turbidity probe measured in NTU, nephelometric turbidity units

All quality assured data were considered as the entire time series. To establish an event-based dataset, data taken during hydrological events were extracted from the continuous datasets by using a rule-based method (based on (Bilotta *et al.*, 2008) defining hydrological events as a period of rainfall and discharge if the discharge increases in response to a period of precipitation above a certain threshold, based on field size. A storm event was considered to start when rainfall occurred after it had been dry for 2 hours and that rainfall was followed by either a net flow rise within the next 8 hours or a rapid flow rise ( $> 0.5 \text{ L s}^{-1} \text{ ha}^{-1}$  within an individual 15-minute time slot) and the flow rose  $> 1 \text{ L s}^{-1} \text{ ha}^{-1}$  within the event. A storm event was considered to end 4 hours after the last rainfall associated with an event. In total, 184 hydrological events (61 for field 2,



64 for field 5 and 59 for field 8) were recorded between 1<sup>st</sup> April 2012 and 1<sup>st</sup> April 2013 using these rules.

To minimize uncertainty in the automated water quality data (SS, TON<sub>N</sub>), hydrological events were ignored if there was > 1h continuous missing data in the event time series, unless data was missing at the start of an event, when flow levels were too low for water to be pumped into the by-pass cell housing the sensors. All TP and TC events were used.

**(Question 5.1)** To compare rates of sediment and macronutrient delivery from intensively managed grasslands to other agricultural land uses, annual yields were calculated and compared to those reported in other grassland studies, mixed agricultural land-use studies and from arable land. To estimate annual yields, the entire time series was used: event-based data as well as data taken between hydrological events. Annual yield estimation is generally highly uncertain, as pollutant concentrations over unmonitored time steps have to be estimated (Bilotta *et al.*, 2010), even with the near-continuous sampling regimes employed in this study. To estimate total yield of SS and TON<sub>N</sub>, rating curves with 95 % confidence intervals were calculated and used to estimate concentrations of unsampled time steps (Bilotta *et al.*, 2010; Glendell & Brazier, 2014). To estimate annual yield of TC and TP with low data coverage, the Walling and Webb Method 5 was used (Walling & Webb, 1985). This method provides the least biased yield estimation from time series with little data coverage, but a continuous discharge record (Walling & Webb, 1985; Littlewood, 1992; Glendell & Brazier, 2014).

**(Question 5.2)** To examine the controlling factors on hydrology and how hydrology affects fluxes and yields of sediment and macronutrients, a) rating curves between discharge and pollutant concentrations were established throughout the entire time series, and b) stepwise-multiple linear regressions were conducted to understand event-based relationships between hydrology and responses of individual pollutants (considered significant at the  $p \leq 0.05$ ) and c) the sedigraph / chemograph shapes and hysteresis effects were examined in relation to the hydrographs. Non-normally distributed variables were log transformed. All statistical analysis was conducted in Genstat (15<sup>th</sup> edition) (VSN International Ltd., Hemel Hempstead, UK).

**(Question 5.3)** Three steps were involved to examine the relative importance of diffuse pollutants through flow conditions and time. a) The percentage contribution of each pollutant to overall annual yields as well as annual yield macronutrient ratios were calculated for all fields. b) The mean / median concentrations and pollutant ratios were contrasted through all monitored baseflow and stormflow periods, as well as further divided into the lower baseflow quartile and the upper stormflow quartile for one example field (field 2) (Melland *et al.*, 2012). The overall duration over which these flow conditions occurred over the entire monitoring time series was expressed as a percentage of the entire time series. c) The fine-scale contribution of pollutants to overall pollution and their ratios were plotted throughout a 34 hour period for one example field (field 5), which includes a storm event followed by a long period of baseflow. Overall, SS, TON<sub>N</sub> and TP were considered over baseflow periods and SS, TON<sub>N</sub>, TP and TC were considered over storm-flow periods.

**(Question 5.4)** To compare water quality from intensively managed grasslands to EU / UK recommended water quality standards, the percentage of 15-minute time-step data that exceeded concentrations recommended by water quality guidelines was calculated (Bilotta *et al.*, 2010). Such concentration-frequency curves express the pollutant delivery data in an ecologically relevant way: providing an indication of the duration of exposure to certain pollutant concentrations (Bilotta *et al.*, 2010; Thompson *et al.*, 2014). Water quality guidelines used are summarized in table 5.2).

Table 5.2. Summary of the water quality guidelines and their specific pollutant concentrations used to compare to the pollutant concentrations measured on the North Wyke Farm Platform.

Pollutant in this study*	Guideline used	Chemical guideline set for	Guideline concentration
<b>SS</b>	EU Freshwater Fisheries Directive	No specified SS size	25 mg SS L <sup>-1</sup>
	lower SS standard than FFD used because FD was suggested to be too high (Bilotta <i>et al.</i> , 2012) study on SS background levels of 638 UK water courses in reference state)	No specified SS size	10 mg SSL l <sup>-1</sup>
<b>TP</b>	'good ecological status' (GES) specifically for the upper Taw catchment (UK Technical Advisory Group (TAG) standard devised for the EU Water Framework Directive)	dissolved molybdate reactive phosphorus (MRP)	< 0.04 mg MRP L <sup>-1</sup>
	'moderate ecological status' (MES) specifically for the upper Taw catchment (UK Technical Advisory Group (TAG) standard devised for the EU Water Framework Directive)	dissolved molybdate reactive phosphorus (MRP)	< 0.15 mg MRP L <sup>-1</sup>
<b>TON<sub>N</sub></b>	EU Nitrates Directive	Nitrate <sub>N</sub> (NO <sub>3</sub> <sup>-</sup> -N)	< 11.3 mg NO <sub>3</sub> <sup>-</sup> -N L <sup>-1</sup>
<b>TC</b>	n.a	n.a	n.a

\* SS, suspended sediment; TP, total phosphorus, TON<sub>N</sub>, total oxidized nitrogen-N; TC, total carbon.

\*<sup>1</sup> n.a., carbon is not included in water quality standards, yet, in terms of freshwater ecosystem health.

## IV. Results & Discussion

Rainfall and the occurrence of hydrological events were similar, but peak flow rates varied between the fields throughout the entire time series (April 2012-April 2013) (Figure 5.2). The sampling year was wet, with 132 % of the average annual rainfall (of the past 40 years) occurring at the site. Results therefore illustrate the response of a landscape that is well connected to its surface waters, a scenario that is likely to occur more often in the future with wetter winters being predicted to occur in the UK with climate change (Jordan *et al.*, 2012).

Hydrographs across the Farm Platform demonstrate a rapid response to rainfall, with high variability across the year with storm runoff-coefficients being as low as 10 % during the summer and reaching as high as 133 % during the winter (Table 5.3). The flashy hydrographs are typical for most areas of managed grasslands with similar soil types and topography (Bilotta *et al.*, 2008). The soil moisture (%) at 10 cm depth was the most variable in all three fields (21 - 46 %), showing the lowest soil moisture levels during summer and the highest during winter / wet periods. Moving down the soil profile, the soil was driest at 20 cm (24 - 34 %) (apart from dry periods, when the topsoil was driest) and was most constant at 30 cm soil depth (29 - 39 %). Soil conditions were considered as dry when soil moisture at 10 cm < 40 %, 20 cm < 30 %, 30 cm < 36 % and near saturation when soil moisture levels were above these thresholds, accounting for high variability and measurement errors. The high rainfall-runoff coefficients reflect both the fast response of these soils caused by the low water storage capacity that heavy clay soils support and the artificial drainage system. A number of events (6 out of 184 in total) had runoff-coefficients higher than 100 %, which may be due to a) spatial variability of rainfall rates, so that a lower total rainfall is calculated for a hydrological event than actually fell on the field, b) errors in rain gauge measurements, c) elevated 'baseflow' at the start of storm events which were still affected by previous rainfall and d) water previously stored in the drainage system or the soil being flushed out in rapidly flowing events.

Table 5.3. General overview of the three fields' hydrological characteristics (mean, median, minimum and maximum) during storm events and number of captured events.

Field		Total Rainfall mm	Total Discharge 1000L	Peak Discharge L s <sup>-1</sup>	Rainfall-runoff coefficient %
2	Mean	15.9	517.2	28.1	46.2
	Median	11.2	352.5	21.4	46.6
	Minimum	2.4	70.4	6.9	12
	Maximum	50	2124.4	97.6	82
	N	61	61	61	61
5	Mean	14.2	586.7	37	63
	Median	9.8	405.6	30.8	60.9
	Minimum	2	52.5	6.8	9.9
	Maximum	50.4	2424.9	105.8	132.7
	N	64	64	64	64
8	Mean	15.8	701.3	38.5	54.3
	Median	11	452.2	32.9	52.7
	Minimum	3.2	87.7	8.6	12.7
	Maximum	46.8	2583.6	103.9	128.7
	N	59	59	59	59

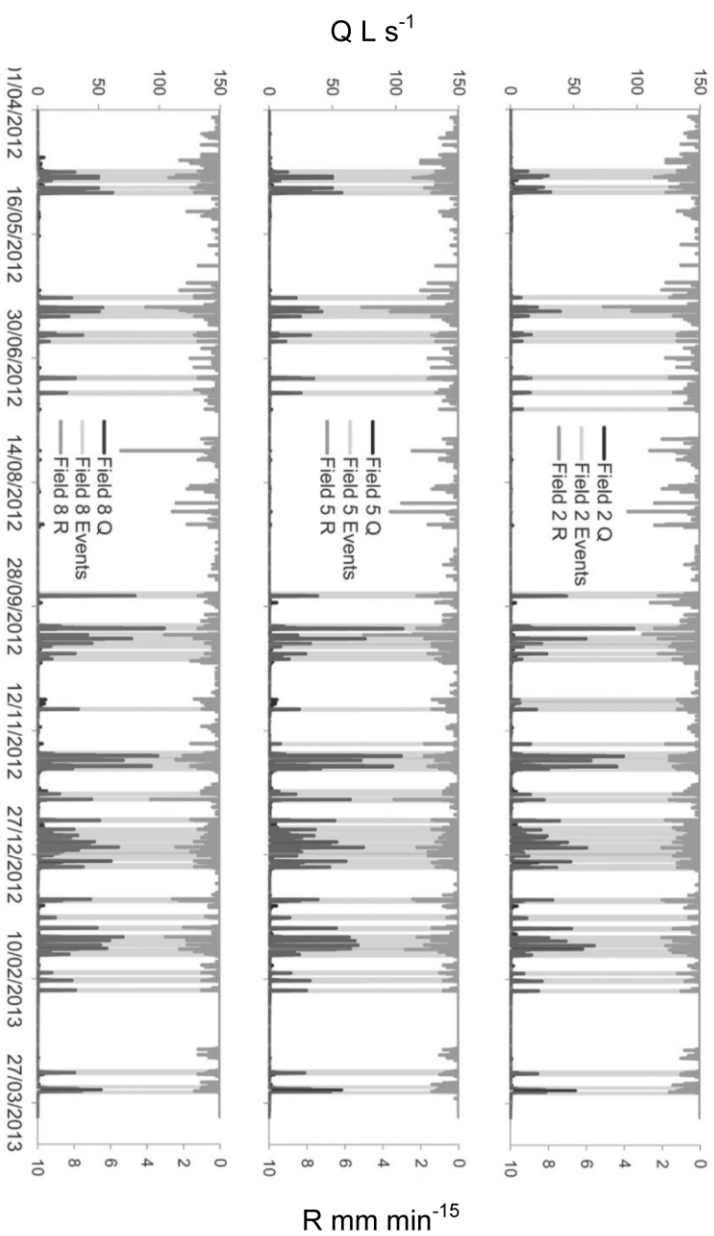


Figure 5.2. Rainfall ( $R \text{ mm min}^{-15}$ ), discharge ( $Q \text{ L s}^{-1}$ ) and hydrological events\* for all three intensively managed grassland sampling fields for the entire sampling duration (April 2012- April 2013). All data was monitored and is expressed at 15-minute time steps. Occurrence of hydrological events was similar for the three fields, but peak flow rates vary between the fields. Soil moisture levels (not included in this figure) were high or near to saturation in mid-end of April, mid-end of June and throughout most of October- March. Note the period of July-August, when no hydrological events occurred, despite high rainfall rates, because soils were dry and/or dried out quickly after rainfall. \*Hydrological events were defined on the basis of rainfall and a discharge response rising above certain thresholds, based on field sizes.

**A. How do rates of sediment and macronutrient delivery from intensively managed grasslands compare to other agricultural land uses?**

Individual hydrological events in these grassland fields can yield up to 29.5 kg SS ha<sup>-1</sup> (> 1.2 µm), 84.5 g TON<sub>N</sub> ha<sup>-1</sup>, 49 g TP ha<sup>-1</sup>, and 7.1 kg TC ha<sup>-1</sup> (Table 5.4). Estimated over the entire sampling duration (April 2012 - April 2013), these grassland fields yield up to 527.4 kg SS ha<sup>-1</sup>, 3 kg TON<sub>N</sub> ha<sup>-1</sup>, 0.9 kg TP ha<sup>-1</sup> and 179 kg TC ha<sup>-1</sup> annually (Table 5.4). TC was approximately composed of 34 % TIC and 66 % TOC. Apart from four TC events, all events for which water quality parameters were measured occurred when the soils were wet / near saturation or saturated (October- March).

Erosion rates from the Farm Platform intensively managed grasslands (annual yields 182.2 - 527.4 kg SS ha<sup>-1</sup>) are comparable to similar grasslands (up to 14.9 kg SS ha<sup>-1</sup> during individual events (Bilotta *et al.*, 2008)); 540 - 1210 kg SS ha<sup>-1</sup> year<sup>-1</sup> (SS > 0.7 µm) (Bilotta *et al.*, 2010)), mixed land use (640 kg ha<sup>-1</sup> year<sup>-1</sup> average erosion rate for 56 mixed land-use catchments (Boardman & Evans, 1994), 255 - 588 kg SS ha<sup>-1</sup> year<sup>-1</sup> in a mixed land-use catchment in the south-west UK (estimated for a 9 month period (Glendell & Brazier, 2014), 116 kg SS ha<sup>-1</sup> year<sup>-1</sup> in a mixed-agricultural tributary to the River Dee in Scotland (Stutter *et al.*, 2008)), and are within the ranges reported for arable land (average erosion rates for clay soils 611 kg ha<sup>-1</sup> year<sup>-1</sup> (Deasy *et al.*, 2009), 85 - 650 kg SS ha<sup>-1</sup> year<sup>-1</sup> on an arable site in England (Withers *et al.*, 2006), 410 - 1910 kg ha<sup>-1</sup> year<sup>-1</sup> on the UK Woburn Erosion Reference Experiment (Quinton *et al.*, 2006)). The erosion rates presented in this study were measured as particles > 1.2 µm. If smaller particles had been included in the measurements, which are known to be preferentially transported from grasslands to surface waters, erosion rates may have been even higher (Bilotta *et al.*, 2007). The high erosion rates from intensively managed grasslands reported here add to the growing evidence that grasslands have previously been underestimated in their erosion rates, which should be acknowledged in land management guidelines and advice.

The  $\text{TON}_\text{N}$  losses from the Farm Platform were low (annual yields 0.92 - 3  $\text{kg ha}^{-1}$ ). Concentrations in discharge waters were similar to those from comparable grasslands (Granger *et al.*, 2010; Sandford *et al.*, 2013), but annual yields were lower than the losses reported in nearby grassland studies in the past (35.8 - 133.8  $\text{kg NO}_3^- \text{ ha}^{-1} \text{ year}^{-1}$ ) (Scholefield *et al.*, 1996). The reduction in N leaching may be attributed to reduced N inputs, controlled by NVZ guidelines in the UK (DEFRA, 2008). Grasslands monitored by Scholefield *et al.* (1996) received more than double the N inputs (between 200 - 400  $\text{kg N ha}^{-1} \text{ year}^{-1}$ ) that the sampled fields in this study received (80  $\text{kg N ha}^{-1} \text{ year}^{-1}$ ). The annual  $\text{TON}_\text{N}$  losses from the Farm Platform were significantly lower than those reported for mixed land use (17.4  $\text{kg NO}_3^- \text{ ha}^{-1} \text{ year}^{-1}$  in a mixed grassland and arable catchment in Scotland (Stutter *et al.*, 2008) and arable land-use (6 - 60  $\text{kg NO}_3^- \text{ ha}^{-1} \text{ year}^{-1}$  in Denmark (Erikson & Vinther, 2002), average losses of 30  $\text{kg NO}_3^- \text{ ha}^{-1} \text{ year}^{-1}$  on the Rothamsted Research Broadbalk Wheat experiment, UK, (Goulding *et al.*, 2000), > 20  $\text{kg NO}_3^- \text{ ha}^{-1} \text{ year}^{-1}$  from tile drained arable land in USA (Schilling *et al.*, 2013).

TP losses reported herein (up to approx. 0.9  $\text{kg ha}^{-1} \text{ year}^{-1}$ ) compare well with typical TP losses reported for UK agricultural catchments (1  $\text{kg P ha}^{-1} \text{ year}^{-1}$  (Heathwaite, 2005)), P losses measured in nearby grasslands (0.21  $\text{kg SRP ha}^{-1} \text{ year}^{-1}$  of soluble reactive P (Hawkins & Scholefield, 1996) event yields of up to 50  $\text{g P ha}^{-1}$  (Bilotta *et al.*, 2008)), other grasslands (0.54 - 0.7  $\text{kg TP ha}^{-1} \text{ year}^{-1}$  in Irish grassland catchments (Jordan *et al.*, 2012)), mixed land-use (0.37  $\text{kg TP ha}^{-1} \text{ year}^{-1}$  in a Scottish mixed catchment (Stutter *et al.*, 2008)), and arable land (Irish arable land 0.18 - 0.79  $\text{kg TP ha}^{-1} \text{ year}^{-1}$  (Jordan *et al.*, 2012), 2  $\text{kg TP ha}^{-1} \text{ year}^{-1}$ , UK, (Smith *et al.*, 2001), 0.17 - 0.73  $\text{kg TP ha}^{-1}$  over one winter on a clay soil, UK (Deasy *et al.*, 2009)). The TP losses add to the growing evidence that grasslands contribute significantly to P levels in surface waters.

The comparison of TC yields from the Farm Platform with yields from grasslands or other land uses is constrained, because a) the majority of C studies are conducted on peaty or natural catchments and b) studies mostly measure dissolved organic carbon (DOC) (Worall *et al.*, 2012) rather than the TC data presented here. Results show that TC was approximately divided into 34 % TIC and 66 % TOC. Despite constraints in comparing DOC and TC / TOC



yields, C exports from these grasslands (up to 179 kg ha<sup>-1</sup> year<sup>-1</sup> (≈ 118 kg TOC ha<sup>-1</sup> year<sup>-1</sup>)) exceeded those of typical UK / European catchments (the average of 85 UK catchments 7.7 - 103.5 kg DOC ha<sup>-1</sup> year<sup>-1</sup> (Hope *et al.*, 1997b)) and the range reported for an agricultural watershed in Midwestern USA (14.1 - 19.5 kg DOC ha<sup>-1</sup> year<sup>-1</sup> (Dalzell *et al.*, 2007)), as well as the range reported for German grasslands (8 - 55 kg DOC ha<sup>-1</sup> year<sup>-1</sup> (Don & Schulze, 2008)). In addition, the TC annual rates are comparable to the combined rate of DOC and total particulate carbon measured over a 9 months period in an agricultural catchment in south-west UK (27.18 - 130.46 TPC + DOC kg ha<sup>-1</sup> (Glendell & Brazier, 2014)). The high rates of C export support the notion that agricultural catchments, particularly pastoral systems, yield higher C losses than forested or semi-natural catchments (Graeber *et al.*, 2012). Increased C losses from agricultural catchments may be caused by manure applications and grazing causing an increase in soil dissolved organic matter concentration through stimulation of microbial activity and increased oxygenation of the agricultural soils (Chantigny, 2003; Heitkamp *et al.*, 2009) and higher erosion rates (Hope *et al.*, 1997a; Quinton *et al.*, 2010) transporting high rates of particulate carbon. The few studies that quantified DOC and particulate carbon in agricultural landscapes showed a high contribution of particulate carbon to overall carbon losses by low DOC-TOC ratios (up to 1.01) (Glendell & Brazier, 2014) and 58 % and 42 % of organic C losses as DOC and particulate organic carbon (POC), respectively (Stutter *et al.*, 2008). Therefore, studies measuring C cycling and C losses from agricultural land to freshwater should include total carbon as up to 50 % of C losses may not be accounted for (Quinton *et al.*, 2006).

The annual yield estimations of SS and TON<sub>N</sub> in this study may be more accurate than those presented in many other water quality studies, owing to the high-resolution sampling. Annual yield estimation is generally uncertain, but uncertainty increases with reduced sampling frequency (Kirchner *et al.*, 2004; Bilotta *et al.*, 2010; Cassidy & Jordan, 2011; Jordan & Cassidy, 2011). Low sampling frequency may either miss transfers by high intensity but low duration and low frequency storm events or may overlook the contribution of baseflow loads to overall yields (Jordan & Cassidy, 2011). Therefore, low-frequency sampling has been demonstrated to generally underestimate total yields by up to 60 % (Cassidy & Jordan, 2011).

Table 5.4. General overview of the three fields' sediment and macronutrient data. All measurements are normalised by field area. Where appropriate, mean median, minimum, maximum and number of captured events are shown.

Field	Suspended sediment (>1.2 µm)			Total oxidized nitrogen-N			Total phosphorus			Total carbon		
	Annual yield * kg ha <sup>-1</sup>	Event yield kg ha <sup>-1</sup>	Peak event conc. mg l <sup>-1</sup> ha <sup>-1</sup>	Annual yield * kg ha <sup>-1</sup>	Event yield g ha <sup>-1</sup>	Peak event conc. mg l <sup>-1</sup> ha <sup>-1</sup>	Annual yield * <sup>1</sup> kg ha <sup>-1</sup>	Event yield g ha <sup>-1</sup>	Peak event conc. mg l <sup>-1</sup> ha <sup>-1</sup>	Annual yield * <sup>1</sup> kg ha <sup>-1</sup>	Event yield kg ha <sup>-1</sup>	Peak event conc. mg l <sup>-1</sup> ha <sup>-1</sup>
2	Mean	191.3	3.5	19.9	11.9	0.2	0.42	7.4	0.16	122.2	2.2	4.5
	Median		2.2	17.3	6	0.1		5.58	0.14		1.9	4.8
	Min	182.2	0.3	6.6	0.2	0	0	0.88	0.04		0.5	2.2
	Max	194.3	17.7	51.4	84.5	2	2	39.13	0.48		6.1	6.4
	N		41	41	41	41	41	18	18		11	11
5	Mean	441.4	5.9	38	16.2	0.2	0.87	10.65	0.22	179.1	2.4	5.2
	Median		4.3	29.3	11.5	0.2		8.1	0.23		2.4	5.3
	Min	433.9	0.5	9.5	4.3	0.1	0	1.09	0.06		0.3	2.7
	Max	527.4	25.5	109.2	70.1	0.3	0.3	49	0.37		7.1	6.9
	N		30	30	42	42	42	18	18		12	12
8	Mean	218.1	3.7	17.8	10.8	0.1	0.44	7.14	0.18	109.4	1.9	3.2
	Median		2.5	14.3	2.5	0		6.18	0.17		1.5	3.3
	Min	213.4	0.4	5.1	0	0	0	0.55	0.03		0.4	1.1
	Max	220.9	17.1	51.1	63.1	0.1	0.1	21.15	0.44		4.6	5.7
	N		37	37	19	19	19	17	17		12	12

\* Calculated with rating curves

\*<sup>1</sup> Calculated with Walling and Webb Method 5 (Walling and Webb, 1985)

It is important to note that erosion rates and losses of TP and TC were equivalent to those reported for mixed agricultural land and arable land use, even though the fertilization rates and stocking densities were relatively low for intensively managed grasslands and the fields had not been ploughed recently, a common management practice in intensively managed grasslands. Therefore, results presented herein demonstrate that sediment, TP and TC losses from intensively managed grasslands are significant.

**B. What are the controlling factors on hydrology and how does hydrology affect fluxes and yields of sediment and macronutrients in intensively managed grasslands?**

Total event rainfall described a significant amount of variance in total event discharge in field 2, field 5 and field 8 ( $R^2 = 0.61, 0.62$  and  $0.77$ , respectively). Also, variance in discharge peaks in all fields were significantly related to total rainfall and peak rainfall intensity in the case of field 2 and field 5, but to a lesser extent ( $R^2 = 0.47, R^2 = 0.52$ , respectively). The sampled fields respond very quickly to rainfall, the start of rising flows during hydrological events often occurs only 15 minutes after rainfall started, depending on antecedent soil moisture conditions. Testing for antecedent soil moisture conditions as a control, sampled events were divided into events that occurred when soils were wet and dry. The amount of total discharge described by total rainfall was higher in Field 2, 5 and 8 when soils were wet ( $R^2 = 0.85, 0.87, 0.94$ , respectively) and in Field 2 and 5 when soils were dry ( $R^2 = 0.82, 0.63$ , respectively) (Figure 5.3).

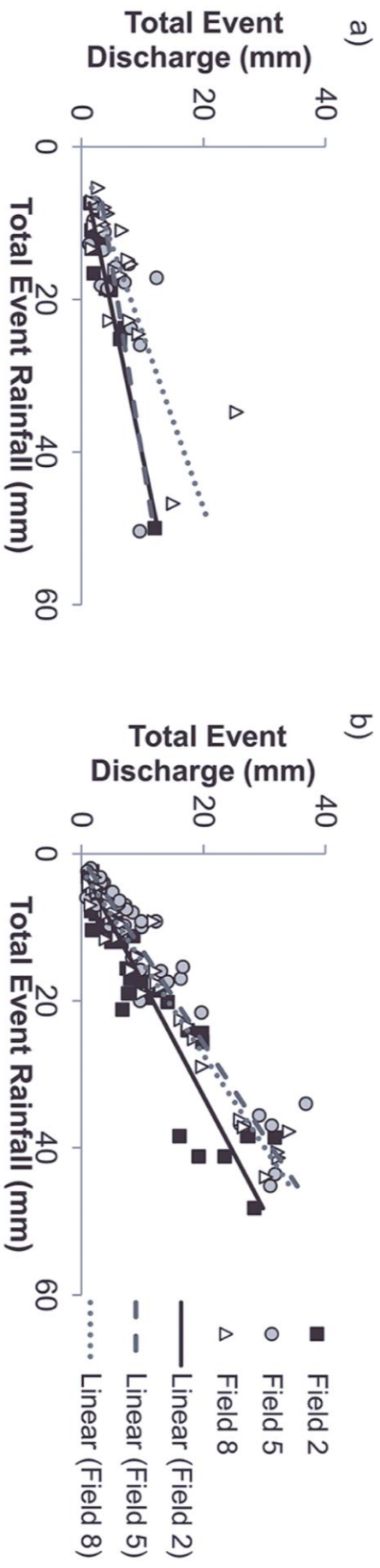


Figure 5.3. Relationship between total event rainfall (mm) and total event discharge (mm, normalised by field area) for events that occurred when a) soils were dry\* and b) soils were near saturation\*, in all three intensively managed grassland fields. A rainfall event of 40 mm total rainfall occurring when antecedent soil conditions are dry is expected to have discharges of approximately 10 - 18 mm. The same rainfall event occurring when soils are wet is likely to trigger 22 - 30 mm of discharge.

\*Antecedent soil moisture conditions were defined as: dry soils when soil moisture was at 10 cm < 40 %, 20 cm < 30 %, 30 cm < 36 % and near saturation when soil moisture levels were above these thresholds.

The flashy discharge response to rainfall indicates a fast lateral movement of water either on the soil surface or through the surface layers via cracks and macropore flow (Granger *et al.*, 2010). The topsoil (10 cm) is the most responsive to rainfall and temperature changes. Upon reaching field capacity in the topsoil, water is most likely to run off laterally down slope rather than further infiltrating into the driest 20 cm soil layer. The 30 cm clay-rich soil layer maintained the most constant soil moisture. Antecedent soil moisture conditions were a controlling factor on discharge, despite soil moisture measurements being highly variable. The highest runoff coefficients occurred when the soil was near saturation prior to a rainfall event, suggesting that hydrological events are mostly driven by saturation excess processes during wet periods (most of the sampling year as it was a particularly wet year) and only a small proportion of events was driven by infiltration excess processes during the summer months (Granger *et al.*, 2010).

Throughout the entire time series, discharge explained significant amounts of variation in concentrations of SS (field 2:  $R^2 = 0.62$ , field 5:  $R^2 = 0.71$ , field 8:  $R^2 = 0.65$ ),  $\text{TON}_N$  (field 2:  $R^2 = 0.5$ , field 5:  $R^2 = 0.76$ , field 8:  $R^2 = 0.24$ ) and TP (field 2:  $R^2 = 0.53$ , field 5:  $R^2 = 0.59$ , field 8:  $R^2 = 0.84$ ), but no variation in TC concentrations. Total storm event discharge explained a large amount of variation in event loads for SS, TP and TC, but only very small amounts or no variation at all for  $\text{TON}_N$  (Figure 5.4). Storm event analysis could not be split into events with dry or wet antecedent soil conditions, because almost all events monitored for water chemistry occurred when soil conditions were wet.

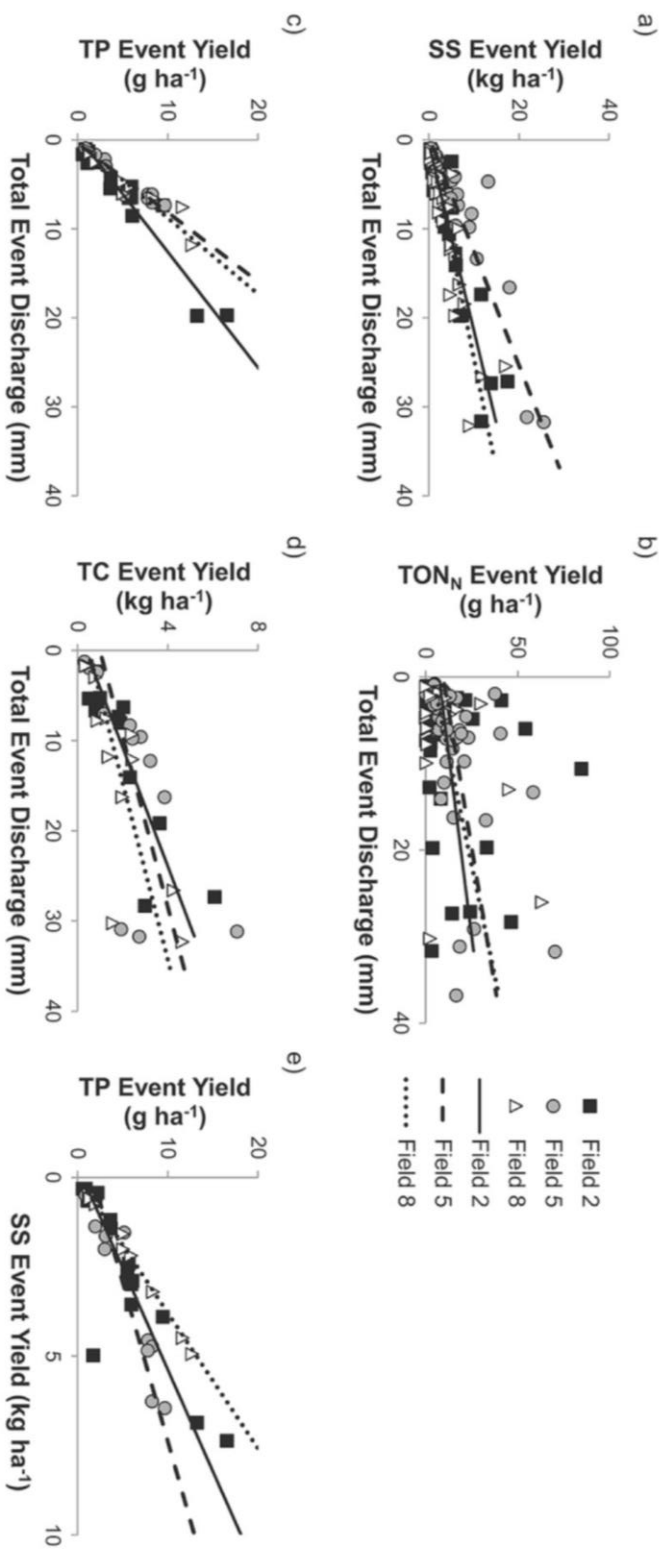


Figure 5.4. Correlation between total event discharge and a) SS event yield\*<sup>1</sup>, b) TON<sub>N</sub> event yield\*<sup>2</sup>, c) TP event yield\*<sup>2</sup>, d) TC event yield\*<sup>3</sup>, and e) correlation between SS event yield and TP event yield\*<sup>5</sup>. Trendlines are only shown and R<sup>2</sup> values given for significant correlations.

\* Field 2: R<sup>2</sup>= 0.81, Field 5: R<sup>2</sup>= 0.8, Field 8: R<sup>2</sup>= 0.82  
<sup>1</sup> Field 2: R<sup>2</sup>= 0.14, Field 5: R<sup>2</sup>= 0.34  
<sup>2</sup> Field 2: R<sup>2</sup>= 0.0.78, Field 5: R<sup>2</sup>= 0.8, Field 8: R<sup>2</sup>= 0.83  
<sup>3</sup> Field 2: R<sup>2</sup>= 0.65, Field 5: R<sup>2</sup>= 0.49, Field 8: R<sup>2</sup>= 0.57  
<sup>4</sup> Field 2: R<sup>2</sup>= 0.77, Field 5: R<sup>2</sup>= 0.96, Field 8: R<sup>2</sup>= 0.99

This study is one of the few studies to combine discharge and pollutant concentrations of SS, TON<sub>N</sub> and TP monitored at synchronous high-resolution time-steps. Such high-frequency monitoring showed very close coupling of hydrological, sediment and macronutrient dynamics. SS, TON<sub>N</sub>, TC and TP showed different behaviours throughout hydrological events. Sedigraphs, TON<sub>N</sub> and TP chemographs showed a consistent response in relation to the hydrograph in all hydrological events (unimodal, bimodal and multimodal) (Figure 5.5). The consistent response of SS, TP and TON<sub>N</sub> throughout baseflow and stormflow (up to a total of 42 storm events monitored in one field for one pollutant) throughout the entire year could not have been detected without such high resolution monitoring (Cassidy & Jordan, 2011). TC dynamics are less understood because of lower frequency monitoring, highlighting the loss of information that occurs at low sampling frequencies (Kirchner *et al.*, 2004).

The sedigraph peak(s) generally preceded the hydrograph peak(s), following a clockwise hysteresis pattern (Figure 5.5). Clockwise hysteresis in SS has previously been reported in field to small catchment-scale studies in temperate grasslands (Granger *et al.*, 2010) as well as large-scale catchments (Asselman, 1999). Clockwise hysteresis indicates that it takes less time to mobilize, transport and deliver SS to the flumes than the time to generate peak discharge (Klein, 1984). Mobilization, transport and delivery may take less time because a) sediment particles may have been deposited in or near the drains at the end of the last hydrological event or from periods of high flows in the same event and can therefore be delivered to the flumes before peak discharge has been generated (Klein, 1984), or b) sediment particles may be easily mobilized even by lower energy flows at the beginning of hydrological events, because grazing livestock can impact soil structure so that resistance of sediment particles to mobilization is reduced (Bilotta *et al.*, 2008), or a combination of both. Therefore, there is an influence of processes that occurred previous to the current storm event, which explains why peak flow was not well correlation with peak SS concentration (Granger *et al.*, 2010). The fine-scale dynamics of hysteresis, with the SS peak often only preceding the hydrograph peak by 15 minutes may not have been shown without such high resolution monitoring (Kirchner *et al.*, 2004; Jordan *et al.*, 2005).

The TP peak either coincided with the SS peak, occurred between the SS and the hydrograph peaks, or coincided with the hydrograph peak, leading to clockwise hysteresis or no hysteresis (Figure 5.5). After the initial TP peak, concentrations dropped rapidly, but not as rapidly as the concentration drops observed for SS. Throughout the entire time series, SS explained significant amounts of TP (62 – 72 %). Higher TP concentrations during hydrological events as opposed to base flow indicates TP sources are mobilized by hydrological transfer from flashy, or fast response runoff (Haygarth *et al.*, 1998). Clockwise hysteresis for P has been shown before for TP as well as PP and SRP in agricultural catchments (House & Warwick, 1998; Bowes *et al.*, 2005). The proportion of PP and SRP in TP could not be inferred from the data in this study. Total P and SS concentration peaks often coincided and a control of SS over TP was confirmed by significant correlation throughout the entire time series, but SRP is still likely to play a role in TP losses, as TP storm concentrations after the first peak (likely to be driven by SS associated P) were still elevated compared to baseflow concentrations. In addition, the proportion of TP and SRP is likely to change both spatially and temporally throughout events and between events (Granger *et al.*, 2010). Total P accumulates at the soil surface either adsorbed to sediment particles or stored in dissolved form in the soil water in the topsoil layer. Total P in both particulate or dissolved forms can then be mobilized by rainwater either through physical mobilization of sediment particles, desorption of P from particles or dissolved P enriched interflow transported through macropores; explaining the likely contribution of SRP and PP to overall TP losses.

Total oxidized N decreased as discharge increased and increased again towards the end of the event;  $\text{TON}_N$  concentrations often fell below the limits of analytical quantification within events ( $< 0.1 \text{ mg TON}_N \text{ L}^{-1}$ ) (Figure 5.5). The reduction of  $\text{TON}_N$  throughout hydrological events with discharge indicates a dilution of  $\text{TON}_N$  by flow. Such N dilution by rainwater has been reported elsewhere for both components of  $\text{TON}_N$  : nitrate ( $\text{NO}_3^-$ ) (Gächter *et al.*, 2004; Granger *et al.*, 2010) and nitrite ( $\text{NO}_2^-$ ) (Granger *et al.*, 2010). Both nitrate and nitrite are formed and held within the soil and are mobilized from soil water by diffusion to water moving through the soil system (Gächter *et al.*, 2004). When water moves rapidly over the soil surface or through the soil macro pores, it has



limited opportunities for diffusion (Granger *et al.*, 2010). When rainwater moves slowly throughout the soil profile, diffusion potential is high and therefore high and relatively stable  $\text{TON}_N$  concentrations emanate as baseflow. However, note that  $\text{TON}_N$  can show a different response to discharge shortly after fertilizer N was applied (Granger *et al.*, 2010).

The TC chemograph varied between storm events, but often TC concentrations decreased slightly as discharge increased and TC concentrations showed a peak prior to the peak discharge, often coinciding with the SS peak (Figure 5.5). TC concentrations in all fields were higher during the summer and reduced throughout the winter. The TC dataset is more uncertain because it had larger data gaps than the other pollutants monitored. Most importantly, if TC data were missing at the start and the end of an event, little indication was given about between-event concentrations. Therefore, less understanding of TC dynamics can be inferred compared to the other pollutant dynamics, highlighting the advantages of high-frequency monitoring. Erosion associated C losses, are likely to play an important role in overall C losses with TC peaks often coinciding with SS peaks and concentrations being overall higher than in studies on analogous grasslands measuring only DOC (Sandford *et al.*, 2013). However, SS did not explain any variation in TC concentrations throughout the year, which may be attributed to the reduction of TC concentrations from summer to winter. This reduction of TC concentrations from summer to winter may be explained by several factors: a) enhanced organic matter decomposition during summer followed by a flushing of C upon rewetting, b) enhanced C inputs by grazing animals and manure additions during the summer, c) higher temperatures and or d) enchytraeid worms influencing microbial activity by soil aeration (Evans *et al.*, 2005).

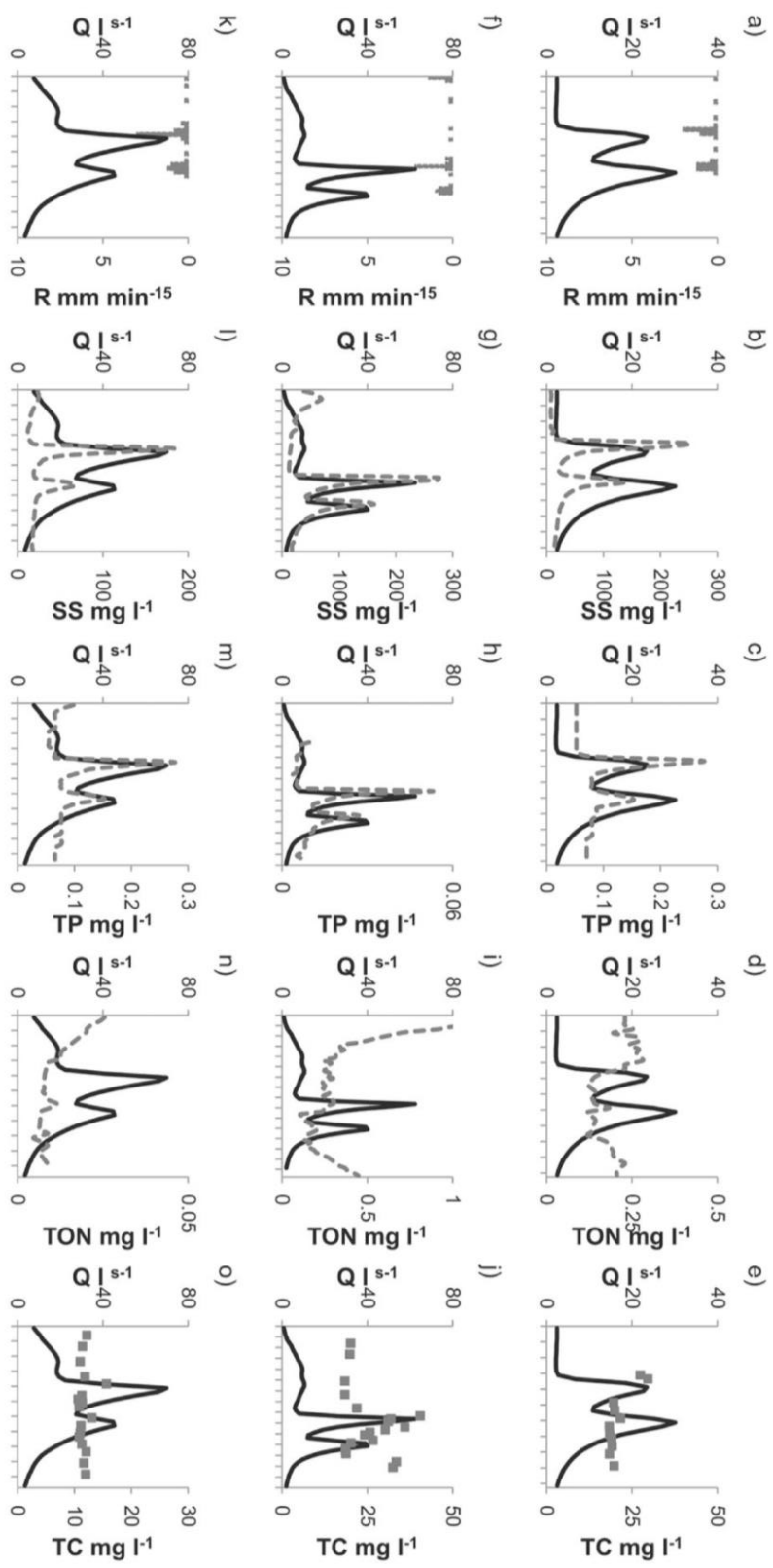


Figure 5.5. Detailed description of one particular storm event which occurred on the 25 - 26/01/2013 in the three intensively managed grassland fields\*. For each field, rainfall (R) and hydrographs (Q) are presented as well as showing hydrograph shape and chemograph / sedigraphs shapes (field 2 a-e), field 5 f-j), field 8 k-o). Each parameter was measured at 15 minute time-steps, apart from TC, for which manual samples are shown as individual dots. The x-axis shows hourly ticks. \* Field 2 start of the hydrological event at 11:45, lasting for 15 h, field 8 start at 16:15, lasting for 10.75 h.

**C. How does the relative importance of diffuse pollutants change from intensively managed grasslands through flow conditions and time?**

The contribution of each pollutant to the overall pollution yields were in the order of SS (61 – 71 %) > TC (29 - 39 %) > TON<sub>N</sub> (0.3 - 0.5 %) > TP (0.13 - 0.14 %) (Table 5.5). Annual yield macronutrient ratios ranged from TC:TON<sub>N</sub> = 60 - 109, TC:TP = 206 - 291 and TON<sub>N</sub>:TP = 2.27 – 4.

Table 5.5. Percentage of the contribution of each pollutant to the overall annual pollutant yield and annual yield macronutrient ratios for each field.

	Field 2	Field 5	Field 8
Total annual pollutant* yield kg ha <sup>-1</sup>	315.62	624.37	328.94
% of total annual pollutant yield:			
SS	60.61	70.7	66.3
TC	38.72	28.7	33.26
TON <sub>N</sub>	0.54	0.48	0.3
TP	0.13	0.14	0.13
Macronutrient ratios:			
TC:TON <sub>N</sub>	71.88	59.7	109.4
TC:TP	290.95	205.86	248.64
TON <sub>N</sub> :TP	4.05	3.45	2.27

\* SS, suspended sediment; TC, total carbon, TON<sub>N</sub>, total oxidized nitrogen-N; TP, total phosphorus

Mean and median pollutant concentrations and ratios in one field (field 2) changed considerably when comparing baseflow and stormflow conditions (Table 5.6). For up to 81 % of the year (if pollutants are assumed to have baseflow behaviour during flow rates < 0.2 L s<sup>-1</sup> when no discharge water was pumped for monitoring) the total pollution concentration (excluding TC) was made up by approximately by 10 times as much SS as TON<sub>N</sub>, approximately 216 times as much SS as TP and approximately 23 times as much TON<sub>N</sub> as TP. During low baseflow conditions, for 15 % up to 65 % of the year (if pollutants are assumed to have lower baseflow behaviour during flow rates < 0.2 L s<sup>-1</sup>), discharge water was made up by 4 times as much SS as TON<sub>N</sub>, 150 times as much SS as TP and

approximately 32 times as much  $\text{TON}_N$  as TP, because  $\text{TON}_N$  concentrations further increased, while SS and TP concentrations further decrease. During storm-flow periods (11 % of the year) or high storm-flow periods (2.8 % of the year), SS and TP concentrations generally increased, while  $\text{TON}_N$  concentrations decreased. SS and TC concentrations were approximately similar with ratios around 1 during storm-flow, but almost twice the concentrations of SS as TC during high storm flows. SS concentration was approximately 100 and > 230 times that of  $\text{TON}_N$  and approximately 380 and 375 times that of TP during storm-flow and high storm-flow conditions, respectively. Macronutrient ratios were  $\text{TC}:\text{TON}_N \approx 100$  and  $100 - 888$ ,  $\text{TC}:\text{TP} \approx 380$  and  $190$  and  $\text{TON}_N:\text{TP} \approx 4$  and  $0.2 - 2$  during storm-flow and high storm-flow, respectively. Base and stormflow periods change highly frequency with stormflow periods occurring at short but frequent bursts (Figure 5.2).

Looking at the representative example of the 34-hour high-resolution period, the relative contribution of each pollutant towards the overall pollution concentration behaved differently with flow, whilst the total pollution concentration increased with flow (Figure 5.6). SS generally contributes most to the combined pollution concentration of  $\text{SS} + \text{TP} + \text{TON}_N$ . The contribution of SS was 99.8 % during the hydrograph peaks but fell to 80 % throughout the post-storm baseflow period, whilst percentage  $\text{TON}_N$  contribution was approximately 14 % at the start of the event, dropped down to almost 0.03 % through hydrograph peaks and then recovered back to 19 % at the end of the shown period. Despite rising TP concentrations with higher flows, the % contribution of TP fell with the hydrographs (down to 0.034 %) and was 0.5 % at the start of the storm event and 0.72 % towards the end of the time series.

Table 5.6. Mean and median pollutant concentrations and their ratios measured in one field (Field 2) during baseflow and stormflow periods as well as further subdivided into the lower quartile of baseflow and upper quartile of stormflow.

Pollutant* concentrations mg L <sup>-1</sup>	All baseflow						Baseflow lower quartile						All stormflow						Stormflow upper quartile					
	32 – 81 % of the year *2			15 - 65 % of the year *2			11 % of the year			2.8 % of the year														
	Mean	Median	N	Mean	Median	N	Mean	Median	N	Mean	Median	N	Mean	Median	N									
SS	8.8	6.4	7364	4.8	3.7	3526	29.6	20.8	2898	29.8	19.6	951												
TC*1							23.4	25.6		13.3	11.6	478												
TON <sub>N</sub>	0.9	0.8	6846	1.0	0.9	3267	0.3	0.2	2715	0.13	0.01	54												
TP	0.04	0.03	2249	0.03	0.025	978	0.059	0.069	1184	0.061	0.073	665												
SS:TC*1							1.3	0.8		2.2	1.7													
SS:TON <sub>N</sub>	10.2	8.5		4.7	4.1		95.5	115.3		229.1	1507.7													
SS:P	218.8	214.7		159.3	148.0		501.7	300.7		488.2	268.5													
TC:TON <sub>N</sub> *1							75.5	142.2		102.2	888.5													
TC:TP *1							396.6	371.0		217.7	158.2													
TON <sub>N</sub> :TP	21.5	25.3		33.7	36.4		5.3	2.6		2.1	0.2													

\* SS, suspended sediment; TC, total carbon, TON<sub>N</sub>, total oxidized nitrogen-N; TP, total phosphorus

\*1 Total carbon was only measured as grab samples during storm events.

\*2 Higher baseflow estimates include the time when there was flow, but not sufficient rates (< 0.2 L s<sup>-1</sup>) for monitoring; assuming that concentrations and ratios during that time is similar to those during baseflow or the lower quartile of baseflow.

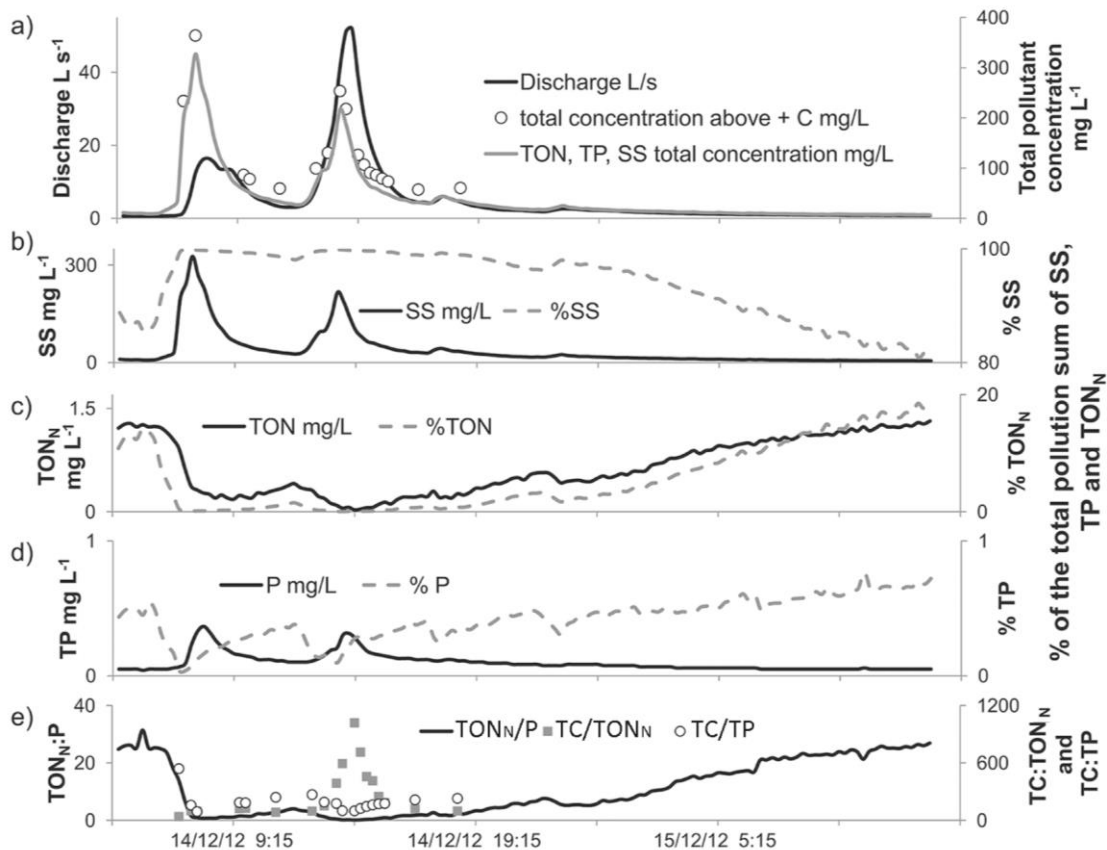


Figure 5.6. Example fine-scale dynamics of multiple pollutants throughout a 34 hour time series for one field (Field 5). a) Discharge and the total pollution concentrations: the sum of TON<sub>N</sub>, TP and SS pollutant concentrations (line), the sum of all pollutants including TC (dots), b-d) SS, TON<sub>N</sub> and TP concentration and their % contribution to the overall pollution concentration (SS+TON<sub>N</sub>+TP), respectively, e) nutrient ratios. SS, TON<sub>N</sub> and TP were monitored continuously at 15 minute steps and TC was analysed at lower resolution by grab samples.

This is the first study to calculate the proportionate contribution of SS and the macronutrients TC, TON<sub>N</sub> and TP to overall losses in intensively managed grasslands. The high annual yield stoichiometric ratios of TC to TON<sub>N</sub> and TP highlight the high TC losses from these grasslands in relation to the other macronutrients (Graeber *et al.*, 2012). Total C may be mobilized and transported disproportionately to N when compared with the source soil TC:TN ratios. Soil TC:TN ratios measured in field 2 one year prior to this study was 9.9 (Chapter 4)

and a nearby agricultural catchment had soil TC:TN ratios of 14.21 (Glendell *et al.*, 2014), both an order of magnitude lower than those found herein in the discharge water (TC:TON<sub>N</sub> = 60 - 100). Therefore, future research should compare soil C:N:P ratios with water C:N:P ratios on the Farm Platform. Additionally, future research should quantify the proportion of TON<sub>N</sub> for overall total N in discharge water for higher certainty in C:N:P ratio calculations. Measuring TON<sub>N</sub> and excluding ammonium N (NH<sub>4</sub><sup>+</sup>) and forms of organic N is likely to represent a high proportion of the overall N, 84 % as reported for a catchment dominated by both grassland and arable land (Stutter *et al.*, 2008), but this needs to be confirmed on the Farm Platform.

The results presented in this paper show that such high-resolution synchronous monitoring of multiple pollutants is required to provide advances in understanding pollutant delivery of multiple pollutants with respect to a) the conditions that aquatic biota are likely to experience and the impacts these conditions may cause and b) to achieve simultaneous pollutant reductions rather than just mitigating individual pollutants.

a) The fine-scale changes of relative SS, TON<sub>N</sub>, TP and TC concentrations shown here indicate the fine-scale changes of water quality, habitat quality, relative nutrient availability and relative occurrence of multiple stressors that aquatic organisms in agricultural catchments are likely to be exposed to (Collins *et al.*, 2011; Thompson *et al.*, 2014). The proportional importance of SS, TP increases from baseflow to stormflow while the proportionate importance of TON<sub>N</sub> falls. Whilst up to 81 % of the entire year is dominated by baseflow, stormflow periods occurred at frequent, but short bursts; demonstrating the frequently changing conditions that aquatic organisms are exposed to. Short-term exposure has been reported to impact on aquatic organisms and ecology (Collins *et al.*, 2011; Thompson *et al.*, 2014), but research assessing the impact of short-term exposures are rare (Collins *et al.*, 2011). Such high resolution, multi-pollutant research can provide useful information for receptor-response studies, for example periods of exposure and dosages and mixtures of exposure (Thompson *et al.*, 2014).

b) Concentrations and yields of N seem to already have been reduced in this NVZ by the current management compared to previous research conducted on the same site (Scholefield *et al.*, 1996), but SS, TP and TC losses are comparable to other grassland sites as well as other land uses. Therefore, the relative importance of SS, TP and TC has increased with the reduction in  $\text{TON}_N$ . Switches in relative importance of pollutants have been demonstrated by N and P switching in their role as limiting nutrients in the Gulf of Mexico (Sylvan *et al.*, 2007), showing the need for simultaneous reductions of multiple pollutants (Pearl, 2009). Simultaneous reduction of diffuse pollution can only be achieved if the impact of agricultural management practices on water quality is understood by monitoring relative pollutant delivery.

#### **D. How does water quality from intensively managed grasslands compare to EU and UK recommended water quality standards?**

Guidelines set for SS and DRP were frequently exceeded by the concentrations of SS and TP measured in this study (Table 5.7). The high-frequency monitoring, including all flow conditions from low to high flows, allowed for accurate and precise calculation of water quality guideline exceedance frequencies and the timing and duration of exposure (Kirchner *et al.*, 2004; Bilotta *et al.*, 2010; Thompson *et al.*, 2014).

11.6 - 13.9 % of all SS samples (low and high flows) exceeded the FFD guideline of  $25 \text{ mg L}^{-1}$ . When the SS standard was lowered to  $10 \text{ mg L}^{-1}$ , 31.4 – 54.1 % of the SS samples exceeded that standard. This lower  $10 \text{ mg L}^{-1}$  is close to the water quality guideline set for turbidity in agricultural eco-regions in the USA (USEPA, 2000). If particles  $< 1.25 \mu\text{m}$  had been included in the suspended sediment measurements, the percentage of all samples exceeding the guideline concentrations would have potentially been even higher. SS on a nearby grassland site, more intensively managed than the Farm Platform, exceeded the FFD guideline for approximately 50 % of the hydrological season (SS  $> 0.7 \mu\text{m}$  (Bilotta *et al.*, 2010)) and two Irish catchments showed an annual exceedance of 8.3 - 17.8



% (Thompson *et al.*, 2014). However, note that the suitability of the blanket guideline (across all water bodies in the UK, all seasons) of 25 mg SS L<sup>-1</sup> has recently been heavily criticised (Bilotta *et al.*, 2012). The high erosion levels from these grasslands are likely to contribute significantly to the documented water quality issues in the receiving Taw River. Low salmonid fish numbers in the Taw are generally attributed to high sedimentation levels and physical degradation of spawning gravels by siltation (Haygarth *et al.*, 2005a).

Approximately half of all the TP discharge water samples failed to meet what is considered as good ecological status (< 0.04 mg SRP L<sup>-1</sup>) and 4.2 – 18.3 % failed to reach moderate ecological quality (< 0.15 SRP mg L<sup>-1</sup>) (TAG, 2008). Therefore, grasslands, which cover 80 % of the Taw River catchment (similar management and soil types to the North Wyke Farm Platform) contribute to the documented P issue in the Taw river (Haygarth *et al.*, 2005a). Note that TP exceedance of the guideline set for soluble reactive P (SRP) may overestimate the true exceedance. However, not only SRP is bioavailable in surface waters, but particulate P and organic P also have the potential to be recycled within rivers and become bioavailable through time (Darch *et al.*, 2013). Elsewhere, for example in the USA, standards are set as TP concentration thresholds; in agriculturally dominated eco-regions around 0.03 - 0.08 mg TP L<sup>-1</sup> (USEPA, 2000), sitting just between the values of good and moderate status that TP concentrations in this study were compared to. Furthermore, climate change scenarios predict wetter winters and drier summers for the UK in the future, which are likely to increase winter discharge events and reduce river flow levels during summers (Jordan *et al.*, 2012), both factors that already cause high P loadings in the Taw River.

TON<sub>N</sub> concentrations in discharge waters did not exceed the Nitrates Directive Nitrate-N guideline of 11.3 mg L<sup>-1</sup>, which is a positive result, as the entire Taw River catchment is designated as a NVZ. However, the fact that TON<sub>N</sub> levels were acceptable under the current guideline does not necessarily mean that these grasslands do not pose a threat to surface waters in terms of N: a) Nitrite, even though only accounting for a small proportion of TON<sub>N</sub> (4 % in Granger *et al.* (2010) on a near-by site), is potentially toxic to aquatic fauna even in very low

concentrations and impacts on ecosystem health by leading to increased biological oxygen demand within surface waters (Lewis & Morris, 1986) and b) there is growing evidence that organic N can be rapidly available to plankton and microorganisms in estuarine and marine environments (See *et al.*, 2006). Therefore, the export of organic N that was not accounted for in this study, may have significant impacts on the receiving Taw estuary, already classified as eutrophic (Maier *et al.*, 2012).

There are no known EU / UK C guidelines in terms of freshwater and marine ecosystem health. The TC concentrations from these grasslands may make a potentially significant contribution to reducing dissolved oxygen in the water and therefore indirectly affecting aquatic fauna and flora (Sandford *et al.*, 2013). Excessive biological oxygen demand have been reported for stretches of the Taw river (Haygarth *et al.*, 2005a). Such results support the need for explicit guidelines for TC in surface waters.

The concentrations found in discharge waters in this study were comparable to the range of concentrations monitored in the Taw River (weekly measured concentrations approx. 400 m downstream from the flume at Field 2: SS: 0 - 31 mg L<sup>-1</sup> (particle sizes not presented), PP + total dissolved P: < 0.02 - 0.37 mg L<sup>-1</sup>, NO<sub>3</sub> + NO<sub>2</sub><sup>-</sup> = TON: 4 - 10.2 mg L<sup>-1</sup>, DOC: 1 - 16 mg L<sup>-1</sup>) (Jarvie *et al.*, 2008). Additionally, a study in the Taw catchment estimated that diffuse sources of P contributed at least 60 % of the annual P flux of the Taw River (Wood *et al.*, 2005). Therefore, the sediment and macronutrient concentrations seen in the discharge waters and yields from these intensively managed grassland fields contribute significantly to overall concentrations and yields in the receiving surface water and dilution is not likely to be high.

Table 5.7. The percentage of all suspended sediment (SS), total P (TP), and total oxidized nitrogen-N (TON<sub>N</sub>) samples exceeding water quality guidelines in the discharge water of three improved grassland fields.

	Field 2	Field 5	Field 8
<b>SS</b>			
> FFD (> 25 mg SS L <sup>-1</sup> ) *	11.64	13.9	13.37
> 10 mg L <sup>-1</sup>	41.88	31.4	54.1
<b>TP</b>			
fail 'good ecological status' (> 0.04 mg DRP L <sup>-1</sup> ) * <sup>1</sup>	49.1	52.3	59.27
fail 'moderate ecological status' (> 0.15 mg DRP L <sup>-1</sup> ) * <sup>1</sup>	7.11	4.2	18.31
<b>TON<sub>N</sub></b>			
fail Nitrates Directive (> 11.3 mg NO <sub>3</sub> <sup>-</sup> -N L <sup>-1</sup> )	0	0	0

\* FFD, EU Freshwater Fisheries Directive.

\*<sup>1</sup> DRP, dissolved reactive phosphorus.

The high resolution monitoring approach herein has shown quality standard exceedances, which regulatory monitoring at considerably coarser resolutions (weekly or monthly) may have missed (Kay *et al.*, 2009). Relying on lower resolution monitoring for classifying rivers for the WFD may lead to wrong classification of water quality status as well as potentially identifying the wrong reasons for failure. The data here has highlighted that, if coarse monitoring for classification only occurred during low flows, SS and TP issues may not have been identified. Identifying the right reason for failure is important in deciding on the best mitigation options in the catchment basin management plan for the water framework directive. Additionally, only monitoring that can identify whether pollutant concentrations fall throughout all flow conditions or only throughout certain conditions have the potential to reliably show the effects of mitigation measures (Kay *et al.*, 2012).

Monitoring pollutant fluxes in discharge generated from fields nested within the farm scale provides advantages over interpreting water quality at the outflow of large catchments. This study has shown the isolated losses of diffuse pollutants mobilized from grassland fields, rather than showing the combined pollution from entire catchments. This isolation is important in reliably monitoring the effects of in-

field management practices, which cannot be disentangled from other pollutant sources, such as on-farm sources like farm yards (Bilotta *et al.*, 2010), or off-farm sources such as septic tanks (Melland *et al.*, 2012). The usefulness of the field or farm scale will become further evident when the effectiveness of future field-based management changes will be assessed on the Farm Platform.

## V. Conclusion

This study adds to the growing evidence that grasslands have been previously underestimated in terms of their erosion rates and TP losses.  $\text{TON}_N$  yields were less than those reported in earlier grassland N studies and arable sites, possibly due to reduced N inputs as a result of NVZ regulations. TC losses were particularly high, adding to the evidence that agricultural catchments and intensively managed grasslands in particular can yield high C losses (**Question 5.1**).

Hydrological events were mostly saturation-excess driven in the winter as opposed to infiltration-excess driven during the summer. Suspended sediment and TP were mobilized and transported by hydrological flushing from the soil surface, while  $\text{TON}_N$  was diluted by rainwater, because diffusion from its source (soil water) is limited by the rapid rainwater movement. Total carbon showed varied responses in hydrological events, with concentrations decreasing from summer to winter. Both dissolved and particulate C are likely to contribute to the overall TC concentrations and yields (**Question 5.2**).

The relative importance of pollutants varied greatly and changed rapidly through flow conditions and time. Total C losses were high in relation to the other macronutrients. The relative importance of SS, TP and TC has increased with the reduction of  $\text{TON}_N$  (**Question 5.3**). Suspended sediment and TP concentrations frequently exceeded EU water quality guidelines and high TC exports are likely to reduce dissolved oxygen in surface waters. Intensively managed grasslands pose a significant threat to water quality (**Question 5.4**).

This study has shown the usefulness of a farm-scale research platform (the North Wyke Farm Platform) and has established a baseline understanding of how this ecosystem functions in terms of multiple pollutants at management-relevant scales. Future work will monitor field to farm-scale perturbations of land management in relation to this baseline understanding to understand the effects of improved land management on these multiple pollutant losses. The overarching aim should be to achieve synchronous reductions in all pollutant losses, which can only be monitored by the high-resolution and multi-pollutant approach used in this paper.

*This chapter added to the growing evidence that conventional temperate intensively managed grasslands contribute significantly to soil erosion and agricultural diffuse pollution.*

*Whilst this chapter answered important questions about intensively managed grassland fields in general, by treating the three fields as examples for typical intensively managed grassland fields, it did not address between-field variation. The three fields showed a range of sediment and macronutrient values, which raises the question whether the fluxes of these three fields are significantly different and if they are different, what may have caused these differences to occur. Subsequent questions arise, such as whether the differences may be linked to differences in the soil nutrient pools available for mobilization, or different potential of mobilization of the pollutants in the three fields. Therefore, between-field differences in terms of water quality linked with between-field differences in soil status were addressed in the next chapter (Chapter 6).*

*The grassland fields that were monitored in this chapter had been managed as permanent grasslands for at least 5 years. However, most grasslands are not managed as permanent grasslands, but ploughing followed by reseeded is part of a normal cycle of managing grassland systems. Therefore, chapter 8 quantified sediment and macronutrient losses in recently ploughed and reseeded grasslands.*

## Chapter 6

### Quantifying the Field-Scale Variation of Ecosystem Structure and Function within an Intensively Managed Grassland

#### **I. Abstract**

One of the major challenges for agriculture today is to manage soil properties and their spatial distribution to optimize productivity and minimize environmental impacts, such as diffuse pollution.

Three conventionally managed grassland fields with uniform short-term management, but with differences in long-term management history, were studied to understand spatial variation of soil properties and the quality of discharge water and to establish a robust baseline understanding of this agro-ecosystem's functioning prior to implementing different grassland management scenarios. Geostatistical sampling pattern and analysis was used to quantify soil spatial variation. Soil status was linked to discharge water quality data from each field in terms of the macronutrients total carbon (TC), total nitrogen in the soil (TN) and total oxidized nitrogen-N in the water (TON<sub>N</sub>) nitrogen, and total phosphorus (TP).

Despite having the same land use and uniform management for at least 6 years, the sampled fields functioned differently; they were different in mean soil properties and their distributions, and different in terms of water quality. Therefore, agricultural fields with different management histories but the same land use cannot be assumed to be similar and it is essential to characterize a baseline to which future effects of mitigation measures can be compared to. Soil and water quality benefits may be gained by recognizing the distribution of soil properties within fields. The mobilization of total oxidised nitrogen-N and total phosphorus from soil sources to water could be explained well, but more research is required to understand total carbon mobilization processes. Total carbon was mobilized disproportionately from the soil total carbon pool.

Future effects of planned grassland management scenarios on the Farm Platform can be analysed reliably as changes from the baseline reported in this study.

## **II. Introduction**

Agricultural practices inevitably affect the physical properties of the soil and nutrient contents to optimize crop production. Those altered soil properties subsequently affect ecosystem services, such as nutrient sources, their mobilization and delivery to surface waters. Latest estimates are that agriculture contributes 81 % of the overall N and 47 % of the overall P pollution in England and Wales (Zhang *et al.*, 2014); there are no published estimates of the C contribution from agriculture to overall carbon loads. Many mitigation measures have been implemented in the past two decades, most of which aim to improve in soil quality and minimize the mobilization of nutrients from agricultural land. The effectiveness of those measures have not (yet) become evident (Johnson & Lord, 2011; van Grinsven *et al.*, 2012).

Effectiveness of mitigation measures might not be detectable (yet), because the legacy of intensive agricultural management takes time to take effect on soils and again time to take effect on water quality (Burt *et al.*, 2011; Horrocks *et al.*, 2014). Therefore, soil status and water quality of surface waters today to some extent reflect past management rather than current management (Burt *et al.*, 2011). Disentangling the interplay between short and long-term management is crucial to fully understand relationships between management and soil and water quality (Burt *et al.*, 2011).

Improvements in soil quality (reduction of excess soil nutrients) and improvements in water quality (reductions of nutrient concentrations and loadings) are often evaluated separately, even though both operate on a continuum from soil to water (Haygarth *et al.*, 2005). Therefore, effects of management should be studied through the entire source-mobilization-delivery continuum, to identify the continuum components that have improved and those that need further improvement (Wall *et al.*, 2011). For example, Johnson & Lord (2011) found a reduction in soil nutrient surpluses in grasslands, but no overall reduction in surface water nutrient concentrations, showing that potential

nutrient sources may have reduced, but their mobilization rates need further mitigation efforts.

Detecting an improvement in soil and water quality by mitigation or management change is often limited by poor understanding of the conventional management, to which post-mitigation data can be compared. Before any new management practice can be quantified, a baseline understanding or characterization of the 'status quo' of the conventional management in both soil properties and resulting water quality is therefore essential (Breuer *et al.*, 2006). Many water quality studies use paired catchment studies involving a baseline characterization (Schilling *et al.*, 2013). However, soil studies often compare soil properties between sites with different management histories without baseline characterization and rely on the fundamental assumption that the sites were similar in terms of soil properties prior to land-use change (Breuer *et al.*, 2006). Wrong inferences may be made about management effects without analyzing management effects relative to baseline conditions. Additionally, monitoring before the change in management and long-term monitoring afterwards should enable us to judge how long it takes for the management to take effect (Wall *et al.*, 2011).

It is not just the average soil conditions in a field that might change as a result of management, but also the spatial distribution of soil properties. Spatial variation exists in agricultural fields (McCormick *et al.*, 2009; Chapter 4), despite the homogenization effect of agricultural management via uniform fertilizer applications, uniform vegetation cover and uniform soil physical management (Glendell *et al.*, 2014). This spatial variation needs to be quantified both between and within agricultural fields so that any alteration in either the overall mean or in the patterns of soil properties can be attributed to changes in management (Li *et al.*, 2010; Glendell *et al.*, 2014). Consequently, it is necessary to adopt a spatial sampling strategy to quantify the spatial distribution of soil properties.

Soil improvement and water quality mitigation measures are generally implemented on individual farms, whereby the farmer decides on field-specific management. Because the field- to farm-scale is the scale at which management decisions are made and at which policies are targeted, farm-scale experiments have been set up to investigate these matters; to provide novel



insight into management effects on the continuum of fine-scale soil processes up to the arrival of pollutants in surface waters.

In light of these research needs, this is a spatially explicit study of soil properties and resultant water quality across a conventionally managed grassland farm-scale experiment in the UK: the North Wyke Farm Platform. Grassland fields with uniform short-term management, but differences in long-term management history were sampled to address the following questions:

**Question 6.1** Does within and between-field variation of soil properties exist in intensively managed grassland fields?

**Question 6.2** Can between-field differences in water quality be explained by between-field differences in soil properties and between-field differences in site characteristics?

**Question 6.3** Does soil and water quality monitoring before management change provide a robust baseline for future comparisons, and are the sampled fields suitable for a paired catchment approach?

### **III. Methods**

#### **A. Field site**

Sampling was conducted on the Rothamsted Research North Wyke Farm Platform in south-west England (Figure 6.1a) between April 2012 and April 2013. The Farm Platform consists of 15 fields, subdivided into three, equal-sized farmlets, which were under the same management during the sampling period, but which will be subjected to different management in the future. Each Farm Platform field is hydrologically isolated so that the water leaving the field by subsurface and surface flow is channelled via French drains into flumes, where both water quantity and quality are monitored.

The three largest fields (approx. 6.5 - 7.5 ha) in each farmlet were chosen for this study, Field 2: Great Field, Field 5: Orchard Dean and Field 8: Higher and Middle Wyke Moor (Figure 6.1b - d). Field characteristics such as soil types,

topography and management are presented in figure 6.1b - d and table 6.1. The soil types are the most common hydrological soil types in England and Wales, covering approximately 13.9 % of the land area (Boorman *et al.*, 1995; Bilotta *et al.*, 2008). The soils are slowly permeable and often waterlogged, creating saturation-excess overland flow (Harrod & Hogan, 2008). Waterlogging occurs mostly between October and March, when a large proportion of the annual rainfall occurs (Harrod & Hogan, 2008). The long-term (40-year) mean annual rainfall (1045 mm) and temperature (9.6 °C) are typical of many of the intensively managed grassland areas in the UK.

Land management over the last 30 years was permanent pasture in field 5, the northern part of field 2 and the eastern part of field 8, whereas the southern part of field 2 was ploughed and reseeded to grass after cultivation for barley in 2007 and the eastern part of field 8 was ploughed and reseeded in 1993. The management for the past 6 years was uniform for the three fields. They were managed conventionally for intensive cattle and sheep production, involving grazing or grass cutting for silage. Inorganic fertilizer and manure were applied in accordance with the Code of Good Agricultural Practice (DEFRA, 2010) and the Nitrate Vulnerable Zone guidelines (DEFRA, 2008) and can therefore be considered to represent a standard management practice. Inorganic fertilizer and manure inputs for each field are listed in table 6.1. In 2011, the fields were used for silage, followed by grazing by cattle and sheep. In 2012 they were mainly used for cattle and sheep grazing, but the animals were taken off the fields early because soil conditions were too wet.

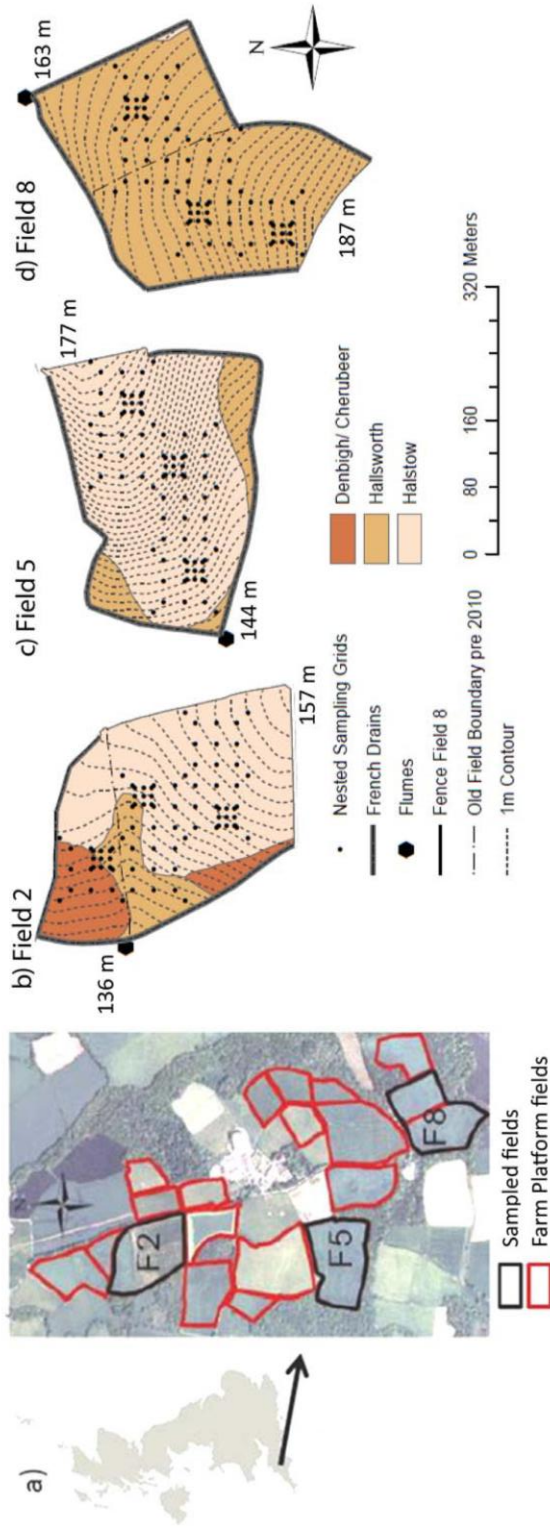


Figure 6.1. Description of the sampling site: the North Wyke Farm Platform. a) Location of the Farm Platform and the location of the three grassland sampling fields within the Farm Platform. b-d) individual sampling field topography, soil types\*, French drains, which channel surface and subsurface flow to flumes for c) field 2, d) field 5 and e) field 8. Field 2 used to be two separate fields until 2010; the old field boundary is presented. Field 8 has two fenced parts; the location of the fence is presented.

\*Names for soil types under international classifications: Denbigh/Cherubeer (Avery, 1980); FAO Stagni-eutric cambisol, USDA: Dystric eutrochrept; Halstow (Avery, 1980); FAO Stagni-vertic cambisol, USDA Aeric haplaquept; Hallsworth (Avery, 1980); FAO Stagni-vertic cambisol, USDA Typic haplaquept (in Harrod and Hogan, 2008).

Table 6.1. Detailed physical site characteristics, short-term inorganic fertilizer and FYM <sup>\*1</sup> inputs, and long-term ploughing history for each sampled field.

Site characteristic	Field 2	Field 5	Field 8
Catchment Size (ha)	6.71	6.59	7.59
Mean slope ± stdev. (%)	6.11 ± 1.56	11.79 ± 3.1	6.86 ± 1.59
Slope Range (%)	0.98 - 9.81	5.26 - 20.89	3.52 - 13.37
Soil Types and Coverage *	Halstow (68%) Denbigh (18%) Hallsworth (14%)	Halstow (84.5%) Hallsworth (15.5%)	Hallsworth (84.7%) Halstow (5.4%)
Inorganic Fertilizer Input (2011-2012)	284 kg N ha <sup>-1</sup> 32 kg P ha <sup>-1</sup>	284 kg N ha <sup>-1</sup> 32 kg P ha <sup>-1</sup>	304 kg N ha <sup>-1</sup> 32 kg P ha <sup>-1</sup>
FYM <sup>*1</sup> Inputs (2011-2012)	176 t	176 t	eastern part: 0 western part: 39.2 t
Ploughing History	<u>northern part:</u> permanent grassland for ≈ 30 years  <u>southern part:</u> ploughed in 2007	permanent grassland for ≈30 years	<u>eastern part:</u> ploughing: 1993  <u>western part:</u> permanent grassland for ≈30 years

\* (Avery, 1980)

<sup>\*1</sup> FYM, Farmyard manure

## B. Soil sampling and statistical analysis

The soil was sampled in June 2012. Soil bulk density (BD), soil organic matter (SOM), total carbon (TC), total nitrogen (TN) and total phosphorus (TP) were measured.

In total 252 soil samples were taken, 84 in each field. All measurements were taken with cores from 0 - 10 cm soil depth, the soil layer that comprises most of the soil-plant-water processes. Sample preparation and analysis except TP followed the methods described in Chapter 4. Total P was determined by a sulphuric acid extraction method on finely ground samples (Saunders & Williams, 1955). In all analyses, assured quality control standards were used to ensure analytical quality. The ratios TC:TN, TC:TP and TN:TP were calculated for each field.

To address **question 6.1**, whether within and between-field variation of soil properties exist, a nested geostatistical sampling pattern was chosen for each field, which captures short-range and large-range variation. A 25 x 25 m grid was supplemented with extra points: 12 broader scale 75 x 75 m points and 3

sets of small-scale 10 x 10 m samples (Figure 1 b-d). All geostatistical analyses were done with GenStat 16<sup>th</sup> edition (VSN International, Hemel Hempstead, UK). The dataset was characterized by testing for normal distribution, calculating the skewness coefficient and detecting outliers. Trend analysis was conducted by fitting linear and quadratic surfaces (Oliver & Webster, 2014). A trend is a gradual variation in space and conflicts with the basic assumption of randomness. Experimental variograms were fitted by Matheron's method of moments and the variograms with the smallest mean square error were chosen (Oliver & Webster, 2014). For datasets with underlying trends, the variograms of the residuals of the fitted trend surface were tested for spatial structure, both in separate steps as well as by combining both steps by residual maximum likelihood (REML) (Oliver & Webster, 2014). Kriging was conducted to visualize spatial distribution of soil properties. Values were predicted for 5 x 5 m blocks in each field. The neighbourhood settings recommended by Oliver & Webster (2014) were used. Cross validation was conducted to validate kriging predictions and variogram model fit (Oliver & Webster, 2014). Kriged estimates were imported into ArcGIS 10 (ESRI, Redlands, CA, USA). To visualise soil properties with underlying trends and no remaining spatial structure of the residuals after fitting the trend, inverse distance weighing was used in ArcGIS. A trend surface would show a gradual increase or decrease of values with the direction of the trend and may be most closely fitting model to describe the distribution of soil properties in fields with underlying trends, but a surface prediction that very closely resembles the raw data was chosen as the aim was to map the distribution of soil properties as realistically as possible. To keep the displays on the surface map as close to the raw data as possible, a maximum of 4 neighbours was used to fill the areas between points. The individual prediction maps for each field were combined to use the same colour classification by using the mosaic tool in ArcGIS 10.

To assess between-field variation, boxplots were used and two-sample t-tests in GenStat 16<sup>th</sup> edition (VSN International, Hemel Hempstead, UK). To identify possible underlying mechanisms causing within-field variation, a) the strength of correlation between individual soils properties were tested by Pearson's correlation coefficients, b) visually similar patterns of distribution were identified on the surface prediction maps, and c) known physical site

characteristics (e.g. topography) and present and past management records were consulted to interpret the effects of land management on soil properties (Oliver & Webster, 2014).

### **C. Hydrology and water quality monitoring**

To address **question 6.2**, whether between-field differences in water quality can be explained by between-field differences in soil properties and between-field differences in site characteristics, monitoring was conducted between June 2013 and April 2014. In summary, hydrology (rainfall and discharge) and the water quality parameters total carbon (TC), total oxidized nitrogen-N ( $\text{TON}_\text{N}$ ), total phosphorus (TP) and suspended sediment (SS) were monitored by automated, semi-automated and manual methods. Griffith *et al.* (2013) describe the instrumentation of the Farm Platform and Chapter 5 describes the specific instrumentation, methodology, data management and quality assurance.

To test for between-field differences in hydrology and water quality, crude two-sample t-tests were used in GenStat, following the work of (Schilling *et al.*, 2013). It is difficult to test for differences between the fields, because the data was not sampled at random, but systematically. However, using t-tests on time series is common practice in the literature (Schilling *et al.*, 2013). To put pollutant losses in the context of potential causal mechanisms, between-field differences in pollutant losses were explored in relation to hypothesized causal factors, such as between-field differences in soil properties and field characteristics, such as topography.

To address question 6.3 a), whether soil and water quality monitoring before management change provides a robust baseline for future comparisons, results of question 6.1 and 6.2 were used. To address question 6.3 b), whether the sampled fields are suitable for a paired catchment approach, the future control catchment (field 5) was paired with the future treatment catchments 2 and 8. Then, linear regression was conducted for discharge and like pollutant concentrations between the paired catchments, a common practice in paired catchment studies (King *et al.*, 2008). Correlations are conducted to show whether the fields / catchments respond to rainfall in similar ways in terms of

flow and pollutant concentrations, which is an important prerequisite that needs to be met in paired field / catchment studies (King *et al.*, 2008; Schilling *et al.*, 2013).

## IV. Results

### A. Does within and between-field variation of soil properties exist in intensively managed grassland fields?

Significant spatial variation was detected both between and within the sampled fields. Mean soil properties were significantly different between the fields (Table 6.2 and boxplots in Figure 6.4). Field 8 had the lowest bulk density ( $0.8 \text{ g cm}^{-3}$ ), followed by field 2 ( $0.9 \text{ g cm}^{-3}$ ) and field 5 with the highest bulk density ( $1 \text{ g cm}^{-3}$ ). SOM, TC and TN concentrations were least in field 2, intermediate in field 8, and largest in field 5 (TC storage in field 2:  $31.6 \text{ t ha}^{-1}$  < field 8:  $33.6 \text{ t ha}^{-1}$  < field 5:  $47.6 \text{ t ha}^{-1}$ ). Total phosphorus content was also largest in field 5, followed by field 2 and least in field 8. TC:TN and TC:TP ratio were smallest in Field 5, intermediate in Field 2 and largest in Field 8, ranging between 8.3 and 8.8 and 33.3 and 36.6, respectively. TN:TP ratio was smallest in field 2 and highest in field 8.

Table 6.2. Summary of the mean and standard deviation (Stdev) values of the measured properties for the three grassland sampling fields. Statistical differences between the fields are indicated by different letters (a,b,c).

Measured soil property *	Field 2		Field 5		Field 8	
	Mean ± Stdev		Mean ± Stdev		Mean ± Stdev	
BD ( $\text{g cm}^{-3}$ )	$0.9 \pm 0.1$	a	$1 \pm 0.1$	b	$0.8 \pm 0.1$	c
Total C ( $\text{g kg}^{-1}$ )	$35.9 \pm 6.4$	a	$49.8 \pm 6.4$	b	$42.2 \pm 6.1$	c
Total N ( $\text{g kg}^{-1}$ )	$4.3 \pm 0.7$	a	$6 \pm 0.7$	b	$4.8 \pm 0.7$	c
Total P ( $\text{g kg}^{-1}$ )	$1.3 \pm 0.3$	a	$1.5 \pm 0.2$	b	$1.2 \pm 0.2$	c
SOM ( $\text{g kg}^{-1}$ )	$88.8 \pm 18.4$	a	$118.2 \pm 12.3$	b	$101.1 \pm 10.4$	c
TC:TN	$8.6 \pm 0.9$	a	$8.3 \pm 0.6$	b	$8.8 \pm 0.6$	c
TC:TP	$34.9 \pm 6.0$	a	$33.3 \pm 3.3$	b	$36.6 \pm 5.8$	c
TN:TP	$3.2 \pm 0.7$	a	$4.0 \pm 0.4$	b	$4.2 \pm 0.6$	b

\* BD, Bulk density; SOM, Soil organic matter

Within-field variation of soil properties occurred over distances of 41.9 m (SOM) to 129.2 m (TP) in field 5, and over distances of 93.7 m (BD) to 173.7 m (SOM) in Field 8 (Table 6.3). Spherical variograms were fitted to the data of field 5 and 8, because they had no underlying trends. A significant quadratic south-north trend was detected in field 2 for each soil property, explaining between 8.6 - 62.8 % of the variation (Table 6.4). There was no spatial structure left in the residuals after the trend fitting and REML was not conducted. Therefore, soil prediction maps for field 2 were established by inverse distance weighting (Figure 6.2).

Table 6.4. Results of quadratic surfaces for field 2. There was no spatial structure left in the residuals.

Field	Variable *	% variance explained by fitted trend
2	BD (g cm <sup>-3</sup> )	30.3
2	SOM (g kg <sup>-1</sup> )	34.1
2	Total C (g kg <sup>-1</sup> )	62.8
2	Total N (g kg <sup>-1</sup> )	50
2	Total P (g kg <sup>-1</sup> )	36.3

\* BD, Bulk density; SOM, Soil organic matter



Table 6.3. Results of geostatistical analysis and spherical variogram model\*/ kriging cross-validation for all soil properties of grassland fields 5 and 8.

Field	Variable *1	Nugget $c_0^*$	Partial Sill $c^*$	Range $r^*$	% variability explained by the model	mean error	mean squared error	mean prediction variance	mean ratio	median ratio
5	BD (g cm <sup>-3</sup> )	0.003	0.01	72.7	64.7	0.001	0.01	0.005	1.23	0.73
5	SOM (g kg <sup>-1</sup> )	27.71	104.40	41.9	36.2	-0.84	143	94.36	1.44	0.59
5	Total C (g kg <sup>-1</sup> )	17.39	14.99	67.4	42	-0.41	31	26.23	1.15	0.70
5	Total N (g kg <sup>-1</sup> )	0.18	1.20	79.4	38.2	-0.03	0.42	0.27	1.38	0.45
5	Total P (g kg <sup>-1</sup> )	0.01	0.01	129.2	58.4	-0.005	0.01	0.015	1.00	0.39
8	BD (g cm <sup>-3</sup> )	0.01	0.01	93.7	59.9	0.0004	0.02	0.01	1.30	0.41
8	SOM (g kg <sup>-1</sup> )	51.35	68.35	173.7	79.1	-0.06	81.83	69.87	1.18	0.41
8	Total C (g kg <sup>-1</sup> )	5.17	28.31	96.3	83.5	0.02	18.45	14.04	1.38	0.45
8	Total N (g kg <sup>-1</sup> )	0.12	0.28	104.0	56	0.003	0.22	0.22	1.04	0.51
8	Total P (g kg <sup>-1</sup> )	0.01	0.02	111.6	89.3	-0.002	0.02	0.02	1.09	0.32

\* equation of the spherical model:  

$$y(h) = c_0 + c \left\{ \frac{3h}{2r} - \frac{1}{2} \left( \frac{h}{r} \right)^3 \right\}$$
 for  $0 < h \leq r$ , when  $h =$  lag distance,  $c_0 =$  nugget,  
 $c =$  sill,  $r =$  range

\*1 BD, bulk density; SOM, Soil organic matter.

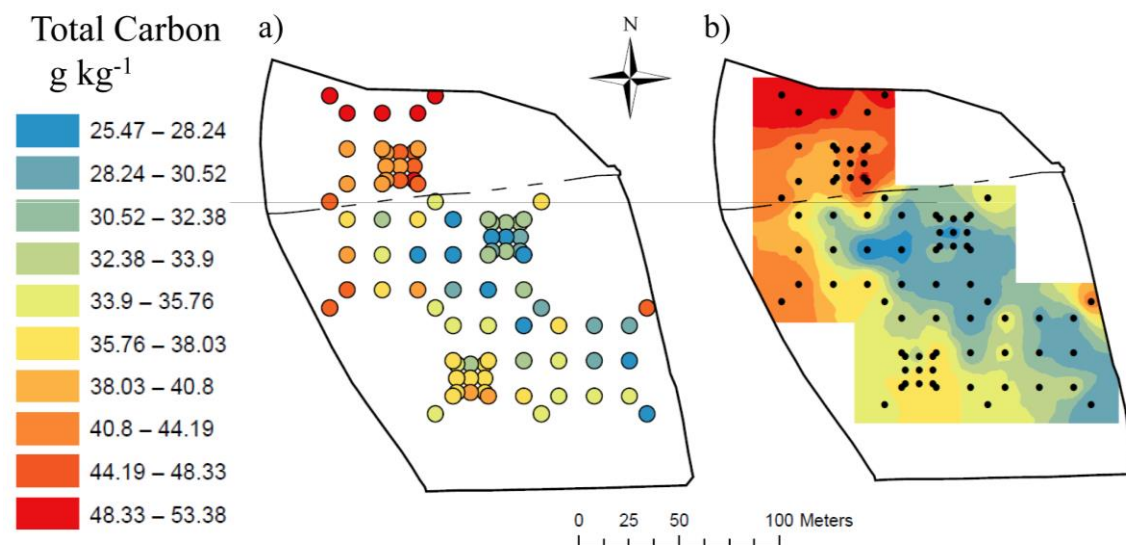


Figure 6.2. Total carbon raw data in field 2 (a) and surface prediction map by inverse distance weighting (b). The inverse distance weighting map very closely resembles the raw data, because only 4 neighbours were chosen to make the predictions.

The surface maps (Figure 6.4) show different distributions of soil properties within the individual fields, across the extent of the sampling (Figure 6.5) and display the significant differences between the three fields. Those soil properties that show similar distributions across the fields were often correlated (Table 6.5).

The north-south trend is evident in the map of field 2. The northern part of the field contained more SOM, TC and TN and has a smaller BD than the southern part. The north-south pattern was not evident in TP concentrations and TP was not correlated with the other soil properties (except TN), but showed large concentrations in the north and the far south with smaller concentrations in between. The northern-part is lower than the southern part and elevation was positively correlated with BD and negatively correlated to SOM, TC and TN.

Field 5 contained a uniform distribution of SOM, TC, TN and TP across the field, confirmed by significant positive correlations between those soil properties. The centre up to the north-east of the field had slightly higher BD, SOM, TC, TN and TP concentrations. Elevation was not correlated with any

soils properties apart from TC (negatively) and no visible pattern was detectable with slope gradient.

Field 8 showed a somewhat different pattern between the fenced-off eastern and western parts of the field with larger SOM, TC, TN and TP concentrations in the eastern part; most of these soil properties were correlated (Table 6.5). The eastern part of field 8 is lower, and elevation was correlated with SOM, TC and TN. There was a patch of larger BD around the fence than in the rest of the field.

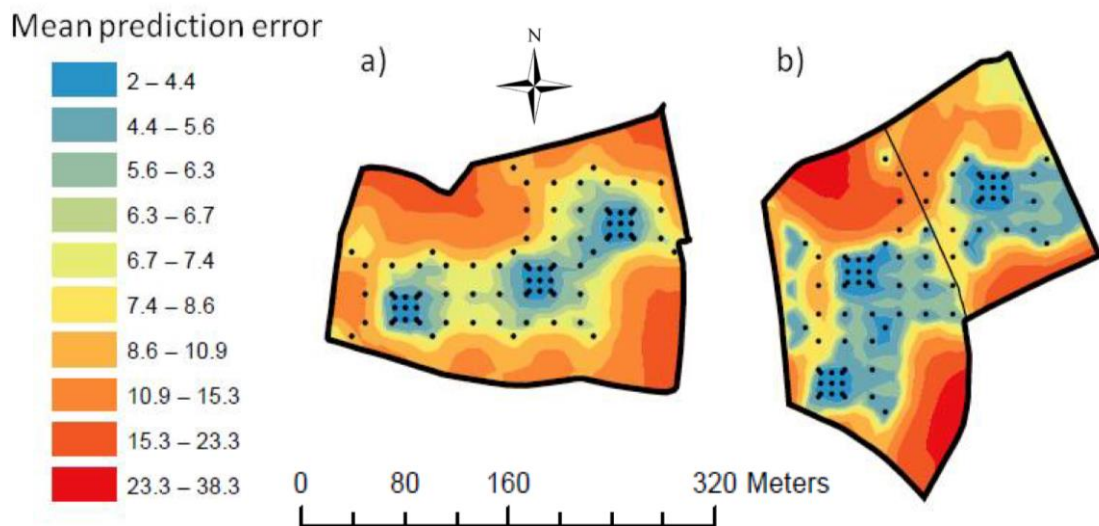


Figure 6.4. Mean prediction error for predicting total carbon by kriging for a) field 5 and b) field 8. The error is smallest when the sampling is most dense. Therefore, only prediction surfaces covering the extent of the sampling area are shown in Figure 6.3.

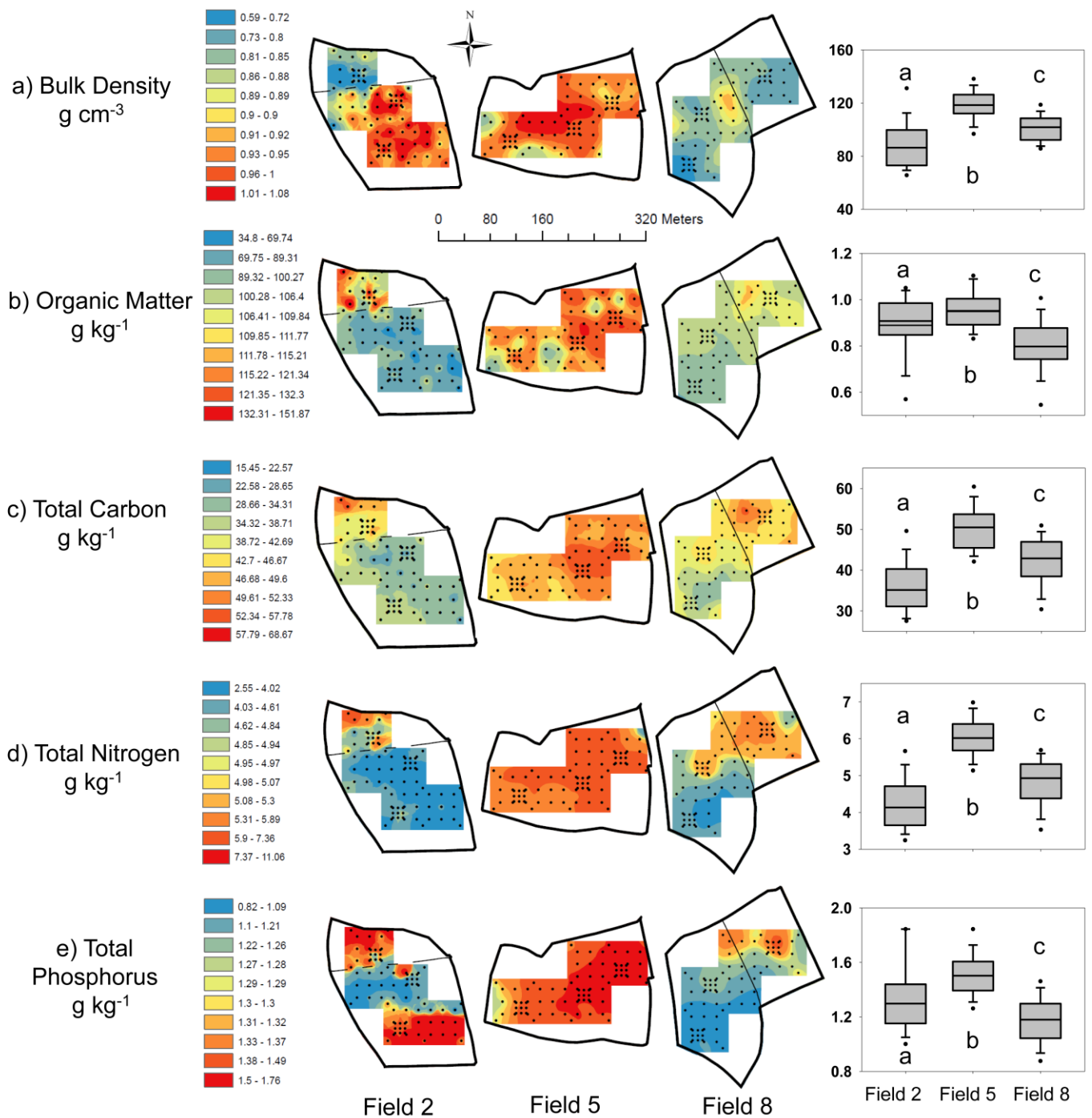


Figure 6.3. Surface prediction maps by inverse distance weighting for field 2 (left) and by kriging for soil properties in field 5 (middle) and field 8 (right), apart from total P in field 8 (inverse distance weighting). Boxplots are showing the significant between-field differences in means of each soil property. Only predictions within the area of the sampling extent are shown. The old dividing field boundary (pre 2010) is shown in field 2, dividing the northern and southern part, affecting distribution patterns of soil properties. The fence between the eastern and western part in field 8 is shown. The boxes visualize the lower to the upper quartile, the line the median and the upper whisker the upper quartile + 1.5 \* the interquartile range and the lower whisker the lower quartile – 1.5 \* the interquartile range. Dots visualize the 5<sup>th</sup> and 95<sup>th</sup> percentile. Significant differences between boxes are shown by different letters (a,b,c), determined by two-sample t-tests.

Table 6.5. Correlation coefficient between the measured soil properties and elevation within each sampling field. Only significant ( $P < 0.5$ ) coefficients are presented.

Field 2	BD	SOM	Total C	Total N	Total P
SOM	-0.43				
Total C	-0.49	0.78			
Total N	-0.36	0.70	0.86		
Total P				0.28	
Elevation	0.44	-0.45	-0.42	-0.25	0.38

Field 5	BD	SOM	Total C	Total N	Total P
SOM					
Total C		0.64			
Total N	-0.26	0.56	0.79		
Total P	-0.26	0.45	0.72	0.66	
Elevation			-0.36		

Field 8	BD	SOM	Total C	Total N	Total P
SOM	0.32				
Total C		0.64			
Total N		0.54	0.87		
Total P		0.45	0.47	0.52	
Elevation		-0.24	-0.40	-0.38	

**B. Can between-field differences in water quality be explained by between-field differences in soil properties and between-field differences in site characteristics?**

There were significant differences between the three fields in terms of mean discharge, mean pollutant concentrations and mean loads, despite large variation (Table 6.6). The relationships of between-field differences in soil properties and differences in water quality properties were not linear across the three fields.

Mean discharge was in the order of field 2 < 5 < 8, but when expressed as a runoff coefficient, the order was field 2 (41 %) < field 8 (46 %) < field 5 (54 %), because the runoff coefficient accounts for the larger volume of rain on the

larger catchment area of field 8. The order of the fields in terms of runoff coefficients also reflects the mean slope and slope range of the fields, as a proxy for the efficiency of field drainage (Table 6.1). Field 5, with the largest runoff coefficients, highest slope and significantly largest soil nutrient contents and storages (Table 6.2) had low mean nutrient concentrations and loads in its discharge water, with mean concentrations of  $\text{TON}_N = 1.17 \text{ mg L}^{-1}$ ,  $\text{TP} = 55.28 \mu\text{g L}^{-1}$ ,  $\text{TC} = 25.76 \text{ mg L}^{-1}$ . Total P, TC and  $\text{TON}_N$  fields' mean nutrient losses did not reflect their relative soil nutrient contents and storages for field 2 and 8. Field 8 with smaller soil TP than field 2 had larger losses of P in its discharge water. Field 2 with the smallest soil TC and TN, has significantly larger mean TC and  $\text{TON}_N$  concentrations ( $23.65 \text{ mg L}^{-1}$ ,  $0.88 \text{ mg L}^{-1}$ , respectively) in the water leaving the field, whereas field 8 with larger TC and TN soil contents lost less TC and  $\text{TON}_N$  in the water ( $27.77 \text{ mg L}^{-1}$ ,  $0.45 \text{ mg L}^{-1}$ , respectively). TC: $\text{TON}_N$  (60-109) and TC:TP ratios (206-291) in the discharge water were an order of magnitude larger than in the soil (TC:TN  $\approx 8.5$ , TC:TP  $\approx 34.5$ ), whereas water  $\text{TON}_N$ :P ratios (3 - 4) and soil TN:TP ratios (3 - 4) were similar.

Table 6.6. Hydrology and water quality characteristics for the three grassland fields and the differences between their means, where appropriate. Different letters (a,b,c) show significant differences, determined by two-sample t-tests). Hydrology and water quality monitoring was conducted from April 2012 - March 2013, with sampling resolutions up to every 15 minutes).

	Field 2	Field 5	Field 8	
Hydrology	Mean Discharge L s <sup>-1</sup> ± stdev	1.2 ± 4.7	1.5 ± 5.6	1.6 ± 6.1
	% of rain as discharge year <sup>-1</sup>	40.5	53.9	46.2
Suspended Sediment	Annual yield kg ha <sup>-1</sup> year <sup>-1</sup>	182.2 - 194.3	433.9 - 527.4	213.4 - 220.9
	Mean conc. mg L <sup>-1</sup> ± stdev	13.4 ± 20.7	14.9 ± 30.8	15.1 ± 17.8
	Mean load mg s <sup>-1</sup> ± stdev	15.4 ± 65.5	24.1 ± 148.9	15.7 ± 69.4
Total oxidised Nitrogen-N	Annual yield kg ha <sup>-1</sup> year <sup>-1</sup>	1.4 - 1.8	2.9 - 3	0.9 - 1
	Mean conc. mg L <sup>-1</sup> ± stdev	0.9 ± 0.6	1.2 ± 0.5	0.5 ± 0.3
	Mean load mg s <sup>-1</sup> ± stdev	0.1 ± 0.2	0.2 ± 0.3	0.05 ± 0.2
	Annual yield kg ha <sup>-1</sup> year <sup>-1</sup>	0.4	0.9	0.4
Total Phosphorus	Mean conc. µg L <sup>-1</sup> ± stdev	48.9 ± 25.7	55.3 ± 50.7	47.6 ± 42.8
	Mean load µg s <sup>-1</sup> ± stdev	30.2 ± 92.3	92.2 ± 257.7	58.9 ± 155.4
	Annual yield kg ha <sup>-1</sup> year <sup>-1</sup>	122.2	179.1	109.4
Total Carbon	Mean conc. mg L <sup>-1</sup> ± stdev	23.7 ± 8.9	25.8 ± 8.4	17.8 ± 7.04
	Mean load mg s <sup>-1</sup> ± stdev	46.3 ± 42.6	72.3 ± 73.6	53.6 ± 47.9
	TC:TON <sub>N</sub>	71.9	59.7	109.4
Annual yield nutrient ratios	TC:TP	290.95	205.9	248.6
	TON <sub>N</sub> :TP	4.1	3.5	2.3

**C. Does soil and water quality monitoring before management change provide a robust baseline for future comparisons, and are the sampled fields suitable for a paired catchment approach?**

Results of question 6.1 and 6.2 characterized the soil and water baseline. The paired future control and treatment catchments were strongly correlated in terms of rainfall ( $r^2 = 0.8$ ) and discharge ( $r^2 = 0.9$ ) and moderately correlated for water quality parameters ( $r^2 = 0.46$  to  $0.69$ ) (Table 6.7).

Table 6.7. Coefficients of determination for each water quality variable between the selected control field (Field 5) and the two future treatment fields (Field 2 and Field 8).

	Field 5 vs Field 2	Field 5 vs Field 8
Precipitation	$r^2 = 0.68$ , N = 35713	$r^2 = 0.69$ , N = 35713
Discharge	$r^2 = 0.89$ , N = 35713	$r^2 = 0.9$ , N = 35713
Suspended Sediment	$r^2 = 0.79$ , N = 8178	$r^2 = 0.82$ , N = 7964
Total oxidised Nitrogen-N	$r^2 = 0.68$ , N = 11045	$r^2 = 0.33$ , N = 10988
Total Phosphorus	$r^2 = 0.62$ , N = 1886	$r^2 = 0.44$ , N = 2026
Total Carbon	$r^2 = 0.65$ , N = 59	$r^2 = 0.55$ , N = 85

## V. Discussion

**A. Does within and between-field variation of soil properties exist in intensively managed grassland fields?**

The fields were significantly different in terms of soil physical properties and nutrient contents, despite having been managed uniformly for at least 6 years. Long-term management differences, such as different ploughing management, rather than short-term management may be identified as causal mechanisms for the differences between the fields.

The soil in the field with the longest time since last ploughing (field 5: at least 30 years) contained most SOM, TC and TN. The field with the intermediate time



since last ploughing (field 8: western part not ploughed for at least 30 years, eastern part ploughed in 1993) had intermediate SOM, TC and TN contents, and the soil in the field with the most recent ploughing (field 2: ploughed in 2007) had the least SOM, TC and TN. Ploughing reduces SOM, TC and TN in the soils by breaking soil aggregates, mixing the topsoil with deeper soil layers and thereby increasing soil aeration, exposing previously protected SOM to mineralisation and increasing SOM decomposition and microbial turnover. In contrast, SOM, TC and TP accumulate in the topsoil of permanent grasslands, because fertilizer and manure applications and direct applications of manures by grazing livestock are made to the soil surface and not mixed with deeper soil layers.

Agricultural fields with different management histories (more than 6 years ago), but the overall same land-use cannot be assumed to be similar in their mean soil properties. Therefore, long-term management history always has to be included when interpreting soil data.

The fields were not only significantly different in the means of soil properties, but also had different within-field spatial variation and different distribution of soil properties. Again, within-field patterns may be affected by different management histories for different areas within fields, but may also be affected by topography and resulting water movement or impacts of grazing animals.

The significant north-south trend in all soil properties in field 2 reflect several influences: different past management in the two field areas (ploughing in the southern part versus permanent grassland in the north, which previously was part of a neighbouring field), topography and resultant water movement down slope towards the south with possible re-deposition of nutrients. These patterns have remained stable since the previous year. Chapter 4 discussed the potential causal mechanisms of the distribution of soil properties in detail. This similarity in the patterns of soil properties and the similar values year-on-year illustrates the relative stability of total nutrients and their within-field patterns.

One or a combination of the following may be responsible for causing the differences between the two parts of the field 8 that are divided by a fence. The western part has the more recent ploughing history (last ploughed in 1993), whereas the eastern part has not been ploughed for approximately 30 years,

which may have resulted in SOM, TC, TN and TP accumulation in the eastern part. Different short-term nutrient management (FYM applications in the eastern part but not in the western part 2 years prior to sampling) may have increased soil SOM, TC, TN and TP contents and storages (Edmaedes, 2003; Dungait *et al.*, 2012). Additionally, the direction of water movement through the field and consequent soil erosion down the slope, generally from the western to the eastern part, may have re-deposited SOM, TC, TN and TP in the eastern part. Bulk density showed a different distribution pattern and was not correlated with other soil properties except SOM and nutrient storage. Bulk density was largest around the fence between the two parts of the field, the area in both parts of the fields where cattle mostly congregate (Page *et al.*, 2005).

In field 5, either the short-term grazing behaviour of livestock or an accumulated effect of longer-term grazing behaviour may have caused the large concentrations in the centre-east of the field. The central eastern area with large concentrations of SOM, TC, TN and TP and large BD coincided with the area where cattle congregate. The large BD may be caused by livestock trampling and the large concentrations of nutrients and SOM by manure inputs by the grazing livestock (Page *et al.*, 2005; Bilotta, 2008).

Such high-resolution geostatistical sampling provides additional information, which cannot be detected by studies which only considering central tendencies between fields. The differences in central tendencies between the fields would not give insight into the field-specific distributions of the soil properties across the fields. Most scientific soil surveys sample in a zigzag or w-pattern across a field and commercial soil surveys may only take one sample per ha, which would have only resulted in 6-7 samples per field (McCormick *et al.*, 2009). The UK National Soil Research Institute dataset would have provided 1-3 values per field ([www.landis.org.uk/soilscapes](http://www.landis.org.uk/soilscapes)). Glendell *et al.* (2014) discuss the discrepancies that may occur when comparing detailed soil sampling datasets with coarser scale data (UK National Soil Research Institute dataset). They found the national dataset to underrepresent the true variation of soil properties found by geostatistical sampling and analysis. The discrepancy between the spatial variation found herein and the national data set would be even larger because this study had a higher sampling resolution (1199 samples km<sup>-2</sup>) than the study by Glendell *et al.* (2014) (5.18 samples km<sup>-2</sup>). Therefore, incorporating

spatial variation by a detailed geostatistical approach is essential to monitor the full effect of agricultural management practices on soil properties reliably.

To incorporate spatial variation in experimental sampling on the Farm Platform, or in agricultural fields in general, optimal sampling strategies should sample distances between 20 m and 80 m (approximately half the range distances), depending on the soil property of interest. The ranges over which spatial variation occurred on the Farm Platform compare to the ranges reported for a single field in an earlier Farm Platform publication (Chapter 4), and compare to the ranges reported for other intensively managed temperate grassland (McCormick *et al.*, 2009) and those reported for arable land (Kerry & Oliver, 2011).

**B. Can between-field differences in water quality be explained by between-field differences in soil properties and between-field differences in site characteristics?**

The fields were not only significantly different in terms of their mean soil properties and their within-field distribution, but were also significantly different in their nutrient concentrations, loads and yields in the discharge water (despite having had the same management for at least 6 years). Between-field differences in soil nutrient sources and between-field differences in their mobilization potential are likely to have caused the differences in water nutrient concentrations, loads and yields (Wall *et al.*, 2011). Question 6.1 already discussed the differences in nutrient sources between fields. Additionally, rainwater moved to the flumes faster and in a larger proportion of rainfall in field 5 < 8 < 2, thereby differently affecting the mobilization of nutrients between the fields. The following discusses the source, mobilization and transport mechanisms that may be responsible for the differences in nutrient concentrations, loads and yields between the fields. Mechanisms of TP and TON<sub>N</sub> transfer can be explained well, as their sources and mobilization mechanisms have been extensively studied, but more TC mechanistic research is required.

Total P delivery to surface waters is known to depend on a combination of different factors: soil TP available for mobilization (Djordjic *et al.*, 2004), hydrological TP mobilization potential by either rapid flows that mobilize sediment particles with adsorbed TP, desorption of TP from sediment particles or transporting dissolved P enriched soil water (McDowell *et al.*, 2001). Soil P is generally only viewed as an indicator of potential P source and has to be considered in combination with other factors such as topography and hydrological connectivity of sources to surface waters (McDowell *et al.*, 2001). Total P is known to be preferentially transported during high flows, by hydrological mobilization and often in association with soil particles (Bilotta *et al.*, 2010; Chapter 5). Slope angle and runoff coefficients can be considered as indicators of hydrological P mobilization potential (Page *et al.*, 2005) and discharge water SS concentrations and loads represent the potential mobilization of P associated with soil particles (Bilotta *et al.*, 2008; Chapter 5). Here, all of those factors were greatest in field 5, which also stores the most TP in the soil, illustrating the potential of this field to yield larger TP losses. The larger TP losses in field 8 than in field 2, even though the order of soil TP content was the reverse, may be explained by field 8 having a steeper slope angle, higher runoff coefficients and larger SS concentrations than field 2. Therefore, the differences in TP losses between the grassland fields may be explained by a combination of available soil TP pool, mobilization potential by hydrological mobilization and sediment associated P transport.

The mode of mobilization of  $\text{TON}_N$  from these grassland soils is thought to be by diffusion of  $\text{TON}_N$  from the soil water to the rainwater moving through the soil system (Gächter *et al.*, 2004; Granger *et al.*, 2010). The amount of  $\text{TON}_N$  delivered to freshwater therefore depends on the available dissolved  $\text{TON}_N$  pool in the soil water and the diffusion potential.  $\text{TON}_N$  losses were largest in field 5, intermediate in field 2 and smallest in field 8. The total N content that was analysed in the soils, containing both organic and inorganic forms of N, does not directly reflect the  $\text{TON}_N$  availability in the soil. The soil TN content was in the order of field 2 < field 8 < field 5, only reflecting the largest N losses in field 5, but not the other two fields' ranking. Rather than comparing soil total N and water  $\text{TON}_N$ , most studies compare inorganic N inputs, or the balance between N inputs and N uptake by crops, but these relationships are generally poor

(Buczko & Kuchenbuch, 2010). Soil TC:TN ratios may be more indicative of the actual concentrations of inorganic N in the soil pool. Research conducted in forests found that the smaller the C:N ratio is, the faster is the rate of SOM turnover, which increases the available nitrate pool in the soil (Mooshammer *et al.*, 2012). If this process was true for grasslands, then the available nitrate pool would be in the order of field 8 < 2 < 5, the same order as the TON<sub>N</sub> delivery to discharge water. The time since last ploughing may also be an indicator of the N pool in the soil occurring as inorganic N, as ploughing increases N mineralisation (Bhogal *et al.*, 2000). The more recent ploughing in field 2 indicates field 2 to have larger concentrations of inorganic N in the soil compared to field 8, despite having smaller overall total soil TC. The opportunities for TON<sub>N</sub> diffusion are small in these sloping grasslands. When rainfall moves rapidly over the soil surface or through macropores, TON<sub>N</sub> concentrations in water are diluted during high flows (Gächter *et al.*, 2004; Granger *et al.*, 2010; Chapter 5). The dilution potential during high flows is in the order of field 8 < 5 < 2 (mean discharge) (Gächter *et al.*, 2004; Granger *et al.*, 2010; Chapter 5). The combination of potential TON<sub>N</sub> pool in the soil and dilution potential between the fields may explain the between-field differences in TON<sub>N</sub> concentrations in discharge waters.

The relationship between available soil TC pool and the amount of TC transported to surface waters in agricultural landscapes is not well documented, because a) most C studies measure dissolved organic carbon in water (DOC) (Worall *et al.*, 2012) rather than total C, thereby ignoring any organic matter particles or carbon adsorbed to sediment particles. b) most C studies are conducted on peaty or semi-natural catchments and c) most studies that are conducted in agricultural catchments do not quantify both soil and water C (for example Sandford *et al.*, 2013). Glendell *et al.* (2014) reported a negative correlation between soil C and water total organic C across an agricultural catchment and a semi-natural upland catchment in the UK. The agricultural catchment had smaller soil TC content and had larger C losses to water than the semi-natural upland catchment. The larger TC losses from the agricultural catchment were attributed to larger soil erosion-driven particulate organic carbon losses. No studies that are comparing soil TC with water TC could be found between agricultural catchments / fields. Herein, it is difficult to explain

the differences in water TC concentrations and yields between the fields for several reasons. a) Water TC was only analysed during storm events and therefore, baseflow TC concentrations and behaviour are not understood (Chapter 5). The ranked differences in soil TC pools between the fields did not reflect the differences in water TC between the fields, apart from field 5 having the largest soil TC pool and the largest amounts of TC in the water. Recent ploughing history and thereby the likely degree of SOM protection in soil aggregates (Liu *et al.*, 2006) may be an explanation for the larger C losses in field 2 with the most recent ploughing history and the smallest TC soil content, compared to field 8 with larger soil C content but longer time since ploughing, but this has not been demonstrated in previous research. The ranked potential of mobilizing sediment associated TC between the fields ( $2 < 8 < 5$ ) did not reflect the water TC concentrations or loads (as found in (Quinton *et al.*, 2006; Glendell & Brazier, 2014). Higher resolution (temporal) research on TC in discharge waters is required, best divided into analysing dissolved and particulate C, as the source, mobilization and transport mechanisms of TC in agricultural landscapes are not yet fully understood. What can be said here though is that, TC was lost disproportionately from the soil carbon pool. C:N and C:P ratios in the water were an order of magnitude larger than in the soils, whereas N:P ratios were similar in the soils and in the water.

The three fields may be considered to be functioning differently. Long-term management differences have affected soil properties and altered soil processes, such as nutrient cycling within and between the fields. Those differences in soil properties and cycling processes and inherent differences in site characteristics, such as field topography, have altered nutrient sources and their mobilization mechanisms to surface waters in a complex manner, so that the fields (possibly even further divided into parts of fields) are now functioning differently.

Long-term management effects, going back at least 6 years, but possibly up to 30 years ago or longer, were still evident in soil properties and resultant water quality. Such long response times are known to occur (Burt *et al.*, 2011). Full SOM turnover times are estimated to take approximately 36 years (Balesdent *et al.*, 1987) and long-term surface nutrient accumulations in grasslands can have

a lost-lasting legacy effect on elevated nutrient concentrations in surface waters (Schärer *et al.*, 2007). Such long-term effects of management still acting on soil properties may indicate how long it can take to see water quality improvements after implementing mitigation measures (decades).

The differences in soil status between the fields, the spatial distribution of soil properties within the fields and the differences in resulting water quality between fields confirms that intensively managed grassland fields, even on the similar soil types, cannot be treated as homogeneous management units. Water quality benefits and possibly productivity and economic benefits may be gained by considering the patterns of soil nutrients and matching nutrient inputs to the heterogeneous nutrient status within individual fields, as with precision farming in arable areas. For example, the two parts in field 2 and the fenced-off parts in field 8 could be treated as different management units (McCormick *et al.*, 2009).

**C. Does soil and water quality monitoring before management change provide a robust baseline for future comparisons, and are the sampled fields suitable for a paired catchment approach?**

The soil and water quality monitoring conducted in this chapter a) provide a robust baseline for future comparisons and b) were found suitable for future paired catchment studies.

a) The fact that the fields were significantly different in terms of soil characteristics as well as water quality does not make these results unsuitable for a robust baseline, but further emphasize the importance of baseline characterization. These fields cannot be assumed to have the same land-use, which is a fundamental assumption that paired site surveys without baseline characterization are based on (Breuer *et al.*, 2006). Therefore, results from such paired site surveys have to be analysed carefully (Breuer *et al.*, 2006). The characterized differences between fields in this paper will serve as a robust baseline, because any future alterations from the relative differences between the fields found in this paper may be identified reliably as an effect of management change.

b) The fields were found to be suitable for a paired catchment approach. To be suitable for a paired catchment approach, fields / catchments do not have to have the same soil nutrient contents or pollutant concentrations in discharge water, but they have to respond to rainfall in similar ways in terms of discharge generation and the behaviour of pollutants with discharge (tested for by linear regressions of time-series) (Jokela & Casler, 2011; Schilling *et al.*, 2013). The future control field (Field 5) was significantly correlated with the future treatment fields (2 and 8) in terms of hydrology and water quality properties throughout the entire time series (Schilling *et al.*, 2013). Significant and positive regression relationships between the fields suggest that rainfall occurs at the same time due to close proximity and the fact that hydrological and water chemical responses to rainfall are similar between the fields (Chapter 5).

The baseline characterization presented in this paper will allow a robust comparison of future soil and water quality to baseline soil and water quality. Any alteration in mean soil properties, their spatial variation and distribution within fields as well as any change in the components of the soil to water source-mobilization-delivery continuum can be identified as future management effects with a high degree of confidence (Jokela & Casler, 2011; Wall *et al.*, 2011; Schilling *et al.*, 2013).

## VI. Conclusion

The three sampled grassland fields were different in mean soil properties, different in spatial variation and the distribution of soil properties within **(Question 6.1)**. Those between-field differences in soil nutrient sources, in combination with mobilization and transport mechanisms have also caused differences in water quality **(Question 6.2)**. They were different despite having had the same land-use and uniform management for at least the past 6 years.

These findings have important implications for further monitoring of management practices on soil and water quality.

- The fields may be considered as functioning differently.



- The differences in soil and water quality between the fields emphasize the importance of baseline characterization and paired catchment approaches.
- Agricultural fields with different management histories, but the overall same land-use cannot be assumed to be similar in terms of mean soil properties or their distribution. Long-term management has to be taken into account when interpreting soil data, and the effect of new management changes have to be monitored long-term.
- High resolution soil sampling approaches are essential to reliably monitor the full effect of agricultural management practices on soil properties; the fine-scale spatial patterns could not have been detected by conventional soil sampling strategies.
- Soil and water quality benefits may be gained by conducting site-specific management; taking into account the distribution of soil properties.
- Carbon is mobilised and delivered to discharge water disproportionately to the carbon in the soil. Mobilization and delivery of carbon needs to be studied further, at high resolution.

The findings in this paper have important implications which are specific to long-term Farm Platform experiments. The fields proved suitable for paired catchment studies (**Question 6.3**). Once the planned management scenarios are implemented, any change occurring in the soil to water continuum components can be identified by before-after comparisons as well as by treatment-field and control-field comparisons and can be considered as the effect of future management with a high degree of confidence.

*This chapter characterized within and between field spatial variation of soil properties as well as between field differences in hydrology and water quality. Between-field differences in soil properties were then linked to between-field differences in water quality to address questions about available pollutant pools in the soils and their mobilization potentials. This chapter has also set a suitable baseline characterization to which future management intervention results can be compared to.*

*This chapter has answered some of the questions that were raised by previous chapters. First, using improved geostatistical methods confirmed the findings presented in chapter 4 rather than proved them to be unreliable. The improved geostatistical method confirmed the north-south differences to be an underlying trend in the dataset in field 2 (Great Field). Improved statistical methods confirm the north-south trend in field 2 that was found by the less reliable methods of kriging used in chapter 4. However, it was true that this north-south trend was in fact overriding spatial variation in this field, so no geostatistics could be conducted. Producing surface prediction maps by using inverse distance weighting in this chapter, neither changed the surface prediction map and the distribution patterns it presented, nor changed the interpretation of what was causing the spatial distribution presented in Chapter 4. The ranges of spatial variation found in this chapter with the improved geostatistics were similar to those presented in chapter 4.*

*Second, this chapter has also addressed the question whether field 2 (Great Field) in chapter 4 was an appropriate example of intensively managed grassland fields given the two previously differently managed parts of the field. However, this chapter has found that each grassland field was different in terms of soil status as well as distribution.*

*Third, this chapter has shown that the three fields are in fact significantly different in terms of their sediment and macronutrient concentrations and fluxes and that a large proportion of those differences may be explained by differences in soil properties between the fields.*

*The results in this chapter also provoked new questions, such as would ploughing homogenize soil properties within fields and between fields, or would the past management legacy remain? Chapter 7 explores these questions by comparing the results from two ploughed and reseeded fields and one grassland control field in the following year with the baseline calibration set in this chapter. Also, the question arises whether ploughing and reseeded would a) alter sediment and nutrient concentrations and fluxes compared to permanent grassland management, and b) whether ploughing and reseeded would alter the relationship between soil status and water quality between the fields, which were addressed in chapter 8.*

## **Chapter 7**

### **The Effects of Ploughing and Reseeding Grasslands on Soil Properties and Spatial Variation**

#### **I. Abstract**

Grasslands are frequently ploughed and reseeded as part of a normal grassland management cycle. Whilst the overall effects of ploughing on soil properties are well known, it remains to be understood, a) whether the magnitude of soil organic matter and nutrient losses with ploughing depends on past management such as sward age or time since last ploughing and b) whether one single ploughing and reseeded event has a significant homogenizing effect on the distribution of soil properties.

After ploughing and reseeded permanent grassland fields with contrasting ploughing histories, a range of soil physical and chemical variables (0 - 10 cm soil depth) were monitored. Mean values of soil properties as well as their spatial variability and distribution were compared to a pre-ploughing baseline period as well as a control field still managed as permanent grassland.

There may have been an effect of sward age; all soil nutrient concentrations were significantly reduced by ploughing the older grassland field but not in the younger grassland field. The expected homogenization effect on the spatial variation and distribution of soil properties was not seen after a single ploughing and reseeded event.

Ploughing and reseeded once did not override the legacy of past management in the intensively managed grasslands monitored; site specific management may be required to reverse past management effects and to reduce spatial variability in these intensively managed grasslands, if desirable.

## II. Introduction

Ploughing followed by reseedling is part of the normal cycle of managing grassland systems (Butler & Haygarth, 2007). It is considered economic to reseed, because dry grass matter yields can improve significantly (Butler & Haygarth, 2007). Also, grasslands are often ploughed whenever “sustainable intensification” measures are imposed, such as re-seeding with newer varieties with improved characteristics, such as high sugar grasses, disease/drought resistant or deeper rooting varieties. The degradation of soil quality, fertility and structure that ploughing and reseedling may bring about, might consequently restrict the long-term sustainability of such intensification measures.

The effect of ploughing on soil properties is generally well understood. Ploughing grasslands is known to cause a decline of soil organic matter (SOM) of 30 - 60 % of its original value over time (0 - 30 cm soil depth) (Grandy & Robertson, 2006; Acharya *et al.*, 2012). Similar declines have been shown in soil macronutrients nitrogen (N) and phosphorus (P) (Eriksen, 2001; Butler & Haygarth, 2007). Such macronutrient reductions occur because soil material that was previously stored in deeper soil horizons is exposed to air and microbes, and soil aggregates which were previously protected from degradation in shallow soil horizons are transformed via mineralization, oxidation, and volatilization as well as losses by erosion and surface runoff (Paustein *et al.*, 2000; Six *et al.*, 2000; Soussana *et al.*, 2004; Kalbitz *et al.*, 2005; Grandy & Robertson, 2006), N: (Kristensen *et al.*, 2003; Hansen *et al.*, 2005), P: (Addiscott & Thomas, 2000; Butler & Haygarth, 2007). Ploughing has also been shown to influence soil bulk density depending on soil depth. For example, surface soil bulk density (0 - 10 cm soil depth) was found to be increased by ploughing, whilst bulk density reduced in deeper layers (10 - 30 cm) (Koch & Stockfisch, 2006).

Whilst the overall effects of ploughing on soil properties are well known, certain aspects need further research. First, it is not well understood whether the magnitude of SOM and nutrient losses with ploughing depends on sward age / the time since last ploughing. Some studies have reported increased SOM and nutrient losses with increasing sward age / increasing time since last

ploughing (for C: (Soussana *et al.*, 2004), for N: (Johnston *et al.*, 1994)), whilst others have shown that, for example organic N is easier to mineralize and lost subsequently the more recently it has been formed (Hansen *et al.*, 2005). However, such research is often conducted in short-term grass leys rather than in longer-term permanent grasslands.

Second, it has never been quantified how ploughing and reseeded of previously disturbed or permanent intensively managed grasslands affects the spatial variation and the distribution of soil properties. It is generally known that agricultural land use, most importantly tillage, homogenizes the distribution of soil properties in contrast to natural environments (Robertson *et al.*, 1993; Paz-Gonzalez *et al.*, 2000; Chiba *et al.*, 2010; Li *et al.*, 2010; Glendell *et al.*, 2014). However, it remains unknown whether a single ploughing / reseeded event alone has a homogenizing effect and / or if it can override past management effects. Therefore, research is needed to quantify whether repeated ploughing / reseeded or individual ploughing operations homogenize soil properties and if so, to what degree.

Additionally, it is challenging to implement robust experimental designs under realistic management and climatic settings (as opposed to studies conducted in controlled environments). Chapter 6 suggested that a combination of 'before ploughing versus after ploughing' and 'control versus ploughed' experimental designs are more robust than soil surveys that compare soil properties between sites with different ploughing histories and rely on the assumption that the sites were similar in terms of soil properties prior to ploughing (Breuer *et al.*, 2006). However, soils are inherently variable and their characteristics at any site are affected by numerous influences, which change through time. Therefore, soil properties in a control field may change, despite receiving the same management, for example changes influenced by climatic variability, soil moisture variability or a legacy of past management (Hopkins *et al.*, 2009). Changes in soil properties in a control field may therefore compromise such experiments.

The main aim of this paper was therefore to study the short-term effect of ploughing and reseeded on soils that were previously managed as permanent grassland fields with different long-term ploughing histories. The aim was to

answer the following research questions by quantifying post / reseeding soil properties (0 - 10 cm soil depth) with respect to soil properties quantified in a permanent grassland control field and soil properties quantified during a baseline period when the fields were still managed as permanent grassland (Chapter 6).

**Question 7.1** Can fields subject to no management change act as controls, or is annual-scale (year-on-year) variability in soil characteristics significant?

**Question 7.2** Does ploughing and reseeding impose a significant change on soil physical properties and soil nutrient contents?

**Question 7.3** Does ploughing and reseeding affect spatial variation and the spatial distribution of soil properties, which in turn may affect herbage yield and therefore productivity?

For subsequent effects of ploughing and reseeding of permanent grasslands on water quality, see the companion paper (Chapter 8).

### **III. Methods**

Soil sampling was conducted on the Rothamsted Research 'North Wyke Farm Platform' in south-west England (Figure 7.1a) in October 2013. The 15 Farm Platform fields are subdivided into three farmlets (Figure 7.1a), which were subjected to different management scenarios. The red and the blue farmlet were ploughed and reseeded with different seed mixtures in July 2013, while the green farmlet remained as a permanent grassland control. The largest field in each farmlet was chosen for sampling, field 2 in the red farmlet, field 5 (control field) in the green farmlet and field 8 in the blue farmlet (Figure 7.1b - d); the same fields that were sampled in the previous year, the baseline period, when all fields were managed as permanent grassland (Chapter 6).

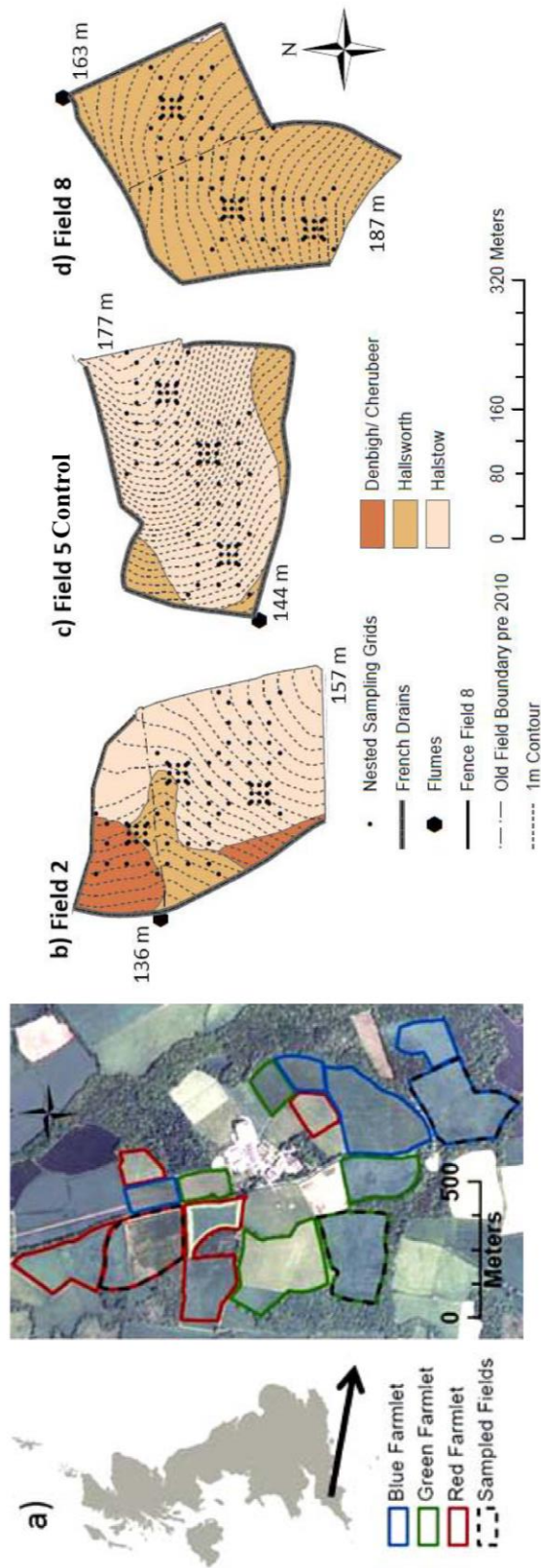


Figure 7.1. Description of the sampling site: the North Wyke Farm Platform, the location of the three farmlets and their component fields and the location of the three sampling fields. b - d) individual sampling field topography, soil types, French drains, which channel surface and subsurface flow to flumes for b) ploughed field 2, c) control field 5 and d) ploughed field 8. Field 2 used to be two separate fields until 2010; the old field boundary is presented. Field 8 has two fenced parts; the location of the fence is presented. Names for soil types under international classifications: Denbigh / Cherubeer (Avery, 1980); FAO Sagni-eutric cambisol, USDA Dystic eutrochrept; Halstow (Avery, 1980); FAO Stagni-vertic cambisol, USDA Aeric haplaquept; Hallsworth (Avery, 1980); FAO Stagni-vertic cambisol, USDA Typic haplaquept (in Harrod and Hogan, 2008).

The treatment fields (field 2 and 8) were first sprayed with glyphosate to kill the vegetation. The seed bed was prepared by ploughing, rolling and power harrowing, and by addition of both farm yard manure (FYM) and mineral fertilizers, followed by seed drilling. Field 2 was resown with the rye grass variety AberMagic and field 8 with a mixture of AberMagic and white clover (AberHerald) (detailed timing of management is given in table 7.1). The control field remained as a conventionally managed grassland field, it received fertilizer and FYM inputs. Field characteristics, recent and past management for each field, including the rates of FYM and fertilizer application prior to sampling, are summarized in table 7.2. Manure and inorganic fertilizer were applied following the Code of Good Agricultural Practice (DEFRA, 2010) and Nitrate Vulnerable Zone guidelines (DEFRA, 2008).

Table 7.1. Detailed timing of management implementation on field 2 and 8.

	Field 2	Field 8	
		east	west
Glyphosate spraying	26-Jun	26-Jun	26-Jun
FYM* spreading	04-Jul	04-Jul	05-Jul
Ploughing	06-Jul	09-Jul	09-Jul
Rolling and Power Harrow	20-Jul	20-Jul	19-20 July
Fertilizer application	22-Jul	22-Jul	22-Jul
Rolling and power harrow	30-Jul	31-Jul	31-Jul
Seed drilling	30-Jul	02-Aug	31-Jul
Herbicide spraying	06-Oct	06-Oct	06-Oct

\* FYM, farm yard manure

The Farm Platform soils are clay loams over shales of the Crackington formation with thin subsidiary sandstone bands (Bilotta *et al.*, 2008; Harrod & Hogan, 2008; Pilgrim *et al.*, 2010). These main soil types are typical for agricultural land managed as grassland and are the most common hydrological soil types, covering 13.9 % of the land area in England and Wales (Boorman *et al.*, 1995; Bilotta *et al.*, 2008). The soils have low water storage capacity, are slowly permeable and often waterlogged, creating saturation-excess overland flow (Harrod & Hogan, 2008; Dixon *et al.*, 2010). A high proportion of rainfall occurs as surface runoff between October and March (Harrod & Hogan, 2008; Dixon *et al.*, 2010). The long-term (40 years) mean annual rainfall (1045 mm)



and temperature (9.6 °C) are also typical of many of the intensively managed grassland areas in the UK (Smith & Trafford, 1976).

Table 7.2. Detailed physical site characteristics, short-term inorganic fertilizer and farm yard manure inputs, and short-term ploughing history for each sampled field.

	Field 2	Field 5 (control)	Field 8
Catchment Size (ha)	6.71	6.59	7.59
Mean slope ± stdev. (%)	6.11 ± 1.56	11.79 ± 3.1	6.86 ± 1.59
Slope Range (%)	0.98 - 9.81	5.26 - 20.89	3.52 - 13.37
French Drain Length (m)	601.8	926.9	983.6
Soil Types and Coverage *	Halstow (68 %) Denbigh (18 %) Hallsworth (14 %)	Halstow (84.5 %) Hallsworth (15.5 %)	Hallsworth (84.7 %) Halstow (5.4 %)
Inorganic Fertilizer Input (2013)	112 kg N ha <sup>-1</sup> 16 kg P ha <sup>-1</sup>	152 kg N ha <sup>-1</sup> 16 kg P ha <sup>-1</sup>	eastern part: 128 kg N ha <sup>-1</sup> ; 16 kg P ha <sup>-1</sup> ; western part: 112 kg N ha <sup>-1</sup> ; 16 kg P ha <sup>-1</sup>
FYM* <sup>1</sup> Inputs (2013)	211 t	171.5 t	eastern part: 98 t western part: 88.2 t
Soil Physical Management (2013)	Ploughed in July 2013, resown with AberMagic (30 kg ha <sup>-1</sup> ) in July 2013	permanent grassland for ≈30 years	Ploughed in July 2013, resown with a mixture of AberMagic (25 kg ha <sup>-1</sup> ) and white clover (AberHerald: 3.5 kg ha <sup>-1</sup> ) in July 2013

\*( Avery, 1980)

\*<sup>1</sup> FYM, Farmyard manure

Each field is hydrologically isolated by French drains, which channel surface and subsurface flows to flumes, where water quantity and quality was monitored for the companion paper on the effects of ploughing on water quality (Chapter 8).

A total of 84 soil samples were taken in each field with a pro-corer in October 2013 after the sward had established in the ploughed fields. Samples were taken from 0-10 cm soil depth, the soil layer that is considered most relevant for the soil-plant-water continuum in grasslands (Schärer *et al.*, 2007).

Samples were analysed for soil physical properties (soil bulk density [BD], soil organic matter [SOM]) and chemical properties (total carbon [TC], total

nitrogen [TN], and total phosphorus [TP]). Sampling was conducted on a nested grid (Figure 7.1 b - d). All sampling and laboratory procedures followed those conducted during the baseline period described in Chapter 4 and 6. Assured quality control standards were used in all analyses to ensure analytical quality. The ratios TC:TN, TC:TP and TN:TP were calculated for each field.

All statistical analysis was conducted in GenStat 16<sup>th</sup> edition (VSN International, Hemel Hempstead, UK). To answer **question 7.1**, whether fields subject to no management change can act as controls, the variation between the grassland baseline (2012) mean soil characteristics (Chapter 6) and the 2013 mean soil characteristics were assessed in the control field by using boxplots and two-sample t-tests. Also, spatial variation and spatial distribution of soil properties in the control field was compared between the baseline (Chapter 6) and this sampling period. To do so, geostatistical analysis was conducted. A full description of the geostatistical analysis is described in Chapter 6. In brief, experimental variograms were plotted which show the variance between sampling points as a function of separation distance. Variogram models were then fitted to the experimental variograms, to describe the continuous function and ignoring point-to-point fluctuations. The variogram functions were then used to visualize the distribution of soil properties across the whole field by predicting values at unsampled locations using kriging (Oliver and Webster, 2014). Datasets with underlying trends, and no spatial structure left in the residuals after trend fitting were visualized by inverse distance weighting, using only 4 neighbours, to keep the surface map as close to the raw data as possible (Chapter 6). Change in spatial variation and soil parameter distributions from the permanent grassland baseline period to the post-ploughing period were assessed by comparing semivariogram parameters, such as range and sills as well as visual assessment of the surface prediction maps (van Meirvenne & Hofman, 1989; Delcourt *et al.*, 1996; Bogaert *et al.*, 2000).

To answer **question 7.2**, whether ploughing / reseeded imposed a change on soil physical properties and soil nutrient contents, changes in mean values between the baseline period and after ploughing were assessed for the treatment fields (field 2 and 8) by boxplots and two-sample t-tests. Additionally, differences between the mean soil characteristics between the ploughed fields

and the control field were visualised by boxplots and tested statistically using two-sample t-tests.

To answer **question 7.3**, whether ploughing and reseeded affect spatial variation and the spatial distribution of soil properties, the same geostatistical analysis as described for question 1 was conducted and results for the treatment fields were compared to those from the baseline period (Chapter 6).

## **IV. Results**

### **A. Can fields subject to no management change act as controls, or is annual-scale (year-on-year) variability in soil characteristics significant?**

Mean soil properties changed significantly in the control field between 2012 and 2013 (Table 7.3). Soil TC increased by 16.2 % (from 49.8 TC g kg<sup>-1</sup> in the previous year (baseline) to 57.9 TC g kg<sup>-1</sup>) and soil N increased by 8.3%, but TP content was reduced by 7.1 % (Table 7.3). Soil organic matter did not change significantly. Bulk density decreased by 16.7 %, from 0.96 down to 0.8 g cm<sup>-3</sup>.

Semivariogram parameters changed in the control field from the previous year to the subsequent sampling period (Table 7.4). The distance over which soil properties varied (range) increased on average by 20 m and the total variance (total sill) decreased in most soil properties, BD (from 0.13 in 2012 to 0.005 in 2013), SOM (from 132.11 in 2012 down to 93.7), TN (from 1.38 in 2012 down to 0.3 in 2013). The distribution of soil properties across the control field remained similar to the previous year. The distribution was fairly uniform, but concentrations of nutrients and bulk density were higher in the middle of the field (Figure 7.3).

Table 7.3. Changes in mean values in the permanent grassland control field from the sampling season 2012 to the sampling season 2013. The direction and % of change is only shown for significant changes ( $p < 0.05$ )

Field	Soil property *		Percentage change	Mean values 2013	Mean values 2012
Control	BD ( $\text{g cm}^{-3}$ )	↓	16.7	0.8	0.96
	Total C ( $\text{g kg}^{-1}$ )	↑	16.2	57.9	49.83
	Total N ( $\text{g kg}^{-1}$ )	↑	8.3	6.5	6
	Total P ( $\text{g kg}^{-1}$ )	↓	7.1	1.4	1.5
	SOM ( $\text{g kg}^{-1}$ )			121.4	118.2

\* BD, Bulk density; SOM, Soil organic matter.

Table 7.4. Results of the geostatistical analysis and spherical variogram model \*/ kriging cross-validation for the control field.

	BD * <sup>1</sup> $\text{g cm}^{-3}$	SOM * <sup>1</sup> $\text{g kg}^{-1}$	Total C $\text{g kg}^{-1}$	Total N $\text{g kg}^{-1}$	Total P $\text{g kg}^{-1}$
Nugget $c_0$ *	0.003	34.4	21.6	0.2	0.02
Partial sill $c$ *	0.002	59.3	13.6	0.2	0.01
Range $r$ *	109.6	291	109.7	96.7	125
% explained by the model	48.7	52.7	43.9	51.3	24.1
mean error	-0.01	-0.002	-0.15	-0.01	0.01
mean squared error	0.01	395.2	45.21	0.48	0.02
mean prediction variance	0.004	358.2	27.78	0.24	0.02
mean ratio	1.48	1.10	1.51	1.78	1.07
median ratio	0.51	0.49	0.57	0.59	0.46

$$y(h) = c_0 + c \left\{ \frac{3h}{2r} - \frac{1}{2} \left( \frac{h}{r} \right)^3 \right\}$$

\* equation of the spherical model:  
= lag distance,  $c_0$  = nugget,  $c$  = sill,  $r$  = range

\*<sup>1</sup> BD, Bulk density; SOM, Soil organic matter

## B. Does ploughing and reseeded impose a significant change on soil physical properties and soil nutrient contents?

Ploughing imposed a significant change on all soil physical properties and soil nutrient contents in field 8, but only on some soil properties in field 2, in relation to the permanent grassland baseline period (Table 7.5).

Field 8 saw a significant reduction of soil organic matter and soil nutrient concentrations, and a significant increase in BD. Ploughing in field 8 reduced SOM concentration by 19.3 % (from 101.14 SOM g kg<sup>-1</sup> during the baseline down to 81.6 SOM g kg<sup>-1</sup> after ploughing, TC by 15.6 % (from 42.23 TC g kg<sup>-1</sup> during the baseline down to 35.87 TC g kg<sup>-1</sup>), TN by 15.6 % ( from 4.81 TN g kg<sup>-1</sup> to 4.06 TN g kg<sup>-1</sup> after ploughing) and TP by 25 % (from 1.16 TP g kg<sup>-1</sup> during the baseline down to 0.87 TP g kg<sup>-1</sup> after ploughing). Bulk density increased significantly after ploughing by 23.8 % (0.99 g cm<sup>-3</sup>) in relation to the baseline period (0.8 g cm<sup>-3</sup>).

Ploughing of field 2 imposed a significant reduction in SOM and total P content, but not in TC and TN. SOM was reduced by 17.7 % (from 88.8 g kg<sup>-1</sup> during the baseline down to 75.4 g kg<sup>-1</sup> after ploughing) and P by 2.3 %. Bulk density increased significantly by 11.2 % (from 0.89 g cm<sup>-3</sup> in the baseline up to 0.99 g cm<sup>-3</sup> after ploughing).

Table 7.5. Changes in mean values with ploughing and reseeded compared to the previous year, when the fields (field 2 and 8) were managed as permanent grassland. The direction and percentage of change is only shown for significant changes (p < 0.05).

Field	Soil property *	Direction of Change	Percentage change	Mean values post plough (2013)	Mean values grassland (2012)
2	BD (g cm <sup>-3</sup> )	↑	11.24	0.99	0.89
	Total C (g kg <sup>-1</sup> )			35.8	35.88
	Total N (g kg <sup>-1</sup> )			4.2	4.25
	Total P (g kg <sup>-1</sup> )	↓	2.3	1.3	1.33
	SOM (g kg <sup>-1</sup> )	↓	17.7	75.4	88.75
8	BD (g cm <sup>-3</sup> )	↑	23.75	0.99	0.8
	Total C (g kg <sup>-1</sup> )	↓	15.1	35.9	42.23
	Total N (g kg <sup>-1</sup> )	↓	15.6	4.1	4.81
	Total P (g kg <sup>-1</sup> )	↓	25	0.9	1.16
	SOM (g kg <sup>-1</sup> )	↓	19.32	81.6	101.14

\* BD, Bulk density; SOM, Soil organic matter.

The differences between the two treatment fields (2 and 8) as well as the control field were altered significantly by ploughing and reseeded. The two treatment fields had been significantly different during the baseline period in all

measured soil properties, but the significant reductions of SOM and soil nutrient contents in field 8 have reduced the difference between the two fields, so that they are now not significantly different in terms of bulk density, TC and TN (Table 7.6; Figure 7.2). The control field had higher SOM and nutrient contents than the ploughed fields, both in the baseline period and after ploughing. However, the difference between the control and the treatment fields further increased with the rise in SOM and soil nutrient contents in the control field and the reduction of SOM and soil nutrients in field 8 (Table 7.6; Figure 7.2).

Table 7.6. Differences between the mean values of the measured soil properties between the two ploughed-reseeded fields 2 and 8 and the grassland control field 5. Statistical differences between the fields are indicated by different letters (a,b,c), determined by two-sample t-tests.

Measured soil property *	Field 2		Control		Field 8	
	Mean ± Stdev		Mean ± Stdev		Mean ± Stdev	
BD (g cm <sup>-3</sup> )	1 ± 0.2	a	0.8 ± 0.1	b	1 ± 0.1	a
Total C (g kg <sup>-1</sup> )	35.8 ± 7.9	a	57.9 ± 4.4	b	35.9 ± 4.8	a
Total N (g kg <sup>-1</sup> )	4.2 ± 0.7	a	6.5 ± 0.5	b	4.1 ± 0.4	a
Total P (g kg <sup>-1</sup> )	1.3 ± 0.3	a	1.4 ± 0.2	b	0.9 ± 0.1	c
SOM (g kg <sup>-1</sup> )	75.4 ± 16	a	121.4 ± 16.5	b	81.6 ± 12.4	c
TC:TN	8.5 ± 0.5	a	9 ± 0.2	b	8.8 ± 0.4	ab
TC:TP	27.8 ± 6.3	a	40.7 ± 4.5	b	41.9 ± 8.4	b
TN:TP	3.2 ± 0.6	a	4.5 ± 0.4	b	4.7 ± 0.9	b

\* BD, Bulk density; SOM, Soil organic matter

### C. Does ploughing and reseeded affect spatial variation and the spatial distribution of soil properties?

Ploughing / reseeded did not affect the spatial variation and spatial distribution of soil properties in field 2, but there were some small effects in field 8.

Spatial variation still existed in the fields after ploughing. Field 2 had a significant north-south trend and no spatial structure left in the residuals after trend fitting, as it had before ploughing (Table 7.7). Therefore, no geostatistics could be conducted, and semivariogram parameters before and after ploughing could not be compared in field 2.

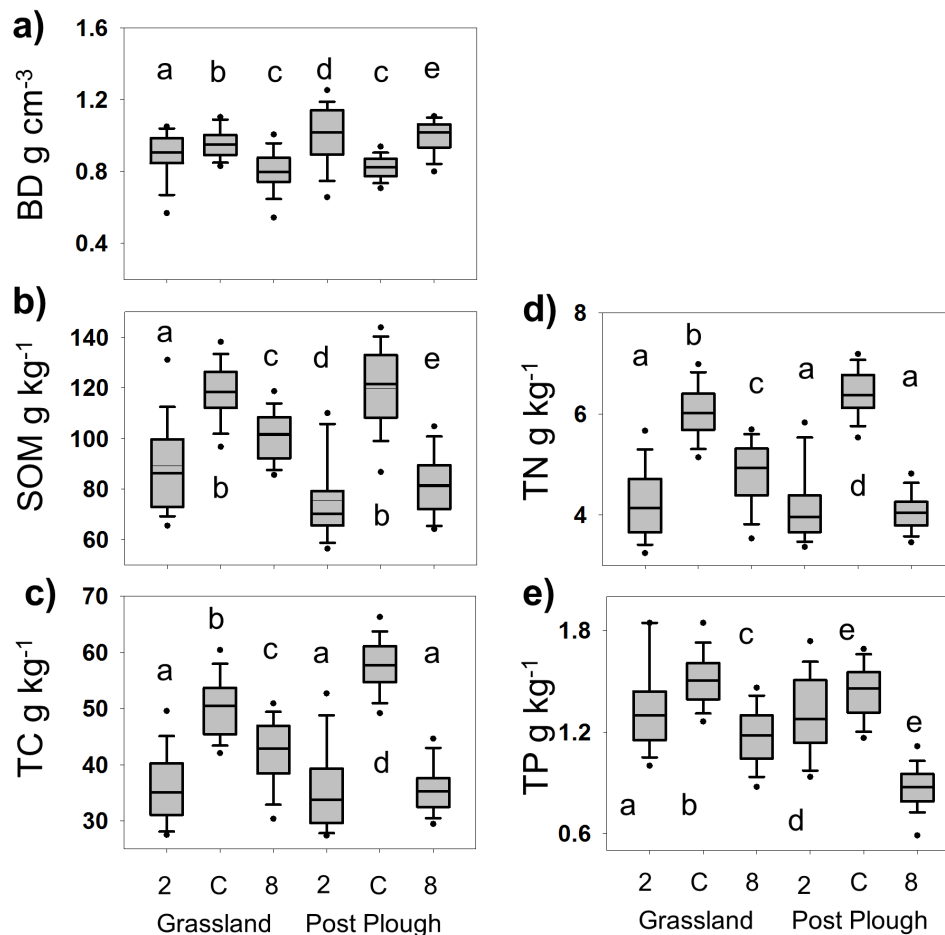


Figure 7.2. Between-field (2 = field 2, C = control field, 8 = field 8) differences in means of each soil property, first during the grassland baseline period and then during the post-ploughing period: a) bulk density (BD), b) soil organic matter (SOM), c) total carbon (TC), d) total nitrogen (TN), and e) total phosphorus (TP). The boxes visualize the lower to the upper quartile, the line the median and the upper whisker the upper quartile + 1.5 \* the interquartile range and the lower whisker the lower quartile - 1.5 \* the interquartile range. Dots visualize the 5<sup>th</sup> and 95<sup>th</sup> percentile. Significant differences are indicated by different letters (a,b,c,d,e,f), determined by two-sample t-tests.

Table 7.7. Results of quadratic trend analysis of all soil properties for Field 2 (all p < 0.001). There was no spatial structure left in the residuals.

Soil property *	% variance explained by fitted trend
BD (g cm <sup>-3</sup> )	36.4
SOM (g kg <sup>-1</sup> )	42.8
Total C (g kg <sup>-1</sup> )	46.5
Total N (g kg <sup>-1</sup> )	52
Total P (g kg <sup>-1</sup> )	50

\* BD, bulk density; SOM, Soil organic matter

Most soil properties in field 8 exhibited a clear spatial structure, except P, for which no geostatistics could be conducted. Semivariogram parameters changed after ploughing, but soil properties behaved in different ways. The ranges over which soil properties varied increased for BD (increase by 43 m) and TC (slight increase by 0.8 m) but ranges decreased for SOM (decreased by 88.7 m) and TN (decreased by 4.2 m) (Table 7.8). Total variance (total sill) increased for BD, SOM and TN, but decreased for TC.

Ploughing did not affect the distribution of soil properties in field 2, but in field 8 (Figure 3). The significant north-south trend that already existed during the baseline period is still visible in the surface maps. The northern part of field 2 still has significantly higher SOM, TC and TN content, the difference between those has not changed. The distribution in field 8 was more uniform after ploughing than it was during the baseline; the two parts of the field were not different anymore.

Table 7.8. Results of geostatistical analysis and spherical variogram model \*/ kriging cross-validation for ploughed and reseeded field 8.

	BD <sup>*1</sup> gcm <sup>-3</sup>	SOM <sup>*1</sup> g kg <sup>-1</sup>	Total C g kg <sup>-1</sup>	Total N g kg <sup>-1</sup>	Total P g kg <sup>-1</sup>
Nugget $c_0$ *	0.01	79.3	11.3	0.09	n.a <sup>*2</sup>
Partial sill $c$ *	0.004	93.9	13.4	0.08	n.a <sup>*2</sup>
Range $r$ *	136.2	84.99	97.1	99.8	n.a <sup>*2</sup>
% explained by the model	33.1	59.1	42.9	88.2	n.a <sup>*2</sup>
mean error	-0.01	-0.21	-0.06	-0.01	n.a <sup>*2</sup>
mean squared error	0.01	155.2	20.5	0.14	n.a <sup>*2</sup>
mean prediction variance	0.01	133.1	17.04	0.12	n.a <sup>*2</sup>
mean ratio	1.03	1.18	1.19	1.13	n.a <sup>*2</sup>
median ratio	0.47	0.59	0.3	0.35	n.a <sup>*2</sup>

$$y(h) = c_0 + c \left\{ \frac{3h}{2r} - \frac{1}{2} \left( \frac{h}{r} \right)^3 \right\}$$

\* equation of the spherical model for  $0 < h \leq r$ , when  $h =$  lag distance,  $c_0 =$  nugget,  $c =$  sill,  $r =$  range

<sup>\*1</sup> BD, bulk density; SOM, Soil organic matter.

<sup>\*2</sup> n.a., total P in field 8 did not have any spatial structure.



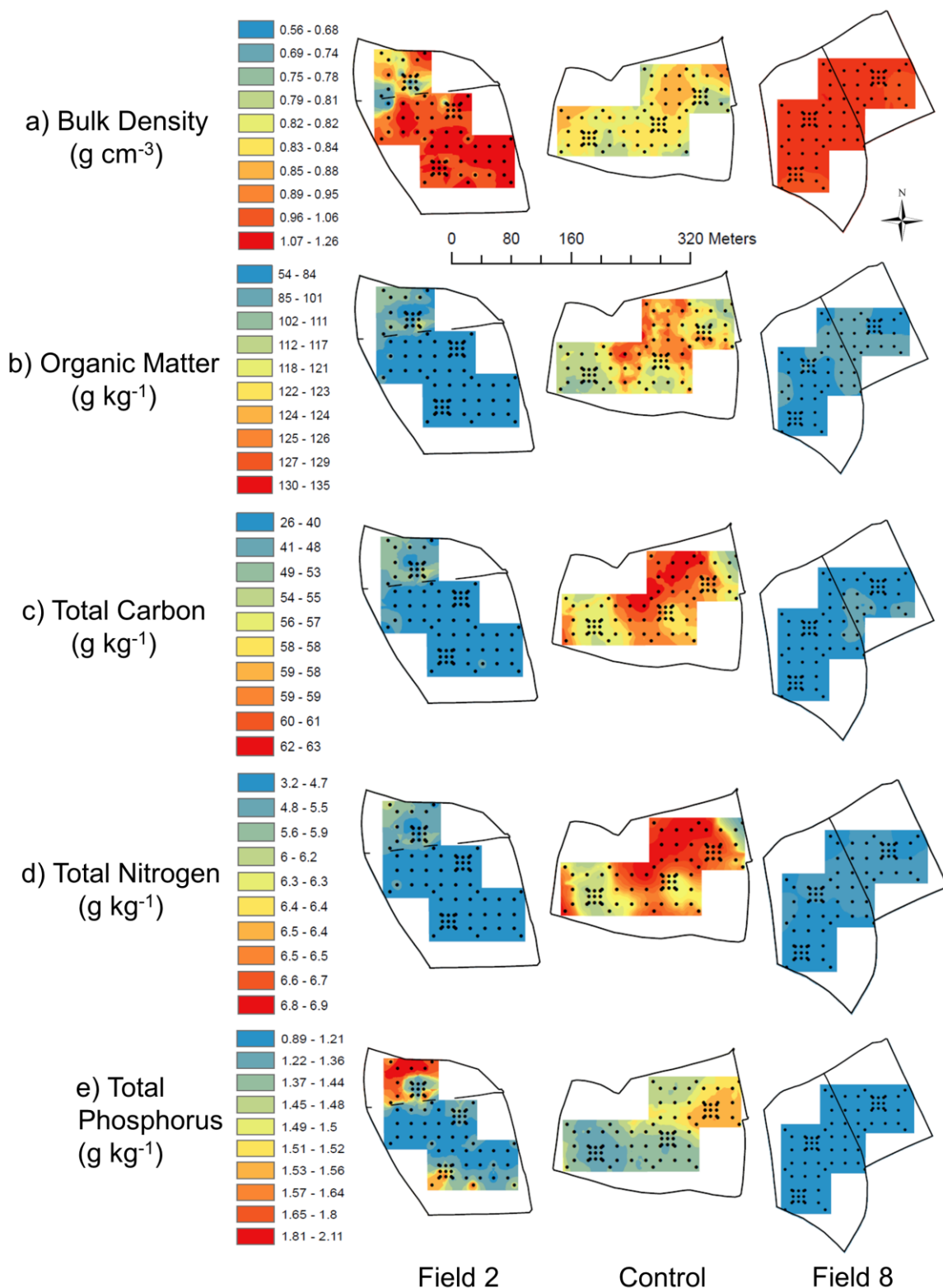


Figure 7.3. Surface prediction maps by inverse distance weighting for ploughed and reseeded field 2 (left) and by kriging for soil properties in the grassland control field 5 (middle) and ploughed and reseeded field 8 (right), apart from total P in field 8 (inverse distance weighting). Only predictions within the area of the sampling extent are shown. In field 2, the old dividing field boundary is shown (pre 2010), dividing the northern and southern part, affecting distribution patterns of soil properties. The fence between the eastern and western part in field 8 is shown.

## V. Discussion

### A. Can fields subject to no management change act as controls, or is annual-scale (year-on-year) variability in soil characteristics significant?

Year-on-year variability was in fact significant in the field that acted as a control for this experiment. The permanent grassland control field showed significant nutrient accumulation in the top 10 cm of soil, despite receiving the same management as the previous year. Such soil surface nutrient accumulations are typical in grassland fields over time (Schaerer *et al.*, 2007). Fertilizer / manure applications as well as direct application of manures by grazing livestock are made to the soil surface and are not mixed with lower soil layers by ploughing (Paustein *et al.*, 2000; Koch & Stockfisch, 2006; Liu *et al.*, 2006). Some authors suggest that grasslands that have not been ploughed for 30 years cease to act as a carbon and nitrogen sinks (Johnston *et al.*, 1994), a finding which could not be confirmed by this research. Bulk density was reduced by 16.7 % even though the management stayed the same. Bulk density is very likely to be affected by year-on-year climatic variability, for example by differences in soil moisture (Hopkins *et al.*, 2009). When soils are wet, as they were during the baseline period, soils tend to swell and thereby increase bulk density. In contrast, when soils are dry, as they were during the 2013 sampling period, soils shrink and therefore bulk density decreases (Hopkins *et al.*, 2009). Whilst all efforts were made to sample soil when in similar soil moisture conditions, it was not possible due to the very different weather occurring in 2012 versus 2013.

There was also year-on-year variability in the spatial variation of soil properties, despite receiving the same management; the semivariogram parameters changed notably. Total variance (sill) within the control field was reduced and the soil properties varied over larger distances (range distances) (Oliver & Webster, 1991; 2014). Therefore, homogenization occurred even though there was no management change. However, such homogenization was not visible in the kriged surface maps, the distribution remained the same as it was in the baseline period.

Even though soil properties changed significantly in the control field, we argue that managed fields can still be used as robust controls when used in combination with pre-management change characterization. Monitoring before and after management change allows for the assessment of relative change; a further increase in differences between control and treatment fields in the case of this study. Such assessment of relative change would have been even more important, if the choice of control field had been different in this study. The field that already had the highest SOM and nutrient content during the baseline period was chosen as the control field, and remained the field with the highest SOM and nutrient contents after the others had been ploughed. Therefore, the lower SOM and nutrient concentrations in the ploughed fields may have been identified rightly as ploughing effects compared to the unploughed field if no baseline characterization had been conducted. However, if another field had been chosen as the control field and there had been no baseline to compare changes in soil properties to, then the effects of ploughing may have not been identified.

The significant year-on-year variability despite the same management found in this study indicates that any soil survey or datasets, for example the UK National Soil Research Institute dataset, only provide a snapshot of the time that the data were taken.

#### **B. Does ploughing and reseeded impose a significant change on soil physical properties and soil nutrient contents?**

Ploughing and reseeded imposed a significant change on soil bulk density in both ploughed fields, but effects on soil nutrient contents varied between the two ploughed fields.

Ploughing in field 8 had the expected effect of reducing SOM, TC, TN and TP concentration (10 cm soil depth). Mixing the nutrient-rich top soil with nutrient-poorer soil lower down the soil profile is likely to have reduced overall soil surface nutrient content (Koch & Stockfisch, 2006). Also, previously protected soil organic matter, including organic C, N and P by macroaggregates and in lower deeper soil horizons, was exposed to microorganisms and physical

degradation by ploughing, resulting in mineralization and oxidation (SOM:(Soussana *et al.*, 2004; Acharya *et al.*, 2012; Beniston *et al.*, 2014), N: (Bhogal, 2000; Kristensen *et al.*, 2003; Eriksen *et al.*, 2004b; Hansen *et al.*, 2005; Eriksen *et al.*, 2006), P: (Addiscott & Thomas, 2000; Butler & Haygarth, 2007). Additionally, some of the degraded SOM and organic nutrients may have been taken up by the new grass cover, or lost by gaseous emissions (CO<sub>2</sub>: (Acharya *et al.*, 2012; Merbold *et al.*, 2014), N<sub>2</sub>O: (Merbold *et al.*, 2014). An increase in BD was also expected, because ploughing breaks up soil structure, such as soil aggregates and porosity, resulting in soil compaction. However, despite the significant changes after ploughing, the mean SOM, nutrient concentrations and BD are still within the range of those reported for grasslands (Shi *et al.*, 2002; McGrath & Zhang, 2003; Clegg, 2006; Amman *et al.*, 2009) and greater (SOM) / smaller (BD) than those reported for arable systems, respectively (Cambardella & Karlen, 1999; Wright & Hons, 2005; Qiu *et al.*, 2011).

Field 2 only experienced significant reductions in SOM and soil TP, but not in soil TC and TN. Additionally, the percentage of SOM reduction in field 2 was smaller than that in field 8. Therefore, the older grassland (field 8, last ploughed > 30 years ago) exhibited more soil nutrient reductions, especially C, after ploughing than the more recently ploughed field 2 (7 years ago). Similar effects of grassland age have been reported on soil TC reductions (Soussana *et al.*, 2004) and for TN release (Hansen *et al.*, 2005). Also, carbon response curves after land use change have shown an exponential loss of SOC after converting permanent grassland (no ploughing) to arable land (frequent ploughing), indicating that most SOC is lost with the first few ploughing events (Popleau *et al.*, 2011, West *et al.*, 2004). A combination of the following explanations is likely to have affected SOM and nutrient contents in the top 10 cm and mitigated any change due to ploughing in field 2. One explanation may be that recent ploughing had mixed soil layers, so that the soil nutrient concentrations of deeper soil layers were already similar to those in the topsoil and further mixing due to ploughing therefore had no effect (Grandy & Robertson, 2006; Koch & Stockfisch, 2006; Baker *et al.*, 2007). Another explanation may be that organic matter in recently ploughed fields was already partially decomposed and readily mineralized nutrients were taken up by grass vegetation at higher

rates in the young grassland field, because biomass production of grass reduces rapidly with age (Eriksen *et al.*, 2004). A further explanation may be that 'older' SOM or SOC is lost preferentially by erosion than 'younger' SOM or SOC, as shown by Beniston *et al.* (2014a).

The fact that the two ploughed fields showed different rates of SOM, C and nutrient reductions after ploughing could not have been detected without baseline characterisation. If the fields had been assumed to have the same mean values of soil properties before ploughing, a basic assumption that a lot of soil surveys are based on (Breuer *et al.*, 2006), it would have been concluded that both fields had significantly lower SOM and soil nutrient contents due to the ploughing and reseeded event.

### **C. Does ploughing and reseeded affect spatial variation and the spatial distribution of soil properties?**

A single ploughing event did not cause the expected homogenizing effect on soil properties. Spatial variation as well as patterns of soil distribution remained similar to those quantified during the permanent grassland baseline period (Chapter 6).

The ranges over which spatial variation occurred could not be compared before and after ploughing in field 2, however, the remaining north-south trend in all soil properties indicates that spatial variation remained broadly unaffected by ploughing / reseeded. The visible differences in soil property distribution maps between the northern and southern part of field 2, that were previously managed differently, remained after ploughing and reseeded. The two parts seemed to be affected in similar ways and the difference between them remained. The north-south difference in field 2 has now been documented for 3 consecutive years, despite ploughing in this study (Chapter 4 and 6). Therefore, the different past management and historical soil properties in the two parts of the field still affect the distribution of soil properties despite intensive management in recent years. The southern part of the field was ploughed and

reseeded 7 years ago whilst the northern part remained as permanent grassland (Chapter 4).

Comparisons of semivariogram parameters before and after ploughing did not reveal any alteration in spatial variation in field 8. The distribution maps in field 8 seem to show uniform distribution. The differences between the two fenced-off parts of field 8 have been reduced (Chapter 6). Those differences had been attributed to differences in long-term ploughing history (most recent difference: the eastern part was ploughed and reseeded 10 years before the sampling in this paper whilst the western part remained as permanent grassland) and short-term differences in FYM applications (3 years prior to this sampling period, eastern part received no FYM, whilst the western part received FYM).

One single ploughing and reseeded event did not show a significant homogenizing effect on the variability or distribution of soil properties. Even though the mean values of soil properties was altered by ploughing, at least in field 8, the distribution and variability of soil properties still seem to be affected by past management and the historical condition of the soils. The fact that long-term management effects are still influencing the distribution and variability of soil properties now indicates long response times of soils to agricultural management, but also how a single ploughing event is not enough to manipulate soils so that they become homogenized enough to be treated as one management unit. For example, field 2 still functions as separate fields and those two parts of the field should instead be managed as two separate management zones. Results of this paper indicate that productivity and economic benefits, and possibly water quality benefits (see companion paper) may be gained by treating the individual field as different management units and field 2 as two separate management units (McCormick *et al.*, 2009; Fu *et al.*, 2010). The soil properties measured in this study may potentially be yield limiting (Zhang *et al.*, 2002). However, the total nutrients measured here do not describe the nutrients that are plant available, at least not under the conventional understanding that mostly inorganic nutrients are available. The spatial variability of inorganic nutrients may differ from those of total nutrients. For example, the spatial variability for NO<sub>3</sub>-N was reported to be a lot higher in

similar temperate grassland studies than that of the total N in this study (ranges an order of magnitude lower than those in this study) (Delcourt *et al.*, 1996; Bogaert *et al.*, 2000) and the NO<sub>3</sub>-N content of soils is continuously changing (van Meirvenne & Hofman, 1989). Therefore, this study indicates that site-specific management is required to homogenize the fields and for potential yield and environmental benefits, but sampling of more specific fractions of nutrients may be required in order to make recommendations of site-specific fertilizer application rates. Once site-specific management is applied, the larger Farm Platform project that this study is nested within, may also provide currently missing information on yield improvements from site specific fertilizer applications in grasslands (Schnellberg *et al.*, 2008) as well as on the time it takes for homogenization of soil properties to occur.

## VI. Conclusion

This study has quantified the immediate effects of ploughing / reseeding of grassland fields with different sward ages on bulk density, soil organic matter and nutrient concentrations (0 - 10 cm soil depth). Additionally, this is the first study to quantify how a single ploughing / reseeding operation in grasslands affects the spatial variation and distribution of soil properties. Results demonstrated that:

- The combination of 'before ploughing vs. after ploughing' and 'control vs. ploughed' was found to be a robust experimental design, despite significant year-on-year variability in the control field (**Question 7.1**). The permanent grassland control field (no ploughing for > 30 years) showed a significant accumulation of TC, TN and TP.
- Ploughing and reseeding increased soil surface bulk density in both ploughed fields (**Question 7.2**).
- There may have been an effect of sward age before ploughing: all soil nutrient concentrations were significantly reduced in the older grassland field (no ploughing for 20 years), but not in the younger grassland field (no ploughing for 7 years) (**Question 7.2**).

- A single ploughing and reseeding operation in the two grassland fields did not show the expected homogenizing effect on soil properties' spatial variation and distribution (**Question 7.3**).
- Ploughing and reseeding once did not override past-management effects that are considered to have caused the distribution of soil properties (**Question 7.3**).
- Field-specific management (the specific management of separate management units within fields) may be required in order to over-ride past management effects, reduce spatial variability within and between fields, which may eventually result in yield gains and on- and off-site environmental benefits

For subsequent water quality effects after ploughing and reseeding of permanent grassland, see the companion paper (Chapter 8).

*This chapter characterized the effects of ploughing and reseeding on soil properties and their distribution in grassland fields with contrasting management histories. This chapter addressed questions that were raised by previous chapters (Chapter 4 and 6), how long the effect of management history lasts. It found that past management effects may still have an effect on how mean soil properties were altered by ploughing and reseeding and that the differences between the two previously differently managed parts in two fields still remained even after ploughing and reseeding the entire field. Therefore, field specific and site specific management in field 2 may have to be employed to homogenize soil properties within fields and between fields, to achieve potential grass production benefits and diffuse water pollution reductions.*

*The results in this chapter also provoked new questions, such as do the changes in mean soil properties by ploughing and reseeding have subsequent effects on diffuse water pollution rates? Therefore, chapter 8 quantified the sediment and macronutrient losses from the same ploughed and reseeded fields and assessed whether the relationship between soil status and water quality between the fields was altered by ploughing and reseeding.*



## **Chapter 8**

### **The Effects of Ploughing and Reseeding Grasslands on Sediment and Macronutrient Delivery to Surface Waters**

#### **I. Abstract**

This study adds to the growing evidence that temperate intensively managed grasslands, particularly ploughed and reseeded grasslands, contribute significantly to soil erosion and diffuse pollution rates.

This study is the first to monitor the effects of ploughing and reseeded in grasslands on the delivery of multiple pollutants and their ratios; sediment and the macronutrients nitrogen, phosphorus and carbon. Two ploughed and reseeded grassland fields and one permanent grassland field were monitored throughout the first hydrological season post-ploughing. Monitoring was conducted at high resolution (up to every 15 minutes) at the North Wyke Farm Platform, UK. Ploughing effects were identified by employing a paired catchment design, comparing back to a pre-characterized permanent grassland baseline period.

Ploughing and reseeded significantly accelerated the losses of sediment and the macronutrients carbon, nitrogen and phosphorus, thereby exacerbating the already significant losses from these grasslands. Additionally, ploughing and reseeded caused a shift in the relative importance of pollutants, with a dramatic increase in the relative importance of N losses. The availability or vulnerability of soil particles and macronutrients to mobilization, irrespective of soils nutrient contents, may be controlling fluxes and yields of sediment and macronutrients from ploughed and reseeded grasslands.

Sediment, nitrogen and phosphorus losses from ploughed and reseeded grasslands frequently exceeded EU water quality guidelines, at higher frequencies than in permanent grasslands. Such accelerated losses from recently ploughed grasslands need to be acknowledged in land management

guidelines and taken into consideration when implementing sustainable intensification practices that involve ploughing and reseeded.

## II. Introduction

Grasslands cover extensive areas of Europe, the USA, Australia and New Zealand (Brazier *et al.*, 2007) and may be widespread sources of diffuse pollution. Whilst evidence has accumulated that demonstrates permanent grasslands to contribute significantly to diffuse pollution (Haygarth, 1997; Preedy *et al.*, 2001; Wood *et al.*, 2005; Bilotta *et al.*, 2008; Bilotta *et al.*, 2010; Granger *et al.*, 2010; Matthews *et al.*, 2010; Sandford *et al.*, 2013; Chapter 5), the diffuse pollution losses from ploughed and reseeded grasslands are less understood; a frequent management practice in grasslands. Additionally, many 'sustainable intensification' measures may include ploughing grasslands and reseeded with newer varieties with improved characteristics such as deep rooting varieties.

There are only few studies that assess the effects of ploughing and reseeded grasslands on diffuse water pollution. In the short-term, ploughing-reseeded has been reported to accelerate erosion (Sharpley, 2003; Grandy & Robertson, 2006; Butler & Haygarth, 2007) and increased losses of macronutrients due to soil organic matter mineralization (nitrogen (N): (Shepherd, 2001; Eriksen *et al.*, 2004; Eriksen *et al.*, 2006; Burt *et al.*, 2008; Burt *et al.*, 2011), phosphorus (P): (Addiscott & Thomas, 2000; Sharpley, 2003; Butler & Haygarth, 2007). Carbon, (C) losses have been shown to be higher after ploughing in general, but have not been quantified in ploughed grasslands before (Owens *et al.*, 2002; Quinton *et al.*, 2006; Kuhn *et al.*, 2009). In the long-term, some studies have found overall reductions of P losses (Sharpley, 2003) as well as no detection of a residual N effect of ploughing (Sharpley, 2003), potentially due to the reduction of nutrient surface accumulation by ploughing and reseeded (Chapter 7). However, several aspects need to be addressed to fully understand diffuse water pollution from ploughed and reseeded grasslands.

First, the effects of ploughing and reseeded on the delivery of some pollutants are better understood than on the delivery of other pollutants, partly

due to using different methods of quantification. For example, N leaching after ploughing is mostly quantified by suction cups in the soil water (Shepherd, 2001; Eriksen *et al.*, 2004; Eriksen *et al.*, 2006), rather than monitoring actual N transport to surface waters as has been done for sediment and phosphorus (Butler & Haygarth, 2007). Carbon losses from grassland, let alone from ploughed grasslands are not well understood. Either, mostly dissolved organic carbon is studied in grasslands (Don & Schulze, 2008; Sandford *et al.*, 2013) or only particulate carbon is studied in recently ploughed arable fields (Owens *et al.*, 2002; Quinton *et al.*, 2006; Kuhn *et al.*, 2009). Total carbon losses, including dissolved and particulate C, have only been quantified once in permanent grasslands (Chapter 5), but never in recently ploughed grasslands. Therefore, the delivery of sediment, N, C and P losses to surface waters have to be monitored after ploughing and reseeding of grasslands.

Second, it is important not only to understand the effects of ploughing and reseeding of grasslands on the losses of individual pollutants but also on their relative losses. It is not the concentration or load of single pollutants, but the relative concentrations or loads of multiple pollutants that impact aquatic ecosystems (Chapter 5). A switch in the relative importance of pollutants following ploughing and reseeding may alter the nature of the original water quality issue, for example, by altering the limiting nutrient in the aquatic system of interest (Sylvan *et al.*, 2007). Therefore, the simultaneous losses of multiple pollutants have to be monitored after ploughing and reseeding of grasslands, to understand whether the relative importance of pollutants is altered (Sylvan *et al.*, 2007, Pearl *et al.*, 2009; Chapter 5).

Third, it is important to understand the mechanisms controlling the losses of diffuse pollutants from ploughed and reseeded grasslands, such as identifying pollutant sources (for example nutrient contents in the soil), the mode of mobilization of pollutants from the source and the flow pathways that transport and delivery pollutants to surface waters (Haygarth *et al.*, 2005). Mechanistic understanding may be improved by employing high resolution monitoring rather than daily sampling (Butler and Haygarth, 2007) or two-weekly sampling (Eriksen *et al.*, 2004) that were employed in previous studies on ploughed grasslands (Kirchner *et al.*, 2004; Jordan *et al.*, 2012; Melland *et al.*, 2012) and

by linking pollutant losses with soil physical and chemical properties (Wall *et al.*, 2011; Haygarth *et al.*, 2005a).

Additionally, it is challenging to reliably identify whether any detected change in water quality parameters between two monitoring periods is evident, for example between a permanent grassland monitoring period and a post ploughing and reseeded monitoring period, are attributed to year-on-year variation or whether these changes are caused by the implementation of ploughing and reseeded. Such inter-annual variation exists for example climatic variation, variation in soil moisture conditions and subsequent variation in runoff generation, which may eventually leads to year-to-year variation in diffuse pollution concentrations, fluxes and yields (Schilling *et al.*, 2013, King *et al.*, 2008). Paired catchment approaches involve a baseline characterization of testing whether catchments respond to rainfall in similar ways in terms of flow and pollutant concentrations, so that changes between the baseline period and the post-management-change period can be identified as management effects rather than year-to-year variation (Schilling *et al.*, 2013, Jokela & Casler, 2011, King *et al.*, 2008).

Therefore, the main aim of this paper was to study the effect that ploughing and reseeded of permanent grassland fields has on water quality in terms of suspended sediment and the macronutrients carbon, nitrogen and phosphorus. High resolution monitoring (up to every 15 minutes) in grassland fields of different sward ages and a permanent grassland control field was conducted, using a paired catchment approach. Results were described in relation to water quality and soil properties during a permanent grassland baseline period (Chapter 5 and 6) and in relation to soil nutrient contents after ploughing (Chapter 7). The main questions were:

**Question 8.1** Can changes be detected between baseline water quality from permanent grasslands the previous year and post-ploughing and reseeded water quality?

**Question 8.2** How do pollutant losses after ploughing and reseeded compare to a permanent grassland control and the permanent grassland baseline period?

**Question 8.3** Have controls on fluxes and yields of sediment and macronutrients changed with respect to the baseline period and what may be controlling pollutants after ploughing?

**Question 8.4** Has ploughing and reseeded affected the relative importance of pollutants through flow conditions and time relative to the permanent grassland baseline period and control field?

**Question 8.5** How does water quality from ploughed and reseeded grassland fields compare to EU / UK recommended water quality standards?

### III. Methods

Hydrology and water quality monitoring was conducted at the Rothamsted Research 'North Wyke Farm Platform' in south-west England between June 2013 and April 2014. This paper / chapter is a companion to Chapter 7, which discusses the effects of ploughing the same grassland fields on soil properties and their spatial variation and distribution. A location map of the Farm Platform can be found therein (Figure 7.1 a). The Farm Platform fields are hydrologically isolated by French drains, so that water leaving the field by either subsurface and/or surface flow is channelled via the drains to flumes, where water quantity and quality was monitored (Chapter 5). The Farm Platform is subdivided into three equal-sized farmlets, which were subjected to different management scenarios. One field in each farmlet was chosen for monitoring, the same fields as during the baseline period, when the farmlets were managed as permanent grasslands (Chapter 5 and 6). The control field (field 5) remained as permanent grassland, while field 2 and field 8 were ploughed and reseeded with different seed mixtures in July 2013. Detailed maps of the chosen fields and their characteristics, detailed timing of ploughing and reseeded operations in field 2 and 8 as well as a detailed description of Farm Platform soils, climate and long-term past management of the sampled fields can be found in chapter 7.

Hydrology and water quality instrumentation of the Farm Platform is described in detail by Griffith *et al.* (2013). In brief, each field is equipped with a tipping bucket rain gauge and each flume is outfitted with a range of automated

or semi-automated water quantity (discharge) and quality monitoring equipment. All data were collected at 15-minute time-steps.

The following water quality parameters were monitored: suspended sediment (SS), and the macronutrients total carbon (TC), total phosphorus (TP) and total oxidized nitrogen-N ( $\text{TON}_N$ ), a combined measurement of nitrate and nitrite. Detailed description of analytical methods, instruments and quality assurance procedures are described in Chapter 5. SS and  $\text{TON}_N$  were monitored continuously by automated sensors that are located in a stainless-steel by-pass cell, into which discharge water is pumped every 15 minutes when discharge rates are  $> 0.2 \text{ L s}^{-1}$  (Griffith *et al.*, 2013; Chapter 5). Continuously monitored nephelometric turbidity units (NTU), were converted to SS ( $\text{mg L}^{-1}$ ) concentrations by establishing rating curves between NTU and manually sampled SS concentrations (analysed by filtration (1.2  $\mu\text{m}$  filters (Anon., 1980; Bilotta *et al.*, 2008; Chapter 5) ( $\text{SS mg L}^{-1} = 0.77 x + 5.7a$ ,  $r^2 = 0.91$ ,  $N = 81$ , where  $x$  is turbidity in nephelometric turbidity units, NTU). Total phosphorus was measured at 15-minute time-steps during the following deployment periods: deployment period 1: 30/10/20013-15/11/2013 (all fields), deployment period 2: 18/12/2013 – 31/12/2013 in field 8 and 18/12/2013 - 7/1/2014 in field 2 and 5. TC was sampled during storm events by flow-proportional auto-sampling and manually analysed in the laboratory. The TC analytical instrument used during the baseline period was replaced by a different analytical instrument (Shimadzu total organic carbon analyser, Shimadzu corporation analytical & measuring instruments division, Japan). As in the previous year, the samples were not filtered, but stirred before analysis. Within the Shimadzu analytical instrument, samples were heated at 680 °C (in contrast to 850 °C in the method during the baseline period) to oxidize all forms of carbon to carbon dioxide, which was then measured by infrared (Chapter 5).

All statistical analysis was conducted in GenStat 16<sup>th</sup> edition (VSN International, Hemel Hempstead, UK). To address **question 8.1**, whether a change in water quality can be detected between the baseline and post-ploughing periods, the control field was paired with the two ploughed and reseeded fields and linear regressions were conducted for hydrology and water quality properties throughout the entire time series (following typical paired

watershed experimental designs (King *et al.*, 2008; Jokela & Casler, 2011; Schilling *et al.*, 2013). The regression equations, regression coefficients and slope of regression lines post-ploughing were compared to those of the baseline period (2012-2013) (Chapter 6). The monitoring methodology was the same during the baseline, methods described in chapter 5 and relevant data discussed in chapter 6.

Three steps were involved in addressing **question 8.2**, how pollutant losses after ploughing compare to a permanent grassland control and the permanent grassland baseline period. a) Summary calculations were made for the entire time series and compared to those calculated during the permanent grassland baseline period (Chapter 5), including mean discharge, time-series precipitation, time-series runoff coefficients, mean time-series pollutant fluxes and loads and total yields. Discharge-concentration rating curves were used to estimate total yield of the monitoring period for SS and TON<sub>N</sub> (Bilotta *et al.*, 2010; Glendell & Brazier, 2014) and the Walling & Webb method 5 (1985) was used to calculate total yields for TC and TP (Walling & Webb, 1985; Littlewood, 1992; Glendell & Brazier, 2014). b) A storm–event dataset was extracted, following the rule-based method described in chapter 5. Storm-event summary statistics like event rainfall, discharge and pollutant yields were calculated and compared to those calculated during the permanent grassland baseline period. c) Two-sample t-tests were conducted to test for differences between pre-ploughing and post-ploughing were tested for each field by conducting two-sample t-tests, and the differences between the two ploughed fields and the control field were tested by conducting two-sample t-tests. For TC, values measured during the baseline and during the post ploughing period could not be compared, because different analytical instruments were used in the two monitoring periods and no cross-instrument calibration was available. Therefore, the relative differences between the treatment and the control fields were compared.

Several steps were involved to address **question 8.3**, whether controls on fluxes and yields of sediment and macronutrients changed with respect to the baseline and what may be controlling pollutant losses after ploughing and reseeded. a) Hydrological controls on individual pollutant concentrations, loads and yields were tested by examining sedigraph / chemograph shapes in relation to hydrographs, conducting time-series rating curves between discharge and

pollutant concentrations and conducting regressions between event-based hydrology and event-based pollutant yields (relevant baseline data in chapter 5). b) Between-field differences in pollutant concentrations, loads and yields were examined in relation to hypothesized causal factors and compared to the relationships found during the baseline period (relevant data in chapter 6). Hypothesized causal factors included soil nutrient contents (relevant data in Chapter 7) and site characteristics including topography.

Two steps were involved with addressing **question 8.4**, whether ploughing and reseeded altered the relative importance of pollutants through flow conditions and time relative to the permanent grassland period, following the methods in chapter 6. a) Total annual pollutant yield was calculated by summing all individual pollutant annual yields for each field. Then, the percentage contribution of each individual pollutant to the total annual pollutant yield for each field was calculated. b) The entire time-series was divided into baseflow and stormflow periods, as well as further divided into the lower baseflow quartile and the upper stormflow quartile for ploughed and reseeded field 2 (Melland *et al.*, 2012). The mean and median pollutant concentrations as well as their ratios were compared throughout these periods of contrasting flow conditions and the duration over which these flow conditions occurred was expressed as a percentage of the entire time series. The results of both these calculations were compared to those calculated during the baseline period (relevant data in chapter 5).

To put the post-ploughing water quality results into a wider context and to address **question 8.5**; how the water quality from ploughed and re-seeded grassland fields compares with EU / UK recommended water quality standards, the percentage of 15-minute time-step data that exceeded the concentrations recommended in EU / UK water quality standards were calculated (Bilotta *et al.*, 2010; Thompson *et al.*, 2014; Chapter 5). EU / UK water quality standards included the 1) EU Freshwater Fisheries Directive (FFD) (25 mg SS L<sup>-1</sup>) and a lower, more appropriate standard suggested by (Bilotta *et al.*, 2012) (10 mg SS L<sup>-1</sup>), 2) what is considered as 'good ecological status' for dissolved molybdate reactive P (MRP) by the UK Technical Advisory Group (TAG) devised for the EU Water Framework Directive (< 0.04 mg MRP L<sup>-1</sup>), and 3) the Nitrates Directive Nitrate-N guideline of 11.3 mg L<sup>-1</sup>. Exceedance frequencies were



compared with those calculated during the baseline period (relevant data in chapter 5).

#### **IV. Results**

Figure 8.1 presents the entire monitoring period in terms of rainfall, discharge and hydrological events for each field. No discharge occurred during the implementation of management change in field 2 and 8, during spraying, fertilizer and FYM applications, when soils were bare or during early grass establishment. The hydrological season started in mid-October, when the vegetation cover was already well established, and a high number of discrete rainfall-runoff events occurred throughout the autumn, winter and spring (field 2: 35 events, field 5: 43 events, field 8: 44 events). The post-ploughing period received less rainfall (1032 mm) compared to the permanent grassland baseline period (1173 mm rainfall for the equivalent time period). However, the temporal distribution of rainfall and discharge was different during the two periods. Even though discharge only occurred for 65 % of the 15-minute time intervals during the post-ploughing period (compared to 93 % during the baseline period), total time-series runoff coefficients (51.2 %) were larger post-ploughing than during the baseline period (48.2 %).

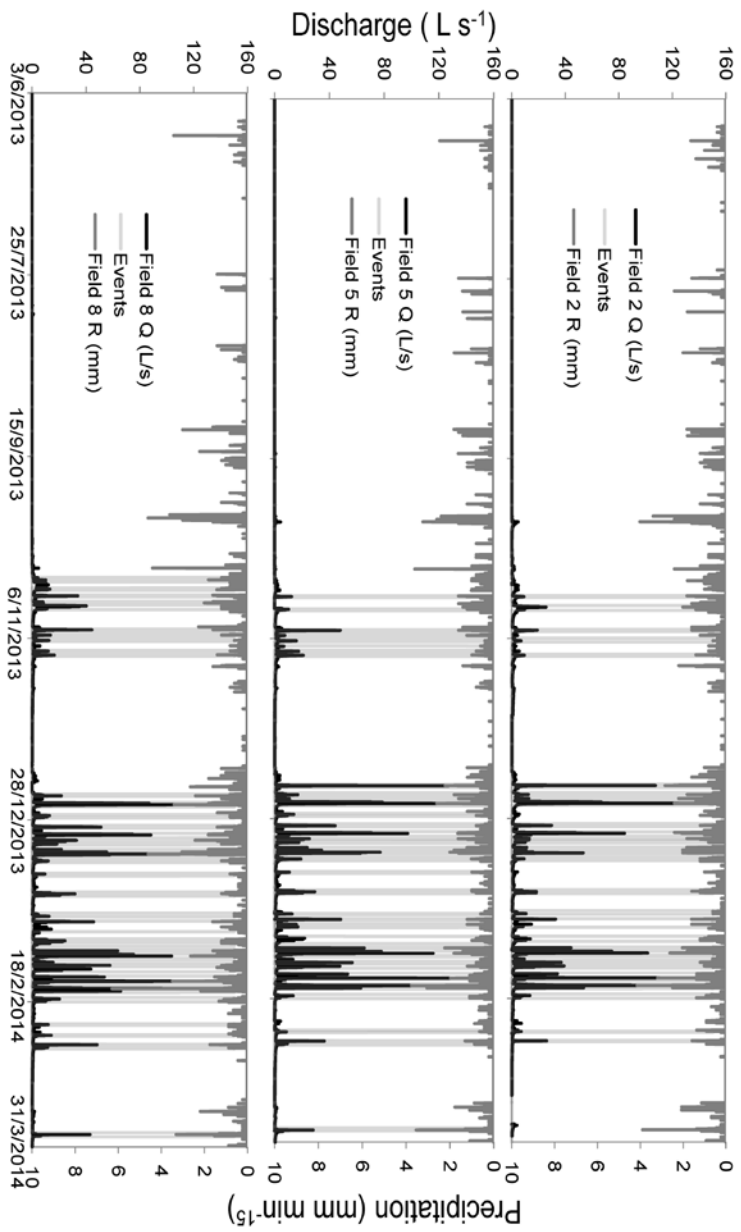


Figure 8.1. Precipitation ( $R \text{ mm min}^{-15}$ ), discharge ( $Q \text{ L s}^{-1}$ ) and hydrological events \* for all three monitored fields, ploughed / reseeded field 2, permanent grassland control field 5, and ploughed / reseeded field 8, for the entire sampling duration (June 2013-April 2014). All data was monitored and expressed at 15-minute time steps. Even though rainfall occurred during the summer, no storm events occurred in the summer and the hydrological season started thereafter.

\*Hydrological events were defined on the basis of rainfall and discharge response rising above a certain threshold, which was based on field sizes.

**A. Can changes be detected between baseline water quality from permanent grasslands the previous year and post-ploughing and reseeded water quality?**

Changes were detected between the baseline period and the post-ploughing and reseeded period. The regression equations and slopes of regression lines between the control field and the ploughed fields changed (positively) relative to the baseline (Figure 8.2; Table 8.1). Regression coefficients were very large for rainfall (ploughed fields versus control field: 0.85 - 0.88) and for discharge (0.88 - 0.92). The pollutant concentrations were still correlated between the ploughed fields and the control field, but regressions were less strong than during the baseline. Additionally, the slopes of all paired control-treatment regression lines increased from the baseline to the post ploughing period (Figure 8.2), because the concentrations in the treatment fields were greater than those in the control field.

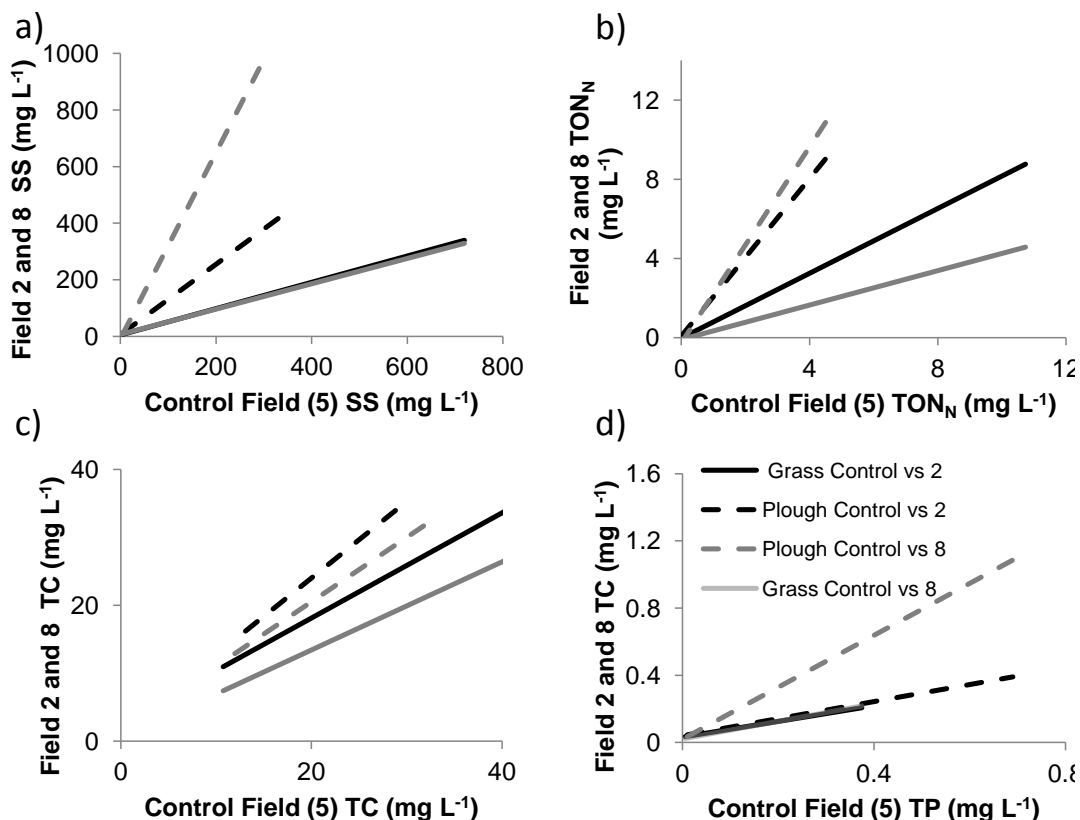


Figure 8.2. Regression relationships between each treatment and control field, for the permanent grassland baseline period (solid lines) and for the post ploughing and reseeded period (dashed lines). a) Suspended sediment (SS), b) total oxidized nitrogen-N (TON<sub>N</sub>), c) total carbon (TC), and d) total phosphorus (TP). The regression equations are given in table 8.1.

Table 8.1. Linear regression between a) the control field and field 8, and b) between the control field and field 2; both for the baseline period when the three fields were managed as permanent grasslands and after ploughing and reseeding, when field 2 and 8 were ploughed and reseeded and the control field remained as permanent grassland.

a) *	Permanent Grassland		After Ploughing	
	Control (Field 5) vs Field 8		Control (Field 5) vs Field 8	
Rain	P<0.001	R <sup>2</sup> = 0.8 y=0.006 + 0.95x	P<0.001	R <sup>2</sup> = 0.85 y= 0.18 + 0.91x
Flow	P<0.001	R <sup>2</sup> = 0.88 y=0.07 + 1.02x	P<0.001	R <sup>2</sup> = 0.85 y=0.19 + 0.91x
SS	P<0.001	R <sup>2</sup> = 0.7 y=7.26 + 0.45x	P<0.001	R <sup>2</sup> = 0.57 y=-8.51 + 3.29
TON <sub>N</sub>	P<0.001	R <sup>2</sup> = 0.46 y= -0.09 + 0.43x	P<0.001	R <sup>2</sup> = 0.36 y=-0.27 + 2.47x
TC	P<0.001	R <sup>2</sup> = 0.49 y= 0.47 + 0.65x	P<0.001	R <sup>2</sup> = 0.84 y= 1.53 + 0.95x
TP	P<0.001	R <sup>2</sup> = 0.51 y=0.02 + 0.52x	P<0.001	R <sup>2</sup> = 0.5 y=0.02 + 1.53x
b) *	Permanent Grassland		After Ploughing	
	Control (Field 5) vs Field 2		Control (Field 5) vs Field 2	
Rain	P<0.001	R <sup>2</sup> = 0.82 y= 0.005 + 0.95x	P<0.001	R <sup>2</sup> = 0.88 y = 0.006 + 0.89x
Flow	P<0.001	R <sup>2</sup> = 0.92 y=0.03 + 0.81x	P<0.001	R <sup>2</sup> = 0.88 y=0.25 + 0.81x
SS	P<0.001	R <sup>2</sup> = 0.6 y=4.87 + 0.47x	P<0.001	R <sup>2</sup> = 0.36 y=5.81 + 1.24x
TON <sub>N</sub>	P<0.001	R <sup>2</sup> = 0.63 y= -0.03 + 0.82x	P<0.001	R <sup>2</sup> = 0.12 y= 0.08 + 1.99x
TC	P<0.001	R <sup>2</sup> = 0.52 y= 1.5 + 1.27x	P<0.001	R <sup>2</sup> = 0.62 y= 2.56 + 0.77x
TP	P<0.001	R <sup>2</sup> = 0.57 y=0.03 + 0.44x	P<0.001	R <sup>2</sup> = 0.1 y=-0.09 + 0.03x

\* SS, suspended sediment; TON<sub>N</sub>, total oxidized nitrogen-N; TC, total carbon; TP, total phosphorus

**B. How do pollutant losses after ploughing and reseeding compare to a permanent grassland control and the permanent grassland baseline period?**

Ploughing and reseeding significantly increased the concentrations, loads and yields of all pollutants relative to the permanent grassland baseline period and the grassland control field (Table 8.2; Figure 8.3). SS and  $\text{TON}_N$  mean concentrations almost doubled in the ploughed fields compared to the baseline period. TP increased from  $49 \text{ mg L}^{-1}$  to  $55.76 \text{ mg L}^{-1}$  in field 2 and from  $47.57 \text{ mg L}^{-1}$  to  $73.04 \text{ mg L}^{-1}$  in field 8. TC losses could not be compared between the baseline and post-ploughing period (change of analytical instrument between the monitoring periods with no cross-calibration available), but TC concentrations, loads and yields increased in the ploughed fields in relation to the control field, which had larger TC losses during the baseline. The ranking of pollutant concentrations, loads and yields was altered; the control field now had consistently lower pollutant concentrations, loads and yields compared to the ploughed fields, even though it had significantly higher pollutant losses than the other two fields during the baseline period (Table 8.2). The ranked order of pollutant losses between the two ploughed fields remained the same, field 8 lost more SS and TP than field 2, but field 2 lost more  $\text{TON}_N$  and TC than field 8.

Table 8.2. Hydrology and water quality characteristics for the two ploughed and reseeded fields (2 and 8) and the permanent grassland control field, and the differences between their means (a,b,c, shows significant differences, determined by two-sample t-tests). Hydrology and water quality monitoring was conducted from April 2012 - March 2013, with a sampling resolution up to every 15 minutes).

	Field 2	Control	Field 8
Hydrology	Mean Discharge (L s <sup>-1</sup> ) ± stdev	0.3 ± 4.7	1.3 ± 5.5
	% of rain as discharge year <sup>-1</sup>	47.8	57.5
Suspended Sediment	Annual yield (kg ha <sup>-1</sup> year <sup>-1</sup> )*	331 - 335	153 - 166
	Mean conc. (mg L <sup>-1</sup> ) ± stdev	22.1 ± 32.6	12.3 ± 14.3
	Mean load (mg s <sup>-1</sup> ) ± stdev	276.3 ± 1908.9	91.9 ± 648.4
Total oxidized Nitrogen-N	Annual yield (kg ha <sup>-1</sup> year <sup>-1</sup> )*	8.2 - 8.5	2.3 - 2.36
	Mean conc. (mg L <sup>-1</sup> ) ± stdev	2.6 ± 4.5	0.8 ± 0.4
	Mean load (mg s <sup>-1</sup> ) ± stdev	4.6 ± 12.1	1.2 ± 1.9
Total Phosphorus	Annual yield (kg ha <sup>-1</sup> year <sup>-1</sup> )*	0.35	0.23
	Mean (µg L <sup>-1</sup> ) ± stdev	55.8 ± 50	34.4 ± 38.5
	Mean load (µg s <sup>-1</sup> ) ± stdev	259.4 ± 108.4	182.4 ± 696.1
Total Carbon	Annual yield (kg ha <sup>-1</sup> year <sup>-1</sup> )*	104	97
	Mean conc. (mg L <sup>-1</sup> ) ± stdev	25.3 ± 6.3	21.3 ± 5.0
	Mean load (mg s <sup>-1</sup> ) ± stdev	373.6 ± 335.1	335.2 ± 352.2

\* Calculated with rating curves.

\*<sup>1</sup> Calculated with Walling and Webb Method 5 (Walling and Webb, 1985).

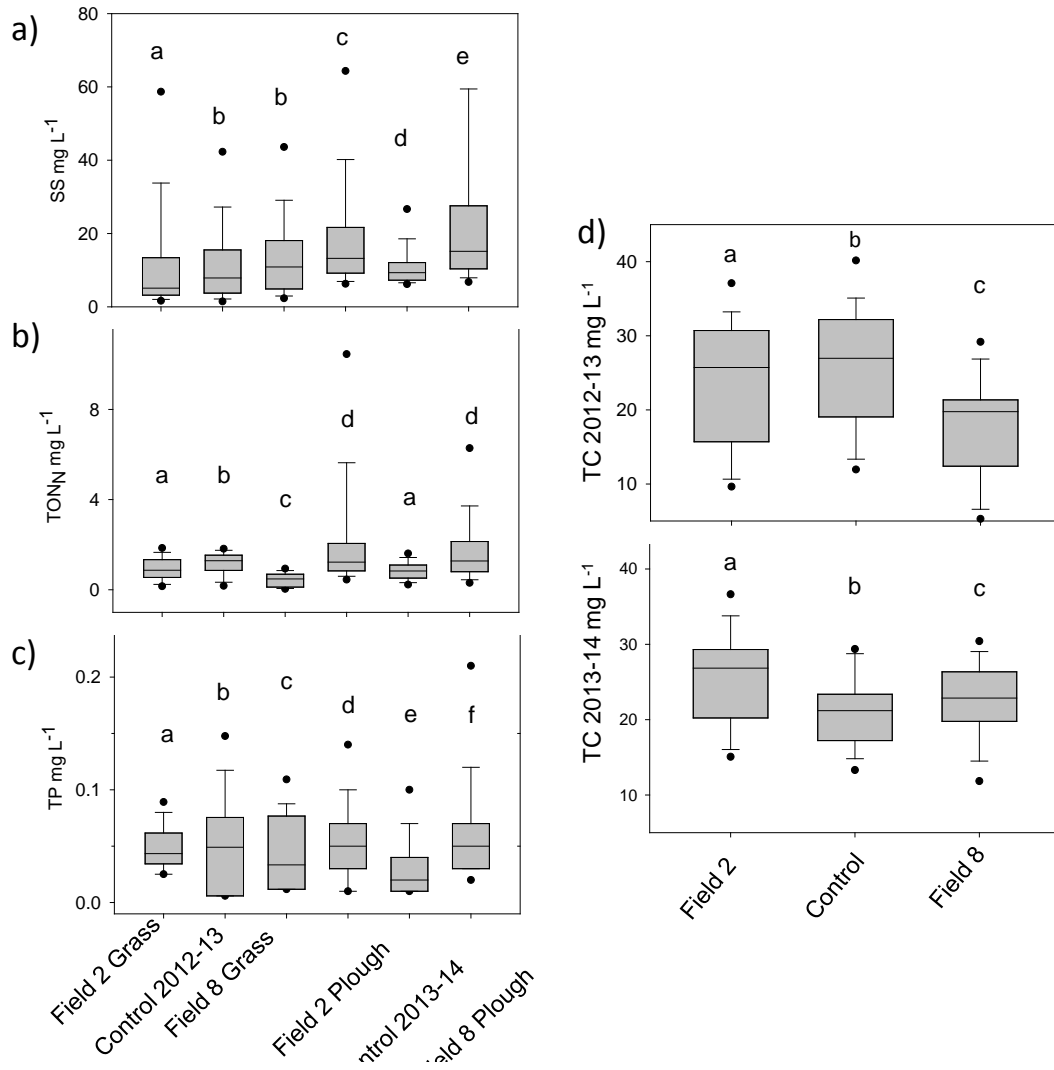


Figure 8.3. Between-field differences in means of each monitored water quality property, for both the permanent grassland baseline period (2012 - 2013) and the post-ploughing treatment period (2013 - 2014), a) suspended sediment (SS), b) total oxidized nitrogen-N (TON<sub>N</sub>), c) total phosphorus (TP) and d) total carbon (TC)\*. Significant differences, determined by two sample t-tests, are visualized by different letters (a,b,c,d,e,f). The boxes visualize the lower to the upper quartile, the line the median and the upper whisker the upper quartile + 1.5 \* the interquartile range and the lower whisker the lower quartile - 1.5 \* the interquartile range. Dots visualize the 5<sup>th</sup> and 95<sup>th</sup> percentile.

\*Different analytical instruments without available cross-calibration were used between the two monitoring periods. Therefore, the relative differences between the treatment and control fields were compared and not comparison could be conducted before and after ploughing.

Table 8.3. General overview of the three fields' event-based hydrological characteristics (mean, median, minimum and maximum) and number of captured events.

Field		Event Total	Event Discharge	Peak Discharge	Rainfall-runoff coefficient
		mm	1000L	L s <sup>-1</sup>	%
2	Mean	15.5	1041.4	35.7	51.64
	Median	12.6	845.5	18.2	49.04
	Minimum	2.5	167.8	6.9	17.68
	Maximum	48	3220.8	126.7	92.08
	N	35	35	35	35
Control	Mean	10.6	577.8	40.00	74.31
	Median	7.6	335.0	21.2	75.19
	Minimum	2.4	119.4	6.8	3.42
	Maximum	39.8	3301.0	142.1	125.86
	N	42	42	42	42
8	Mean	16.0	593.1	36.1	45.95
	Median	12.1	343.4	20.5	47.66
	Minimum	2.8	83.7	8.0	16.06
	Maximum	64.8	3411.0	132.5	72.80
	N	44	44	44	44



Table 8.4. Overview of storm event water quality data for the two ploughed and reseeded fields (2 and 8) and the permanent grassland control field. Water quality data includes peak event concentrations and event yields of suspended sediment and macronutrients. All measurements are normalised by field area. Where appropriate, mean median, minimum, maximum and number of captured events are shown.

Field	<u>Suspended Sediment</u> ( $>1.2 \mu\text{m}$ )			<u>Total Oxidized Nitrogen</u>			<u>Total Phosphorus</u>			<u>Total Carbon</u>		
	peak event conc.	event yield	peak event conc.	peak event conc.	event yield	peak event conc.	peak event conc.	event yield	peak event conc.	event yield	peak event conc.	event yield
	$\text{mg L}^{-1} \text{ha}^{-1}$	$\text{kg ha}^{-1}$	$\text{mg L}^{-1} \text{ha}^{-1}$	$\text{mg L}^{-1} \text{ha}^{-1}$	$\text{g ha}^{-1}$	$\mu\text{g L}^{-1} \text{ha}^{-1}$	$\mu\text{g L}^{-1} \text{ha}^{-1}$	$\text{g ha}^{-1}$	$\text{mg L}^{-1} \text{ha}^{-1}$	$\text{mg L}^{-1} \text{ha}^{-1}$	$\text{mg L}^{-1} \text{ha}^{-1}$	$\text{kg ha}^{-1}$
	Mean	26.40	8.79	0.20	60.36	23.02	6.43	4.70	2.77			
	Median	17.74	3.31	0.16	29.10	16.39	2.83	4.60	2.20			
2	Min	1.07	0.27	0.09	5.28	2.98	0.22	3.81	1.13			
	Max	83.27	54.55	0.88	579.05	114.75	44.51	5.73	5.70			
	N	34	34	32	32	29	29	10	10			
	Mean	14.32	3.45	0.13	24.98	16.99	4.49	3.77	1.99			
	Median	10.40	1.15	0.14	20.89	13.66	1.89	3.63	1.53			
Control	Min	4.53	0.39	0.05	2.63	1.52	0.35	2.53	0.43			
	Max	37.24	17.40	0.26	135.58	56.15	38.65	4.90	5.31			
	N	31	31	41	41	36	36	11	11			
	Mean	39.48	11.75	0.29	68.86	44.02	10.34	3.55	2.00			
	Median	32.76	3.23	0.17	25.22	34.91	3.08	3.52	1.22			
8	Min	5.44	0.21	0.06	4.20	5.27	0.59	2.90	0.46			
	Max	101.46	77.77	1.96	686.45	134.39	72.94	4.18	4.81			
	N	44	44	44	44	22	22	10	10			

**C. Have controls on fluxes and yields of sediment and macronutrients changed with respect to the baseline period and what may be controlling pollutants after ploughing?**

Controls on fluxes and yields of sediment and macronutrients changed after ploughing with respect to the baseline period. The relationships between pollutant concentrations and discharge remained the same, but the ploughed fields, despite having significantly lower soil nutrient contents compared to the control field (Chapter 7), yielded significantly more macronutrients than the control field; a reversal from the baseline period. The ranked order of losses and soil contents between the two treatment fields did not change with ploughing.

The pollutants' behaviour with respect to discharge was the same after ploughing. Suspended sediment and TP peaks preceded or coincided with the hydrograph peaks, but the SS peaks were generally higher in ploughed fields than in the control field. Total oxidized N was diluted by high flows, but both high base-flow  $\text{TON}_N$  concentrations and lower diluted storm-flow concentrations were consistently higher in the ploughed fields compared to the control field. Total C illustrated mixed behaviour with discharge, from peak TC concentrations coinciding or preceding with peak discharge to dilution of TC by high flows. Therefore, the time-series rating curves between discharge and pollutant concentrations remained significantly positive for SS, TP and TC, and significantly negative for  $\text{TON}_N$ , but the variance explained by discharge was smaller in all fields compared to the baseline period, including the control field (Flow versus SS: 25.3 % - 61.4 %, TP: 9.7 % - 16.8 %,  $\text{TON}_N$ : 20.2 % - 46.0 %, TC: 20.8 % - 53.2 %).

What was different in this monitoring period compared to the baseline was that  $\text{TON}_N$  concentrations were large as soon as discharge occurred after the dry summer (no discharge for 3 months), and gradually declined throughout the first few months of discharge (Figure 8.3). Also, TC concentrations in the ploughed fields showed a pattern that was not seen during the baseline period. TC concentrations always increased with discharge before the high flow events in December, and high discharge caused a dilution of TC concentrations during the high flow events after December.

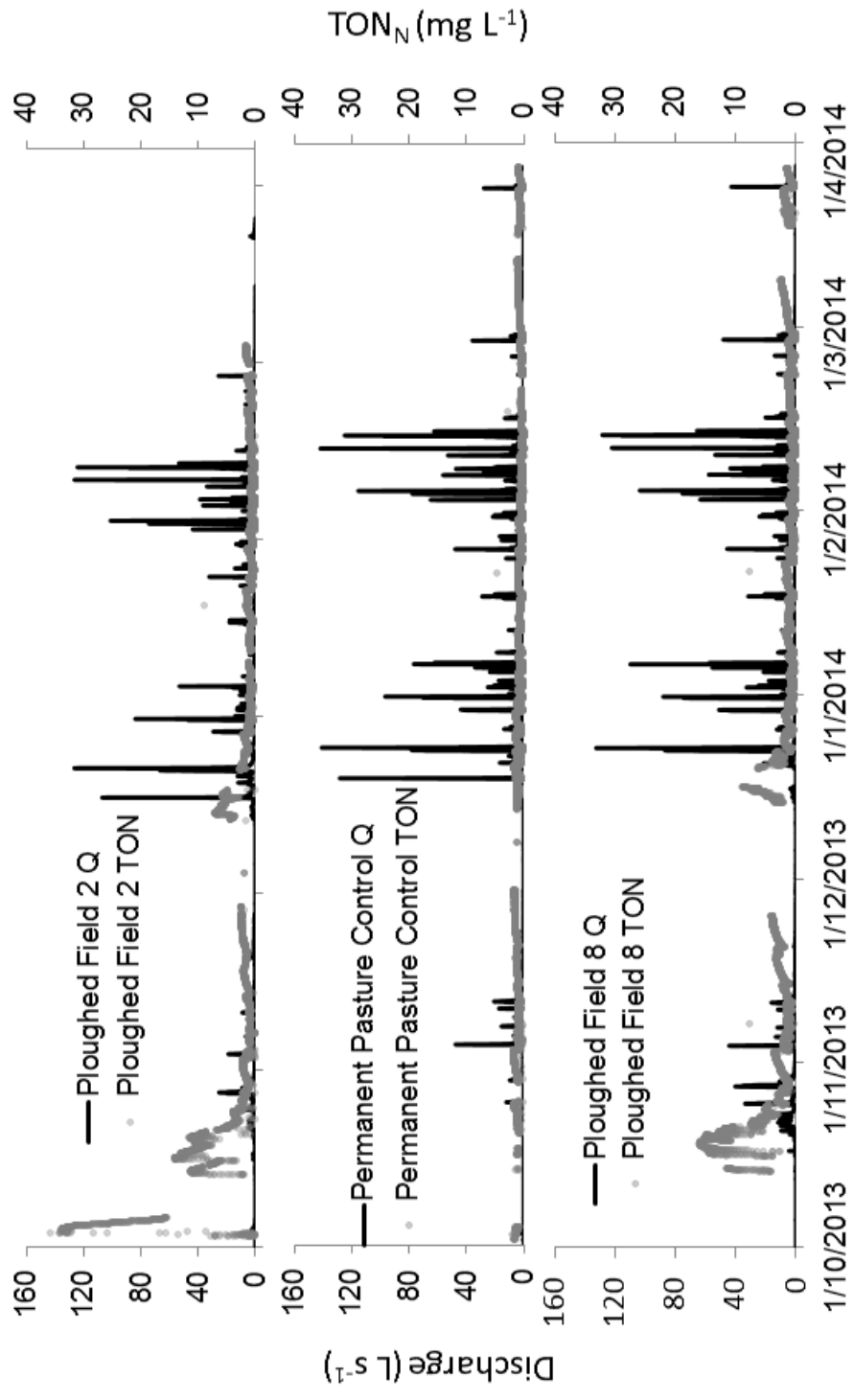


Figure 8.4. Total oxidized Nitrogen-N ( $\text{TON}_N$ ) concentrations ( $\text{mg L}^{-1}$ ) for all three monitoring fields, ploughed / reseeded field 2, permanent grassland control field, ploughed / reseeded field 8, for the sampling duration in which discharge occurred (October 2013 – April 2014). All data was monitored and expressed at 15-minute time steps.

**D. Has ploughing and reseeded affected the relative importance of pollutants through flow conditions and time relative to the permanent grassland baseline period and control fields?**

The relative importance of pollutants through flow conditions and time changed after ploughing and reseeded relative to the permanent grassland baseline period and the control field. Ploughing and reseeded did not affect the contribution of individual pollutants to the overall total pollutant yield, the order was SS > TC > TON<sub>N</sub> > TP before and after ploughing / reseeded and in the control field (Table 8.1). However, the proportions of contribution to overall pollution losses and macronutrient ratios were altered after ploughing and reseeded. The contribution of SS increased by approximately 10 – 14 %, TON<sub>N</sub> by approximately 1.7 %, whilst TC reduced by approximately 10 % and TP reduced by 0.1 – 0.9 %. The TC:TON<sub>N</sub> ratio reduced by approximately 30 – 70, TC:TP remained similar and TON<sub>N</sub>:TP increased by approximately by 10. However, TON<sub>N</sub>:TP ratio also increased in the control field in 2013 compared to the control field in 2012.

Table 8.5. Percentage of the contribution of each pollutant to the overall annual pollutant yield and annual yield macronutrient ratios for the two ploughed and reseeded grassland fields (Field 2 and 8) and the permanent grassland control.

	Field 2	Control	Field 8
Total annual pollutant* yield kg ha <sup>-1</sup>	446.66	265.33	642.87
% of total annual pollutant yield:			
SS	74.75	62.34	83.44
TC	23.21	36.69	16.00
TON <sub>N</sub>	1.95	0.88	0.51
TP	0.08	0.09	0.05
Macronutrient ratios:			
TC:TON <sub>N</sub>	11.89	41.61	31.46
TC:TP	296.26	423.30	311.73
TON <sub>N</sub> :TP	24.91	10.17	9.91

\* SS, suspended sediment; TC, total carbon, TON<sub>N</sub>, total oxidized nitrogen-N; TP, total phosphorus

Ploughing also altered the mean and median pollutant concentrations and ratios in field 2 during different flow conditions, compared to those reported for field 2 during the baseline period (Table 8.6). Mean and median pollutant concentrations and ratios changed considerably between baseflow and stormflow conditions, as was the case in the previous year when the field was managed as permanent grassland. Baseflow occurred for up to 56 % of the time series (if pollutants are assumed to show the same behaviour at flow rates  $< 0.2 \text{ L s}^{-1}$ , when no discharge water was monitored, as they do during baseflow  $> 0.2 \text{ L s}^{-1}$ , when discharge water was monitored). Generally, SS and TP concentrations increased with rising flow rates, whilst  $\text{TON}_N$  decreased with rising flow rates, the same behaviour as was observed during the permanent grassland baseline period. However, SS: $\text{TON}_N$  ratios were always smaller after ploughing than before ploughing, SS:TP slightly larger and  $\text{TON}_N$ :TP always greater.

Ploughing / reseeded altered the differences between macronutrient ratios in water and macronutrients ratios in the soil. The TC: $\text{TON}_N$  ratio in water was closer to that in the soil after ploughing than during the baseline period and  $\text{TON}_N$ :TP ratios were greater than those in soil, a rise relative to the baseline period.

Table 8.6. Mean and median pollutant concentrations and their ratios measured in one ploughed / reseeded field (Field 2) during baseflow and stormflow periods as well as further subdivided into the lower quartile of baseflow and upper quartile of stormflow.

pollutant * concentrations mg L <sup>-1</sup>	All baseflow			Baseflow lower quartile			All stormflow			Stormflow upper quartile		
	35 - 56 % * <sup>2</sup>			11 - 42 % * <sup>2</sup>			9.5 % * <sup>2</sup>			4.7 % * <sup>2</sup>		
	Mean	Median	N	Mean	Median	N	Mean	Median	N	Mean	Median	N
SS	13.1	10.8	5942	10.5	8.1	593	42.2	26.3	2671	60.9	41.3	1388
TC* <sup>1</sup>							25.3	26.9	140	24.6	25.7	122
TON <sub>N</sub>	3.0	1.4	8954	5.0	1.9	1528	1.0	0.7	2571	0.96	0.58	1268
TP	0.05	0.05	5457	0.03	0.02	717	0.065	0.060	2309	0.070	0.060	1122
SS:TC							1.7	1.0		2.5	1.6	
SS:TON <sub>N</sub>	4.3	7.6		2.1	4.4		44.4	39.8		63.5	71.1	
SS:TP	251.5	216.6		420.4	406.0		648.8	438.3		870.3	687.7	
TC* <sup>1</sup> :TON <sub>N</sub>							26.6	40.7		25.6	44.4	
TC* <sup>1</sup> :TP							389.2	447.5		351.7	429.0	
TON <sub>N</sub> :TP	58.1	28.6		200.8	93.0		14.6	11.0		13.7	9.7	

\* SS, Suspended sediment; TC, Total carbon; TON<sub>N</sub>, Total oxidised nitrogen-N; TP, Total phosphorus

\*<sup>1</sup> Total carbon was only measured as grab samples during storm events.

\*<sup>2</sup> Duration expressed as percentage of the entire time series. Discharge occurred 65.7 % of the time-series (3/6/2013-3/4/2-14). Higher baseflow estimates include the time when there was flow, but not sufficient rates (< 0.2 L s<sup>-1</sup>) for monitoring; assuming that concentrations and ratios during that time is similar to those during baseflow or the lower quartile of baseflow.

**E. How does water quality from ploughed and re-seeded grassland fields compare to EU / UK recommended water quality standards?**

EU water quality guidelines for SS and TP were frequently exceeded in all fields, but the ploughed fields had larger exceedance frequencies than the control field (Table 8.5). Exceedance frequencies increased in the ploughed fields, and decreased in the control field in relation to the baseline period. Approximately 20 - 30 % of all SS samples from the ploughed fields exceeded the Freshwater Fisheries Directive (FFD) (control field: 7 %) and 70 – 80 % exceeded the lower 10 mg L<sup>-1</sup> standard (control field: 42.77 %). Approximately 50 % of all TP samples in the ploughed fields did not to meet good ecological status (control: 22 %). TON<sub>N</sub> occasionally exceeded the Nitrates Directive in the ploughed fields (2 - 3%), but not at all in the control field; an increase with respect to the baseline period.

Table 8.7. The percentage of all suspended sediment (SS), total P (TP), and total oxidized nitrogen-N (TON<sub>N</sub>) samples exceeding water quality guidelines in the discharge water of two ploughed and reseeded grassland fields (Field 2 and 8) and a permanent grassland control.

	Field 2	Control	Field 8
<b>SS</b>			
> FFD (>25 mg SS L <sup>-1</sup> ) *	20.13	6.69	28.39
> 10 mg L <sup>-1</sup>	69.57	42.77	77.69
<b>TP</b>			
fail 'good ecological status' (> 0.04 mg DRP L <sup>-1</sup> ) * <sup>1</sup>	55.55	22.06	52.39
fail 'moderate ecological status' (> 0.15 mg DRP L <sup>-1</sup> ) * <sup>1</sup>	3.41	1.64	6.88
<b>TON<sub>N</sub></b>			
fail Nitrates Directive (> 11.3 mg NO <sub>3</sub> <sup>-</sup> -N L <sup>-1</sup> )	3.94	0	2.86

\* FFD, EU Freshwater Fisheries Directive.

\*<sup>1</sup> DRP, dissolved reactive phosphorus.

A summary of the key effects of ploughing and reseeded on the monitored diffuse pollutants is presented in table 8.8.

Table 8.8. Summary of key effects of ploughing and reseeded on multiple pollutants from grasslands.

	Suspended Sediment	Total Phosphorus	Total oxidized Nitrogen-N	Total Carbon
concentrations, loads and yields	↑	↑	↑	↑
relative importance	↑	↓	↑	↓
exceedance of water quality guidelines	↑	→	↑	↑

## V. Discussion

### A. Can change be detected between baseline (permanent grasslands the previous year) and post-ploughing?

This study is the first to use a paired design to assess the effects of ploughing and reseeded on diffuse water pollution from grasslands. A significant change between the baseline period and post-ploughing was detected. The response of pollutants to discharge was changed by the management intervention of ploughing and reseeded. While rainfall and discharge were highly correlated between the control field and the treatment fields, both in the baseline period and post-ploughing, the regression equations and slopes of regression lines of pollutants between the control field and the treatment fields changed in agreement with the work of several researchers (Bishop *et al.*, 2005; King *et al.*, 2008; Jokela & Casler, 2011; Schilling *et al.*, 2013; Veum *et al.*, 2009), albeit at a different observation scale. The fundamental requirement of paired studies was met (that the catchments (or fields in this case) respond to rainfall in similar ways); regressions for discharge were as strong as 0.88 and 0.92. Therefore, only 8 – 12 % of the changes in water quality may be explained by altered discharge, but most of the variability can be attributed to the effects of ploughing and reseeded and its subsequent effects on how the field-scale systems



responded. Consequently, despite inter-annual variability in rainfall and discharge, change seen after ploughing cannot be attributed to changes in extrinsic factors such as the weather, but can be attributed to the management change itself.

**B. How do pollutant losses after ploughing and reseeding compare to a permanent grassland control and the permanent grassland baseline period?**

Pollutant losses, in terms of concentrations, loads and yields increased in the treatment fields in the first hydrological season after ploughing and reseeding compared to their losses when they were managed as permanent grassland and compared to the permanent grassland control field. Therefore, the ranking in terms of pollutant losses reversed, the ploughed and reseeded fields had significantly larger pollutant losses than the control field.

Such increases in SS and TP losses were expected from previous research on ploughed and reseeded grassland reported in the literature (SS: Sharpley, 2003; Grandy & Robertson, 2006; Butler & Haygarth, 2007; TP: Addiscott & Thomas, 2000; Sharpley, 2003; Butler & Haygarth, 2007). This is, however, the first study to demonstrate the increase of N and C losses in discharge water after ploughing and reseeding of grasslands.

Chapter 5 showed that pollutant losses from permanent grasslands (> 6 years without ploughing and reseeding) were similar to or exceeded those reported for mixed land-use and even arable land, especially in terms of SS, TP and TC. Here, ploughing the same fields accelerated the already significant losses of SS, TP, TC and  $\text{TON}_N$ . Therefore, the contribution of grasslands to overall agricultural diffuse pollution may have been underestimated, especially immediately after ploughing permanent grasslands (Chapter 5 and references therein).

**C. Have controls on fluxes and yields of sediment and macronutrients changed with respect to the baseline and what may be controlling pollutants after ploughing?**

Ploughing and reseeded changed the controls on fluxes and yields of sediment and macronutrients. Pollutants were mobilized and transported by the same processes as during the permanent grassland baseline, demonstrated by the same behaviour with discharge as during the baseline period, but the relationships between soil nutrient content and nutrient losses in discharge water reversed. The control field with the highest nutrient contents (nutrient source) compared to the ploughed fields had the lowest nutrient losses. Therefore, the availability or vulnerability of soil particles and soil nutrients for mobilization (in combination with site characteristics, such as topography), irrespective of the soil nutrient contents, may be controlling sediment and nutrient fluxes and yields after ploughing. The following section discusses these mobilization processes and how availability or vulnerability to mobilization may have altered with ploughing and reseeded.

Suspended sediment was mobilized and transported by physical detachment and hydrological transfer in all fields (Chapter 5), but sediment particles were more vulnerable to mobilization after ploughing and reseeded compared to the permanent grassland baseline period and the control field. The soil is less stable after ploughing and therefore more vulnerable to detachment (Butler & Haygarth, 2007). Particles previously protected as macroaggregates are broken down resulting in less dense and smaller microaggregates, which can be more easily detached (Grandy & Robertson, 2006). Further protection by dense root biomass is also reduced after ploughing and reseeded (Gyssels, 2005; Acharya *et al.*, 2012). Therefore, more sediment was detached and transported to the flumes in the ploughed and reseeded fields compared to the control field, as has been observed in arable landscapes when bare soil is exposed particularly in the autumn months (Grandy & Robertson, 2006).

Total P was mobilized and transported by hydrological transfer during high flows, in a similar manner like SS in all fields (House & Warwick, 1998; Bowes *et al.*, 2005), but increased rates of TP were mobilized after ploughing and

reseeded even though the ploughed fields had lower soil TP contents than during the baseline period and the control field (Chapter 7). Increased mobilization and transport of TP, especially sediment-associated TP in ploughed fields may be due to a higher potential for sediment-bound P to be transported (Butler & Haygarth, 2007). The sediment transported to the flumes in ploughed fields may be enriched with P compared to grassland fields, because ploughing increases soil P sorption capacity by aggregate break down and soil mixing (Sharpley, 2003; Butler & Haygarth, 2007). Ploughing exposes soil particles that were previously protected from sorption by aggregates, soil particles from lower soil horizons with high P sorption capacity as well as smaller soil particles with higher surface areas (Sharpley, 2003; Butler & Haygarth, 2007). Therefore, the proportion of TP transported as particulate P may be increased after ploughing, as was reported by Butler and Haygarth (2007), who distinguished between particulate and dissolved P in their analysis.

Total oxidized N was mobilized by diffusion of dissolved oxidised N in the soil water to rain water in all fields, with greater diffusion and therefore mobilization when the rain water is slowly moving through the soil matrix during low flows (Gächter *et al.*, 2004; Granger *et al.*, 2010, Chapter 5). The availability of  $\text{TON}_N$  to mobilization by diffusion increased with ploughing. Ploughing and reseeded causes mineralization of previously protected organic matter and with that mineralization of organic N, so that the overall N content may be reduced but the mineral proportion of N may have increased (Bhogal, 2000; Shepherd, 2001; Eriksen *et al.*, 2004; Hansen *et al.*, 2005). The increased mineral soil N is not all utilized by the re-sown vegetation and therefore becomes excess N, readily available for diffusion from the soil water and is gradually washed out (Bhogal, 2000; Shepherd, 2001; Eriksen *et al.*, 2004; Hansen *et al.*, 2005; Bernsten *et al.*, 2006). The suggested increase in soil mineral N after ploughing is confirmed by the higher soil TC:TN ratios in the ploughed field than the control field (Chapter 6, Mooshammer *et al.*, 2012).

Total oxidized N concentrations were large with the onset of discharge and decreased continuously until the onset of high flows at the end of December, a pattern that was not seen during the baseline sampling period. The “flushing” of mineral N after a long dry period has been reported before (Shepherd, 2001)

and may be attributed to a) high SOM turnover and additional FYM and N fertilizer inputs over the summer that were not all taken up by the vegetation (Shepherd, 2001; Gächter *et al.*, 2004) and b) increased rates of N mineralization in rewetting soils after a long dry period (Frier & Schimel, 2002). Rewetting may cause microbes to release intracellular solutes, which can then be rapidly mineralized by other microbes and transported to surface waters (Frier & Schimel., 2002).

Total oxidized N concentrations in discharge water were gradually reduced throughout the monitoring period, and were comparable to those in the control field at the end of the monitoring period. It remains to be quantified whether a residual ploughing increase of N losses will remain or whether N losses will revert back to pre-ploughing levels long-term (Shepherd, 2001).

The mobilization processes of TC are not as well understood compared to the other pollutants. This is partly because less research has been conducted on TC mechanisms from grasslands or agricultural land (Chapter 5), but also because the monitoring resolution for TC in this study was much lower than that for the other pollutants (Chapter 5). Water leaving the ploughed fields had consistently greater TC concentrations, loads and yields in discharge water, despite having significantly lower soil TC contents (Chapter 7), a reversal of the baseline period (Chapter 6). An increase in the TC content of SS (or what was herein considered as SS: particles above a certain size, which can also include coarse organic matter particles) is often seen after ploughing (Owens *et al.*, 2002; Haygarth *et al.*, 2006; Kuhn *et al.*, 2009). The large TC content of SS may be due to either increased binding of SOM to sediment after ploughing or mobilization of lighter SOM-sediment microaggregates that were previously protected in heavier macroaggregates (Grandy & Robertson, 2006). Also, it may be light, labile organic matter particles which become more vulnerable to mobilization (Lal, 2005; Grandy & Robertson, 2006; Zhang *et al.*, 2006). Light organic matter particles may have been 'washed out' by the first storm events followed by little particulate SOM being transported once the high-flow storm events started end-December. Dissolved C may also be more vulnerable / available to mobilization after ploughing, as SOM that was previously protected in macroaggregates now gets dissolved in the soil water or by rainwater moving over and through the soil matrix (Six *et al.*, 2000).

**D. Has ploughing and reseeded affected the relative importance of pollutants through flow conditions and time relative to the permanent grassland baseline period and control field?**

This is the first study to present macronutrient ratios and pollutant ratios in discharge water from ploughed and reseeded grasslands. In addition to accelerating diffuse pollutant losses, ploughing and reseeded altered the relative importance of pollutants. SS and  $\text{TON}_N$  concentrations increased at similar rates, but greater rates than those of TC and TP losses. Therefore, the relative importance of TC and TP reduced with ploughing and reseeded. The largest increase in relative importance was that of  $\text{TON}_N$ , which is particularly important as the Farm Platform is situated within a Nitrate Vulnerable Zone, where eutrophication of the River Taw is an issue (Haygarth *et al.*, 2005a; EA, 2009; Maier *et al.*, 2012). Long-term monitoring therefore is required to quantify the effect of ploughing and reseeded on diffuse water pollution, to see whether there is a long-term shift in the relative importance of pollutant losses. The fact that ploughing and reseeded altered the short-term relative importance of pollutants emphasizes the need for synchronous monitoring of multiple pollutants to identify management practices that (ideally) simultaneously reduce all pollutants.

The anticipated mobilization and transport pathways were confirmed by the changing  $\text{TON}_N$ :TP ratios with flow conditions. High  $\text{TON}_N$ :TP ratios during low flows and a dramatic reduction in  $\text{TON}_N$ :TP ratios during high flows confirms slow subsurface flows to be mobilizing and transporting N, whereas high surface runoff flows are mobilizing and transporting P (Green *et al.*, 2007). With the rise of  $\text{TON}_N$  concentrations and losses after ploughing, TC: $\text{TON}_N$  overall yield ratios have become closer to the soil source TC:TN ratios, showing that these are lost more in proportion of the available source compared to the baseline period (Chapter 6).

**E. How does water quality from ploughed and re-seeded grassland fields compare to EU / UK recommended water quality standards?**

Ploughing and reseeded exacerbated the frequencies by which SS and TP from grassland exceeded EU / UK water quality guidelines (Chapter 5). The lower, more appropriate 10 mg SS L<sup>-1</sup> guideline was exceeded by 70 – 80 % throughout the sampling period and more than 50 % of TP samples did not meet good ecological status. Additionally, the Nitrates Directive (11.3 mg L<sup>-1</sup>) was exceeded for 2 - 3 % of the time series, which was not exceeded during the permanent grassland monitoring period. Therefore, recently ploughed and reseeded grasslands do not comply with water quality guidelines. More regular ploughing of the grasslands in the Taw catchment (to pursue so-called sustainable intensification of farming), the receiving catchment of the Farm Platform, covered by approximately 80 % grassland, may exacerbate already documented SS, TP and N problems (Haygarth *et al.*, 2005a; EA, 2009; Maier *et al.*, 2012). Additionally, exceedance frequencies may have been a lot higher if the summer had not been as dry. Heavy rainfall during spraying, when soils were bare, and immediately after fertilizer and FYM applications, would have most likely caused high summer pollutant concentrations and exacerbated guideline exceedance frequencies (Preedy *et al.*, 2001). Pollutant concentrations from these ploughed grassland fields would also exceeded water quality standards set outside the EU, such as in the USA (SS guideline similar to the lower 10 mg L<sup>-1</sup> standard used here and the P standard lower than the good ecological standard (USEPA, 2000).

The amount of 15-minute time-steps that exceeded the Nitrates directive may seem low, but N losses from ploughed grasslands are likely to impose a threat to the receiving surface water. Several fractions of N that are likely to impact on aquatic biota are not included in the Nitrate-N standard. For example, Nitrite, a small component of TON<sub>N</sub>, is known to be toxic to aquatic fauna even at low concentrations (Lewis & Morris, 1986; Granger *et al.*, 2010). Also, organic N mobilization and transport is likely to have increased after ploughing with increased erosion of SOM, and organic N has been demonstrated to be bioavailable (See *et al.*, 2006). Therefore, N guidelines outside the EU are set

for total N (USEPA, 2000). The high TC concentrations from these ploughed grasslands may pose a threat to surface water quality, even though C guidelines have not yet been set for surface waters (Edwards *et al.*, 2008; Sandford *et al.*, 2013; Chapter 5).

It remains to be quantified, whether exceedance frequencies remain high after ploughing grasslands or whether there may be long-term pollutant reductions. Any potential water quality benefits of sustainable intensification measures that include ploughing and reseeded of grasslands will have to compensate for those short term accelerated diffuse pollution rates reported here.

## VI. Conclusion

This is the first study to monitor the effects of ploughing and reseeded of grasslands on the delivery of multiple pollutants, sediment and the macronutrients N, P and C, at high resolution. Monitoring was conducted throughout the first hydrological season after ploughing and therefore this paper reports on the short-term effects of ploughing and reseeded grasslands. A paired experimental design was employed so that data from ploughed and reseeded field could be compared to a pre-monitored baseline period when the fields were managed as permanent grasslands, as well as a permanent grassland control field during both the baseline and the post-ploughing period.

A clear effect of ploughing and reseeded on water quality could be detected with help of the paired design (**Question 8.1**): Ploughing and reseeded of grasslands caused accelerated pollutant losses in the first hydrological season after ploughing and reseeded with respect to previous losses when all fields were managed as permanent grassland and to a grassland control field (**Question 8.2**). Even though such diffuse pollution increases after ploughing and reseeded were to be expected, this is the first study in ploughed and reseeded grasslands to demonstrate SS and TP losses at such high resolution and the first study to measure actual N losses in discharge water and to demonstrate TC losses from ploughed and reseeded grasslands. High

resolution monitoring gave insight into pollutant dynamics and the comparison with soil conditions gave insight into mobilization of nutrients with respect to the soil nutrient pools; water quality in combination with soil conditions has never been quantified in ploughed and reseeded grasslands. The controls on fluxes and yields of sediment and macronutrients have changed with ploughing and reseeded: pollutants still responded to discharge the same way as during the permanent grassland baseline, but the relationship between soil nutrient content and nutrient losses have reversed. The availability or vulnerability of soil particles and macronutrients to mobilization, irrespective of soil nutrient contents, may be controlling fluxes and yields of sediment and macronutrients from ploughed/reseeded grassland fields (**Question 8.3**). Ploughing and reseeded caused a shift in the relative importance of pollutants, with a dramatic increase in the relative importance of N losses (**Question 8.4**).

Compliance with water quality guidelines is challenging a year after ploughing/ reseeded permanent grasslands. A general increase of percentage exceedance was seen compared to the baseline period or the permanent grassland control. Ploughing / reseeded grasslands is very likely to exacerbate the already existing water quality issues in terms of all SS, P, N and C in the receiving surface water, the Taw River (**Question 8.5**).

This study contributes to the growing evidence that grasslands significantly contribute to overall agricultural diffuse pollution, especially even more so after ploughing and reseeded.



*This chapter quantified the effects of ploughing and reseeded grasslands on sediment and macronutrient fluxes and yields and their relative importance. It has addressed questions that were raised by previous chapters. Ploughing and reseeded accelerated the fluxes and yields of sediment and the macronutrients carbon, nitrogen and phosphorus, thereby exacerbating the high diffuse pollution rates that were presented from permanent grasslands, which were found to be similar to or exceeding the losses reported from other grasslands, mixed land-use and arable sites. Therefore, regularly ploughing and reseeded grasslands increases the threat that grasslands pose to receiving surface waters (question raised by chapter 5). Ploughing and reseeded has also altered the relationship between soil status and water quality status between the fields; suggesting a shift from the importance of the available source in the soil controlling the between-field differences in water quality, to mobilization pathways controlling the between-field differences in water quality (question raised by chapter 6 and chapter 7). As this chapter only addressed the short-term effects of ploughing and reseeded on soil erosion and diffuse pollution, further questions were raised about the long-term effects.*

*The next chapter concludes this thesis by summarising the key findings of this thesis and discussing areas of further research.*

## **Chapter 9**

### **Summary, Areas of Further Research, and Conclusions**

#### **I. Summary of key findings**

This thesis presents an improved understanding of the effects of different grassland management practices on the soil-to-water transfer continuum. The initial focus describes the effect of permanent grassland management (permanent for at least 6 years with the same management, but different grassland management > 6 years ago) on soil and water quality. The latter part of this thesis studies the short-term effects of ploughing and reseeded of permanent grassland fields, again on soil and water quality. A before / after (permanent grassland baseline characterization followed by treatment implementation of ploughing and reseeded) and control / treatment experimental design (one field remained as the baseline management whilst two other fields were ploughed and reseeded) was employed and proved to be useful in detecting the effects of management change. A significant change after ploughing and reseeded was detected despite high year-to-year variation both in soil and water properties.

Figure 9.1 shows the original conceptual framework setting out the overall aim of this PhD and the specific questions that were asked to increase the understanding of the effects of the different grassland management approaches on the individual soil-to-water transfer continuum components, from source, mobilization & transport to delivery to surface waters and the potential impacts of those diffuse pollutants in the receiving surface waters. These questions were addressed in five results chapters / papers. The following chapter summarises the key findings, split into two parts, first the effects of conventional permanent grassland management (Figure 9.2) and second the effects of ploughing and reseeded (Figure 9.3).

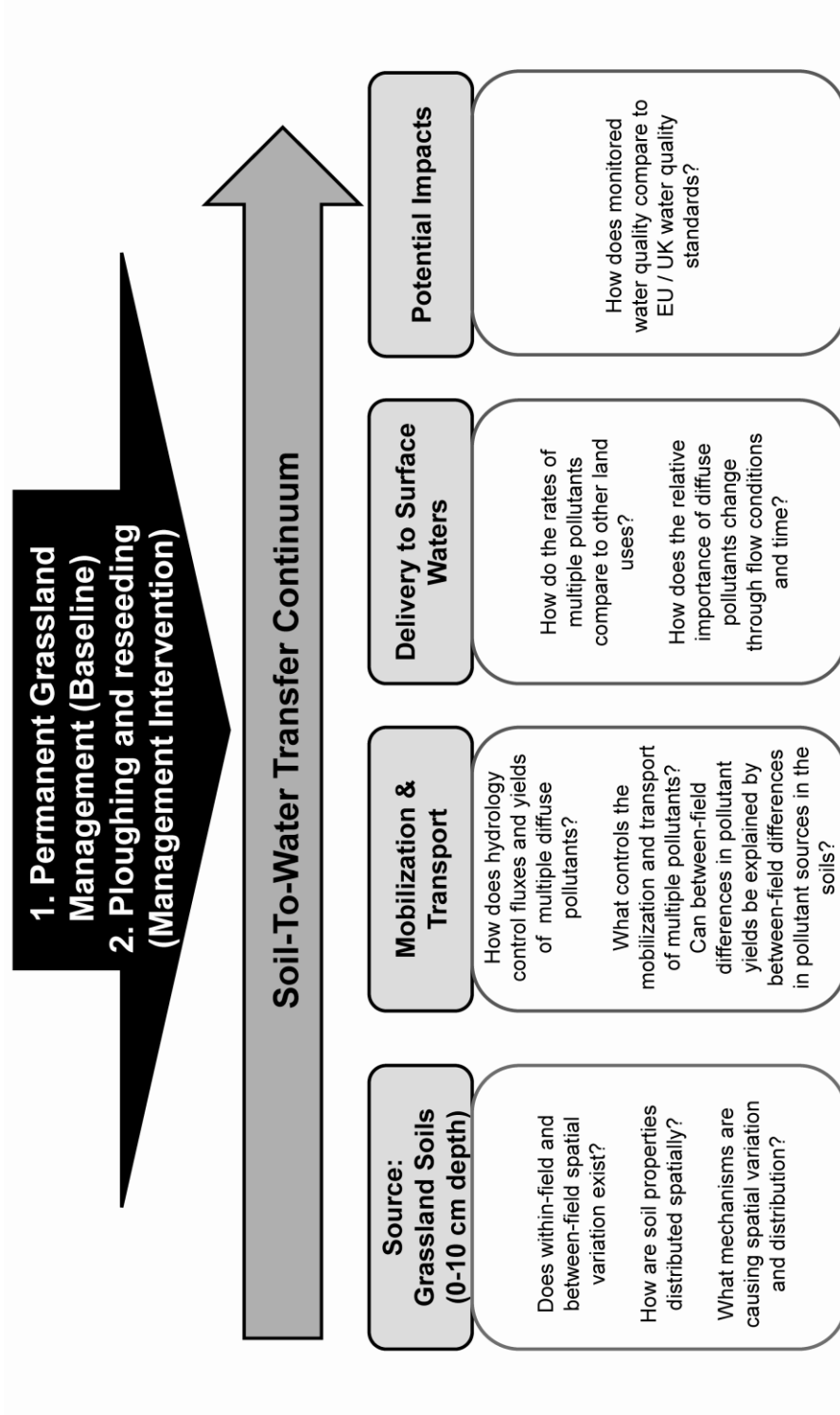


Figure 9.1. Conceptual framework setting out the overall aim of this PhD “Understanding the effects of different grassland management practices on the soil-to-water transfer continuum” and how they were addressed. The effects of two different grassland management practices (black arrow) were monitored on the soil-to-water transfer continuum. Each individual component of the continuum (light grey boxes) was addressed with specific research questions (white boxes).

## **A. The effects of permanent conventional grassland management on the soil-to-water transfer continuum**

This section summarises the knowledge that was gained by this thesis towards understanding the effects of permanent conventional grassland management on each component of the soil-to-water transfer continuum (Figure 8.2).

Source: Pollutant sources were shown to be spatially variable within grassland fields, despite homogeneous fertilizer application, homogeneous physical soil management and homogeneous crop cover for the past 5 years. Therefore, the three grassland fields did not provide uniform soil sources for diffuse pollution. Spatial variation existed within fields and the three sampled fields were significantly different in terms of their mean soil properties. Soil nutrient contents were comparable to those in other grasslands and greater than those reported for arable sites. The distribution of soil properties was significantly different in each field and also significantly different between areas within fields. The soil properties varied over lag distances of 40 - 111 m, depending on the soil property of interest illustrating that future soil sampling strategies to characterize soil quality should take these levels of spatial variation into account. Between-field and within-field spatial variation was mostly caused by past management influences, but also by topography and resulting water movement through fields as well as the aggregation of grazing livestock in certain areas of the fields. Soil nutrients accumulate at the soil surface over the time since last ploughing in permanent grasslands.

Mobilization & Transport: Discharge was mostly dependent on antecedent soil moisture conditions and high flows were caused by saturation-excess rather than infiltration-excess overland flow. Sediment and P were mobilized by hydrological flushing from the soil surface, whereas  $\text{TON}_N$  was mobilized by diffusion from soil water. Total C mobilization processes were not clear, but were likely to be a mixture of hydrological flushing of sediment-associated C and diffusion of dissolved C. Total C was lost disproportionately to the soil TC pool, C:N and C:P ratios in the water were an order of magnitude higher than those in the soils, whereas N:P ratios in water were similar to those in the soil. The size of the available soil source pool (soil nutrient content) and the

mobilization potential (water movement through the field, caused by a combination of rainfall and topography) explained the differences in diffuse water pollution concentrations and rates between the fields. The field with the greatest soil nutrient contents had the highest diffuse nutrient losses.

Delivery to Surface Waters: Sediment, TP and TC delivery from permanent grasslands were similar to or exceeded those reported for other grasslands, mixed land-use and arable sites, whereas  $\text{TON}_\text{N}$  losses were less than those reported from arable studies and earlier grassland studies. The relative importance of pollutants varied greatly and changed rapidly through flow conditions and time. In short, the relative importance of SS, TP and TC increased during high flows, whilst the relative importance of  $\text{TON}_\text{N}$  increased during low flows.

Potential Impacts: Permanent grasslands pose a significant threat to water quality. Sediment and P concentrations frequently exceeded EU and UK water quality guidelines. High TC exports are likely to reduce dissolved oxygen in the receiving surface water. Even though  $\text{TON}_\text{N}$  did not exceed the  $\text{NO}_3^-$  guidelines, organic N that was not monitored here may have significant impacts on receiving waters.

Overall, the three sampled fields can be considered to be functioning differently, or areas of individual fields were functioning differently. Long-term management differences (more than 6 years ago) have affected soil properties and altered soil processes, such as nutrient cycling within and between fields. Those differences in soil properties and nutrient cycling processes, in combination with inherent differences between the fields (such as within-field topography) support different nutrient sources and mobilization potentials which subsequently caused the differences in sediment and nutrient delivery to surface waters from the fields.

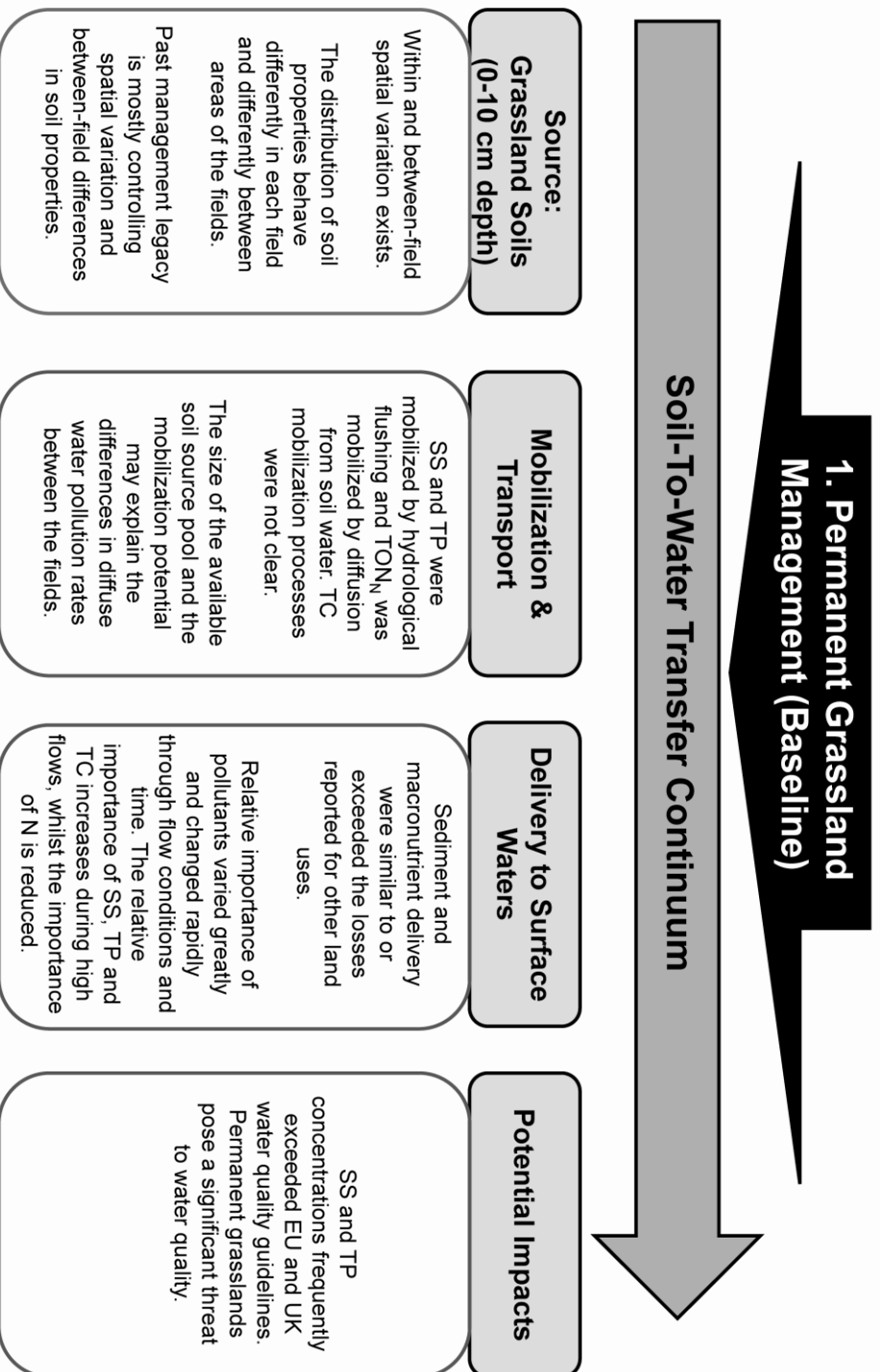


Figure 9.2. Summary of the effects of permanent grassland management on the soil-to-water transfer continuum and its individual components.

## **B. The effects of ploughing and reseeding grasslands on the soil-to-water transfer continuum**

This section summarises the knowledge that was presented in this thesis towards understanding the effects that ploughing and reseeding of grasslands has on each component of the soil-to-water transfer continuum (Figure 8.3). The effects of ploughing and reseeding are discussed as a change from those of the permanent conventional grassland management.

Source: Ploughing and reseeding grassland fields caused significant increases in soil surface bulk density. There may have been an effect of sward age in terms of soil nutrients: all nutrient concentrations were significantly reduced in the older grassland field (no ploughing for 20 years), but not in the younger grassland field (no ploughing for 6 years). Spatial variation between and within fields remained after ploughing and reseeding; a single ploughing operation did not override pre-existing differences between the fields. Between-field differences and spatial variation within the fields are still likely to be caused by different past management practices.

Mobilization & Transport: The processes by which specific diffuse pollutants were mobilized and transported remained the same after ploughing and reseeding. But the availability or vulnerability of soil particles and macronutrients to mobilization, irrespective of soils nutrient contents, increased after ploughing and reseeding. Ploughing and reseeding reduced the TC:TON<sub>N</sub> ratio in receiving surface water, so that they were closer to those in the soil compared to the permanent grassland period, but TON<sub>N</sub>:TP ratios were an order of magnitude greater than those in the soil.

Delivery: Ploughing and reseeding of grasslands exacerbated the already significant diffuse pollution rates from grasslands. The transport and delivery of all diffuse pollutants significantly increased after ploughing. Total oxidized N had the greatest relative increase in concentrations after ploughing. The relative importance of SS and TON<sub>N</sub> increased after ploughing, whilst the relative importance of TC and TP decreased.

Potential impacts: The threats that permanent grasslands pose were exacerbated by ploughing and reseeded. With the significant increase in all pollutant losses, EU / UK water quality guidelines for SS and P were exceeded even more frequently than during the permanent grassland period.  $\text{TON}_\text{N}$  exceeded the nitrate water quality standard in the ploughed fields after ploughing and reseeded.

Despite an additional year of uniform management across the two ploughed and reseeded fields, the fields can still be considered to be functioning differently. Long-term management differences affected soil properties and altered soil processes, so that the fields subsequently responded differently to ploughing and reseeded in terms of soil properties and water quality.



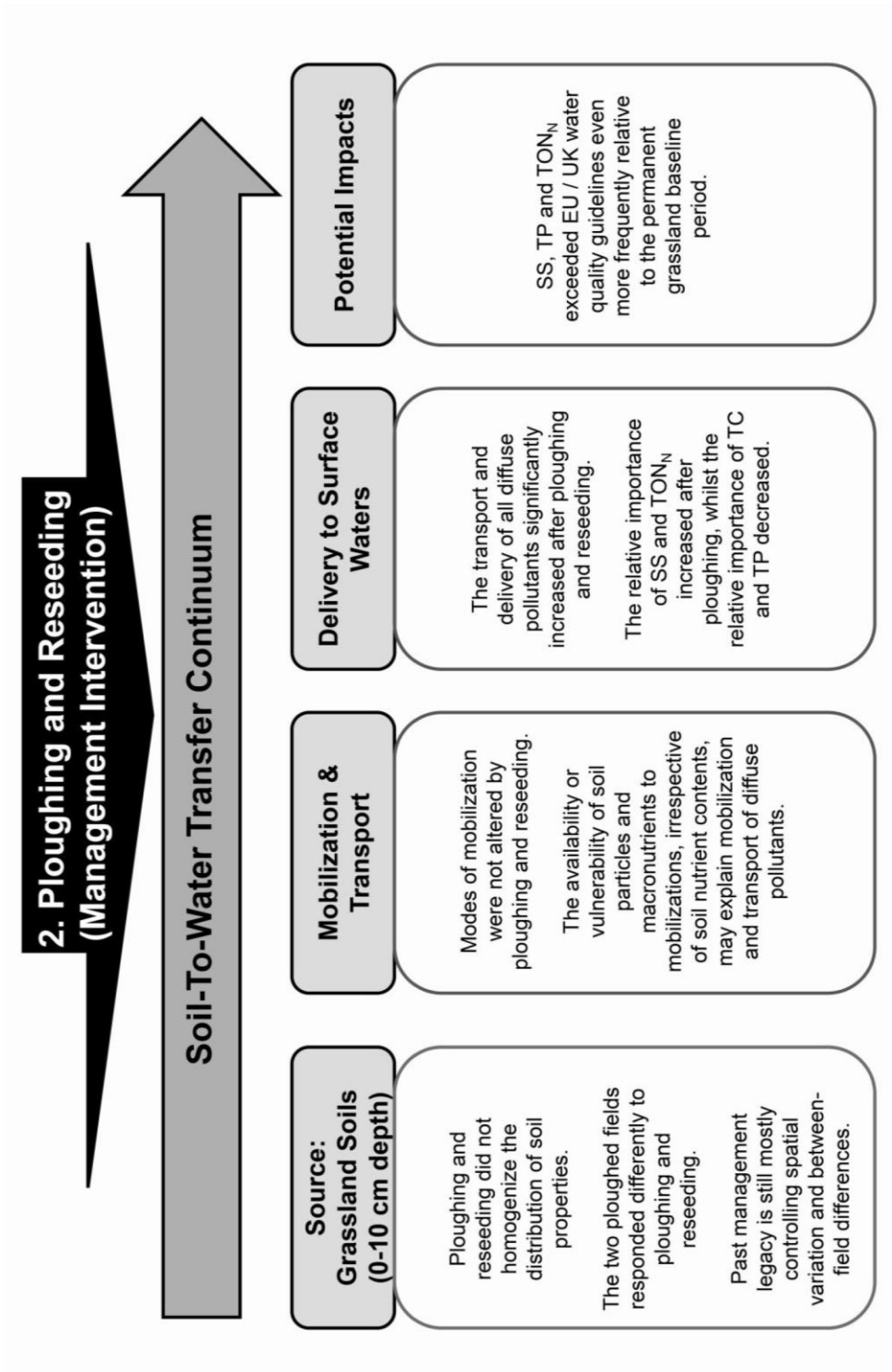


Figure 9.3. Summary of the effects of ploughing and reseeded on the soil-to-water transfer continuum and its individual components. Findings are expressed as changes relative to the permanent grassland effects in figure 9.2.

### **C. Implications of the research findings: for future research, for policy making and farm management advice**

The findings of this thesis have important implications for future research, for policy making as well as for sustainable farm management advice:

- This thesis contributed to the growing evidence that grasslands contribute significantly to agricultural diffuse pollution, both when managed as permanent intensively managed grasslands as well as recently ploughed and reseeded grasslands. Additionally, the rates of diffuse pollution from grasslands were found not to comply with EU / UK water quality regulations. Such sediment and nutrient losses from intensively managed grasslands should be acknowledged in land management guidelines and advice for future compliance with surface water quality standards. Simply advising farmers or encouraging farmers by policies to convert arable land to grassland is not sufficient to reduce diffuse pollution rates. More specific advice is required, such as emphasizing the importance of extensive management, the importance of alleviating over-fertilization and surface accumulation in permanent grasslands and accelerated diffuse pollution rates shortly after ploughing and reseeded. Additionally, caution should be taken in prescribing any “sustainable intensification” measures that include ploughing and reseeded in grasslands, unless the long-term benefits of those measures have been shown to outweigh the short-term diffuse pollution costs after ploughing and reseeded.
- This thesis provided an insight into the relative importance of multiple diffuse pollutants. The relative importance of pollutants varied greatly and changed rapidly through flow conditions and time. In short, the relative importance of SS, TP and TC increased during high flows, whilst the relative importance of  $\text{TON}_\text{N}$  increased during low flows. Additionally ploughing and reseeded caused a shift in relative importance of each pollutant, by consistently increasing the relative importance of N. Additionally, insight into the relative importance of pollutants through flow conditions and time have advanced the understanding of mobilization processes. The shift of relative importance

after management intervention and the frequent changes in the relative importance of pollutants through flow conditions highlights the importance of simultaneously monitoring multiple pollutants at high resolution for a) research purposes and b) regulatory monitoring to classifying water quality status and identifying the reasons of water quality failures. The overarching aim should be to understand the effects of mitigation measures or sustainable intensification measures on multiple pollutants and their relative importance, to avoid shifting from one water quality issue to another. Lower resolution monitoring may miss certain flow conditions and may therefore lead to a wrong classification of surface waters and / or potentially identifying the wrong reasons for non-compliance, subsequently resulting in implementation of inappropriate mitigation measures.

- This thesis presented evidence of existing spatial variation of soil properties within and between fields as well as differences in diffuse pollution rates between fields, despite at least 6 years of uniform management across all fields. Agricultural fields with the same land use and short-term management history (up to 6 years ago) but contrasting long-term management histories cannot be assumed to be similar in terms of mean soil properties or diffuse losses. High-resolution spatial sampling should be conducted in soil surveys to capture spatial variation, reduce uncertainty and to detect the distribution of soil properties and their underlying processes, which would not be detected by studies which only consider central tendencies between fields by taking a few samples per field. Such differences between fields highlight a) the importance of baseline characterization, b) importance of paired experimental design and c) the potential limitations of soil surveys that assume fields of the same land-use to be 'the same'. Site specific management or precision agriculture may be useful tools to homogenize soil properties and potentially gain improved yields and water quality benefits in such grasslands with high soil spatial variation.
- Most results in this thesis have emphasized the influence of past management on soil spatial variation within fields, on differences between fields in terms of soil properties and diffuse pollution losses, and past

management also had an influence on how those fields responded to ploughing and reseeded. Additionally, ploughing did not override spatial variation which is continuing to be caused by past management legacy. Such long-term effects of management still acting on soil properties and subsequently water quality indicates how long it may take to see soil and water quality improvements after implementing mitigation measures. Therefore, long-term management history always has to be included when interpreting soil data, where possible, and baseline characterization is essential prior to assessing the effects of mitigation measures.

## **II. Areas of further research**

Several areas of further research have been recognized, which can be grouped into four main themes: 1) long-term continuation with the monitoring on the Farm Platform that was started in this thesis to assess long-term effects of management, 2) modelling of the water quality data, 3) more detailed monitoring of fractions of nutrients rather than just total nutrients, and 4) combining the soil and water quality data / research with other relevant research / data to gain a more holistic understanding of the sustainability of the grassland management systems.

### **A. Long-term continuation of the monitoring**

This thesis quantified the short-term effects of ploughing and reseeded on soil properties and water quality, but the long-term effects remain to be studied. A long-term continuation of the monitoring that was conducted in this thesis may establish whether ploughing and reseeded causes a long-term acceleration of diffuse pollution or whether multiple pollutant losses are reduced over time as was found for individual nutrients by Sharpley (2003) compared to the losses from permanent grasslands. Additionally, long-term monitoring will quantify whether the different seed mixtures that were sown onto the two ploughed fields

have an effect on soil nutrient contents and nutrient losses, specifically in terms of potentially reduced N losses linked to the legume- ryegrass mixture that was reseeded in field 8. Another important aspect of long-term management will be to explore how long the effects of management legacy last in these fields without the implementation of site-specific management and whether the fields accumulate soil surface nutrients at different rates depending on their management history.

## **B. Modelling the hydrology and water quality dataset**

Second, an important implication of the finding of this thesis was that the significant diffuse pollution losses from grasslands need to be included in policies and management decisions. Modelling of the data would develop a more detailed understanding of the fine-scale (hysteresis) relationships between hydrology and water quality, so that the detailed understanding gained by this dataset can eventually be included in land-use based models a) to provide more accurate estimates of pollutant yields than those that were provided in this thesis by rating curves and the Walling & Web method 5, b) correct the estimation of grassland contribution towards overall pollutant loads in catchments in land-use based models, c) to predict future water quality from grasslands and finally d) to integrate those models into models used for policy decision making, such as the models used to designate NVZ target catchments.

## **C. More detailed monitoring of nutrient fractions**

Third, this thesis quantified total nutrients in soils and in water. However, monitoring individual forms of nutrients in both soil and water may add further to the understanding of the individual soil-to-water components.

Quantifying organic and inorganic fractions as well as particulate and dissolved fractions of nutrients in the discharge water may give further insight into mobilization processes, such as the proportion of TC, TP and TN that is mobilized and transported by erosion processes. Additionally, comparing how

the relative importance of particulate versus dissolved and organic versus inorganic nutrients change throughout flow conditions and time will give even further insight into mobilization processes throughout flow conditions and time. Quantifying total N and its fractions will clarify what proportion of TN was not quantified in this thesis by only analysing for  $\text{TON}_N$  and therefore, total N losses can be calculated as well as macronutrient ratios in soil and water can be better compared. Apart from quantifying the fractions of TC, more insight may be gained by generally monitoring C at higher resolution. This thesis quantified total C in water at lower resolution than the other pollutants; TC samples were taken flow proportionately during storm events, but not at baseflow. Therefore, little inference could be made about C dynamics throughout all flow conditions and TC annual yields were less certain than those estimated for the other pollutants.

The total soil nutrient contents quantified in this thesis do not necessarily represent the fraction of nutrients that are available or vulnerable to mobilization and transport by subsurface or surface flows. Analysing for a range of other soil properties may be more useful as indicators of diffuse pollution available nutrients. For example, quantifying water extractable fractions of nutrients and SOM may better describe the proportion of the total nutrients that are available to mobilization and transport by rainwater (Embacher *et al.*, 2007). Additionally, pH may be an influencing factor determining the mobilization of certain fractions of nutrients (for example P :Turner & Haygarth, 2013).

Results in this thesis suggested that potential yield and water quality benefits may be gained by site-specific management. However, the total nutrients measured do not describe the nutrients that are plant available, at least not under the conventional understanding that mostly inorganic nutrients are available. Therefore, more specific sampling of plant available nutrient fractions may be required to make recommendations about site-specific fertilizer application rates.

#### **D. Towards a holistic understanding and assessment of the sustainability of different grassland management practices**

This thesis took a holistic approach to quantifying the soil-to-water continuum in grasslands as well as considering multiple agricultural diffuse pollutants. However, assessing the sustainability of grassland management practices does not only include soil and water quality related aspects, but a whole range of other ecosystem services. Only a full assessment of productivity and economic impacts as well as environmental impacts of different management practices can lead to a reliable assessment of the sustainability of management practices. Therefore, adding the data and understanding that was gained in this thesis to data that is already being monitored on the Farm Platform will provide a holistic dataset. Already monitored data on the Farm Platform includes productivity monitoring (grass yields, live weight gain, nutritional quality of the grass crop and meat quality), monitoring of green-house gas emissions (CO<sub>2</sub> and N<sub>2</sub>O), monitoring of soil biodiversity. Additionally, economic aspects should be included, because before a 'sustainable management practice' can be advised or encouraged by policies, the costs of implementing such practices and its profits needs to be quantified and / or the amount of compensation that policies may have to provide for implementing such management practices.

The Farm Platform provides an excellent opportunity for further research into precision agriculture or specific site management in grasslands. Once high resolution sampling has provided information on the distribution of yield limiting soil properties, site specific fertilizer applications could be employed followed by quantifying, whether such specific fertilizer applications a) alter the spatial distribution of soil properties (homogenization) and over what time scales, b) improve yields and provide financial benefits, c) provide reductions of diffuse pollution rates. Furthermore, the data gathered by soil sampling can be used to ground truth new remote sensing technologies to further the development of precision agriculture in grasslands, which at the moment is mostly researched and implemented in arable land (Schnellberg *et al.*, 2008).

### **III. Conclusion**

This PhD thesis advanced the understanding of the effects of different grassland management practices on the soil-to-water transfer continuum by using a holistic approach: monitoring soil properties at high spatial resolution and water quality properties at high temporal resolution. The most important finding was that grasslands cannot be considered as a tool to resolve erosion and runoff issues from agricultural land, but that intensively managed grasslands, both permanently managed as well as managed as plough-reseeds, contribute significantly to surface water pollution. Therefore, grasslands have to be carefully managed in terms of soil structure (surface compaction) and soil nutrient management (reducing surface accumulation of nutrients). Additionally, this PhD thesis highlighted the existence of soil spatial variation within fields and differences between fields in terms of soil properties and resulting water quality, despite being subjected to the same management and land use; thereby showing the need for site specific management in grasslands. The relative importance of diffuse pollutants changed with grassland management practice, through time and flow conditions, highlighting the importance of simultaneous monitoring of multiple diffuse pollutants. All findings emphasized the strong influence of past management on the functioning of grassland fields today. The findings of this PhD thesis should be acknowledged in further research, land management guidelines and advice for future compliance with surface water quality standards.



## References

- Acharya, B.S., J. Rasmussen & J. Eriksen. 2012. Grassland carbon sequestration and emissions following cultivation in a mixed crop rotation. *Agriculture, Ecosystems and Environment*, **153**, 33-39.
- ADAS. 2011. *Nitrates Directive Consultation Document. The evidence base for assessing the impacts of the NVZ Action Programme on water quality across England and Wales*. Ltd, A.U., Wolverhampton
- Addiscott, T.M. 1988. Long-term leakage of nitrate from bare unmanured soil. *Soil Use and Management*, **4**, 91-95.
- Amman, C., C. Spirig, J. Leiffield & A. Neftel. 2009. Assessment of the nitrogen and carbon budget of two managed temperate grassland fields. *Agriculture, Ecosystems & Environment*, **133**, 150-162.
- Amundson, R., A.T. Austin, E.A.G. Schnuur, K. Yoo, V. Matzek, C. Kendall, et al. 2003. Global patterns of the isotopic composition of soil and plant nitrogen. *Global Biogeochemical Cycles*, **17**.
- Armstrong, A.C. & E.A. Garwood. 1991. Hydrologic consequences of artificial drainage of grasslands. *Hydrological Processes*, **5**, 157-174.
- 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. A soil classification for England and Wales. *Soil Survey Technical Monograph No 14*, Harpenden.
- Bailey, A., J. Quinton, M. Silgram, C. Stevens & B. Jackson. 2007. Determining the cost effectiveness of solutions to diffuse pollution: the case of in-field mitigation options for phosphorus and sediment loss. *International Farm Management Association Congress*, 657-664.
- Baker, J.M., T.E. Ochsner, R.T. Venterea & T.J. Griffis. 2007. Tillage and soil carbon sequestration- What do we really know. *Agriculture, Ecosystems and Environment*, **118**, 1-5.

Balesdent, J., A. Mariotti & B. Guillet. 1987. Natural  $^{13}\text{C}$  abundance as a tracer for studies of soil organic matter dynamics. *Soil Biology and Biochemistry*, **19**, 25-30.

Balmford, A. & W. Bond. 2005. Trends in the state of nature and their implications for human well-being. *Ecological Letters* **8**, 1218-1234.

Beniston, J.W., S.T. DuPont, J.D. Glover, R. Lal & J.A.J. Dungait. 2014. Soil organic carbon dynamics 75 years after land-use change in perennial grassland and annual wheat agricultural systems. *Biogeochemistry*, **120**, 37-49.

Beniston, J.W., M.J. Shipitalo, R. Lal, E.A. Dayton, D.W. Hopkins, F. Jones, A. Joynes, J.A.J. Dungait. 2014. Carbon and macronutrient losses during accelerated erosion under different tillage and residue management. *European Journal of Soil Science*, **66**, 218-225.

Bennett, E.M. & P. Balvanera. 2007. The future of production systems in a globalized world. *Frontiers in Ecology and the Environment*, **5**, 191-198.

BfN. 2009. *Kurzfassung der Agrarumwelt- und Naturschutzprogramme. Skripten* 253. Bundesamt für Naturschutz,

Bernoux, M., C.C. Cerri, C. Neill & J.F.L. de Moraes. 1998. The use of stable isotopes for estimating soil organic matter turnover rates. *Geoderma*, **82**, 43-58.

Bhogal, A., D.V. Murphy, S. Fortune, M.A. Shepherd, D.J. Hatch, S.C. Jarvis, *et al.* 2000. Distribution of nitrogen pools in the soil profile of undisturbed and reseeded grasslands. *Biology and Fertility of Soils*, **30**, 356-362.

Bilotta, G.S., R.E. Brazier & P.M. Haygarth. 2007a. The impacts 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., R.E. Brazier & P.M. Haygarth. 2007b. Processes affecting transfer of sediment and colloids, with associated phosphorus from intensively farmed grasslands: erosion. *Hydrological Processes*, **21**, 135-139.

Bilotta, G.S., R.E. Brazier, P.M. Haygarth, C.J.A. Macleod, P. Butler, S. Granger, *et al.* 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. & R.E. Brazier. 2008. Understanding the influence of suspended solids on water quality and aquatic biota. *Water Research*, **42**, 2849-2861.

Bilotta, G.S., T. Krueger, R.E. Brazier, P. Butler, J. Freer, J.M.B. Hawkins, *et al.* 2010. Assessing catchment-scale erosion and yields of suspended solids from improved temperate grassland. *Journal of Environmental Monitoring*, **12**, 731-739.

Bilotta, G.S., N.G. Burnside, L. Cheek, M.J. Dunbar, M.K. Grove, C. Harrison, *et al.* 2012. Developing environment-specific water quality guidelines for suspended particulate matter. *Water Research*, **46**, 2324-2332.

Bishop, P.L., W.D. Hively, J.R. Stedinger, M.R. Rafferty, J.L. Lojpersberger & J.A. Bloomfield. 2005. Multivariate analysis of paired watershed data to evaluate agricultural best management practice effects on stream water phosphorus. *Journal of Environmental Quality*, **34**, 1087-1101.

Biswas, A., B.C. Si & F.L. Walley. 2008. Spatial relationship between 15N and elevation in agricultural landscapes. *Nonlinear Processes in Geophysics*, **15**, 397-407.

Blackstock, K.L., J. Ingram, R. Burton, K.M. Brown & B. Slee. 2010. Understanding and influencing behaviour change by farmers to improve water quality. *Science of the Total Environment*, **23**, 5631-5618.

Blake, L., S. MErcik, M. Koerschens, S. Moskal, P.R. Poulton, K.W.T. Goulding, *et al.* 2000. Phosphorus content in soil, uptake by plants and balance in three European long-term field experiments. *Nutrient Cycling in Agroecosystems*, **56**, 263-275.

BMEL. Bundesministerium für Ernährung und Landwirtschaft. 2014. <http://www.bmel.de/DE/Landwirtschaft/Foerderung-Agrarsozialpolitik/Texte/Cross-Compliance.html>. "accessed" 13/10/2014.

Blume, H.P., G.H. Bruemmer, R. Horn, E. Kandeler, R. Koegel-Knabner, R. Kretschmar, *et al.* 2010. *Lehrbuch der Bodenkunde*. Spektrum Akademischer Verlag, Heidelberg, D.

Boardman, J. & R. Evans. 1994. *Conserving soil resources: European perspectives*. CABI, Wallingford, UK.

Boerner, R.E.J., A.J. Scherzer & J.A. Brinkman. 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.

Bogaert, N., J. Salomez, A. Vermoesen, G. Hofman, O. Van Cleemput & M. Van Mairvenne. 2000. Within-field variability of mineral nitrogen in grassland. *Biological Fertility of Soil*, **32**, 186-193.

Bol, R., J. Eriksen, P. Smith, M.H. Barnett, K. Coleman & B.T. Christensen. 2005. The natural abundance of  $^{13}\text{C}$ ,  $^{15}\text{N}$ ,  $^{34}\text{S}$  and  $^{14}\text{C}$  in archived (1923-2000) plant and soil samples from the Askov long-term experiments on animal manure and mineral fertilizer. *Rapid Communication in Mass Spectrometry*, **58**, 3216-3226.

Bol, R., N.J. Ostle, K.J. Petzke, C. Chenu & J. Balesdant. 2008. Amino acid  $^{15}\text{N}$  in long-term bare fallow soils: influence of annual N fertilizer and manure applications. *European Journal of Soil Science*, **4**, 617-619.

Boorman, D.B., J.M. Hollis & A. Lilly. 1995. *Hydrology of soil types: A hydrologically based classification of the soils of the United Kingdom*. Institute of Hydrology Natural Environmental Research Council.

Bowes, M.J., W.A. House, R.A. Hodgkinson & D.V. Leach. 2005. Phosphorus-discharge hysteresis during storm events along a river catchment: the River Swale, UK. *Water Research*, **39**, 751-762.

Boutton, T.W., S.R. Archer, A. Midwood, S.F. Zitzer & R. Bol. 1998.  $^{13}\text{C}$  values of soil organic carbon and their use in documenting vegetation change in a subtropical savanna ecosystem. *Geoderma*, **82**, 5-41.

Brauman, K.A., G.C. Daily, T. Duarte, Ka'leo & H. Mooney, A.,. 2007. The nature and value of ecosystem services: An overview highlighting hydrological services. *Annual Review of Environment and Resources*, **32**, 67-98.

Brazier, R.E., G.S. Bilotta & P.M. Haygarth. 2007. A perspective on the role of lowland, agricultural grasslands in contributing to erosion and water quality problems in the UK. *Earth surfaces, processes and landforms*, **32**, 964-967.

Breuer, L., J.A. Huisman, T. Keller & H.-G. Frede. 2006. Impact of a conversion from cropland to grassland on C and N storage and related soil properties: Analysis of a 60-year chronosequence. *Geoderma*, **133**, 6-18.

Bruck, H., C. Jureit, M. Hermann, A. Schulz & B. Sattelmacher. 2001. Effects of water and nitrogen supply on water use efficiency and carbon isotope discrimination in edible canna (*Canna edulis* Ker-Gawler). *Plant Biology*, **3**, 326-334.

Brown, L.E., G. Mitchell, J. Holden, a. Folkard, N. Wright, N. Beharry-Borg, *et al.* 2010. Priority water research questions as determined by UK practitioners and policy making. *Science of the Total Environment*, **409**, 256-266.

Buckley, C. & P. Carney. 2013. The potential to reduce the risk of diffuse pollution from agriculture while improving economic performance at farm level. *Environmental Science & Policy*, **24**, 101-109.

Buczko, U. & R.O. Kuchenbuch. 2010. Environmental indicators to assess the risk of diffuse nitrogen losses from agriculture. *Environmental Management*, **45**, 1201-1222.

Burt, T.P., N.J.K. Howden, F. Worrall & M.J. Whelan. 2008. Importance of long-term monitoring for detecting environmental change: lessons from a lowland river in south east England. *Biogeosciences Discussions*, **5**, 2369-2379.

Burt, T.P., N.J.K. Howden, F. Worrall, M.J. Whelan & M. Bieroza. 2011. Nitrate in United Kingdom rivers: policy and its outcomes since 1970. *Environmental Science and Technology*, **45**, 175-181.

Burt, T.P., N.J.K. Howden & F. Worall. 2014. On the importance of very long-term water quality records. *Wiley Interdisciplinary Reviews: Water*, **1**, 41-48.

Butler, P.J. & P.M. Haygarth. 2007. Effects of tillage and reseeding on phosphorus transfers from grassland. *Soil Use and Management*, **23**, 71-81.

Cambardella, C.A. & D.L. Karlen. 1999. Spatial analysis of soil fertility parameters. *Precision Agriculture*, **1**, 5-14.

Cardenas, L.M., S.P. Cuttle, B. Crabtree, A. Hopkins, A. Shepherd, D. Scholefield, *et al.* 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.

Carpenter, S.R., H.A. Mooney, J. Agard, D. Capistrano, R.S. DeFries, S. Diaz, *et al.* 2009. Science for managing ecosystem services: Beyond the millennium ecosystem assessment. *Proceedings of the National Academy of Sciences of the United States*, **106**, 1305-1312.

Carstensen, J., D.J. Conley, J.H. Andersen & G. Aertebjerg. 2006. Coastal eutrophication and trend reversal: A Danish study. *Limnology Oceanography*, **51**, 398-408.

Cassidy, R. & P. Jordan. 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.

Chadwick, D.R., John, F., Pain, B.F., Chambers, B.J., Williams, J. 2000. Plant uptake of nitrogen from the organic nitrogen fraction of animal manures: a laboratory experiment. *The Journal of Agricultural Science*, **134**, 159-168.

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.

Chiba, M., S. Vieira, R., A. Gonzalez, S.C.F. Dechen & I.C. De Maria. 2010. Alterations and spatial variability of soil fertility in successive years under no tillage systems. *Bragantia, Campinas*, **69 Suplemento**, 29-38.

Choi, W.J., H.M. Ro & E.A. Hobbie. 2003a. Patterns of natural <sup>15</sup>N in soils and plants from chemically and organically fertilized uplands. *Soil Biology and Biochemistry*, **35**, 1493-1500.

Choi, W.J., H.M. Ro & S.M. Lee. 2003b. Natural <sup>15</sup>N abundances of inorganic nitrogen in soil treated with fertilizer and compost under changing soil moisture regimes. *Soil Biology and Biochemistry*, **35**, 1289-1298.

Clegg, C.D. 2006. Impact of cattle grazing and inorganic fertiliser additions to managed grasslands on the microbial community composition of soils. *Applied Soil Ecology*, **31**, 73-82.

Collins, A.L., P.S. Naden, D.A. Sear, J.I. Jones, I.D.L. Foster & K. Morrow. 2011. Sediment targets for informing river catchment management: international experience and prospects. *Hydrological Processes*, **25**, 2112-2129.

Conley, D.J., H.W. Pearl, R.W. Howarth, D.F. Boesch, S.P. Seitzinger, K.E. Havens, *et al.* 2009. Controlling eutrophication: Nitrogen and Phosphorus. *Science*, **323**, 1014-1015.

Constanza, R., R. d'Arge, R. de Groot, S. Farber, M. Grasso, B. Hannon, *et al.* 1997. The value of the world's ecosystem services and natural capital. *Nature*, **387**, 253-260.

Constanza, R., R. de Groot, P. Sutton, S. van der Ploeg, S.J. Anderson, I. Kubiszewski, *et al.* 2014. Changes in the global value of ecosystem services. *Global Environmental Change*, **26**, 152-158.

Cordell, D., J.-O. Drangert & W. S. 2009. The story of phosphorus: Global food security and food for thought. *Global Environmental Change*, **19**, 292-305.

Cournane, F., MdCowell, R., Littlejohn, R., Condon, L. 2011. Effects of cattle, sheep and deer grazing on soil physical quality and losses of phosphorus and suspended sediment losses in surface runoff. *Agriculture, Ecosystems and Environment*.

Creamer, R.E., F. Brennan, O. Fenton, M.G. Healy, S.T.J. Lalor & G.J. Lanigan. 2010. Implications of the proposed Soil Framework Directive on agricultural systems in Atlantic Europe- a review. *Soil Use and Management*, **26**, 198-211.

DAFM. Department of Agriculture, Food and the Marine, Ireland. 2014a. <http://www.agriculture.gov.ie/farmerschemespayments/crosscompliance/>. "accessed" 13/10/2014.

DAFM. Department of Agriculture, Food and the Marine, Ireland. 2014b. [www.agriculture.gov.ie/farmerschemespayments/](http://www.agriculture.gov.ie/farmerschemespayments/) <<http://www.agriculture.gov.ie/farmerschemespayments/>>. "accessed" 10/10/2014.

Daily, G.C., S. Alexander, P.R. Ehrlich, L. Goulder, J. Lubchenco, P.A. Matson, *et al.* 1997. Ecosystem services: benefits supplied to human societies by natural ecosystems. *Issues in Ecology*, **2**, 1-18.

Dalzell, B.J., T.R. Filley & J.M. Harbor. 2007. The role of hydrology in annual organic carbon loads and terrestrial organic matter exports from a midwestern agricultural watershed. *Geochemica et Cosmochemica Acta*, **71**, 1448-1462.

Darch, T., M.S.A. Blackwell, J.M.B. Hawkins, P.M. Haygarth & D. Chadwick. 2013. A meta-analysis of organic and inorganic phosphorus in organic fertilisers, soils and water: implications for water quality. *Critical Reviews in Environmental Science and Technology*, **44**, 2172-2202.

Davies, B.E. 1974. Loss-on-ignition as an estimate of soil organic matter. *Soil Science Society of America Proceedings*, **38**, 150-151.

Deasy, C., J.N. Quinton, M. Silgram, A.P. Bailey, B. Jackson & C.J. Stevens. 2009. Mitigation options for sediment and phosphorus loss from winter-sown arable crops. *Journal of Environmental Quality*, **38**, 2121-2130.

DeBeats, S., Poesen, J., Gysels, G., Knapen, A. 2006. Effects of grass roots on the erodibility of topsoils during concentrated flow. *Geomorphology*, **76**, 54-67.

DEFRA. 2005a. *Entry Level Stewardship Handbook*. DEFRA, Department for Environment Food & Rural Affairs, London.

DEFRA. 2006. *Cross compliance guidance for soil management*. DEFRA, Department for Environment Food & Rural Affairs, London.

DEFRA. 2007a. *Cross compliance summary of key points*. DEFRA, Department for Environment Food & Rural Affairs, London.

DEFRA. 2007b. *Guide to cross compliance in England- Version 1*. DEFRA, Department for Environment Food & Rural Affairs, London.

DEFRA. 2007c. *Single Payment Scheme- management of habitats and landscape features: guidance for cross compliance in England*. DEFRA, Department for Environment Food & Rural Affairs, London.

DEFRA. 2008. *The nitrate pollution prevention regulation 2008- guidance for farmers in the NVZ*. DEFRA, Department for Environment, Food and Rural Affairs, London.



DEFRA. 2009. *Protecting our water, soil and air: a Code of Good Agricultural Practice for farmers, growers and land managers*. The Stationary Office, Norwich, UK.

DEFRA. 2010. *RB209 Defra: Fertilizer Manual, 8th edition*. DEFRA, The Stationary Office, Norwich, UK.

DEFRA. Department for Environment Food and Rural Affairs. 2013. Nitrate Vulnerable Zones for England and Wales.

<http://adlib.everysite.co.uk/adlib/defra/content.aspx?doc=95402&id=98406>

"accessed" 10/10/2014.

DEFRA. Department for Environment Food and Rural Affairs. 2014. The new common agricultural policy schemes in England: August 2014 update.

<https://www.gov.uk/government/publications/cap-reform-august-2014-update-including-greening-how-it-works>. "accessed" 01/10/2014.

deGroot, R.S., R. Alkemade, L. Braat, L. Hein & L. Willemsen. 2010. Challenges in integrating the concept of ecosystem services and values in landscape planning, management and decision making. *Ecological Complexity*, **7**, 260-272.

Delcourt, H., P.L. Darius & J. De Baerdemaeker. 1996. The spatial variability of some aspects of topsoil fertility in two Belgian fields. *Computers and Electronics in Agriculture*, **14**, 179-196.

Dick, J., C. Andrews, D.A. Beaumont, S. Benham, D.R. Brooks, S. Corbett, *et al.* 2011a. A comparison of ecosystem services delivered by 11 long-term monitoring sites in the UK environmental change network. *Environmetrics*, **22**, 639-648.

Dick, J.M., R.I. Smith & R.M. Scott. 2011b. Ecosystem service and associated concepts. *Environmetrics*, **22**, 598- 607.

Dixon, E.R., M.S.A. Blackwell, M.S. Dhanoa, Z. Berryman, N. de la Fuente Martinez, D. Junquera, *et al.* 2010. Measurement at the field scale of soil  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  under improved grassland. *Rapid Communications in Mass Spectrometry*, **24**, 511- 518.

Djodjic, F., K. Boerling & L. Bergstroem. 2004. Phosphorus leaching in relation to soil type and soil phosphorus content. *Journal of Environmental Quality*, **33**, 678-684.

Don, A. & E.D. Schulze. 2008. Controls on fluxes and export of dissolved organic carbon in grasslands with contrasting soil types. *Biogeochemistry*, **91**, 117-131.

Doody, D.G., R.H. Foy & C.D. Barry. 2012. Accounting for the role of uncertainty in declining water quality in an extensively farmed grassland catchment. *Environmental Science and Policy*, **24**, 15-23.

Dungait, J.A.J., L.M. Cardenas, M.S. Blackwell, L. Wu, P.J.A. Withers, D.R. Chadwick, *et al.* 2012. Advances in the understanding of nutrient dynamics and management in UK agriculture. *Science of the Total Environment*, **434**, 39-50.

Dunkerley, D. 2008. Rain even properties in nature and in rainfall simulation experiments: a comparative review with recommendations for increasingly systematic study and reporting. *Hydrological Processes*, **22**, 4415-4435.

EA. 2009. *River Basin Management Plan, South West River Basin District. Annex A: Current state of our waters.*

EC. European Commission. 2012. Map of surface water bodies affected by pollution pressures associated with agriculture. [http://ec.europa.eu/environment/water/water-framework/facts\\_figures/pdf/Agricultural\\_pressures2012.pdf](http://ec.europa.eu/environment/water/water-framework/facts_figures/pdf/Agricultural_pressures2012.pdf). "accessed" 10/10/2014

EC. European Commission. 2012b. Water Framework Directive implementation reports by member state. [http://ec.europa.eu/environment/water/water-framework/impl\\_reports.htm](http://ec.europa.eu/environment/water/water-framework/impl_reports.htm). "accessed" 13/10/2014.

EC. European Commission. 2014a. Withdrawal of the proposal for a Soil Framework Directive. [http://ec.europa.eu/environment/soil/process\\_en.htm](http://ec.europa.eu/environment/soil/process_en.htm). "accessed" 28/8/2014

EC. European Commission Joint Research Centre. 2014b. EC Nitrate Vulnerable Zones Interactive Map. <http://fate-gis.jrc.ec.europa.eu/geohub/MapView.aspx?id=2>. "accessed" 10/10/2014

Edmaedes, D.C. 2003. The long-term effects of manures and fertilisers on soil productivity and quality: a review. *Nutrient Cycling in Agroecosystems*, **66**, 165-180.

Edwards, A.C., D. Kay, A.T. McDonald, C. Francis, J. Watkins, J.R. Wilkinson, *et al.* 2008. Farmyards, an overlooked source for highly contaminated runoff. *Journal of Environmental Management*, **87**, 551-559.

EEA. 2012. European waters- assessment of status and pressures. European Environment Agency, Copenhagen, DK.

Eghball, B., Gilley, J.E., Baltensprenger, D.D., Blumenthal, J.M. 2002. Long-term manure and fertilizer application effects on phosphorus and nitrogen runoff. *Transactions of the American Society of Agricultural Engineers*, **45**, 687-694.

Elser, J.J. & J. Urabe. 1999. The stoichiometry of consumer-driven nutrient recycling: Theory, observations, and consequences. *Ecology*, **80**, 735-751.

Elser, J.J., R.W. Sterner, E. Gorokhova, W.F. Fagan, T.A. Markow, J.B. Cotner, *et al.* 2000. Biological stoichiometry from genes to ecosystems. *Ecology Letters*, **3**, 540-550.

Elser, J.J., M.E.S. Bracken, E.E. Cleland, D.S. Gruner, W.S. Harpole, H. Hillebrand, *et al.* 2007. Global Analysis of nitrogen and phosphorus limitation on primary producers in freshwater, marine and terrestrial ecosystems. *Ecology Letters*, **10**, 1-8.

Embacher, A., A. Zsolnay, A. Gattinger & J.C. Munch. 2007. The dynamics of water extractable organic matter (WEOM) in common arable topsoils: 1. Quantity, quality and function over a three year period. *Geoderma*, **139**, 11-22

Natural England. 2008. Higher Level Stewardship Handbook. NE 108.

Natural England. 2014. Catchment Sensitive Farming  
<http://www.naturalengland.org.uk/ourwork/farming/csf/>. "accessed" 13/10/2014.

EPA. Environmental Protection Agency. 2014. <http://www2.epa.gov/laws-regulations/summary-clean-water-act>. "accessed" 13/10/2014.

Eriksen, J. 2001. Nitrate leaching and growth of cereal crops following cultivation of contrasting temporary grasslands. *Journal of Agricultural Sciences*, **136**, 271-281.

Eriksen, J., F.P. Vinther & K. Soegaard. 2004. Nitrate leaching and N<sub>2</sub>-fixation in grasslands of different composition, age and management. *Journal of Agricultural Science*, **142**, 141-151.

Eriksen, J., L. Pedersen & J.R. Jorgensen. 2006. Nitrate leaching and bread-making quality of spring wheat following cultivation of different grasslands. *Agriculture, Ecosystems and Environment*, **116**, 165-175.

Erikson, J.M. & F.P. Vinther. 2002. Nitrate leaching in grazed grasslands of different composition and age. In: *Multi-function grasslands- quality forage, animal products and landscapes*, pp. 682-683. European Grasslands Federation, Zurich, Ch.

Evans, C.D., D.T. Monteith & D.M. Cooper. 2005. Long-term increases in surface water dissolved organic carbon: Observations, possible causes and environmental impacts. *Environmental Pollution*, **137**.

Evans, R. 2005. Monitoring water erosion in lowland England and Wales: A personal view of its history and outcomes. *Catena*, **64**, 142-161.

Evans-White, M.A., B.E. Haggard & J.T. Scott. 2013. A review of stream nutrient criteria development in the United States. *Journal of Environmental Quality*, **42**, 1002-1014.

Foley, J.A., R. Defries, G.P. Asner, C. Barford, G. Bonan, S.R. Carpenter, *et al.* 2005. Global consequences of land use. *Science*, **309**, 570-574.

Foley, J.A., N. Ramankutty, K.A. Brauman, E.S. Cassidy, J.S. Gerber, M. Johnston, *et al.* 2011. Solutions for a cultivated planet. *Nature*, **478**, 337-342.

Foresight. 2011. *The Future of Food and Farming: Challenges and choices for global sustainability. Final Project Report.* . The Government Office for Science,, London

Foth, H.D. & L.M. Turk. 1972. *Fundamentals in Soil Science*. John Wiley, New York, USA.

Franzluebbers, A.J. 2002. Water infiltration and soil structure related to organic matter and its stratification with depth. *Soil & Tillage Research*, **66**, 197-205.

Freibauer, A., D.A. Rounsevell, P. Smith & J. Verhagen. 2004. Carbon sequestration in the agricultural soils of Europe. *Geoderma*, **122**, 1-23.

Frier, N. & J.P. Schimel. 2002. Effects of drying-rewetting frequency on soil carbon and nitrogen transformations. *Soil Biology & Biochemistry*, **34**, 777-787.

Fu, W., H. Tunney & C. Zhang. 2010. Spatial variation of soil nutrients in a dairy farm and its implications for site-specific fertilizer applications. *Soil and Tillage Research*, **106**, 185-193.

Fullen, M.A., C.A. Booth & R.T. Brandsma. 2006. Long-term effects of grass ley set-aside on erosion rates and soil organic matter on sandy soils in east Shropshire, UK. *Soil and Tillage Research*, **89**, 122-128.

Gächter, R., S.M. Steingruber, M. Reinhardt & B. Wehrli. 2004. Nutrient transfers from soil to surface waters: differences between nitrate and phosphate. *Aquatic Sciences*, **66**, 117-122.

Garcia, A.M., T.L. Veith, P.J.A. Kleiman, C.A. Rotz & L.S. Saporito. 2008. Assessing manure management strategies through small-plot research and whole-farm modelling. *Journal of Soil and Water Conservation*, **63**, 204-211

Gerzebeck, M.H., G. Haberhauer & H.J. Kirchmann. 2001. Nitrogen distribution and <sup>15</sup>N natural abundances in particle size fractions of a long-term agricultural field experiment. *Soil Science*, **164**, 475-481.

Glendell, M. & R.E. Brazier. 2014. Accelerated export of sediment and carbon from a landscape under intensive agriculture. *Science of the Total Environment*, **476-477**, 643-656.

Glendell, M., S.J. Granger, R. Bol & R.E. Brazier. 2014. Quantifying the spatial variability of soil physical and chemical properties in relation to mitigation of diffuse water pollution. *Geoderma*, **214**, 25-41.

Golchin, A., J.M. Oades, J.O. Skjemstad & P. Clarke. 1995. Structural and dynamic properties of soil organic matters as reflected by  $^{13}\text{C}$  natural abundances, pyrolysis mass spectrometry and solid-state  $^{13}\text{C}$  NMR spectroscopy in density fractions of an oxisol forest and pasture. *Australian Journal of Soil Research*, **33**, 59-76.

Govers, G., Vandaele, K., Desmet, P., Poesen, J., Bunte, K. 1994. The role of tillage in soil redistribution on hillslopes. *European Journal of Soil Science*, **45**, 469-478.

Goovaerts, P. 1998. Geostatistical tools for characterizing the spatial variability of microbiological and physio-chemical soil properties. *Biology and Fertility of Soils*, **27**, 315-334.

Goovaerts, P. 1999. Geostatistics in soil science: state-of-the-art and perspectives. *Geoderma*, **89**, 1-45.

Gordon, L.J., C.M. Finlayson & M. Falkenmark. 2010. Managing water in agriculture for food production and other ecosystem services. *Agricultural Water Management*, **97**, 512-519.

Goulding, K.W.T., P.R. Poulton, E.P. Webster & M.T. Howe. 2000. Nitrate leaching from the Broadbalk Wheat Experiment, Rothamsted, UK, as influenced by fertilizer and manure inputs and the weather. *Soil Use and Management*, **16**, 244-250.

Graeber, D., J. Gelbrecht, M.T. Pusch, C. Anlanger & D. Von Schiller. 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.

Grandy, A.S. & G.P. Robertson. 2006. Aggregation and Organic Matter Protection Following Tillage of a Previously Uncultivated Soil. *Journal of the Soil Science Society of America*, **70**, 1398-1406.

Granger, S.J., J.M.B. Hawkins, R. Bol, Whitem S.M., P. Naden, G. Old, *et al.* 2010. High temporal resolution monitoring of multiple pollutant responses in drainage from an intensively managed grassland catchment caused by a summer storm. *Water, Air and Soil Pollution*, **205**, 377-393.

Green, M.B., J.L. Nieber, G. Johnson, J. Magner & B. Schaefer. 2007. Flow path influence on an N:P ratio in two headwater streams: A paired watershed study. *Journal of Geophysical Research*, **112**, 1-11.

Griffith, B., J.M.B. Hawkins, R.J. Orr, M.S.A. Blackwell & P.J. Murray. 2013. The North Wyke Farm Platform: Methodologies used in remote sensing of the water quantity and quality of drainage water. In: *International Grassland Congress 15-19 September, 2013*, pp. 1453-1455. New South Wales Department of Primary Industry, Sydney, Australia.

Gyssels, G., Poesen, J., Buchet, E., Li, Y. 2003. The importance of plant root characteristics in controlling concentrated flow erosion rates. *Earth Surface Processes and Landforms*, **28**, 371-384.

Gyssels, G., Poesen, J., Buchet, E., Li, Y. 2005. Impact of plant roots on the resistance of soils to erosion by water: a review. *Progress in Physical Geography*, **29**, 189-217.

Hamilton, S.K. 2012. Biogeochemical time lags may delay responses of streams to ecological restoration. *Freshwater Biology*, **57**, 43-57.

Hancock, G.R., T. Wells, C. Martinez & C. Dever. 2015. Soil erosion and tolerable soil loss: Insights into erosion rates for a well-managed grassland catchment. *Geoderma*, **237-238**, 256-265.

Hansen, J.P., J. Eriksen & L.S. Jensen. 2005. Residual nitrogen effect of a dairy crop rotation as influenced by grass-clover ley management, manure type and age. *Soil Use and Management*, **21**, 278-286.

Harpole, W.S., J.T. Ngai, E.E. Cleland, E.W. Seabloom, E.T. Borer, M.E.S. Bracken, *et al.* 2011. Nutrient co-limitation of primary producer communities. *Ecology Letters*, **14**, 852-862.

Harris, G.L. & A.L. Heathwaite. 2012. Why is achieving good ecological status in rivers so difficult? *Freshwater Biology*, **57**, 91-2017.

Harrod, T.R. & D.V. Hogan. 2008. The soils of North Wyke and Rowden. <http://www.northwyke.bbsrc.ac.uk/pages/soilsofnw.html>, Accessed: 08/2014.

Hart, M.R., B.F. Quin & M.L. Long Nguyen. 2004. Phosphorus runoff from agricultural land and direct fertilizer effects: a review. *Journal of Environmental Quality*, **33**, 1954-1972.

Hawkins, J.M.B. & D. Scholefield. 1996. Molybdate-reactive phosphorus losses in surface and drainage waters from permanent grassland. *Journal of Environmental Quality*, **25**, 727-732.

Haygarth, P.M., P.J. Chapman, S.C. Jarvis & R.V. Smith. 1998. Phosphorus budgets for two contrasting grassland farming. *Soil Use and Management*, **14**, 160-167.

Haygarth, P.M., L.M. Condon, A.L. Heathwaite, B.L. Turner & G.P. Harris. 2005. The phosphorus transfer continuum: linking source to impact with an interdisciplinary and multi-scale approach. *Science of the Total Environment*, **344**, 5-14.

Haygarth, P.M., L. Hepworth & S.C. Jarvis. 1998. Forms of phosphorus transfer in hydrological pathways from soil under grazed grassland. *European Journal of Soil Science*, **49**, 54-72.

Haygarth, P.M., F.L. Wood, A.L. Heathwaite & P.J. Butler. 2005a. Phosphorus dynamics observed through increasing scales in a nested headwater-to-river channel study. *Science of the Total Environment*, **344**, 83-106.

Haygarth, P.M. & K. Ritz. 2009. The future of soils and land use in the UK: Soil systems for the provision of land-based ecosystem services. *Land Use Policy*, **26S**, S187-S197.

Haygarth, P.M., H.P. Jarvie, S.M. Powers, A.N. Sharpley, J.J. Elser, J. Shen, *et al.* 2014. Sustainable phosphorus management and the need for a long-term perspective: the legacy hypothesis. *Environmental Science and Technology*, **48**, 8417-8419.

Haynes, R.J. & R. Naidu. 1998. Influence of lime, fertilizer and manure applications on soil organic matter content and soil physical conditions: a review. *Nutrient Cycling in Agroecosystems*, **51**, 123-137.



Heathwaite, A.L., Dils, R.M., Carvalho, L., Brazier, R.E., Pope, L., Hughes, M., Phillips, G., May, L. 2005. A tiered risk-based approach for predicting diffuse and point source phosphorus losses in agricultural areas. *Science and the Total Environment*, **344**, 225-239.

Heckrath, G., P.C. Brookes, P.R. Poulton & K.W.T. Goulding. 1995. Phosphorus leaching from soils containing different phosphorus concentrations in the Broadbalk experiment. *Journal of Environmental Quality*, **24**, 904-910.

Heitkamp, F., J. Paupp & B. Ludwig. 2009. Impact of fertiliser type and rate on carbon and nitrogen pools in a sandy Cambisol. *Plant and Soil*, **319**, 259-275.

Hering, D., A. Borja, J. Carstensen, L. Carvalho, M. Elliott, C.K. Feld, *et al.* 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.

Hodkinson, R.A. & P.J.A. Withers. 2007. Sourcing, transport and control of phosphorus loss in two English headwater catchments. *Soil Use and Management*, **23**, 92-103.

Hogberg, P. 1997. <sup>15</sup>N natural abundance in soil-plant systems. *New Phytologist*, **137**, 179-203.

Hope, D., M.F. Billett & M.S. Cresser. 1997a. Exports of organic carbon in two river systems in NE Scotland. *Journal of Hydrology*, **193**, 61-82.

Hope, D., M.F. Billett, R. Milne & T.A.W. Brown. 1997b. Exports of organic carbon in British rivers. *Hydrological Processes*, **11**, 325-344.

Hopkins, D.W., I.S. Waite, J.W. McNicol, P.R. Poulton, A.J. Macdonald & A.G. O'Donnell. 2009. Soil organic carbon contents in long-term experimental grassland plots in the UK (Palace Leas and Parl Grass) have not changed consistently in recent decades. *Global Change Biology*, **15**, 1739-1754.

Horrocks, C.A., J.A.J. Dungait, L.M. Cardenas & K.V. Heal. 2014. Does extensification lead to enhanced provision of ecosystem services from soils in UK agriculture? *Land Use Policy*, **38**, 123-128.

House, W.A. & M.S. Warwick. 1998. Hysteresis of the solute concentration/discharge relationship in rivers during storms. *Water Research*, **32**, 2279-2290.

Howden, N.J.K., T.B. Burt, F. Worall, S.A. Mathias & M.J. Whelan. 2013. Farming for water quality: balancing food security and nitrate pollution in UK river basin. *Annals of the Association of American Geographers*, **103**, 397-407.

Jarvie, H.P., P.M. Haygarth, C. Neal, C. Butler, B. Smith, P.S. Naden, *et al.* 2008. Stream water chemistry and quality along an upland-lowland rural land-use continuum, south-west England. *Journal of Hydrology*, **350**, 215-231.

Jepperson, E., J.P. Jensen, M. Sondergaard & T.L. Lauridsen. 2005. Response of fish and plankton to nutrient loading reduction in eight shallow Danish lakes with special emphasis on seasonal dynamics. *Freshwater Biology*, **50**, 1616-1627.

Johnson, D. & E. Lord. 2011. *Assessment of trends in N and P balance in Agriculture, by sector, with likely causes. EPCRS Farmework project 14627 for Environment Agency.*

Johnston, A.E., J. McEwan, P.W. Lan, M.V. Hewitt, P.R. Poulton & D.P. Yeoman. 1994. Effects of one to six years old rye grass- clover leys on nitrogen and on subsequent yields and fertilizer nitrogen requirements of the arable sequence winter wheat, potatoes, winter wheat, winter beans (*Vicia faba*) grown on a sandy loam soil. *Journal of Agricultural Science*, **122**, 73-89.

Jones, J.I., J.F. Murphy, A.L. Collins, D.A. Sear, P.S. Naden & P.D. Armitage. 2012. The impact of fine sediment on macro-invertebrates. *River Research and Applications*, **28**, 1055-1071.

Jokela, W. & M. Casler. 2011. Transport of phosphorus and nitrogen in surface runoff in a corn silage system: Paired watershed methodology and calibration period results. *Canadian Journal of Soil Science*, **91**, 479-491.

Jordan, C., S.O. McGuckin & R.V. Smith. 2000. Increased predicted losses of phosphorus to surface waters from soils with high Olsen-P concentrations. *Soil Use and Management*, **16**, 27-35.

Jordan, P., J. Arnscheidt, H. McGrogan & S. McCormick. 2005. High-resolution phosphorus transfer at the catchment scale: the hidden importance of non-storm transfers. *Hydrology and Earth System Sciences Discussions*, **9**, 685-691.

Jordan, P., A. Arnscheidt, H. Mcgrogan & S. McCormick. 2007. Characterising phosphorus transfers in rural catchments using a continuous bank-side analyser. *Hydrology and Earth System Sciences Discussions*, **11**, 372-381.

Jordan, P. & R. Cassidy. 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., A.R. Melland, P.-E. Mellander, G. Shortle & D. Wall. 2012. The seasonality of phosphorus transfers from land to water: Implications for trophic impacts and policy evaluation. *Science of the Total Environment*, **434**, 101-109.

Kalbitz, K., D. Schwesig, J. Rethemeyer & E. Matzner. 2005. Stabilization of dissolved organic matter by sorption to the mineral soil. *Soil Biology & Biochemistry*, **37**, 1319-1331.

Kallis, G. & D. Butler. 2001. The EU water framework directive: measures and implications. *Water Policy*, **3**, 125-142.

Kay, P., A.C. Edwards & M. Foulger. 2009. A review of the efficacy of contemporary agricultural stewardship measures for ameliorating water pollution problem of key concern to the UK water industry. *Agricultural Systems*, **99**, 67-75.

Kay, P., R. Grayson, M. Phillips, K. Stanley, A. Dodsworth, A. Hanson, *et al.* 2012. The effectiveness of agricultural stewardship for improving water quality at the catchment scale: Experiments from an NVZ and ECSFDI watershed. *Journal of Hydrology*, **422**, 10-16.

Kerry, R. & M.A. Oliver. 2011. Soil geomorphology: Identifying relations between the scale of spatial variation and soil processes using the variogram. *Geomorphology*, **130**, 40-54.

King, K.W., P.C. Smiley, B.J. Baker & N.R. Fausey. 2008. Validation of paired watersheds for assessing conservation practices in the Upper Big Walnut Creek watershed, Ohio. *Soil and Water Conservation*, **63**, 380-395.

Kirchner, J.W., X. Feng, C. Neal & A.J. Robson. 2004. The fine structure of water-quality dynamics: the (high-frequency) wave of the future. *Hydrological Processes*, **18**, 1353-1359.

Kristensen, H.L., K. Deboz & G.W. McCarty. 2003. Short-term effects of tillage and mineralization of nitrogen and carbon in soil. *Soil Biology & Biochemistry*, **35**, 979-986.

Klein, M. 1984. Anti-clockwise hysteresis in suspended sediment concentration during individual storms: Holbeck catchment, Yorkshire, England. *Catena*, **11**, 251-257.

Koch, H.J. & N. Stockfisch. 2006. Loss of soil organic matter upon ploughing under a loess soil after several years of conservation tillage. *Soil Tillage Research*, **86**, 73-83.

Kuhn, N.J., T. Hoffmann, W. Schwanghart & M. Dotterweich. 2009. Agricultural soil erosion and global carbon cycle: controversy over? *Earth Surface Processes and Landforms*, **34**, 1033-1038.

Kriszan, M., W. Amelung, J. Schellberg, T. Gebbing & W. Kuehbauch. 2009. Long-term changes of the <sup>15</sup>N natural abundance of plants and soil in a temperate grassland. *Plant and Soil*, **325**, 157-169.

Lal, R. 2001. Soil degradation by erosion. *Land Degradation & Development*, **12**, 519-539.

Lal, R. 2005. Soil erosion and carbon dynamics. *Soil & Tillage Research*, **81**, 137-142.

Lewis, W.M. & D.P. Morris. 1986. Toxicity of nitrite to fish: a review. *Transactions of the American Fishery Society*, **115**, 183-195.

Li, J., D. Richter, A. Mendoza & P. Heine. 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. p. 81. Institute of Hydrology, Wallingford, UK.

Liu, X., S.J. Herbert, A.M. Hashemi, X. Zhang & G. Ding. 2006. Effects of agricultural management on soil organic matter and carbon transformation- a review. *Plant Soil and Environment*, **52**, 531-543.

- Liu, X.J., A.R. Mosier, A.D. Halvorson, C.A. Reule & F.S. Zhang. 2007. Dinitrogen and N<sub>2</sub>O emissions in arable soils: effect of tillage N source and soil moisture. *Soil Biology and Biochemistry*, **39**, 2262-2370.
- Lord, E.I., Anthony, S.G., Goodlass, G. 2002. Agricultural nitrogen balance and water quality in the UK. *Soil Use and Management*, **18**, 363-369.
- Lord, E., Shepherd, M., Silgram, M., Goodlass, G., Gooday, R., Anthony, S.G., Davison, P., Hodgkinson, R. 2007. *Investigating the effectiveness of NVZ action programme measures: development of a strategy for England*. DEFRA.
- Maier, G., G.A. Glegg, A.D. Tappin & P.J. Worsfold. 2012. A high resolution temporal study of phytoplankton bloom dynamics in the eutrophic Taw Estuary (SW England). *Science of the Total Environment*, **434**, 228-239.
- Mariott, C.A., G. Hudson, D. Hamilton, R. Neilson, B. Boag, L.L. Handley, *et al.* 1997. Spatial variability of soil total C and N and their stable isotopes in an upland Scottish grassland. *Plant and Soil*, **196**, 151-162.
- Marschner, H. 2012. *Mineral nutrition of higher plants. Third edition*. Academic Press, Elsevier, San Diego, USA.
- Matlack, G.R. 2009. Long-term changes in soils of second-growth forest following abandonment from agriculture. *Journal of Biogeography*, **36**, 2066-2075.
- Matson, P.A., W.J. Parton, A.G. Power & M.J. Swift. 1997. Agricultural intensification and ecosystem properties. *Science*, **277**, 504-509.
- Matthews, G.P., G.M. Laudone, A.S. Gregory, N.R.A. Bird, A.G. Matthews & W.R. Whalley. 2010. Measurement and simulation of the effect of compaction on the pore structure and saturated hydraulic conductivity of grassland and arable soil. *Water Resources Research*, **46**, 1-13.
- McCormick, S., C. Jordan & J.S. Bailey. 2009. Within and between-field spatial variation in soil phosphorus in permanent grassland. *Precision Agriculture*, **10**, 262-276.

McDowell, R.W., A.N. Sharpley, L.M. Condron, P.M. Haygarth & P.C. Brookes. 2001. Processes controlling soil phosphorus release to runoff and implications for agricultural management. *Nutrient Cycling in Agroecosystems*, **59**, 269-284.

McGonigle, D.F., R.C. Harris, C. McCamphill, S. Kirk, R. Dils, J. Macdonald, *et al.* 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.

McGrath, D. & C. Zhang. 2003. Spatial distribution of soil organic carbon concentrations in grassland of Ireland. *Applied Geochemistry*, **18**, 1629-1639.

MEA. 2005. *Millenium Ecosystem Assessment: Ecosystems and human wellbeing: synthesis*. Island Press, Wahington DC

Melland, A.R., P.-E. Mellander, P.N.C. Murphy, D.P. Wall, S. Mehan, O. Shine, *et al.* 2012. Stream water quality in intensive cereal cropping catchments with regulated nutrient management. *Environmental Science & Policy*, **24**, 58-70.

Mellander, P.-E., A.R. Melland, P. Jordan, D.P. Wall, P.N.C. Murphy & G. Shortle. 2012. Quantifying nutrient transfer pathways in agricultural catchments using high temporal resolution data. *Environmental Science & Policy*, **24**, 44-57.

Merbold, L., W. Eugster, J. Stieger, M. Zahnister, D. Nelson & N. Buchmann. 2014. Greenhouse gas budget (CO<sub>2</sub>, CH<sub>4</sub> and N<sub>2</sub>O) of intensively managed grassland following restoration. *Global Change Biology*, **20**, 1913-1929.

Montgomery, D.R. 2007. *Dirt: The erosion of civilizations*. University of California Press, Berkeley.

Mooshammer, M., W. Wanek, J. Schneckner, B. Wild, S. Leitner, F. Hofhansl, *et al.* 2012. Stoichiometric control of nitrogen and phosphorus cycling in decomposing beech leaf litter. *Ecology*, **93**, 770-782.

Murray, P.J., B.A. Griffith, R.J. Orr, A. Shepherd, M.S.A. Blackwell & J. Hawkins, M.B. 2013. The North Wyke Farm Platform: A new UK national capability for research into sustainability of agricultural temperate grassland management. In: *International Grassland Congress 15-19 September, 2013*. New South Wales Department of Primary Industry, Sydney, Australia.

NEA. 2011. *UK National Ecosystem Assessment: Synthesis of the key findings*.

Newell-Price, P., D. Harris, D. Taylor, J.R. Williams, S.G. Anthony, D. Duethemann, *et al.* 2011. *An inventory of mitigation methods and guide to their effects on diffuse water pollution, greenhouse gas emissions and ammonia emissions from agriculture*.

Nimmo-Smith, R.J., G.A. Clegg, R. Parkinson & J.P. Richards. 2007. Evaluating the implementation of the nitrates directive in Denmark and England using an Actor-Orientated Approach. *European Environment*, **17**, 124-144.

Oliver, M.A. & R. Webster. 1986. Combining nested sampling and linear sampling for determining the scale and form of spatial variation of recognized variables. *Geographical Analysis*, **18**, 227-242.

Oliver, M., R. Webster & J. Gerrard. 1989a. Geostatistics in physical geography, Part 2: Applications. *Transactions of the Institute of British Geographers*, **14**, 270-286.

Oliver, M., R. Webster & J. Gerrard. 1989b. Geostatistics in physical geography: Part 1: Theory. *Transactions of the Institute of British Geographers*, **14**, 259-269.

Oliver, M.A. & R. Webster. 1990. Kriging: a method of interpolation for geographical information systems. *International Journal of Geographical Information Systems*, **4**, 313-332.

Oliver, M.A. & R. Webster. 1991. How geostatistics can help you. *Soil Use and Management*, **7**, 206-217.

Oliver, M.A. & R. Webster. 2014. A tutorial guide to geostatistics: Computing and modelling variograms and kriging. *Catena*, **113**, 56-69.

Owens, P.N., R.W. Malore, D.L. Hothem, G.C. Starr & R. Lal. 2002. Sediment carbon concentration and transport from small watersheds under various conservation tillage practices. *Soil & Tillage Research*, **67**, 65-73.

Page, T., P.M. Haygarth, K.J. Beven, A. Joynes, T. Butler, C. Keeler, *et al.* 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.

Parris, K. 2011. Impact of agriculture on water pollution in OECD countries: recent trends and future prospects. *International Journal of Water Resources Development*, **27**, 33-52.

Paustein, K., J. Six, E.T. Elliot & H.W. Hunt. 2000. Management options for reducing Co<sub>2</sub> emissions from agricultural soils. *Biogeochemistry*, **48**, 147-163.

Paz-Gonzalez, A., S. Vieira, R., & M.T. Taboada Castro. 2000. The effect of cultivation on the spatial variability of selected properties of an umbric horizon. *Geoderma*, **97**.

Pearl, H.W. 2009. Controlling Eutrophication along the freshwater-marine continuum: dual nutrient (N and P) reductions are essential. *Estuaries and Coasts*, **32**, 593-601.

Peukert, S., R. Bol, W. Roberts, C.J.A. Macleod, P.J. Murray, E.R. Dixon, *et al.* 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.

Peukert, S., B.A. Griffith, P.J. Murray, C.J.A. Macleod & R.E. Brazier. 2014a. Intensive management in grasslands causes diffuse water pollution at the farm-scale. *Journal of Environmental Quality*, **43**, 2009-2023.

Pilgrim, E.S., Macleod, J.A. Ch, S.A. Blackwell, R. Bol, D.V. Hogan, *et al.* 2010. Interaction among agricultural production and other ecosystem services delivered from European temperate grassland systems. *Advances in Agronomy*, **109**, 117-154.

Poeplau, C., A. Don, L. Vesterdal, J. Leifeld, B. Van Wesemael, J. Schumacher, A. Gensior. 2011. Temporal dynamics of soil organic carbon after land-use change in the temperate zone – carbon response functions as a model approach. *Global Change Biology*, **17**, 2415-2427.

Power, A.G. 2010. Ecosystem services and agriculture: tradeoffs and synergies. *Philosophical Transactions of the Royal Society*, **365**, 2959-2971.



Powlson, D.S., P.J. Gregory, W.R. Whalley, J.N. Quinton, D.W. Hopkins & A.P. Whitmore. 2011. Soil management in relation to sustainable agriculture and ecosystem services. *Food Policy*, **36**, S72-S87.

Preedy, N., K. McTiernan, R. Matthews, L. Heathwaite & P. Haygarth. 2001. Rapid incidental phosphorus transfer from grassland. *Journal of Environmental Quality*, **30**, 2105-2112.

Pretty, J.N., C. Brett, D. Gee, R.E. Hine, C.F. Mason, J.I.J. Morison, *et al.* 2000. An assessment of the total external costs of UK agriculture. *Agricultural Systems*, **65**, 113-136.

Pretty, J.N., C.F. Mason, D.B. Nedwell, R.E. Hine, S. Leaf & R. Dils. 2003. Environmental Costs of Freshwater Eutrophication in England and Wales. *Environmental Science and Technology*, **37**, 201-208.

Pretty, J., W.J. Sutherland, J. Ashby, J. Auburn, D. Baulcombe, M. Bell, *et al.* 2010. The top 100 questions of importance to the future of global agriculture. *International Journal of Agricultural Sustainability*, **8**, 219-236.

Quinton, J.N., P. Strauss, N. Miller, E. Azazoglu, M. Yli-Halla & R. Uusitalo. 2003. The potential for soil phosphorus tests to predict phosphorus losses in overland flow. *Journal of Plant Nutrient and Soil Sciences*, **166**, 432-437.

Quinton, J.N., J.A. Catt, G.A. Wood & J. Steer. 2006. Soil carbon losses by water erosion: Experimentation and modelling at field and national scales in the UK. *Agriculture, Ecosystems & Environment*, **112**, 87-102.

Quinton, J.N., G. Govers, K. Van Oost & R.D. Bardgett. 2010. The impact of agricultural soil erosion on biogeochemical cycling. *Nature Geoscience*, **3**, 311-314.

Qiu, W., D. Curtin & M. Beare. 2011. Spatial variability of available nutrients and soil carbon under arable cropping in Canterbury. *The New Zealand Institute for Plant and Food Research, Ltd.*

Roberts, W.M., M.I. Stutter & P.M. Haygarth. 2011. Phosphorus retention and remobilization in vegetated buffer strips: A review. *Journal of Environmental Quality*, **41**, 389-399.

Robertson, G.P., J.R. Crum & B.G. Ellis. 1993. The spatial variability of soil resources following long-term disturbances. *Oecologia*, **96**, 451-456.

Rossel, R.A., J.C. Gasperoni & J.A. Galantini. 2001. Soil organic matter evaluation. In: *Assessment methods for soil carbon* (eds. Lal, R., Kimble, J.M., Follett, R.F. & Stewart, B.A.). Lewis Publishers, London, New York, Washington.

Sandford, R.C., J.M.B. Hawkins, R. Bol & P.J. Worsfold. 2013. Export of dissolved organic carbon and nitrate from grassland in winter using high temporal resolution, in situ UV sensing. *Science of the Total Environment*, **456**, 384-391.

Sardanas, J., A. Rivas-Ubach & J. Penuelas. 2012. The elemental stoichiometry of aquatic and terrestrial ecosystems and its relationship with organismic lifestyle and ecosystem structure and function: a review. *Biogeochemistry*, **111**, 1-39.

Saunders, W.M.H. & E.G. Williams. 1955. Observations on the determination of total organic phosphorus in soils. *Journal of Soil Science*, **6**, 254-267.

Schärer, M., C. Stamm, T. Vollmer, E. Frossard, A. Oberson, H. Flühler, *et al.* 2007. Reducing phosphorus losses from over-fertilized grassland soils proves difficult in the short term. *Soil Use and Management*, **23**, 154-164.

Schilling, K.E., C. Jones, S., & A. Seeman. 2013. How paired is paired? Comparing nitrate concentrations in three Iowa drainage districts. *Journal of Environmental Quality*, **42**, 1412-1421.

Schnellberg, J., M.J. Hill, R. Gerhards, M. Rothmind & M. Braun. 2008. Precision agriculture on grasslands: applications, perspectives and constraints. *European Journal of Agronomy*, **29**, 59-71.

Scholefield, D., K.C. Tyson, E.A. Garwood, A.C. Armstrong, J. Hawkins & A.C. Stone. 1996. Nitrate leaching from grazed grassland lysimeters: effects of fertiliser input, field drainage, age of sward and patterns of weather. *Journal of Soil Science*, **44**, 601-613.

Schroeder, J.J., Scholefield, D., Cabral, F., Hofman, G. 2004. The effects of nutrient losses from agriculture on ground and surface water quality: the

position of science in developing indicators for regulation. *Environmental Science and Policy*, **7**, 15-23.

See, J.H., D.A. Bronk & A.J. Lewitus. 2006. Uptake of Spartina-derived humic nitrogen by estuarine phytoplankton in nonaxenic and axenic culture. *Limnology and Oceanography*, **51**, 2290-2299.

Selles, F., R.E. Karamanos & R.G. Kachanoski. 1986. The spatial variability of nitrogen-15 and its relation to the variability of other soil properties. *Journal of the Soil Science Society of America*, **50**, 105-110.

Senbayram, M., L. Dixon, K.W.T. Goulding & R. Bol. 2008. Long-term influence of manure and mineral nitrogen applications on plant and soil <sup>15</sup>N and <sup>13</sup>C values from the Broadbalk Wheat Experiment. *Rapid Communications in Mass Spectrometry*, **22**, 1735-1740.

Sharpley, A., H.P. Jarvie, A. Buda, L. May, B. Spears & P. Kleimann. 2013. Phosphorus legacy: Overcoming the effects of past management practices to mitigate future water quality impairment. *Journal of Environmental Quality*, **42**, 1308-1326.

Sharpley, A.N. 2003. Soil mixing to decrease surface stratification of phosphorus in manured soils. *Journal of Environmental Quality*, **32**, 1375-1384.

Shearer, G. & D.H. Kohl. 1986. N<sub>2</sub>-fixation in field settings: estimations based on natural <sup>15</sup>N abundance. *Australian Journal of Plant Physiology*, **13**, 699-756.

Shepherd, M.A., Hatch, D.J., Jarvis, S.C., Bhogal, A. 2001. Nitrate leaching from reseeded pasture. *Soil Use and Management*, **17**, 97-105.

Shi, Z., K. Wang, J.S. Bailey, C. Jordan & A.H. Higging. 2002. Temporal changes in the spatial distribution of some soil properties on a temperate grassland site. *Soil Use and Management*, **18**, 353-362.

Siegling, K. & H. Kage. 2006. N balance as an indicator of N leaching in an oilseed rape- winter wheat- winter barley rotation. *Agriculture, Ecosystems & Environment*, **115**, 261-269.

Silveira, M.L.A. 2005. Dissolved organic carbon and bioavailability of N and P as indicators of soil quality. *Scientia Agricola*, **62**, 502-508.

Six, J., E.T. Elliott & K. Paustein. 2000. Soil macroaggregate turnover and microaggregate formation: a mechanism for C sequestration under no-tillage agriculture. *Soil Biology & Biochemistry*, **32**, 2099-2103.

Smart, S., L.C. Maskell, M.J. Dunbar, B.A. Emmet, S. Marks, L.R. Norton, *et al.* 2010. An integrated assessment of countryside survey data to investigate ecosystem services in Great Britain. *CS Technical Report No. 10/07*.

Smith, L.P. & B.D. Trafford. 1976. *Climate and drainage*. HMSO, London, UK.

Smith, K.A., D.R. Jackson & P.J.A. Withers. 2001. Nutrient losses by surface run-off following the application of organic manures to arable land. 2. Phosphorus. *Environmental Pollution*, **112**, 53-60.

Smith, V.H., S.B. Joye & R.W. Howarth. 2006. Eutrophication of freshwater and marine ecosystems. *Limnology Oceanography*, **51**, 351-355.

Smith, V.H. & D.W. Schindler. 2009. Eutrophication science: where do we go from here? *Trends in Ecology and Evolution*, **24**, 201-207.

Soussana, J.-F., P. Loiseau, N. Viuichard, E. Ceschia, J. Balesdent, T. Chevallier, *et al.* 2004. Carbon cycling and sequestration opportunities in temperate grasslands. *Soil Use and Management*, **20**, 219-230.

Stafford, J.V. 2000. Implementing precision agriculture in the 21st century. *Journal of Agricultural Engineering Research*, **76**, 267-275.

Stalnacke, P., A. Grimvall, C. Libiseller, M. Laznik & I. Kokorite. 2003. Trends in nutrient concentrations in Latvian rivers and the response to the dramatic change in agriculture. *Journal of Hydrology*, **283**, 184-205.

Stavi, I. & R. Lal. 2011. Variability of soil physical quality in uneroded, eroded and depositional cropland sites. *Geomorphology*, **125**, 85-91.

Stevens, C.J. & J.N. Quinton. 2009. Diffuse pollution swapping in arable agricultural systems. *Critical Reviews in Environmental Science and Technology*, **39**, 478-520.

Stevens, C.J., J.N. Quinton, A.P. Bailey, C. Deasy, M. Silgram & D.R. Jackson. 2009. The effects of minimum tillage, contour cultivation and in-field vegetative barriers and soil erosion and phosphorus loss. *Soil Tillage Research*, **106**, 145-151.

Stevens, C.J., Quinton, J.N. 2009. Policy implication of pollution swapping. *Physics and Chemistry of the Earth*, **34**, 589-594.

Strock, J.S., Porter, P.M., Russelle, M.P. 2004. Cover cropping to reduce nitrate loss through subsurface drainage in the Northern U.S. corn belt. *Journal of Environmental Quality*, **33**, 1010-1016.

Stutter, M.I., S.J. Langer & R.J. Cooper. 2008. Spatial and temporal dynamics of stream water particulate and dissolved N, P and C forms along a catchment transect, NE Scotland. *Journal of Hydrology*, **350**, 187-202.

Sutherland, R.A., C. van Kessel, R.E. Farrell & D.J. Pennock. 1991. Landscape-scale variations in plant and nitrogen-15 natural abundance. *Journal of the Soil Science Society of America*, **57**, 169-178.

Sutherland, W.J., S. Armstrong-Brown, P.R. Armsworth, T. Brereton, J. Brickland, C.D. Campbell, *et al.* 2006. The identification of 100 ecological questions of high policy relevance in the UK. *Journal of Applied Ecology*, **43**, 617-627.

Swinton, S.M., F. Lupi, G.P. Robertson & S.K. Hamilton. 2007. Ecosystem services and agriculture: Cultivating agricultural ecosystems for diverse benefits. *Ecological Economics*, **64**, 245-252.

Sylvan, J.B., Quigg A., S. Tozzi & J.W. Ammerman. 2007. Eutrophication-induced phosphorus limitation in the Mississippi River plume: evidence from fast repetition rate fluorometry. *American Society of Limnology and Oceanography*, **52**, 2679-2685.

TAG, U. 2008. UK Environmental standards and conditions (Phase 2). UK Technical Advisory Group on the Water Framework Directive.

Tan, Z. & R. Lal. 2005. Carbon sequestration potential estimates with changes in land use and tillage practice in Ohio, USA. *Agriculture, Ecosystems & Environment*, **111**, 140-152.

Thompson, J., R. Cassidy, D.G. Doody & R. Flynn. 2014. Assessing suspended sediment dynamics in relation to ecological thresholds and sampling strategy in two Irish headwater catchments. *Science of the Total Environment*, **438-469**, 345-357.

Tiessen, H. & J.W.B. Stewart. 1982. Particle-size fractions and their use in studies on soil organic matter: 2. Cultivation effects on organic matter composition in size fractions. *Journal of the Soil Science Society of America*, **47**, 509-514.

Turnbull, L., J. Wainwright, R.E. Brazier & R. Bol. 2010. Biotic and abiotic changes in ecosystem structure over a shrub-encroachment gradient in the southwestern USA. *Ecosystems*, **13**, 1239-1255.

Turner, B.L. & P.M. Haygarth. 2000. Phosphorus forms and concentrations in leachate under four grassland soil types. *Soil Science Society of America*, **64**, 1090-1099.

Turner, B.L. & M.S.A. Blackwell. 2013. Isolating the influence of pH on the amounts and forms of soil organic phosphorus. *European Journal of Soil Science*, **64**, 249-259.

Ulen, B., M. Bechmann, Foelsterm J., H.P. Harvie & H. Tunney. 2007. Agriculture as a phosphorus source for eutrophication in the north-west European countries, Norway, Sweden, United Kingdom and Ireland: a review. *Soil Use and Management*, **23**, 5-15.

USEPA. US Environmental Protection Agency. 2000. Ecoregional Nutrient Criteria Documents for rivers and streams <http://www2.epa.gov/nutrient-policy-data/ecoregional-nutrient-criteria-documents-rivers-and-streams>. "accessed" 22/4/2014.

van Grinsven, H.J.M., H.F.M. ten Berge, T. Dalgaard, B. Fraters, P. Durand, A. Hart, *et al.* 2012. Management, regulation and environmental impacts of nitrogen fertilization in Northwestern Europe under the Nitrates Directive; a benchmark study. *Biogeosciences Discussions*, **9**, 7353-7404.

van Kessel, C., R.E. Farrell & D.J. Pennock. 1993. Carbon-13 and nitrogen-15 natural abundance in crop residues and soil organic matter. *Journal of the Soil Science Society of America*, **58**, 382-389.

van Meirvenne, M. & G. Hofman. 1989. Spatial variability of soil nitrate nitrogen after potatoes and its change during winter. *Plant and Soil*, **120**, 103-110.

Verstraeten, G., J. Poesen, K. Gillijns & G. Govers. 2006. The use of riparian vegetate filter strips to reduce river sediment loads: an overestimated control measure? *Hydrological Processes*, **20**, 4259-4267.

Wall, D., P. Jordan, A.R. Melland, P.-E. Mellander, C. Buckley, S.M. Reaney, *et al.* 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., P.N.C. Murphy, A.R. Melland, S. Mechan, O. Shine, C. Buckley, *et al.* 2012. Evaluating nutrient source regulations at different scales in five agricultural catchments. *Environmental Science & Policy*, **24**, 34-43.

Walling, D.E. & B.W. Webb. 1985. Estimating the discharge of contaminants to coastal waters by rivers- some cautionary comments. *Marine Pollution Bulletin*, **16**, 488-492.

Wang, L., A.S. Butcher, M.E. Stuart, D.C. Goody & J.P. Bloomfield. 2013. The nitrate time bomb: a numerical way to investigate nitrate storage and lag time in the unsaturated zone. *Environmental Geochemistry and Health*, **35**, 667-681.

Ward, R.C. & M. Robinson. 2000. *Principles of hydrology fourth edition*. McGraw-Hill Publishing Company, Maidenhead, UK.

Watzka, M., K. Buchgraber & W. Wanek. 2006. Natural <sup>15</sup>N abundance of plants and soils under different management practices in a montane grassland. *Soil Biology and Biochemistry*, **38**, 1564-1576.

Webb, B.W. & D.E. Walling. 1985. Nitrate behaviour in streamflow from a grassland catchment in Devon, UK. *Water Research*, **19**, 1005-1016.

Webster, R., S.J. Welham, J.M. Potts & M.O. Oliver. 2006. Estimating the spatial scales of recognizes variables by nested sampling, hierarchical analysis of variance and residual maximum likelihood. *Computers & Geosciences*, **32**, 1320-1333.

West, T.O., G. Marland, A. W. King, W.M.Post. 2004. Carbon management response curves: Estimates of temporal soil carbon dynamics. *Environmental Management*, **33**, 507-518.

Whitehead, P. & J. Crossman. 2012. Macronutrient cycles and climate change: Key science areas and an international perspective. *Science of the Total Environment*, **434**, 262-267.

Wilson, G.A. & K. Hart. 2000. Financial motivation or conservation concern? EU farmers' motivations for participation in voluntary agri-environmental schemes. *Environment and Planning*, **32**, 2161-2185.

Wilson, G.A., K. Hart. 2001. Farmers participation in agri-environmental schemes: towards conservation-oriented thinking? *Sociologia Ruralis*, **41**, 254-274.

Withers, P.J.A., Hodgkinson R.A., A. Bates & C.M. Withers. 2006. Some effects of tramlines on surface runoff, sediment and phosphorus mobilization on an erosion-prone soil. *Soil Use and Management*, **22**, 245-255.

Wood, F.L., A.L. Heathwaite & P.M. Haygarth. 2005. Evaluating diffuse and point phosphorus contributions to river transfers at different scales in the Taw catchment, Devon, UK. *Journal of Hydrology*, **304**, 118-138.

Worall, F. & T.P. Burt. 2007. Flux of dissolved organic carbon from UK rivers. *Global Biogeochemical Cycles*, **21**.

Worall, F., E. Spencer & T.P. Burt. 2009. The effectiveness of nitrate vulnerable zones for limiting surface water nitrate concentration. *Journal of Hydrology*, **370**, 21-28.

Worall, F., Davies, A. Bhogal, A. Lilly, M. Evans, K. Turner, *et al.* 2012. The flux of DOC from the UK- Predicting the role of soils, land use and net watershed losses. *Journal of Hydrology*, **448**, 149-160.

Wright, A.L. & F.M. Hons. 2005. Tillage impacts on soil aggregation and carbon and nitrogen sequestration under wheat cropping sequences. *Soil & Tillage Research*, **84**, 67-75.



Zhang, N., M. Wang & N. Wang. 2002. Precision agriculture- a worldwide overview. *Computers and Electronics in Agriculture*, **36**, 113-132.

Zhang, J., T.A. Quine, S. Ni & F. Ge. 2006. Stocks and dynamics of SOC in relation to soil redistribution by water and tillage erosion. *Global Change Biology*, **12**, 1834-1841.

Zhang, X., Liu, X., Zhang, M., Dahlgren, & R.A. Dahlgren. 2010. A review of vegetated buffers and a meta-analysis of their mitigation efficacy in reducing nonpoint source pollution. *Journal of Environmental Quality*, **39**, 76-84.

Zhang, Y., A.L. Collins, N. Murdoch, D. Lee & P.S. Naden. 2014. Cross sector contributions to river pollution in England and Wales: Updating waterbody scale information to support policy delivery for the Water Framework Directive. *Environmental Science & Policy*, **42**, 16-32.