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Identifying multiple pollutant catchment risks for the selection and targeting of water industry catchment management interventions: Development, implementation and testing of the CaRPoW framework

School of Energy, Environment and Agrifood

EngD
Academic Year: 2014 - 2015

Supervisor: Prof. Ian Holman and Dr. Paul Burgess
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This thesis is submitted in partial fulfilment of the requirements for the degree of Doctor of Engineering

ABSTRACT

Water companies are continually adopting catchment management as a way of improving the quality of raw water prior to treatment. The catchments from which raw water is abstracted are often heterogeneous which regularly presents multiple pollutant issues and variability in the spatial distribution of pollutant-contributing areas. For catchment management to be effective, it is crucial that water companies select and target appropriate interventions at multi-pollutant high risk areas. Within this thesis a conceptual framework is developed to disaggregate and compare multiple pollutant risks in drinking water catchments to aid water companies in this decision making process.

A review of pollutant processes highlights links between pollutants often mitigated using catchment management and therefore confirms the feasibility for a multi-pollutant framework. Criteria were developed with water industry catchment management professionals to determine framework requirements. No current framework or model fully meets these criteria.

The Catchment Risk to Potable Water(CaRPoW) framework was therefore developed which disaggregates pollutants risks according to the Source-Mobilisation-Delivery continuum. Models for various pollutants that match the defined criteria were developed for each component of the framework and applied to the River Ugie catchment, a lowland agricultural drinking water source catchment in the North East of Scotland, UK.

Within the limits of uncertainty for both the models and monitoring data, the models were capable of representing total catchment load for each pollutant reasonably well. Similarly approximately half of the models were able to replicate the spatial distribution of pollutants loads. Given the relative simplicity of the models, the scale at which processes are represented and uncertainty in validation data, the models provide a reasonable representation of catchment loading (risk) for the pollutants modelled.

Spatial comparison of the outputs highlights concurrence in risks between pollutants and the potential for multiple benefits. A methodology to select and target interventions was demonstrated for the pesticides chlorotoluron and metaldehyde. The majority of high risk areas were best mitigated using source control interventions; however certain fields were better mitigated using mobilisation and delivery interventions thus confirming the need for informed intervention selection depending on the field.

Finally a retrospective economic analysis using data from Scottish Water's catchment management project highlights theoretical savings upwards of £30,000 in monitoring costs. Additionally, comparison of applications to Scottish Water's incentive scheme against CaRPoW outputs suggests discrepancies in the interventions applied for and funded.

Overall this thesis has improved understanding on the representation of multiple pollutant processes at the catchment scale within one conceptual framework and provided a decision support methodology to aid water industry catchment management projects going forward.

Keywords:

Catchment Management, Water Industry, Diffuse Pollution, Model, Drinking Water

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2, 4-D	2,4-Dichlorophenoxyacetic acid
AET	Actual Evapotranspiration
ANCOVA	Analysis Of Covariance
APLE	Annual Phosphorus Loss Estimator
BADC	British Atmospheric Data Centre
BCPC	British Crop Protection Council
BFI	Baseflow Index
CAPEX	Capital Expenditure
CaRPoW	Catchment Risk to Potable Water
CatchIS	Catchment Information System
Chl	Chlorotoluron
CMPP	Mecoprop-p
CSA	Critical Source Area
DEFRA	Department of the Environment Fisheries and Agriculture
DOC	Dissolved Organic Carbon
DTC	Demonstration Test Catchment
DWI	Drinking Water Inspectorate
DWQR	Drinking Water Quality Regulator
DWD	Drinking Water Directive
UKWIR	United Kingdom Water Industry Research
EFSA	European Food Standards Agency
EU	European Union
FOCUS	Forum of the Co-ordination of Pesticide Fate Models and their Use
GAC	Granular Activated Carbon
HER	Hydrologically Effective Rainfall
HGCA	Home Grown Cereals Authority
IACS	Integrated Administration and Control System
LCM	Land Cover Map
LPID	Land Parcel Identifier
MCPA	2-methyl-4-chlorophenoxyacetic acid
Metd	Metaldehyde

Metz	Metazachlor
MMMF	Modified Morgan Morgan Finney
MORECS	Meteorological Office Rainfall and Evapotranspiration Calculation System
N	Nitrogen
NERM	Nitrogen Export Risk Matrix
NGO	Non-Governmental Organisation
NIRAMS	Nitrogen Risk Assessment Model Scotland
NLEAP	Nitrate Leaching Potential
NVZ	Nitrate Vulnerable Zone
OFWAT	The Water Services Regulation Authority
Olsen-P	Olsen Phosphorus
OPEX	Operational Expenditure
PCV	Prescribed Concentration Value
SNH	Scottish Natural Heritage
PET	Potential Evapotranspiration
PIT	Phosphorus Indicators Tool
PP	Particulate Phosphorus
PPDB	Pesticide Properties Database
PPP	Plant Protection Products
PSYCHIC	Phosphors and Sediment Yield Characterisations In Catchments
RE	Relative Error
RMSE	Root Mean Square Error
SAC	Scottish Agricultural College
HOST	Hydrology Of Soil Types
SAGIS	Source Apportionment Geographical Information System
SASA	Scottish Agricultural Statistics Agency
SCS	Soil Conservation Service
SDRN	Scottish Detailed River Network
SEISMIC	Spatial Environmental Information System for Modelling the Impact of Chemicals
SEPA	Scottish Environment Protection Agency
SLM	Sustainable Land Management

S-M-D	Source-Mobilisation-Delivery
SNIFFER	Scotland and Northern Ireland Forum For Environmental Research
SR15	Strategic Review 15
SRP	Soluble Reactive Phosphorus
SSKIB	Scottish Soils Knowledge and Information Base
SW	Scottish Water
UK	United Kingdom
WaSim	Water Simulation
WFD	Water Framework Directive

Chapter 1. Introduction

1.1 Research context

1.1.1 Catchment management for water quality

The variable nature of catchment water quality affects multiple aspects of the environment and society. In response to poor water quality, regulations implemented in the latter half of the 20th century to control point source pollution (e.g. European Union Urban Waste Water Directive 91/271/EEC) have resulted in general catchment water quality improvements in developed countries (Jarvie et al., 2002; Kinniburgh and Barnett, 2009). Nevertheless the control of point sources has somewhat shifted the focus to tackling diffuse pollution (Orr et al., 2007; Edwards and Withers, 2008). By its nature diffuse pollution is not conducive to the same regulatory controls as point sources and therefore an integrated approach at the catchment scale (catchment management) has been adopted as the primary mechanism for its control (Keirle and Hayes, 2007; Harris, 2013). Internationally this has been enshrined in legislation such as the Watershed Approach Framework in the United States (EPA, 1996) and the formation of Catchment Management Authorities in Australia (New South Wales Government, 2003).

The European approach is centred on the EU Water Framework Directive (WFD) which aims to achieve a ‘good’ ecological and chemical status for all EU water bodies (2000/60/EC; Holzwarth, 2002). Catchment management is intertwined within the WFD where improving the status of water bodies is predicated on the designated competent authority in each member state outlining a programme of measures within river basin management plans to improve a range of water quality parameters, some of which are directly related to diffuse pollution control (Holzwarth, 2002).

Aside from national and international legislative drivers a number of other sectors have been incentivised to implement catchment management to improve water quality. A key adopter of the approach is water companies who are reliant on catchment water quality for the provision of clean drinking water (Keirle and Hayes, 2007). With encouragement from regulators (e.g. the Water Services Regulation Authority (OFWAT) and the Drinking Water Inspectorate (DWI) in England and Wales and the Water Industry Commission for Scotland (WICS) and the Drinking Water Quality Regulator (DWQR) in Scotland) uptake in the sector has been large in recent years. So much so that all of the major drinking water suppliers in the United Kingdom have some form of catchment management at varying degrees of implementation (Spiller et al., 2013). Commitment to the approach has been in response to a variety of drivers. Compliance with both the EU Drinking Water Directive (DWD) and the WFD (2000/60/EC) are key, with article 7 of the WFD stating that member states should aim at "avoiding deterioration in their [water companies] quality to reduce the level of purification treatment required in the production of drinking water" (2000/60/EC). In some circumstances catchment management has been adopted in response to deteriorating raw water quality where the design limits of treatment works are being stretched and there is a threat to compliance with the DWD. Water companies are also incentivised by non-legislative drivers such as the increasing operational costs of treatment and striving to promote sustainability in their practices (UKWIR, 2012).

In accordance with the DWD water companies are required to remove an assortment of different pollutants to maintain compliance (98/83/EC). There are also other pollutants that are not directly regulated by the DWD or cause issues with the treatment process that are problematic to water companies. Subsequently water company catchment management schemes have tended to focus on the following pollutants:

- Nitrate (directly regulated under the DWD)
- Phosphorus (eutrophic issues in reservoirs)
- Pesticides (directly regulated under the DWD)
- Dissolved Organic Carbon (DOC)/water colour (issues with disinfection by-products which are regulated under the DWD)
- Sediment (issues with turbidity and is a conduit for other pollutants)

Although multiple pollutants often manifest in the same catchment, most water industry catchment management schemes are reactionary and emphasise single pollutant issues in isolation. Arguably water companies have therefore missed the opportunity to implement catchment management in a truly integrated way so that interventions are selected on the basis of multiple pollutant mitigation.

1.1.2 Catchment heterogeneity and current approaches to intervention selection and targeting

The occurrence of different pollutants within drinking water supply catchments is often dependent on a heterogeneous mix of varying land uses, soil types, hydrology, geology and anthropogenic influences. The spatial distribution of the processes that define overall catchment pollutant risk for different pollutants are therefore disproportional, and subsequently Critical Source Areas (CSAs) exist (Strauss et al., 2007; White et al., 2009; Doody et al., 2012). Many water industry catchment management schemes offer funding for land owners to implement interventions on their land (e.g. Scottish Water's Sustainable Land Management Scheme). For such schemes to be successful it is important that interventions are selected according to the dominant processes that promote high risk critical source areas (Doody et al., 2012). By doing this, interventions can be selected that will pay back benefits for more than one pollutant (Gooday et al., 2014). At the same time comparing pollutants in this way will also highlight where risks do not match and consequently where there is the potential for pollutant swapping (Stevens and Quinton, 2009). In this thesis 'pollutant swapping' refers to incidences where interventions implemented to mitigate the drinking water contamination risk of one pollutant increases the risk of another.

Adopting such an approach will make sure maximum benefits to water quality are achieved from minimal investment. Accordingly, money will not be invested on interventions unlikely to have a positive (or even negative) impact on catchment water quality. The targeted approach will similarly reduce disruption to other catchment stakeholders which is an important consideration when the uptake of interventions by land owners is considered (Beharry-Borg et al., 2013). Overall, selecting and targeting interventions at CSAs has the potential to improve the efficacy and efficiency of catchment management.

Consequently methodologies are required that are able to characterise, define and break down multiple pollutant risks at the catchment scale to predict where CSAs may exist, and select appropriate interventions accordingly. Such an approach is representative of what Beven and Alcock (2012) describe as “Models of everything everywhere”; these being simple generic models and frameworks capable of implementation in many situations to develop understanding of complex catchment processes for decision making.

There are previous methodologies and frameworks that have been developed, however none specifically meet these requirements. For example the Nutrient Export Risk Matrix (Hewett et al., 2009, 2004), the Phosphorus Indicators Tool (Heathwaite et al., 2003) and CatchIS modelling framework (Brown et al., 2002) are able to define critical source areas for nitrate, phosphorus and pesticide respectively i.e. single pollutants. Other approaches are applicable to more than one pollutant but only target one component of risk; for example the SciMap modelling framework (Lane et al., 2009) which characterises pollutant risk on hydrological connectivity alone. Some frameworks and models do consider multiple pollutants but are only applicable to certain land use and soil types (e.g. Granger et al., 2010), only consider one risk component (e.g Dawson and Smith, 2010) or do not allow for easy comparison between different pollutants (Gascuel-Odoux et al., 2009). As of yet, no “model of everything everywhere” exists that is generic, can be applied to multiple pollutants, specifically breaks down the components of pollutant risk and allows for multiple pollutant comparison for the purposes of measure selection i.e. which intervention to target where.

There is therefore a niche both within the water industry and wider catchment management research for a methodology capable of defining and comparing multiple pollutant risks at a scale that allows for interventions to be specifically targeted at the dominant components that constitute CSAs for multiple pollutants.

1.2 Aims and objectives

1.2.1 Aim

The overarching aim of the thesis is to develop a conceptual framework and associated modelling methodologies capable of identifying and comparing high risk areas in catchments for multiple pollutants so that catchment management interventions can be effectively selected and targeted.

1.2.2 Objectives

To achieve the broad aim set out in section 1.2.1 the following objectives have been formulated, each one relating to a specific chapter in the thesis:

1. Assess the feasibility of considering multiple pollutants within the same conceptual framework by reviewing the processes that constitute catchment risk for the pollutants mitigated in water industry catchment management schemes (Chapter 2).
2. Develop criteria with water industry professionals to outline the industry requirements for a conceptual modelling framework (Chapter 3).
3. Critique current methodologies and frameworks against the industry defined criteria and outline a new conceptual framework (Chapter 3).
4. Develop modelling methodologies to populate the conceptual framework developed in objective 3, capable of representing the components of risk using a quantifiable metric (Chapter 4).
5. Apply the framework and associated modelling methodologies to the River Ugie catchment and assess the utility of the framework for representing multiple pollutant risk against catchment water quality data (Chapter 5).
6. Compare the risk outputs of different pollutants to identify where multiple benefits and pollutant swapping may be prevalent and develop a methodology to select and target interventions using model outputs in the River Ugie catchment (Chapter 6).

7. Determine how the framework fits within Scottish Water's (SW) and other water companies catchment management processes, and conduct a retrospective economic analysis to quantify the benefits of implementing the methodologies developed (Chapter 7).

1.3 Research Contribution

The thesis contributes to the development of catchment management within the water industry in a number of ways. The framework developed is the first of its kind capable of being applied generically for the specific purpose of selecting and targeting catchment management interventions when multiple pollutants are an issue. Likewise the results of applying the framework and associated models has highlighted a number of key constraints that must be considered by water companies when selecting and targeting interventions. The analysis of scheme applications against model outputs has outlined a number of disparities between the interventions applied for by land managers and those that are likely to have the most positive impact on water quality.

Aside from the specifics of the water industry the research also contributes to wider understanding on pollutant processes at the catchment scale. The development of models within the framework has already contributed to understanding on pesticide mobilisation for example and it is hypothesised that the continual development of models within the framework will contribute to a better understanding of more complex processes. The approach also constitutes one of the first attempts at modelling pollution swapping within the context of catchment management interventions where multiple pollutants are concerned. More specifically the research builds on the concepts of the Source-Mobilisation-Delivery continuum by developing the theory for pollutants other than phosphorus for which it was first developed. Likewise the addition of landscape barrier and enhancement features within the structural connectivity model represents the first time this has been done using generic data.

Overall the research provides a step in the right direction for catchment management decisions within the water industry to be made upon a pragmatic integrated understanding of catchment processes.

1.4 Thesis structure

The thesis is structured as 8 chapters with a separate analysis that sits as an appendix but is still discussed in some parts of the thesis. The structure is detailed by the illustration in Figure 1.1 and detailed below.

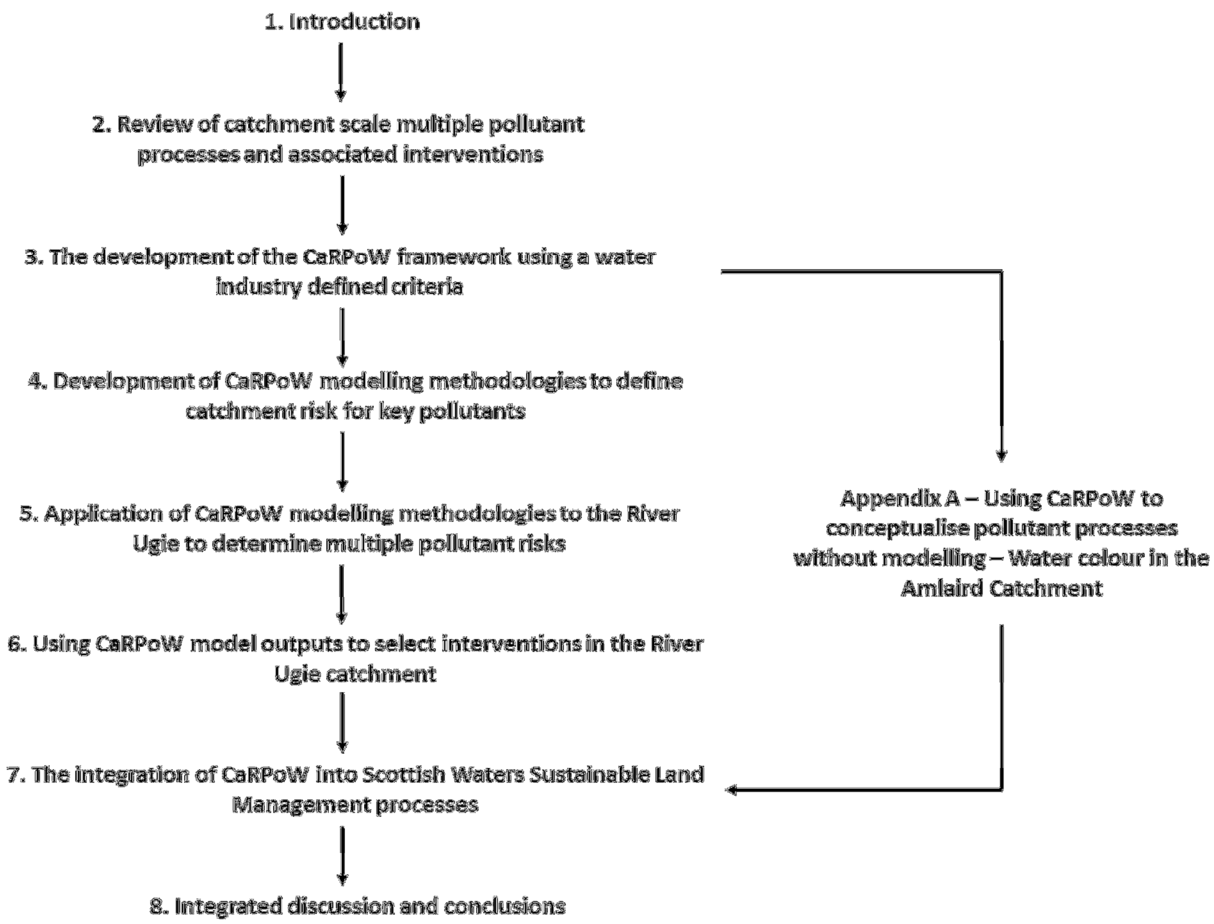


Figure 1.1 - Thesis structure

Chapter 2 reviews the dominant processes and deterministic variables within the source-mobilisation-delivery continuum for the pollutants of concern to the water industry. The purpose of the review is to ascertain similarities and differences between pollutants to assess the feasibility of considering multiple pollutants within the same conceptual framework. Intervention options are also considered and categorised by pollutant and processes targeted.

Chapter 3 initially sets out criteria for the development of a conceptual framework developed in conjunction with catchment management professionals within Scottish Water. Current frameworks and models are then critiqued against the criteria to determine if a new framework is required. The new CaRPoW (Catchment Risk to Potable Water) framework, developed on the back of the industry defined criteria, is then outlined.

The framework can be used with modelling or to qualitatively conceptualise pollutant process understanding in a catchment. In the thesis, Chapters 4 and 5 outline the method of using the framework for modelling purposes. Models are applied and validated in the River Ugie catchment for nitrate, phosphorus, sediment and pesticides. A separate analysis is also included in appendix A which applies the framework in a qualitative sense to an upland catchment (Amlaird) with DOC/water colour issues where catchment data are not available to model pollutant processes.

Chapter 6 outlines the methodology for using the modelled risk outputs from Chapter 5 to select and target interventions. Modelled outputs for each pollutant are compared to assess potential for multiple benefits or pollutant swapping. The intervention selection and targeting methodology is then applied to the pesticides chlorotoluron and Metaldehyde as a detailed example. The limitations of the overall methodology and post-processing steps required after modelling are discussed.

Chapter 7 discusses Scottish Water’s Sustainable Land Management (SLM) processes and where the CaRPoW methodology can be used. A retrospective economic analysis is conducted to highlight potential savings generated from using CaRPoW at the beginning of the SLM process. Finally a blueprint is detailed for an updated SLM or general catchment management approach making full use of the CaRPoW framework.

Chapter 8 assesses if the aim and objectives of the thesis have been met by discussing each objective in turn. Key contributions and implications of the research to both the water industry and wider catchment management research are discussed and recommendations for future work are outlined.

Chapter 2. Literature review of multiple pollutant processes and associated interventions

2.1 Introduction

The aim of Chapter 2 is to review the dominant processes from source to delivery of the pollutants included in catchment management schemes and the associated interventions that could therefore contribute to drinking water protection. It is necessary to complete this review before the generic conceptual framework is developed in Chapter 3, as evidence for the process links between different pollutants must be established as a conceptual basis for a new framework. This chapter does not provide a review of pollutant modelling methodologies or frameworks. Such a review comes later in Chapter 3 once criteria have been developed to benchmark methodologies against.

The chapter starts by identifying the method of reviewing pollutant processes within the source-mobilisation-continuum. Each pollutant is taken in turn and the dominant processes and controlling variables detailed. Dominant processes are compared and potential opportunities for multiple benefits and issues with pollutant swapping identified. Finally interventions are reviewed in the context of which pollutant processes they mitigate to identify measures capable of mitigating multiple pollutants. The following structure is therefore followed:

- 2.2 The Source-Mobilisation-Delivery (S-M-D) Continuum
- 2.3 Review of dominant processes within the S-M-D continuum for different pollutants
- 2.4 Process links between pollutants
- 2.5 Interventions within the S-M-D continuum

The review of pollutant processes (section 2.3) and pollutant process comparison (section 2.4) have been published as part of Bloodworth et al. (2015).

2.2 The Source-Mobilisation-Delivery (S-M-D) continuum

The dominant processes of the identified pollutants (pesticides, nitrate, phosphorus, sediment and DOC/colour) are reviewed within the context of the Source-Mobilisation-Delivery (S-M-D) continuum. The S-M-D continuum was originally developed to conceptualise phosphorus processes within a catchment (e.g. Haygarth et al., 2005), but has more recently been applied to other pollutants in heavy soiled grassland environments (Granger et al., 2010). The continuum describes the cascade of processes from source to water body. It follows a similar approach to the widely used source-pathway-receptor model in pollutant fate assessment but has been developed specifically for a hydrological context. The selection of the continuum for the review of pollutant processes is based upon its cross-scale and cross-pollutant applicability. The parts of the continuum are described in sections 2.2.1 to 2.2.3.

2.2.1 Source processes

Source processes refer only to how pollutants are derived in a catchment, with no emphasis placed on their movement or delivery to the water body. In the classification scheme of Granger et al. (2010) source processes are split into three groupings, external, cycled and internal. External sources are those pollutants applied outside of the natural system and are often anthropogenically derived (e.g. pesticides). Cycled sources relate to external pollutants that may have been incorporated into the system and modified in some way (for example the cycling of nutrients by livestock). Internal sources are pollutants derived within the ‘natural’ system and are often associated with the soil, lithology or vegetation processes.

2.2.2 Mobilisation processes

Mobilisation refers to the processes by which sources become mobile following an input of energy (usually hydrological). Mobilisation processes are characterised as solubilisation, detachment and incidental by Haygarth et al. (2005) and Granger et al. (2010). Solubilisation relates to biological and chemical processes such as desorption, mineralisation and the release of material following biological degradation that contribute to soluble pollutants mobilised in soil water (Granger et al., 2010).

Pollutants attached to soil particles that are eroded via processes such as raindrop impact and hydraulic shear constitute detachment processes (Granger et al. 2010). Incidental processes include both detachment and solubilisation processes but relate to the rapid mobilisation of externally applied substances in close proximity to application e.g. mobilisation of phosphorus following manure application (Haygarth et al., 1999; Withers et al., 2003).

2.2.3 Delivery processes

Delivery processes refer to the pathways in which mobilised pollutants travel before reaching a water body (receptor). Pathways are largely hydrological and can be split into high energy pathways such as surface runoff and macropore flow or low energy processes such matrix throughflow associated with groundwater recharge (Reichenberger et al., 2007). For some pollutants there may be more direct pathways not associated with hydrology such as spray drift with pesticides and direct inputs of nutrients by livestock (Reichenberger et al., 2007).

Delivery processes can be altered via anthropogenic activities such as the installation of agricultural tile drainage which may reduce the incidence of infiltration excess overland flow and increase macropore or bypass flow (Geohring et al., 2001).

2.3 Review of dominant processes within the S-M-D continuum for different pollutants

The method for reviewing pollutant processes within the continuum is based on similar work by Granger et al. (2010) where the dominant processes are outlined for each component of the continuum for each pollutant. In this review however more pollutants are reviewed and processes are related to different land uses and soil types. The key catchment variables controlling the likely dominance of one process over another are also detailed where appropriate.

2.3.1 Pesticides

Agricultural land use is the most important factor in determining the strength and importance of the source term for pesticides as it defines the timing, frequency and rate of active ingredient application (Hunt et al., 2006). This is certainly the case for sources applied to fields that are mobilised and delivered during hydrological events via runoff, drainflow and leaching processes (Leu et al., 2004; Reichenberger et al., 2007). Less common but nevertheless important pesticide sources can come as a result of poor practice, with spray drift, overspray and point source spills all potentially important source processes (Reichenberger et al., 2007). Although less understood in the context of overall source load, pesticides from amenity land uses such as golf courses can also be important (e.g. King and Balogh, 2010). The availability of a source for mobilisation is dependent on the half-life of the pesticide i.e. the rate at which it degrades within the environment (Webb et al., 2004). It is therefore an important consideration in the source strength of different substances.

Pesticides can be mobilised in solution or attached to particles, the ratio of which is informed by soil properties and the sorption and solubility characteristics of the pesticide (Wauchope et al., 2002; Gavrilescu, 2005). Nevertheless even pesticides with high sorption strengths are dominated by soluble mobilisation (e.g. Wu et al., 2004). Important soil characteristics influencing partitioning include the organic carbon and clay content which provide sorption sites; and physical properties such as porosity for instance which limits water storage capacity and hence the likelihood of sorption (Spark and Swift, 2002; Arias-Estévez et al., 2008). Where prevalent, particulate pesticide mobilisation is dependent on the soil properties that influence erosion rates e.g. texture and topographical features such as slope (Arias-Estévez et al., 2008). Rainfall characteristics relating to timing, duration and intensity are important for the onset of particulate associated mobilisation (i.e. erosion processes), mobilisation of soluble pesticides recently applied to the soil and mobilisation of pesticides in stored soil water if the soil is at or near field capacity (Kladivco et al., 2001; Nolan et al., 2008; Lewan et al., 2009).

Pesticides are associated with both high and low energy hydrological and non-hydrological delivery processes (Reichenberger et al., 2007). As with mobilisation, the dominant delivery process in a given context is somewhat dependent on pesticide properties where highly soluble and low sorbing substances can be more associated with low energy hydrological processes such as leaching and throughflow (Kördel et al., 2008), as well as high energy runoff and drainflow processes. In contrast substances that are less soluble with higher sorption strengths can be more related to higher energy runoff and preferential delivery processes (Riise et al., 2004; Reichenberger et al., 2007). Soil properties are similarly important for determining dominant pesticide delivery. Where soils are lighter for example, a higher prevalence of slower leaching and throughflow pesticide delivery processes may be present (Leu et al., 2004). Whereas heavier soils (higher clay content) promote faster runoff processes and drainflow where artificial drains are present (Akay and Fox, 2007; Brown and van Beinum, 2009).

Related to both mobilisation and delivery processes, the proximity and characteristics of the first rainfall event after applications are very important; with heavy rainfall soon after an application likely to lead to a larger proportion of the pesticide source being mobilised and delivered (Louchart et al., 2001; Guo et al., 2004). The prevalence of non-hydrological delivery processes, such as volatilisation, spray drift and overspray are reliant on poor practice, application technique, proximity to water body, pesticide properties (e.g. volatility) and weather (e.g. wind and temperature) (Gil and Sinfort, 2005; FOCUS, 2008).

Overall pesticide processes can be highly variable depending on the characteristics of the catchment and the pesticide. However a few key points can be drawn from the review that are relevant in many contexts:

- Pesticide source strength is generally highest in agricultural land uses (arable in particular).
- The first rainfall event after application is crucial for the availability of sources for mobilisation but also the proportion of available source that is mobilised and delivered.
- Pesticide mobility is highly dependent on sorption strength (unless particulate mobilisation is very high).

- High energy runoff and drainflow process contribute the highest mobilised and delivered pesticide loads.

2.3.2 Nitrate

Nitrate sources associated with agricultural land uses are related to a surplus within the soil (Di and Cameron, 2002), inorganic fertilisers (Domburg et al., 1998) or livestock manure/slurry application and direct excreta (Hooda et al., 2000). Agricultural sources are generally diffuse in nature, however point sources can exist on farm steadings where slurry storage is poorly managed (Edwards et al., 2008). Other non-agricultural sources are generally point sources and related to wastewater treatment discharges from municipal works and localised septic tanks (Withers et al., 2011). The proportion and prevalence of nitrate sources in a catchment are therefore dependent on the type of agriculture (although variability is high within each agricultural system e.g. different stocking rates and fertiliser requirements) and the presence of other point sources. Temporally, diffuse sources are generally higher in the autumn and winter months when leaching rates are high and uptake by plants is low (Jarvie et al., 2010). Nitrate sources can be depleted by the nitrification process, where, through a series of reduction reactions nitrate is converted to nitrogen gas (Rivett et al., 2008). Denitrification rates are generally higher in anaerobic conditions and therefore soils that are waterlogged for periods of the year will have higher denitrification rates than freely draining soils (Rivett et al., 2008). Denitrification is therefore an important process in the availability of nitrate sources for mobilisation.

Due to its very high solubility, nitrate mobilisation is dominated by solubilisation processes (Di and Cameron, 2002; Granger et al., 2010). Solubilisation is closely related to soil moisture content, which is dependent on the properties of the soil (e.g. porosity and texture) and inputs from rainfall (Torbert et al., 1999). The incidental mobilisation of ammoniacal-N (that can be nitrified to nitrate) from livestock manures and nitrate from inorganic fertilisers can occur in some isolated areas. It is dependent on low soil infiltration capacity (Butler et al., 2008) and the proximity of the application to hydrologically effective rainfall events (Smith et al., 2001).

The high solubility of nitrate means that approximately 5 times more nitrate is delivered via low energy leaching processes than higher energy surface runoff in both arable and grassland systems (Pärn et al., 2012). Variables that promote or increase nitrate losses via throughflow and leaching are soils with low field capacities and high hydraulic conductivity (Bergström and Johansson, 1991), a lack of cover crops during the autumn and winter period (Macdonald et al., 2005) and land management activities such as the installation of artificially drainage that increase the hydraulic conductivity in the soil (Singleton et al., 2001). Ammoniacal-N and nitrate mobilised incidentally can also be delivered via high energy surface runoff and preferential flow (e.g. Ming-kui et al., 2007), however the occurrence of such processes is less common.

Nitrate processes are generally well defined and understood across multiple land uses. Key points from the review include:

- High nitrate sources are generally associated with arable and intensive grassland land uses, although the proportion of nitrate inputs from wastewater treatment can be high depending on their presence in a catchment.
- Mobilisation is almost exclusively in a soluble form due to nitrate's high solubility.
- Delivery processes are dominated by low energy leaching and throughflow.

2.3.3 Phosphorus

Phosphorus follows a similar source profile to nitrate with sources available from added inorganic fertiliser, applied and excreted livestock waste, internally within the soil where a phosphorus surplus is present and point sources (Edwards and Withers, 1998; Withers et al., 2003; Hodgkinson and Withers, 2007). In agricultural catchments both diffuse and point sources of phosphorus can be high. Diffuse sources exist in the form of applied fertiliser and applied or excreted manure, and points sources from farmyards and wastewater effluent discharges (Macintosh et al., 2011). The strength of either source depends on the type of livestock and stocking rate for livestock inputs

(Smith, 1998; Withers et al., 2001), the fertiliser application rate, usually determined by the phosphorus status of the soil (DEFRA, 2010) and the occurrence of wastewater discharges for point sources (Macintosh et al., 2011).

Unlike nitrate, phosphorus mobilisation has been demonstrated to be mobilised significantly in particulate, soluble and incidental forms (Granger et al., 2010). Given the high sorption strength of phosphorus, particulate phosphorus detachment is thought of as the dominant phosphorus mobilisation process (Kleinman et al., 2011). High rates of phosphorus detachment require significant rainfall inputs but are further augmented by vulnerable soil textures, tillage practices, livestock poaching and soil compaction (Van Oost et al., 2006; Bilotta et al., 2010). Although particulate processes dominate, the mobilisation of soluble reactive phosphorus is perhaps more important given its critical role in the eutrophic processes that cause water companies issues (Crossman et al., 2013). The mobilisation of phosphorus in solution is largely a result of desorption when the phosphorus equilibrium of the soil is tipped or via the dissolution of phosphorus compounds (Styles et al., 2006). The exceedance of the phosphorus equilibrium in the soil is particularly prominent in over fertilised agricultural soils, with a low sorption strength, low organic carbon content and high soil moisture content (Hooda et al., 2000; Mcdowell et al., 2001; Djodjic et al., 2004). When a fertiliser and manure application or excretal phosphorus input coincides with a hydrologically effective rainfall event there is potential for incidental mobilisation (Preedy et al., 2001). The effect of incidental mobilisation is unclear however it is thought effects tend to be localised (Withers et al., 2003).

Surface runoff is understood to be the dominant delivery mechanism for both particulate and soluble phosphorus in both arable and grassland catchments (Mcdowell et al., 2001; Haygarth et al., 2006; Bilotta and Brazier, 2008). Effective rainfall inputs (Shigaki et al., 2007), along with soil properties (texture), topography and land management activities such as tillage practices and compaction (Silgram et al., 2010) are important drivers of phosphorus delivery via surface runoff. More recent research however has highlighted the importance of both natural (macropores) and artificial (drains) preferential flow in the delivery of both soluble and particulate phosphorus (e.g. Heathwaite and Dils, 2000; Smith et al., 2015). Preferential flow pathways generally become an issue when the texture of the soil (heavy soils) is conducive of macropore formation (van Es et al., 2004) or poorly drained soils are under drained (Hodgkinson et al., 2002). Although not as common a delivery mechanism as high energy processes there is evidence for soluble phosphorus to be delivered via lower energy throughflow and leaching processes (e.g. Börling, 2003).

The key dominant processes identified from the phosphorus review include:

- Sources from both diffuse (fertiliser, soil and manure) and point (farm yards and wastewater discharges).
- Mobilisation dominated by the particulate form however in certain circumstances (e.g. when phosphorus sorption capacity of the soil is exceeded) soluble phosphorus mobilisation is very important.
- Delivery dominated by high energy processes with preferential processes important where soil type and land management activities promote them.

2.3.4 Sediment

Sediment is important as it often provides a conduit for other pollutants (e.g. pesticides and phosphorus) and is directly related to turbidity which is regulated under the DWD (Lawler et al., 2006). Sediment is derived 'naturally' within a catchment from erosive processes on land and from bed and bank erosion within the river system (Walling, 2005). With land based sediment erosion, vegetation is an important controlling variable, and therefore areas of land that have limited or no vegetation (e.g. bare soil following crop harvesting) contribute a large proportion of total sediment load (Collins et al., 2009). Other sediment sources within the catchment can arise from urban and sewage treatment, where contributions can be large. Carter et al., (2003) for example reported that 19-22% and 14-18% of total annual sediment load was sourced from urban areas and sewage treatment effluent respectively.

By its nature sediment mobilisation is via detachment processes, which requires significant energy inputs (Granger et al., 2010). Land based sediment sources are generally detached via hydraulic detachment or rain drop action (Morgan, 2005). However certain land management activities such as the livestock poaching (Skinner et al., 1997) may exacerbate sediment detachment from both land and also river bank sources where livestock have access.

Sediment delivery is dominated by high energy runoff processes, meaning that the proportion of sediment that is mobilised and delivered to the water body is reliant on runoff having enough energy to sustain sediment suspension or saltation (Blake et al., 2012). When energy is not maintained along the runoff pathway sediment is deposited (Morgan, 2005). Subsequently the majority of sediment is delivered to surface waters in the highest energy most intense runoff events (Smith et al., 2003). More recent studies have also started to demonstrate the significance of sediment delivery in sub-surface drains, where macropores in the soil provide a connection between mobilised sediment and sub-surface drainage (e.g. Deasy et al., 2009).

The key processes from the sediment review include:

- Sediment can be sourced from land, bank and bed erosion as well as from urban and wastewater discharges. The proportion of each depends on catchment features relating to land use and soil type.
- Mobilisation is wholly via detachment processes that require high energy from hydrological or land management processes.
- Delivery is largely via surface runoff although there is evidence that high energy preferential processes can contribute.

2.3.5 DOC/Colour

Dissolved Organic Carbon (DOC) (as a proxy for water colour) is largely sourced from the dissolution of organic matter in soil and vegetation, and a much smaller proportion from atmospheric deposition (Dawson and Smith, 2007). There is therefore a distinct relationship between the DOC concentration of surface waters and the organic carbon content of the soils that they drain (Clark et al., 2004; Holden, 2005; Buckingham et al., 2008). In the United Kingdom by far the largest loads of DOC come from rivers that drain catchments with a large proportion of peat soils (Billett et al., 2010).

DOC is solely mobilised by solubilisation processes the rate of which depends on organic matter decomposition in the soil (Dawson and Smith, 2007). In peatlands the rate of organic matter decomposition is dependent on pH, temperature and water table depth (Bonnett et al., 2006). This promotes distinct seasonality in DOC production and mobilisation, with higher rates of decomposition and release in the summer and autumn seasons compared to the winter and spring (Dawson et al., 2011). These processes explain intra-annual variations in DOC production and mobilisation but they do not provide an explanation for the observed increasing trend of DOC in UK surface waters over the land 40 years (Evans et al., 2005). Potential explanations for this include a reduction in acid deposition resulting from sulphur emission controls (e.g. Evans et al., 2006), increases in temperature driving increased rates of decomposition (e.g. Freeman et al., 2001), CO_2 enrichment from increasing emissions (e.g. Freeman et al., 2004) and upland management practices such as drainage, moorland burning and land use change that affect local hydrology (e.g. Yallop and Clutterbuck, 2009). Although evidence exists for all of these explanations there is no one driver that fully explains trends in all catchments.

In peatland catchments DOC is delivered via both high energy surface runoff and preferential flow processes (especially in degraded peat with large peat pipes and macropores) as well as low energy throughflow processes (Clark et al., 2008; Holden, 2005). There is a distinct variability in the literature on the dominance of any one process, however a number of studies have quantified the importance of large runoff events in the overall annual flux of DOC. For example Clark et al., (2007) found that in one catchment 50% of the annual DOC flux was exported in 10% of runoff events.

Key processes from the DOC review include:

- Soils with high organic matter content (e.g. peatlands) provide the largest source for DOC in the UK.
- The mobilisation of DOC in solution is dependent on the rate of organic matter decomposition which is dependent on pH, temperature and water table depth.

- DOC can be transported by both low and high energy processes however there is evidence in the literature that the largest loads are delivered in high energy delivery pathways.

2.4 Process links between pollutants

If processes and their controlling variables are similar between different pollutants then there is a possibility that certain interventions may be able to mitigate multiple pollutants. Conversely, if processes are different between pollutants then there is a possibility that pollutant swapping may occur if an intervention alters the dominant process in an area (Stevens and Quinton, 2009). For example increasing infiltration capacity in a soil to reduce surface runoff may increase mobilisation and delivery via slow throughflow and leaching processes (e.g. Roberts et al., 2009).

Process links and dissimilarities for the dominant processes between the different pollutants within the S-M-D continuum are summarised in Figure 2.1. Source processes are characterised according to which land use type the pollutant is most associated with. Mobilisation processes are split into soluble, particulate or incidental mobilisation. Delivery processes are defined by high energy runoff or preferential flow processes and lower energy lateral throughflow or deep leaching to groundwater.

With the exception of DOC the sources of most of the pollutants reviewed are associated with agricultural land uses. This means that risks are likely to exist in spatially similar areas for these pollutants and therefore source related interventions may mitigate multiple agriculturally derived pollutants.

The mobilisation of these sources highlights a different picture however. Sediment and particulate phosphorus by their nature are both mobilised via particulate detachment processes. Some pesticides may also be mobilised via particulate processes if sorption strength is high however the majority will be mobilised in solution. This is comparable with nitrate and soluble reactive phosphorus which is also mobilised in solution. Pesticides and phosphorus can be mobilised incidentally suggesting interventions that limit their application in close proximity to rainfall events are important. Overall there are some pollutants that could be mitigated with similar mobilisation interventions. At the same time however not all pollutants are subject to the same mobilisation processes, and therefore care must be taken to limit pollution swapping.

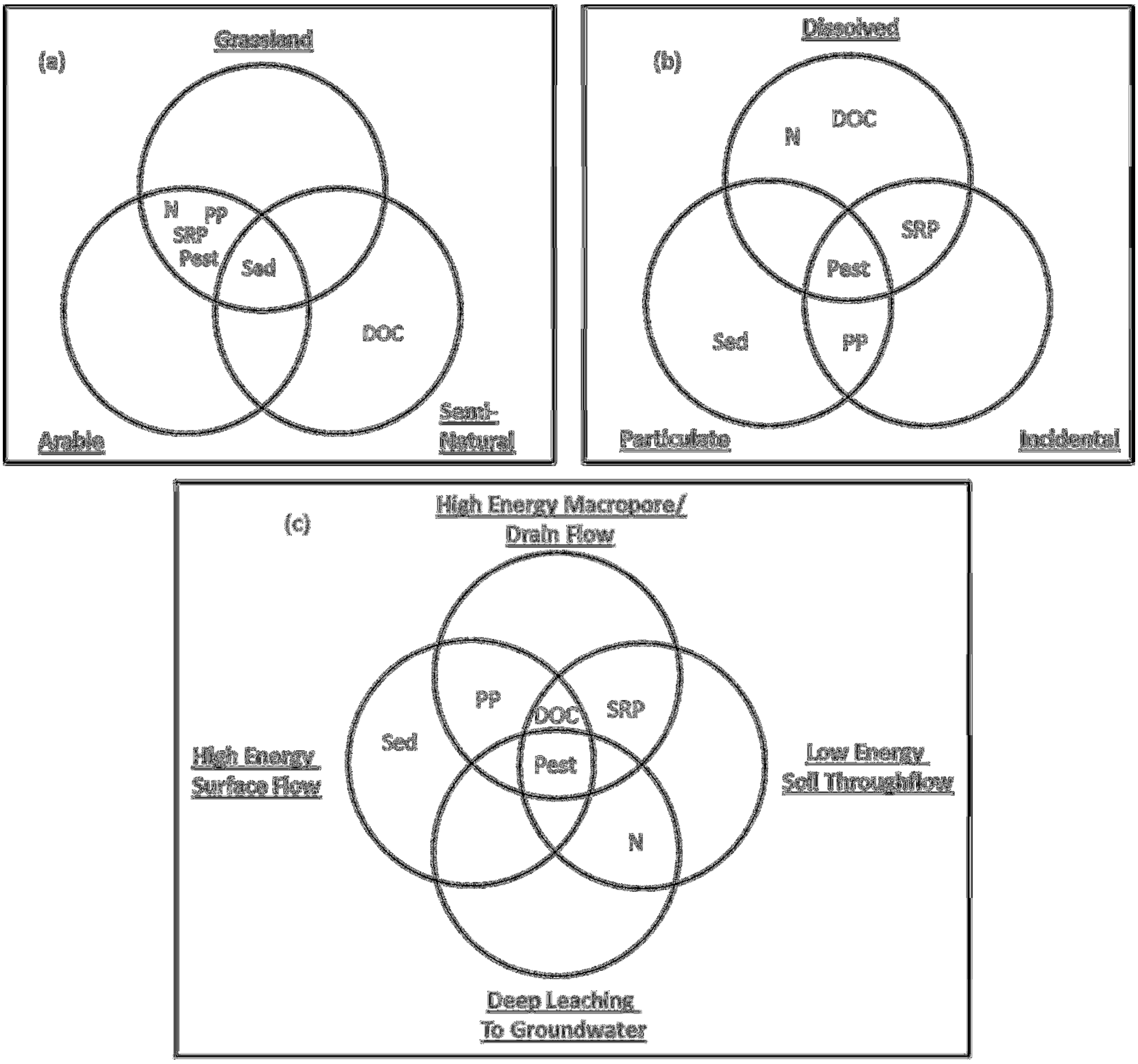


Figure 2.1 - Process linkages between the water industry priority pollutants framed within the (a) Source, (b) Mobilisation and (c) Delivery continuum (adapted from Granger et al., 2010). Pest – Pesticides, PP – Particulate Phosphorus, SRP – Soluble Reactive Phosphorus, N – Nitrate, Sed – Sediment, DOC – Dissolved Organic Carbon. Note: Figure also found in Bloodworth et al. (2015).

Similarly the dominant delivery processes are variable across the different pollutants. Pesticides have the potential to be delivered by all delivery mechanisms depending on the substance and the conditions of the catchment. Sediment and particulate phosphorus on the other hand are associated with higher energy surface and preferential flow pathways. Soluble reactive phosphorus and DOC can be transported via both high and low energy pathways (although their sources are not linked). The only pollutant that is largely delivered via slower energy processes is nitrate.

This review and analysis demonstrates that it is possible to link the processes of different pollutants in order to highlight where benefits may be achieved by mitigating a certain process. At the same time it has also highlighted where care needs to be taken for pollutants that do not have matching processes when selecting interventions.

2.5 Interventions within the S-M-D continuum

A large spectrum of interventions is available to mitigate the range of pollutants reviewed. This section outlines some of the interventions available to water companies and classifies them by pollutant and which part of the S-M-D continuum they mitigate. The review is by no means exhaustive and does not go into detail on the effectiveness of each intervention for each pollutant. More detailed reviews and intervention inventories are available such as Vinten et al. (2005), Reichenberger et al., (2007), Kay et al. (2009), Newell Price et al. (2011) which go into detail on measure effectiveness, potential uptake etc.

Table 2.1 outlines a range of interventions selected from the various reviews detailed above. Each intervention is described and classified according to the S-M-D continuum and associated with the pollutants they potentially mitigate. A column is also included on the potential for pollutant swapping for each intervention. It is important to note that the literature on pollutant swapping for many of the interventions is sparse; where a reference is not included potential for pollutant swapping is speculative based on process understanding. Likewise pollutant swapping with other problem pollutants identified is only considered. There is also a column that details if the intervention is available in Scottish Water's Sustainable Land Management Incentive Scheme; this column is for use in Chapters 6 and 7.

Table 2.1 demonstrates that there is a large selection of interventions available to mitigate the pollutants reviewed. With perhaps the exception of artificial wetlands, very few interventions are able to mitigate all pollutants. However, very few of the interventions actually promote pollutant swapping (although evidence in the literature for pollutant swapping is often sparse). The interventions that may be subject to pollutant swapping can fall into any part of the continuum. For example altering land use or substituting pesticides has the potential to swap the source of one pollutant for another. Likewise measures that increase the infiltration capacity of the soil have the potential to reduce incidental mobilisation but increase solubilisation processes. In a similar vein many of the speculative pollutant swapping incidences identified tend to be related to mitigating surface runoff and subsequently increasing the risk of preferential and slower sub surface flow processes.

Table 2.1 - Inventory of measures detailing which part of the continuum they mitigate and for which pollutants. Interventions have been selected on the basis that they mitigate the pollutants threatening drinking water sources as reviewed in section 1.1.1. The majority of the interventions in the table have been derived from the inventory of measures provided by Newell-Price et al. (2011), the reviews of Kay et al. (2009), Reichenberger et al. (2007) and Vinten et al. (2005), various papers on mitigation options for DOC in peatlands or those available in Scottish Water's Sustainable Land Management Scheme

Measure	Available in SLM Incentive Scheme?	Description	S, M or D?	Pollutants mitigated	Potential pollutant swapping?	Reference
1. Do not apply pollutant at high risk times	**x**	Avoid applying either nutrients (inorganic and organic) or pesticides at times of high risk i.e. in heavy rainfall or when soil moisture is high to reduce losses to surface water	S, M, D	P and N (in manure and fertiliser form), Pesticides	none	Vinten et al. (2005); Kay et al. (2009); Newell-Price et al. (2011)
2. Do not apply pollutant to high risk areas	**x**	Avoid applying P to soil with a high P index, do not apply fertiliser (organic and inorganic) or pesticides to areas susceptible to rapid transport to water bodies (dependant on soil type, topography etc.)	S, M, D	P and N (in manure and fertiliser form), Pesticides	none	Vinten et al. (2005); Kay et al. (2009); Newell-Price et al. (2011)
3. Conversion of arable land to grassland/woodland	**x**	Conversion to grassland will reduce inputs of inorganic fertiliser and pesticides, but may increase manure inputs	S	P, N (inorganic), Sediment and Pesticides	none	Reichenberger et al. (2007); Kay et al. (2009); Newell-Price et al. (2011)

4. Establish autumn cover crops	x	Establish cover crop to protect soil at high risk time and reduce mobilisation and transport of pollutants	M, D	PP and N; Pesticides to a certain extent but only particle associated pesticides (results largely unknown); Sediment	Potential for extra pesticides to be used to remove cover crop in the spring	Vinten et al. (2005); Reichenberger et al. (2007); Kay et al. (2009) Newell-Price et al. (2011)
5. Harvest crops early and establish autumn crops	x	Earlier harvesting will leave bare soils in period of low loss and autumn crops would improve soil structure at high risk times	M, D	P (main particulate), Sediment and to a lesser extent N. Pesticides due to potential losses in autumn rainfall events	none	Vinten et al. (2005); Newell-Price et al. (2011)
6. Cultivate in spring	x	Cultivation in spring increases likelihood of uptake of mineralised N by plants and reduces losses of P in surface runoff at high risk times	M, D	P (mainly particulate) and N	none	Vinten et al. (2005); Newell-Price et al. (2011)
7. Adopt reduced tillage systems and cultivate across slope	✓	More direct tillage systems retain organic matter content and reduces soil erosion; cultivation across slope reduces rill erosion	M, D	Mainly particulate P; Pesticides (although results are mixed depending on pesticide and other independent factors such as soil type etc.); Sediment	Increased infiltration potential for N increases? (e.g. Catt et al., 2000)	Vinten et al. (2005); Reichenberger et al. (2007); Kay et al. (2009); Newell-Price et al. (2011)
8. Strip Cropping	✓	Cultivate across contours leaving strips in between to act as filters of runoff and throughflow. The larger the width of the filter strip the better. Effectively an in field buffer strip	M, D	Potential to be effective for nutrients and pesticides but mainly for sediment.	none	Vinten et al. (2005)

9. Manage tramlines effectively	x	Use tines to disrupt tramlines or avoid creating tramlines so that infiltration is increased and surface runoff reduced	D	P (mainly in particulate form); potentially pesticides transported in overland flow; Sediment	Increased infiltration potential for N increases?	Kay et al. (2009); Newell-Price et al. (2011)
10. Edge of field and riparian buffers	x	Use of buffer strips to intercept overland flow	D	Largely P in particulate form; pesticides transported in surface runoff (edge of field more so than riparian); Sediment	Some evidence that riparian buffers increase SRP release (Roberts et al., 2011); minimal effect in N also (Leeds-Harrison et al. 1999)	Vinten et al. (2005); Reichenberger et al. (2007); Kay et al. (2009) Newell-Price et al. (2011)
11. Loosen compacted grassland soils	✓	Reduce compaction in grasslands by machinery and livestock by soil spiking and aeration to increase infiltration and reduce surface runoff	M, D	Most effective on PP; Sediment	Minimal effect on N in literature - potential for leaching?	Newell-Price et al. (2011)
12. Allow deterioration of artificial field drainage	x	Reduce preferential flow pathways and leaching by allowing drainage to deteriorate	M, D	N, pesticides and to a lesser extent PP - Although has potential to increase surface runoff	Increase in runoff - potential increase in sediment and PP? Potential for poor crop management and extra competition from weeds leads to extra pesticide use.	Reichenberger et al. (2007); Newell-Price et al. (2011)
13. Plant crops with improved N use efficiency	x	The use of plants that are efficient in N usage will require less fertiliser inputs and thus fewer N losses	S	N	none (assuming no extra pesticide requirements)	Newell-Price et al. (2011)

14. Efficient fertiliser and pesticide use	**x**	Correct machine calibration and a system to analyse appropriate fertiliser/pesticide requirement will minimise unnecessary fertiliser application, usage of fertiliser and manure in conjunction to meet nutrient requirements	S	N, SRP and pesticides	none	Newell-Price et al. (2011)
15. Reduce inorganic fertiliser use	**x**	Reducing inorganic fertiliser use will reduce short term losses and long term build up of P in soils.	S	N and P (soluble in short term and particulate in long term)	none (unless offset by organic fertiliser use)	Newell-Price et al. (2011)
16. Use direct fertiliser application technologies	**x**	Using direct application technologies will reduce incidental losses of fertiliser and increase nutrient uptake by plants	S, M	N and SRP	None (unless artificial drains active in close proximity to application)	Vinten et al. (2005); Kay et al. (2009); Newell-Price et al. (2011)
17. Reduce Manure Spreading on Land	**x**	Reduce overall manure application rate	S	All nutrient forms	Potential for increase in inorganic fertiliser use?	Vinten et al. (2005)
18. Better manage livestock dietary inputs/needs	**x**	Reduce the dietary inputs of N and P to livestock and match dietary needs to individual or groups of animals as current intakes are largely excreted	S	N and P in excretal form	none	Vinten et al. (2005); Newell-Price et al. (2011)
19. Reduce grazing time, reduce grazing in high risk periods and reduce overall stocking rates	**x**	Reduce amount of time livestock are in field by housing overnight and in winter seasonally; Reduce stocking rates when soil moisture is high to prevent poaching; reduce overall stocking rates to reduce manure inputs and poaching	S, M	N and P in manure form and reduces PP from less poaching; Sediment	none	Vinten et al. (2005); Newell-Price et al. (2011)

20. Appropriate livestock feeding and watering	**x**	Frequent movement of in field feeders to reduce poaching and manure inputs in concentrated areas; Place water troughs in a firm base to reduce poaching; use a water trough system rather than letting cattle drink straight from the water body	S, M	N and P in manure form and reduces PP from less poaching; Sediment	none	Newell-Price et al. (2011)
21. Effective slurry storage	**x**	Increase storage of slurry so that it can be applied at appropriate times	S	N and P but most effective for SRP	none	Newell-Price et al. (2011)
22. Site solid manure heaps away from water bodies and drains/Store manure on solid base and collect leachate	**x**	Site manure heaps at least 10m from water bodies and drains to reduce pollutant losses in surface runoff and drainflow	S, M, D	N and P (although reductions small)	none	Newell-Price et al. (2011)
23. Change from liquid to solid manure handling system	**x**	Pollutants less likely to be lost from solid manure storage to water bodies	S, M	More so for N and SRP	none	Newell-Price et al. (2011)
24. Transport manure between farms	**x**	Transport excess manure to farms with extra capacity to minimise field application at high risk times	S	Relatively effective for all N and P forms	Potential to increase source risk in other areas for nutrients?	Newell-Price et al. (2011)
25. Minimise livestock access to water bodies	✓	Construct fences and bridges so that livestock have no contact with water bodies to reduce bank poaching and direct manure inputs	S, M	Small decreases in N and P forms	none	Vinten et al. (2005); Newell-Price et al. (2011)
26. Effective farm infrastructure management	✓	Site gateways and farm tracks away from high risk areas i.e. away from the bottom of slopes or water bodies, make sure tracks drain to appropriate	S, M, D	Small reductions in N forms, more effective for PP losses	none	Newell-Price et al. (2011)

		areas etc.				
27. Hedge Establishment	x	Establish hedges along fence lines to break surface runoff pathways	D	Small reductions in N forms, more effective for PP losses, reduction in pesticides transported in surface runoff and by wind; Sediment	none	Reichenberger et al. (2007); Newell-Price et al. (2011)
28. Barrier Ditches	✓	Excavation of a ditch in between field and water body to collect surface runoff and intercept pollutants.	D	Potential to work for all nutrient forms, sediment and pesticides although use is relatively unproven	none	Vinten et al. (2005)
29. Reduce Water Course Maintenance	✓	Allow water courses to behave naturally in order to promote pollutant degradation with vegetation etc.	D	Potential to work for all nutrient forms, sediment and pesticides although use is relatively unproven	Potential increased pesticide use where unfavourable weeds grow e.g. rushes	Vinten et al. (2005)
30. Artificial wetlands	✓	Construct wetlands to capture runoff and degrade pollutants.	D	Small reductions in N forms, more effective for PP and sediment losses; reduction in pesticides transported in surface runoff and for strong sorbing pesticides	none	Schulz (2004); Vinten et al. (2005); Reichenberger et al. (2007); Gregoire et al. (2008); Kay et al. (2009) Newell-Price et al. (2011)

31. Vegetated Barriers	x	Vegetated fences to reduce runoff to a certain extent but mainly for wind driven pollutants – potential to reduce sediment erosion for wind blow affected soils	D	Small potential for nutrients in runoff but mainly for spray drift pesticides	none	Vinten et al. (2005); Reichenberger et al. (2007).
32. Soil incorporation	x	Incorporate potential pollutant into soil to reduce losses in surface runoff	M, D	Potential to reduce some pesticides dependant on characteristics e.g. sorption strength. Shown reduced P losses but has potential to Increase N losses via leaching.	Potential to increase losses via sub-surface delivery?	Vinten et al. (2005); Reichenberger et al. (2007); Kay et al. (2009); Newell-Price et al. (2011)
33. Low drift spray nozzles	x	Specialist nozzles attached to pesticide sprayers that creates coarse pesticide droplets less likely to be conveyed via spray drift	M, D	Potential to reduce pesticide losses via spray drift massively but high variability depending on nozzle	none	Kay et al. (2009); Reichenberger et al. (2007).
34. Product Substitution	✓	Substituting a problem pesticide with another that is either less mobile in the environment or can be kept below the 0.1 µg L-1 limit at the abstraction point	S	Pesticides - Highly dependent on the pesticide substitute as another problem could be potentially created	Potential to swap one pesticide for another	Reichenberger et al. (2007).
35. Maintain Soil Organic Matter Content	✓	Maintain a high soil organic matter content to increase pesticide sorption	M	Pesticides - Dependent on pesticide K_{oc} value; P	Potential increase in DOC?	Kay et al. (2009)
36. Pesticide loading and wash down area (with or without biobed)	✓	Created a specific area where pesticide spraying equipment can be maintained and cleaned to reduce point source losses. The addition of a biobed may further improve losses.	S	Pesticides - although effectiveness at catchment scale load reduction is uncertain	none	Reichenberger et al. (2007).

37. Grip Blocking	✓	Block artificial peatland drainage channels to restore high water table and reduce fast preferential flow processes	S, M, D	DOC - Has been proven effective in some cases but not others	Some studies have shown an short term increase on DOC concentrations	Armstrong et al. (2009; Wallage et al. (2006); Kay et al. (2009)
38. Peatland Revegetation	✓	Reseeding of peatlands with natural vegetation type e.g. *Sphagnum* mosses. This is to restore water tables previously lowered by heather	S, M, D	DOC - Although effectiveness relatively unproven	none	Waddington et al, (2008); Kay et al. (2009)

2.6 Conclusions

The review of pollutant processes within the S-M-D continuum for the pollutants of concern to the water industry has highlighted a few key points. Firstly many process similarities have been identified between different pollutants. This is encouraging and suggests that there is a high potential for multiple pollutants to be mitigated with the implementation of a single intervention. At the same time there are also some disparities between pollutant processes that must be considered when selecting interventions to limit incidents of potential pollution swapping. These realisations are further demonstrated by the range of different interventions available to target different aspects and processes of the continuum. Interventions have been outlined that are very effective for certain pollutants, but ineffective and potentially have a negative effect on other pollutants. Overall the review has demonstrated that it is possible for multiple pollutants to be considered in conjunction with one another when determining which processes are high risk and how best to deal with them. This therefore outlines the potential for a methodology capable of defining CSAs in a catchment for multiple pollutants, based on an understanding of the processes that constitute pollutant risk and subsequently informs which interventions are likely to be most appropriate.

Chapter 3. The development of the CaRPoW (Catchment Risk to Potable Water) framework using a Water Industry derived criteria

3.1 Introduction

What is clear from Chapter 2 is that the pollutants often included in water industry catchment management schemes have a range of variable and relatively complex processes enacting on them. Nevertheless the review demonstrated that in a number of cases there is parity between the processes of a number of pollutants. Similarly a number of interventions are capable of mitigating processes for more than one pollutant. As a result, there is scope for a conceptual framework capable of identifying and comparing catchment risk from multiple pollutants for the purposes of intervention selection and targeting. This chapter outlines the development of such a conceptual framework.

Firstly, water industry defined criteria are developed to understand the requirements of a new framework and against which current frameworks and models are compared. Following this, the newly developed CaRPoW framework is presented to meet the requirements of the water industry criteria. The chapter takes on the following structure:

- 3.2 Water industry criteria – Outlines the criteria developed with water industry professionals for a new conceptual framework.
- 3.3 Assessment of Frameworks against criteria – Current frameworks and models are compared against the criteria.
- 3.4 The CaRPoW framework – The new CaRPoW framework is presented to match the requirements of the water industry defined criteria.
- 3.5 Chapter conclusions

The criteria, framework and model review, and outlined CaRPoW framework have been published in Bloodworth et al. (2015).

3.2 Defining the framework properties with water industry defined criteria

As the framework is to be developed for use within the water industry and the outputs to be used by water industry professionals it was deemed necessary to develop criteria to inform framework development. The final criteria are also used to benchmark current models and frameworks against i.e. assess if currently available models and frameworks are suitable.

The methodology used to develop the criteria was based on a modified version of the method developed by Graves et al. (2005) for Agro-Forestry modelling. The purpose of the method is to structure end user defined requirements for models within 9 sub-sections including: model background, systems modelled, model objectives, the viewpoint of analysis, spatial scale, temporal scale, generation and use of data, platform and interface, and inputs and outputs (Graves et al., 2005). Structuring the criteria in this way was deemed beneficial for benchmarking current models and frameworks against, and to provide a definitive blueprint for a new framework if required. Although the Graves et al. (2005) methodology was initially derived for a different purpose its techniques were deemed transferable for any kind of environmental modelling.

The criteria are divided into 9 key sub-sections as documented in Table 3.1.

In total three end users were selected for criteria development who are involved in water quality regulation, catchment management and EU water framework directive implementation within SW. The criteria sub-sections were explained to each end user and they were asked to provide input to each of the sections. After collation a final set of criteria was agreed between all parties which formed the basis of the conceptual framework and subsequent modelling methodology. The final agreed criteria are shown in the second column in Table 3.1.

Table 3.1 - Water industry defined criteria for a conceptual framework with criteria sub-sections according to Graves et al (2005) in the first column and the outlined criteria for the framework in the second.

Criteria sub-sections	Water company defined criteria
1. Background - General information on framework/model	1.1 Operate in English
	1.2 Supporting methodology for drinking water source protection decisions
2. Systems Modelled - Components of the system represented by framework/model	2.1 Represents lowland and upland systems; arable, grassland and moorland dominated systems
	2.2 Focus on surface water systems although consideration of groundwater made in some capacity
3. Objectives	3.1 Characterise dominant diffuse pollution processes from source to delivery in drinking water catchments
	3.2 Assess spatial and temporal variation in process characterisations
	3.3 Classify risk of pollutant characterisations
	3.4 Compare risk classifications between different pollutants
	3.5 Select and target interventions according to the high risk areas
4. Viewpoint of analysis - Who the methodology is being developed for	4.1 Modelled from the viewpoint of a water company with a focus on abstracted raw water quality
5. Spatial scale and arrangement	5.1 Field/land unit scale
6. Temporal scale	6.1 Monthly for some model components but output to be seasonal or annual risk

7. Generation and use of data - How the framework/model is used	7.1 GIS methodology with potential to derive information from other models if necessary 7.2 Potential for framework to be used in a qualitative assessment
8. Platform and interface	8.1 Initial development in spatial modelling platform
9. Inputs and outputs	9.1 Inputs are spatial-temporal datasets and parameters defined by user 9.2 First output is modular to represent components of pollutant risk 9.3 Second output combined total risk output with all modules 9.4 Third output is risk comparison between pollutants 9.5 Intervention options selected according to process characterisation in post-processing of outputs 9.1 – 9.3

3.3 Conceptualising Pollutant Processes for Catchment Management

The synthesis of the modelling criteria in Table 3.1 forms the basis for the development of a conceptual framework on which modelling methodologies are founded.

There is a relatively large body of previous work that attempts to conceptualise pollutant processes at various scales in order to select and target interventions for the purposes of catchment management. Such investigations cover a range of different spatio-temporal scales, pollutants, modelling types and systems. For example, there are conceptual frameworks such as FARMSCOPER (Gooday et al., 2014) that work at the farm scale and the classification system developed by Granger et al. (2010) for grasslands with heavy soils attempt to group processes for better conceptual understanding. Likewise modelling methodologies such as the Phosphorus Indicators

Tool (Heathwaite et al., 2003) operationalise such frameworks into models able to spatially delineate risk.

Before deciding if a unique methodology to meet the criteria in Table 3.1 is required a number of current frameworks and modelling methodologies are explored to assess whether they meet the outlined criteria. For a model or framework to be included in the analysis it either has to be a framework that attempts to classify or characterise pollutant processes or a modelling methodology that uses such a conceptualisation of pollutant processes. Frameworks and models applied only to the UK or Northern Europe that cover at least one of the key pollutants were selected on the basis of similar agro-climatic conditions .

Frameworks and models have been identified from literature searches using search engines such as Web of Science and SCOPUS. The types of search terms used included “diffuse pollution conceptual framework”, “diffuse pollution catchment risk model”, “water quality protection framework”, “multiple diffuse pollution mitigation model” etc. Initially frameworks and models detailed in journal papers were searched for, however further searches for technical reports (especially with Scotland and UK specific models) were warranted. The reported outcomes of a workshop on “the spatial targeting of agri-environment measures for mitigation diffuse water pollution” was also utilised (Naden, 2013).

In total 12 models and frameworks were identified and selected for analysis against the modelling criteria. Of these, 9 were models and 3 were frameworks for process conceptualisation. Table 3.2 assesses each of the frameworks and models against the criteria outlined in Table 3.1.

Table 3.2 - Comparison of current frameworks and models against the water industry defined modelling criteria (table in Bloodworth et al., 2015). Column headings relate to criteria sub-sections as outlined in table 3.1.

Related Criteria Sub-Sections		1, 4	2	2	2	3	3	3	3	5, 6	7, 8, 9
Framework/ Model	**Reference**	**Drinking Water Specific?**	**Land uses represented**	**Pollutants represented**	**Hydrological Systems Represented?**	**Separate Source-Mobilisation-Delivery?**	**Pollutant Comparison?**	**Intervention Targeting?**	**Transferable, Generic Methodology?**	**Spatio-temporal scale?**	**Platform and Outputs**
Phosphorus Indicators Tool	Heathwaite et al. (2003)	×	Upland and Lowland - Grassland, Arable, Semi-Natural,	Soluble and Particulate Phosphorus	Surface Water	S-M-D	×	×	× (principles could possibly be generic)	$1km^2$ - Annual	GIS risk maps - total and component risk
FARMSCOPER	Gooday et al. (2014)	×	Lowland - Grassland and Arable	Soluble and Particulate Phosphorus, Nitrate, Sediment, Pesticides	Surface Water and Groundwater	S-M-D	✓	✓	✓	Farm Scale - Annual	Numerical assessment
Granger et al (2010)	Granger et al. (2010)	×	Upland and Lowland - Grassland	Soluble Phosphorus, Particulate Phosphorus, Nitrate, Nitrite, Ammonia, Fine Sediment	Surface Water and Groundwater	S-M-D	✓	×	✓	n/a	Qualitative classification

NERM	Hewett et al. (2004)	×	Upland and Lowland - Grassland and Arable	Nitrate and Phosphorus	Surface Water and Groundwater	×	✓ (Potentially Implicit)	✓	✓	Farm Scale - n/a	Qualitative Classification
SNIFFER - Diffuse Pollution Screening Tool	Sniffer (2006)	×	Upland and Lowland - Grassland, Arable, Semi-Natural,	Phosphorus, Nitrate, Sediment, Pesticides, Metals	Surface Water and Groundwater	×	×	×	✓	$1km^2$ - Annual	GIS Risk Maps
SCiMap	Lane et al. (2009)	×	Upland and Lowland - Grassland, Arable, Semi-Natural,	Potential for all pollutants	Surface Water	D	×	×	✓	User Defined - n/a	GIS Risk Maps - Total risk
SAGIS	Comber et al. (2013)	✓(but not exclusively)	Upland and Lowland - Grassland, Arable, Semi-Natural,	Phosphorus, Nitrate, Sediment, Metals	Surface Water	×	×	×	✓	Catchment scale - Annual	GIS Risk Maps - Total risk
CatchIS	Brown et al. (2002)	✓	Lowland - Grassland, Arable, Semi-Natural,	Pesticides, Nitrate	Surface Water and Groundwater	×	×	×	×	Catchment scale - Daily (time series), Annual (spatial risk)	GIS Risk Maps - Total risk
Foster and MacDonald (2000)	Foster and Mcdonald (2000)	✓	Upland and Lowland - Grassland, Arable, Semi-Natural,	Cryptospridium, Pesticides, Oil and grease, Colour, Trace Metals, Faecal Bacteria, Lead, Phosphorus, Nitrate	Surface Water	×	×	×	✓	Catchment scale - Annual	GIS Risk Maps - Total risk

Grayson et al. (2012)	Grayson et al. (2012)	✓	Upland - Grassland and Semi-Natural	DOC/Water Colour	Surface Water	×	×	×	×	Catchment scale - Annual	GIS Risk Maps
PSYCHIC Model	Davison et al. (2008)	×	Upland and Lowland - Grassland, Arable, Semi-Natural,	Soluble Phosphorus, Particulate Phosphorus and Sediment	Surface Water	S-M-D	×	×	×	$1km^2$ Grid (Tier 1), Farm Scale (Tier 2) - Monthly	GIS Risk Maps - total and component risk
The Territ'eau Framework	Gascuel-Odoux et al. (2009)	×	Upland and Lowland - Grassland, Arable, Semi-Natural,	Phosphorus, Nitrate, Sediment and Pesticides	Surface Water	×	×	✓	✓	Field to catchment scale - Annual	GIS Risk Maps - Total risk

Table 3.2 shows that none of the models and frameworks meets the industry defined criteria. Failure to do so stems from a number of causes, including not representing the full range of pollutants, not being able to represent processes and at a detailed enough spatial scale, not being developed for drinking water protection purposes, not being a generic transferrable methodology and not covering all land use and soil types.

This is somewhat unsurprising as most of the frameworks have not been developed for the purposes of drinking water protection, meaning they are unlikely to fully meet the expectations of the industry. Exceptions to this include CatchIS (Brown et al., 2002), Foster and MacDonald (2000), SaGIS (Comber et al., 2013) and Grayson et al. (2012) which have all been developed with inputs from water companies or with drinking water source protection in mind. These models that are water industry specific fall down because they only represent a single pollutant (e.g. CatchIS, Grayson et al., 2012) or they do not suitably represent the necessary processes to make informed decisions about which interventions to select and target within the catchment (Foster and MacDonald, 2000; SaGIS).

The framework and model that gets closest to the criteria is the Territ'eau framework (Gascuel-Odoux et al., 2009) which assesses the 'fate' and 'transfer' of pesticides, sediment, phosphorus and nitrates. The modular structure however is based on that of the individual pollutants rather than the continuum of processes. This makes it difficult to disaggregate and compare the components of risk between the different pollutants and therefore identify potential multiple benefits and pollutant swapping.

This small literature review of available models and frameworks highlights the need for a new framework that is able to meet the industry defined criteria in Table 3.1. Aside from the needs of the water industry, the review has also highlighted the relative dearth of diffuse pollution models that consider and compare the risks of multiple pollutants. Thus the development of a new framework will not only meet the needs of water industry catchment management schemes but also in identifying shared spatial pollutant risks in general.

3.4 The CaRPoW framework

The CaRPoW (Catchment Risk for Potable Water) has been developed in response to the industry criteria and the need for generic frameworks that can compare multiple pollutant risk (Figure 3.1). CaRPoW builds on previous conceptual classification frameworks of pollutant processes by Heathwaite et al. (2003), Haygarth et al. (2005) and Granger et al. (2010). Such classifications divide pollutant processes into three separate groupings according to source, mobilisation and delivery i.e. the Source-Mobilisation-Delivery continuum (Haygarth et al., 2005).

Although initially developed for phosphorus the S-M-D continuum has been applied to other pollutants in certain land types (e.g. Granger et al. 2010) and is loosely based on the classic Source-Pathway-Receptor approach of environmental risk assessments (e.g. Leo et al., 2008). The continuum has also been applied within a spatial modelling platform to identify areas with high agricultural phosphorus loading (the Phosphorus Indicators Tool, Heathwaite et al. 2003).

The key benefit of using the S-M-D continuum within CaRPoW is that its modular structure allows the components of pollutant risk to be clearly displayed to the end user (requirement 9.2 of the criteria). It does this by first of all calculating the risk within each module and then combining these to give an overall risk value. Deriving risk in this manner gives ultimate transparency to the end user as to where and how risk is propagated in a catchment.

Likewise it gives the added benefit of identifying where particular measures will be suited in a catchment rather than only identifying where risks are. The review of catchment management interventions in Chapter 2 highlights where different measures fit into different parts of the continuum. Thus by highlighting which part of the continuum dominates overall risk, the most appropriate measure can be selected and targeted.

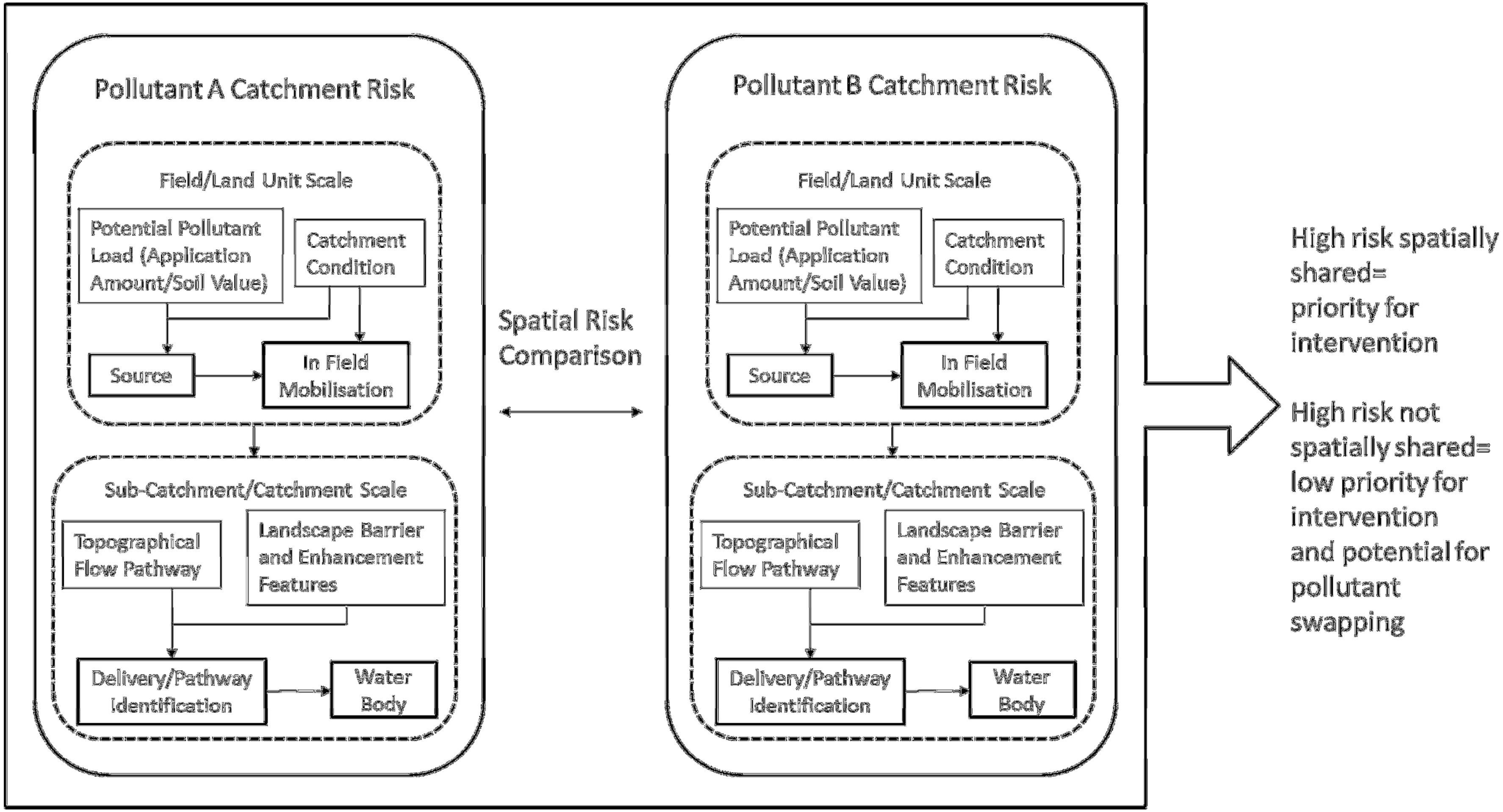


Figure 3.1 - The CaRPoW framework (figure also found in Bloodworth et al. 2015) developed from the water industry defined criteria in table 3.1. The framework disaggregates catchment pollutant risk and allows multiple pollutant comparison to aid intervention selection and targeting.

Within the original S-M-D continuum, components work at a range of differing scales. The source component works at the soil profile and field scale, mobilisation at the soil profile scale and the delivery component at a range of scales from the soil to the catchment (Haygarth et al., 2005). In CaRPoW the scales are much more defined to ease process conceptualisation for the end user and simplify modelling processes implemented within the framework. CaRPoW is divided into two different scales with source and mobilisation working at the field/land unit scale (unique combination of land use, soil type and drainage) and delivery/connectivity at the catchment scale.

The main utility of CaRPoW is as a framework within which to fit modelling methodologies to represent each of the three components (source, mobilisation and delivery) for each pollutant. The benefit of this approach is that as model capabilities and process understanding develop, the models placed within the framework can be updated to improve catchment risk representation and understanding.

However for catchments that do not have the data availability to model pollutant processes and subsequently catchment risk at the scales represented by CaRPoW (i.e. high resolution data are not available to represent the processes that differentiate spatial risk), the framework can be used in a purely qualitative manner to frame process understanding and aid decision making.

Both approaches are demonstrated in this thesis with the modelling approach demonstrated in Chapters 4-6 for pesticides, nitrate, phosphorus and sediment and the qualitative assessment in Appendix A for DOC.

The following sections detail each part of the CaRPoW framework and how it works to conceptualise overall catchment risk.

3.4.1 Source risk

The original source component of the S-M-D refers to how a pollutant is derived in a catchment and can be broadly characterised as internal sources i.e. those ‘naturally’ derived from the system, external sources i.e. those applied to the soil and cycled sources i.e. externally added pollutants that are cycled and redistributed within the system. Some pollutants can be derived from multiple source types (e.g. phosphorus), whereas others fall into one category (e.g. externally applied pesticides).

In CaRPoW the source component does not consider any ‘losses’ of pollutant and is therefore considered a source potential. Where in the original S-M-D framework the source component works from the soil profile to the field scale in CaRPoW it works at the ‘land unit’ scale. In this instance a land unit is defined as an area of land with unique land use, soil and drainage characteristics as defined by the input datasets.

3.4.2 Mobilisation risk

In the original S-M-D continuum the mobilisation component split phosphorus into soluble and particle associated forms and outlines solubilisation and detachment as the two key mobilisation processes (Haygarth et al., 2005; Granger et al., 2010). Mobilisation in CaRPoW is different to the conventional S-M-D as it considers mobilisation as the proportion of the source mobilised to the edge of a field in a given year. It therefore not only considers the form of the pollutant (i.e. in solution, particulate or incidental), but also the dominant within field delivery pathway. It can therefore be considered ‘within field mobilisation’ and consider aspects of both mobilisation and delivery within the traditional sense of the S-M-D.

The importance (and risk) of different mobilisation types and pathways will subsequently differ according to the pollutant and land unit typology. For example a high sorbing pesticide on a land unit type with a potential for large amounts of runoff and high soil erosion will have a high risk of particulate mobilisation. In contrast nitrate on a freely draining soil will have a high risk of solubilisation mobilisation.

3.4.3 Delivery risk

Delivery or connectivity is similar to mobilisation but it considers movement beyond the land unit scale i.e. movement of the pollutant beyond the edge of the field. It aims to represent the routing of pollutants from mobilisation at the land unit to the receptor (water body). Conceptually, flow routing is driven by topography however there is a consideration for features within the landscape that either enhance or restrict connectivity to the receptor.

Thus the highest risk index in the delivery component will be land units that are on direct and enhanced flow routes to the water body. As with mobilisation, delivery accounts for the proportion of the mobilised pollutant that reaches the water body.

3.4.4 Overall risk and pollutant comparison

In the simplest process risk characterisation the three modules can be considered in isolation if interventions that only fit to one type are feasible. However, to further delineate risk all three can be considered in conjunction with one another so that the areas with the highest risk are sources that are easily mobilised and well connected to the water body. Where all three components are considered together, 'risk' accounts for the total average annual pollutant load contributed by each field to the outlet of the catchment (where water is abstracted for drinking water treatment) i.e. the risk posed by each field to overall catchment raw water for a certain pollutant.

Either total risk or each individual risk component can be compared to make an assessment of the similarities and differences between the process risk characterisations of each pollutant. Risk outputs are compared to test for spatial relationships. If risk outputs are positively correlated then there is a potential for interventions to have a beneficial impact on both pollutants. If however there is a negative correlation then caution should be taken in selecting interventions as there may be a potential for pollutant swapping, or at least no potential for multiple benefits.

3.4.5 Selecting interventions

Selection of different interventions between the three modules will often be indicative of other factors not considered in the model. For example, social factors on the ground i.e. land owners will have the final say as to which interventions they would be willing to implement (Christensen et al., 2011). Nevertheless the recommended interventions for individual fields can be determined by making an assessment of the main component of risk within the field (i.e. source, mobilisation or delivery). An exhaustive list of interventions (Table 2.1 for example) can then be cross referenced against which risk component they mitigate and for which pollutant.

3.5 Chapter conclusions

The inherent need for a new framework that is capable of helping water companies make decisions on which measures to target where in a catchment has been demonstrated by assessing current available models and frameworks against a water company defined criteria. The CaRPoW framework, which key premise is in the disaggregation of the components of pollutant risk within a generic framework, has been developed with these criteria in mind. The main use of the framework is to model each risk component for the spatial delineation of pollutant risk. The framework can also be used to conceptualise pollutant risk in a catchment where data availability does not permit a modelling approach. The main modelling utility of the framework is demonstrated in Chapters 4-6 of the thesis whilst the qualitative conceptualisation is demonstrated for a catchment in appendix A.

Chapter 4. Development of CaRPoW modelling methodologies to define catchment risk for agricultural pollutants

4.1 Introduction

Chapter 4 outlines the modelling approaches developed to fit within the CaRPoW framework for the agriculturally associated pollutants pesticides, nitrate, phosphorus and sediment. DOC modelling approaches are not outlined in this chapter as qualitative approaches are discussed in Appendix A. Methodologies have been selected and developed according to the criteria developed in conjunction with water industry professionals, as outlined in Chapter 3. Where possible as much process based understanding has been included within the methods without sacrificing model simplicity and introducing over parameterisation. Methods have been selected and developed with the view that they can be applied to all catchments with readily available input data. Likewise, where possible models have been selected that have been developed and tested for UK conditions, or conditions similar to the UK. Non-catchment specific parameter values are presented along with the models in this chapter, whereas catchment specific parameters are detailed in Chapter 5.

The chapter is split into the following sections:

- Section 4.2 details where uncertainty is taken into account
- Section 4.3 describes source methodologies for the key pollutants
- Section 4.4 outlines the water balance methodology implemented as well as pollutant mobilisation methodologies
- Section 4.5 outlines the hydrological connectivity or connectivity methodologies
- Section 4.6 outlines how final risk is calculated for each field.
- Section 4.7 concludes and summarises the chapter

4.2 Incorporating uncertainty

In some instances it is necessary to incorporate known uncertainties within the models. For example, pesticide sorption strength (K_{oc}) and half-life (DT_{50}) are variable within the literature and therefore models are run with the variable parameter ranges. Similarly, although the models are based on annual averaged climate data, the models are run with an average year as well as a representative 'dry' and 'wet' year. Thus, some of the model outputs are stochastic and are comparable against observed pollutant loading values which also incorporate uncertainty (methodology in section 5.5).

Uncertainty ranges are discussed in more detail within the relevant model methodology and model setup sections (Chapter 4 and 5).

4.3 Source methods

The conceptualisation of source processes in Chapters 2 and 3 dictate that source methodologies should only consider the potential mass of a pollutant available for mobilisation. Methodologies are therefore relatively simple when compared to mobilisation and delivery. However there are certain variables that are considered within the source methodologies that influence pollutant availability. All source methodologies output a mass of pollutant per hectare available for mobilisation unless otherwise stated.

4.3.1 Pesticide source methods

Key pesticide sources include the load applied to the field, loads potentially available for mobilisation during application (i.e. overspray and spray drift) and loads available from pesticide sprayer loading and washdown areas (Reichenberger et al., 2007). Although sources from sprayer loading and washdown areas may be significant, it would be extremely difficult to implement them in a CaRPoW style methodology without knowledge of which farms have areas where sprayers are loaded and washed down. This source type is therefore discounted within the methodology. Similarly applications for amenity purposes (e.g. golf courses) and hard surfaces (e.g. roads and railways) are not considered.

Likewise, it is assumed that correct practices are followed by pesticide users in the catchment and therefore unintended losses during application from processes such as spray drift and over spray are deemed negligible and not included in the model. This therefore limits the pesticide source term to pesticides that have been applied to the field and are therefore potentially available for mobilisation via hydrological processes.

In its simplest form the application term is the mass of pesticide (g) applied per hectare per month. A monthly time step is required for the mobilisation methodology, although overall risk is presented annually in the output.

Equation 4.01 is used to derive this rate.

$$\boldsymbol{App_{c\,t}} = \boldsymbol{App_{\max\,c\,t}} \cdot \boldsymbol{F_{app}} \qquad 4.01$$

Where $App_{c\,t}$ is the adjusted application rate for crop c at time t, (kg ha^{-1} month^{-1}) $App_{\max\,c\,t}$ is the maximum application rate for the crop c at time t (kg ha^{-1} month^{-1}) and F_{app} is the fraction of the total crop area the product is applied to according to pesticide use statistics as not all cropped fields will receive an application.

Upon application pesticides are assumed to equilibrate instantly between soil solution and that sorbed to the soil bulk (Brown and Hollis, 1996). Partitioning between the two phases is dependent on the sorption strength to organic carbon of each pesticide and the organic carbon content of the soil (equation 4.02).

$$K_d = K_{oc}\,F_{oc} \qquad (4.02)$$

Where K_d is the soil organic carbon content adjusted pesticide sorption coefficient (l kg^{-1}), K_{oc} is the sorption coefficient for organic carbon (l kg^{-1}) and F_{oc} is the fraction of the soil that is organic carbon.

The proportion of applied pesticide in soil water and bound to the soil is calculated with equations 4.03 and 4.04.

$$App_{part} = \left(\frac{K_d}{K_d + 1}\right) \qquad (4.03)$$

$$App_{sol} = \left(\frac{-K_d}{K_d + 1}\right) + 1 \tag{4.04}$$

Where $App_{part}$is the proportion of applied pesticides attached to soil and $App_{sol\,t}$the proportion of of applied pesticide in soil solution.

The mass of pesticide in the soluble fraction is assumed to be available for mobilisation and is therefore derived from equation 4.05.

$$App_{cSol\,t} = App_{c\,t} \,.\, App_{sol} \tag{4.05}$$

4.3.2 Phosphorus source

Diffuse phosphorus sources are split into those sources internal to the soil both in soluble and particulate forms and those that are applied to the soil surface that constitute a separate source before incorporation into the soil (Granger et al., 2010). The key sources considered in the CaRPoW phosphorus methodology are therefore soil soluble phosphorus, soil particulate phosphorus, soluble phosphorus in applied fertilisers (both organic and inorganic) and soluble phosphorus in grazing livestock excreta.

The PIT (Heathwaite et al., 2003) and PSYCHIC (Davison et al. 2008) models have been developed using a Source-Mobilisation-Delivery in a similar way to CaRPoW. The CaRPoW phosphorus methodologies were therefore adapted from these models as they have been developed and well tested in the UK using readily available data.

Soluble phosphorus held within the soil is calculated using equation 4.05.

$$SolubleSoilP_{mass} = OlsenP \,.\, Soilv \,.\, \rho \tag{4.06}$$

Where $SolubleSoilP_{mass}$ is the mass of soluble soil P in the soil (mg ha^{-1}), $OlsenP$ is the mass of Olsen P in the soil (mg kg^{-1}), $Soilv$ is the soil volume (m^3 ha^{-1}) and ρ is the bulk density of the soil (kg m^{-3}).

Within both PIT and PSYCHIC soil soluble phosphorus is based on soil Olsen-P content as derived from soil property databases. Unfortunately the Scottish Soil Property database does not include data on Olsen-P or any soluble phosphorus fraction. Soluble soil phosphorus concentration was therefore based on soil texture and land use using default values presented by Davison et al. (2008) shown in Table 4.1.

Table 4.1- Soil Olsen-P values from Davison et al. (2008) for CaRPoW land use classes

	Olsen P (mg kg^{-1}) by land use			
Soil category	Winter and Spring Cereals	Row Crops	Intensive grass	Semi-Natural and Woodland
Sandy	42	45	25	21
Light	32	41	26	21
Medium/heavy	27	30	22	20

The particulate P source is dependent on the total phosphorus content of the soil, for each soil type the mass of total P in the topsoil was calculated using equation 4.07

$$TotalSoilP_{mass} = TotalSoilP \, . \, Soilv \, . \rho b \tag{4.07}$$

Where $TotalSoilP_{mass}$ is the total P mass (mg ha^{-1}), $TotalSoilP$ is the total P mass as derived from SSKIB (mg kg^{-1}).

Total soil phosphorus is based on the soil phosphorus content by soil association as documented in the SSKIB (Scottish Soils Knowledge and Information Database).

Phosphorus potentially sourced from fertilisers is dependent on the application rate of both organic and inorganic fertiliser to a field (kg ha^{-1} yr^{-1}).

$$FertiliserP = InorgPFert + OrgPFert \tag{4.08}$$

Where $FertiliserP$ is the potential available soluble P from fertiliser (kg ha^{-1} yr^{-1}), $InorgPFert$ is the potential available P from inorganic fertiliser (kg ha^{-1} yr^{-1}) and $OrgPFert$ is the potential P source available from organic fertiliser (kg ha^{-1} yr^{-1}).

In practice the amount of P applied to the land for each crop is dependent on the P status of the soil, as determined by regular soil testing (DEFRA, 2010). This makes it difficult to derive unique P application values for each field without having access to detailed soil P information on field by field basis. Previous investigations have used average P fertiliser applications derived from fertiliser surveys conducted by the UK government (e.g. Heathwaite et al., 2003, Davison et al. 2008) and from survey data in other countries (e.g. Kovacs et al. 2012).

Data on phosphorus fertiliser application are collated by the Scottish Government for a subset of Scottish farms. For each agricultural land use type the average phosphorus application rate is given for each. It is difficult to ascertain the proportion of inorganic and organic fertiliser for certain catchments and therefore the statistics assume that total applied phosphorus includes both organic and inorganic fertiliser in one combined value. Application rates are detailed specifically for the River Ugie catchment in Chapter 5 using a subset of the Scottish Government statistics.

P sources from direct livestock excreta are dependent on the stocking rate of each field multiplied by the annual output of phosphorus from each livestock type (kg ha^{-1} yr^{-1}). Livestock P sources only account for that available to plants i.e. soluble P.

$$LivestockP_{grazed} = LivestockDensity\,.\,LivestockPRate \qquad (4.09)$$

Where $LivestockP_{grazed}$ is the annual livestock P available (kg ha^{-1} yr^{-1}), $LivestockDensity$ is the density of livestock (livestock units per ha^{-1}) and $LivestockPRate$ is the annual available P output per unit of livestock per annum (kg yr^{-1}).

Livestock excreta will not cover the whole field and therefore not all of the phosphorus excreted by livestock will interact with runoff for potential mobilisation. To account for this a reduction factor is introduced based on the Annual Phosphorus Loss Estimator

(APLE) Model (Vadas et al., 2009). The reduction factor assumes that 1kg of excreta will cover an area of 0.2636 m^2 (James et al., 2007). Percentage excreta coverage for each field is derived using this value and the excretal mass output which in turn is used in the reduction factor equation 4.10.

$$ReductionFactor = \frac{1.2\,(250\,.\,PercCover)}{(250\,.\,PercCover) + 73.1} \qquad (4.10)$$

Where $PercCover$ is the percentage area coverage of excretal manure in each field.

The total livestock P source term is therefore calculated as the annual grazing output multiplied by the reduction factor (equation 4.11).

$$LivestockP = LivestockP_{grazed}\,.\,ReductionFactor \qquad (4.11)$$

Where $LivestockP_{grazed}$ is the total annual P output of livestock when grazing (kg ha^{-1} yr^{-1}) and $LivestockP$ is the total annual livestock P available for mobilisation after reduction (kg ha^{-1} yr^{-1}).

In CaRPoW, total livestock numbers are established from the statistics at a parish level. Livestock numbers are divided amongst the grassland fields within each parish according to area to give a potential grazing density for both cattle and sheep per field. Livestock is assumed to be mixed. The output and P content of livestock excreta is determined using lookup values from Chambers et al. (2001) (Table 4.2). Livestock are assumed to be overwintered during the months of November, December, January and February therefore reducing the annual output by 40% (which is assumed to be included in the organic fertiliser source). Note cattle phosphorus outputs values have been averaged across the different types of cattle because stocking values for individual cattle types is not available at the parish level.

Table 4.2 - Livestock excretal mass, available P content and total annual available P output for use in CaRPoW phosphorus source models (derived from Chambers et al., 2001)

Livestock Type	Total annual excretal mass (kg)	Available P content of excreta (g kg)	Total annual P output (kg)
Cattle	12410	2.1	26.06
Sheep	1496	1.2	1.80

The Total, soluble and particulate phosphorus source potential is subsequently calculated using equations 4.12 to 4.14.

$$TotalP_{source} = TotalSoilP_{mass} + SoilSolubleP + FertiliserP + LivestockP \quad (4.12)$$

$$ParticulateP_{source} = TotalSoilP_{mass} \quad (4.13)$$

$$SolubleP_{source} = SoilSolubleP + FertiliserP + LivestockP \quad (4.14)$$

Where $TotalP_{source}$ is the total potential P source (kg ha^{-1} yr^{-1}), $ParticulateP_{source}$ is the particulate P source (kg ha^{-1} yr^{-1}), $SolubleP_{source}$ is the soluble P source (kg ha^{-1} yr^{-1}), $SoilSolubleP$ is the total P in soil solution (kg ha^{-1} yr^{-1}), $FertiliserP$ is the total applied fertiliser (kg ha^{-1} yr^{-1}) per field and $LivestockP$ is the total P excreted by livestock per field (kg ha^{-1} yr^{-1}).

4.3.3 Nitrate source

Nitrate modelling methodologies can be inherently complex due to the myriad of processes that determine the balance of nitrogen in the soil. To maintain model simplicity and generalisation a simple nitrate source methodology was developed using adapted versions of the Nitrogen Risk Assessment Model Scotland (Dunn et al.,

2004) and the later Dunn et al. (2013) nitrate model, both of which have been developed and tested in Scotland.

Both methods use a fairly simple nitrate soil balance approach which derives an excess of nitrate in the soil available for mobilisation at the end of the growing season. The overall nitrate balance is highlighted in equation 4.15.

$$availN_t = (fertN_t.\,(1 - denitN_t\,)) - cropN_t + minerN_t + depN_t \qquad (4.15)$$

Where $availN_t$ is the nitrate available at the end of the growing season per field (kg ha^{-1} yr^{-1}), $fertN_t$ are nitrate inputs from fertilisers (both inorganic and organic) (kg ha^{-1} yr^{-1}), $cropN_t$ is the nitrate offtake from crops (kg ha^{-1} yr^{-1}), $depN_t$ is the atmospheric deposition of nitrate (kg ha^{-1} yr^{-1}), $minerN_t$ is the nitrate mineralised from organic matter (kg ha^{-1} yr^{-1}) and $denitN_t$ is the proportion of fertiliser denitrified (unitless coefficient).

The majority of farmers will decide how much N fertiliser to use according to soil testing, the previous crop grown and advice from agronomists (SAC, 2013). This proposes difficulties in assigning indiscriminate fertiliser inputs for different crop types in N models. However generalisations can be made from the recommendations provided by the Scottish Agricultural College (SAC) in their technical guidance notes (SAC, 2013). The guides use information on previous crop type, soil properties and rainfall statistics to offer annual N requirement recommendations. The guides are similar to the DEFRA fertiliser manual (DEFRA, 2010) but altered for Scottish conditions. It is difficult to make a distinction between types of fertiliser applied to each field. Interviews with agronomists (methodology and full results detailed in Chapter 5 and Appendix D) showed that there was high variability between farms in the proportions of organic and inorganic fertilisers used. The SAC methodology can circumvent this by only providing a total applied N value that can be derived from either organic or inorganic fertilisers.

Model testing by Dunn et al. (2013) showed that the best results for livestock grazed areas were achieved by assuming a set nitrate excess value of 22 kg ha^{-1} yr^{-1}, i.e. equation 4.15 is not used for livestock and the 22 kg ha^{-1} yr^{-1} is set as a coefficient. This value was similarly adopted in CaRPoW as well to maintain model consistency

Crop offtake values were taken from the lookup tables in Dunn et al. (2013) which are based on literature values. Offtake values not included in Dunn et al. (2013) such as carrots and cabbages were derived from DEFRA (2010) and Sylvester-Bradley (1993). Offtake values are shown in appendix B.2 for all crops.

Nitrogen deposition was set at 8 kg ha^{-1} yr^{-1} for all land uses and mineralisation values were derived according to land use as per the NIRAMS model (Dunn et al., 2004). Denitrification values were based on HOST soil classes so that freely draining soils had minimal fertiliser nitrification, soils that were periodically waterlogged had 20% fertiliser denitrification and soils with water logging for large periods of the year had 35% fertiliser denitrification. This is based on work by Vinten (1999) and has been adapted to be based on HOST soil classes from the NIRAMS model (Dunn et al., 2004).

4.3.4 Sediment source

The erosion methodology combines both the source and mobilisation components in one method and is therefore outlined in section 4.4.4.

4.4 Mobilisation methodologies

Mobilisation methodologies differ for each of the pollutants, however to maintain model consistency hydrological inputs to each of the different methods are based on the same field water balance model.

4.4.1 Field scale soil water balance modelling

A 1D soil water balance model, WaSim (Hess and Counsell, 2000), is used to generate ‘runoff’ and ‘drainflow’ values for each soil, land use and drainage combination (herein referred to as a ‘field’). WaSim was chosen for its simplicity in implementation and transparency in model inputs. The model has also been proven successful at partitioning rainfall into both quick flow and slow flow responses in UK catchments (e.g. Hess et al., 2010; Holman et al., 2011) which is its primary function within CaRPoW.

A simplified description of the model for the purposes of CaRPoW is presented below. More detailed descriptions of the model are given by Hess and Counsell (2000), Holman et al. (2011) and Warren and Holman (2011).

WaSim splits the soil column into 5 segments. When the soil moisture content exceeds field capacity water drains from upper to lower segments. Surface runoff includes both infiltration excess (as determined by the SCS curve number method) and saturation excess runoff. If drains are present drainflow occurs when the water table rises above the depth of drains. In the traditional model set up recharge is determined as the water moving from the bottom compartment in freely draining soils without drains. However in CaRPoW undrained soils are set up with wide spaced, deep drains to represent the slow flow component. Water is removed from the soil via actual evapotranspiration (soil evaporation and plant transpiration) using the methods of Ritchie (1972), Allen et al. (1998) and Brisson (1998). The model is illustrated by the diagram in Figure 4.1.

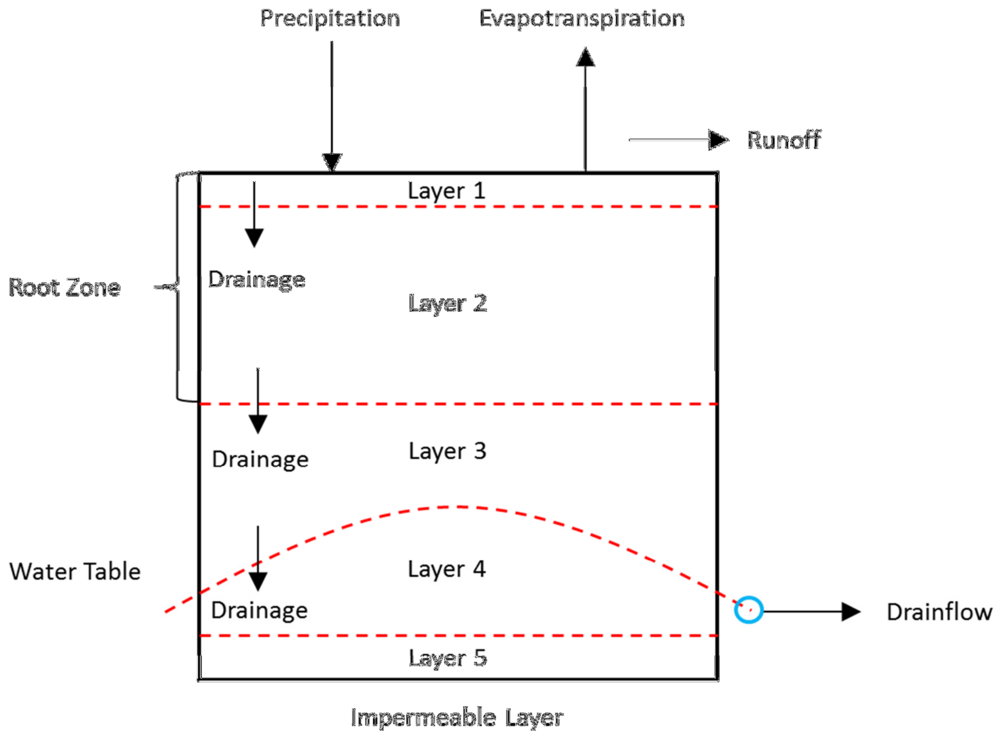


Figure 4.1 - Illustration of the WaSim water balance model used in CaRPoW (adapted from Hess and Counsell, 2000 and Warren and Holman, 2011)

The two climate inputs WaSim requires are daily rainfall and potential evapotranspiration. A simple method of calculating potential evapotranspiration with limited input parameters was required for applicability to most areas. The temperature based method outlined by Oudin et al. (2005) (equation 4.16 and 4.17) was chosen for this reason and also because it has been validated against Met Office MORECS data by Kay and Davies (2008).

$$PE_t = \frac{R_e}{\lambda\,\rho_w}\,\frac{T_a+5}{100} \quad \text{if} \quad T_a + 5 > 0 \tag{4.16}$$

$$PE_t = 0 \quad \text{if} \quad T_a + 5 < 0 \tag{4.17}$$

Where PE_t is Potential Evapotranspiration (mm day^{-1}), R_e is extra-terrestrial radiation (MJ m^2 day^{-1}), λ is the latent heat flux (set as 2.45 MJ kg^{-1}), ρ_w is the density of water (set as 1000 kg m^{-3}) and T_a is the mean daily air temperature (˚C). Note that all negative PET values are set to zero in this method.

To use the equation above R_e was calculated using the method outlined by Allen et al. (1994) (equations 4.18 to 4.21).

$$R_e \;= 37.6\, d_r\, (\omega_s \sin\varphi_l \sin\delta + \cos\varphi \cos\delta \sin\omega_s) \tag{4.18}$$

Where R_e is total daily extra-terrestrial radiation (MJ m^{-2} d^{-1}), d_r is the relative distance to the Earth, δ is the solar declination, φ_l is the latitude and ω_s is the sunset hour angle (rad)

$$\omega_s = \arccos(-\tan\varphi \tan\delta) \tag{4.19}$$

$$d_r \;= 1 + 0.033 \cos\left(\frac{2\pi}{365}J\right) \;=\; 1.0.033 \cos\,(0.0172\;\mathrm{J}) \tag{4.20}$$

$$\delta = 0.409\, sin\left(\frac{2\pi}{365}J - 1.39\right) = 0.409 \sin(0.0172\, J - 1.39) \tag{4.21}$$

Where J is the Julian Day.

All of the WaSim model parameter inputs are detailed in appendix B.3 including ‘Crops’, ‘Soil’, ‘Drainage’ and ‘Soil Curve Number’.

The 30 year daily output for each field from WaSim is manipulated into a few key monthly parameters to be used in the pesticide fate model. The R statistical programming language (R Core Team, 2014) is used to derive the parameters in Table 4.3.

Table 4.3 – Derived average monthly values extracted from the 30 year WaSim model run used in the CaRPoW mobilisation methodologies

Parameter	Unit	Description
Total Average Monthly Runoff	mm	Average monthly runoff (saturated and infiltration excess)
Total Average Monthly Drainflow	mm	Average total monthly slow flow component (drainflow in drained soils and recharge in freely drained soils)
Total Average Monthly HER	mm	Average total monthly Hydrological Effective Rainfall (Runoff + Drainflow)
Total Average Monthly Rainfall	mm	Average total monthly rainfall
Total Average Monthly AET	mm	Average total monthly actual evapotranspiration
Days to Runoff	days	Average number of days per month between runoff events
Days to Drainflow	days	Average number of days per month between drainflow events
Runoff Proportion	proportion (0-1)	Proportion of total HER as runoff
Drainflow Proportion	proportion (0-1)	Proportion of total HER as drainflow
Topsoil Water Content	$cm^3\ cm^{-3}$	Average topsoil water content per month

4.4.1.1 Selection of wet and dry years

All hydrological inputs to the CaRPoW mobilisation and delivery methodologies are therefore based on total monthly values averaged from a daily 30 year model run. It is also important to assess the differences in model outputs between wet and dry rainfall years as well as the average to determine potential uncertainty ranges based on the hydrological inputs to the pollutant models.

The same 30 year WaSim input rainfall dataset is used to assess the thresholds for what are considered wet and dry years within the catchment. Initially the distribution of total annual rainfall for the period of the record is assessed to make sure there is a relatively normal distribution of total annual rainfall. The years are grouped in 100mm incremental rainfall classes from the minimum to the maximum. An example of binned rainfall data overlain by a normal distribution curve are shown in Figure 4.2.

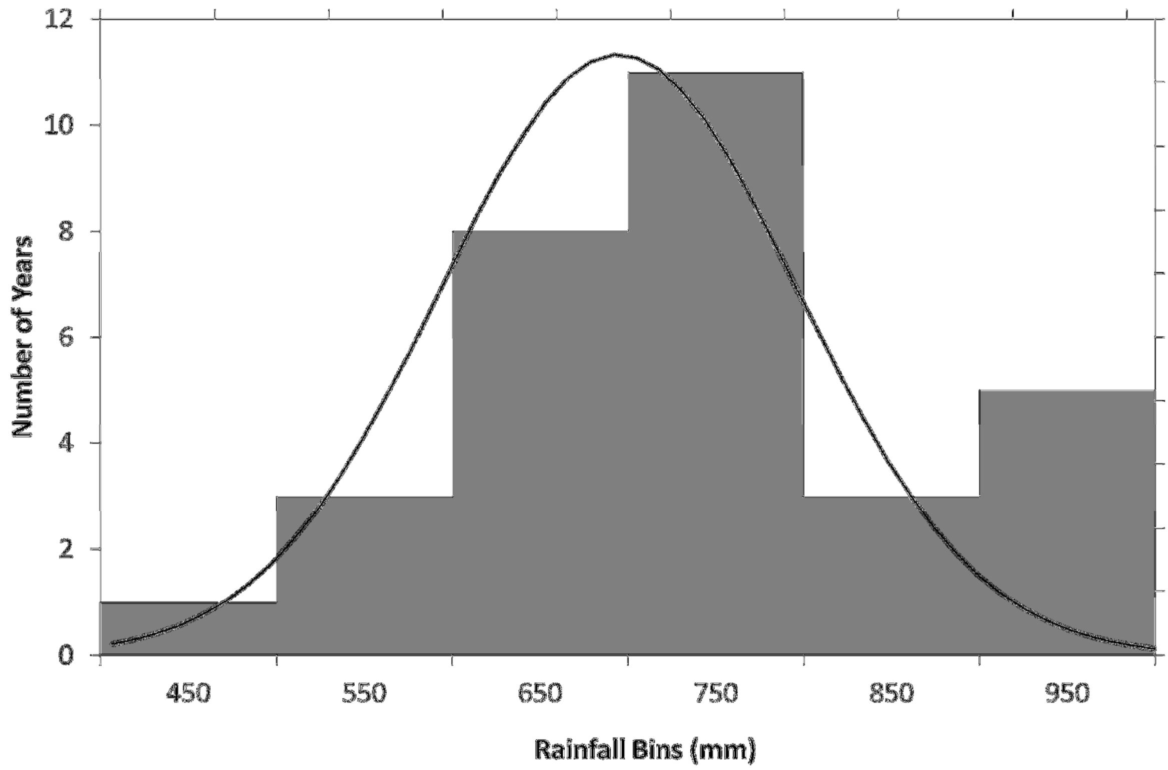


Figure 4.2 - Example rainfall distribution (Forehill rain gauge, Peterhead, UK) with normal distribution curve overlay. Rainfall has been grouped in 100 mm classes by year.

Wet years and dry years are selected according to which matches the top and bottom 20th percentiles closest respectively.

4.4.2 Pesticide mobilisation

Pesticide mobilisation is based on the pesticide fate component of the SWATCATCH (not to be confused with the Soil Water Assessment Tool) methodology of Brown and Hollis (1996) and the methodology of Pullan (2014) (which is an update of

SWATCATCH). Both methodologies assess the movement of pesticides within soil water following mobilisation via hydrologically effective rainfall on a daily time step.

Within the CaRPoW pesticide mobilisation methodology the concepts of SWATCATCH are adapted to create a monthly assessment of pesticide mobilisation based on the first effective rainfall event after pesticide application. This is on the premise that the first effective rainfall event is the most important for pesticide mobilisation (e.g. Louchart et al., 2001; Guo et al., 2004), an assumption that is tested in Chapter 5.

The overall equation (4.22) multiplies the concentration of the pesticide in the soil water, by the volume of water mobilised within the soil to give a mass flux of pesticide per month per hectare.

$$MobilisedFlux_t = C_{int}.V_{mob} \tag{4.22}$$

Where $MobilisedFlux_t$ is the mobilised flux (µg ha^{-1} month^{-1}), C_{int} is the concentration of pesticide in the interactive water zone at the time of the first runoff event (µg l^{-1}) and V_{mob} is the volume of water mobilised based on average soil water content values halfway between field capacity and saturation (l ha^{-1} month^{-1}).

The concentration of the pesticide in the soil water at the time of mobilisation is a function of its degraded mass at time t and the water content of the interactive fraction of the soil.

$$C_{int} = \frac{PestMassCoef_{sol}t}{\theta_{int}.d_{tRO}} \tag{4.23}$$

Where $PestMassCoef_{sol}t$ is the mass of pesticide in solution after degradation (µg), θ_{int} is the interactive soil water content (cm^3 cm^{-3}) and d_{tRO} is the depth penetrated in the soil before runoff event (mm).

The mass of pesticide available at time of mobilisation is the soluble source term from the pesticide source methodology multiplied by a degradation factor. To maintain model simplicity it is assumed that all pesticide applied is either degraded or mobilised within each month, i.e. there is no carry over.

$$PestMassCoef_{sol}t = (1 \,.\, Degradation) \tag{4.24}$$

Where $PestMassCoeff_{sol}t$ is a coefficient representing the mass of pesticide left in the soil after degradation and $Degradation$ is a coefficient derived from equation 4.25 to represent the mass of pesticide degraded before the first runoff event.

$$Degradation = e^{Avgt_{days}\left(\frac{-ln(2)}{DT_{50}}\right)} \tag{4.25}$$

Where DT_{50} is the half life of the pesticide (days), Avg_t is the mean number of days between application and first effective rainfall event per month (days).

To maintain model simplicity it is assumed that at the time of runoff or drainflow the soil moisture content is set half way between field capacity and saturation for every event. The reason for doing this is it is difficult to represent the variability in antecedent conditions for each drainflow and runoff events using the averaged WaSim model outputs. Therefore the interactive water fraction is the difference between the soil water content between field capacity and saturation and the water content at permanent wilting point.

$$\theta_{int} = \left(\frac{\theta_{fc} + \theta_{sat}}{2}\right) - \theta_{pwp} \tag{4.26}$$

Where θ_{int} is the water content of the interactive soil water ($cm^3\ cm^{-3}$), θ_{fc} is the soil water content at field capacity ($cm^3\ cm^{-3}$), θ_{sat} is the soil water content at saturation ($cm^3\ cm^{-3}$) and θ_{pwp} is the soil water content at permanent wilting point ($cm^3\ cm^{-3}$).

The depth penetrated by the pesticide is a function of the time between application and mobilisation, the unsaturated hydraulic conductivity (calculated using equation 4.27) and a retardation factor (4.31) (Brown and Hollis, 1996 and Pullan, 2014).

$$d_{tRO} = t.\left(\frac{K(\theta_t)}{RF_t}\right) + 2 \quad (4.27)$$

Where d_{tRO} is depth penetrated before runoff event (mm), t is the average time between application and runoff event per month (days), $K(\theta_t)$ is the hydraulic conductivity at field capacity (mm day^{-1}) and RF_t is the retardation factor (Unitless).

The hydraulic conductivity at field capacity is calculated after van Genuchten (1980) as:

$$K(\theta_t) = K_{sat}.\theta_{*fc}{}^{0.5}.\left[1 - \left(1 - \theta_{*fc}{}^{\frac{1}{m}}\right)^{m}\right]^{2} \quad (4.28)$$

Where $K(\theta_t)$ is the unsaturated hydraulic conductivity of the soil (mm day^{-1}), θ_{*fc} is the dimensionless water content at field capacity (-), m is a dimensionless curve number and K_{sat} is the saturated hydraulic conductivity (mm day^{-1}).

The dimensionless curve number m is calculated using equation 4.29 after van Genuchten (1980)

$$m = 1 - \left(\frac{1}{n}\right) \quad (4.29)$$

Where n is the dimentionless van Genuchten parameter related to soil type.

The dimensionless water content at field capacity can be calculated from equation 4.30.

$$\theta_{*fc} = \frac{\left(\frac{\theta_{fc} + \theta_{sat}}{2}\right) - \theta_r}{\theta_{sat} - \theta_r} \quad (4.30)$$

Where θ_{*fc} is the dimensionless water content at field capacity, θ_{fc} is the water content of the topsoil at field capacity (cm^3 cm^{-3}), θ_{sat} is the water content at soil saturation (cm^3 cm^{-3}) and θ_r is the water content at residual water content (assumed as 0.5 x θ_{pwp}) (cm^3 cm^{-3})

The unitless retardation factors accounts for any further sorption of the pesticide as it penetrates further into the soil column and is a factor of the pesticides sorption characteristics (adapted from Brown and Hollis, 1996).

$$RF_t = 1 + \left(\frac{K_{oc.}F_{oc.}p_b}{\theta_{int}}\right) \tag{4.31}$$

Where RF_t is the unitless retardation factor, K_d is the sorption coefficient of the pesticide (l kg^{-1}) and p_b is the bulk density of the top soil (g cm^{-3}).

The volume of water mobilised in the soil is dependent on the volume of the mobile fraction, the depth the pesticide has penetrated in the soil and the ratio between the unsaturated hydraulic conductivity and the saturated hydraulic conductivity (after Pullan, 2014).

$$V_{mob} = \theta_{mob}.d_{tRO}.\frac{K(\theta_{fc})}{K_{sat}} \tag{4.32}$$

Where V_{mob} is the volume of water mobilised (l day^{-1}), $K(\theta_t)$ is the unsaturated hydraulic conductivity (mm day^{-1}), K_{sat} is the saturated hydraulic conductivity (mm day^{-1}), θ_{mob} is the mobilised soil water content (cm^3 cm^{-3}) and d_{tRO} is the penetrated depth between application and mobilisation (mm).

The mobilised water content is calculated as the difference between the assumed water content at time t (month) and the water content at 200 KPa.

$$\theta_{mob} = \left(\frac{\theta_{fc} + \theta_{sat}}{2}\right) - \theta_{200} \tag{4.33}$$

Where θ_{mob} is the water content of the soil mobilised ($cm^3\ cm^{-3}$) and θ_{200} is the water content of the soil at 200 KPa ($cm^3\ cm^{-3}$).

4.4.3 Phosphorus mobilisation

The different nature of the phosphorus sources represented in CaRPoW (soluble vs particulate, within the soil vs. applied to soil) makes it difficult to represent mobilisation of the four sources using one methodology. Other phosphorus models that attempt to represent the source-mobilisation-delivery continuum such as the Phosphorus Indicators Tool (Heathwaite et al., 2003) and the PSYCHIC model (Davison et al. 2008) therefore keep the different source and mobilisation methodologies separate. In keeping with this CaRPoW also separates them so that transparency in the drivers of phosphorus risk is maintained.

4.4.3.1 Particulate phosphorus

To maintain model consistency the most appropriate methodology to represent phosphorus mobilisation is to use the same Modified Morgan-Morgan-Finney (MMMF) erosion modelling approach that has been adopted in the suspended sediment methodology.

This approach therefore simply takes the total phosphorus source potential and multiplies it by the amount of eroded soil per year as determined by MMMF (section 4.4.5).

$$PP = TP_{soil} \, . Sed_{mob} \tag{4.34}$$

Where PP is the annual loss of particulate phosphorus per field (kg), TP_{soil} is the mass of total phosphorus contained in the top soil (kg $tonne^{-1}$) and Sed_{mob} is the total mass of soil eroded per field (tonnes).

This methodology has been used successfully on a monthly time step in the PSYCHIC model (Strömqvist et al. 2008; Davison et al. 2008).

4.4.3.2 Soluble phosphorus in soil water

The mobilisation of soluble phosphorus held within the soil follows the PSYCHIC model methodology of Davison et al. (2008). Firstly the soil Olsen P source is converted to a concentration in runoff and drainflow using the relationship in equation 4.35 derived by Flynn and Withers (2001).

$$SP_{conc} = 40(OlsenP)^{0.33} \tag{4.35}$$

Where SP_{conc} is the concentration of soluble P from soil water in runoff or drainflow (µg l^{-1}).

This Figure is then multiplied by runoff or drainflow to give a load of exported soluble P.

$$SP_{runoff} = SP_{conc} . Q_{runoff} . 10^{-9} \tag{4.36}$$

$$SP_{drainflow} = SP_{conc} . Q_{drainflow} . 10^{-9}. Drain_{coeff} \tag{4.37}$$

Where SP_{runoff} and $SP_{drainflow}$ are the mobilised soluble P in runoff and drainflow respectively (kg), Q_{runoff} and $Q_{drainflow}$ are the discharge values for runoff and drainflow respectively (mm). For the drainflow equation an additional attenuation factor is included to represent further attenuation of P during the movement of soluble P from soil water to drain. In CaRPoW $Drain_{coeff}$ is set at 0.1 after Davison et al. (2008).

4.4.3.3 Soluble Incidental phosphorus mobilisation from fertiliser and excretal phosphorus

The final two P sources considered in CaRPoW are incidental losses from fertiliser and manure, i.e. losses directly from fertiliser and excreted manure with the onset of rainfall driven runoff and drainflow processes.

A method is therefore required that accounts for any degradation and incorporation of these sources before they are mobilised as well as the calculation of an actual coefficient of mobilisation. Within PSYCHIC (Davison et al., 2008) an attempt is made to account for the assumed exponential degradation/incorporation of P from fertiliser and manure by deriving a P 'half-life' related to cumulative rainfall. However, because of the high uncertainty in the timing of fertiliser and excretal phosphorus application at the monthly scale, this methodology was deemed unsuitable.

An alternative methodology that has been developed for an annual time frame is the methodology presented by Vadas et al. (2009), known as the Annual Phosphorus Loss Estimator. This model provides a medium between the simplistic approaches of PIT for example and the more complex physically based approach of PSYCHIC.

It utilises annual rainfall and runoff values combined with a distribution factor to output a value for the amount of P lost in runoff from manure and fertiliser. The equations for both manure and fertiliser are shown in equations 4.38 and 4.39.

$$IncidentalP_{manure} = P_{manure} \,.\, (R_{annual} / Q_{annual}).\, Dist_{manure} \qquad (4.38)$$

$$IncidentalP_{fertiliser} = P_{fertiliser} \,.\, (R_{annual} / Q_{annual}).\, Dist_{fertiliser} \qquad (4.39)$$

Where $IncidentalP_{manure/fertiliser}$ is the incidental loss of P (kg ha^{-1} yr^{-1}), $P_{manure/fertiliser}$ is the P source content of manure/fertiliser (kg ha^{-1} yr^{-1}), R_{annual} is total annual rainfall (mm^{-1}), Q_{annual} is the total annual runoff (mm^{-1}) and $.Dist_{manure/fertiliser}$ is the distribution factor between runoff and infiltration. The distribution factors are calculated using equations 4.40 and 4.41 after Vadas et al. (2007) and Vadas et al. (2008).

$$Dist_{manure} = (Q_{annual}/R_{annual})^{\,0.225} \qquad (4.40)$$

$$Dist_{fertiliser} = 0.034 \,.\, e^{3.4\,.(Q_{annual}/R_{annual})} \qquad (4.41)$$

4.4.4 Nitrate mobilisation

The N mobilisation methodology must represent a coefficient of mobilisation for the available N at the end of the growing season as determined by the N balance of the source methodology.

The work undertaken by Dunn et al. (2004, 2013) in Scotland for a distributed Nitrogen model uses an equation from the NLEAP model (Shaffer et al., 1994) to represent the proportion of available N lost via leaching.

This therefore assumes that N is only lost via leaching processes i.e. slower, through the soil drainage. This is based on the general conceptualisation in the literature that available N is held within the soil pores in solution and therefore any mobilisation is driven by slower processes through the soil as faster hydrological processes bypass stored soil water (Quinn, 2004; Granger et al., 2010).

The equation derived from the NLEAP methodology for N loss via leaching is shown in equation 4.42.

$$N_{mob} = 1 - (e^{-KNL\,.\,(\frac{Q_{drain}}{\theta_{sat}})}) \tag{4.42}$$

Where N_{mob} is the coefficient of N mobilisation (-),KNL is a leaching coefficient set at 0.7 for Scottish conditions by Dunn et al. (2004) although the standard set figure for the NLEAP method of 1.2 is also tested, Q_{drain} is the total drainage in the winter period following the growing season (mm) and θ_{sat} is the water content of the soil at saturation (mm).

4.4.5 Sediment mobilisation

The Modified Morgan-Morgan-Finney (MMMF) model (Morgan, 2001, Morgan and Duzant, 2008) has been selected as the best way of representing soil erosion in the methodology because of its level of suitable process presentation and application to British conditions (Davison et al., 2008). The MMMF comprises two forms of soil erosion, that by rain drop action and that by runoff shear. The calculation of erosion by raindrop action adheres to the full methodology of the MMMF. However to align modelling methods and keep simplicity the runoff input to the erosion model is based on the runoff values as modelled by WaSim as opposed to the runoff methodology used in the MMMF model.

Using mean values of rainfall over the period for an average year, a selected dry and a selected wet year the effective rainfall is calculated as per equation 4.43.

$$Rf = R(1 - PI)\frac{1}{cosS} \quad (4.43)$$

Where Rf is effective rainfall (mm), R is mean total monthly rainfall (mm), PI is potential interception (proportion between zero and one) and S is slope (degrees). Interception (PI) is based on average values derived from Morgan and Duzant (2008). It must be noted that values for PI are likely to be variable for crops between months, thus PI may be over or under estimated for both the cereal type and row crops land uses as the PI values derived from Morgan and Duzant (2008) are based on averages over the growing period. PI values for the generalised land use classes are averaged from the different vegetation types in each class from Morgan and Duzant (2008), these values are shown in Table 4.4.

Table 4.4 - Variables by land use used in the MMMF (Modified Morgan Morgan Finney) soil erosion model (adapted from Morgan and Duzan, 2008)

Land Use Class	PI	CC	PH
Cereal Type	0.38	0.75	1
Grassland	0.28	0.85	0.1
Semi-Natural	0.26	0.82	0.4
Woodland	0.25	0.96	27.5
Row Crops	0.16	0.6	0.7

Effective rainfall is partitioned between direct throughfall (DT; mm) and leaf drainage (LD; mm). Leaf drainage is determined by the proportion of effective rainfall intercepted by the vegetation canopy (equation 4.44).

$$LD = Rf\ CC \tag{4.44}$$

Where CC is the proportion of canopy cover from 0-1. Canopy cover values have been averaged from Morgan and Duzant (2008) using the same land use groupings as for PI (Table 4.4). Direct throughfall is therefore the proportion of effective rainfall that is not accounted for by leaf drainage.

$$DT = Rf - LD \tag{4.45}$$

Kinetic energy for both DT and LD are calculated using empirically derived equations for UK conditions. The kinetic energy of DT is based on work by Marshall and Palmer (1948).

$$KE(DT) = DT(8.95 + 8.44\ log_{10}I) \tag{4.46}$$

Where $KE(DT)$ is the kinetic energy of DT and I (mm hr^{-1}) is the intensity of rainfall which is set at 10 mm hr^{-1} for the UK.

Kinetic energy of LD is derived as a function of plant height (PH) using techniques developed by Brandt (1990). Plant height values are again derived from averages for the land use classes (Table 4.4). If plant height is below 0.15 m KE(LD) is assumed to be negligible.

$$for\ PH < 0.15 \quad KE(LD) = 0 \tag{4.47}$$

$$for\ PH > 0.15 \quad KE(LD) = (15.8\ x\ PH^{0.5}) - 5.87 \tag{4.48}$$

Total kinetic energy of effective rainfall is therefore an addition of KE(DT) and KE(LD)

$$KE = KE(LD) + KE(DT) \tag{4.49}$$

Particle detachment is a function of both detachment by raindrop and detachment by runoff. In the updated MMMF rain drop detachment is a function of three separate equations according to the sand, silt and clay content of the soil, the stone cover on the ground and the kinetic energy of effective rainfall (Morgan and Duzant, 2008). Data on these mineral soil properties are not available for all soil types however. Therefore the original methodology of Morgan (2001) is used with parameter values from Davison et al. (2008) (Table 4.5).

$$F_{org} = K\ x\ KE\ x\ 10^{-3} \tag{4.50}$$

Where F_{org} is the detachment of soil by raindrop (kg m-^{2}) and K is the erodibility of the soil (g J^{-1}) (as per Davison et al., 2008, Table 4.5).

Table 4.5 - Variables by soil texture class used in the Modified Morgan Morgan Finney (MMMF) soil erosion model (adapted from Morgan, 2001 and Davison et al., 2008)

Soil Texture Class	K	COH
Sand	1.2	2
Loamy sand	0.3	2
Sandy loam	0.7	2
Loam	0.8	3
Silt	1	(-)
Silt loam	0.9	3
Sandy clay loam	0.1	3
Clay loam	0.7	10
Silty clay loam	0.8	9
Sandy clay	0.3	(-)
Silty clay	0.5	10
Clay	0.05	12
Organic	0.8	9

Detachment by runoff in the MMMF is again dependant on the sand, silt and clay concentrations, thus the original method is employed.

$$H_{org} = ZQ^{0.5} \sin S(1 - GC)\, 10^{-3} \tag{4.51}$$

Where H_{org} is the detachment of sediment by runoff shear (kg m^{-2}), Z is a factor that accounts for the detachability of soils and is derived using equation 4.52, Q is the total annual runoff (mm), S is the slope angle (degrees) and GC is ground cover (unitless proportion from 0-1).

$$Z = \frac{1}{(0.5\ COH)} \tag{4.52}$$

Where COH is the cohesivity of soils (kPa) using values according to Davison et al. (2008) (Table 4.5).

Total soil detachment is derived from the addition of detachment by raindrop and runoff.

$$Erosion = F + H \tag{4.53}$$

All eroded material mobilised within the field is not likely to be mobilised to the edge of the field and may be subject to deposition within the field. To account for this a deposition term is introduced based on the equations developed in Morgan and Duzant (2008). To maintain model simplicity the bare soil deposition equations were implemented in CaRPoW for all land use types as knowledge on soil tillage practices was not available on a field by field basis. Initially the flow velocity of runoff is calculated using equation 4.54.

$$v = \frac{1}{n}\, d^{0.67} S^{0.5} \tag{4.54}$$

Where v is the flow velocity, n is the mannings roughness coefficient (set at 0.015 as per Morgan and Duzan, 2008), d is the depth of flow (set at 0.005 m as per Morgan and Duzan, 2008) and S is the slope of the field.

Using this flow velocity value the particle fall number is calculated for each soil particle class (silt, sand and clay) using equations 4.55.

$$N_f(c,z,s) = \frac{l\, v_s(c,z,s)}{v\, d} \tag{4.55}$$

Where l is length of the slope (set to 1 metre in CaRPoW) and $v_s(c,z,s)$ is the fall velocity of clay, silt and sand (m s^{-1}) set at 0.000002 m s^{-1}, 0.00006 m s^{-1} and 0.0002 m s^{-1} respectively.

The overall percentage deposition of each particle class is therefore calculated using the relationship obtained by Tollner et al. (1976) in equation 4.56.

$$DEP(c,z,s) = 44.1(N_f(c,z,s))^{0.29} \tag{4.56}$$

Due to the lack of soil mineral property data the deposition term is averaged over the three particle sizes.

$$DEP = \frac{\sum N_f(c,z,s)}{3} \tag{4.57}$$

This equation can give values over 100% which in reality are impossible; thus maximum values are set to 100%.

Total sediment eroded and transported in runoff is therefore calculated using equation 4.58.

$$TotErosion = \ Erosion\,(1 - \left(\frac{DEP}{100}\right)) \tag{4.58}$$

The transport capacity of the runoff is calculated to account for the ability of runoff process to transport detached material. It is derived using equation 4.59.

$$TC = (1 - GC)Q^2 \sin S \, 10^{-3} \tag{4.59}$$

Where TC is the transport capacity of the runoff (kg m^{-2}).

The overall erosion rate for the field is the lowest value of the total detachment and the transport capacity of runoff, so that the limiting factor i.e. detachment or transport is accounted for (Morgan, 2005).

Within the CaRPoW methodology mobilised sediment is directed in runoff or via sub-surface preferential flow (artificial drainage). Using the methodology developed in Davison et al. (2008) eroded sediment is assigned a pathway according to the proportion of rainfall directed as flow in each pathway (from WaSim), see equations 4.60 and 4.61.

$$Erosion_{RO} = Erosion \, . \frac{Q_{RO}}{R} \tag{4.60}$$

$$Erosion_{Drain} = Erosion \, . \frac{Q_{Drain}}{R} \, . \propto_{SedDrain} \tag{4.61}$$

.

Where $Erosion_{RO}$ and $Erosion_{Drain}$ represent eroded sediment mobilised in runoff and drainflow respectively (kg). Q_{RO} and Q_{Drain} flow volume in runoff and drainflow (mm), R is rainfall (mm) and for drainflow an extra coefficient ($\propto_{SedDrain}$) is added to represent sediment entrainment in the soil structure (set at 0.2).

4.5 Delivery/Connectivity

Once pollutants are mobilised in the field, flow is routed to the hydrographic network using a travel time approach as a measure of connectivity. The premise being that the faster any water containing mobilised pollutants can be delivered to the river network the less time it has to degrade and attenuate in the catchment, and the higher the risk of delivery.

The approach used for integrating travel time into a connectivity measure is similar to the approach adopted by Buchanan et al. (2013). The travel time approach is based on the integration of the kinematic wave approximation with Manning's n. This is implemented with principles of Variable Source Area hydrology so that more runoff is directed to the wetter parts of the catchment. The travel time approach was selected over other methodologies because of its inclusion of the Manning's roughness coefficient, which allows for adaptability when including barrier and enhancement features within the landscape.

The WaSim model used in the mobilisation section has already derived runoff values using the curve number method for each field. Assuming that saturation is driven by topography a topographic wetness index can be used to spatially distribute the WaSim runoff output into wetness classes so that the runoff is proportioned to those areas of the field most likely to generate the highest proportion of runoff.

Topographic wetness index is based on the TOPMODEL index with K_{sat} substituted in for transmissivity (as per Buchanan et al., 2013) (equation 4.62).

$$\lambda = \ln\left(\frac{\alpha}{K_{sat}.D\,.\tan\beta}\right) \tag{4.62}$$

Where λ is the topographic wetness index (unitless), α is the upslope contributing area (m^2), K_{sat} is the saturated hydraulic conductivity of the soil (m day^{-1}), D is the depth of the soil (set at 1 metre in this instance) and β is the topographic slope (m m^{-1}).

The sum of λ is calculated for each field. The number of cells in each field is also calculated in the field calculator by dividing the area of the field by the area of one grid cell.

WaSim runoff is then distributed to wetness classes within each field using equation 4.63.

$$Q_{dist} = \left(\frac{Q\,\lambda}{\sum \lambda_{Field}}\right) \tag{4.63}$$

Where Q_{dist} is the distributed WaSim Runoff (m) and λ_{Field} are topographic index values within a field.

The travel time for each cell is computed from the integrated kinematic wave approximation and Manning's equations (e.g. Melesse and Graham, 2004; Buchanan et al., 2013). Firstly the runoff value equated from equation 4.63 needs to be converted to a flow velocity as per equation 4.64.

$$q = \frac{Q_{dist}}{t} \tag{4.64}$$

Where q is the flow velocity over the cell (m s^{-1}) and t is the period of the record i.e. one year (s). It is important to note that at an annual timescale (as in CaRPoW) equation 4.64 will give unrealistic flow velocity values. However the final travel time approach is normalised and therefore connectivity is relative within the catchment.

$$TT_i = \frac{L^{0.6} n^{0.6}}{q^{0.4} \beta^{0.3}} \tag{4.65}$$

Where TT is the travel time across each cell i (s^{-1}), L is the length travelled (i.e. cell size), n is the Manning's coefficient and q is the flow velocity (m s^{-1}).

Manning's roughness values are varied for each land use class and also for finer detailed barrier and enhancement features present in the catchment. For example, barrier features at the edge of fields that could potentially slow flow have a higher Manning's n than urban areas where flow is likely to be quickly propagated. Values for Manning's roughness have been derived from Chow (1959) and are detailed in Table 4.6.

Table 4.6 – Manning's roughness values (Chow, 1959) for CaRPoW mobilisation land use classes

CaRPoW Mob	Manning's N	Related Land Cover from Chow (1959)
Winter Cereals	0.04	Normal mature field crops
Spring Cereals	0.04	Normal mature field crops
Grassland	0.03	Normal short grass
Semi-Natural	0.06	Normal Light Brush with some trees
Woodland	0.1	Normal heavy stand of timber, a few down trees, little undergrowth, flood stage below branches
Row Crops	0.035	Normal mature row crops
Roads or Man Made Surface	0.016	Normal smooth asphalt
Urban	0.016	Normal smooth asphalt
Boundary Barriers	0.07	Normal medium brush, winter
Unclassified	0.03	Normal short grass

The measure of connectivity is the cumulative travel time along each flow path. This is done by altering the flow path length of each cell to the river network with the travel time function as the weighting (Equation 4.66).

$$Connectivity = \sum TT \, . \, FlowPathLength \tag{4.66}$$

Where $FlowPathLength$ is the length along the flow path of each cell to the river (m).

The connectivity metric is normalised from 0-1 to create a unitless coefficient in the final risk equation.

4.6 Final risk

The calculation of the final risk for each pollutant in each field is a simple multiplication of the three component modules (as per equation 4.67).

$$Risk_t = Source_t \,.\, MobilisedCoef_t \,.\, Connectivity \tag{4.67}$$

Where $Risk_t$ is the risk (g ha^{-1} yr^{-1}) and $Source_t$ is the mass of pollutant source (g ha^{-1} yr^{-1}).

4.7 Conclusions

This chapter has outlined the modelling methodologies developed to fit within the CaRPoW framework for pesticides, phosphorus, nitrate and sediment. Source methods relate to potential load of a pollutant in the catchment and have been either newly developed (pesticides) or adapted from other methodologies in the literature (phosphorus, nitrate and sediment). The hydrological component of all of the mobilisation methodologies has been based on derived average monthly outputs from the 1D soil water balance model set up for every field (unique combinations of soil, land use and drainage characteristics). At the same time a method to extract the hydrological characteristics of representative wet years and dry years has been outlined. The pesticide mobilisation methodology is based on an adapted version of the SWATCATCH model (Brown and Hollis, 1996; Pullan, 2014) that assesses the mobilisation of pesticides in the first hydrological event following application. This is based on the assumption that the first hydrological event is the most important for pesticide mobilisation. Phosphorus mobilisation methodologies are split three ways depending on the phosphorus source, with the methodology from the PSYCHIC model (Davison et al., 2008) adapted for soil soluble phosphorus and soil particulate phosphorus, and the APLE model Vadas et al. (2009) used for incidental soluble phosphorus mobilisation from fertiliser and manure. Sediment mobilisation is based on the Modified Morgan-Morgan-Morgan-Finney model (Morgan, 2001; Morgan and Duzan, 2008). The delivery component uses the same methodology for all pollutants and is based on an adapted version of the Travel Time Approach (Melesse and Graham, 2004; Buchanan et al., 2013). The approach was selected because of the inclusion of Manning's roughness values that allow barrier features in the landscape to impact on connectivity. Finally the overall risk calculation is presented which multiplies the source load by the modelled mobilisation and delivery coefficients to provide a total risk load for each field in a catchment.

Chapter 5. Application of CaRPoW modelling methodologies in the River Ugie to determine multiple pollutant risks

5.1 Introduction

Chapter 5 applies the methods outlined in Chapter 4 to a case study catchment, the River Ugie in the North East of Scotland. The chapter starts by describing the characteristics of the River Ugie catchment and its water quality issues. Catchment specific data inputs required that were not outlined in Chapter 4 are identified and outlined. The practical implementation of CaRPoW is briefly outlined along with the methods used to validate the models. Results are presented for the 4 pollutant groupings modelled and validated against spatially distributed pollutant loading data. The ability of the models to represent both spatial and temporal loads in the catchment are discussed and explanations explored where there are discrepancies.

The chapter is structured as follows:

- 5.2 The River Ugie Catchment – a description of the characteristics and water quality issues in the Ugie catchment.
- 5.3 Sources and Selection of Model Input Data – Input data to the model are outlined and any data assumptions justified.
- 5.4 Implementation of CaRPoW – a practical description of how CaRPoW has been implemented in the Ugie
- 5.5 Model validation methodology– an outline of the methods employed to validate the CaRPoW modelling methodologies against hydrological and water quality data.
- 5.6 Model results and discussion – Model results are presented and discussed for the water balance model component, the validation of the pesticide fate model assumptions and the ability of the models to replicate total and spatial pollutant load.
- 5.6 Conclusions – Provides a conclusion to the chapter

5.2 River Ugie catchment

5.2.1 Catchment characteristics

The River Ugie catchment is situated in the North East of Scotland approximately 40 km to the north of Aberdeen (Figure 5.1). The catchment drains an area of 335 km^2 from West to East, where it flows into the North Sea at the town of Peterhead. The river is split into two main branches, the North and South Ugie, which confluence approximately 10km to the west of Peterhead (SEPA, 2011). The catchment is low lying with a maximum elevation of 235m in the headwaters, making the catchment characteristic of a lowland river system.

Land use is split between intensive grassland and arable agriculture, with some patches of managed forestry and rough grazing. Soil types are strongly characterised by parent material, which accounts for the diverse range of soil types found in the catchment. To the west of the catchment where elevations are highest soils are dominated by the Countesswells, Foudland and Hatton associations, which have parent materials of granitic glacial till, argillaceous schist and red sandstone till respectively. Countesswells and Foudland mainly comprise free draining iron podzols and non-calcareous gleys whereas Hatton consists of iron podzols, non-calcareous gleys, peaty gleys and brown forest soils. The lowlands are largely composed of the Tarves association which is derived from intermediate and basic gneisses and comprises brown forest soils and non-calcareous gleys. Undefined alluvium soils are found along the river corridors and there are patches of basin peat on the margins of the catchment (Soil Survey of Scotland Staff, 1970-1981).

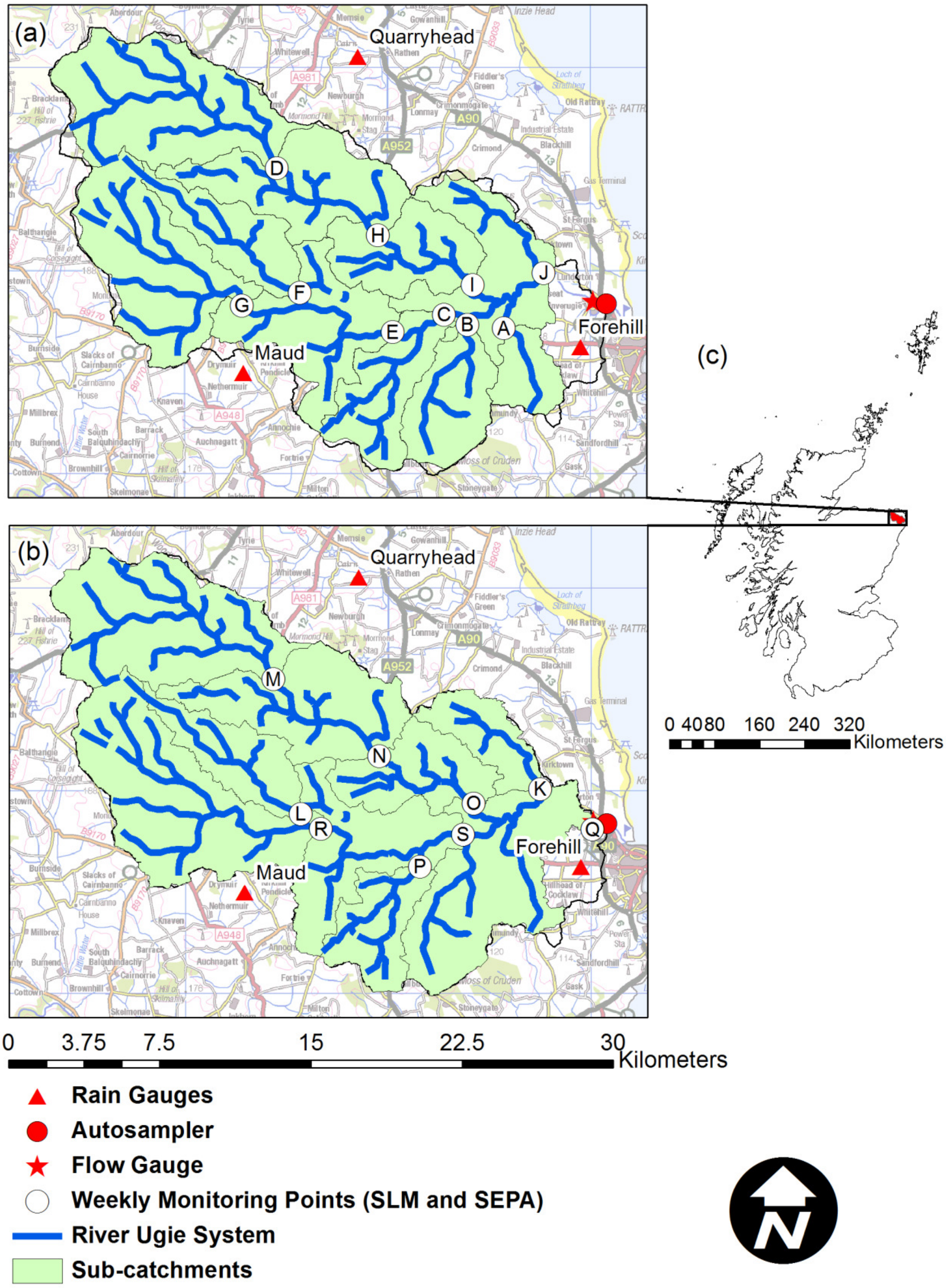


Figure 5.1 - (a) SLM (Sustainable Land Management) monitoring points, (b) SEPA monitoring points and (c) the location of the River Ugie catchment. Note river network broken in places by lakes not displayed

The river is used by Scottish Water as a drinking water source for the town of Peterhead and the surrounding area, a population of approximately 40,000 people. During certain periods of the year Scottish Water detects pesticide concentrations in the raw abstracted water above the regulatory limit of 0.1 $\mu g\ L^{-1}$ as set by the EU Drinking Water Directive (98/83/EC). There is no specific pesticide removal process at the works, therefore leading to occasional drinking water quality failures at customers' taps. In response to this the Drinking Water Quality Regulator (DWQR) and the Economic Regulator (Water Industry Commission for Scotland) in Scotland advised Scottish water to reduce the number of water quality failures attributed to pesticides in the Ugie. Scottish Water has adopted a twin track approach by building a new granular activated carbon (GAC) process at their works in conjunction with a catchment management initiative to reduce pesticide loads in the catchment, in order to reduce the operational expenditure of the GAC process. Identified pesticide pressures also mean that the catchment is part of the Voluntary Initiative, which monitors pesticide concentrations in the river and works closely with farmers to reduce the risk of pesticides entering the river.

The catchment also has nutrient pressures as identified by SEPAs WFD water body classification (SEPA, 2011) and is therefore one of SEPAs priority catchments for diffuse pollution. Nitrate pressures also mean it has a Nitrate Vulnerable Zone (NVZ) designation which restricts the spreading of fertilisers and manure during certain periods of the year.

5.2.2 Measured data

The Scottish Water catchment management initiative known as Sustainable Land Management (SLM) started in 2010 with 6 drinking water catchments in the scheme, of which the River Ugie is one. It was recognised that a monitoring strategy was required beyond the regulatory water quality samples taken at the treatment works to better understand the nature of the problem within the catchment, identify high risk sub-catchments and monitor intervention effectiveness.

As a result, since June 2011 weekly grab water samples have been collected at 10 spatially diverse monitoring locations in the catchment (See Figure 5.1a). These samples are collected in the same order each week by the Scottish Water sampling teams and refrigerated immediately before being analysed for a large suite of pesticides and other water quality parameters (see appendix C.2 for the range of pesticides).

To test the assumption that the first hydrologically effective rainfall event following pesticide application is the most important for pesticide mobilisation and delivery, a programme of storm sampling was initiated in the catchment as part of this research. A more detailed description of the sampling and analysis techniques used are outlined in Appendix C as only short summary is given here.

An autosampler was installed at the point where water is abstracted from the River Ugie for the Forehill water treatment works (Figure 5.1). The sampler was setup to be remotely triggered during storm events. Initially the sampler was setup to collect a 2 litre sample every 2 hours over a 24 hour period. However it was soon realised that this often did not capture the full storm hydrograph and therefore the sampling programme was adjusted to a 2 litre sample collected every 4 hours over a 48 hour period. A more detailed outline of the field and laboratory methodology can be found in Appendix C.

Data for nitrates, phosphorus and suspended sediment are collected by the Scottish Environment Protection Agency (SEPA) as part of their diffuse pollution priority catchment work. Sampling locations differ from Scottish Water's and are detailed in Figure 5.1. Sampling is also not as frequent and varies between monitoring points from fortnightly to monthly.

Pollutant sub-catchment loadings were derived using the concentration data in conjunction with discharge data collected from the catchment. Discharge data was derived from a flow gauge downstream of sample point 10 in Figure 5.1 that is operated and maintained by SEPA. The station is cableway rated using the velocity-area method and has been operating since 1971 (Marsh and Hannaford, 2008).

Flow measurements for each individual sub-catchment were modelled using the Low Flows Enterprise model (Wallingford Hydro Solutions, 2013). The method for calculating flow follows the methodology of Goody et al. (2010), where the LFE model is used to find analogous gauged catchments and calculate the daily mean flow for each ungauged catchment.

Modelled discharge values for each sub-catchment were used in conjunction with observed concentration values to calculate sub-catchment loads for model validation. There are different levels and types of uncertainty associated with the many techniques of calculating pollutant load. Generally the fewer measurements there are in a record the greater the uncertainty as it is unlikely that the full concentration-discharge dynamic is fully captured (Defew et al., 2013). A range of load calculation methods were therefore implemented using available data to provide a load uncertainty range for each pollutant in each sub-catchment.

5.2.2.1 Loading methods

Loading methodologies can be split into two types, interpolation and extrapolation techniques (Walling and Webb, 1981). Interpolation or numeric integration techniques assume that the conditions of the river at the time of sampling are representative of the conditions of the river for the period in between samples (Defew et al., 2013). Extrapolation techniques define a relationship between concentration and discharge that is applied to periods that are not sampled.

Extrapolation techniques are only applicable where discharge is a driver of pollutant load. This is the case for phosphorus and suspended sediment, but because pesticides are only applied at certain times of the year and nitrate is generally associated with low energy leaching processes extrapolation techniques were not deemed suitable.

Interpolation methods from Defew et al. (2013) were implemented for all pollutants and are outlined in equations 5.01-5.06.

$$Total\ Load = K\left(\sum_{i=1}^{n}\frac{C_i}{n}\right)\left(\sum_{i=1}^{n}\frac{Q_i}{n}\right) \tag{5.01}$$

$$Total\ Load = K\left(\sum_{i=1}^{n}\frac{C_i}{n}\right)\overline{Q_r} \tag{5.02}$$

$$Total\ Load = K\sum_{i=1}^{n}\left(\frac{C_iQ_i}{n}\right) \tag{5.03}$$

$$Total\ Load = K\left(\sum_{i=1}^{n}C_i\overline{Q_p}\right) \tag{5.04}$$

$$Total\ Load = K\frac{\sum_{i=1}^{n}(C_iQ_i)}{\sum_{i=1}^{n}Q_i}\overline{Q_r} \tag{5.05}$$

$$Total\ Load = K\sum_{i=1}^{n}(C_iQ_i) \tag{5.06}$$

Where $Total\ Load$ is in kg for nutrients and suspended sediment and g for pesticides, K is the time conversion factor (seconds), C_i is the measured instantaneous concentration (mg l^{-1} or µg l^{-1}), Q_i is the instantaneous measures discharge ($m^3\ s^{-1}$), $\overline{Q_r}$ is the average discharge for the period of the record ($m^3\ s^{-1}$) and $\overline{Q_p}$ is the mean discharge in between samples ($m^3\ s^{-1}$).

Uncertainty in the loading calculations is heavily dependent on the sampling resolution (weekly for pesticides, monthly for nutrients and suspended sediment). Previous investigations have determined uncertainty by assessing each against a ‘true load’ calculated using high resolution monitoring (e.g. Defew et al., 2013). Such high resolution is not available for the Ugie therefore making this impossible in this research.

Uncertainty was therefore assessed according to the method outlined in Richards (1998) which devises upper and lower ranges of loads calculated via interpolation. The technique is based on the assumption that concentration changes linearly between samples. In the method, concentration values are interpolated linearly by time, to the boundary of each observed sample. Each sample observation therefore has three associated concentration values, the actual observed concentration and two associated concentrations from the linear interpolation. The method assumes that within that time period the concentration will not be above the highest of the three values or below the lowest therefore giving an upper and lower loading estimate. In reality of course this is unlikely to be true, especially where there are significant periods of time between samples, however it does give an estimation of uncertainty.

For phosphorus and suspended sediment log-log regression equations are derived for the relationship between concentration and discharge. Daily discharge values are then substituted into the regression equation to derive concentration values for each day. Equation 5.07 is then used to calculate annual load.

$$Total\ Load = K\left(\sum_{i=1}^{n}(C_c Q_c)\right) \tag{5.07}$$

Where C_c is the estimated daily concentration value (mg l^{-1} or µg l^{-1}) and Q_c is the mean daily discharge ($m^3\ s^{-1}$).

Uncertainty in the regression equations is based on the confidence intervals of each regression equation. At the 95% confidence limit upper and lower values of the intercept and slope of each regression are implemented to give upper and lower load ranges for each sample location.

The loading values are adjusted for the sub-catchments that contain a nested sub-catchment, so that the effect of area is taken away. Consulting Figure 5.1a this means that sub-catchment C is adjusted by subtracting the load of sub-catchment E, sub-catchment I by subtracting the load of sub-catchment H and so on. Likewise loads of phosphorus, nitrate and sediment are adjusted to include loads from wastewater treatment works using values from SEPA (2011).

5.3 Sources and selection of model input data and parameters

5.3.1 Climate data

The two key climate data inputs used in CaRPoW are daily rainfall and temperature, over a 30 year period for the WaSim water balance model. Although rainfall is spatially diverse, rain gauge measurements represent a single measurement at a single location. There are three rain gauges representative of the Ugie at Forehill, Maud and Quarryhill where data are available (see Figure 5.1). The Forehill rain gauge was chosen because of the length of its record and the fact that temperature measurements are also taken. Both temperature and rainfall data were obtained from the British Atmospheric Data Centre (BADC) for the period of the WaSim model run (1980-2012).

5.3.2 Soil data

Soils data are based on the 1:25000 Scottish Soils dataset from the James Hutton Institute, with soil properties obtained from the Scottish Soils Knowledge and Information Base (SSKIB) and SEISMIC databases. The soils properties used in CaRPoW are outlined in Table 5.1. Soil hydrological properties were also obtained from the SEISMIC soils database held at Cranfield University. Within these soil classifications, 4 broad land use classes are available for each soil series (arable, permanent grass, ley grass and other). Model runs were completed for all four soil property types and matched to the soil and land use combinations present in the catchment.

Soil types were assigned HOST classifications according to Boorman et al. (1995). The HOST classifications were used in conjunction with land use to make an assessment on the presence of artificial drainage, i.e. if the HOST classification relates to a water logged, poorly drained soil and the land use is agricultural then field drains are assumed to be installed. HOST class was also used to assign each soil an SCS curve number depending on 5 different soil conditions and 6 different land uses according to Holman et al. (2011).

Table 5.1 - Soil properties used in the various CaRPoW methodologies and the symbols representing them in the model equations

Soil Property	Symbol	Method used in
Total P (g kg)	*TotalPSoil*	Phosphorus Source
Bulk Density (g cm^{-3})	ρb	Phosphorus Source, Pesticide Mobilisation
Water Content at 0kPa, 5kPa, 200kPa and 1500kPa (cm3 cm3)	θ_{sat}, θ_{fc}, θ_{200}, θ_{pwp}	Pesticide mobilisation, WaSim Model
Saturated Hydraulic Conductivity (m day)	K_{sat}	Pesticide mobilisation, WaSim Model
van Genuchten n parameter (-)	*n*	Pesticide mobilisation
Organic carbon content (%)	F_{oc}	Pesticide source
SCS curve number (-)	*N*	WaSim Model
Erodibility of the soil parameter (-)	*K*	Modified Morgan-Morgan-Finney erosion model
Cohesivity of the soil parameter (-)	*COH*	Modified Morgan-Morgan-Finney erosion model
Soil properties used to infer information:		
HOST Classification	HOST	Presence of drains, Nitrate Source

5.3.3 Land use

Land use data has been obtained and adapted from the IACS dataset. This is an annually updated dataset created by the Scottish Government from the single farm payment application forms completed by land owners across Scotland. Each field within a catchment has an associated Land Parcel ID (LPID) that is assigned a land use.

The dataset is in an excel spread sheet format and added to the LPID shapefile for the Ugie catchment, both provided by the Scottish Government.

This dataset only covers the land within the catchment that is used for agricultural production, meaning other areas of land are classified according to the CEH Land Cover 2007 dataset (Morton et al., 2011). Land use classes are not concurrent across the two different datasets and therefore a CaRPoW land use classification system was developed from the amalgamation of the two datasets to accurately capture the detail required by the modelling methods. Two different land use classifications have been created for the CaRPoW methodology for both the source and mobilisation methodologies. The source classification is more detailed and separates out individual crop types at the level required to distinguish between different pesticide and fertiliser applications. The mobilisation classification is less detailed and relates to the vegetation types modelled in the WaSim soil water balance model (see section 5.3.4). Both classifications and the original IACS and CEH land cover map classes they relate to are shown in Table 5.2 for the Ugie catchment.

Table 5.2 - Land use classes for the source and mobilisation methodologies assigned to Integrated Administration and Control System (IACS) and Land Cover Map (LCM) land use classifications

	IACS and LCM land use classes	**CaRPoW source class**	**CaRPoW mobilisation class**
IACS Classes	ARABLE SILAGE FOR STOCK FEED	Stock Feed	Row Crops
	CARROTS	Carrots	Row Crops
	EX STRUCTURAL SET-ASIDE (AFFORESTED LAND ELIGIBLE	Woodland	Woodland
	EX STRUCTURAL SET-ASIDE (AFFORESTED LAND ELIGIBLE FOR SFPS)	Woodland	Woodland
	FALLOW	Semi-Natural	Semi-Natural
	FALLOW LAND FOR MORE THAN 5 YEARS	Semi-Natural	Semi-Natural
	GRASS OVER 5 YEARS	Permanent Grass	Grassland

GRASS UNDER 5 YEARS	Ley Grass	Grassland
KALE AND CABBAGES FOR STOCKFEED	Cabbages	Row Crops
LFASS INELIGIBLE ENVIRONMENTAL MANAGEMENT	Semi-Natural	Semi-Natural
MIXED CEREALS	Other Cereals	Winter Cereals
NEW WOODLAND (ELIGIBLE FOR SFPS)	Woodland	Woodland
NORMAL SETASIDE - 5 YEAR UNDER WGS	Semi-Natural	Semi-Natural
NORMAL SETASIDE - NAT REGEN (AFTER CEREALS)	Semi-Natural	Semi-Natural
NORMAL SETASIDE - NAT REGEN (AFTER OTHER CROPS)	Semi-Natural	Semi-Natural
NORMAL SETASIDE - SOWN GRASS COVER	Semi-Natural	Semi-Natural
NORMAL SETASIDE - WILD BIRD COVER	Semi-Natural	Semi-Natural
OPEN WOODLAND(GRAZED)	Rough Grazing	Semi-Natural
OTHER CROPS FOR STOCK FEED	Stock Feed	Row Crops
OTHER VEGETABLES	Other Vegetables	Row Crops
POSITIVE ENVIRONMENTAL MANAGEMENT	Semi-Natural	Semi-Natural
PROTEIN PEAS	Other Vegetables	Row Crops
RAPE FOR STOCK FEED	Winter Oilseed Rape	Winter Cereals
RASPBERRIES	Soft Fruit	Row Crops
RASPBERRIES GROWN IN OPEN SOIL UNDER TEMPORARY WALK-IN STRUCTURES	Soft Fruit	Row Crops
ROUGH GRAZING	Rough Grazing	Grassland
SEED POTATOES	Potatoes	Row Crops
SETASIDE AGRICULTURAL PRODUCTION - ARABLE	Semi-Natural	Semi-Natural
SETASIDE AGRICULTURAL PRODUCTION - FORAGE	Rough Grazing	Semi-Natural
SFPS BEING CLAIMED ON AGRI-	Semi-Natural	Semi-Natural

	ENVIRONMENTAL OPTIONS		
	SHOPPING TURNIPS/SWEDES	Turnips	Row Crops
	SPRING BARLEY	Spring Barley	Spring Cereals
	SPRING OATS	Spring Oats	Spring Cereals
	SPRING OILSEED RAPE	Spring Oilseed Rape	Spring Cereals
	SPRING WHEAT	Spring Wheat	Spring Cereals
	STRAWBERRIES	Soft Fruit	Row Crops
	STRAWBERRIES GROWN IN OPEN SOIL UNDER TEMPORARY WALK-IN STRUCTURES	Soft Fruit	Row Crops
	STRUCTURAL SETASIDE - WGS, FWPS OR SFGS	Semi-Natural	Semi-Natural
	TRITICALE	Other Cereals	Winter Cereals
	TURNIPS/SWEDES FOR STOCK FEED	Turnips	Row Crops
	WARE POTATOES	Potatoes	Row Crops
	WHOLE CROP CEREALS	Other Cereals	Winter Cereals
	WILD BIRD SEED	Semi-Natural	Semi-Natural
	WINTER BARLEY	Winter Barley	Winter Cereals
	WINTER OATS	Winter Oats	Winter Cereals
	WINTER OILSEED RAPE	Winter Oilseed Rape	Winter Cereals
	WINTER OILSEED RAPE ENERGY	Winter Oilseed Rape	Winter Cereals
	WINTER WHEAT	Winter Wheat	Winter Cereals
LCM Classes	Arable and horticulture	Winter Wheat	Winter Cereals
	Bog	Semi-Natural	Semi-Natural
	Broadleaved, mixed and yew woodland	Woodland	Woodland
	Coniferous woodland	Woodland	Woodland
	Freshwater	Lochs	Lochs

Heather	Semi-Natural	Semi-Natural
Heather grassland	Semi-Natural	Semi-Natural
Improved grassland	Grassland	Grassland
Inland rock	Semi-Natural	Semi-Natural
Rough grassland	Rough Grazing	Grassland
Suburban	Urban	Urban
Unclassified	Unclassified	Unclassified
Urban	Urban	Urban

5.3.4 Vegetation parameters

The WaSim soil balance model requires parameters for each vegetation type in order to calculate actual evapotranspiration (Table 5.3). The Julian dates relating to the stages of crop growth (planting, emergence, 20% crop cover, full crop cover, max root depth, full plant maturity and harvest) were derived from combining local information extracted from the agronomist interview (section 5.3.6.1 and Appendix D), information from the HGCA crop manuals for cereal crop and oilseed rape (HGCA 2005, 2008, 2012) and the crop calendars produced by Holman et al. (2005). Crop parameters for semi-natural and grassland vegetation types were assumed to be constant year round, i.e. max root depth achieved at planting date and no harvest. The woodland vegetation type was assumed to follow a pattern of leaf development in the spring (represented by planting date) and defoliation in the autumn (represented by harvest). The maximum root depth achievable by any of the vegetation type was set at maximum soil depth (assumed to be 1.5 metres).

Table 5.3 - Vegetation parameters used in the WaSim water balance model (derived from Holman et al., 2004)

Variable	Grassland	Row Crops	Winter Cereals	Spring Cereals	Semi-Natural	Woodland
Planting Date (Julian day)	1	105	273	74	1	74
Harvest Date (Julian day)	365	170	351	175	365	324
Emergence Date (Julian day)	1	31	11	15	1	105
20% Coverage Date (Julian day)	1	46	41	18	1	115
Full Coverage Date (Julian day)	1	92	183	76	1	130
Vegetation Maturity Date (Julian day)	365	133	273	122	365	302
Maximum Root Depth Date (Julian day)	1	92	162	76	1	74
Planting Depth (m)	0.70	0.08	0.03	0.03	0.35	1.50
Maximum Root Depth (m)	0.70	0.75	1.50	1.50	0.35	1.50
WaSim Crop Coefficient (-)	100	110	110	110	100	114
WaSim P Fraction (-)	0.5	0.5	0.5	0.5	0.5	0.71

5.3.5 Topography data

The underlying dataset for topography model inputs (e.g. slope) was the NextMap 5m Digital Terrain Model dataset for the River Ugie catchment. Before analysis the dataset was hydrologically corrected by filling in pitted artefacts in the dataset using the TauDEM pit filling tool (Tarboton, 2012). The DTM was further treated by ‘burning’ the detailed river network, so that flow is forced along known drainage channels. The river network dataset burned into the DTM is the Scottish Detailed River Network (SDRN), which is based on hydrological features present in the Ordnance Survey (OS) Mastermap Dataset. The SDRN was burned into the DTM using the Whitebox GAT decay function methodology with a depth of 2m and a decay function of 10m (Lindsay, 2014). This methodology better directs flow into burned drainage channels than simply subtracting the depth of the river network away from the DTM.

The barrier features implemented within the delivery/connectivity module of the methodology (section 4.4) are derived from the OS Mastermap dataset. Within the dataset line features are classified with a “physicalPresence” attribute where any line classified as an “Obstructing Feature” is above 0.3 metres and obstructs passage by foot (Ordnance Survey, 2004). It was assumed that any line feature that is a physical obstruction also provides a hindrance to water movement across the landscape and thus has a higher Manning’s n value in the connectivity methodology. Barrier features were buffered by 5 metres and rasterised to a 5 metre cell size to match that of the NextMap DTM.

5.3.6 Pollutant specific parameters

Where parameter values are concurrent across all Scottish catchments they are detailed in the CaRPoW methodology in section 4. This section outlines the specific input parameters used for the River Ugie catchment.

5.3.6.1 Pesticide specific data

Two key pesticide property parameters are required by the model, sorption coefficient (K_{oc}) and half-life (DT_{50}). The main sources of pesticide property information are from the University of Hertfordshire Pesticide Property Database (2015) and the various European Food Standard Agency Risk Assessments for the pesticides of interest. Parameter values derived from these sources are highly variable (Table 5.4). Thus the model was run with the upper, lower and mean parameter values to provide an uncertainty range of model outputs for pesticides.

Table 5.4 - Pesticide specific CaRPoW model parameters (derived from the Hertfordshire Pesticide Properties Database, European Food Safety Agency risk assessments or agronomist interviews).

Pesticide	Organic carbon to water coefficient - K_{oc} ($l\ kg^{-1}$)	Soil DT_{50} (Days)	Crops applied to (according to agronomist interviews and EFSA risk assessments)
2, 4-D	16-68	1.2-94.6	Ley Grass, Spring Barley, Spring Wheat
Chlorotoluron	108-384	26-42	Spring Barley, Winter Barley, Spring Wheat, Winter Wheat
CMPP	20-43	6.3-8.2	Spring Barley, Winter Barley, Spring Wheat, Winter Wheat, Spring Oats, Winter Oats, Ley Grass
MCPA	10-157	7-41	Spring Barley, Winter Barley, Spring Wheat, Winter Wheat, Spring Oats,, Ley Grass, Permanent Grass
Metaldehyde	34-240	6.6-19.5	Winter Oilseed Rape, Winter Wheat, Winter Barley, Potatoes, Ley Grass, Brassicas, Other Vegetables
Metazachlor	29.2-75.1	2.8-21.3	Winter Oilseed Rape, Spring Oilseed Rape, Brussel Sprouts, Cabbage, Cauliflower, Turnips/Swedes

Application rate and timings have been obtained from a number of different sources. Maximum application rates were selected from the British Crop Protection Council pesticide manual (BCPC, 2013). At the same time the number of applications allowed per year is noted from the BCPC manual so that any restrictions on annual application rate are carried through in the model. The application rates used for each pesticide on each crop type can be found in Appendix B.

When assessing the timing of applications it is important to understand the specific uses of each pesticide within the study catchment. Although general information is available on application timings for various pesticide and crop combinations it has been shown that regional differences can be important (Dolan et al., 2014). Dolan et al. (2014) identified agronomists as a key information source for catchment managers in order to understand the nature and drivers of pesticide use in individual catchments. Using a similar methodology to Dolan et al. (2014) a number of semi-structured interviews were conducted with agronomists to ascertain the key crop rotations, pests and pesticide usage in the River Ugie catchment. The questionnaire is shown in Appendix D with questions split into 4 parts:

1. Cropping practices
2. Pest Issues
3. Pesticide usage
4. Nutrient management

The first section includes questions relating to cropping practices in the catchment and the second relates to specific pest issues for the crops outlined in part one and the methods of dealing with them. Part three specifically deals with the 6 pesticides highlighted as problematic in Scottish Water's monitoring data, questions relate to the uses of each and potential alternatives. The final section relates to fertiliser application for the crop identified in section one.

To gauge the number of agronomists operating in the River Ugie catchment the author attended a meeting arranged with agronomists as part of Scottish Water's Sustainable Land Management Incentive Scheme. A short presentation was given outlining the information requirements after which agronomists were asked to express an interest in taking part in the study. It was stressed that only independent agronomists were wanted for the study to remove bias from agronomists linked to specific chemical suppliers.

The questionnaire driven interview was first of all tested in a pilot with one of the agronomists who expressed an interest in the initial meeting. Feedback was requested from the participant and amendments made to the questionnaire

All interviews were conducted face to face at the offices of the participants. Participants were asked to sign a consent form, a copy of which is included in Appendix D. The interviews started with the author outlining the purpose of the study and the uses of the information acquired. The interview was recording for transcription at a later date. Although there was a structure to the interview the author used their judgement to ask follow up questions to certain answers and tangents to the questions were allowed if they were relevant to the purposes of the study.

In total three independent agronomists agreed to be interviewed. The relatively small number of agronomists sampled reflects the catchment size and the limited number of independent agronomists representing farmers in the catchment. An example anonymised questionnaire response is outlined in Appendix D.4.

Using the outputs from the interviews along with other application timing information from European Food Standards Agency (EFSA) pesticide risk assessments the application timings in Appendix B were devised. If applications had the potential to be applied over a two month time window the application rate was split between months equally.

Outputs from the agronomist interviews highlighted the fact that pesticide applications are pest dependant and therefore not all fields with the same crop type will receive the same application rate, or even an application at all. Without specific application rate data from individual farms the best option available was to use the Science and Advice for Scottish Agriculture (SASA) pesticide usage statistics (Reay, 2010; Watson et al., 2012; Watson et al., 2013) to reduce the maximum application rate by the proportion of the product applied to each individual crop in the Grampian region of Scotland (where the River Ugie is situated).

5.3.6.2 Nitrate specific parameters

Nitrate specific parameters relate to the derivation of the values for each component of the source equation (equation 4.11 in section 4.2.3). Values for mineralisation, denitrification, livestock N and atmospheric deposition have been detailed in the nitrate source methodology section (4.2.3). The methods of deriving crop offtake and fertiliser N values are also detailed in section 4.2.3 and the values used in the model can be found in appendix B.

All other parameter values for the nitrate mobilisation methodology are detailed in methodology section 4.3.4.

5.3.6.3 Phosphorus specific parameters

Phosphorus parameters derived for the River Ugie catchment are mostly inputs to the source methodology. Annual fertiliser applications rates have been derived from the Scottish Government statistics for phosphorus fertiliser use. Fertiliser application rates were matched to the CaRPoW source land use classifications; values for the years 2008-2012 are detailed in Table 5.5.

Table 5.5 - Phosphorus fertiliser application rates per year used in CaRPoW models (derived from Scottish Fertiliser Use Statistics)

	Phosphorus fertiliser application rate (kg ha^{-1} yr^{-1})					
CaRPoW Source Land Use	**2008**	**2009**	**2010**	**2011**	**2012**	**Average**
Cabbages	42	53	48	38	48	45.8
Carrots	42	53	48	38	48	45.8
Ley Grass	26	23	28	22	24	24.6
Other Cereals	42	53	48	38	48	45.8
Other Vegetables	42	53	48	38	48	45.8
Permanent Grass	13	12	12	10	10	11.4
Potatoes	149	145	139	136	109	135.6
Rough Grazing	0	0	0	0	0	0
Semi-Natural	0	0	0	0	0	0
Soft Fruit	0	0	0	0	0	0
Spring Barley	46	46	48	51	50	48.2
Spring Oilseed Rape	45	46	39	34	43	41.4
Spring Wheat	56	52	44	43	47	48.4

Spring Oats	26	28	39	38	35	33.2
Stock Feed	34.5	39.5	39	32	37	36.4
Turnips	42	53	48	38	48	45.8
Winter Barley	59	45	50	52	50	51.2
Winter Oilseed Rape	45	46	39	34	43	41.4
Winter Wheat	56	52	44	43	47	48.4

P sources from livestock are based on the stocking density and annual phosphorus output of each livestock type, as detailed in section 4.2.2. In the Ugie catchment stocking density is based on parish level agricultural census data collected annually by the Scottish Government. Values for stocking density for each parish are outlined in Table 5.6. It should be noted that because of missing data on other livestock types at the parish level only cattle and sheep are included in the analysis.

5.3.6.4 Sediment specific parameters

There are no Ugie specific sediment parameters derived in the methodology; all parameters used in the modelling methodologies have been detailed in section 4.3.5.

Table 5.6 - Detailed outline of parish livestock numbers (2012) and how this translates to stocking density in the River Ugie catchment

Parish	Parish area (ha)	Total cattle in parish	Total sheep in parish	Total parish area within Ugie catchment (ha)	Percentage parish area within the Ugie	Adjusted cattle numbers	Adjusted sheep numbers	Total grassland area in parish (ha)	Cattle stocking density (animals per ha)	Sheep stocking density (animals per ha)
Aberdour	5809	2894	3035	1887	32	940	305	427	2.20	0.72
Crimond	2548	1647	2541	166	7	107	7	78	1.39	0.09
King Edward	7186	2600	4900	30	0	11	0	19	0.55	0.00
Longside	6984	5850	3923	6469	93	5419	5019	1896	2.86	2.65
Lonmay	4838	3859	4553	1441	30	1149	342	403	2.85	0.85
New Deer	10846	12558	11806	5270	49	6102	2965	1676	3.64	1.77
Old Deer	10933	8949	10555	7945	73	6504	4727	2038	3.19	2.32
Peterhead	3903	1628	2010	1603	41	669	275	460	1.45	0.60
St Fergus	3434	1820	1664	525	15	278	43	69	4.02	0.61
Strichen	5747	8488	6440	4872	85	7195	6099	1226	5.87	4.98
Tyrie	4633	4289	1834	2924	63	2707	1709	757	3.58	2.26

5.4 Implementation of CaRPoW modelling methodologies

5.4.1 Model implementation format

All source and mobilisation methodologies were coded in the R programming language (R Core Team, 2014) with results outputted as ESRI shapefiles. The equations developed in the delivery/connectivity module were coded as python scripts within an ArcGIS toolbox. Outputs from the delivery/connectivity module were in a raster format that is assigned to the 'fields' in the source and mobilisation shapefile outputs using a zonal statistics function. The purpose of this was to make sure the outputs from the three modules were in the same shapefile format for calculation of final risk using R.

5.4.2 Data pre-processing

To achieve the correct data structure for use in the models some of the GIS data inputs outlined in section 5.3 require pre-processing. The hydrological correction of the DTM for the delivery/connectivity methodology has already been discussed. However the most important pre-processing step was the creation of a shapefile which delineates 'fields' within the catchment, the resolution at which the source and mobilisation methodologies operate.

Within CaRPoW 'fields' were classified as unique combinations of land use, soil type and drainage. However traditional field boundaries as dictated by the IACS dataset are also maintained so that model outputs can be easily assigned to physical fields. To achieve this, the derived land use dataset, soils dataset and OS Mastermap dataset for the catchment were combined. The OS Mastermap dataset is included so that urban areas are appropriately captured within the data structure for the purposes of the delivery/connectivity component. An example output of this process is shown in Figure 5.2.

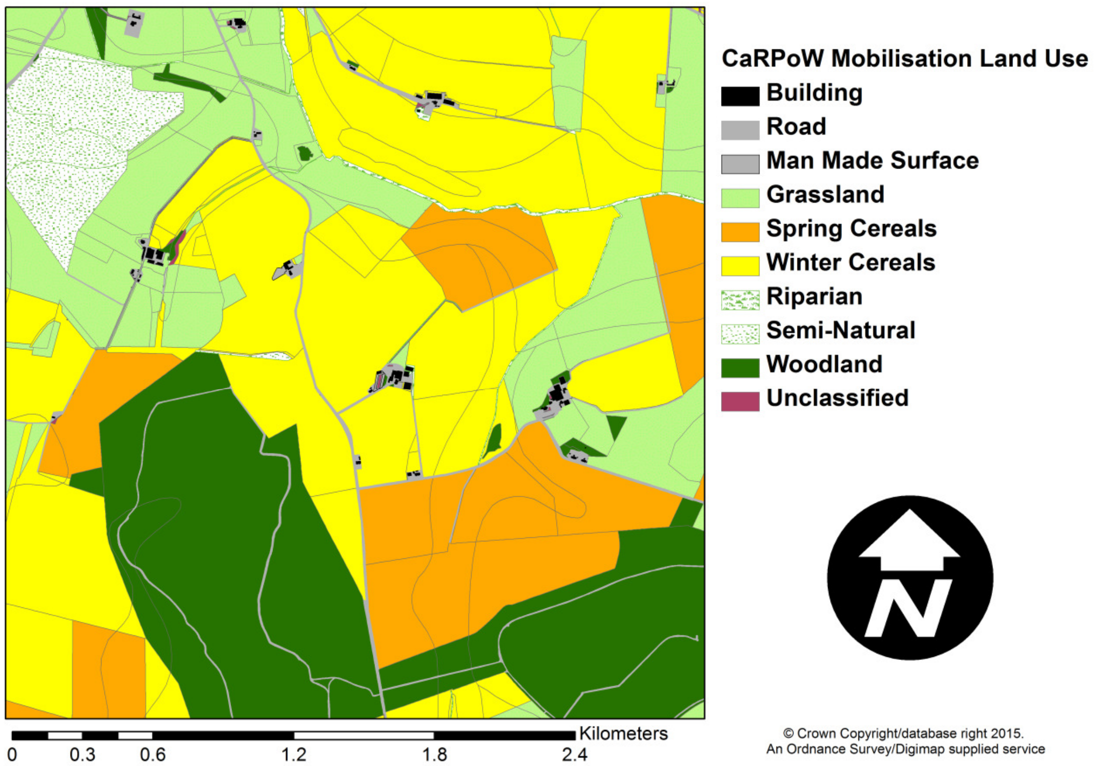


Figure 5.2 - Example of CaRPoW mobilisation land use coverage with integrated OS Mastermap features as used in the CaRPoW model.

5.4.3 WaSim model setup

Climate, vegetation and soil parameters implemented for the River Ugie catchment within WaSim have been outlined in section 5.3.

Model inputs for the Ugie equated to 26 different soil types each with 4 sets of parameters relating to land use (arable, ley grass, permanent grass and other), 5 different soil conditions that alter the SCS curve number (as per Holman et al., 2011), 6 different crop types and 2 drainage conditions. In total 6,240 WaSim model runs were completed for the Ugie to represent every possible soil, land use and drainage combination.

5.5 Model validation methodology

All CaRPoW model outputs are validated against the loading data described in section 5.2.2.1 in two different ways. Firstly the ability of the models to accurately calculate pollutant loads is determined statistically using Root Mean Square Error (RMSE) and Relative Error (RE). Both tests have been used previously in diffuse pollution load model testing by Strömqvist et al. (2008) for example. The RMSE is used to assess the error between the predicted values (modelled load) and the observed values (calculated load) for each sub-catchment. The RMSE is calculated using equation 5.08.

$$RMSE = \sqrt{\frac{\sum_{i=1}^{n} P_i - O_i}{n}} \tag{5.08}$$

Where $RMSE$ is the total RMSE between modelled and observed loads (g for pesticides, kg for other pollutants), P_i are the individual modelled values for each sub-catchment (g for pesticides, kg for other pollutants), O_i are the individual loading values for each sub-catchment (g for pesticides, kg for other pollutants) and n is the number of sub-catchments. RMSE is assessed across the range of model and load values by assessing the different combinations of minimum, median and maximum values within the RMSE test.

Relative error assesses the percentage difference between the modelled and observed values and provides a semblance of whether the model under or over predicts (negative values are an under prediction, positive an over prediction). RE is calculated using equation 5.09 against the same range of values as the RMSE.

$$RE = \frac{100}{n} \sum \frac{(P_i - O_i)}{O_i} \tag{5.09}$$

Where RE is the relative error between the modelled and observed loads (%).

The second type of model validation is to assess the accuracy of the model in predicting the spatial arrangement of risks in the catchment. Simple linear regression analysis is used to assess the best fit relationships within the uncertainty ranges between modelled and observed loads as delineated by sub-catchment. It is important however to assess how the relationship changes under the different uncertainty ranges of both the model outputs and loading calculations. The ANCOVA (Analysis of Covariance) method is therefore implemented to assess the difference between the slope values of the regression models of the CaRPoW model outputs and data within their associated uncertainty ranges. ANCOVA outputs were interpreted using a 95% confidence. When $P<0.05$, regression models across the uncertainty ranges were deemed to be significantly similar and hence the correlation relationships consistent across the model and data uncertainty ranges.

5.6 Model results and discussion

5.6.1 Water balance model

Validation of the water balance methodology is difficult as no data are available on the runoff, drainflow, recharge or evapotranspiration for individual fields in the River Ugie catchment. Similarly the model does not output a river discharge value which is what most hydrological models are validated against. Instead the water balance model is validated using the methodology of Holman et al. (2011) where an indicative baseflow index (BFI) is calculated for each unique soil, drainage and land use combination. These are subsequently upscaled according to the proportion of each unique combination in the catchment to give an overall predicted BFI. The indicative BFI is derived according to the proportion of the long term average Hydrological Effective Rainfall (surface runoff and drainflow) to long term average rainfall (equation 5.10).

$$BFI = 1 - \frac{R}{HER} \tag{5.10}$$

Where BFI is the baseflow index (proportion from 0-1), R is the long term average runoff (mm) and HER is the Hydrologically Effective Rainfall (mm).

The indicative baseflow index can be compared to the baseflow index for the River Ugie as calculated by the methodology of Gustard et al., (1992) which is used for low flows estimation in the UK.

The CEH hydrometric register (Marsh and Hannaford, 2008) states the River Ugie's baseflow index as **0.63**. The indicative baseflow index as derived from upscaled WaSim outputs is **0.60**. The small difference between the two BFI values is encouraging and suggests that WaSim and the associated input parameter assumptions provide a good representation of the partitioning between slow and fast flow processes in the catchment. This is important to the models utility as the partitioning of flow is important for the selection of interventions e.g. increasing soil infiltration to reduce runoff versus installation of wetlands at artificial drain outfalls.

5.6.2 Model functionality within the CaRPoW framework

The functionality of the model is described and discussed in this section using the example of metaldehyde with the dominant land use over the 2008-2012 period. The source, mobilisation, connectivity and final risk model outputs are detailed in Figures 5.3 to 5.6 respectively. The outputs for all other pollutants using land use data from 2012 and the dominant land use (2008-2012) are shown in Appendix E. Risk is classified into 5 groups according to Natural Jenks (Jenks, 1967), with the lowest class set to zero i.e. no risk.

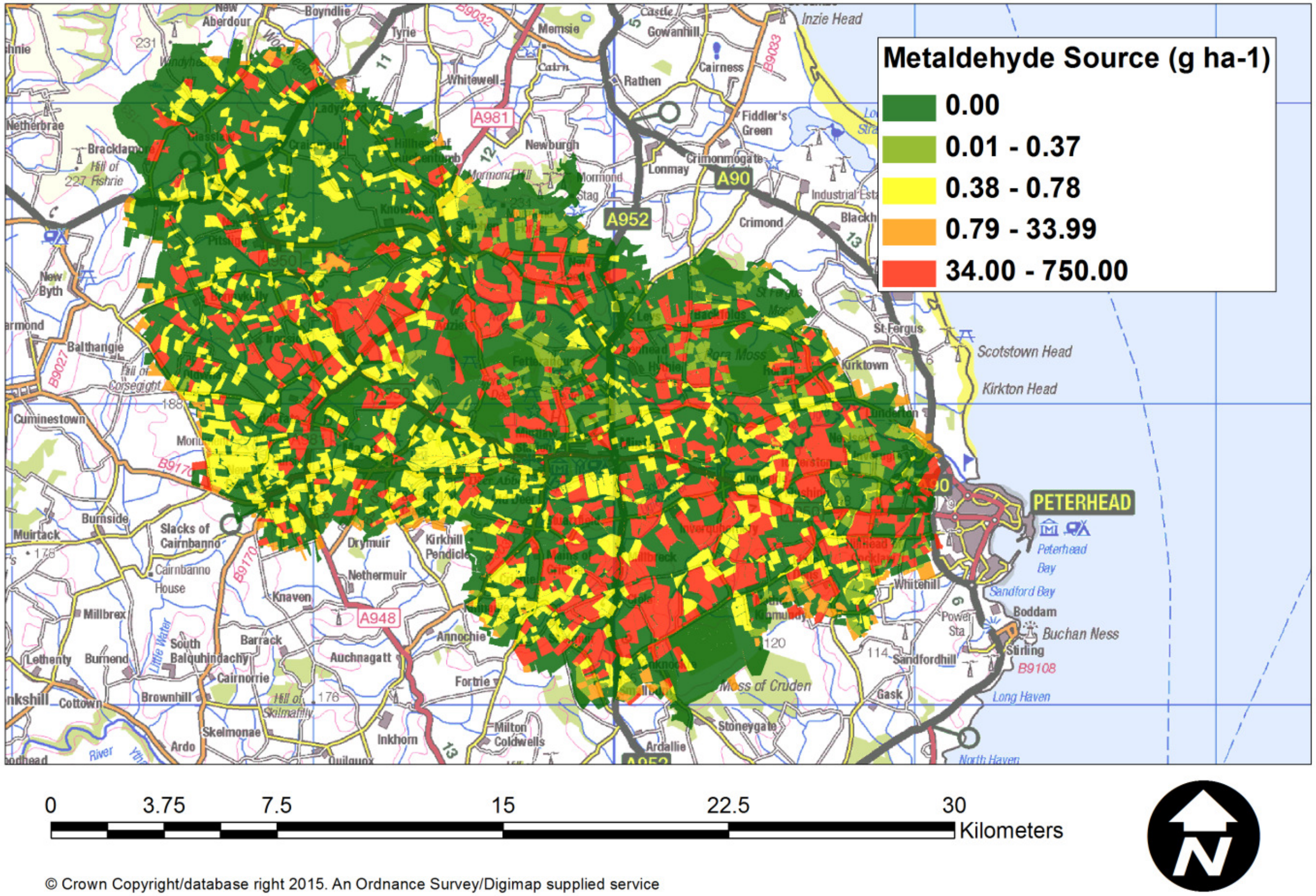


Figure 5.3 - Annual metaldehyde source risk for dominant land use (2008-2012) in the River Ugie catchment

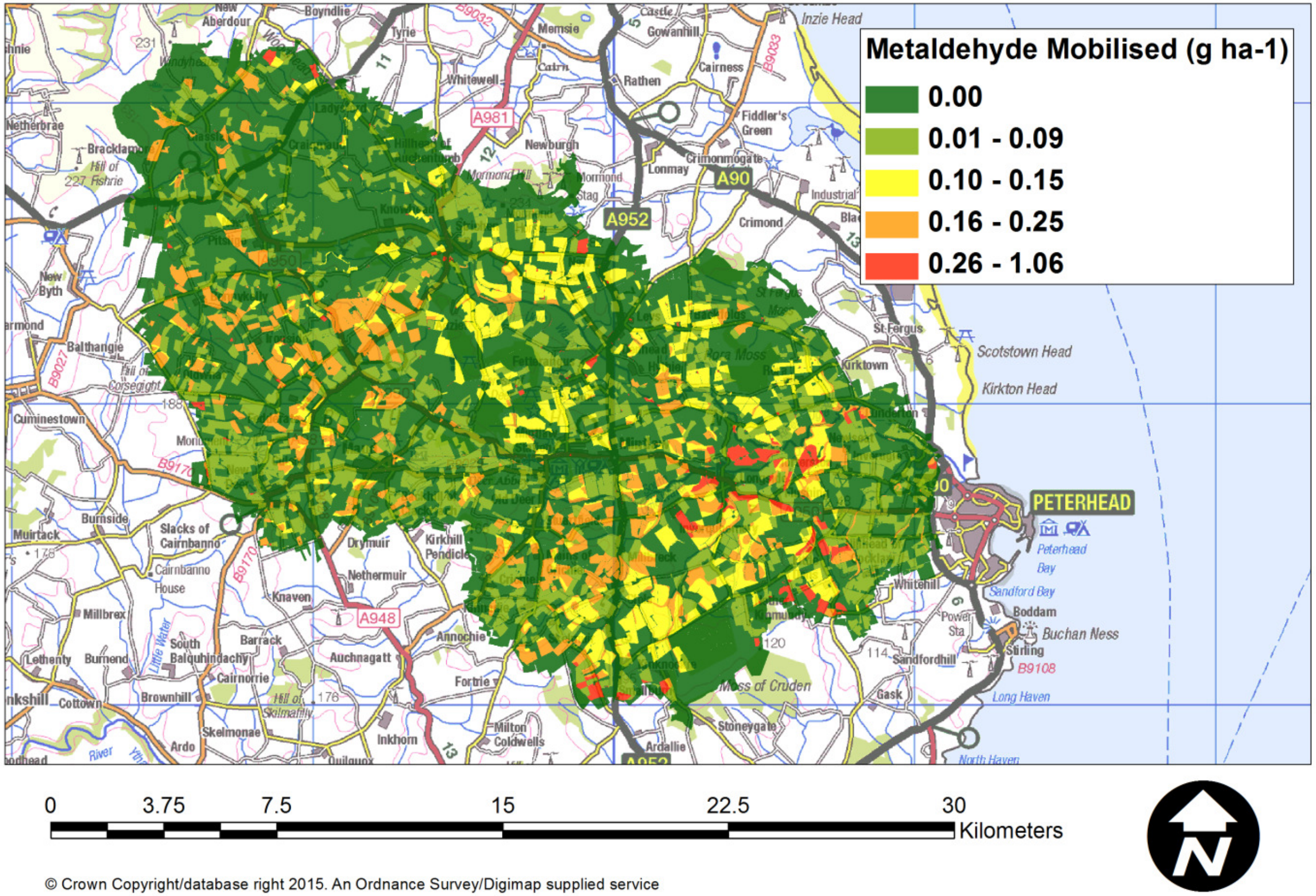


Figure 5.4 - Annual metaldehyde mobilised for dominant land use (2008-2012) in the River Ugie catchment (Source Risk multiplied by Mobilisation coefficient)

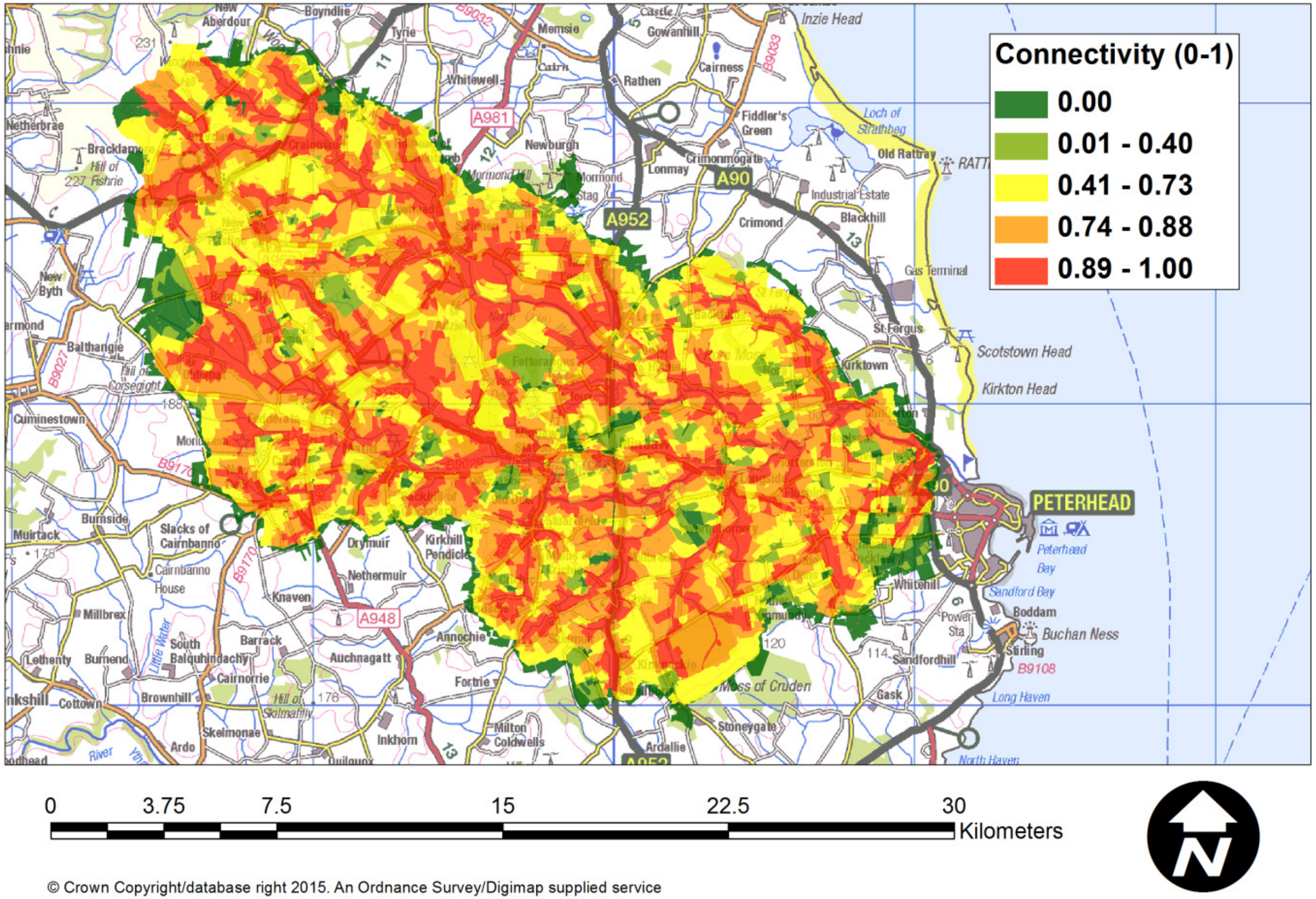


Figure 5.5 - Connectivity risk for dominant land use (2008-2012) in the River Ugie catchment

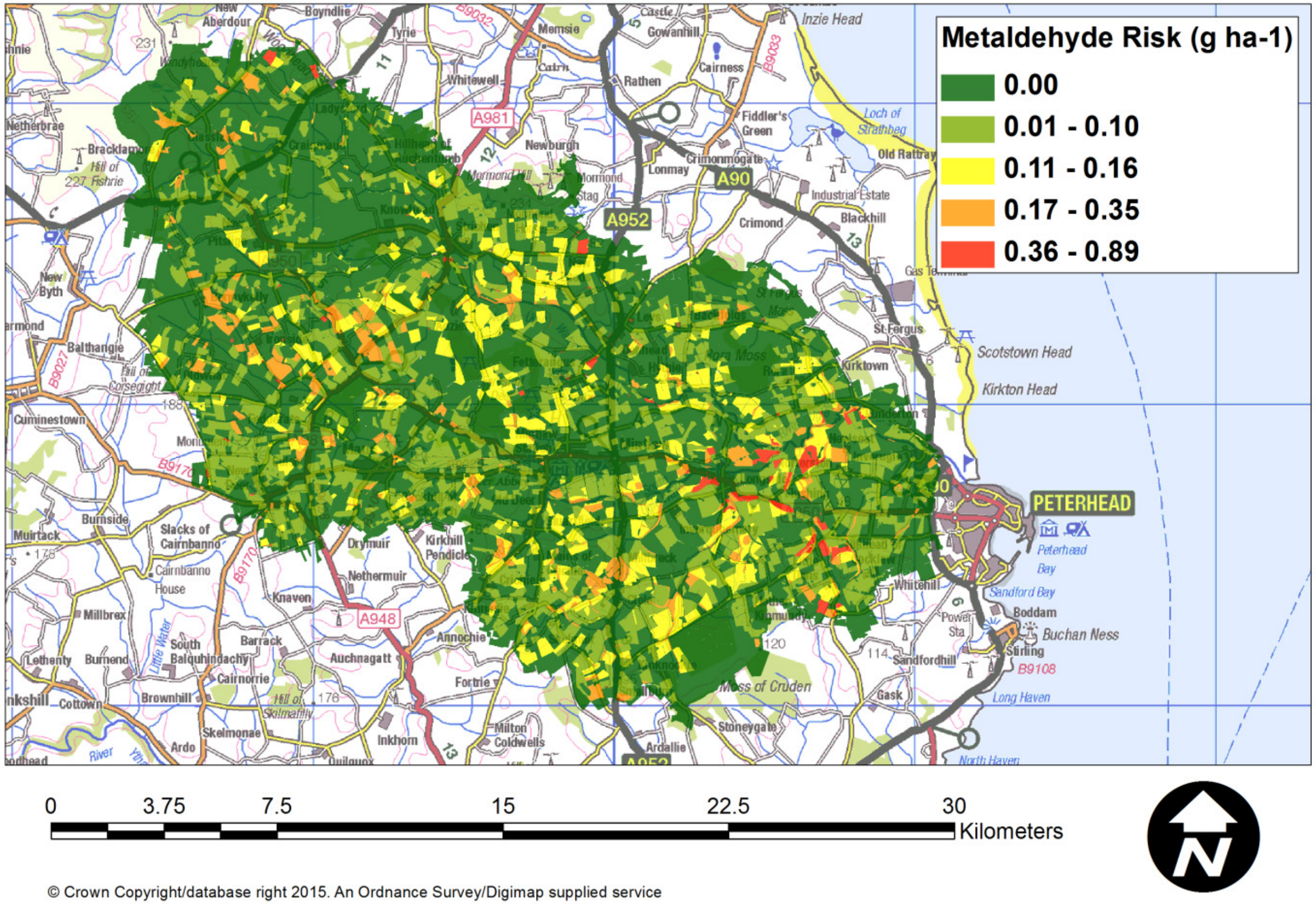


Figure 5.6 - Annual metaldehyde final risk for dominant land use (2008-2012) in the River Ugie catchment

Visual inspection of the model component outputs for metaldehyde highlights how risk changes through the model structure. Understandably, overall risk (Figure 5.6) only exists where there is an initial source potential (Figure 5.3). A proportion of the source is mobilised in every field except where organic soils are present. However the highest source risks do not necessarily correspond to the highest mobilisation risk. An example of this is shown in Figure 5.7 where one field has a higher source risk and lower mobilisation risk (0.23% of source mobilised) and the other has a lower source risk and a higher mobilisation risk (1.52% of source mobilised).

Connectivity/delivery risk is highest along the corridors of the hydrographic network, which is to be expected as runoff travel times will increase the further away from the water body. Pockets of unconnected areas exist within the catchment where areas of land drain to water bodies (such as unconnected ditched and ponds) that are not connected to the main River Ugie network.

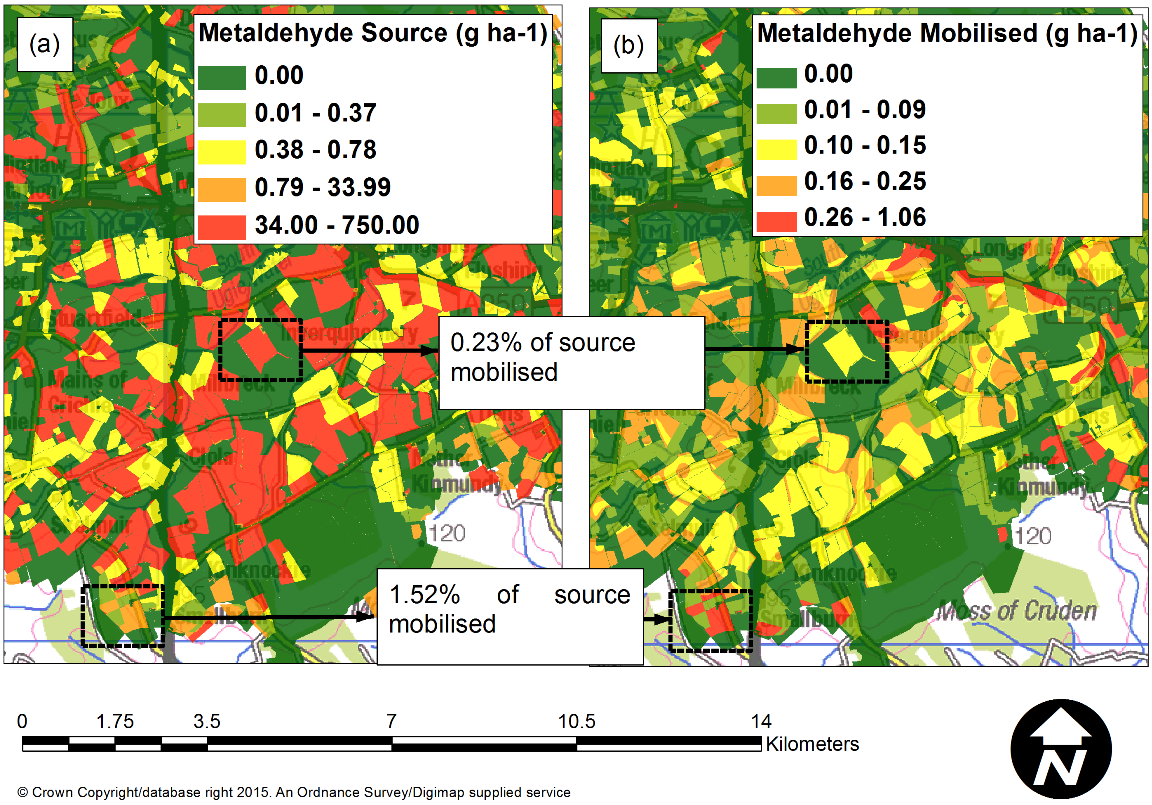


Figure 5.7 - Example of how risk transfers through the models with metaldehyde outputs. Note the variability in pesticide mobilisation meaning that the highest source risks do not always relate to the highest overall risk.

The average transfer of risk from source to water body for the catchment is detailed in Table 5.7 for each pollutant using the dominant land use classification model output (sediment is not included because it does not have a separate source methodology). Transfer of source load to the water body is generally low for most pollutants except nitrate where around half of the surplus (available source) is delivered to the water body. Higher percentage nitrate losses are in line with other studies such as Allingham et al. (2002) who found an average 60.1% loss of soil nitrate surplus to leaching. All of the pesticides have less than 1% of the applied load reaching the water body which is consistent with field investigations (e.g. Leu et al., 2004; Riise et al., 2004). Fertiliser P delivery to the Ugie was around 1% of applied fertiliser, which is in the lower range of applied P fertiliser losses identified in a review of literature by Hart et al., 2004 (0.03% - 42%). However most of the studies reviewed were plot studies not taking into account P losses at the catchment scale and thus fertiliser P losses in CaRPoW are likely to be lower. Percentage mobilisation and delivery of livestock P was lower than fertiliser P and corresponds well to the 0.4% loss for solid manure found by Heathwaite et al. (1998). It must be noted that this study was based on applied solid manure rather than directly excreted manure as no studies could be found on percentage P mobilisation from directly excreted manure. Likewise no field studies were found that derived the proportion of soil Soluble P and Total P that is mobilised or delivered from the source. However it is reasonable to assume that less of the soil P would be mobilised as it is locked up in the soil and has less interaction with surface and subsurface hydrology than the fertiliser and livestock P.

Table 5.7 - Average percentage load transfer from source to delivery for each pollutant with dominant land use from 2008-2012.

Pollutant	Average percentage of source load mobilised	Average percentage of source load delivered	Average percentage of mobilised load delivered
2, 4-D	0.05	0.04	80.00
Chlorotoluron	0.52	0.39	75.00
CMPP	0.18	0.14	77.78
MCPA	0.26	0.2	76.92
Metaldehyde	0.42	0.31	73.81
Metazachlor	0.12	0.09	75.00
Fertiliser P	1.21	0.97	80.17
Livestock P	0.75	0.61	81.33
Soil Soluble P	0.004	0.003	75.00
Soil Total P	0.0004	0.0003	75.00
Nitrate	64.2	52.16	81.25
Sediment	N/A	N/A	78.58

The proportion of mobilised pollutants delivered to the River Ugie ranges from 73.81% - 81.33%. The variability in percentage delivered is driven by the spatial arrangement of mobilisation in relation to areas of high connectivity, as the delivery component is the same for all pollutants.

The fact that the proportion of the source mobilised for each pollutant matches literature values well suggests that the models developed and employed within the framework are able to reproduce the source-mobilisation-delivery continuum reasonably well.

5.6.3 Testing model assumptions – The first rainfall event in the pesticide model

Most of the models implemented within CaRPoW are based on methodologies that have been previously developed and proven in other catchments. The pesticide mobilisation model, however, is a new adaptation of a daily pesticide fate model into a monthly output (that is aggregated to annual) that assumes the first rainfall event after application is the most important for the mobilisation and delivery of pesticides.

A series of hydrological events were sampled using the methodology outlined in section 5.2.2 and Appendix C to test this assumption. The following section details the results of the event sampling and discusses them within the context of the CaRPoW pesticide modelling methodology.

Twelve events in total were attempted to be sampled between April 2014 and April 2015, although on two occasions the sampler failed and no samples were taken (events 7 and 10). A variety of event magnitudes were represented with a peak discharge of 1.84 $m^3 s^{-1}$ (23/06/2014) for the smallest event and 21.13 $m^3 s^{-1}$ for the largest (14/11/2014). The timing of the ten events sampled throughout the year and the two failed sample runs are outlined in the time series graph of discharge and rainfall in Figure 5.8.

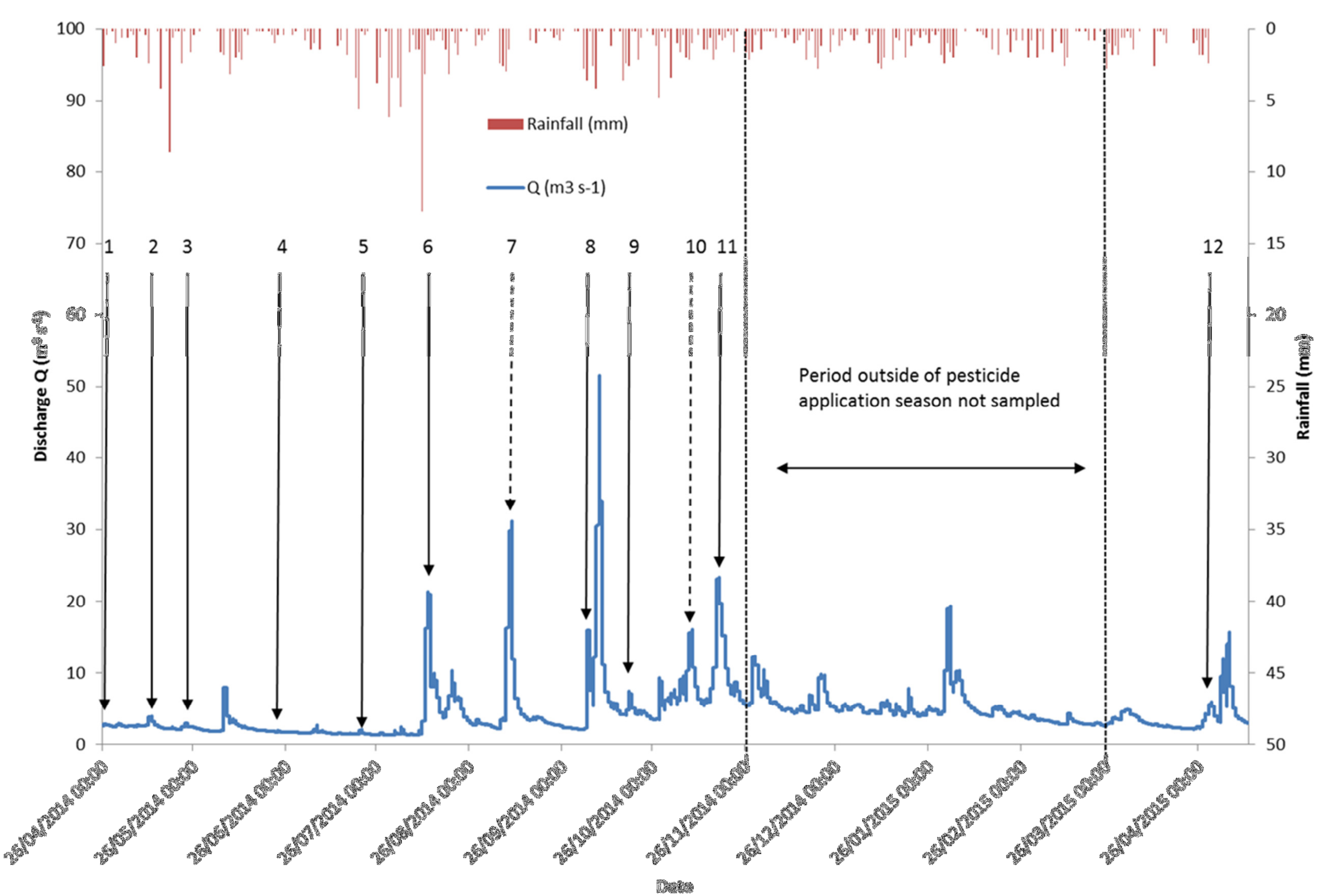


Figure 5.8 - Time series of discharge and rainfall for the period of storm sampling for model validation. Note – Events 7 and 9 was triggered but the sampler failed

Figure 5.6 shows that the majority of the major hydrological events within pesticide application periods were captured by the sampling, with the exception of events 7 and 10 which were missed when the sampler failed.

All sampled events detected at least one pesticide above the limit of detection (variable depending on pesticide), however not all events had pesticides in concentrations above the PCV (Permitted Concentration Value) which is 0.1 µg l^{-1} for pesticides (Table 5.8). All of the 6 pesticides identified by Scottish Water as problematic (2, 4-D, chlorotoluron, CMPP, MCPA, metaldehyde and metazachlor) were observed above the PCV value in at least one event, some of them in multiple events. Other pesticides observed above the PCV value not picked up by normal regulatory sampling include Clopyralid, Diuron and Triclopyr.

Table 5.8 - Peak discharge and pesticides detected above the permitted concentration value (PCV) for drinking water during storm sampling.

Event Number	**Date Sampler Triggered**	**Peak Discharge During Sampling (m^3 s^{-1})**	**Pesticides Above PCV Limit (0.1 µg l^{-1})**	**Pesticides Above Limit of Detection**
1	26/06/2014	3.2	CMPP	Atrazine, Carbendazim, Chlorotoluron, Clopyralid, Dicamba, CMPP, Methiocard, Tebuconazole
2	10/05/2014	3.82	None	2, 4-D, Chlorotoluron, MCPA, CMPP, Metazachlor, Metsulfuron-Methyl

3	22/05/2014	3.22	Clopyralid	2, 4-D, Carbendazim, Clopyralid, Dicamba, Diuron, Epoxiconazole, MCPA, CMPP, Metazachlor, Metsulfuron-Methyl, Tebuconazole, Tribenuron-Methyl
4	23/06/2014	1.91	None	2, 4-D, Chlorotoluron, Dicamba, MCPA, Metazachlor, Tebuconazole
5	20/07/2014	1.99	Diuron	2, 4-D, Chlorotoluron, Clopyralid, Diuron, Epoxiconazole, Isoproturon, MCPA, CMPP, Metaldehyde, Metazachlor, Tebuconazole,
6	10/08/2014	15.452	Diuron, Triclopyr	2, 4-D, Atrazine, Carbendazim, Chlorotoluron, Clopyralid, Diuron, Epoxiconazole, Isoproturon, Linuron, MCPA, CMPP, Metaldehyde, Metazachlor, Metsulfuron-Methyl, Monuron, Propiconazole, Tebuconazole, Triclopyr
7 (Sampler Failure)	08/09/2014	30.23	N/A	N/A

8	04/10/2014	15.96	Metaldehyde, Metazachlor	Carbendazim, Chlorotoluron, Cyproconazole, Diuron, Epoxyconazole, Isoproturon, MCPA, CMPP, Metaldehyde, Matazachlor, Methiocarb, Metsulfuron-Methyl, Teuconazole
9	18/10/2014	7.42	Chlorotoluron	Chlorotoluron, MCPA, Metaldehyde, Metazachlor, Tebuconazole
10 (Sampler Failure)	06/11/2014	15.83	N/A	N/A
11	14/11/2014	21.13	Chlorotoluron	Chlorotoluron, CMPP, Metaldehyde, Metazachlor, Tebuconazole
12	26/04/2015	4.25	2, 4-D, CMPP, MCPA	2, 4-D, Chlorotoluron, Clopyralid, MCPA, CMPP, Metazachlor, Tebuconazole

Loadings for both the individual storms and the total year (calculated from the 41 samples taken during the SLM monitoring) were calculated using method E from Defew et al. (2013). The aggregated loads from the storm samples and the total loads for the year presented in Table 5.9 show that a large proportion of the total annual load is derived from the 10 events sampled. This is particularly telling of the importance of the storm events considering that the two largest discharge events on 08/09 and 08/10 were not sampled. The inclusion of these storm events in the sampling may have increased the percentage contribution of the storm events to total annual load.

The data therefore highlights the importance hydrological events in terms of the total annual pesticide load from the catchment. To determine the importance of the first event after application the data must be discussed with reference to pesticide application dates.

Table 5.9 - Total annual loads calculated from Sustainable Land Management (SLM) monitoring data and total loads from event samples for the 6 problem pesticides in the River Ugie 04/2014 – 04/2015

Pesticide	Total Loads from event sampling (Apr 2014 - Apr 2015) (g)	Total Loads from SLM catchment monitoring data (Apr 2014 - Apr 2015) (g)	Percentage contribution from event sampling (g)
2, 4-D	389	892	43
Chlorotoluron	975	1294	75
CMPP	378	691	54
MCPA	316	563	56
Metaldehyde	851	1319	64
Metazachlor	871	1403	62

It is difficult to speculate on which events constitute the “first event after application” in general terms for the catchment without exact knowledge of when pesticides were applied. However judgement can be made by using the information gleaned from the agronomist interviews as outlined in section 5.2.6.1 and Appendix D in conjunction with the pesticide loadings of individual events (data not shown).

2, 4-D and MCPA are applied in the late spring for ragwort in grassland and in the early summer for cereal crops. The highest loadings of both substances were found in events 6 and 12 which relate to both a summer and spring events respectively. Chlorotoluron loads were highest in events 6, 8 and 11. Events 8 and 11 are likely to relate to the application of chlorotoluron in winter cereals, and event 6 to the application in some instances to spring barley. Loads of CMPP were highest in events 1 and 6 which relate to their use on spring cereals. Finally the highest metaldehyde and metazachlor loads were present in storms 7 and 9. Metazachlor is applied to oilseed rape in this period, and metaldehyde to oilseed rape, winter wheat and potatoes.

The large contribution of the events to total annual load and the proximity of the highest event loadings to the application periods of specific pesticides suggest that the first hydrologically effective rainfall event following application is very important to overall load contribution and catchment pesticide risk. The assumptions taken in the CaRPoW pesticide fate model are therefore deemed acceptable.

5.6.4 Model performance – Total and spatial load prediction

5.6.4.1 Total load prediction

The ability of the models to accurately predict catchment and sub-catchment pollutant loads are discussed in this section. Box and whisker plots for total predicted load and total observed load for the whole Ugie catchment are shown in Figures 5.9 and 5.10 for the years 2012 and 2013.

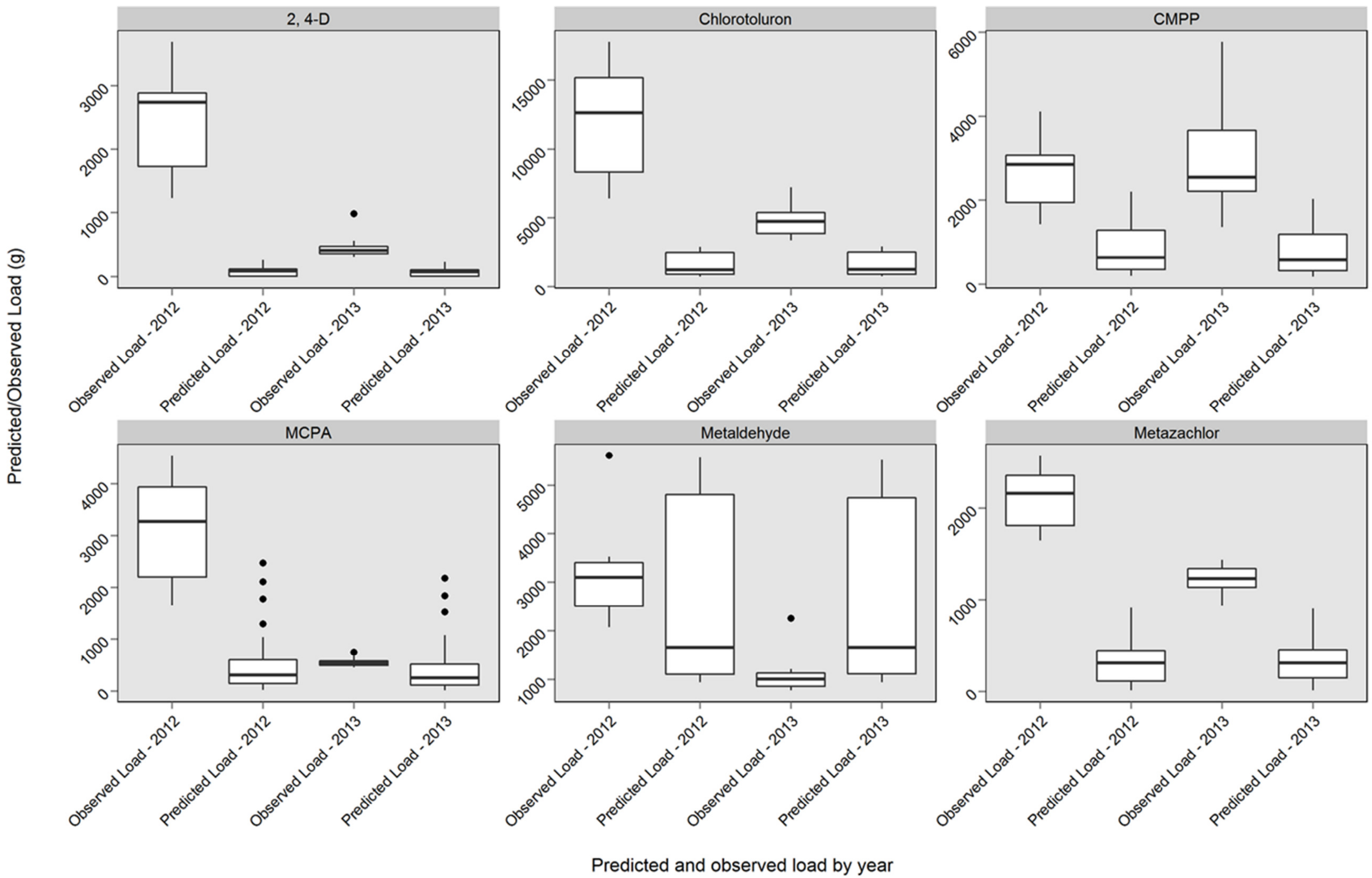


Figure 5.9 - Box and whisker plots of total predicted (CaRPoW) and observed catchment load with uncertainty ranges for pesticides in the years 2012 and 2013

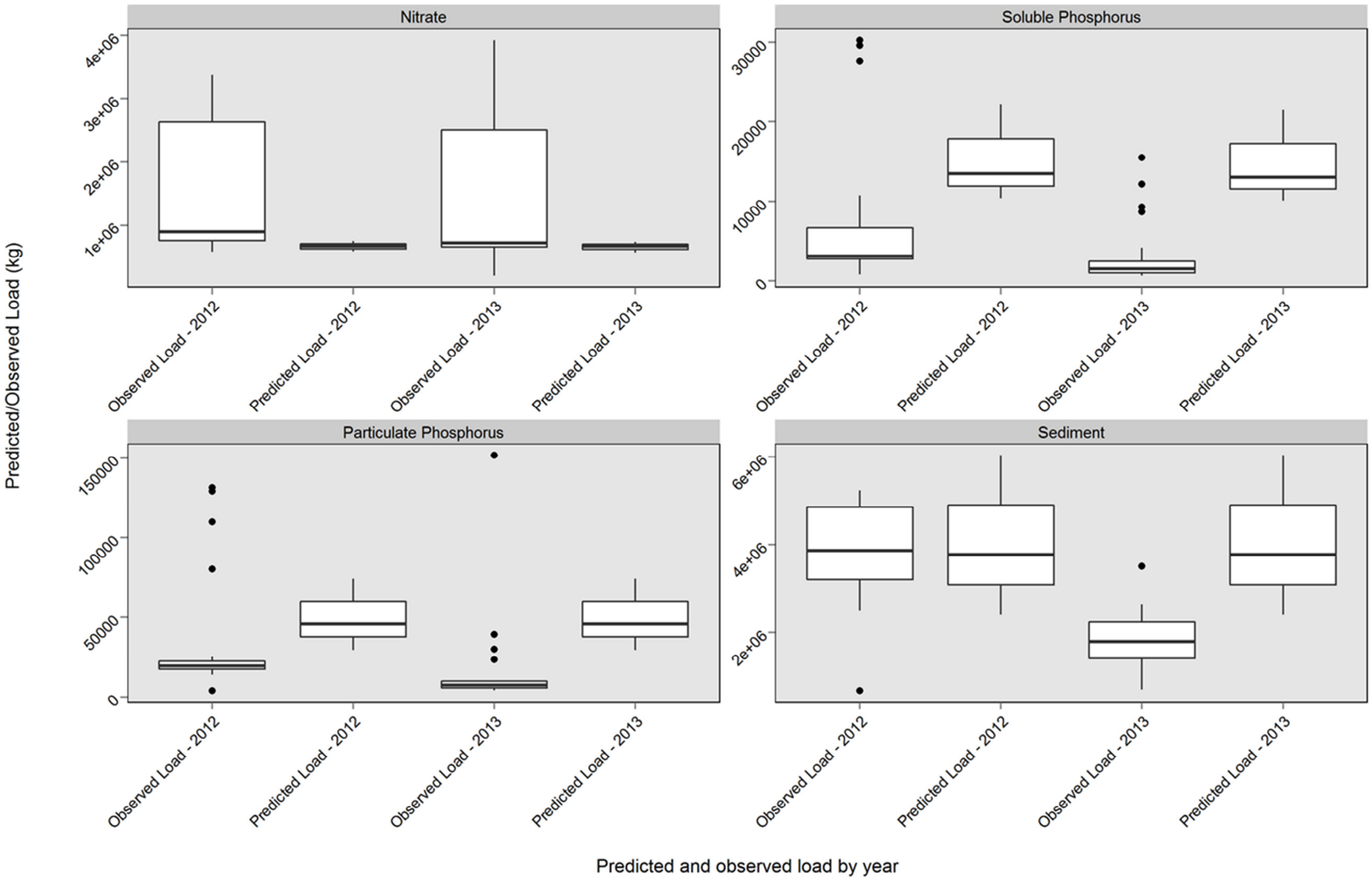


Figure 5.10 - Box and whisker plots of total predicted (CaRPoW) and observed catchment load with uncertainty ranges for Nitrate, Phosphorus and Sediment in the years 2012 and 2013

Analysis of the box plot for pesticides in Figure 5.9 shows that, within uncertainty ranges, the predicted loads are in the same order of magnitude as observed loads with the exception of chlorotoluron and 2, 4-D, which the model under predicts by a factor of 5. Overall there is a general under prediction in load for all pesticides across the two modelled years.

The results from the comparison of maximum, minimum and mean loads within the uncertainty ranges for predicted against observed using Root Mean Square Error are shown in Table 5.10. For pesticides the RMSE is generally lower in 2013 than in 2012 suggesting that the model performs better at predicting overall loads in 2013. When the best case scenarios are selected from within the uncertainty ranges of predicted and observed load the RMSE is less than 1000g for all pesticides.

Metaldehyde was consistently the best predicted pesticide over the two years with RMSE values of 92g and 21g respectively. Chlorotoluron was the least well predicted with RMSE values of 996g and 216g.

However when the relative error is considered chlorotoluron is predicted favourably with -18% and -12% error suggesting that higher RMSE values are likely a result of the higher overall loads of chlorotoluron predicted by the model and observed in the catchment. With the exception of 2, 4-D in 2012 (-62%) all pesticide predictions are below 50% RE when the best scenario of predicted and observed loads are considered within the uncertainty ranges. According to Brown et al. (2002), given the constraints of modelling pesticides at the catchment scale, predictions within a factor of 10 of observed values are generally acceptable for the purposes of policy and regulation. Even considering the worst case RE values in Table 5.10 only CMPP and metaldehyde in 2013 have RE values over 1000%. Therefore according to the acceptability limits of Brown et al. (2002) the model predicts pesticide loads well at the catchment scale.

Table 5.10 - Root Mean Square Error (RMSE) (g) and Relative Error (RE) (%) for predicted catchment pesticide load against observed load for the years 2012 and 2013 with different combinations of minimum, maximum and median loads within uncertainty ranges (values in green represent lowest error and red highest error) – Values rounded to the nearest whole number

	Minimum, Maximum and Median Predicted and Observed Load Combinations (Predicted - Observed)								
	RMSE (g)								
Pollutant	Min Min	Min Med	Min Max	Mid Min	Mid Mid	Mid Max	Max Min	Max Med	Max Max
				2012					
2, 4-D (g)	376	733	1561	349	705	1534	293	650	1478
Chloroltoluron (g)	1681	3312	6540	1524	3155	2834	996	4149	5855
CMPP (g)	375	785	1269	236	646	1130	260	150	634
MCPA (g)	458	949	1589	375	866	1505	317	174	814
Metaldehyde (g)	324	596	1601	92	364	1369	1144	873	132
Metazachlor (g)	490	665	871	399	573	780	205	380	586
Nitrate (kg)	145628	21488	1250969	171786	4670	1224810	199292	32176	1197305
Soluble Phosphorus (kg)	3155	2307	7574	4115	3267	6614	6893	6045	3836
Particulate Phosphorus (kg)	8373	3297	34386	13563	8487	29196	22509	17433	20250
Sediment (kg)	618131	449468	12672839	1056152	11447	12234818	1785150	717552	11505820
				2013					
2, 4-D (g)	90	130	333	66	106	309	17	57	260
Chloroltoluron (g)	476	1203	2421	316	856	819	216	2150	1729
CMPP (g)	361	749	1776	236	623	1651	223	164	1191
MCPA (g)	129	162	238	55	88	164	556	523	447
Metaldehyde (g)	73	21	484	304	209	253	1526	1431	968
Metazachlor (g)	281	380	487	186	285	392	2	97	204
Nitrate (kg)	174917	34405	1447055	206364	65852	1415608	228207	87695	1393765
Soluble Phosphorus (kg)	3136	2882	2043	4055	3800	1124	6723	6468	1544

Particulate Phosphorus (kg)	9137	7133	40266	14327	12323	35076	23273	21269	26130
Sediment (kg)	649558	184387	53352034	1080861	615690	52920732	1798167	1332996	52203425
					Relative Error (%)				
					2012				
2, 4-D (%)	-100	-100	-100	-88	-91	-93	-62	-71	-78
Chloroltoluron (%)	-79	-85	-92	-65	-75	-87	-18	-43	-70
CMPP (%)	-85	-88	-92	-55	-61	-77	56	36	-20
MCPA (%)	-98	-99	-99	-73	-79	-84	146	90	48
Metaldehyde (%)	-44	-58	-70	0	-26	-47	233	145	75
Metazachlor (%)	-99	-99	-100	-78	-84	-88	-34	-51	-62
Nitrate (%)	119	29	-78	130	65	-55	146	86	-52
Soluble Phosphorus (%)	375	320	43	472	424	76	773	758	183
Particulate Phosphorus (%)	863	222	56	1354	379	131	2210	651	262
Sediment (%)	469	53	-7	760	127	34	1232	254	104
					2013				
2, 4-D (%)	-100	-100	-100	-77	-79	-87	-28	-36	-59
Chloroltoluron (%)	-49	-64	-77	-16	-40	-62	93	37	-12
CMPP (%)	-75	-39	-83	-29	120	-47	171	1132	133
MCPA (%)	-97	-97	-98	-37	-49	-61	479	368	260
Metaldehyde (%)	32	182	-41	137	416	7	692	1620	259
Metazachlor (%)	-99	-99	-99	-67	-76	-82	2	-28	-44
Nitrate (%)	243	24	-54	279	66	-47	302	80	-44
Soluble Phosphorus (%)	786	2338	45	981	3137	81	1626	5008	198
Particulate Phosphorus (%)	3312	380	67	5173	632	155	8336	1062	307
Sediment (%)	63	83	-44	116	171	-18	208	313	25

Visual analysis of loads at the sub-catchment level offers some explanation for the error margins in prediction at the catchment scale. Taking CMPP as an example, Figure 5.11 highlights the effect that an under prediction in sub-catchment H has on the prediction of overall loads. Although uncertainty in the observed load is large the lowest observed load value is still higher than the largest load prediction by a factor of 2.5. Whilst not shown, large observed loads for individual sub-catchments are evident for 2, 4-D, chlorotoluron and MCPA also. Errors in the model predictions presented in Table 5.10 are therefore often a result of large under prediction in one or two sub-catchments, opposed to large under prediction across all sub-catchments. The only pesticide in which the latter is the case is metazachlor which has a general under prediction in all sub-catchments (Figure 5.12).

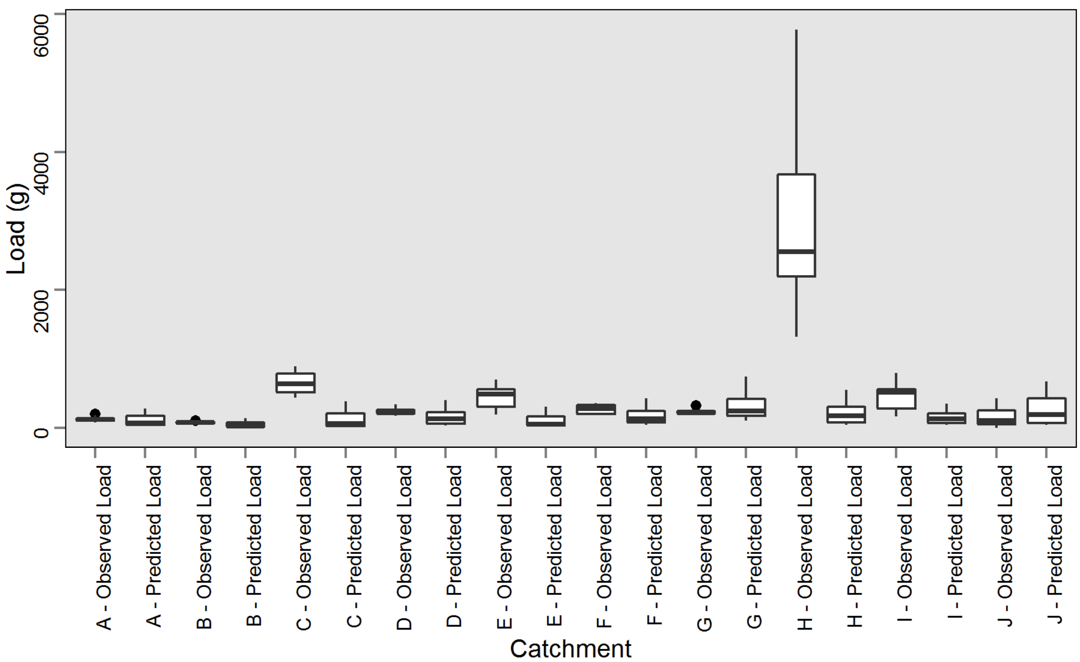


Figure 5.11 - Box and whisker plot of total observed CMPP loads and predicted CMPP loads (CaRPoW) with uncertainty ranges for each sub-catchment in the River Ugie for the 2011-2012 period

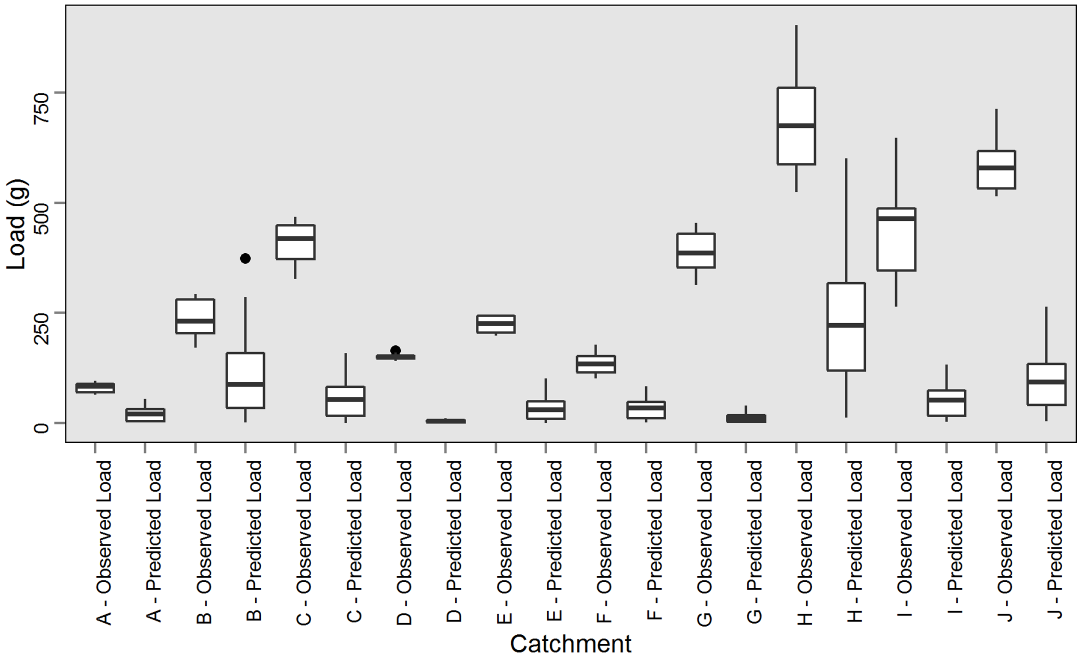


Figure 5.12 - Box and whisker plot of total observed Metazachlor loads and predicted Metazachlor loads (CaRPoW) with uncertainty ranges for each sub-catchment in the River Ugie for the 2011-2012 period

Predicted nitrate loads are within the uncertainty range of calculated observed loads for both 2012 and 2013 (Figure 5.13). According to the RMSE values the model is better at predicting nitrate load in 2012 (4670 kg lowest RMSE within uncertainty range) than in 2013 (34404 kg lowest RMSE within uncertainty range). The RE on the other hand suggests that 2013 loads (24 % lowest RE within uncertainty range) were better predicted than 2012 loads (29 % lowest RE within uncertainty range). Discrepancies between the two error statistics are likely to stem from the very large uncertainty range in the calculated observed loads, which makes it difficult to assess how well the model has performed.

Visual analysis of the loads for individual sub-catchments using Figure 5.13 suggests that the largest uncertainty in calculated observed load comes from sub-catchments K, L and P. Generally however, loads are predicted reasonably well for individual sub-catchments. Subsequently, this suggests that large RMSE and RE values are a result of the high uncertainty range for calculated observed load.

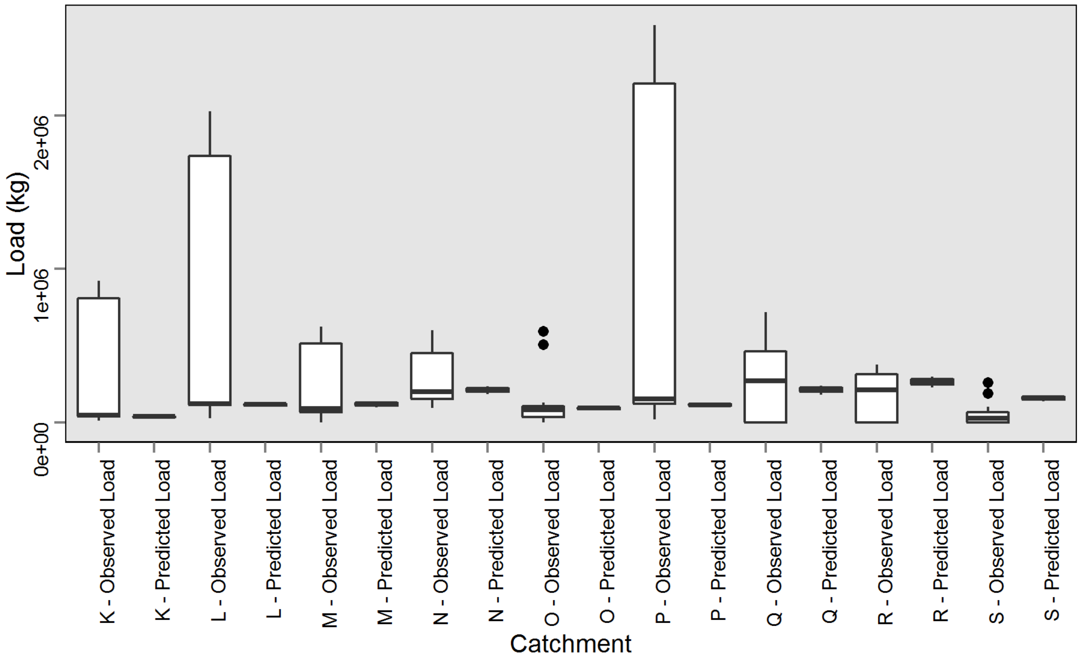


Figure 5.13 - Box and whisker plot of total observed Nitrate loads and predicted Nitrate loads (CaRPoW) with uncertainty ranges for each sub-catchment in the River Ugie for the 2011-2012 period

Soluble phosphorus is over predicted by the model by a factor of approximately 2 within the uncertainty ranges of the model and calculated observed loads for the two years (Figure 5.14). RMSE suggests that the model better predicts 2013 soluble P (1123.89 kg for 2013 compared to 2307 kg for 2012); however the RE is much closer at 42% and 45% for 2012 and 2013 respectively. Analysis of the predictions for individual sub-catchments suggests that the RMSE and RE values may be skewed by the large calculated observed load range for sub-catchment Q (shown in Figure 5.14).

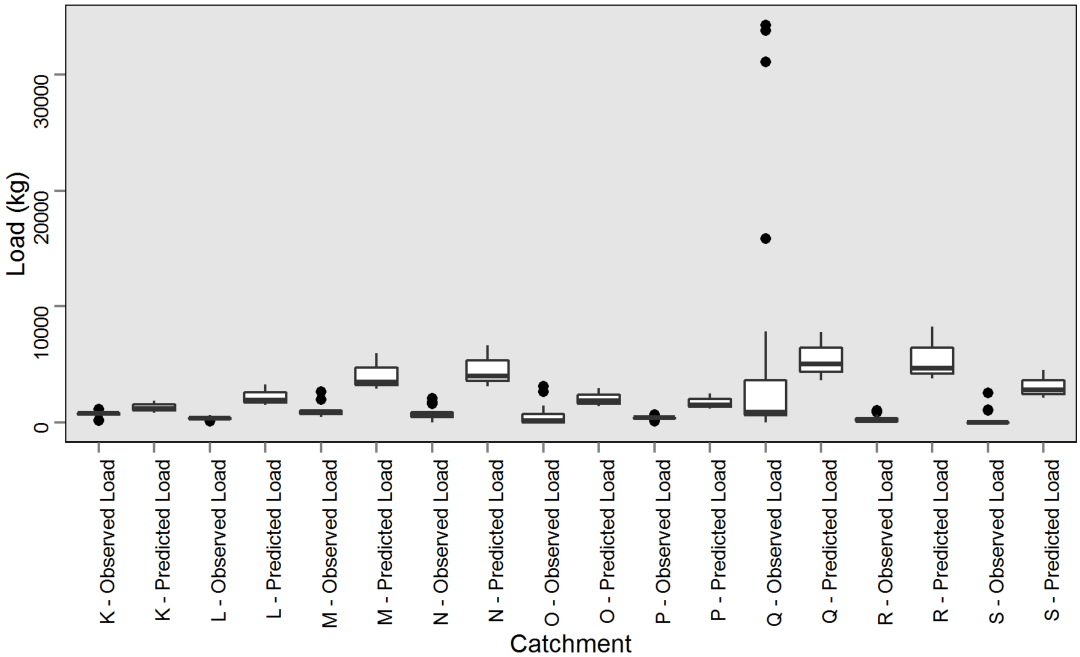


Figure 5.14 - Box and whisker plot of total observed Soluble Phosphorus loads and predicted Soluble Phosphorus loads (CaRPoW) with uncertainty ranges for each sub-catchment in the River Ugie for the 2011-2012 period

Particulate phosphorus follows a similar pattern to soluble phosphorus with over prediction in both years (Figure 5.15). However 2012 loads are predicted better than 2013 when RMSE and RE are considered (lowest RMSE is 3297 kg for 2012 and 7133 kg for 2013, whilst the lowest RE is 55% for 2012 and 67% for 2013). The same skew in the loading for sub-catchment Q is present and somewhat likely to affect both RMSE and RE values (similar to soluble phosphorus).

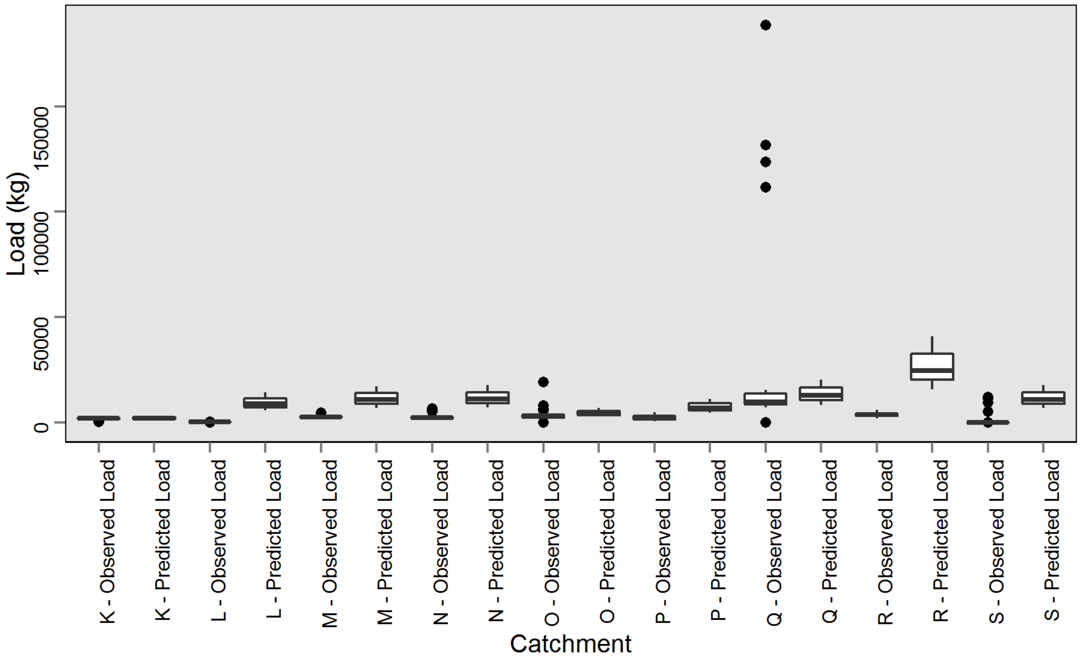


Figure 5.15 - Box and whisker plot of total observed Particulate Phosphorus loads and predicted Particulate Phosphorus loads (CaRPoW) with uncertainty ranges for each sub-catchment in the River Ugie for the 2011-2012 period

Visual comparison of the two years for suspended sediment (Figure 5.10) suggests that the model predicts sediment load well for 2012 and over predicts for 2013. This is confirmed by the lowest RMSE and RE values within the uncertainty ranges, 11446.61 kg and -7% respectively for 2012 and 615690 kg and -18% for 2013. Again sub-catchment Q has a much higher observed load than the other catchments which is under predicted by the model.

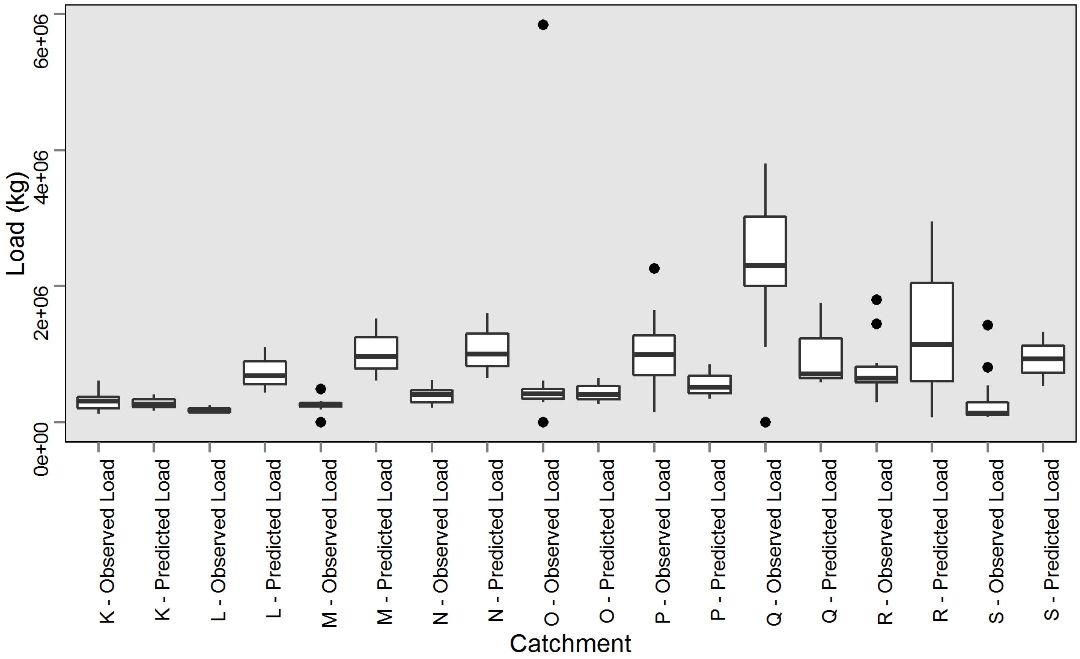


Figure 5.16 - Box and whisker plot of total observed Sediment loads and predicted Sediment loads (CaRPoW) with uncertainty ranges for each sub-catchment in the River Ugie for the 2011-2012 period

5.6.4.2 The spatial distribution of loads

Although predicting total catchment loading is crucial to validating the processes represented in the model, the most important aspect in the context of selecting and targeting measures is to assess if relative spatial risk is accurately represented. Figures 5.17 and 5.18 display the percentage median modelled and observed load contributions of each sub-catchment in the Ugie for the two years modelled (2012-2013).

Visual analysis of Figure 5.17 shows that for the pesticides that do not match as well (2, 4-D, CMPP and MCPA), the model generally under predicts sub-catchments with much higher contribution in the observed load (e.g. sub-catchments E and F for 2, 4-D, sub-catchment H for CMPP and sub-catchment 4 for MCPA). The other three pesticides generally match well although Chlorotoluron is over predicted in sub-catchments D and F somewhat, but not to the detriment of their ranked contribution (i.e. they still have a small overall modelled contribution).

In Figure 5.18 nitrate visually matches well to the observed load percentage contribution. In contrast, an under prediction in the load contribution of sub-catchment Q somewhat affects the performance of the model for sediment and particulate phosphorus. Equally the spatial representation of soluble reactive phosphorus is generally hampered by an under prediction in sub-catchment K and an over-prediction in sub-catchments R and S.

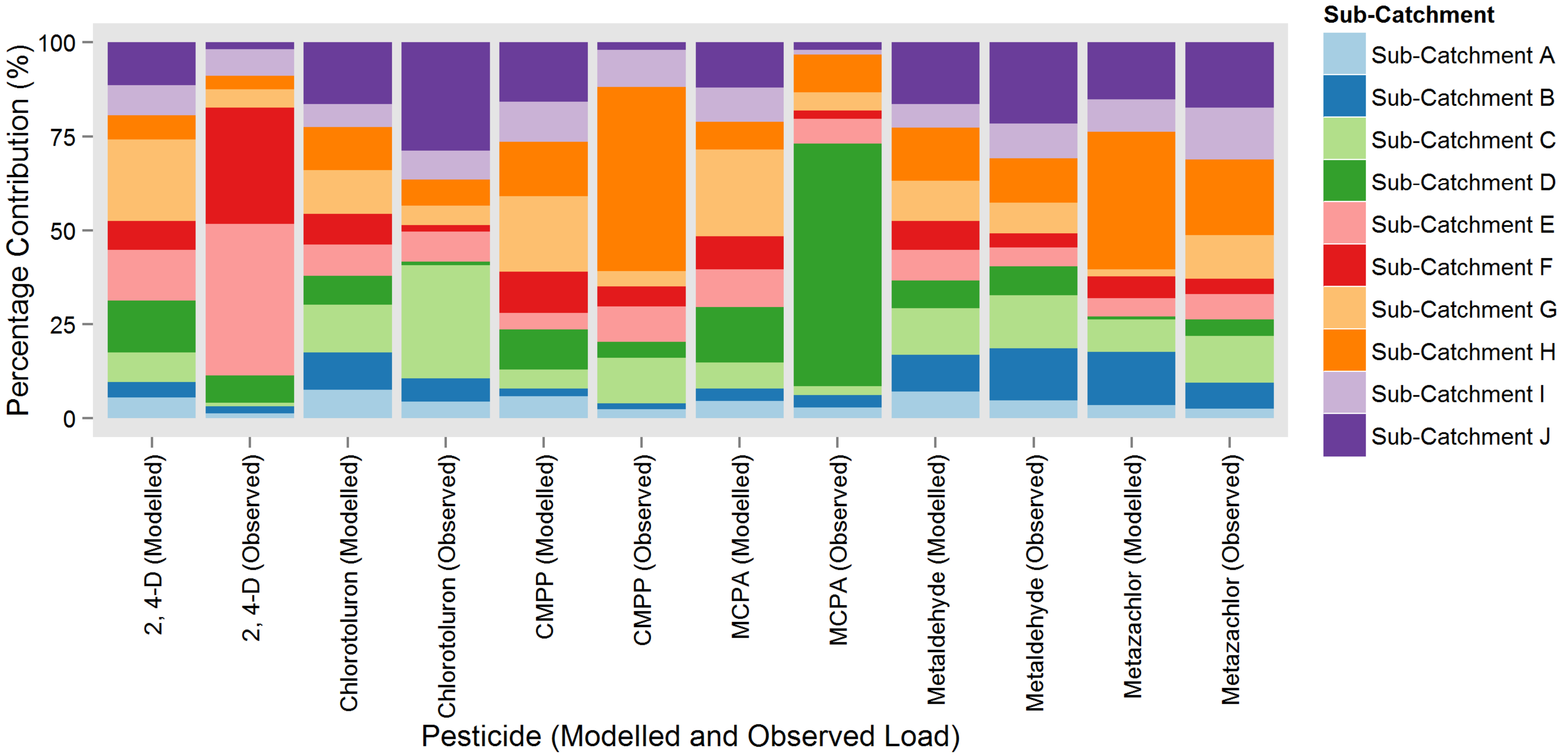


Figure 5.17 - Stacked bar chart representing percentage contribution of each sub-catchment for each pesticide from the median modelled and observed loads (total 2012-2013)

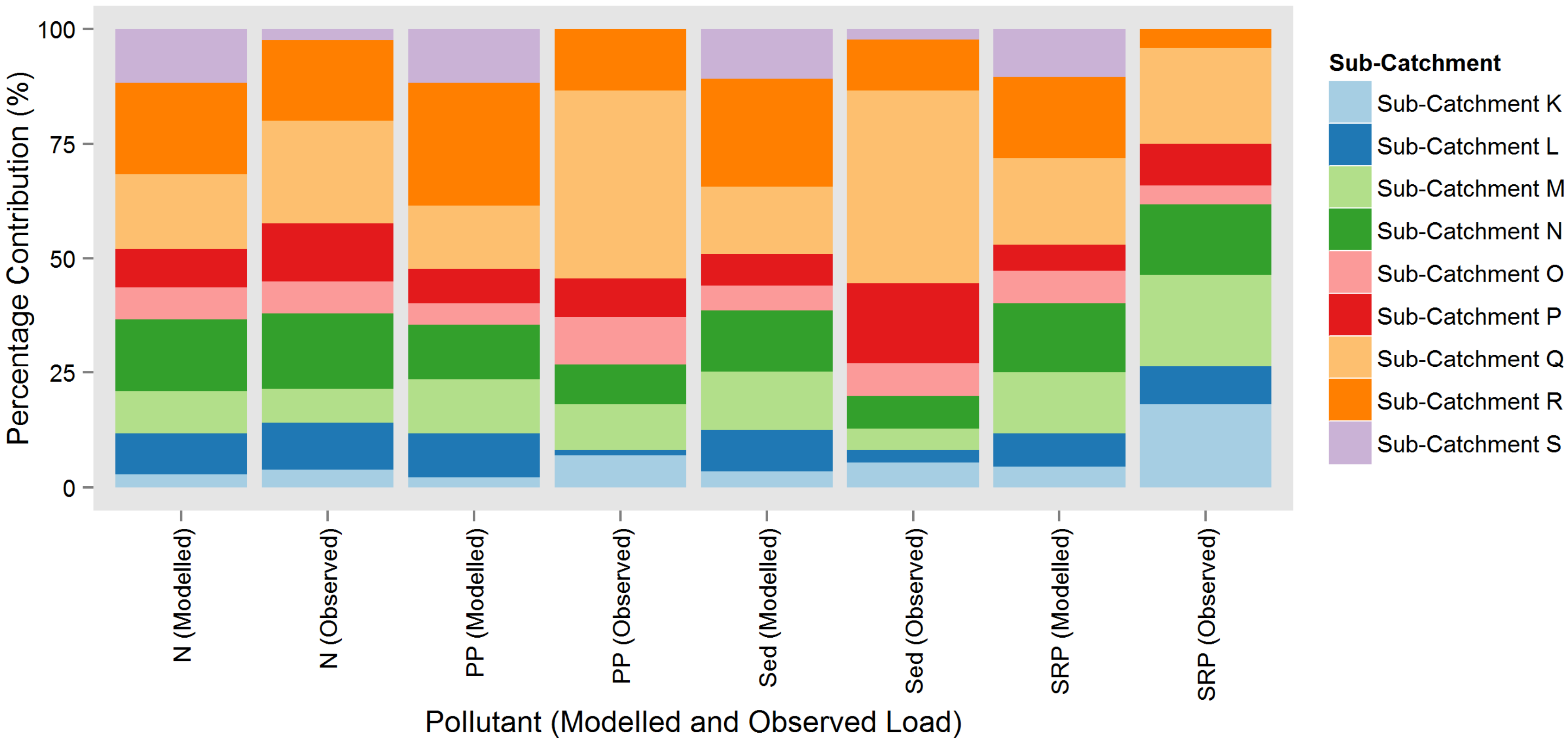


Figure 5.18 - Stacked bar chart representing percentage contribution of each sub-catchment for nutrients and sediment from the median modelled and observed loads (total 2012-2013). N – Nitrate, PP – Particulate Phosphorus, Sed – Sediment, SRP – Soluble Reactive Phosphorus.

The performance of the model in representing pollutant load spatially is assessed statistically using the linear regression and ANCOVA methods detailed in section 5.5. Figures 5.19 and 5.20 illustrate examples of the variability (for chlorotoluron and nitrate) in the linear regression relationships when the uncertainty ranges of modelled load and observed load are high. Both figures demonstrate the potential variation in the spatial relationships of the modelled and predicted loads when the uncertainty ranges are considered for each. The grey area on the two figures represents the 95% confidence intervals for the mean value regression equation. In both examples it suggests that the uncertainty ranges of each point fall within the 95% confidence interval.

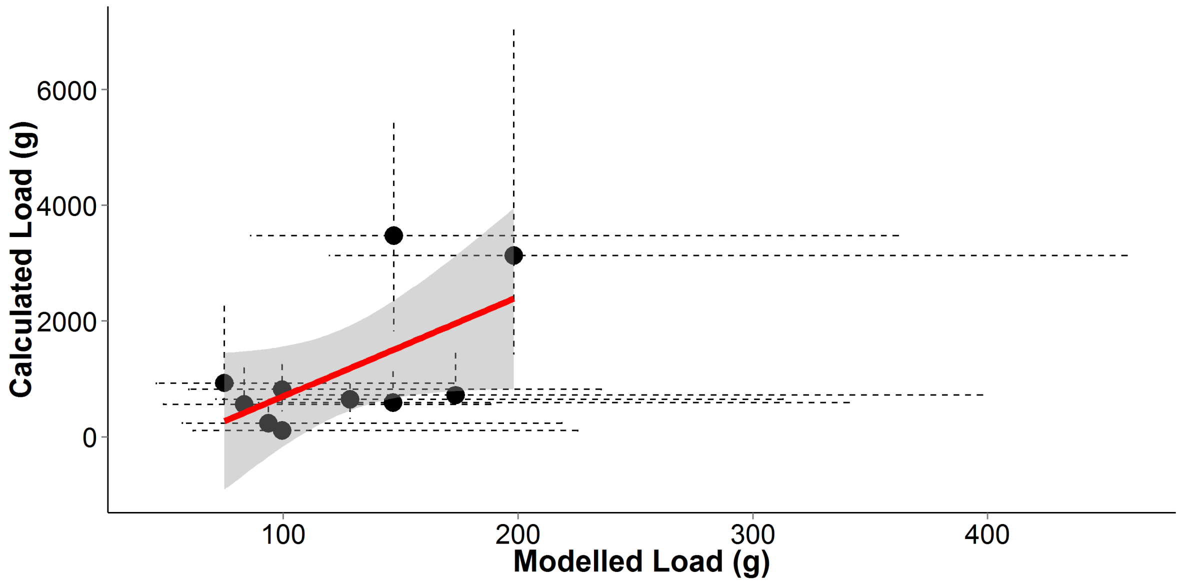


Figure 5.19 - Chlorotoluron 2012 scatter plot with median modelled and observed load regression best fit line. Modelled and observed load uncertainty ranges are displayed with error bars for each point. The grey area represents the 95% confidence interval.

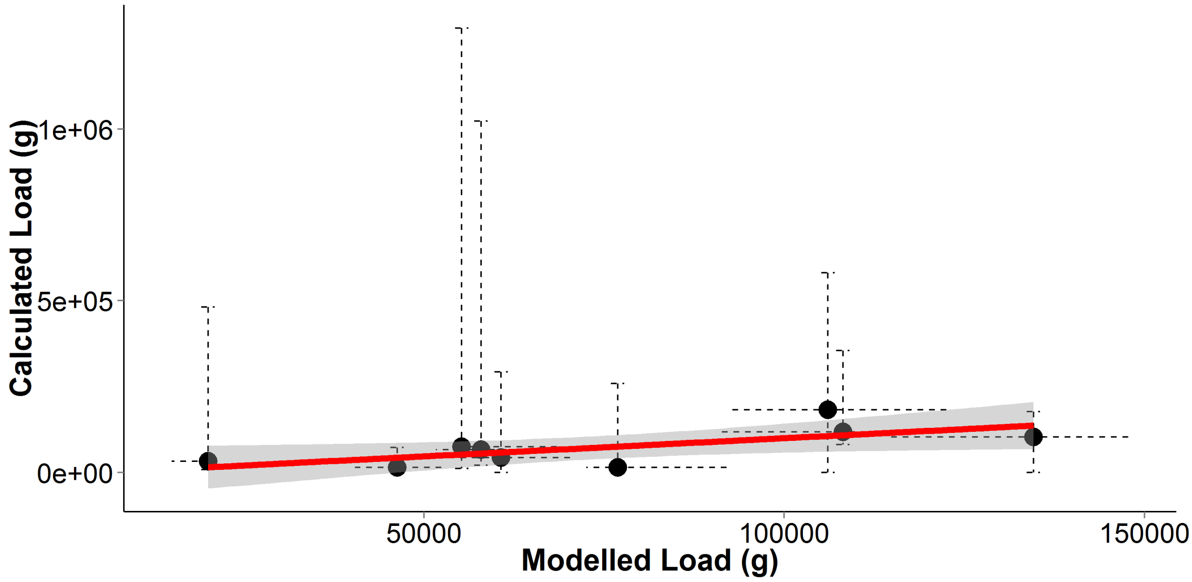


Figure 5.20 - Nitrate 2012 scatter plot with median modelled and observed load regression best fit line. Modelled and observed load uncertainty ranges are displayed with error bars for each point. The grey area represents the 95% confidence interval.

The R^2 and associated significance ($p < 0.05$) for the best fitting linear regression equations between sub-catchment aggregated model and observed load within the uncertainty ranges are displayed in Table 5.11.

Within the uncertainty ranges of both the modelled and observed loads half of the modelled loads are significantly correlated to the observed loads. The best matched pollutants (i.e. significant relationships across all model runs) are chlorotoluron, metaldehyde, metazachlor and nitrate. Others such as 2, 4-D, MCPA and soluble phosphorus are significantly correlated on one year but not the other. Modelled CMPP, particulate phosphorus and sediment loads do not have any significant correlation with observed loads in the two modelled years, although all best fit relationships are weak positive correlations. Spatial correlation is generally better for 2013 than 2012 across all pollutants, with the exception of nitrate and CMPP which are better matched to observed loads in 2012.

Table 5.11 - Best fit R^2 values and associated significance for linear regression analysis between modelled and observed loads within uncertainty ranges for aggregated sub-catchments in the River Ugie.

Pollutant	Model run	Best Fit (R^2)	Regression significance ($p < 0.05$ - in bold)	ANCOVA p value (difference in slope insignificant at $p>0.05$ - in bold)
2, 4-D	2012	0.177	0.23	< 0.05
	2013	0.5	**0.02**	**0.06**
	2012-2013 Total	0.24	0.15	< 0.05
Chlorotoluron	2012	0.54	**0.01**	< 0.05
	2013	0.81	**0.0003**	< 0.05
	2012-2013 Total	0.67	**0.003**	< 0.05
CMPP	2012	0.07	0.44	< 0.05
	2013	0.04	0.54	**0.94**
	2012-2013 Total	0.08	0.4	**0.85**
MCPA	2012	0.38	**0.06**	< 0.05
	2013	0.49	**0.02**	< 0.05
	2012-2013 Total	0.21	0.18	< 0.05
Metaldehyde	2012	0.64	**0.005**	< 0.05
	2013	0.83	**0.0002**	< 0.05
	2012-2013 Total	0.82	**0.0003**	< 0.05
Metazachlor	2012	0.41	**0.04**	< 0.05
	2013	0.85	**0.0001**	< 0.05
	2012-2013 Total	0.66	**0.004**	< 0.05
Nitrate	2012	0.93	**0.00002**	**0.99**
	2013	0.61	**0.01**	**0.96**

	2012-2013 Total	0.79	**0.001**	**0.98**
Soluble Phosphorus	2012	0.34	**0.09**	**0.68**
	2013	0.53	**0.02**	**0.86**
	2012-2013 Total	0.34	**0.09**	**0.71**
Particulate Phosphorus	2012	0.14	0.32	**0.64**
	2013	0.26	0.16	**0.92**
	2012-2013 Total	0.12	0.37	**0.88**
Sediment	2012	0.26	0.16	**0.16**
	2013	0.26	0.16	**0.30**
	2012-2013 Total	0.27	0.15	**0.18**

Results of the ANCOVA analysis used to assess the variance in the relationship between observed and predicted across the uncertainty ranges are also shown in Table 5.11. Where $P < 0.05$ there is a significant difference between the slopes of the regression relationships and therefore the spatial relationship between the modelled and observed loads is variable within the uncertainty ranges.

ANCOVA results show that the majority of the pesticide linear regression models have significantly different linear regression slopes (with the exception of 2, 4-D in 2013 and CMPP in 2013 and 2012-2013). The relationship between the modelled loads and the observed loads subsequently differs significantly across the uncertainty ranges. Though this is not the case for nitrate, both forms of phosphorus and sediment have p-values above 0.05, suggesting no significant difference in the relationship between modelled load and observed load across the uncertainty ranges.

While this is the case, it does not necessarily mean that the pesticide modelled loads are poorly validated against the observed loads. Instead it suggests there is much more variation across the uncertainty ranges for pesticides when compared to the other pollutants. Referring back to Figure 5.7, the discrepancies in the ANCOVA analysis are potentially explained by the wide variation in both modelled and observed uncertainty ranges for pesticides.

5.6.4.3 Discussion of total and spatial load results

Considering the relative simplicity and annual temporal resolution the models provide a reasonable prediction of total catchment loads for all of the pollutants. Taking the assertion from Brown et al. (2002) that model outputs within a factor of 10 of observed values are suitable for regulation and policy use, all models outputs are deemed suitable within predicted and observed load uncertainty ranges. Where spatial load predictions are concerned most pollutants match well with the exception of phosphorus and sediment which are heavily affected by a large and uncertain observed load in one of the sub-catchments.

Within this section possible explanations for the inconsistencies between some of the modelled and observed, total and spatial loads will be discussed.

The general under prediction in loads across all of the pesticides and the spatial mismatch in predicted and observed loads for some pesticides could stem from a number of causes. Although the analysis in section 5.6.3 backs the importance of the first rainfall event assumption, there is still a percentage of the total annual load not accounted for by the events in the analysis. The extra load could be from the carry over and loss of pesticides from the soil between hydrological events or via source and mobilisation mechanisms not considered by the model. For example only losses from pesticides applied to the land and mobilised in hydrological pathways are considered and not losses related to poor practice such as spills, incorrect sprayer wash down, spray drift and overspray (Reichenberger et al., 2007). Such a mechanism could potentially explain the differences between the spatial distribution of CMPP predicted and observed load. Examination of the observation data collected by Scottish Water for each sub-catchment suggests that a large peak in CMPP concentration (3.65 µg L^{-1}) was detected during May 2013 in sub-catchment H (the highest proportional CMPP load). Interestingly this does not correspond to a period of high flow (2.54 m^3 s^{-1}, which equates to Q69 (CEH, 2015)), which potentially suggests a point source either as overspray, spray drift or through poor practice (e.g. a spill, spray wash down). Nevertheless this does not explain the poor CMPP relationship in 2013 which could be attributed to another source not considered by CaRPoW, such as an amenity use of CMPP in golf courses for example which can be a significant source (King and Balogh, 2010).

It is also assumed that the percentage of the crop that receives an application is representative of the Scottish Pesticide Use statistics. In reality the percentage of crop that receives an application may be much higher for certain crops than others in the Ugie, meaning that the source term in the model is too low. Such an assertion offers another explanation for the poor spatial representation of CMPP which is applied to 17% of winter barley, 68% of spring barley, 35% of winter wheat, 67% of spring wheat, 43% of winter oats and 57% of spring oats according to the pesticide use statistics. The information gathered from agronomists stipulates that CMPP is mainly used on spring crops, meaning the percentage application may be higher for these crops and lower for winter barley, winter oats and winter wheat.

Application type is also an important consideration that may explain the poor spatial correlation between predicted and observed loads for 2, 4-D and MCPA. Both substances can be broadcast and spot applied (BCPC, 2013). Currently there is no information or dataset available that can delineate how the substances are applied in the Ugie. Subsequently, establishing the spatial distribution of the source term on land use and application rate alone may lead to a poor spatial match. The pesticide use statistics reinforce this as only 0-2% and 1-47% of grasslands (depending on type) have 2,4-D and MCPA applied to them respectively (Reay, 2010).

The well matched total and spatial load prediction of nitrate loads in the catchment suggests that the methodology of Dunn et al. (2004) represents nitrate processes in the catchment well. Although originally developed for a coarser scale ($1km^2$) the models utility has been proven at the field scale, against aggregated predicted load at least. The results also further reinforce the Scotland specific parameters developed and implemented by Dunn et al. (2004; 2013). Where differences between observed and predicted are present, they can be attributed to the large uncertainty range in the observed loads as outlined in section 5.3.6.1.

General over prediction in the phosphorus models and the poor spatial representation of loads could be due to a number of causes. The low frequency of sampling upon which observed loading values are calculated hold the prospect of being unrepresentative of true loads in the catchment. This is particularly the case for phosphorus where mobilisation and hence the largest quantity of annual load is driven by the largest hydrological events (Heathwaite and Dils, 2000). There is a possibility that the monthly sampling frequency upon which loads are calculated will not capture the most important phosphorus loading event, and thus annual load is underrepresented. The high uncertainty in the observed loads may also explain some of the poor spatial representation of load for soluble phosphorus. Over prediction in sub-catchments R and S and an under prediction in sub-catchment K seem to drive the poor relationship. Interestingly the wastewater treatment works (WWTW) with the largest total phosphorus load contribution are in sub-catchments R and S (Maud WWTW in sub-catchment R contributes 888 kg P per annum and Stuartfield WWTW and Mintlaw WWTW contribute 465 and 2294 kg P per annum respectively in sub-catchment S). When the WWTW phosphorus loads are not subtracted from the observed load, the modelled and observed loads are better matched for soluble phosphorus (best case linear regression relationship for total load over the 2 years within uncertainty ranges is significant at $p < 0.05$ with an R^2 of 0.82). The wastewater loading rates are therefore either incorrect and command a lower proportion of total P load in the catchment or the overall calculated total P load is under calculated.

Other causes for over prediction potentially stem from the parameter values used within the models. Fertiliser application rate for example was based on the Scottish Fertiliser use statistics for each crop type, which is based on a sub-sample of different farm types in Scotland. These figures take no account of the P status of the soil, which would be crucial in the selection of P application rate for a farmer (DEFRA, 2010). Likewise soil soluble P values were derived from Davison et al. (2008) due to a lack of information within the Scottish Soils dataset. In reality soil soluble P will be highly variable according to local land use and soil conditions and not just represented by soil texture, as per the Davison et al. (2008) values.

Particulate phosphorus losses are dependent on the total P values of the Scottish Soils Knowledge and Information Base. Such values have been generated from survey data collected in the 1970s and 1980s, which may be unrepresentative of current soil P status. This is the likely cause of model over prediction for phosphorus P as sediment losses (upon which particulate P mobilisation is based) are fairly well represented by the model (with the exception of over prediction in 2013).

The over prediction of sediment load in 2013 may be due to the same low frequency validation data issues as phosphorus (i.e. missing peaks in sediment load). An alternative explanation is that 2013 was the second driest year (614 mm) within the 30 year climate record used in the model. Although a representative dry year (1994) is included in the uncertainty range of the sediment model there is a possibility this is still not able to predict dry year conditions well.

The poor spatial prediction of particulate phosphorus and sediment loads could stem from the same cause as the models are linked. Both models heavily under predict both pollutants in sub-catchment Q (Figure 5.18), which again could be related to the uncertainty in the observed load calculations. Observed loads in this sub-catchment are calculated using the disaggregation procedure outlined in section 5.2.2. Any upstream load that is under calculated from the observation data upstream is propagated in the disaggregation procedure to calculate observed load in sub-catchment Q (i.e. the loads of nested catchments are subtracted from sub-catchment Q to calculate its load contribution). Hence, the load in sub-catchment Q may be calculated higher than it is in reality.

Aside from the pollutant specific causes for model misrepresentation already discussed there are more general model constraints for all pollutants, which could offer explanations. Perhaps the largest is the representation of small temporal scale processes within CaRPoW. The phosphorus, nitrate and sediment models are all based on averaged annual hydrological values for runoff and drainflow, which means the magnitude of frequency of storm events (important for the mobilisation of phosphorus and sediment in particular) are not captured. Although the pesticide methodology considers the first rainfall event after application, which does give some sense of sub-annual temporality, it does so using averaged data. Therefore, this does not account for the magnitude and frequency of storm events driving the pollutant dynamics upon which the observed loads are calculated. Due to this, averaged observed loads from a longer term monitoring programme may well match better to the CaRPoW modelling outputs as intra-annual variation would be averaged out (Strömqvist et al., 2008). Unfortunately such records were not available at the time of this project.

Likewise, many of the coefficients and variables considered in the modelling methodologies are based on values derived from small scale empirical studies that are not specific to the Ugie catchment. Having such generalised parameters forms the main essence of the CaRPoW framework i.e. an adaptable framework that can be generalised to all catchments. However, their use is likely to be less accurate in predicting actual conditions than perhaps catchment specific empirically derived parameters would.

Within the various methodologies there are a number of pollutant sources and processes not considered that will have an effect on pollutant loading in the catchment. For example, there is no consideration for any in-river processing of pollutants. In reality once pollutants are delivered to the river system they are likely to undergo biological and chemical breakdown (pesticides) (e.g. Chinalia and Killham, 2006), be depleted by in-river biological processing (nutrients) (e.g. Jarvie et al., 2005) or in the case of sediment become entrained within the river system (e.g. Smith et al., 2003). Likewise, sources not considered include but are not exhaustive of, the amenity use of pesticides, nutrients from septic tank systems and within river sources of sediment from bank and bed erosion.

Finally, there are certain characteristics of the years modelled which may explain some of the disparity between observed and modelled loads. For example, although the annual rainfall for 2012 was close to the average for the catchment (798.8 mm for

2012 compared to the annual average of 790.5 mm) the monthly rainfall totals for April and August were much higher than averages for the 1980-2012 period with 79.4 mm and 104.8 mm of rainfall recorded compared to monthly averages of 47.7 mm and 61.7 mm respectively. Such high monthly rainfall for these two months has potential implications for the source, mobilisation and delivery of the pollutants modelled. High rainfall during April for example may increase the proportion of applied 2, 4-D to ley grasslands, MCPA to barley and grasslands and CMPP to ley grasslands to be mobilised and delivered to water bodies. Likewise, more rainfall in August coupled with mild temperatures has the potential to increase slug populations (Choi et al., 2004), which in turn could potentially lead to more widespread applications of metaldehyde and higher mobilisation and delivery rates. A wet August also has the potential to push back the cereal harvest to later in the year which subsequently means that the next crop in the rotation is sown later in the year. If the next crop in the rotation if Oilseed Rape then metazachlor applications are likely to be later in the year where rainfall is likely to be more frequent therefore potentially increasing the likelihood of mobilisation and delivery. All pesticides in 2012 were somewhat under predicted and even though representative wet and dry years were modelled nuances in monthly rainfall totals are not considered. As a result, monthly and annual variations between years must be considered as a potential explanation for model discrepancies.

5.7 Conclusions

This chapter has outlined how the CaRPoW framework and associated modelling methodologies from Chapter 4 have been applied to the River Ugie catchment in the North East of Scotland. The water balance model that provides all of the hydrological input variables to the models has been shown to reproduce catchment baseflow index well against the reference baseflow index for the catchment. It is therefore reasonable to assume that averaged hydrological inputs to the models relating to the ratio of fast to slow hydrological processes are appropriate for use.

The transfer of risk throughout the models has been demonstrated with examples selected that highlight how high risk fields are derived in the catchment. Interestingly the highest source fields do not necessarily correspond to the highest overall risk fields, which suggest that all three risk components play an important role in defining a field's overall risk. The average percentage loss of the sources of most pollutants compare favourably to values in the literature.

The prediction of total load and more importantly the spatial prediction of loads in the catchment have been reproduced well for approximately half of the pollutants in the catchment. Where the models do not predict total and spatial loads well, it has been attributed to either uncertainty in the calculation of observed load or via uncertainties associated within the simplified, averaged and generalised CaRPoW methodologies.

Overall given the complexity in representing catchment risk at the scales attempted and the uncertainties associated with various aspects of the methodology, the models provide an acceptable reproduction of total and spatial risk within the River Ugie. The next phase of the CaRPoW process is to assess the interaction of risk between different pollutants and develop a methodology to select appropriate interventions according to the dominant component of risk.

Chapter 6. Using CaRPoW Model Outputs to Select Measures in the River Ugie Catchment

6.1 Introduction

Chapter 6 demonstrates and discusses how the CaRPoW risk model outputs can be used to select and target interventions in high priority areas. The methodology for comparing pollutant risk is outlined, along with model output post-processing used to determine the potential for risk to be mitigated within each risk component. The methodology is demonstrated and applied to all pollutants to assess the proportion of high risk land areas and risk components. A more detailed examination of the process is then presented, using the pollutants chlorotoluron and metaldehyde as examples. Selected interventions options are discussed in the context of multiple benefits and pollution swapping. Finally the limitations of the methodology and the subsequent post-modelling requirements for decision making are discussed. The chapter is split into the following sections:

- 6.2 Methodology to select and target interventions
- 6.3 Application of the intervention selection methodology to the River Ugie – Results and discussion
- 6.4 Limitations of the measure selection process and subsequent post modelling requirements
- 6.5 Conclusions

6.2 Methodology to select and target interventions

The purpose of this methodology is to ascertain which fields are the highest risks for each pollutant and to select interventions able to mitigate the high risk according to the dominant risk component (source, mobilisation or delivery). The process is illustrated by the Figure 6.1 and explained in this section.

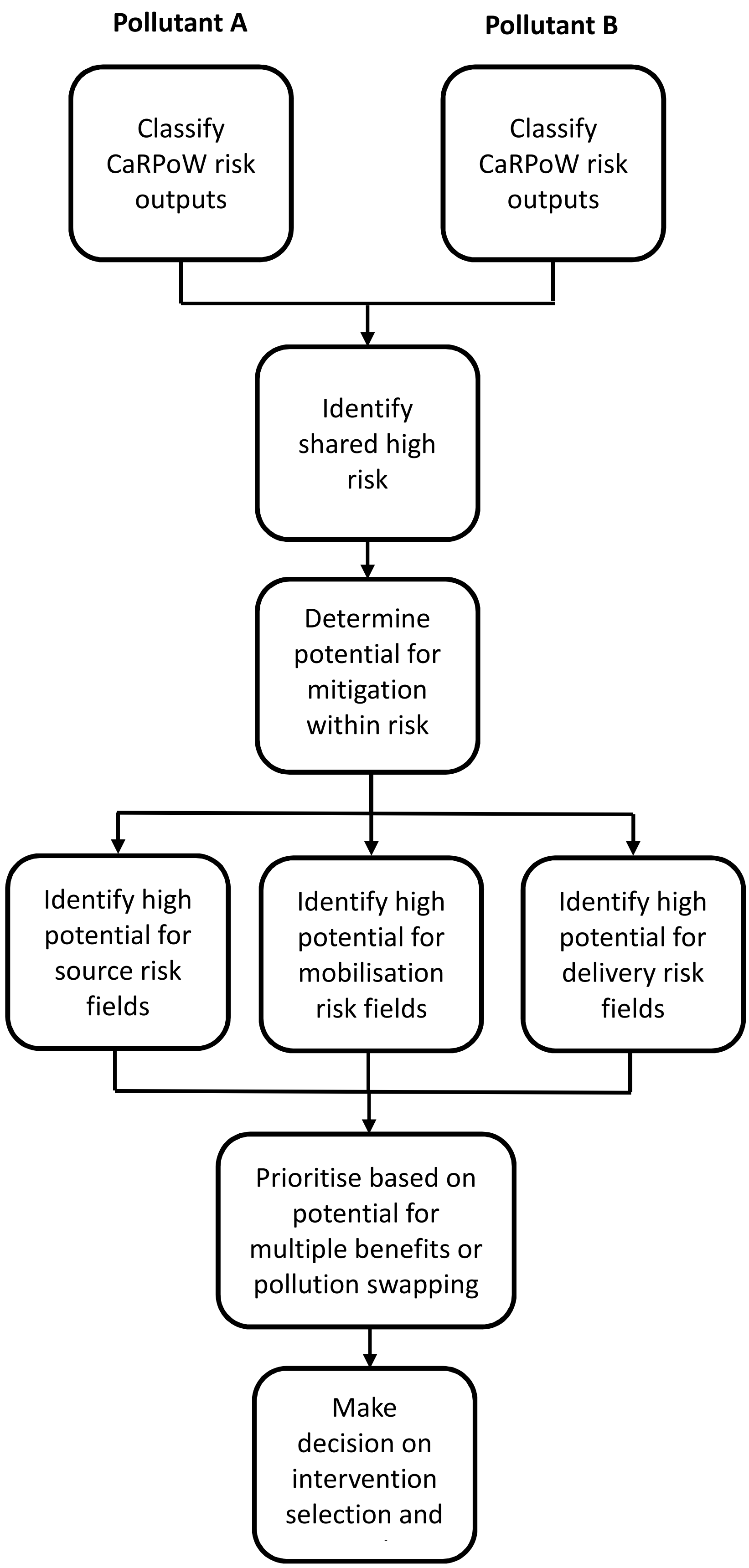


Figure 6.1 - Process of selecting and targeting interventions using CaRPoW model outputs

The first step is to identify where pollutant risks are spatially correlated, as a measure of potentially obtainable multiple benefits. Spearman's rank is used to assess the spatial correlation of modelled risk outputs between different pollutants. A correlation is deemed moderate to strong if r^2 is above 0.5 and significant at the 95% confidence interval ($p < 0.05$).

Once shared risks have been identified the highest risk areas of the catchment are delineated. When assessing single catchments the highest risk fields are determined by selecting the upper quartile of risk. Consequently the perception of 'high risk' is wholly relevant in the context of the catchment. If multiple catchments are to be included in the analysis then the percentile of risk must be assessed across all catchments. It is important that high risk is determined from the pollutant risk per hectare metric ($g\ ha^{-1}$) to reduce the effect of field area.

Where two or more pollutants are being assessed the high risk field outputs are compared to further delimit the number of fields considered to have the highest risk, i.e. a field is only deemed high risk if it is high risk for all pollutants.

After identifying the highest risk fields, potentially appropriate intervention options are selected on the basis of which component of risk (Source, Mobilisation or Delivery) is the most important to overall risk. This is done by assessing where the particular risk component for the field fits within the distribution of the component in all fields across the whole catchment. The premise for this is that the highest percentile risk components are the dominant component of risk and thus where intervention efforts should be focused to mitigate risk. Considering the risk components within their overall distribution also presents a spectrum for what is achievable with the implementation of certain interventions, i.e. what is the minimum risk that can be achieved in the catchment by implementing a particular intervention.

The groupings for the percentile of each risk component in each field within the overall distribution are shown in Table 6.1. Each of the fields that fall within these groups are assigned a classification from low to very high potential for intervention.

Table 6.1 - Risk component percentile groupings and associated potential for intervention classifications from CaRPoW risk model outputs to identify potential of fields for intervention.

Risk Component Percentile (per field)	Potential for Intervention
80 – 100	Very High Potential
60 – 80	High Potential
40 – 60	Moderate Potential
<40	Low Potential

The different spatial scale at which the delivery component works (sub-catchment) merits a slightly different methodology for determining if delivery interventions are preferable. For example, a delivery intervention such as an artificial wetland has the potential to mitigate risk in more than one field if fields are connected within a sub-catchment. It may therefore be preferable to use delivery interventions where high risk fields are clustered and connected.

Such an evaluation is conducted by assessing the upstream risk against the area for each stream or ditch segment in the catchment. The purpose of this is to judge the practicality of connectivity measures such as in ditch wetlands. One of the main considerations for the size of wetland implemented is the volume of flow that passes through the channel, which in turn is dependent upon the upstream drainage area (Millhollon et al., 2009). Thus, it is more practical to target connectivity measures at streams and ditches that have comparatively small drainage areas and high pollutant risk. Splitting the stream and ditch network into segments and dividing the upstream contributing area by the total pollutant risk in that area is the method implemented to assess this (equation 6.01).

$$Conn_{Potential} = \frac{Risk}{a} \tag{6.01}$$

Where $Conn_{Potential}$ is the connectivity potential of the stream segment (g ha^{-1}), $Risk$ is the total pollutant risk in the upstream area (g) and a is the drainage area of the stream segment (ha).

Once the key risk components of each field have been assessed the inventory of measures detailed in Chapter 2 (Table 2.1) is referred to. Interventions are selected according to the pollutant and risk component targeted. Where multiple pollutants are concerned interventions can be selected that mitigate all pollutants considered. At this final stage the interventions selected are cross referenced for the potential for pollution swapping. This is done by using information on the interventions in the inventory and by assessing the risk level in the fields for the pollutants not targeted by the intervention. So, if for example the intervention selected increases the risk of another pollutant and that pollutant is already of a moderate to high risk in the field, the end user may wish to consider an alternative intervention.

6.3 Application of the intervention selection methodology to the River Ugie – Results and discussion

6.3.1 Pollutant risk comparison

The results of the Spearman's rank correlation for the total risk of all of the pollutants modelled with the dominant land use 2008-2012 are displayed using the correlation matrix in Figure 6.2. Of the 45 pollutant relationships tested 16 are moderately to strongly correlated (r^2 => 0.5). Whilst a further 15 have significant weak positive correlations (0.2<= r^2 =<0.5). The remaining 14 are poorly correlated (-0.2<= r^2 =<0.2). None of the pollutants are weakly, moderately or strongly negatively correlated (r^2 => -0.2).

The strongest correlation is between particulate phosphorus and sediment (significant at r^2 0.97), which is unsurprising given the fact that the particulate phosphorus methodology is dependent on the erosion methodology. Other notable strong positive correlations exist between chlorotoluron and CMPP (r^2 = 0.78), chlorotoluron and nitrate (r^2 = 0.68), metaldehyde and CMPP (r^2 = 0.86), CMPP and MCPA (r^2 = 0.78), metaldehyde and MCPA (r^2 = 0.67) and soluble phosphorus and sediment (r^2 = 0.60). Some of these relationships are somewhat expected, especially between the pesticides which are applied to similar land uses. Likewise nitrate which is weakly or strongly correlated to a number of the pesticides has a high risk associated with arable crops, upon which many pesticides are applied.

Further inspection of the scatter plots in Figure 6.2 offers some interesting insights into the nature of the relationships between the different pollutants. There appears to be a variable that affects the slope of the relationship between some of the pollutants. The relationship between nitrate and each of the pesticides chlorotoluron, metaldehyde and CMPP, and the relationship between sediment and particulate phosphorus highlights this most distinctly. Stepwise linear regression analysis was used to determine the variables driving such differences in regression slope.

The relationships between nitrate and pesticides were best explained by the addition of percentage organic matter content (e.g. addition of organic carbon content increases r^2 from 0.28 to 0.40 for relationship between chlorotoluron and nitrate). The important role this variable play in the nature of the relationships is anticipated as the organic matter content of the soil affects how much of the applied pesticide source is available, which incidentally is not considered for nitrate in the model. The variability of the slope regression for particulate phosphorus and sediment was explained by soil association (r^2 improves from 0.88 to 0.94 with addition of soil association variable). In CaRPoW soil association dictates the phosphorus content of the soil, meaning the importance of the soil association in the relationship is anticipated.

These results highlight instances where risks are spatially concurrent between different pollutants (e.g. nitrate and certain pesticides, sediment and particulate phosphorus) and thus where there is potential for multiple pollutant mitigation. Equally they indicate poor risk relationships between pollutants that must be scrutinised when measures are selected to avoid the potential for pollutant swapping.

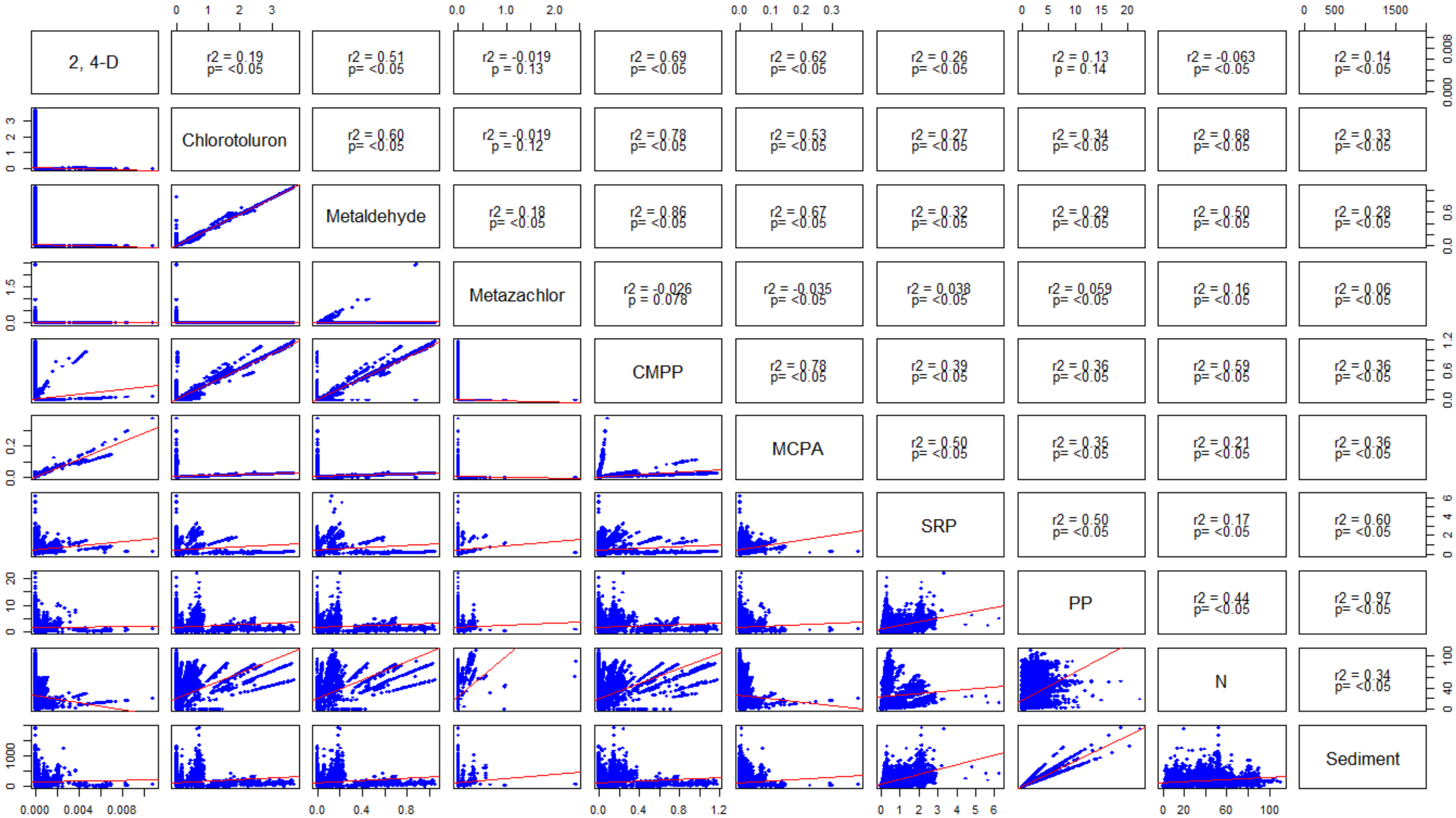


Figure 6.2 - Spearman's correlation matrix for all pollutants modelled with the dominant land use 2008-2012 (units are g ha^{-1} for pesticides and kg ha^{-1} for other pollutants

6.3.2 Selection of interventions

General catchment wide statistics are presented first of all, which outline the designation of the high risk classification for each pollutant and the proportion of the high risk classification that contain the highest risk class for the source, mobilisation and delivery components. The analysis of dominant components at the catchment scale also gives a semblance of the sensitivity of each model to the individual risk components. Following this chlorotoluron and metaldehyde are used as examples within the catchment to demonstrate how the methodology is used in more detail to select and target specific interventions.

6.3.2.1 General results for all pollutants and model risk component sensitivity

Table 6.2 details the area of land constituting the highest percentile overall risk (75th percentile) and highest risk component potential for each pollutant modelled (80th percentile) with the dominant land use classification 2008-2012.

Table 6.2 - Area of land designated high risk (75th percentile) for each pollutant and the proportion of the high risk land area classified as the highest source, mobilisation and delivery class (upper 80th percentile) modelled using the dominant land use classification 2008-2012.

Pollutant	Area total high risk (Ha)	Proportion of total high risk area highest source risk class (Ha, percentage of high risk area in brackets)	Proportion of total high risk area highest mobilisation risk (Ha, percentage of high risk area in brackets)	Proportion of total high risk area highest delivery risk (Ha, percentage of high risk area in brackets)
2, 4-D	2155.4	534.4 (24.7%)	58.7 (2.7%)	218.6 (10.1%)
Chlorotoluron	978.8	727.5 (74.3%)	134.5 (13.7%)	304.7 (31.1%)
CMPP	3991.6	2262.8 (56.6%)	180.8 (4.5%)	258.8 (6.5%)
MCPA	5822.7	3403.1 (58.45%)	165.1 (2.83%)	555.5 (9.5%)
Metaldehyde	2509.8	1662.9 (66.2%)	197.1 (7.85%)	377.0 (15.0%)

Metazachlor	179.9	36.9 (20.6%)	21.3 (11.88%)	31.0 (17.3%)
Nitrate	7323.6	5558.0 (75.9%)	6422.0 (87.68%)	542.0 (7.4%)
Soluble Phosphorus	16997.1	Fertiliser - 5044.8 (68.9%)	Fertiliser - 0 (0%)	1369.2 (8.1%)
		Excreta - 16997.1 (100%)	Excreta - 29.6 (0.2%)	
		Soil Soluble P - 0 (0%)	Soil Soluble P Runoff - 3100.4 (18.2%)	
			Soil Soluble P Drainflow - 5419.9 (31.9%)	
Particulate Phosphorus	18710.5	0 (0%)	Particulate P Runoff - 5672.4 (30.3%)	1277.8 (6.8%)
			Particulate P Drainflow - 6367.2 (34.0%)	
Sediment	6571	n/a	Sediment Runoff - 4549.2 (69.2%)	1465.5 (22.3%)
			Sediment Drainflow - 2568.7 (39.1%)	

The land area designated the highest risk is variable for each pollutant, which is a reflection of the overall risk load for the whole catchment (i.e. the spatial coverage of risk) and the distribution of risk for each pollutant. For example, model results from Chapter 5 show that modelled chlorotoluron load (risk) is larger than modelled MCPA load (risk). However, the risk classification presented here designates more land to the MCPA high risk classification than the chlorotoluron classification does. This suggests that for chlorotoluron a smaller area of land contributes a disproportional area of total risk, whereas the risk is more evenly distributed across the catchment for MCPA, i.e. more land falls into the highest risk category. Making such an assessment is beneficial when mitigating certain pollutants, as fewer interventions are required to reduce higher risk for chlorotoluron.

A large proportion of the high risk areas for many of the pollutants are also designated the highest source risk classification. This either suggests that many of the pollutants are source driven, i.e. overall risk is highly dependent on the presence of a large source availability or the models are overly sensitive to the source component in comparison to mobilisation and delivery.

A few exceptions to this include soil soluble and particulate phosphorus, which both have 0% high source risk within the total source risk areas. There is conceivably a suggestion here that these models are more sensitive to the mobilisation and delivery components, as confirmed by the percentage of high risk areas with high risk mobilisation and delivery classifications. Likewise 2, 4-D and metazachlor have lower potential for source interventions than the other pesticides suggesting the models are either more sensitive to mobilisation and delivery or the models are equally sensitive to all three components.

A large percentage of very high potential mobilisation intervention classifications are present for nitrate, particulate phosphorus and sediment. Which suggests interventions that limit the movement of these pollutants in field, such as contour ploughing and cover crops (Kay et al., 2009; Deasy et al., 2010) may reduce their mobilisation and reduce overall risk.

A large proportion of the high risk land area for chlorotoluron and sediment have a very high potential for delivery interventions, suggesting that breaking up transfer pathways between the mobilised source and the water body are important for these pollutants. The installation of wetlands and in ditch barriers may be useful interventions for these pollutants (Gregoire et al., 2008).

Such results give an indication of the key risk components for each pollutant at the catchment scale, however the real utility of the framework is in the assessment of individual high risk areas on a case by case basis for the selection and targeting of specific interventions.

6.3.2.2 Detailed selection of interventions example – Chlorotoluron and Metaldehyde

Chlorotoluron and metaldehyde have been selected as examples for the detailed methodology in section 6.2 to be applied. Their selection is based on the fact that their risks are well correlated (r^2 = 0.60), their loads (risk) are well represented at the catchment scale and spatially by the CaRPoW pesticide models (results in Chapter 5) and they are both high priority for mitigation in the catchment as designated by Scottish Water.

Results from the shared high risk fields for the two pesticides are displayed in Figure 6.3. A larger area of land is classified as high risk within the metaldehyde risk classification (Figure 6.3a) when compared to the risk classification of chlorotoluron (Figure 6.3b). The spatial distributions of high risk areas for metaldehyde are also more varied, the majority of the high risk chlorotoluron areas are to the east of the catchment and generally along the river corridors.

In total 842 ha of the catchment has a shared high risk classification for chlorotoluron and metaldehyde. Spatially, there are shared high risk fields across the whole catchment, however Figure 6.3c shows that there is a larger cluster of shared risk in the East of the catchment. Of the shared risk areas 599.0 ha (71%) and 692.1 ha (82%) are very high potential for source control for chlorotoluron and metaldehyde respectively. These statistics suggest that metaldehyde may better be controlled at source across the shared risk areas; however both have a high potential for source control. Interestingly the area of land with very high potential for mobilisation interventions is 135.5 ha for both substances suggesting similar mobilisation controls. What is less surprising is that both substances have 286 ha of land classified as high potential for connectivity interventions, as they both use the same connectivity metric.

A small subset of the shared high risk fields can be scrutinised further to demonstrate the measure selection process. The spatial patterns of source, mobilisation and delivery potential for each pollutant are shown in Figure 6.4 for the cluster of high risk fields delineated by the black box in Figure 6.3c. For these fields the potential for source control is very high across the majority of the fields. Mobilisation potential is high for most of fields, with only a few instances of fields with a very high potential for mobilisation interventions. The potential for connectivity interventions is much more varied across the fields, with only a small number having a very high potential for connectivity. Of these a smaller amount are within the catchments of stream segments that have a very high potential for connectivity according to the upstream risk over area method.

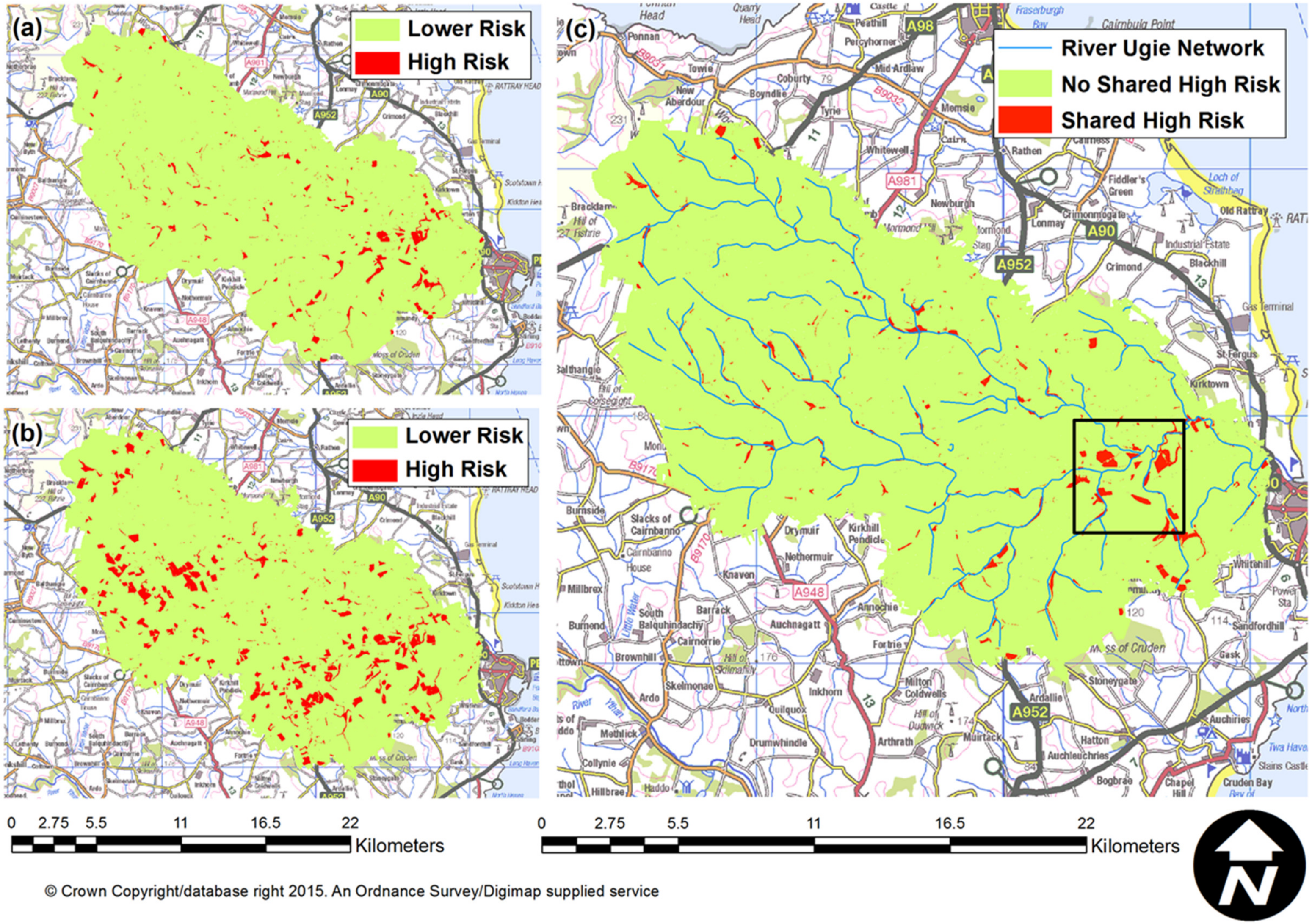


Figure 6.3 – CaRPoW modelled (a) high risk areas for chlorotoluron, (b) high risk areas for metaldehyde, (c) shared high risk areas for chlorotoluron and metaldehyde

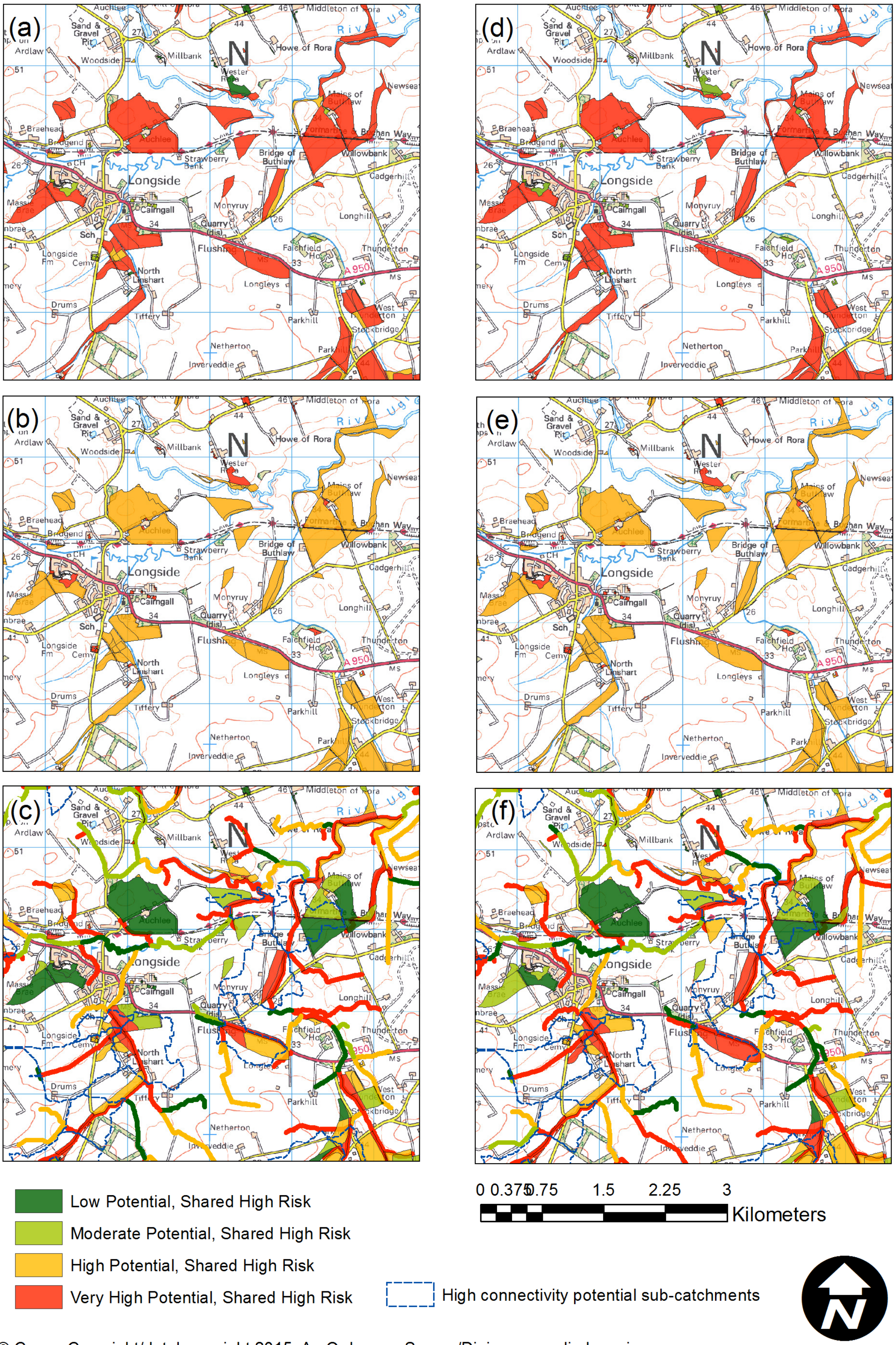


Figure 6.4 - Chlorotoluron source (a), mobilisation (b) and delivery (c) potential and metaldehyde source (d), mobilisation (e) and delivery (f) potential for shared high risk fields within the area highlighted in Figure 6.3c

Based on this assessment the most effective intervention strategy for the majority of the fields is source control. The inventory of measures in Chapter 2 (Table 2.1) details the main source control intervention for pesticides as product substitution. Chlorotoluron and metaldehyde serve two different purposes (broad leaf weed and slug control respectively), which dictates that two separate product substitutions are required to mitigate the source risk. Potential alternatives to the two substances include pendimethalin and diflufenican for chlorotoluron (Gerald Banks, personal communication) and methiocarb and ferric phosphate for metaldehyde. Issues with product substitution for the two substances arise when pollutant swapping is considered. Chlorotoluron for example is used to tackle a range of weed problems and its substitution may require the use of more than one other substance (Dolan et al., 2014). Metaldehyde is used over ferric phosphate because of its lower cost (Gerald Banks, personal communication) and over methiocarb because of its lower ecotoxicity (EFSA, 2010). Even if product substitution mitigates the risk of chlorotoluron and metaldehyde there is potential for the risk to be transferred to the substituted substances which have the same limits under the EU Drinking Water directive (0.1 $\mu g\ l^{-1}$). Product substitution therefore should be limited to the highest risk areas and even then there is a risk of breaching the total pesticide limit of 0.5 $\mu g\ l^{-1}$ if more substances are used within the catchment. Other source control options relate to land use change, which is only considered as a last resort in the face of pesticide license removal (Dolan et al., 2014), and is therefore an unlikely intervention option for water companies.

Subsequently, there are more mobilisation intervention options available for the fields that have a high or very high mobilisation potential. Before mobilisation intervention decisions can be made however a further analysis step is required to determine the ratio of slow flow to fast flow within each high risk field, as certain interventions have the potential to increase the ratio of slow to fast flow processes (e.g. breaking soil compaction). It is important therefore to make sure that fast flow processes are the main driver of pollutant mobilisation, especially where artificial drainage is present as increasing infiltration through breaking soil compaction for example, may increase risk. Of the shared high risk fields only 19.8% are assumed to have artificial drainage using the methodology outlined in Chapter 5 (section 5.3.2). Figure 6.5a details the spatial distribution of drained fields and Figure 6.5b the proportion of fast flow processes for each shared high risk field. The majority of the fields have a runoff proportion between 0.6 and 0.8, with no artificial drainage. What is interesting, is that the fields with the highest mobilisation are actually the fields with the lowest proportion of fast flow processes and have drains present, which implicates the importance of artificial drainage in pesticide mobilisation. In the fields that are very high potential for mobilisation interventions, with a high fast flow proportion and no artificial drains, interventions that increase infiltration such a contour ploughing, reducing compaction, strip contouring etc. would be viable options for reducing both chlorotoluron and metaldehyde mobilisation. Whereas in the fields that have a very high potential for mobilisation intervention, but have a low fast flow proportion and drains present, interventions that increase infiltration and hence drainflow may not be recommended.

Figures 6.4c,f delineate in blue the stream segment sub-catchments within the example area that have a very high pollutant potential according to the upstream risk over contributing area method (i.e. red coloured stream segments) and contain a shared high risk field with a very high potential for both chlorotoluron and metaldehyde connectivity intervention. These are the areas that are most important for connectivity interventions, where artificial wetlands and ditch seepage barriers are potentially best placed in an effort to reduce connectivity and mitigate upstream risk.

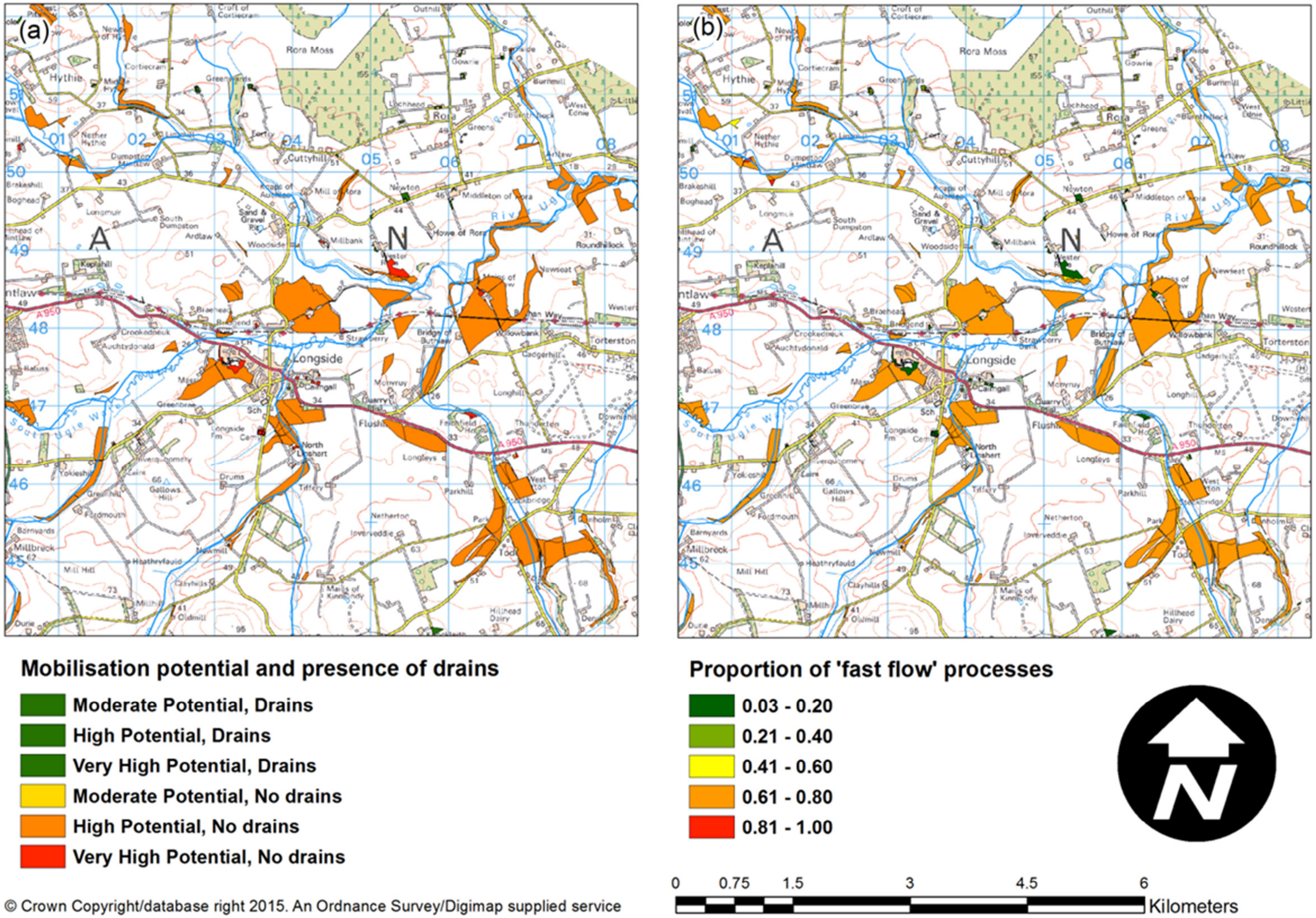


Figure 6.5 – CaRPoW modelled (a) mobilisation intervention potential and the presence of artificial drainage in shared chlorotoluron and metaldehyde high risk fields and (b) the proportion of fast flow processes in shared high risk chlorotoluron and metaldehyde fields

Potential pollutant swapping and multiple benefits are assessed by analysing the intervention potential of the different risk components for all pollutants in the fields where high risk is shared between chlorotoluron and metaldehyde. Table 6.3 presents the percentage of the shared high risk fields within each intervention potential class for the risk components of all pollutants. Examination of the total risk classifications in the first row of Table 6.3 gives an insight as to which pollutants have shared high risks with chlorotoluron and metaldehyde in the catchment, and may therefore also be mitigated by selected interventions. For example, 60% of the shared high risk fields for chlorotoluron and metaldehyde are also high risk for CMPP. Likewise 85%, 80% and 67% of nitrate, soluble phosphorus (fertiliser, excreta and soil soluble P) and soil particulate phosphorus respectively are also high risk.

Looking in more detail into the risk components gives some ideas as to which interventions might promote such multiple benefits. For instance, 89% of the shared risk fields with nitrate have a high source interventions potential, suggesting that the land use changes that benefit chlorotoluron and metaldehyde source risk may also benefit nitrate. 77% of the shared risk area is of a very high potential for interventions that target fast flow mobilisation in undrained areas for soluble phosphorus. Interventions that improve infiltration in these areas such as contour ploughing may also be beneficial to soluble phosphorus in these areas. Over 20% of the sub-catchments that contain a shared high risk field for chlorotoluron and metaldehyde have a very high connectivity over upstream area potential for all pollutants. In these sub-catchments connectivity interventions may provide huge multiple benefits across all pollutants (Brix, 1994; Reichenberger et al., 2007; Haygarth et al., 2012; Kröger et al., 2012).

Table 6.3 - The percentage of the shared risk area for chlorotoluron and metaldehyde in each intervention potential class for all pollutants therefore highlighting the potential for multiple benefits or pollution swapping.

		Percentage area for shared chlorotoluron and metaldehyde high risk fields											
Risk intervention potential component	**Category**	**Chl**	**Metd**	**2, 4-D**	**CMPP**	**MCPA**	**Metz**	**N**	**FertP**	**ExcrtP**	**SolP**	**PP**	**Sed**
Total risk category	High Risk	100	100	0	60	8	0	85	n/a	n/a	80*	67	55
	Lower Risk	0	0	100	30	92	100	15	n/a	n/a	20*	33	45
Source risk intervention potential	Very High	71	82	0	31	0	0	89	100	0	1	0	n/a
	High	12	1	0	52	21	0	6	0	0	5	1	n/a
	Moderate	7	17	0	17	20	0	0	0	0	12	5	n/a
	Low	10	0	100	0	59	100	5	0	100	82	94	n/a
Mobilisation risk intervention potential - all drainage types	Very High	16	16	16	16	16	16	14	2	0	Slow - 14 Fast - 77	Slow - 9 Fast - 41	Slow - 16 Fast - 52
	High	81	81	83	81	81	83	9	12	0	Slow - 3 Fast - 6	Slow - 5 Fast - 8	Slow - 0 Fast - 6
	Moderate	2	2	1	2	2	1	0	26	100	Slow - 0 Fast - 1	Slow - 18 Fast - 14	Slow - 0 Fast - 28
	Low	0	0	0	0	0	0	77	60	0	Slow - 83 Fast - 15	Slow - 68 Fast - 37	Slow - 84 Fast - 14
Mobilisation risk intervention potential - no artificial drains assumed	Very High	2	2	2	2	2	2	1	2	0	Slow - 2 Fast - 77	Slow - 1 Fast - 38	Slow - 2 Fast - 51

	High	78	78	78	78	78	78	2	11	0	Slow - 1 Fast - 1	Slow - 1 Fast - 7	Slow - 0 Fast - 2
	Moderate	1	1	1	1	1	1	0	23	80	Slow - 0 Fast - 0	Slow - 16 Fast - 11	Slow - 0 Fast - 25
	Low	0	0	0	0	0	0	77	44	0	Slow - 77 Fast - 2	Slow - 62 Fast - 24	Slow - 78 Fast - 3
Mobilisation risk intervention potential - artificial drains assumed	Very High	14	14	14	14	14	14	13	0	0	Slow - 12 Fast - 0	Slow - 8 Fast - 4	Slow - 14 Fast - 1
	High	3	4	5	3	3	5	7	1	0	Slow - 2 Fast - 4	Slow - 4 Fast - 2	Slow - 0 Fast - 5
	Moderate	2	1	0	2	2	0	0	2	20	Slow - 0 Fast - 1	Slow - 2 Fast - 3	Slow - 0 Fast - 2
	Low	0	0	0	0	0	0	0	17	0	Slow - 6 Fast - 15	Slow - 6 Fast - 15	Slow - 5 Fast - 11
Connectivity risk intervention potential	Very High	34	34	34	34	34	34	34	34	34	34	34	34
	High	27	27	27	27	27	27	27	27	27	27	27	27
	Moderate	17	17	17	17	17	17	17	17	17	17	17	17
	Low	22	22	22	22	22	22	22	22	22	22	22	22
Upstream connectivity risk potential	Very High	28	28	21	28	21	0	26	n/a	n/a	20	22	24
	High	35	34	24	29	25	0	29	n/a	n/a	26	25	24

Moderate	28	28	24	26	25	0	22	n/a	n/a	26	24	23
Low	9	10	31	17	29	100	23	n/a	n/a	28	29	29

Chl – Chlorotoluron, Metd – Metaldehyde, Metz – Metazachlor, N- Nitrate, FertP – Fertiliser phosphorus, ExcrtP – Excretal phosphorus, SolP – Soil soluble phosphorus, PP – Particulate soil phosphorus, Sed – Sediment

*Values relate to combined risk for fertiliser P, excreta P and soil soluble P

In converse, there are certain interventions that must be selected with caution when the risk components of other pollutant components are considered. For example, although not delineated in the model, nitrate is predominantly mobilised via slower flow processes. 13% of the shared risk area is under drained with a high potential for nitrate mobilisation intervention. This suggests that any mobilisation interventions implemented to increase infiltration could actually exacerbate nitrate mobilisation (and potentially pesticide mobilisation) in these areas. Equally, from a source risk perspective excretal phosphorus sources are low in the shared risk fields as they are largely arable. Any conversion of land from arable to grassland for the purposes of pesticide source reduction could potentially lead to an increase in the risk associated with excretal P, although this must be weighed up against reductions in fertiliser P. Synonymous with this are the sources of some of the pesticides, where for example a shift from winter cereals (as most of the shared high risk areas are) to another land use such as oilseed rape may increase metazachlor use. Connectivity interventions may be the most preferable where pollution swapping is potentially an issue, as attenuating pollutants with in ditch wetlands for example have been shown to reduce load for all of the pollutants modelled (Brix, 1994; Reichenberger et al., 2007; Haygarth et al., 2012; Kröger et al., 2012).

6.4 Limitations of the measure selection process and subsequent post modelling requirements

Although intervention selection results have not been presented for all modelled pollutants, the methodology has been demonstrated and discussed for two key example pollutants in the context of the highest risk areas, most important risk components and possibility for multiple benefits for pollutant swapping. However, there are certain limitations, uncertainties and other factors that must be considered when using the outputs in the intervention selection and targeting decision making process.

Primarily all of the uncertainties and limitations identified in the risk models in Chapter 5 are carried through to the intervention selection and targeting methodology. The delineation of the high risk fields and intervention potential classifications of the risk components are dependent on the risk models. Within the uncertainty ranges of the model, there is therefore potential variation in the classification of the fields used to select and target interventions. Similarly, a number of the pollutants modelled in Chapter 5 were not represented spatially as well as others. Although much of the disparity between modelled and observed spatial loads can be attributed to the poor quality of observation data or the fact that data are not available to represent processes at the scale desired, the end user needs judge whether the models are reliable enough to make intervention decisions. Such considerations are common in the use of many models for decision support (e.g. de Kok et al., 2008). This also potentially affects the validity of the pollutant spatial risk comparison in section 6.3.1.

Questions must also be asked as to whether the processes represented in the model are enough to base intervention selection decisions upon. Referring to the aims in Chapter 1, the purpose of the framework is to give water companies a better understanding of where pollutant risks are derived in their catchments, and potentially how best to deal with them. What the methodology does not do is explicitly determine the potential effectiveness of an intervention implemented in a certain catchment location. This is because the models are somewhat constrained by the simplicity of the processes and scales they represent. They provide more of a guidance in the decision making processes rather than a definitive intervention process representation. To do this for mobilisation and delivery interventions for example, would require a more detailed assessment of landscape microtopography and mobilisation processes (Needelman et al., 2007; Diaz et al., 2012). However, even within the relative simplicity of the methodology it is able to break down the components of risk and give the end user a better understanding of which intervention grouping is potentially best suited to an area.

The present uncertainties and limitations in the selection process mean there are a few recommended steps to be taken before a final intervention decision is made. It is important that consultation is sought by the relevant land owner for any intervention recommended by the model in a certain area. The socio-economic aspect of intervention selection is not considered during model interventions selection, but is crucial in the decision making process. Previous studies have highlighted heterogeneity in the preferences of farmers and land managers for different interventions and levels of uptake (Espinosa-Goded et al., 2010; Christensen et al., 2011; Beharry-Borg et al., 2013). Consequently, one intervention is not likely to be acceptable to land owners in all areas and because of this the end user of the model must treat each land owner on a case by case basis. Where land owners are not approached to implement interventions on their land, but instead apply willingly to a water company funded agri-environment scheme for example, the model outputs can be better used to make decisions on which interventions to fund. Such a process is based on the level of risk in the area where the application has been made and if the intervention addresses the main component of that risk; this method will be explored in more detail in Chapter 7.

The uncertainties and limitations in process representation within the model structure mean that site visits are vital before making final decisions. It is difficult to validate pollutant mobilisation and connectivity but any proposed source interventions can be verified with land owners, i.e. confirmation of land use, application of contaminant etc. Ground truthing can also be used to assess the suitability of mobilisation and delivery interventions. Although there is a dearth in guidance on the practical site considerations for many interventions, site assessments must be undertaken to make sure that selected interventions are practically suitable (Vinten et al., 2005). For example, contour ploughing may be recommended by the model where surface runoff mobilisation is high, but practically contour ploughing is often not suitable on steep slopes where mobilisation may be high (Quinton and Catt, 2004). Likewise, some assumptions in the model relating to the presence of artificial drainage must be verified as this will greatly affect the type of mobilisation and delivery intervention selected.

6.5 Conclusions

In this chapter the methodology used to compare CaRPoW risk outputs for different pollutants and select interventions is outlined and applied to the River Ugie catchment. Spearman's rank correlation highlights the pollutants which have a highly correlated spatial risk and therefore might be mitigated using the same targeted intervention. Examples of such pollutants include certain pesticides such as metaldehyde and chlorotoluron but also different pollutant groups such as nitrate and chlorotoluron. Conversely, some of the pollutants are poorly spatially correlated where caution must be exercised when selecting interventions because of the potential for pollutant swapping. The slope of the correlation relationship appears to be affected by soil parameters for a number of the pollutants.

Designation of the modelled risk into a high and lower risk category according to the upper 25th percentile highlights variability in the area of land contributing to the highest risk. In relation to risk components the source component has the highest percentage intervention potential class (top 20th percentile) for most of the pollutants with the exception of particulate phosphorus, which suggests that source strength is the predominant component of risk within the models.

Taking chlorotoluron and metaldehyde as examples only a small area of the catchment (842 ha) has shared high risk between the two pollutants. In these areas source risk is the predominant component of risk, suggesting source control measures are likely to be the most effective. However, there are also fields that receive important risk contributions from the mobilisation and delivery components as well. More detailed assessment against other pollutants highlights areas of land where multiple benefits can be achieved with some interventions, but at the same time highlights instances where measures that increase the risk of other pollutant, e.g. increasing infiltration may exacerbate nitrate pollution.

Overall the utility of the methodology for selecting the interventions groupings based on the important components of modelled risk has been demonstrated. However, uncertainties and limitations in the methodologies mean that decisions based on model outputs also need to be considered in conjunction with site assessments of the high risk areas and consultation with land owners.

Chapter 7. The integration of CaRPoW into Scottish Water's Sustainable Land Management processes – A retrospective economic analysis

7.1 Introduction

An EngD thesis requires that a section or theme in the thesis is dedicated to a business evaluation of the knowledge generated by the research. This can be in the form of a marketing, economic, investment, technology management, cost-benefit, or legal analysis of the research outcomes in the context of the industry the research is undertaken within. Therefore, this chapter assesses the business integration of the CaRPoW framework in both Scottish Water and the wider water industry.

Initially the chapter details the catchment management processes developed by Scottish Water thus so far and identifies key aspects of the process where CaRPoW could be utilised. A retrospective economic analysis is undertaken to assess theoretical savings generated by implementing CaRPoW from the start of Scottish Water's Sustainable Land Management (SLM) scheme. Catchment monitoring locations and applications to the incentive scheme are evaluated against CaRPoW model outputs to benchmark theoretical savings and missed opportunities for investment between 2011 and the end of 2014. The analysis has been limited to savings made within Scottish Water's current sustainable land management scheme and is therefore concerned with the way in which the efficacy and efficiency of the scheme can be improved. The reason for doing this is to limit the analysis to data readily available from the scheme and to initially assess what impacts CaRPoW has on the efficiency of the scheme rather than the wider benefits of adopting the approach. It is recognised however, that there is scope for widening the analysis to assess other benefits of the framework such as the reduction in treatment costs, reduction in time spent on the ground by catchment officers etc. These analyses would potentially provide further economic benefits to Scottish Water, but were not included in the analysis.

Finally, a redesign of the SLM process and a blueprint for water quality catchment management with the full integration of CaRPoW is presented and discussed in relation to how it potentially improves the efficiency, uptake and success of catchment management.

The chapter takes the following structure:

- 7.2 The Sustainable Land Management project process
- 7.3 Retrospective economic analysis
- 7.4 The use of CaRPoW going forward – Redesigning the SLM and water industry catchment management processes
- 7.5 Conclusions

7.2 The Sustainable Land Management (SLM) process

7.2.1 The current SLM process

Scottish Water's SLM project was set up to improve drinking water quality within a number of drinking water supply catchments. Throughout its progression, the project has gone through a number of stages that are detailed in the flow diagram in Figure 7.1.

All stages of the SLM process are in consultation with other catchment stakeholders. For example, the catchment selection process involves engagement with organisations such as SEPA and Scottish Natural Heritage (SNH), right the way through to the funding of measures which includes close communication with land owners.

The initial catchment selection process back in 2010 narrowed down a long list of catchments identified from the raw water quality report into 6 catchments to be included in the project. Catchments were selected according to a number of criteria including potential Operational Expenditure (OPEX) (e.g. chemical and energy costs) savings, Capital Expenditure (CAPEX) (e.g. investment in new treatment processes) savings, opportunity for measure success, if they are within the SEPA priority catchment scheme, potential for multiple benefits and presence of a regulatory interest. Catchment selection in the second phase of the scheme for Strategic

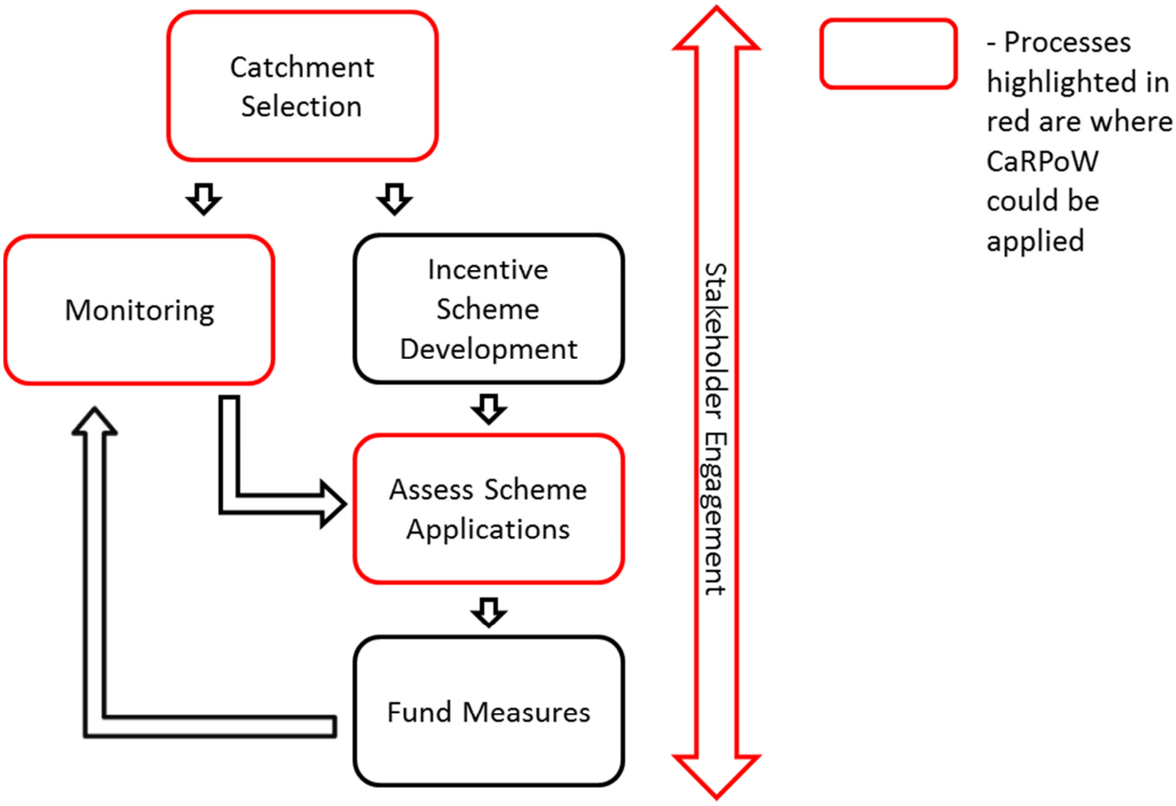


Figure 7.1 – Current Sustainable Land Management flow diagram from catchment selection to the funding of measures (processes marked in red are there CaRPoW may be applicable)

Review 2015 (SR15) is based on water quality trigger levels (half of PCV for Trihalomethanes or Total Organic Carbon for example), the proportion of the catchment with organic soils, access to the catchment, drinking water safety plan risk rating and cost of monitoring. Priority catchments in SR15 are largely related to upland water quality issues.

Once catchments are included in the SLM project, a monitoring programme is designed to determine spatial water quality patterns and develop a more detailed picture of water quality dynamics in the catchment. A pragmatic approach is taken to monitoring in order to capture the necessary spatial variance in water quality at a reasonable cost, at sites that are easily accessible.

The incentive scheme has so far gone through two iterations, with changes in the way interventions are funded and additions made to the list of funded items. 31 items are available for funding in the latest incentive scheme, these are documented in Table 2.1

in Chapter 2. Certain interventions are only eligible in some catchments depending on the water quality issue.

Applications to the scheme are assessed against set criteria following confirmation they are within the incentive scheme catchment. Farms with applications are subject to a visit by a catchment liaison officer who completes a determination report with the help of decision trees to make judgments as to whether to fund the items in the application. The decision trees prioritise certain sub-catchments for intervention according to results from the monitoring programme and if the interventions applied for will mitigate the pollutants of concern in the catchment. An example of a decision tree for pesticides in the Ugie is shown in Figure 7.2 in section 7.3. A final decision is made on an application at a determination meeting involving the catchment liaison officer and the catchment management technical lead.

Monitoring continues over the course of these processes to assess the potential effect implemented interventions have on raw water quality.

7.2.2 CaRPoW and the current SLM process

There are a number of parts of the current SLM process that may benefit from the application of the CaRPoW framework. The processes marked in red in Figure 7.1 have been highlighted as examples of such processes.

During catchment selection CaRPoW could be used in two ways. Firstly, it can be used to define overall pollutant risks between different catchments. Identifying which catchments have the highest total risk may inform which catchments to include in the SLM programme. Secondly, the spatial distribution of risk in the catchment may inform whether SLM is feasible within each catchment. If, for example, risks are concentrated to one area of a catchment the perception may be that targeted efforts in a small high risk area may realistically mitigate the issue. Whereas distributed risk across the whole catchment (especially in large catchments) may be more difficult to mitigate from a practical and economic perspective.

Once catchments have been selected CaRPoW can be used in the design of the monitoring programme. Given the uncertainties and limitations of some of the modelling methodologies it may be unacceptable to remove monitoring entirely from some areas of the catchment. However, CaRPoW could be used to distribute the frequency of monitoring between low and high risk areas, e.g. to make decisions on which catchment areas are monitored weekly and which are monitored fortnightly. This is particularly beneficial for pesticide monitoring which has very high analytical costs relative to other pollutants.

The main application of CaRPoW and the purpose for which it was developed is to make decisions on which applications to the incentive scheme should be prioritised for funding. Applications to the scheme can be assessed against the CaRPoW outputs to see if they are within high risk areas for the pollutant they aim to mitigate, target the dominant component of that risk and determine if they provide any mitigation or enhancement of other pollutants. Again, the framework should be used in conjunction with the analysis of monitoring data and possibly a farm visit (although applications may not require a farm visit if they are in a low risk area according to CaRPoW and the monitoring data).

The outputs of CaRPoW are useful from the standpoint of stakeholder engagement, especially as a tool to communicate pollutant issues in a catchment. The high resolution of the model outputs allows land owners to visualise where there land sits within the pollutant risk for the whole catchment. Such visual engagement may prove important in the decision of the land owner to apply to the scheme or even change practices at their own initiative.

7.3 Quantifying the benefit of CaRPoW in the current process – retrospective economic analysis

To demonstrate and quantify the economic effect of including CaRPoW in the processes detailed in section 7.2 a theoretical retrospective economic analysis can be undertaken using the costs accrued by the SLM project from 2010 – 2014. Presently, the River Ugie catchment is at the stage of assessing scheme application and funding measures. Therefore the model outputs will first of all be used to assess theoretical savings generated by using CaRPoW to design the monitoring programme in the Ugie catchment. Following this, CaRPoW outputs will be included in the scheme application decision making process and mock decisions made on which applications to fund. The catchment selection process is not included in the analysis as CaRPoW has only been applied to the River Ugie catchment in this project.

7.3.1 Operational cost savings from catchment monitoring

From June 2011 until August 2011, the ten monitoring locations in the catchment were sampled on a fortnightly basis. The initial fortnightly programme was not deemed high enough resolution to capture temporal variability in pesticide concentrations, which is the reason it was switched to a weekly sampling programme in August 2011. Budgetary restraints and the identification of problem sub-catchments meant that sampling was moved back to a fortnightly basis from March 2015.

The catchment was sampled 172 times from June 2011 until the end of 2014, giving a total of 1720 samples. In total it costs £450 to sample all ten locations in the same visit. Each of these samples costs £141.73 to process and analyse for the full suite of pesticides, meaning that Scottish Water spent £321,175.60 on sampling and analysis in the Ugie catchment from June 2011 until the end of 2014.

In section 7.2 it was hypothesised that the CaRPoW outputs could be used to assess the monitoring requirements in a catchment by determining which sub-catchments were high risk and therefore designing a monitoring programme around this. Taking the ten sub-catchments monitored in the Ugie for SLM, the average modelled risk (load) per hectare can be calculated to give an idea as to which catchments are on average higher risk for the 6 pesticides modelled. Results are presented in Table 7.1 alongside the results from the first year of monitoring as an extra validation step for using the CaRPoW approach to design monitoring strategies.

The first possibility is to assess whether any sub-catchments are consistently low risk for all pesticides and could therefore be removed from monitoring completely. Across all pesticides, sub-catchment D stands out as consistently low risk based on CaRPoW outputs. However, results from the first year of monitoring show that the sub-catchment had a high load of MCPA which was not represented by CaRPoW. Due to the uncertainties in some aspects of the CaRPoW approach detailed in Chapter 5 (e.g. capturing intra-annual variability, representing point source risk), removing monitoring from all sub-catchments completely may be too uncertain.

Thus, the second possibility is to assess whether the frequency of sampling can be reduced for certain pesticides in certain low risk sub-catchments. This allows costs to be reduced but also reduces the associated uncertainties of not sampling in all sub-catchments all together. Tailoring the monitoring programme frequency first requires an understanding of which pesticides are grouped in analysis suites together as they are not tested for individually. In the case of the priority pesticides in the Ugie 2, 4-D, MCPA and CMPP are in the same suite, with chlorotoluron and metazachlor together in a different suite. Only metaldehyde has its own separate test.

Sub-catchments in which theoretical savings can be made from reduced monitoring according to both CaRPoW risk and validated by the first year of monitoring can be selected on the basis that all pesticides in the suite are relatively low risk. Consulting Table 7.1, certain sub-catchments stand out as low risk across the different pesticide suites. For example, sub-catchment B is low risk across the pesticides 2, 4-D, CMPP and MCPA which are in the same suite. Likewise, sub-catchments D, E and G are low risk for the pesticides chlorotoluron, metaldehyde and metazachlor. A case could therefore be made for removing these analyses from these sub-catchments completely or reducing the frequency in which these analyses are undertaken on samples from these sub-catchments. The potential savings of either removing these analyses or reducing the frequency over the course of the monitoring period are shown in Table 7.2.

Table 7.1 - Predicted and observed load for each pesticide and all sub-catchments, numbers in brackets are sub-catchment rank for predicted and observed load

(a)

	Predicted/Observed Load (g ha^{-1})											
Sub-catchment	**2, 4-D**		**Chlorotoluron**		**CMPP**		**MCPA**		**Metaldehyde**		**Metazachlor**	
	CaRPoW	**Year 1 Sampling**	**CaRPoW**	**Year 1 Sampling**	**CaRPoW**	**Year 1 Sampling**	**CaRPoW**	**Year 1 Sampling**	**CaRPoW**	**Year 1 Sampling**	**CaRPoW**	**Year 1 Sampling**
A	0.0002 (8)	0.0173 (6)	0.1235 (4)	0.6337 (3)	0.0395 (7)	0.0943 (6)	0.0056 (9)	0.0770 (3)	0.0365 (4)	0.1422 (4)	0.0045 (6)	0.0348 (9)
B	0.0001 (10)	0.0131 (8)	0.1342 (3)	0.2753 (5)	0.0201 (10)	0.0192 (10)	0.0043 (10)	0.0322 (5)	0.0384 (3)	0.2201 (1)	0.0113 (2)	0.0676 (5)
C	0.0002 (6)	0.0187 (5)	0.1791 (1)	1.3253 (1)	0.0510 (5)	0.2697 (1)	0.0102 (4)	0.0239 (6)	0.0487 (1)	0.1691 (3)	0.0084 (4)	0.1170 (3)
D	0.0002 (7)	0.0231 (4)	0.0382 (10)	0.0223 (10)	0.0233 (9)	0.0305 (8)	0.0072 (8)	0.4150 (1)	0.0114 (10)	0.0305 (10)	0.0004 (9)	0.0192 (10)
E	0.0001 (9)	0.3240 (2)	0.0686 (9)	0.2319 (7)	0.0282 (8)	0.1045 (3)	0.0073 (7)	0.0511 (4)	0.0195 (9)	0.0545 (7)	0.0021 (8)	0.0367 (8)
F	0.0003 (3)	0.3535 (1)	0.1221 (5)	0.1460 (9)	0.0747 (1)	0.0998 (5)	0.0131 (3)	0.0195 (8)	0.0346 (5)	0.0365 (8)	0.0034 (7)	0.0410 (7)
G	0.0004 (2)	0.0173 (7)	0.0833 (8)	0.1576 (8)	0.0626 (2)	0.0275 (9)	0.0168 (1)	0.0216 (7)	0.0232 (8)	0.0340 (9)	0.0004 (10)	0.0442 (6)
H	0.0002 (5)	0.0110 (10)	0.0859 (7)	0.2376 (6)	0.0507 (6)	0.1029 (4)	0.0076 (6)	0.0933 (2)	0.0341 (6)	0.1015 (6)	0.0270 (1)	0.0978 (4)
I	0.0004 (1)	0.0578 (3)	0.0905 (6)	0.4858 (4)	0.0617 (3)	0.1813 (2)	0.0140 (2)	0.0000 (9)	0.0292 (7)	0.1319 (5)	0.0083 (9)	0.1355 (1)
J	0.0003 (4)	0.0113 (9)	0.1378 (2)	0.9942 (2)	0.0549 (4)	0.0482 (7)	0.0092 (5)	0.0000 (9)	0.0450 (9)	0.2200 (2)	0.0106 (3)	0.1263 (2)

Table 7.2 - Theoretical cost savings made by tailoring the monitoring programme according to CaRPoW risk outputs (validated by results from first years of monitoring)

Pesticide and Sub-catchment	Retrospective theoretical cost savings made by switching to fortnightly monitoring (2011-2014)	Retrospective theoretical cost savings made for removing analysis from monitoring location completely (2011-2014)
2, 4-D, CMPP and CMPA - Sub-catchment D	£2,435.52	£4,871.04
Chlorotoluron and Metazachlor - Sub-catchments D, E and G	£7,322.04	£14,633.08
Metaldehyde - Sub-catchments D, E and H	£6,277.14	£12,554.28
Total savings	£16,034.70	£32,058.40

The largest savings are generated by reducing the frequency of analysis or removing the analysis for chlorotoluron, metazachlor and metaldehyde in sub-catchments D, E and G. This is arguably the least uncertain option for tailored monitoring also as these pollutants are consistently low risk across both CaRPoW and in the results from the first year of monitoring used for validation.

Overall aggregated savings generated by either lowering the sampling frequency or removing the analysis from identified low risk sub-catchments using CaRPoW represent approximately 5% and 10% of the total monitoring spend respectively. The analysis therefore outlines significant theoretical cost savings by using CaRPoW to tailor the monitoring program in the Ugie, without detriment to the overall quality of the monitoring program.

7.3.2 Assessment of SLM scheme applications against CaRPoW

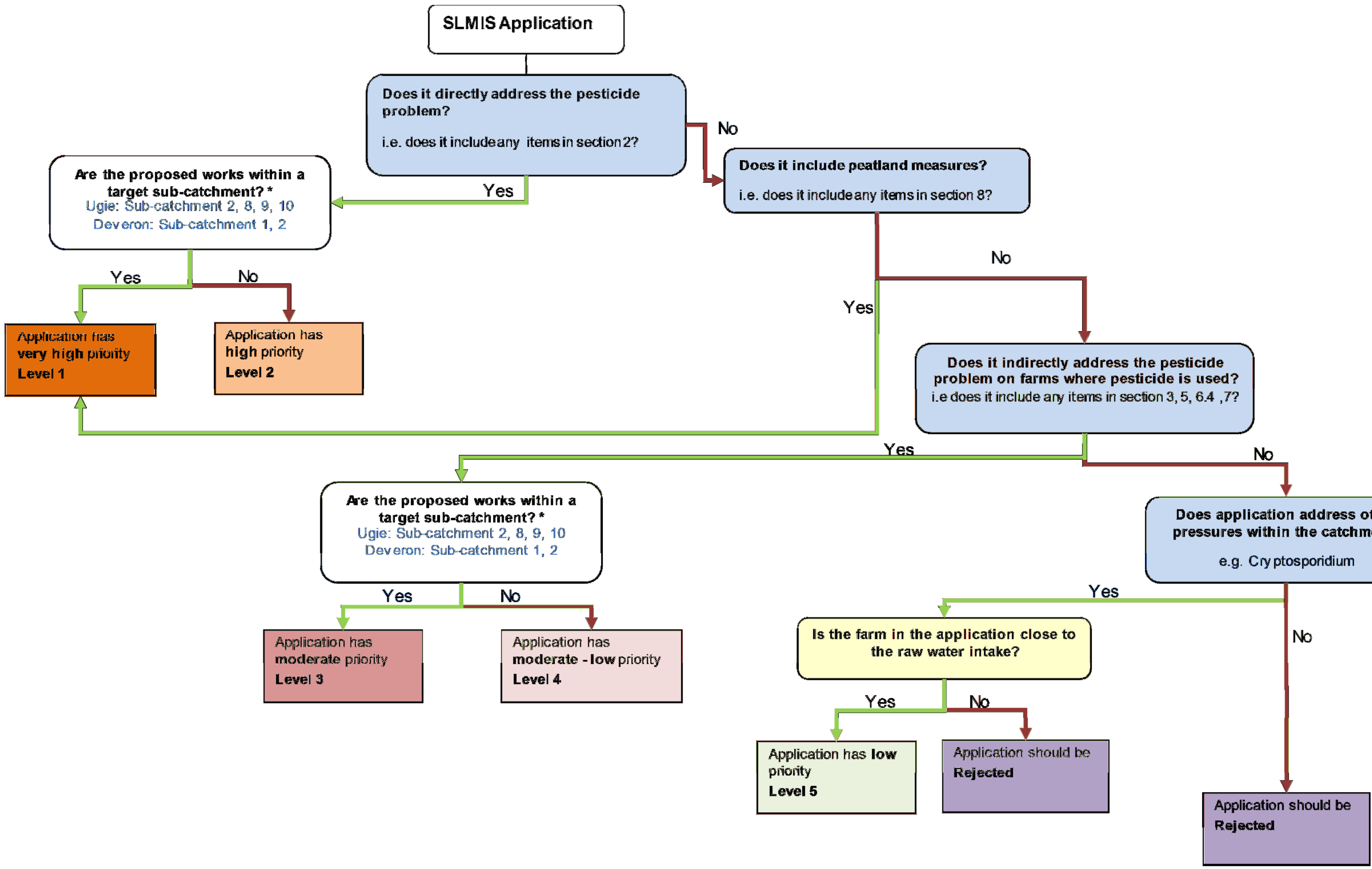
The first applications to the SLM incentive scheme in the Ugie catchment came through in October of 2012 and since then 29 applications have gone through the full SLM process. This includes the generation of a determination report that details all capital items applied for and if the application is accepted according to the decision tree process detailed in Figure 7.2. The 29 applications were for items totalling £116,737.24, of which £42,233.17 have been funded. A full break down of the types of interventions applied for and funded is shown in Table 7.3.

Table 7.3 - Interventions applied for and funded within the Sustainable Land Management Incentive Scheme in the River Ugie catchment since October 2012

Intervention	Total Applied Funding	Total Accepted Funding
Alternative livestock watering	£61,338.80	£20,462.75
Livestock fencing	£35,429.44	£10,953.42
Pesticide loading area	£680	£408
Pesticide biobed	£18,999	£11,399
Gate relocation	£290	£0
Total	£116,737.24	43,223.17

The current SLM decision making process for the River Ugie catchment using the decision tree approach (shown in Figure 7.2) is in place so that preference is given to interventions that mitigate pesticide risk in high risk catchments (according to the monitoring results). The tree goes through a number of decisions to classify applications as very high, high, moderate, moderate-low, low priority or rejected. There are a few decisions in the tree that could benefit from using CaRPoW outputs, these are highlighted by the red boxes in Figure 7.2.

The decision marked (a) in Figure 7.2 determines if the intervention is in a high risk sub-catchment. The risk outputs from CaRPoW can be used in this decision to prioritise interventions if they are classified as high risk (75th percentile) for pesticides and if the risk component they target has a very high potential for intervention. In decision (b), CaRPoW can be used to assess if indirect pesticide interventions are within high risk and high potential for intervention areas. Decision (c) assesses if the intervention mitigates risk for other pollutants. Here, the CaRPoW outputs for the other pollutants (nitrate, phosphorus and sediment) can be used in a similar manner to pesticides to decide if the application is low priority or rejected.



* Target sub-catchments are subject to periodic review

Note: The benefits to drinking water quality will be assessed during the farm visit and will consider; connectivity, topography, soil type, land use and livestock numbers

Figure 7.2 - Scottish Water's decision tree for prioritising capital items applied for in the River Ugie in the Sustainable Land Management Incentive Scheme. Processes highlighted in red are potential parts of the decision tree where CaRPoW outputs could be used in the decision making process.

A retrospective analysis can be conducted that uses CaRPoW within the decision tree process to categorise interventions into the priority classes. For confidentiality reasons applications cannot be discussed individually and therefore applications are analysed collectively. The outputs of the decision making process using CaRPoW for each decision category are presented in the graph in Figure 7.3.

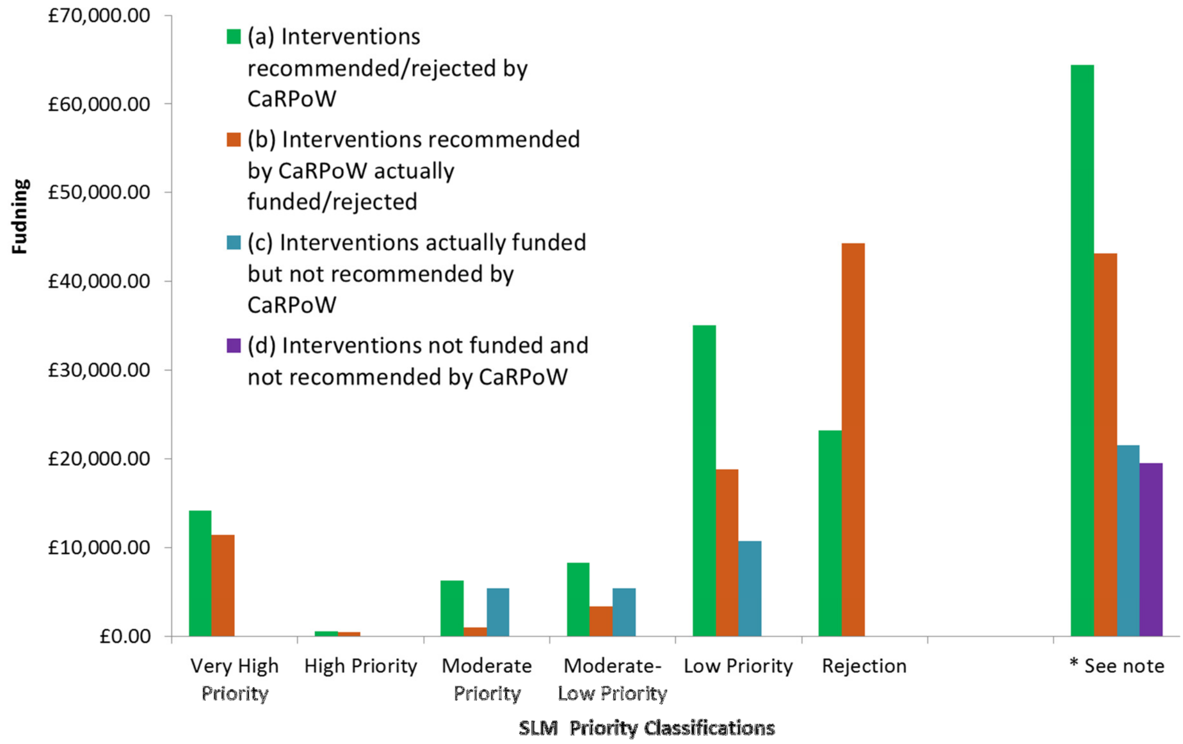


Figure 7.3 - Graph to show the value of interventions within each category of the SLM decision tree for (a) value of interventions recommended/rejected by CaRPoW in total, (b) value of interventions recommended/rejected by CaRPoW that have been funded, (c) value of interventions funded but not recommended by CaRPoW and (d) interventions neither funded or recommended by CaRPoW. * This category represents the total value of interventions either recommended (a), funded (b and c) or not funded (d)

Of all the measures applied for only one item, a pesticide biobed, directly mitigates pesticide risk and falls within a CaRPoW high risk area for any of the 6 pesticides. Therefore, this is the only item that is of a very high priority (according to the SLM priority classes) for funding. Although this is the case, it is the largest value single item at £18,999.00 and therefore constitutes 16% of the total funding applied for.

The only other measure that directly addresses pesticide risk from the applications is a pesticide loading area. However, according to the outputs of CaRPoW this does not fall within a high risk area for any of the 6 pesticides and therefore is only a high rather than very high priority for funding if CaRPoW is used to make the decision. It must be noted however that both of the items that directly address pesticide issues mitigate a point source risk, which is not represented by the CaRPoW risk outputs. For this reason it may be decided that both or neither are of a very high priority.

Of the other interventions applied for only the gate relocation and livestock fencing have potential indirect mitigation impacts on pesticides, as both potentially limit runoff losses. Of the £35,429.44 of livestock fencing applied for, only £2741.48 is within a high risk pesticide area with a very high potential for pesticide delivery mitigation according to CaRPoW. These livestock fencing items are therefore given a moderate preference for funding. The single application for gate relocation is not in a CaRPoW high risk pesticide area and is therefore not given moderate priority.

The largest proportion of the total funding applied for is given a low priority classification by CaRPoW. These are predominantly applications for alternative livestock watering and livestock fencing that do not mitigate pesticide risk indirectly but do mitigate a high risk of phosphorus, nitrate or sediment. A total of £48,598.74 is allocated to this low priority status, with £30,461.20 and £18,137.54 of this consisting of alternative watering and livestock fencing respectively.

The remaining interventions applied for are rejected by CaRPoW on the grounds that they do not mitigate pesticide risk directly or indirectly, and are not located in the CaRPoW high risk areas of the catchment for other pollutants modelled. The intervention types that fall into this category are alternative livestock watering, livestock fencing and the one application for gate relocation.

Compared to the actual number of interventions funded the addition of CaRPoW to the decision making process generally increases the level of funding recommended. An extra £21,186.10 of items are recommended for funding by CaRPoW over what was funded using the decision tree. There are a number of possible reasons for this. Firstly, the percentage contribution of funding Scottish Water can provide to measures changed in 2014 to a higher percentage contribution of 60%, which means a proportion of the interventions before this time would receive less funding than the 75% value used in this retrospective analysis. Secondly, there is a likelihood that interventions would be placed in a lower priority category if they did not fall in a high risk sub-catchment as delineated by the monitoring. The addition of CaRPoW removes the constraints of sub-catchments by detailing specific high risk fields. There may be for example a small number of high risk fields within overall low risk sub-catchments (as determined by monitoring) that are suitable for intervention. Finally, the decision tree approach was only adopted towards the end of 2013, meaning many of the decisions on funding were not made with this approach and therefore items may have been funded in less preferable areas.

The use of CaRPoW within the approach also highlights interventions that were funded and not recommended by CaRPoW. In total £21,488.53 or approximately 50% of the total funding given to land owners would not have been recommended by CaRPoW. Such a large proportion of measures funded in lower risk areas potentially means that investment was made in areas on interventions that may not have a significant effect on raw water quality. Interestingly this figure is close to the extra investment recommended by CaRPoW for interventions that were not funded, suggesting that the level of investment was correct just for the wrong applications.

Contrary to the monitoring, the retrospective analysis of the scheme application decision making process with CaRPoW outputs does not highlight where Scottish Water could have saved money but instead where they may have missed opportunities to reduce pollutant risk by rejecting or funding certain applications recommended or not recommended by CaRPoW. The extra detail the addition of the CaRPoW outputs provides in the decision making process allows for more informed decision to be made beyond that of the current decision tree methodology.

7.4 The use of CaRPoW going forward – Redesigning the SLM and catchment management process

Sections 7.2 and 7.3 define where CaRPoW can fit within the current SLM process from catchment selection to the funding of measures. But what if the whole SLM process and other catchment management schemes had been designed around the principles of CaRPoW from the beginning? Although many water companies in the UK have adopted catchment management (Spiller et al., 2013), each company's approach has been slightly different. For example Scottish Water have developed an incentive scheme method where land owners are voluntarily encouraged to apply for funding from Scottish Water, herein referred to as the 'incentive scheme approach'. Other companies such as Wessex Water have adopted a more targeted approach where specific high risk land users in their catchments are offered funding for alternative practices that limit impact on water quality (Wessex Water, 2011). Within this section this is herein referred to as the 'targeted funding approach'. A different approach entirely has been adopted by Yorkshire Water for example, where full collaboration is sought with a multitude of stakeholders and land users are encouraged to adopt practices that are low impact on water quality without large financial incentives from the water company (Yorkshire Water, 2015), herein referred to as the 'targeted engagement approach'. Although these approaches differ they all require targeted monitoring and interventions. This section provides a potential blueprint going forward, based on the original SLM process, which is applicable to the three identified catchment management approaches, making full use of the CaRPoW approach.

A few key steps have been added to the current SLM process flow diagram that maximise the use of CaRPoW in every possible decision making process. The updated framework from catchment selection to measure targeting is shown in Figure 7.4, boxes coloured red are where CaRPoW is used.

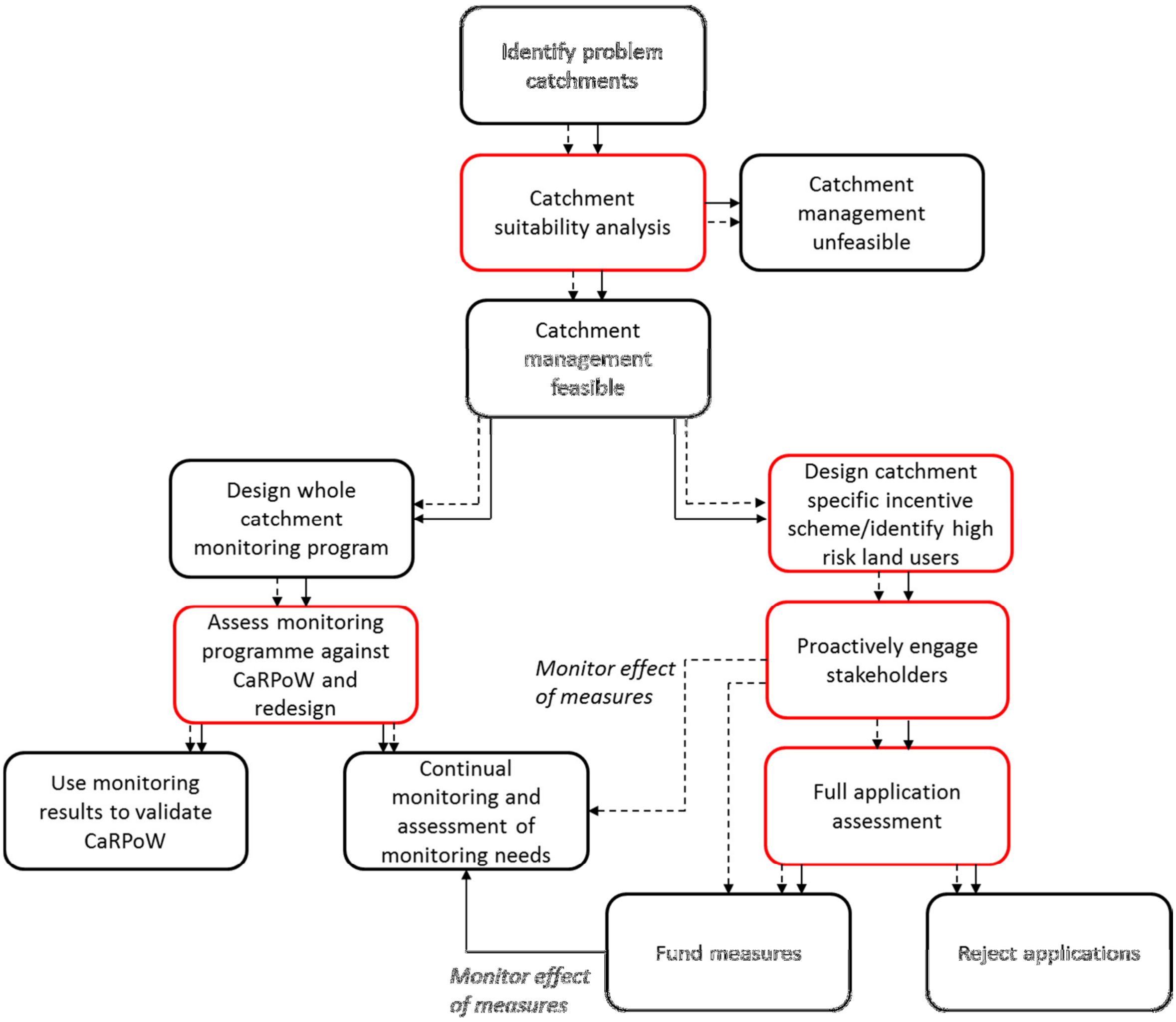


Figure 7.4 - Reworking of the SLM (Sustainable Land Management) process chain to maximise CaRPoW use in the decision making process and create a blueprint for the catchment management process. Solid arrows represent processes with the SLM approach (i.e. an incentive scheme approach), dashed line arrows represent alternative approaches (i.e. targeted funding and targeted engagement approaches).

The identification of problem catchments is no different to the original SLM process, with catchments identified according to the analysis of raw water quality data from regulatory monitoring at drinking water treatment works. Where CaRPoW is introduced is in the delineation of problem catchments into those potentially not suitable for catchment management and those potentially suitable for catchment management. Here, CaRPoW risk models are generated for each problem catchment and analysed to assess the feasibility of catchment management. If risks are concentrated, easily defined and the components of risk mitigated with the interventions available then catchment management may be deemed feasible and the catchment moves to the next phase. If risks are highly dispersed then it may be economically unviable to mitigate risks with catchment management interventions and the catchment is deemed unfeasible for catchment management. This approach is applicable to all three of the identified approaches.

Initially, monitoring programs are designed for suitable catchments that provide the necessary spatial coverage to capture all major branches in the hydrological network. Likewise samples are analysed for all pollutants of concern in the catchment. Such monitoring runs until a suitable enough dataset is obtained to (i) validate CaRPoW modelling outputs against and (ii) identify opportunities for the frequency of monitoring to be downgraded. Once this dataset is established it is used in conjunction with CaRPoW outputs to redesign the monitoring programme so that frequency of monitoring is reduced in identified low risk areas to lower expenditure without compromising data integrity (as per the analysis in section 7.3.1). This is seen as an iterative process and is likely to alter year on year, especially in arable catchments with variable crop rotation patterns (Ulén et al., 2005). Monitoring is required by all three catchment management approaches.

For the SLM approach the incentive scheme of each catchment can be designed in a way so that it is tailored according to the risk profile determined by CaRPoW. In the scheme at present a large range of different measures are offered, many of which do not mitigate the pollutant of concern. This means that a lot of effort is made by the land owner to apply for measures that will never be accepted at the application assessment stage. Previous research has highlighted the importance of reduced paperwork in the likely participation of farmers in agri-environment schemes (Ruto and Garrod, 2009). Introducing CaRPoW into the design of the incentive schemes to limit the interventions available may reduce the amount of applications made by farmers who are unlikely to be successful in securing funding, i.e. increasing the percentage of overall applications funded. One way of doing this is to first of all limit the areas of the catchment in which applications can be made, i.e. stipulating in the incentive scheme guidance where preference will be given to applications based on the high risk parts of the catchment delimited by CaRPoW. Secondly, the dominant components of risk in these areas can also be identified in the incentive scheme documentation, so that land owners are encouraged to apply for interventions that target the specific component of risk in high risk areas. This approach not only reduces the amount of effort required on the part of the land owner but it also increases the likelihood of targeted measures mitigating the pollutant issue. For catchment management approaches that do not have an incentive scheme (targeted funding and targeted engagement approaches), high risk areas are identified at this stage for targeted funding or stakeholder engagement.

Following the design of the incentive scheme, stakeholders within the catchment can be proactively encouraged to apply for funding. This highlights the benefits of a tailored scheme as catchment liaison officers can target high risk areas and promote interventions in these areas that tackle the key component of risk. Again, the benefits of this targeted approach are that less applications are likely to be made for funding that are unlikely to be accepted, which reduces the use of resources in both promoting the scheme and processing applications. Likewise, reducing the amount of rejected applications is likely to improve the credibility and reputation of the water company with catchment stakeholders. At this stage the visit by a catchment liaison officer will also provide an opportunity to ‘ground truth’ the outputs of CaRPoW. For the other two approaches stakeholders in high risk areas are either approached and offered funding for specific interventions (targeted funding approach) or are proactively encouraged to adopt low impact practices off their own initiative (targeted engagement approach).

Applications for funding can subsequently be assessed using the current decision tree approach with the addition of CaRPoW as per the methodology used on section 7.3.2. If previous processes that prioritise certain areas of the catchment and interventions have been successful there should be less applications at this stage, but the applications should be for interventions that have a higher likelihood of being at a very high priority.

Monitoring of water quality in the catchment continues to assess the effectiveness of interventions implemented in all three approaches. At this stage the implementation of interventions can inform the regular reassessment of monitoring needs.

The key benefits of adopting the cascade of processes detailed in Figure 7.4 for catchment management making full use of the CaRPoW framework for the decisions discussed can be summarised in the following points:

- Optimising selection of catchments suitable for catchment management based on distribution of risk in a catchment rather than total risk (derived from water quality data) improves overall efficacy of catchment management.
- A tailored monitoring programme using CaRPoW captures necessary water quality parameters without the need for a full extensive catchment wide monitoring programme and therefore saves costs.
- Tailoring which measures are targeted where in a catchment based on high risks and the potential for intervention reduces disruption to catchment stakeholders, and potentially increases the successful number of applications in the incentive scheme approach.
- CaRPoW outputs provide tools for catchment staff on the ground to proactively engage land owners in high risk areas. It allows for the illustration of the problem and how it can best be mitigated.
- Implementing CaRPoW in the decision tree process further informs and strengthens the decision making process.

7.5 Chapter conclusions

This chapter has assessed the current SLM process from catchment selection to the funding of measures to determine where CaRPoW could be utilised best. Within the current process CaRPoW could be used for catchment selection, monitoring programme design and the selection of interventions. To test these assertions a retrospective economic analysis was used to evaluate theoretical savings and missed opportunities in the River Ugie catchment, using data from the SLM scheme since its inception in 2010 through to the end of 2014. The analysis shows that Scottish Water could have made savings up to around £32,000 (accounting for uncertainties) by using CaRPoW to design the monitoring programme. In the assessment of funded scheme applications the analysis showed that Scottish Water invested approximately £21,000 in measures in low risk areas according to CaRPoW that could have been invested on interventions in higher risk areas.

The analysis presents a first step in assessing the economic benefits of using the CaRPoW approach with data that were readily available to be used in the analysis. Further, more in depth analysis where data are available such as determining potential reductions in treatment costs, reducing the time spent on the ground by catchment officers or undertaking a cost-benefit analysis against other selection and targeting approached for example will strengthen the case for CaRPoW to be adopted by Water companies wanting to better select and target interventions.

On the back of these analysis and using lessons learned from the current SLM processes along with the development of CaRPoW, a new blueprint for SLM and catchment management in the future has been developed. The new process cascade utilises CaRPoW fully to maximise the efficiency of the catchment management process to improve its efficacy and improve collaboration with other catchment stakeholders.

Chapter 8. Integration of findings and conclusions

8.1 Introduction

The research detailed in each of the chapters in this thesis relate to at least one of the objectives set out in the introduction. Subsequently all chapters contribute to the main aim of the thesis which is:

"to develop a conceptual framework and associated modelling methodologies capable of identifying and comparing high risk areas in catchments for multiple pollutants so that catchment management interventions can be effectively selected and targeted."

To directly address this aim the final chapter collates the findings and conclusions from the chapters to assess whether each objective has been met and the overall aim of the thesis achieved.

Following this, findings are integrated and discussed within the context of the thesis' contributions to (i) the water industry and (ii) the wider scientific community surrounding catchment management research. Recommendations for future work are outlined as a result of the integration of findings in the context of both industry and research. Finally, overall conclusions from the thesis are presented.

The final chapter therefore takes the following structure:

- 8.2 – Have the aim and objectives of the research been met? - integration of research findings
- 8.3 – Contributions the research findings make to industry and wider catchment management decision making and pollutant modelling research
- 8.4 - Recommendations for future work
- 8.5 – Conclusions

8.2 Have the aim and objectives of the research been met? - Integration of research findings

Objective 1 - Assess the feasibility of considering multiple pollutants within the same conceptual framework by reviewing the processes that constitute catchment risk for the pollutants mitigated in water industry catchment management schemes (Chapter 2).

The review of pollutant processes framed within the Source-Mobilisation-Delivery continuum covered in Chapter 2 highlighted the dominant processes that constitute pollutant risks in a catchment. Various similarities and differences between the processes of each pollutant within each component of the continuum were identified. For example, the majority of the pollutants, with the exception of DOC, are associated with agricultural land uses (arable and grassland). Although this is the case, the processes that dominate their mobilisation and delivery are often distinctly different. For nitrate and phosphorus this is the case, with the former largely associated with slower leaching processes in solution and the latter with higher energy runoff and preferential flow processes in particulate form.

Interventions were similarly reviewed within the context of the S-M-D continuum and the multiple pollutants considered by water industry catchment management schemes. The review highlighted a variety of interventions that target different aspects of the continuum and are capable of mitigating multiple pollutants. At the same time, there were a small number of interventions reviewed that provided positive benefits for some pollutants and negative for others, i.e. there is potential for pollutant swapping.

The identification of parity and disparity between the processes of the pollutants of concern to the industry and with different interventions highlights the potential for (i) pollutants to be considered in the same conceptual framework and (ii) the potential for multiple benefits to be achieved by the careful selection and targeting of certain interventions. Subsequently, the review confirms the feasibility of including multiple pollutants in the same conceptual framework for the purposes of defining pollutant risk and targeting interventions, and therefore objective 1 is met.

Objective 2 - Develop criteria with water industry professionals to outline the industry requirements for a conceptual modelling framework (Chapter 3).

The criteria developed in Chapter 3 details the requirement for a conceptual framework capable of defining pollutant risk for the selection and targeting of interventions from a water industry perspective. A few key examples include:

- A focus on surface drinking water sources.
- To be able to operate at the field scale.
- Represent the components of pollutant risk individually so that the main component of pollutant risk can be determined.
- Assessment of spatial and temporal variations in the components of pollutant risk.
- Ability to compare the risks of different pollutants.
- GIS based modelling framework with the potential to be used qualitatively to improve conceptual understanding.

Current frameworks and models that define risk and/or select and target interventions were assessed against the criteria to determine if a new framework was required. None of the 12 frameworks and models assessed met the criteria fully. Generally they were either focused on single pollutants or did not disaggregate pollutant risk into its constituent components in order to make decisive intervention decisions.

The developed criteria therefore provide a blueprint for what the water industry requires in order to make decisions on which interventions to target where.

Objective 3 - Critique current methodologies and frameworks against the industry defined criteria and outline a new conceptual framework (Chapter 3).

The niche identified by objective 2 led to the development of a new framework that is capable of meeting the requirements of the industry defined modelling criteria, the Catchment Risk to Potable Water (CaRPoW) framework.

The framework disaggregates the risk posed by a pollutant into its constituent parts according to the principles of the S-M-D continuum. There are a few key differences however. Within CaRPoW both the source and mobilisation components work at the field scale (unique combination of land use, soil type and drainage). The mobilisation component represents the proportion of the source component that is mobilised to the edge of the field and therefore includes both the form the pollutants takes (soluble or particulate) and the within-field pathway (slow or fast flow pathway). The delivery component works at the sub-catchment scale to determine the proportion of pollutant mobilised to the edge of the field that reaches the water body and is based on principles of hydrological connectivity. All of these three components combine to provide overall pollutant risk for each field within a catchment.

The framework therefore allows for appropriate interventions to be selected based on the main component of risk. The subsequent development of modelling methodologies for each component for each pollutant also allows for pollutants' risks to be compared for the purposes of determining where multiple benefits or pollution swapping may exist. The framework can also be used as a way of conceptualising pollutant risk in a catchment qualitatively, where data availability does not allow for appropriate process representation with modelling.

Objective 4 - Develop modelling methodologies to populate the conceptual framework developed in objective 3, capable of representing the components of risk using a quantifiable metric (Chapter 4).

The main purpose of CaRPoW is as a modelling framework, with models that represent each component of the framework (source, mobilisation and delivery). Models were developed for each pollutant mitigated by Scottish Water's SLM scheme with the exception of DOC.

Methodologies have been selected and adapted from the literature to represent the various components of risk within CaRPoW. A soil water balance model (WaSim) was used to represent any hydrological inputs to the pollutant mobilisation and delivery models. Hydrological inputs were based on averages from a 30 year model run (1980-2010) and for a representative wet year and dry year for each unique combination of land use, drainage and soil. A range of parameters were extracted from the model outputs to be used in a number of the risk models. Examples include annual runoff, annual drainflow, and average number of days between runoff events for example.

Source models provide an output in mass (grams for pesticides and kilograms for other pollutants) of the pollutant per hectare per year. Some of the source models are simple and only provide the mass of a pollutant applied to the field or present in the soil (e.g. phosphorus), others are slightly more complex and account for the partitioning of an applied pollutant between soluble and particulate (e.g. pesticides) or are part of a balance with the source term being the surplus from the balance (e.g. nitrate).

The mobilisation methodologies are variable for each pollutant but the outputs provide coefficients that represent the proportion of the source term that is mobilised to the edge of the field per year. For certain pollutants, e.g. pesticides and soluble phosphorus the WaSim soil water balance model is used to proportion the mobilisation of the pollutant into slow and fast hydrological pathways (i.e. runoff vs drainflow or leaching).

The delivery component is based on the representation of hydrological connectivity, developed using a travel time approach methodology similar to Buchanan et al (2013). The methodology varies the Manning's roughness value in the travel time equation according to land use, with barrier features (e.g. field boundaries) included. Travel time is normalised into a coefficient (0-1) therefore meaning that connectivity is relative to the catchment.

Final catchment risk is calculated by multiplying the three different model outputs together to give a risk value to each field in kg ha^{-1} yr^{-1}.

Overall the methodologies have been developed to be applicable to any catchment that has a high resolution input data. The idea behind the CaRPoW approach however, is that different models can be used within each of the components depending on the level of process understanding or data availability in the catchment. The models developed here fulfil the requirements of the criteria outlined in objective 2.

> *Objective 5 - Apply the framework and associated modelling methodologies to the River Ugie catchment and assess the utility of the framework for representing multiple pollutant risk against catchment water quality data (Chapter 5).*

The models developed in objective 4 were applied and validated in the River Ugie catchment, in the North East of Scotland. Six pesticides, nitrate, soluble phosphorus, particulate phosphorus and sediment were modelled in the catchment using specific land use data from 2012 and a derived land use dataset selecting the dominant land use classification in each field from 2008-2012. The models were validated against sub-catchment pollutant load data collected by either SW or SEPA.

The water balance model performed well when the predicted baseflow index was compared against the known baseflow index for the catchment. This suggests hydrological inputs to the models derived from WaSim provided a reasonable representation of hydrological conditions in the catchment over the period of the model run.

The models predicted total loads within the catchment reasonably well within the ranges of uncertainty for the models and the calculated observed loading data. Where there were discrepancies between the total modelled and observed loads, it was generally a result of a high load from a particular sub-catchment in the observed dataset that was not represented by the models. This was hypothesised to either be a result of poor temporal resolution in the observed water quality data or the fact that the models are based on annually averaged hydrological inputs from a 30 year dataset, which is unlikely to represent intra-annual variations in hydrology and therefore mobilisation and delivery year on year.

The prediction of spatial loads within the catchment was more varied with around half of the pollutants modelled, represented well spatially. Spatial disparity between the predicted and observed loads of the other pollutants was generally a result of a large under or over prediction in one particular sub-catchment, which again is a function of the limitations of representing variable loads between years with averaged models. For some of the pesticides that were poorly represented (2, 4-D, MCPA, CMPP), it was also hypothesised that the spot application method these pesticides are generally applied by could not be well represented by the land use defined source term alone. Land use data could not distinguish application differences between fields with the same land use, which may explain some of the spatial disparity in loads.

Given the relative simplicity of the models and the complexity of the processes driving pollutant movement in a catchment, the models provide a reasonable representation of pollutant loads and hence total and spatial risk in the catchment.

> *Objective 6 - Compare the risk outputs of different pollutants to identify where multiple benefits and pollutant swapping may be prevalent and develop a methodology to select and target interventions using model outputs in the River Ugie catchment (Chapter 6).*

A methodology was developed to use the outputs from the models in the Ugie to select and target catchment management interventions based on the upper quartile of risk for each pollutant. Spearman's rank analysis was used to highlight pollutants that have shared spatial risks and therefore the potential to be mitigated with single interventions. At the same time pollutants that were not well correlated were flagged as potential for pollutant swapping.

Analysis of the highest risk areas for each pollutant within the distribution of overall risk showed some interesting results. For example, the highest risk for the pesticide chlorotoluron was distributed to a much smaller area than other pesticides, potentially suggesting fewer interventions are required to mitigate the highest risk. Assessment of the components of risk in the highest risk areas for each pollutant at the catchment scale demonstrate that many of the pollutants (with a few exceptions) have high source risk, suggesting source interventions may be the most suitable or models are most sensitive to the source component.

A more in depth application of the intervention selection methodology was applied to the pesticides chlorotoluron and metaldehyde. Firstly the shared high risk areas of the catchment were delineated and fields within the shared risk classification analysed for the dominant risk component. This allowed for interventions to be selected depending on the main component of risk in each field. Intervention selection was further delineated by assessing the risks of other pollutants in the shared risk fields in an attempt to select interventions with multiple mitigation benefits.

Intervention selection using the model outputs are subject to the limitations and uncertainties of the models themselves. As a result there are a number of steps recommended to be taken, centred on ground truthing visits to sites designated high risk before final intervention decisions are made.

> *Objective 7 - Determine how the framework fits in with conventional catchment management processes and conduct a retrospective economic analysis to quantify the benefits of implementing the methodologies developed (Chapter 7).*

Scottish Water's catchment management processes were scrutinised to determine where CaRPoW could be used to improve their efficiency and efficacy. It was hypothesised that CaRPoW could be used in the catchment selection process, the design of monitoring strategies and in the decision making process for which interventions to fund from applications to the incentive scheme.

To test these hypotheses a retrospective economic analysis was undertaken to determine theoretical savings or opportunities missed by implementing CaRPoW. Firstly, the monitoring programme in the River Ugie was assessed from 2010 – 2014. It was determined that within the bounds of acceptable uncertainty using CaRPoW to design the monitoring programme could have saved Scottish Water approximately £32,000. The analysis of scheme applications using CaRPoW with Scottish Waters' decision tree process showed that around £21,000 was actually invested in interventions that were of a low priority according to CaRPoW. Interestingly interventions amounting to a similar figure were not funded by Scottish Water, but were of a higher priority within CaRPoW and would be recommended for funding. This analysis theoretically highlights where in the current process CaRPoW generates savings and aids in the decision making process.

The catchment management process, from catchment selection to making decisions on interventions, was redesigned for all water industry catchment management approaches with the full integration of CaRPoW. Overall the implementation of CaRPoW determines which catchments are best suited for a catchment management approach, the most effective monitoring strategy, the areas of the catchment most at risk for different pollutants and the main components of risk so that incentive schemes, targeted interventions or stakeholder engagement can be tailored according to the risk profile of the catchment. The potential benefit of this new blueprint for catchment management with CaRPoW reduces the costs of implementation, improves efficacy of the approach and limits disruption to other catchment stakeholders.

Overall the findings and learning generated under each objective have meant that the main aim of the thesis has been achieved.

8.3 Contributions and implications of the research findings to the water industry and wider catchment management research

8.3.1 Water industry

The increased uptake of catchment management by water companies (Dolan et al., 2012; Spiller et al., 2013) has exposed a requirement for a new methodology capable of aiding in the intervention selection and targeting decision making process (Naden et al., 2013). The key contribution this thesis makes to the water industry (and its main aim) is the development of the CaRPoW framework which occupies this identified niche. Beyond this main contribution there are a few key findings generated under the thesis objectives that provide further contributions and implications to industry.

The majority of current catchment management programmes within water companies are reactionary and therefore generally focussed on single pollutant issues. By identifying process links between a range of problem pollutants the thesis demonstrates that water companies can be more proactive and pragmatic in their approach to intervention selection and targeting. By doing this, the pollutants of concern to the water company can be mitigated as well as other pollutants, which provide wider environmental benefits when legislation such as the WFD (60/2000/EC) are considered. This further strengthens the reputation of the water company and provides opportunities for collaboration with other organisations wanting to improve catchment water quality (e.g. NGO's, government agencies etc.).

The application of the framework and associated modelling methodologies to the River Ugie catchment effectively demonstrates the usefulness of the approach to the water industry, but also offers a few key considerations. The application of the approach in a modelling context is only applicable if data are available at a scale capable of representing key pollutant processes. A few key cases within the thesis highlight this implication. For example, the pesticides 2, 4-D and MCPA were poorly represented spatially as the distribution of their application in the catchment was not well represented by land use data alone. In these circumstances it may be beneficial for CaRPoW to be used in a qualitative sense for conceptual understanding as demonstrated by the use of the framework for colour in the Amlaird catchment (Appendix A).

Results from the validation of the modelling against calculated loads in the catchment highlighted uncertainty in some of the model results and perhaps more importantly in the loading calculations. Model uncertainties arise from the generic, average approach adopted which was a key requirement of the water industry defined criteria in Chapter 3. Whereas uncertainties in the loading data come from the relatively low frequency of water quality monitoring upon which pollutant loads are derived. There is an argument that catchment management decisions should not be made using models with systemic uncertainty, but instead with a general agreement between stakeholders as to which action going forward is best (Bevan and Alcock, 2012). However, Bevan and Alcock (2012) argue that the use of such models negates the potential disagreement in priorities between different stakeholders and provides better insights into which measures are likely to be most appropriate. If models such as CaRPoW are to be used for decision making, it is vital that such uncertainties are considered by water companies. With this in mind it would be prudent for water companies to follow up any recommendations CaRPoW makes with suitable field based investigations.

The findings from the comparison of SLM incentive scheme applications to the CaRPoW outputs highlight an important disparity between the dominant components of catchment risk and the interventions applied for. The analysis showed that the majority of interventions applied for within the scheme (livestock fencing and alternative watering) do not actually directly mitigate pesticide risk, and the uptake of interventions that do directly address pesticide risk components (product substitution and artificial wetlands) was very poor. This finding affirms an important aspect of catchment management, which is the willingness of land managers and farmers to implement interventions (Blackstock et al., 2010; Beharry-Borg et al., 2013). Arguably, the interventions in the scheme that directly mitigate pesticides are more disruptive to the land owner than some of the others that may potentially add value to the farm (e.g. livestock fencing), which has potentially limited their uptake (Espinosa-Goded et al., 2010). Increasing the awareness among farmers of their impact on water quality and the importance of certain interventions is therefore required to increase the uptake of interventions that mitigate the dominant risk components of problem pollutants and improve catchment water quality (Merrilees and Duncan, 2005).

The contributions and implications of the research to water industry catchment management schemes are also applicable to other organisations wanting to characterise diffuse pollution processes for the purposes of intervention selection and targeting. For example Catchment Sensitive Farming officers in England could use the framework and models to assess risk on farms wanting to apply for a grant from the Countryside Stewardship scheme (Natural England, 2015), such a use also extends to SEPAs diffuse pollution priority catchment work where farmers are encouraged to apply for funding from the Scottish Rural Development Fund (DPMAG, 2012). Similarly, the framework can also be used by other catchment management organisations to define risks and prioritise interventions e.g. Rivers Trusts and NGO's (e.g. the RSPB).

8.3.2 Catchment management decision making and pollutant modelling research

The findings generated within the thesis also have wider contributions and implications to general catchment management decision making and catchment scale pollutant modelling research outside of the specific application to the water industry.

Beven and Alcock (2012) argue that within catchment management decision making there is a need for "models of everything everywhere". That is, there is a need for simple models capable of being applied in many places in order to drive understanding and learning about complex catchment processes. The development of CaRPoW and its associated methodologies can be seen as the development of a model for everything (multiple pollutants), everywhere (generic application).

To a certain extent, the findings from the thesis have developed learning on catchment pollutant processes by identifying the successes and limitations of the methodologies. For example the simple pesticide fate model developed upon the basis of the first rainfall event after application was successful at representing pesticide loading in the catchment for a number of the pesticides modelled. These outcomes further build on the understanding of pesticide mobilisation dynamics and suggest that simple models provide a reasonable representation of pesticide mobilisation (as validated by the storm sampling). In converse, the poor spatial representation of some of the pesticide source processes (i.e. spot applied pesticides) suggests that higher resolution input data are required to effectively represent source processes at the field scale. Therefore, there is a development in understanding in what can and cannot be represented with the generally applied modelling approaches of CaRPoW. In turn this drives future model development and catchment process understanding.

Comparing the risk of multiple pollutants within the same modelling framework also adds to understanding on the shared risk components of different pollutants. Subsequently, this builds on emerging research on the interactions of different pollutants within a catchment and the phenomena of multiple pollutant benefits from interventions and pollutant swapping (Stevens and Quinton, 2009). For example, the spatial concurrence of nitrate risk with some of the pesticides outlines potential for multiple benefits with single interventions, especially in the shared high risk areas that have a high potential for mobilisation and delivery interventions. Not only are spatial interactions in the risks of these pollutants highlighted, but also the interactions of their source, mobilisation and delivery processes. A comparison approach of this kind has rarely been utilised in other models and is something that is unique within CaRPoW for the purposes of decision making.

The novel approach taken in the representation of pollutant delivery at the catchment scale also adds to the literature on hydrological connectivity representation. A variety of different modelling approaches have been developed previously (Bracken et al., 2013). Many of the methodologies developed are based on topography as a driver of water movement across a catchment, where the steeper the slope and the shorter the distance to a water body the higher the connectivity (e.g. Lane et al., 2009; Buchanan et al., 2013). However, very few of the methods include physical landscape features that either enhance (e.g. ditches) or reduce (e.g. hedged field boundaries) connectivity. The approach developed within the thesis explicitly considers such landscape features within a topographical representation of hydrological connectivity and therefore builds upon the capabilities of topography based hydrological connectivity models.

8.4 Recommendations for future work

There are a number of recommendations for future research that aim to reduce the uncertainty in the modelling methods, initiate the implementation of CaRPoW or develop new research tangents using the CaRPoW approach. These include but are not exclusive of:

- Applying the CaRPoW methodology in more drinking water source catchments to test the generic applicability of the approach and models. Specifically, testing the methodology in catchments with different characteristics to the River Ugie. The framework could also be implemented outside of the UK context for drinking water source protection in both Europe and Internationally.
- Using the CaRPoW framework to assess the risks of more pollutants than those in this thesis. Potential candidates (and pollutants that concern the water industry in some catchments) include bacteriological pollutants (e.g. faecal indicator organisms, cryptosporidium, E.coli etc.) and heavy metals (e.g. manganese).
- The criteria developed in chapter 3 was for Scottish catchments where the predominate drinking water sources are from surface water catchments. Future work could therefore go into adapting the framework for groundwater sources where mobilisation concerns the movement of a pollutant through the soil and into an aquifer and delivery the transit time of the pollutant across the aquifer to the borehole from which water is abstracted. Such work will widen the applicability of the framework to areas that are dominated by groundwater.
- Higher resolution data needs to be collected on the risk components of certain pollutants to improve the load prediction. For example, a more detailed understanding of where spot applied pesticides are likely to be

applied. Integrating local knowledge from agronomists and farmers may elucidate this understanding (Dolan et al., 2014). Similarly, detailed data on vegetation patterns and the condition of peat soils (Parry et al., 2015) would allow DOC and colour modelling within the CaRPoW approach.

- A better methodology is required to collect water quality data against which to validate the spatial CaRPoW models. The grab samples and targeted storm events were still open to high uncertainty when calculating annual loads with the various load calculation methods. The use of passive samplers for pesticides (e.g. Alvarez et al., 2008) and real time turbidity and nutrient sensors (e.g. Owen et al., 2012) could be a useful future research avenue for spatial model validation. Similarly the automated water quality sampling stations implemented in the Demonstration Test Catchment (DTC) project (e.g. Outram et al., 2014) represent a key step forward in high resolution monitoring and will provide a much more reliable dataset against which to validate models such as CaRPoW.
- Likewise more research is required to better understand some of the processes represented by CaRPoW at the catchment scale. Hydrological connectivity for example is not fully understood and no unified theory of connectivity at the catchment scale is accepted (Bracken et al., 2013). As monitoring improves (e.g. with the DTC project) and more is understood, models can be updated within the CaRPoW approach which will better be able to represent risks in drinking water catchments.
- Research on the potential impacts of future scenarios of environmental change (climate change and land use change, e.g. Dunn et al., 2012) on the risks posed by multiple pollutants can be undertaken using the CaRPoW framework to determine future risks to potable water supplies.
- The development of a methodology within CaRPoW to assess the effectiveness of interventions is recommended. Involving the incorporation of field data on the effectiveness of measures at reducing multiple pollutant loads would be one possible way of achieving this (e.g. Cherry et al., 2008).

By doing this, a further dimension to the decision making process would be added, allowing the effectiveness of different intervention scenarios to be assessed.

8.5 Conclusions

In conclusion, this thesis has demonstrated the development of a water industry defined methodology capable of identifying multiple diffuse pollution risks within a catchment for the selection and targeting of catchment management interventions. The CaRPoW framework has been developed on the basis that catchment diffuse pollution processes can be disaggregated into source, mobilisation and delivery groupings. The relative dominance of these process groupings defines the risk posed by an area of land within a catchment and interventions can be selected according to the most dominant risk component in each land area. Modelling methodologies were developed for each risk component and implemented in a case study catchment. Over half of the models represented the spatial distribution of pollutant loads successfully within the limits of uncertainty for both the models and the validation data. The unsuccessful model predictions were hypothesised to be because of the simple averaged nature of the model methods developed or uncertainty in the poor resolution of water quality data against which models were validated. Future work therefore lies in the collection of higher resolution model input and model validation data. When a real world catchment management programme was compared against model outputs theoretical savings and missed opportunities for intervention investment were identified. Overall the approach developed gives water companies and other implementers of catchment management a better insight into the spatial distribution of diffuse pollution risks within their catchments, and a mechanism to prioritise parts of the catchment for certain interventions.

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APPENDICES

Appendix A - Using CaRPoW to conceptualise pollutant processes without modelling – Water colour in the Amlaird Catchment

A.1 Introduction

In Chapters 4-7 of the thesis, the CaRPoW framework has been used with models to represent catchment processes for pesticides, nutrients and sediment in the River Ugie catchment. There are however, pollutants and catchments where data availability means that the catchment pollutant processes that define spatial risk cannot be represented by models. In these instances CaRPoW can be used by end users to frame conceptual understanding of processes in the catchment, attempt to explain catchment monitoring results, better understand the nature of potential spatial risks and get a better idea overall of how best to mitigate the problem.

One such pollutant that falls into this category is Dissolved Organic Carbon (DOC), which is linked to water colour issues in drinking water supply catchments (Grand-Clement et al., 2014). The analysis of pollutant processes from Chapter 2 of the thesis shows that the source and mobilisation of DOC, within the relatively small upland catchments that they are a problem, is heavily dependent on small scale processes driven by differences in vegetation, microtopography and soil structure (Holden, 2005). Models that can represent DOC losses spatially are subsequently either highly parameterised process based models such as the ECOSSE model (Smith et al., 2007) or are simple GIS based methodologies that use generic datasets, but operate at scales unable to delineate intra-catchment risk (e.g. Grayson et al., 2012). At present there are no simple models that use generic datasets applicable to the CaRPoW framework for DOC.

Therefore, this appendix applies the CaRPoW framework in a conceptualisation capacity to the Amlaird drinking water supply catchment which is characterised by high water colour. Results from monitoring are outlined and discussed to highlight spatial-temporal patterns of DOC losses in the catchment. Such patterns are then discussed in reference to the components of the CaRPoW framework to give the end user a better understanding of the water colour problem in Amlaird and offer insights into potential spatial differences in risk.

A.2 Catchment characteristics and field methodology

The Amlaird catchment is a small, 9.3 km^2 catchment to the south of East Kilbride in Central Scotland, United Kingdom. The catchment contains two connected reservoirs (Lochgoin and Craigendunton) that supply the Amlaird Water Treatment works. The catchment has a unique hydrology that is illustrated in Figure A-1. An intake pipe connects numerous locations in the catchment to the Lochgoin Reservoir, which subsequently supplies Craigendunton. A large proportion of the area to the east and north of the catchment is therefore connected to the Lochgoin Reservoir, as well as the Birk Burn. The catchment is relatively homogenous with soil types consisting of predominantly blanket peatland with only a small area of mineral soil to the north of Lochgoin and organo-mineral soils along the stream corridors. Land uses are limited to rough moorland with some plantation forestry to the south of the catchment. Topographically the catchment sits high upon a plateau with a maximum elevation of 356 metres to the east of the catchment, with drains to a minimum elevation of 244 metres at the Craigendunton Reservoir. This makes the catchment relatively flat considering its elevation. Anthropogenic influence is widespread as the catchment houses a large proportion of the Whitelee Windfarm, which began construction in 2005 and consists of 215 turbines and 90km of gravel road infrastructure.

The water treatment works at Amlaird (approximately 3 km to the south west of the catchment) experiences high levels of water colour during certain periods of the year which causes disinfection by-product issues when water is treated with chlorine. The catchment was originally included within Scottish Water's Sustainable Land Management scheme and subsequently a fortnightly monitoring programme was set up in mid-2011 to monitor various points in the catchment for Colour, Dissolved Organic Carbon, Total Organic Carbon and Manganese. As part of this EngD research two water level loggers were installed at the Loch Burn and Birk Burn monitoring locations (sites selected according to ISO 1100-1) and rating curves were developed (using BS EN ISO 748:2007 and ISO 1100-2) so that discharge data from the catchment could be derived.

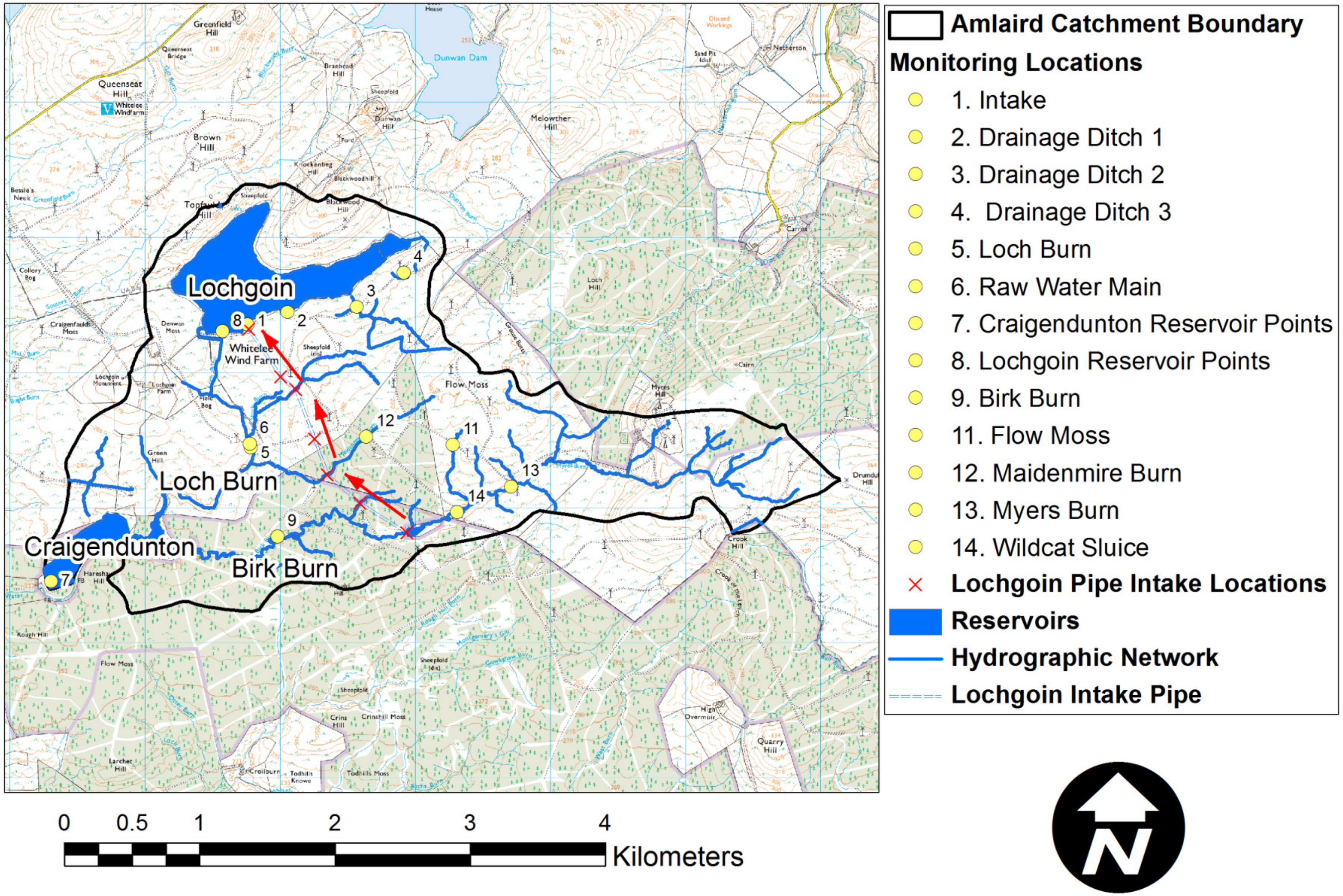

Figure A-1 – Mapped outlined of the Amlaird drinking water supply catchment with unique catchment piped hydrology illustrated by red arrows (location of intake pipe)

A.3 Presentation and discussion of monitoring results

The results from the monitoring are presented in this section to frame the problem and to extricate some of the processes that may be operating on DOC dynamics in the catchment before the CaRPoW framework is applied. For ease of analysis the monitoring points can be split into three groupings, those that drain the catchment (the 3 drainage ditches, Lochgoin Intake, Birk Burn, Myers Burn, Maidenmire Burn, Wildcat Sluice and Flow Moss), those that are either reservoirs or drain from the reservoirs (Lochgoin, Craigendunton, Raw Water Main and Raw Water Tap) and those that have both reservoir and catchment inputs (Loch Burn). DOC concentrations averaged over the three groups for the period of monitoring are plotted against rainfall and discharge form the Loch Burn Gauge and Air Temperature from the nearby Auchincruivie climate station in Figure A-2.

A distinct seasonal pattern is evident with the highest DOC concentrations in the summer and early autumn and the lowest in the winter. The pattern corresponds to temperature with a slight time lag between peak temperatures and peak DOC concentration. Such patterns have been observed in other Scottish catchments (Dawson *et* al., 2008; Dawson et al., 2011; Dinsmore et al., 2013) and catchments in other temperate areas (Koehler et al., 2009), suggesting a causal link between temperature and DOC concentration in surface waters.

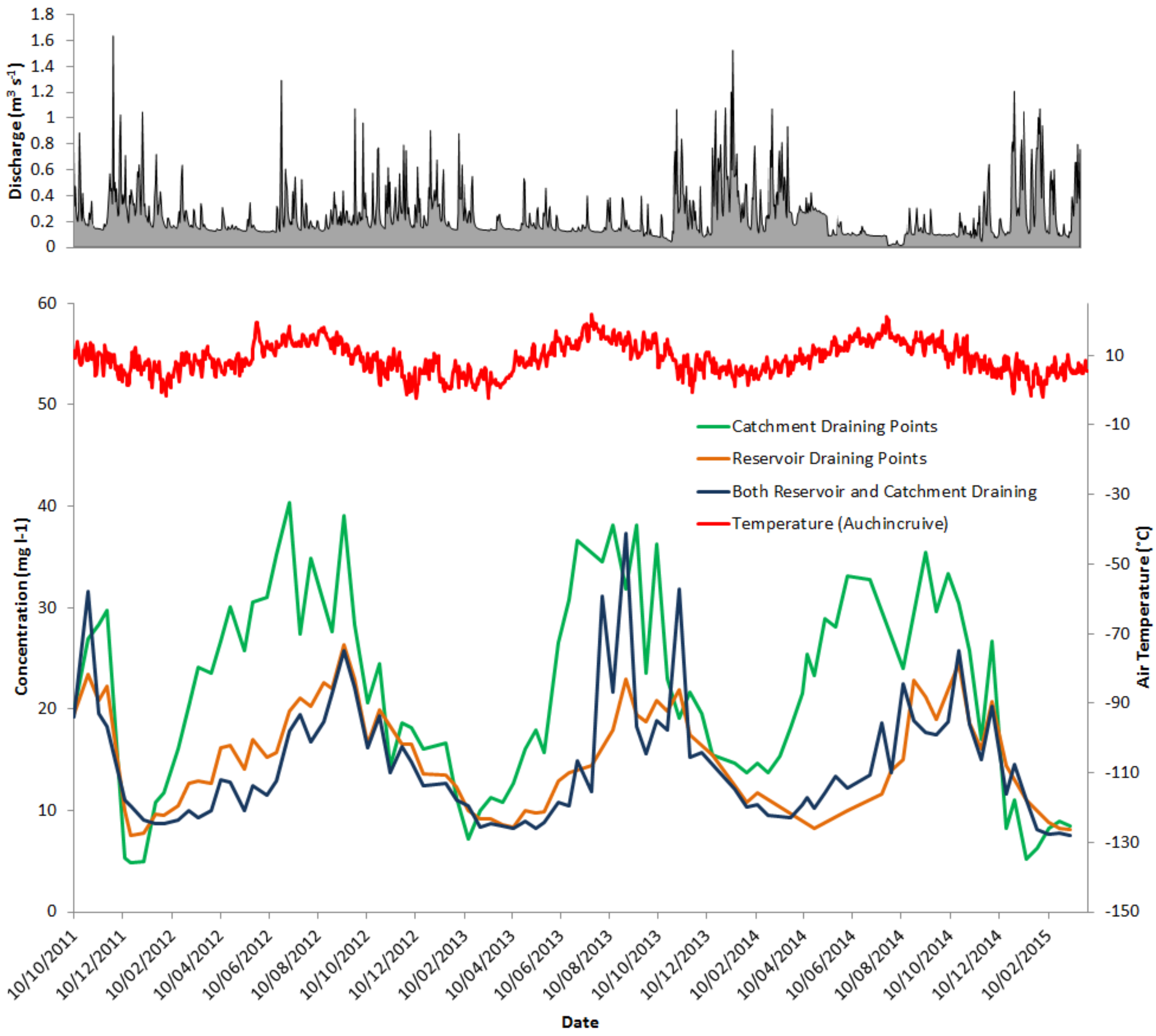

Figure A-2 – DOC (Dissolved Organic Carbon) concentrations for Amlaird averaged across multiple monitoring points, plotted against air temperature from the Auchincruive Gauge and Discharge from the Loch Burn gauge

There also appears to be a lag in the peak DOC concentration in the monitoring points that drain from the reservoirs or are a mixture of the two when compared to those that drain the catchment alone. In the three years of monitoring, peak concentration in the catchment draining monitoring points is generally in July, whereas in the other points peak concentrations are in September or early October. This lag phenomenon is consistent with research in larger lake catchments, such as those found in North America (Goodman et al., 2011; Lottig et al., 2013), where lakes in the stream network act as 'hydrological buffers' to DOC concentration discharge dynamics. If the discharge-concentration dynamics of the Loch

Burn (fed by the Lochgoin reservoir) are analysed this phenomenon holds true for Amlaird also. With no lag, the correlation coefficient between discharge and DOC concentration is -0.056, i.e. an insignificant (at 95% confidence interval), very weak negative correlation. Using a cross correlation function, a lag time of 1 month gives a significant correlation coefficient of 0.463 between discharge and concentration. This potentially suggests that the Lochgoin reservoir lags DOC dynamics in the catchment by 1 month. The discharge-concentration relationship for the Birk Burn (which is not fed by a reservoir) is somewhat affected by the fact that there are very few high discharge events at the times samples were taken, making it difficult to pass judgement on the poorly correlated relationship.

When the relationship between discharge and DOC load is considered the picture is a little different. DOC loading has been calculated for the Loch Burn and Birk Burn streams using the loading methodologies outlined in Defew et al. (2013); more detail on the methods is presented in Chapter 5 in the main thesis. In both the Birk and Loch burns, instantaneous DOC flux correlates well with discharge over the period of the record (least square linear regression R^2 values of 0.72 and 0.98 are significant at $p < 0.05$ for Loch Burn and Birk Burn respectively). Interestingly, DOC loads are highest during the winter months when concentrations are lowest. This is likely a reflection of the higher discharge values in the winter and/or the fortnightly grab sampling missing key storm events in the summer and autumn when high DOC production in the soil coincides with high discharge. Other studies have however found similar higher loads in UK catchments in the winter (Buckingham et al., 2008).

The average (over the 7 load calculation methods used) total annual DOC loads for the full three years of sampling are shown in Table A-1. Across the 3 years Loch Burn consistently contributes approximately four times more DOC load to the Craigendunton reservoir than the Birk Burn. This is likely to stem from the larger discharge values found in the Loch Burn which are around a magnitude larger than the Birk Burn.

Table A-1 - Annual DOC (Dissolved Organic Carbon) loads and average discharge for the Loch and Birk burns over the three years of monitoring

	Annual DOC Load (kg)		Average Discharge ($m^3\ s^{-1}$)	
Year	Loch Burn	Birk Burn	Loch Burn	Birk Burn
2012	111041	27978	0.24	0.03
2013	104337.93	27559	0.23	0.03
2014	94451	25773	0.22	0.03

Given the relatively sparse temporal resolution of the water quality sampling regime the annual loads must be treated with some caution. The reason for this is at certain periods of the year the Birk Burn has a higher discharge than the Loch Burn (as illustrated in Figure A-3). None of the water quality samples were taken on days where the flow was higher in the Birk Burn which may suggest that the annual loads calculated may be underestimated. This is especially prevalent considering the many examples in the literature that highlight the important contribution of individual storm events to annual DOC flux (e.g. 50% of flux transported during 10% of the time, Clark et al., 2007).

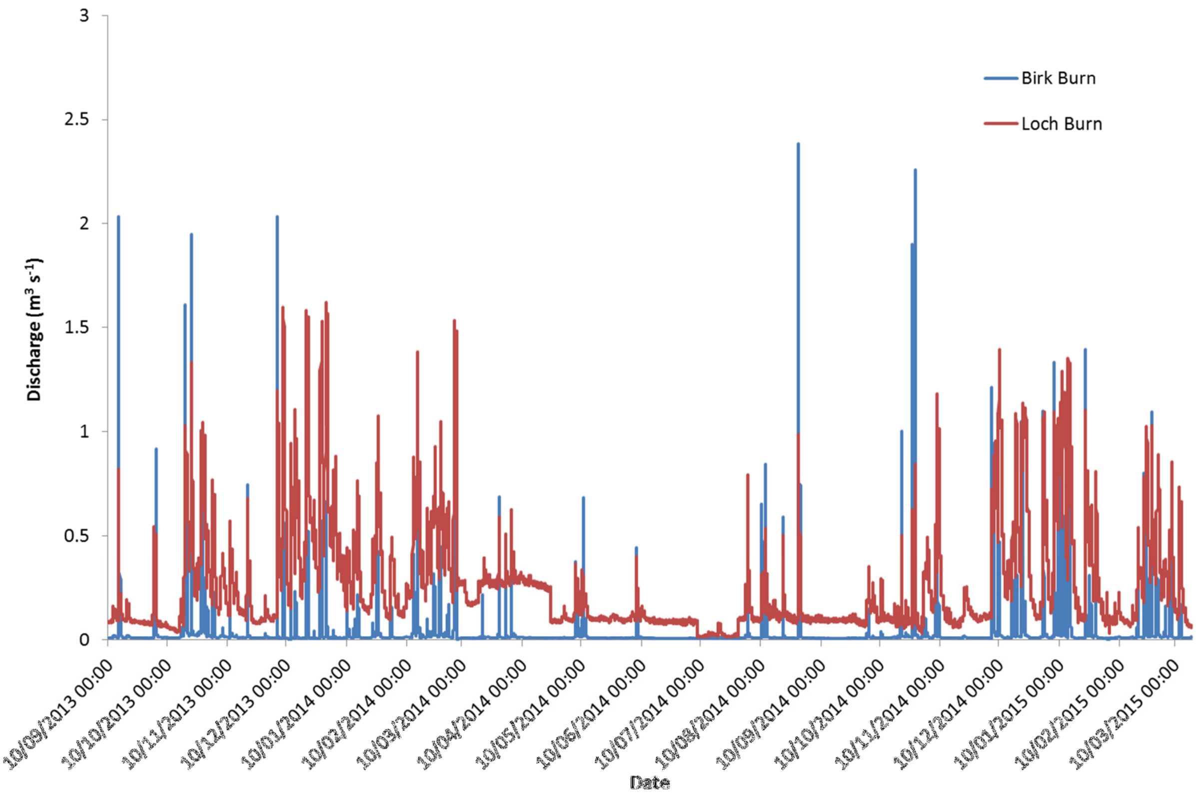

Figure A-3 - Recorded discharge of the Birk and Loch burns over the period of monitoring using a derived ratings curve.

A.4 Applying CaRPoW to conceptualise DOC processes in the Amlaird Catchment

Using the review of processes from Chapter 2 of the thesis, available spatial data and knowledge gathered from field work the CaRPoW framework is used to conceptualise the processes that potentially explain the spatio-temporal patterns detailed in section 3.

A.4.1 Source

Chapter 2 of the thesis highlights the importance of high soil organic carbon content and in particular the presence of peat soils. Of the 9.35 km^2 land area in the catchment, 6.89 km^2 is classified as blanket peat, 0.87 km^2 are organo-mineral soils (peaty podzols and gleys) and 0.85 km^2 are mineral soils according to the Scottish 1:25000 scale soil classification (the remainder of the catchment constitutes the two reservoirs). The dominance of peat and organo-mineral soils perhaps explains why there is a water colour issue, but does not give much insight into the spatial differences of source risk within the catchment i.e. based on soil classification alone source risk is largely equal across the catchment. Spatial differences in DOC sources based on soil are therefore likely attributed to smaller scales not represented by the soil classification data alone. One such small scale variability may be the vegetation type found on the peat.

The best available land cover data for the Amlaird catchment comes from the Land Cover Map 2007. According to the LCM 2007, the catchment consists of 5.20 km^2 of 'Bog', 1.85 km^2 of 'Coniferous Forestry', 0.59 km^2 of 'Acid Grassland' and 0.55 km^2 of 'Heather Grassland", with the rest of the catchment made up of either the reservoirs or a small area of 'Improved Pasture'. The coniferous forestry proportion of the catchment is largely positioned in the Birk Burn proportion of the catchment as detailed in Figure A-4. Thus, the main distinct differences in vegetation type from the LCM classification that can be made are the plantation forestry in the south of the catchment and the moorland vegetation types such as Calluna, Sedges, Molinia and Sphagnum found in the moorland land covers (Armstrong et al., 2012). Although few studies have been conducted on the difference in DOC concentration and fluxes under forested and moorland peat it has been shown that concentrations of DOC are higher under forests but fluxes higher from moorlands (Buckingham et al., 2008). Bearing this in mind, source risk under the forested sites may be higher (as concentrations are higher) but overall risk (i.e. flux) which depends on mobilisation, may be lower. Where greater variability within the source component may be present is in the DOC concentrations under different moorland vegetation species which are not delineated by the best available land cover data. Armstrong et al. (2012) for example, found that soil and catchment drainage water DOC concentrations were highest under *Calluna vulgaris* (heather) and Sedges than under *Sphagnum* and *Molinia*. However, this study is one of the only investigations into DOC production under different vegetation types and the causality of the difference between vegetation types is not confirmed, only speculated. Although there is some delineation between heather grassland and bog land covers there is not enough detail in the LCM dataset to make formative decisions on source strength based on vegetation type.

It has been well documented that DOC production in the soil is often associated with a lowering of the water table and aeration of the peat which increases microbial activity (Clark et al., 2009). Such draw down has been associated with activities such as the construction of drainage channels (Gibson et al., 2009), moorland burning (Yallop et al., 2009) and more recently wind farm activities (Waldron et al., 2009). The catchment has a complex drainage network that is a relic of agricultural drainage and it has also housed a large proportion of the Whitelee wind farm since 2005. Although more research is required on the effects of such activities on DOC production they must be considered as a contributor to the potential variation in source risk. At present the drainage networks have not been extensively mapped in the catchment, nor are updated maps on the wind farm infrastructure and associated forestry activities available. Without these datasets it is difficult to attribute spatial patterns to them; however they must be considered as potential contributors to spatial risk in the catchment going forward.

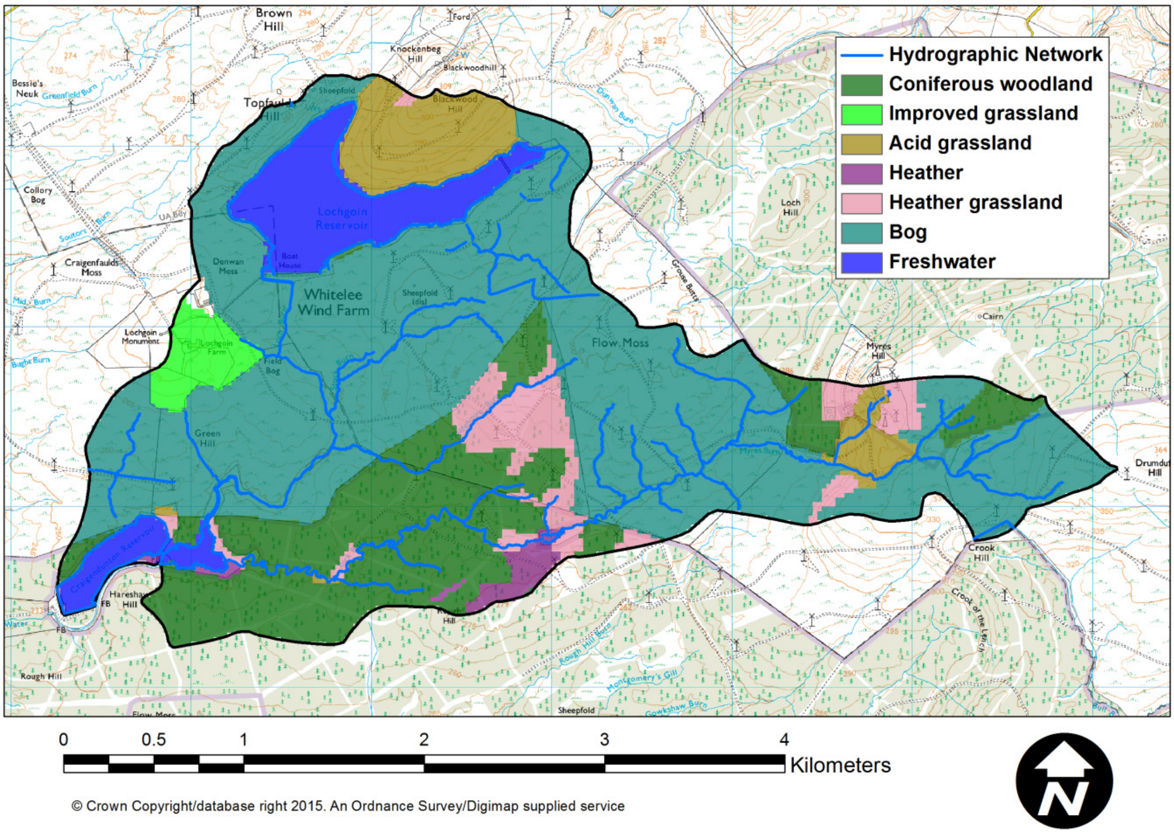

Figure A-4 - Land cover map 2007 classifications (Morton et al., 2011) for the Amlaird drinking water supply catchment

A.4.2 Mobilisation

DOC mobilisation is largely associated with fast flow runoff events where DOC held in the soil is ‘flushed’ by rainfall inputs (Worral et al., 2002). Such a relationship is found in the Amlaird catchment, with the significant ($p < 0.05$) positive relationships observed between

DOC load and discharge in both the Loch and Birk Burns. Spatially defining where runoff processes are more prevalent in the catchment is more difficult for a catchment like Amlaird when compared to the Ugie for example. The relative homogeneity of the soil and land cover datasets mean that the differentiation of runoff processes by unique combinations of soil type and land use will not define runoff processes at a scale small enough to potentially determine mobilisation risk. A different analysis is therefore required to make some inferrals on which parts of the catchment may contribute more runoff than others.

One possible indication of runoff generating areas could be to use the Topographic Wetness Index, as originally developed by Kirkby (1975). The topographic wetness index calculates the ratio of the slope to the specific upslope contributing area to give a semblance of which parts of the catchment are most likely to generate runoff when topography is the main control (Sørensen et al., 2006). Topographic wetness index is shown in Figure A-5 for the Amlaird catchment using a 5 m resolution NextMap DTM with slope calculated using the D-infinity method (Tarboton, 1997). The relatively flat nature of the catchment means TWI is fairly consistent across the catchment apart from a few places such as the areas surrounding the burns, the slope to the north of Lochgoin and the area known as Myers Hill in the eastern part of the catchment that have higher TWI values. Based on topography alone these areas may be associated with a higher DOC mobilisation risk. However, there is one key variable in the mobilisation of DOC that is not accounted for by TWI. In recent years the presence of macropores or 'peat pipes' have been found to be key factors in the rapid mobilisation of DOC from peat soils (Holden et al., 2012). It is difficult to determine where peat pipes are prevalent in a catchment using generic datasets, although there is evidence to suggest the formation of pipes is more prevalent in degraded or drier peat (Holden *et* al., 2012; Smart et al., 2013). Hence, the same land management activities that relate to the DOC source term (drainage, burning, wind farms and forestry activities) may also increase the mobilisation of DOC as well.

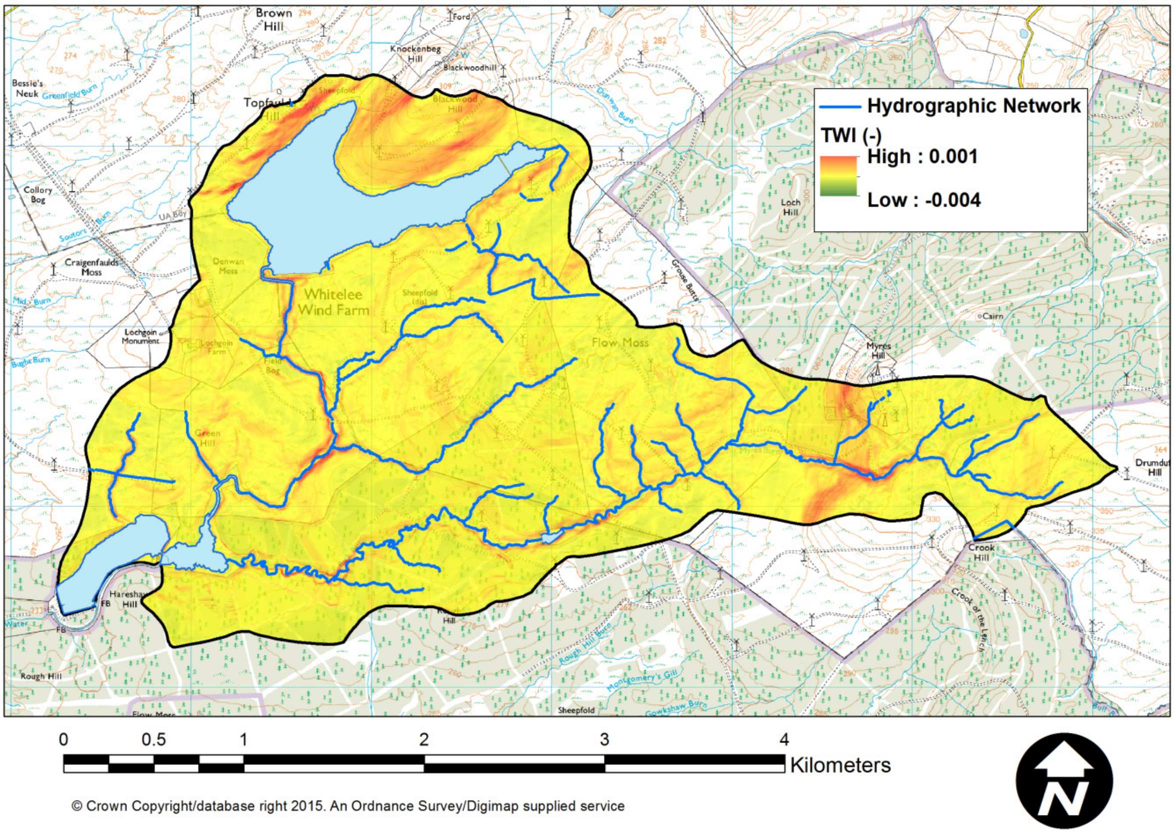

Figure A-5 - Topographic Wetness Index in the Amlaird catchment using NEXTMap 5m DTM

A.4.3 Delivery/Connectivity

Determining which areas of the catchment are most connected to the Craigendunton reservoir is complicated by the unusual hydrology of the catchment. As outlined in Chapter 2, an intake pipe takes water from a number of burns in the eastern half of the catchment and delivers it into the Lochgoin Reservoir. This effectively means that a proportion of water draining from this part of the catchment drains straight into the Craigendunton Reservoir (well connected) and another portion drains into Lochgoin (less well connected). The proportion of discharge from these intakes that is delivered to Lochgoin is not known. But based on visual field observations the intake pipe only has significant flow during periods of heavy rainfall, suggesting water is only transmitted through the pipe above a certain discharge threshold in the burns.

As a result, catchment connectivity is complicated given that the majority of DOC load is transmitted during periods of elevated discharge. Employing a methodology to assess connectivity such as that used in the Ugie for example would be inaccurate, as the area to the east of the intake points would have a higher connectivity score than its actual connectivity would suggest.

The influence of the reservoirs in catchment connectivity is also an important consideration. The data analysis in Chapter 3 has shown the approximate 1 month lag effect the Lochgoin and Craigendunton Reservoirs have on concentrations in the catchment when compared to the water bodies draining straight from the catchment. There is a large body of literature that shows the effects of lakes on DOC losses from the hydrological continuum, with Molot and Dillon (1997) finding between 38-70% loss of DOC inputs within lakes. One way of assessing this for Amlaird is to look at the flow and DOC load contributions for the Loch and Birk Burns as this gives an indication of proportional contribution of DOC when related to discharge contribution. Taking total discharge from 2014, the Loch Burn contributes 85% of the total flow into the St Mary's loch (which feeds Craigendunton) but only contributes 73.8% of the DOC load. Although this does not factor for differences in source inputs it does potentially highlight retention or loss of DOC in the Lochgoin reservoir and hence provides evidence for lower connectivity risk. Conversely, the discrepancy could be a result of the high uncertainty in the loading calculations and no significant difference between the two systems is evident.

The presence of artificial drainage channels must also be considered as features that enhance connectivity in the catchment. Drainage channels have been shown to increase flow velocities above overland flow rates and therefore increase the speed at which water is delivered to the natural stream network, even though they actually reduce maximum flood peak because of dryer antecedent conditions (Lane and Milledge, 2013). The speed at which the drainage channels deliver water, along with increases in overall water yield from the drains when compared to blocked drains or intact peat across the full range of hydrological conditions, consequently increases connectivity and DOC export (Turner et al., 2013).

A.4.4 Overall risk

Based on the outcomes of the process conceptualisation, within the three CaRPoW components the highest risk areas of the catchment are likely to be *Calluna* land cover on disturbed and drained blanket peat, in the wettest parts of the catchment, in an area that does not drain through the Lochgoin reservoir.

Based on this, potential candidate sites for the highest risk classification are the area of the catchment that drains Myers Hill (shown in Figure A-6) which has a mixture of peat and peaty gley soil types, heather and acid grassland LCM classification, the highest TWI value in the catchment and partly drains directly into the Craigendunton Reservoir. Unfortunately the Wildcat Sluice and Myers burn sample locations detailed in Figure A-1 were only sampled 10 times because of access issues. Nevertheless during these sampling periods average DOC concentrations were the first and fourth highest respectively, when compared to the other sampling points, potentially suggesting that the area of the catchment detailed in Figure A-6 is high risk.

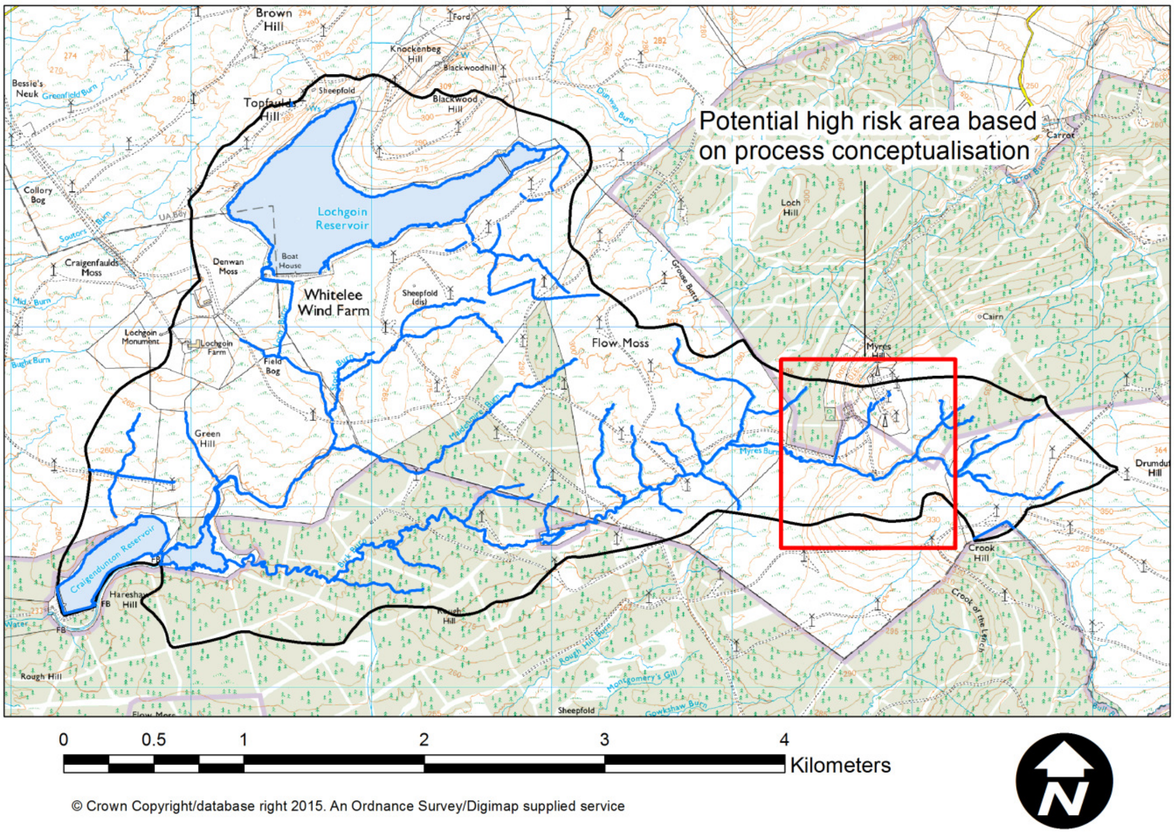

Figure A-6 - Potential high risk area for DOC in the Amlaird catchment based on process conceptualisation within the CaRPoW framework

A.5 Conclusions

Where data are unavailable or not detailed enough to be used to model pollutant risk in a catchment, the CaRPoW framework can be used to conceptualise pollutant processes with data that is avaialbe and give end users a better insight into where risks might be in a catchment. These principles were applied to an analysis of the Amlaird catchment which is a small upland reservoir catchment with a water colour issue.

Results were presented from 3 years of monitoring to outline the nature of the problem and discussed within the context of the CaRPoW framework where DOC processes were conceptualised and explanations offered for the patterns observed in the monitoring data.

Source processes could be spatially defined to a certain extent using available soil and land use data, although more detailed data on land cover and peat disturbance would have provided more detail. Spatial catchment wetness was defined using the TWI but this did not give any indication of mobilisation pathway which required more information on peat structure and condition. Connectivity was hard to define because of the complex hydrology in the catchment, although the lag and loss of DOC caused by the Lochgoin reservoir was observed in the data.

Bringing the three components together, an area of the catchment known as the Myers Hill to the east was specualted as the highest risk area of the catchment and where peatland restoration should be focused. However to make more formative decisions on where to focus efforts more detailed data is required on the condition of the peat and the spatial arrangement of human activities (wind farm and drainange) in the catchment.

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Appendix B CaRPoW model input parameters

B.1 Pesticide parameters

Table B-1 - CaRPoW pesticide model input parameters (crops applied to, application rate and application timing). Data derived from maximum application rates as per produce guidance and application date from agronomist interviews.

Pesticide	Crop	Application Rate (g ha^{-1})	Application Date
2, 4-D	Spring Barley	10	May/June
	Spring Wheat	12.5	May/June
	Ley Grass	33	April/May and August/September
Chlorotoluron	Spring Barley	35	April/May
	Winter Barley	1260	October
	Winter Wheat	1085	October/November
	Spring Wheat	175	April/May
CMPP	Spring Barley	538.2	May/June
	Winter Barley	374.4	May/June
	Winter Wheat	388.8	May/June
	Spring Wheat	552	May/June
	Spring Oats	593.4	May/June
	Winter Oats	552	May/June
	Ley Grass	41.4	April/May
MCPA	Spring Barley	82.5	April/May
	Winter Barley	16.5	April/May
	Winter Wheat	8	September/October
	Spring Wheat	346.5	September/October
	Spring Oats	49.5	April/May/June
	Ley Grass	247.5	April/May/June
	Permanent Grass	16.5	April/May/June
Metaldehyde	Winter Oilseed Rape	750	August/September/October/November
	Winter Barley	750	August/September/October/November
	Winter Wheat	750	August/September/October/November
	Potatoes	750	August/September/October/November
	Ley Grass	7.48	August/September/October/November
	Brussles Sprouts	750	August/September/October/November
	Cabbage	750	August/September/October/November
	Cauliflower	750	August/September/October/November
	Lettuce	750	August/September/October/November
	Turnips	750	August/September/October/November
	Other Veg	750	August/September/October/November
Metazachlor	Winter Oilseed Rape	1250	August/September
	Spring Oilseed Rape	750	April/May

Brussles Sprouts	735	April/May
Cabbage	705	April/May
Cauliflower	750	April/May
Turnips	652.5	April/May

B.2 Nitrate CaRPoW parameters

Table B-2 - Crop nitrogen offtake values (Derived from Nix, 2013)

Crop Type	Nitrogen Offtake Value (kg ha^{-1})
Cabbages	72
Carrots	255
Ley Grass	0
Lochs	0
Other Cereals	140
Other Vegetables	63
Permanent Grass	0
Potatoes	115
Rough Grazing	0
Semi-Natural	20
Soft Fruit	22
Spring Barley	110
Spring Oilseed Rape	100
Spring Wheat	110
Spring Oats	105
Stock Feed	20
Turnips	20
Unclassified	0
Urban	0
Winter Barley	140
Winter Oats	140
Winter Oilseed Rape	130
Winter Wheat	170
Woodland	20

Table B-3 - Nitrogen fertiliser application rates according to crop type, previous crop type and soil texture class (Derived from SAC technical guidance notes)

		Nitrogen fertiliser application rate (kg ha^{-1})				
		Soil texture class				
Crop type and previous crop number		Clay Loam	Loamy Sand	Organic	Sandy Loam	Sandy Silt Loam
Cabbages						
	0	340	340	340	340	340
	1	340	340	340	340	340
	2	330	330	330	330	330
	3	320	320	320	320	320
	4	300	300	300	300	300
	5	250	250	250	250	250
	6	210	210	210	210	210
Carrots		230	230	230	230	230
	0	60	60	60	60	60
	1	60	60	60	60	60
	2	50	50	50	50	50
	3	40	40	40	40	40
	4	20	20	20	20	20
	5	0	0	0	0	0
	6	0	0	0	0	0
Ley Grass						
	0	290	290	290	290	290
	1	290	290	290	290	290
	2	290	290	290	290	290
	3	290	290	290	290	290
	4	290	290	290	290	290
	5	290	290	290	290	290
	6	290	290	290	290	290
Other Cereals						
	0	200	200	80	200	200
	1	200	200	80	200	200
	2	190	190	70	190	190
	3	180	180	60	180	180
	4	160	160	40	160	160
	5	130	130	10	130	130
	6	90	90	0	90	90
Other Vegetables						
	0	0	0	0	0	0
	1	0	0	0	0	0
	2	0	0	0	0	0

	3	0	0	0	0	0
	4	0	0	0	0	0
	5	0	0	0	0	0
	6	0	0	0	0	0
Permanent Grass						
	0	0	250	250	250	250
	1	0	250	250	250	250
	2	250	250	250	250	250
	3	250	250	250	250	250
	4	250	250	250	250	250
	5	250	250	250	250	250
	6	250	250	250	250	250
Potatoes						
	0	100	100	100	100	100
	1	100	100	100	100	100
	2	90	90	90	90	90
	3	80	80	80	80	80
	4	70	70	70	70	70
	5	50	50	50	50	50
	6	0	0	0	0	0
Soft Fruit						
	0	40	40	40	40	40
	1	40	40	40	40	40
	2	30	30	30	30	30
	3	20	20	20	20	20
	4	0	0	0	0	0
	5	0	0	0	0	0
	6	0	0	0	0	0
Spring Barley						
	0	130	130	50	130	130
	1	130	130	50	130	130
	2	120	120	40	120	120
	3	110	110	30	110	110
	4	90	90	10	90	90
	5	60	60	0	60	60
	6	20	20	0	20	20
Spring Oats						
	0	130	130	50	130	130
	1	130	130	50	130	130
	2	120	120	40	120	120
	3	110	110	30	110	110
	4	90	90	10	90	90
	5	60	60	0	60	60
	6	20	20	0	20	20

Spring Oilseed Rape						
	0	100	100	20	100	100
	1	100	100	20	100	100
	2	90	90	20	90	90
	3	80	80	0	80	80
	4	60	60	0	60	60
	5	30	30	0	30	30
	6	0	0	0	0	0
Spring Wheat						
	0	130	130	50	130	130
	1	130	130	50	130	130
	2	120	120	40	120	120
	3	110	110	30	110	110
	4	90	90	10	90	90
	5	60	60	0	60	60
	6	20	20	0	20	20
Stock Feed						
	0	110	110	110	110	110
	1	110	110	110	110	110
	2	100	100	100	100	100
	3	90	90	90	90	90
	4	70	70	70	70	70
	5	40	40	40	40	40
	6	0	0	0	0	0
Turnips						
	0	110	110	110	110	110
	1	110	110	110	110	110
	2	100	100	100	100	100
	3	90	90	90	90	90
	4	70	70	70	70	70
	5	40	40	40	40	40
	6	0	0	0	0	0
Winter Barley						
	0	180	180	80	180	180
	1	180	180	80	180	180
	2	170	170	70	170	170
	3	160	160	60	160	160
	4	140	140	40	140	140
	5	110	110	10	110	110
	6	70	70	0	70	70
Winter Oats						
	0	180	180	80	180	180
	1	180	180	80	180	180
	2	170	170	70	170	170

3	160	160	60	160	160
4	140	140	40	140	140
5	110	110	10	110	110
6	70	70	0	70	70
Winter Oilseed Rape					
0	230	230	110	230	230
1	230	230	110	230	230
2	210	210	90	210	210
3	190	190	70	190	190
4	140	140	40	140	140
5	110	110	0	110	110
6	70	70	0	70	70
Winter Wheat					
0	200	200	80	200	200
1	200	200	80	200	200
2	190	190	70	190	190
3	180	180	60	180	180
4	160	160	40	160	160
5	130	130	10	130	130
6	90	90	0	90	90

B.3 WaSim model inputs

Table B-4 - WaSim crop input parameters (Derived from Holman et al. 2004)

Crop Type	Planting date (Julian Day)	Harvest Date (Julian Day)	Emergence Date (Julian Day)	20% crop coverage date (Julian (Day)	Full Cover Date (Julian Day)	Crop Maturity Date (Julian Day)	Maximum Root Depth Date (Julian Day)	Planting depth (m)	Maximum root depth (m)	Maximum coverage (%)	WaSim Crop Coefficient	P Fraction
Grassland	1	365	1	1	1	365	1	0.7	0.7	100	100	0.5
Row Crops	105	170	31	46	92	133	92	0.08	0.75	100	110	0.5
Winter Cereals	273	351	11	41	183	273	162	0.03	1.5	100	110	0.5
Spring Cereals	74	175	15	18	76	122	76	0.03	1.5	100	110	0.5
Semi-Natural	1	365	1	1	1	365	1	0.35	0.35	100	100	0.5
Woodland	74	324	105	115	130	302	74	1.5	1.5	100	114	0.71

Table B-5 - WaSim soil input parameters (Derived from SEISMIC soil properties databse)

Soil Association, HOST Number and Land Use Type	Water content at saturation (%)	Water content at field capacity (%)	Water content at permanent wilting point (%)	P Fraction	Tau Drainage Coefficient	Hydraulic Conductivity (m day^{-1})
Alluvial Soils 7 - AR	0.42	0.336	0.137	0.5	0.36	1.36
Alluvial Soils 7 - LE	0.425	0.34	0.139	0.5	0.36	1.41
Alluvial Soils 7 - OT	0.435	0.348	0.137	0.5	0.36	3.58
Alluvial Soils 7 - PG	0.425	0.34	0.139	0.5	0.36	1.41
Corby 5 - AR	0.3475	0.278	0.094	0.5	0.69	0.6
Corby 5 - LE	0.35125	0.281	0.0957	0.5	0.69	0.6
Corby 5 - OT	0.40375	0.323	0.121	0.5	0.69	9.28
Corby 5 - PG	0.35125	0.281	0.096	0.5	0.69	0.6
Countesswells 17 - AR	0.3675	0.294	0.118	0.5	0.69	0.4
Countesswells 17 - LE	0.37125	0.297	0.12	0.5	0.69	0.41
Countesswells 17 - OT	0.45	0.36	0.14	0.5	0.69	9.26
Countesswells 17 - PG	0.3625	0.29	0.12	0.5	0.69	0.41
Countesswells 14 - AR	0.3675	0.294	0.118	0.5	0.69	0.4
Countesswells 14 - LE	0.37125	0.297	0.12	0.5	0.69	0.41
Countesswells 14 - OT	0.45	0.36	0.14	0.5	0.69	9.26
Countesswells 14 - PG	0.3625	0.29	0.12	0.5	0.69	0.41
Countesswells 15 - AR	0.3675	0.294	0.118	0.5	0.69	0.4
Countesswells 15 - LE	0.37125	0.297	0.12	0.5	0.69	0.41
Countesswells 15 - OT	0.45	0.36	0.14	0.5	0.69	9.26
Countesswells 15 - PG	0.3625	0.29	0.12	0.5	0.69	0.41
Durnhill 15 - AR	0.4925	0.394	0.16	0.5	0.36	11.65
Durnhill 15 - LE	0.4925	0.394	0.16	0.5	0.36	11.65
Durnhill 15 - OT	0.4925	0.394	0.16	0.5	0.36	11.65
Durnhill 15 - PG	0.4925	0.394	0.16	0.5	0.36	11.65
Foudland 14 - AR	0.4075	0.326	0.14	0.5	0.36	0.29
Foudland 14 - LE	0.41125	0.329	0.142	0.5	0.36	0.29
Foudland 14 - OT	0.4875	0.39	0.16	0.5	0.36	9.27
Foudland 14 - PG	0.4	0.32	0.14	0.5	0.36	0.29
Foudland 17 - AR	0.4075	0.326	0.14	0.5	0.36	0.29
Foudland 17 - LE	0.41125	0.329	0.142	0.5	0.36	0.29
Foudland 17 - OT	0.4875	0.39	0.16	0.5	0.36	9.27
Foudland 17 - PG	0.4	0.32	0.14	0.5	0.36	0.29
Hatton 24 - AR	0.28625	0.229	0.12	0.5	0.36	0.4
Hatton 24 - LE	0.3775	0.302	0.122	0.5	0.36	0.41
Hatton 24 - OT	0.425	0.34	0.139	0.5	0.36	8.91
Hatton 24 - PG	0.37875	0.303	0.122	0.5	0.36	0.41
Hatton 6 - AR	0.28625	0.229	0.12	0.5	0.36	0.4

Hatton 6 - LE	0.3775	0.302	0.122	0.5	0.36	0.41
Hatton 6 - OT	0.425	0.34	0.139	0.5	0.36	8.91
Hatton 6 - PG	0.37875	0.303	0.122	0.5	0.36	0.41
Hatton 15 - AR	0.28625	0.229	0.12	0.5	0.36	0.4
Hatton 15 - LE	0.3775	0.302	0.122	0.5	0.36	0.41
Hatton 15 - OT	0.425	0.34	0.139	0.5	0.36	8.91
Hatton 15 - PG	0.37875	0.303	0.122	0.5	0.36	0.41
Peterhead 24 - AR	0.43375	0.347	0.217	0.5	0.06	0.08
Peterhead 24 - LE	0.44125	0.353	0.219	0.5	0.06	0.09
Peterhead 24 - OT	0.44125	0.353	0.218	0.5	0.06	0.09
Peterhead 24 - PG	0.44125	0.353	0.218	0.5	0.06	0.09
Skelmuir 24 - AR	0.495	0.396	0.219	0.5	0.06	12.79
Skelmuir 24 - LE	0.495	0.396	0.219	0.5	0.06	12.79
Skelmuir 24 - OT	0.495	0.396	0.219	0.5	0.06	12.79
Skelmuir 24 - PG	0.495	0.396	0.219	0.5	0.06	12.79
Skelmuir 26 - AR	0.495	0.396	0.219	0.5	0.06	12.79
Skelmuir 26 - LE	0.495	0.396	0.219	0.5	0.06	12.79
Skelmuir 26 - OT	0.495	0.396	0.219	0.5	0.06	12.79
Skelmuir 26 - PG	0.495	0.396	0.219	0.5	0.06	12.79
Strichen 24 - AR	0.37375	0.299	0.118	0.5	0.36	0.38
Strichen 24 - LE	0.3775	0.302	0.12	0.5	0.36	0.38
Strichen 24 - OT	0.45625	0.365	0.144	0.5	0.36	7.82
Strichen 24 - PG	0.37875	0.303	0.12	0.5	0.36	0.38
Strichen 17 - AR	0.37375	0.299	0.118	0.5	0.36	0.38
Strichen 17 - LE	0.3775	0.302	0.12	0.5	0.36	0.38
Strichen 17 - OT	0.45625	0.365	0.144	0.5	0.36	7.82
Strichen 17 - PG	0.37875	0.303	0.12	0.5	0.36	0.38
Tarves 17 - AR	0.37125	0.297	0.124	0.5	0.36	0.33
Tarves 17 - LE	0.375	0.3	0.126	0.5	0.36	0.34
Tarves 17 - OT	0.3975	0.318	0.132	0.5	0.36	0.32
Tarves 17 - PG	0.375	0.3	0.126	0.5	0.36	0.34
Tarves 24 - AR	0.37125	0.297	0.124	0.5	0.36	0.33
Tarves 24 - LE	0.375	0.3	0.126	0.5	0.36	0.34
Tarves 24 - OT	0.3975	0.318	0.132	0.5	0.36	0.32
Tarves 24 - PG	0.375	0.3	0.126	0.5	0.36	0.34
Tarves (BRANK) - AR	0.4725	0.378	0.162	0.5	0.36	0.15
Tarves (BRANK) - LE	0.49	0.392	0.17	0.5	0.36	0.17
Tarves (BRANK) - OT	0.47125	0.377	0.131	0.5	0.36	0.58
Tarves (BRANK) - PG	0.49	0.392	0.126	0.5	0.36	0.34
Tarves (HG) - AR	0.39875	0.319	0.149	0.5	0.36	0.25
Tarves (HG) - LE	0.4075	0.326	0.152	0.5	0.36	0.28
Tarves (HG) - OT	0.4375	0.35	0.146	0.5	0.36	0.35
Tarves (HG) - PG	0.4075	0.326	0.152	0.5	0.36	0.28
Tipperty - AR	0.4725	0.378	0.238	0.5	0.06	0.06

Tipperty - LE	0.48125	0.385	0.24	0.5	0.06	0.07
Tipperty - OT	0.54875	0.439	0.305	0.5	0.06	0.01
Tipperty - PG	0.48	0.384	0.24	0.5	0.06	0.07
Organic Soils 12 - AR	0.7625	0.61	0.3	0.5	0.06	2.79
Organic Soils 12 - LE	0.7625	0.61	0.3	0.5	0.06	2.79
Organic Soils 12 - OT	0.7625	0.61	0.3	0.5	0.06	2.79
Organic Soils 12 - PG	0.7625	0.61	0.3	0.5	0.06	2.79
Organic Soils 29 - AR	0.7625	0.61	0.3	0.5	0.06	2.79
Organic Soils 29 - LE	0.7625	0.61	0.3	0.5	0.06	2.79
Organic Soils 29 - OT	0.7625	0.61	0.3	0.5	0.06	2.79
Organic Soils 29 - PG	0.7625	0.61	0.3	0.5	0.06	2.79
North Mormond 24 - AR	0.473	0.36	0.157	0.5	0.36	0.215
North Mormond 24 - LE	0.482	0.373	0.164	0.5	0.36	0.242
North Mormond 24 - OT	0.805	0.617	0.303	0.5	0.36	50.94
North Mormond 24 - PG	0.482	0.376	0.165	0.5	0.36	0.251
Mixed Bottom Land 7 - AR	0.42	0.336	0.137	0.5	0.36	1.36
Mixed Bottom Land 7 - LE	0.425	0.34	0.139	0.5	0.36	1.41
Mixed Bottom Land 7 - OT	0.435	0.348	0.137	0.5	0.36	3.58
Mixed Bottom Land 7 - PG	0.425	0.34	0.139	0.5	0.36	1.41
Boyndie 5 - AR	0.545	0.359	0.128	0.5	0.69	1.29
Boyndie 5 - LE	0.59	0.389	0.135	0.5	0.69	1.99
Boyndie 5 - OT	0.801	0.612	0.301	0.5	0.69	50.55
Boyndie 5 - PG	0.593	0.391	0.199	0.5	0.69	2.05

Table B-6 - WaSim drainage input parameters

Drainage scenario	Diameter (m)	Depth (m)	Spacing (m)	Depth to impermeable layer (m)
No drains	0.11	0.5	75	1.5
Drains	0.11	0.5	20	1.5

Table B-7 - WaSim soil curve number parameter inputs (Derived from SEISMIC soil property database)

		Curve number based on land use					
Soil Association, HOST Number and Land Use Type	**Soil Condition**	**Grassland**	**Row Crops**	**Winter Cereals**	**Spring Cereals**	**Semi-Natural**	**Woodland**
Alluvial Soils 7 - AR	1	58	70	69	69	58	55
	2	61	75	73	73	61	55
	3	69	78	75	75	69	60
	4	79	81	76	76	79	66
	5	86	88	84	84	86	77
Alluvial Soils 7 - LG	1	58	70	69	69	58	55
	2	61	75	73	73	61	55
	3	69	78	75	75	69	60
	4	79	81	76	76	79	66
	5	86	88	84	84	86	77
Alluvial Soils 7 - OT	1	58	70	69	69	58	55
	2	61	75	73	73	61	55
	3	69	78	75	75	69	60
	4	79	81	76	76	79	66
	5	86	88	84	84	86	77
Alluvial Soils 7 - PG	1	58	70	69	69	58	55
	2	61	75	73	73	61	55
	3	69	78	75	75	69	60
	4	79	81	76	76	79	66
	5	86	88	84	84	86	77
Corby 5 - AR	1	30	61	58	58	30	30
	2	39	65	61	61	39	30
	3	49	67	63	63	49	36
	4	68	72	65	65	68	45
	5	79	81	76	76	79	66
Corby 5 - LG	1	30	61	58	58	30	30
	2	39	65	61	61	39	30
	3	49	67	63	63	49	36
	4	68	72	65	65	68	45
	5	79	81	76	76	79	66
Corby 5 - OT	1	30	61	58	58	30	30
	2	39	65	61	61	39	30
	3	49	67	63	63	49	36
	4	68	72	65	65	68	45
	5	79	81	76	76	79	66
Corby 5 - PG	1	30	61	58	58	30	30
	2	39	65	61	61	39	30

	3	49	67	63	63	49	36
	4	68	72	65	65	68	45
	5	79	81	76	76	79	66
Countesswells 17 - AR	1	71	77	77	77	71	70
	2	74	82	81	81	74	70
	3	79	85	83	83	79	73
	4	86	88	84	84	86	77
	5	89	91	88	88	89	83
Countesswells 17 - LG	1	71	77	77	77	71	70
	2	74	82	81	81	74	70
	3	79	85	83	83	79	73
	4	86	88	84	84	86	77
	5	89	91	88	88	89	83
Countesswells 17 - OT	1	71	77	77	77	71	70
	2	74	82	81	81	74	70
	3	79	85	83	83	79	73
	4	86	88	84	84	86	77
	5	89	91	88	88	89	83
Countesswells 17 - PG	1	71	77	77	77	71	70
	2	74	82	81	81	74	70
	3	79	85	83	83	79	73
	4	86	88	84	84	86	77
	5	89	91	88	88	89	83
Countesswells 14 - AR	1	71	77	77	77	71	70
	2	74	82	81	81	74	70
	3	79	85	83	83	79	73
	4	86	88	84	84	86	77
	5	89	91	88	88	89	83
Countesswells 14 - LG	1	71	77	77	77	71	70
	2	74	82	81	81	74	70
	3	79	85	83	83	79	73
	4	86	88	84	84	86	77
	5	89	91	88	88	89	83
Countesswells 14 - OT	1	71	77	77	77	71	70
	2	74	82	81	81	74	70
	3	79	85	83	83	79	73
	4	86	88	84	84	86	77
	5	89	91	88	88	89	83
Countesswells 14 - PG	1	71	77	77	77	71	70
	2	74	82	81	81	74	70
	3	79	85	83	83	79	73
	4	86	88	84	84	86	77
	5	89	91	88	88	89	83
Countesswells 15 - AR	1	71	77	77	77	71	70

	2	74	82	81	81	74	70
	3	79	85	83	83	79	73
	4	86	88	84	84	86	77
	5	89	91	88	88	89	83
Countesswells 15 - LG	1	71	77	77	77	71	70
	2	74	82	81	81	74	70
	3	79	85	83	83	79	73
	4	86	88	84	84	86	77
	5	89	91	88	88	89	83
Countesswells 15 - OT	1	71	77	77	77	71	70
	2	74	82	81	81	74	70
	3	79	85	83	83	79	73
	4	86	88	84	84	86	77
	5	89	91	88	88	89	83
Countesswells 15 - PG	1	71	77	77	77	71	70
	2	74	82	81	81	74	70
	3	79	85	83	83	79	73
	4	86	88	84	84	86	77
	5	89	91	88	88	89	83
Durnhill 15 - AR	1	71	77	77	77	71	70
	2	74	82	81	81	74	70
	3	79	85	83	83	79	73
	4	86	88	84	84	86	77
	5	89	91	88	88	89	83
Durnhill 15- LG	1	71	77	77	77	71	70
	2	74	82	81	81	74	70
	3	79	85	83	83	79	73
	4	86	88	84	84	86	77
	5	89	91	88	88	89	83
Durnhill 15 - OT	1	71	77	77	77	71	70
	2	74	82	81	81	74	70
	3	79	85	83	83	79	73
	4	86	88	84	84	86	77
	5	89	91	88	88	89	83
Durnhill 15 - PG	1	71	77	77	77	71	70
	2	74	82	81	81	74	70
	3	79	85	83	83	79	73
	4	86	88	84	84	86	77
	5	89	91	88	88	89	83
Foudland 14 - AR	1	71	77	77	77	71	70
	2	74	82	81	81	74	70
	3	79	85	83	83	79	73
	4	86	88	84	84	86	77
	5	89	91	88	88	89	83

Foudland 14 - LG	1	71	77	77	77	71	70
	2	74	82	81	81	74	70
	3	79	85	83	83	79	73
	4	86	88	84	84	86	77
	5	89	91	88	88	89	83
Foudland 14 - OT	1	71	77	77	77	71	70
	2	74	82	81	81	74	70
	3	79	85	83	83	79	73
	4	86	88	84	84	86	77
	5	89	91	88	88	89	83
Foudland 14 - PG	1	71	77	77	77	71	70
	2	74	82	81	81	74	70
	3	79	85	83	83	79	73
	4	86	88	84	84	86	77
	5	89	91	88	88	89	83
Foudland 17 - AR	1	71	77	77	77	71	70
	2	74	82	81	81	74	70
	3	79	85	83	83	79	73
	4	86	88	84	84	86	77
	5	89	91	88	88	89	83
Foudland 17 - LG	1	71	77	77	77	71	70
	2	74	82	81	81	74	70
	3	79	85	83	83	79	73
	4	86	88	84	84	86	77
	5	89	91	88	88	89	83
Foudland 17 - OT	1	71	77	77	77	71	70
	2	74	82	81	81	74	70
	3	79	85	83	83	79	73
	4	86	88	84	84	86	77
	5	89	91	88	88	89	83
Foudland 17 - PG	1	71	77	77	77	71	70
	2	74	82	81	81	74	70
	3	79	85	83	83	79	73
	4	86	88	84	84	86	77
	5	89	91	88	88	89	83
Hatton 24 - AR	1	78	80	80	80	78	77
	2	80	86	85	85	80	77
	3	84	89	87	87	84	79
	4	89	91	88	88	89	83
	5	89	91	88	88	89	83
Hatton 24 - LG	1	78	80	80	80	78	77
	2	80	86	85	85	80	77
	3	84	89	87	87	84	79
	4	89	91	88	88	89	83

	5	89	91	88	88	89	83
Hatton 24 - OT	1	78	80	80	80	78	77
	2	80	86	85	85	80	77
	3	84	89	87	87	84	79
	4	89	91	88	88	89	83
	5	89	91	88	88	89	83
Hatton 24 - PG	1	78	80	80	80	78	77
	2	80	86	85	85	80	77
	3	84	89	87	87	84	79
	4	89	91	88	88	89	83
	5	89	91	88	88	89	83
Hatton 6 - AR	1	71	77	77	77	71	70
	2	74	82	81	81	74	70
	3	79	85	83	83	79	73
	4	86	88	84	84	86	77
	5	89	91	88	88	89	83
Hatton 6 - LG	1	71	77	77	77	71	70
	2	74	82	81	81	74	70
	3	79	85	83	83	79	73
	4	86	88	84	84	86	77
	5	89	91	88	88	89	83
Hatton 6 - OT	1	71	77	77	77	71	70
	2	74	82	81	81	74	70
	3	79	85	83	83	79	73
	4	86	88	84	84	86	77
	5	89	91	88	88	89	83
Hatton 6 - PG	1	71	77	77	77	71	70
	2	74	82	81	81	74	70
	3	79	85	83	83	79	73
	4	86	88	84	84	86	77
	5	89	91	88	88	89	83
Hatton 15 - AR	1	71	77	77	77	71	70
	2	74	82	81	81	74	70
	3	79	85	83	83	79	73
	4	86	88	84	84	86	77
	5	89	91	88	88	89	83
Hatton 15 - LG	1	71	77	77	77	71	70
	2	74	82	81	81	74	70
	3	79	85	83	83	79	73
	4	86	88	84	84	86	77
	5	89	91	88	88	89	83
Hatton 15 - OT	1	71	77	77	77	71	70
	2	74	82	81	81	74	70
	3	79	85	83	83	79	73

	4	86	88	84	84	86	77
	5	89	91	88	88	89	83
Hatton 15 - PG	1	71	77	77	77	71	70
	2	74	82	81	81	74	70
	3	79	85	83	83	79	73
	4	86	88	84	84	86	77
	5	89	91	88	88	89	83
Peterhead 24 - AR	1	78	80	80	80	78	77
	2	80	86	85	85	80	77
	3	84	89	87	87	84	79
	4	89	91	88	88	89	83
	5	89	91	88	88	89	83
Peterhead 24 - LG	1	78	80	80	80	78	77
	2	80	86	85	85	80	77
	3	84	89	87	87	84	79
	4	89	91	88	88	89	83
	5	89	91	88	88	89	83
Peterhead 24 - OT	1	78	80	80	80	78	77
	2	80	86	85	85	80	77
	3	84	89	87	87	84	79
	4	89	91	88	88	89	83
	5	89	91	88	88	89	83
Peterhead 24 - PG	1	78	80	80	80	78	77
	2	80	86	85	85	80	77
	3	84	89	87	87	84	79
	4	89	91	88	88	89	83
	5	89	91	88	88	89	83
Skelmuir 24 - AR	1	78	80	80	80	78	77
	2	80	86	85	85	80	77
	3	84	89	87	87	84	79
	4	89	91	88	88	89	83
	5	89	91	88	88	89	83
Skelmuir 24 - LG	1	78	80	80	80	78	77
	2	80	86	85	85	80	77
	3	84	89	87	87	84	79
	4	89	91	88	88	89	83
	5	89	91	88	88	89	83
Skelmuir 24 - OT	1	78	80	80	80	78	77
	2	80	86	85	85	80	77
	3	84	89	87	87	84	79
	4	89	91	88	88	89	83
	5	89	91	88	88	89	83
Skelmuir 24 - PG	1	78	80	80	80	78	77
	2	80	86	85	85	80	77

	3	84	89	87	87	84	79
	4	89	91	88	88	89	83
	5	89	91	88	88	89	83
Skelmuir 26 - AR	1	78	80	80	80	78	77
	2	80	86	85	85	80	77
	3	84	89	87	87	84	79
	4	89	91	88	88	89	83
	5	89	91	88	88	89	83
Skelmuir 26 - LG	1	78	80	80	80	78	77
	2	80	86	85	85	80	77
	3	84	89	87	87	84	79
	4	89	91	88	88	89	83
	5	89	91	88	88	89	83
Skelmuir 26 - OT	1	78	80	80	80	78	77
	2	80	86	85	85	80	77
	3	84	89	87	87	84	79
	4	89	91	88	88	89	83
	5	89	91	88	88	89	83
Skelmuir 26 - PG	1	78	80	80	80	78	77
	2	80	86	85	85	80	77
	3	84	89	87	87	84	79
	4	89	91	88	88	89	83
	5	89	91	88	88	89	83
Strichen 24 - AR	1	78	80	80	80	78	77
	2	80	86	85	85	80	77
	3	84	89	87	87	84	79
	4	89	91	88	88	89	83
	5	89	91	88	88	89	83
Strichen 24 - LG	1	78	80	80	80	78	77
	2	80	86	85	85	80	77
	3	84	89	87	87	84	79
	4	89	91	88	88	89	83
	5	89	91	88	88	89	83
Strichen 24 - OT	1	78	80	80	80	78	77
	2	80	86	85	85	80	77
	3	84	89	87	87	84	79
	4	89	91	88	88	89	83
	5	89	91	88	88	89	83
Strichen 24 - PG	1	78	80	80	80	78	77
	2	80	86	85	85	80	77
	3	84	89	87	87	84	79
	4	89	91	88	88	89	83
	5	89	91	88	88	89	83
Strichen 17 - AR	1	71	77	77	77	71	70

	2	74	82	81	81	74	70
	3	79	85	83	83	79	73
	4	86	88	84	84	86	77
	5	89	91	88	88	89	83
Strichen 17 - LG	1	71	77	77	77	71	70
	2	74	82	81	81	74	70
	3	79	85	83	83	79	73
	4	86	88	84	84	86	77
	5	89	91	88	88	89	83
Strichen 17 - OT	1	71	77	77	77	71	70
	2	74	82	81	81	74	70
	3	79	85	83	83	79	73
	4	86	88	84	84	86	77
	5	89	91	88	88	89	83
Strichen 17 - PG	1	71	77	77	77	71	70
	2	74	82	81	81	74	70
	3	79	85	83	83	79	73
	4	86	88	84	84	86	77
	5	89	91	88	88	89	83
Tarves 17 - AR	1	71	77	77	77	71	70
	2	74	82	81	81	74	70
	3	79	85	83	83	79	73
	4	86	88	84	84	86	77
	5	89	91	88	88	89	83
Tarves 17 - LG	1	71	77	77	77	71	70
	2	74	82	81	81	74	70
	3	79	85	83	83	79	73
	4	86	88	84	84	86	77
	5	89	91	88	88	89	83
Tarves 17 - OT	1	71	77	77	77	71	70
	2	74	82	81	81	74	70
	3	79	85	83	83	79	73
	4	86	88	84	84	86	77
	5	89	91	88	88	89	83
Tarves 17 - PG	1	71	77	77	77	71	70
	2	74	82	81	81	74	70
	3	79	85	83	83	79	73
	4	86	88	84	84	86	77
	5	89	91	88	88	89	83
Tarves 24 - AR	1	78	80	80	80	78	77
	2	80	86	85	85	80	77
	3	84	89	87	87	84	79
	4	89	91	88	88	89	83
	5	89	91	88	88	89	83

Tarves 24 - LG	1	78	80	80	80	78	77
	2	80	86	85	85	80	77
	3	84	89	87	87	84	79
	4	89	91	88	88	89	83
	5	89	91	88	88	89	83
Tarves 24 - OT	1	78	80	80	80	78	77
	2	80	86	85	85	80	77
	3	84	89	87	87	84	79
	4	89	91	88	88	89	83
	5	89	91	88	88	89	83
Tarves 24 - PG	1	78	80	80	80	78	77
	2	80	86	85	85	80	77
	3	84	89	87	87	84	79
	4	89	91	88	88	89	83
	5	89	91	88	88	89	83
Organic Soils 12 - AR	1	78	80	80	80	78	77
	2	80	86	85	85	80	77
	3	84	89	87	87	84	79
	4	89	91	88	88	89	83
	5	89	91	88	88	89	83
Organic Soils 12 - LG	1	78	80	80	80	78	77
	2	80	86	85	85	80	77
	3	84	89	87	87	84	79
	4	89	91	88	88	89	83
	5	89	91	88	88	89	83
Organic Soils 12 - OT	1	78	80	80	80	78	77
	2	80	86	85	85	80	77
	3	84	89	87	87	84	79
	4	89	91	88	88	89	83
	5	89	91	88	88	89	83
Organic Soils 12 - PG	1	78	80	80	80	78	77
	2	80	86	85	85	80	77
	3	84	89	87	87	84	79
	4	89	91	88	88	89	83
	5	89	91	88	88	89	83
Organic Soils 29 - AR	1	78	80	80	80	78	77
	2	80	86	85	85	80	77
	3	84	89	87	87	84	79
	4	89	91	88	88	89	83
	5	89	91	88	88	89	83
Organic Soils 29 - LG	1	78	80	80	80	78	77
	2	80	86	85	85	80	77
	3	84	89	87	87	84	79
	4	89	91	88	88	89	83

	5	89	91	88	88	89	83
Organic Soils 29 - OT	1	78	80	80	80	78	77
	2	80	86	85	85	80	77
	3	84	89	87	87	84	79
	4	89	91	88	88	89	83
	5	89	91	88	88	89	83
Organic Soils 29 - PG	1	78	80	80	80	78	77
	2	80	86	85	85	80	77
	3	84	89	87	87	84	79
	4	89	91	88	88	89	83
	5	89	91	88	88	89	83
North Mormond 24 - AR	1	78	80	80	80	78	77
	2	80	86	85	85	80	77
	3	84	89	87	87	84	79
	4	89	91	88	88	89	83
	5	89	91	88	88	89	83
North Mormond 24 - LE	1	78	80	80	80	78	77
	2	80	86	85	85	80	77
	3	84	89	87	87	84	79
	4	89	91	88	88	89	83
	5	89	91	88	88	89	83
North Mormond 24 - OT	1	78	80	80	80	78	77
	2	80	86	85	85	80	77
	3	84	89	87	87	84	79
	4	89	91	88	88	89	83
	5	89	91	88	88	89	83
North Mormond 24 - PG	1	78	80	80	80	78	77
	2	80	86	85	85	80	77
	3	84	89	87	87	84	79
	4	89	91	88	88	89	83
	5	89	91	88	88	89	83
Mixed Bottom Land 7 - AR	1	58	70	69	69	58	55
	2	61	75	73	73	61	55
	3	69	78	75	75	69	60
	4	79	81	76	76	79	66
	5	86	88	84	84	86	77
Mixed Bottom Land 7 - LE	1	58	70	69	69	58	55
	2	61	75	73	73	61	55
	3	69	78	75	75	69	60
	4	79	81	76	76	79	66
	5	86	88	84	84	86	77
Mixed Bottom Land 7 - OT	1	58	70	69	69	58	55
	2	61	75	73	73	61	55

	3	69	78	75	75	69	60
	4	79	81	76	76	79	66
	5	86	88	84	84	86	77
Mixed Bottom Land 7 - PG	1	58	70	69	69	58	55
	2	61	75	73	73	61	55
	3	69	78	75	75	69	60
	4	79	81	76	76	79	66
	5	86	88	84	84	86	77
Boyndie 5 - AR	1	30	61	58	58	30	30
	2	39	65	61	61	39	30
	3	49	67	63	63	49	36
	4	68	72	65	65	68	45
	5	79	81	76	76	79	66
Boyndie 5 - LE	1	30	61	58	58	30	30
	2	39	65	61	61	39	30
	3	49	67	63	63	49	36
	4	68	72	65	65	68	45
	5	79	81	76	76	79	66
Boyndie 5 - OT	1	30	61	58	58	30	30
	2	39	65	61	61	39	30
	3	49	67	63	63	49	36
	4	68	72	65	65	68	45
	5	79	81	76	76	79	66
Boyndie 5 - PG	1	30	61	58	58	30	30
	2	39	65	61	61	39	30
	3	49	67	63	63	49	36
	4	68	72	65	65	68	45
	5	79	81	76	76	79	66

Appendix C Pesticide storm sampling methodology

Chapter 5 of the thesis uses the data generated from a storm sampling regime in the River Ugie to test the assumption that the first rainfall event after application is the most important for pesticide mobilisation and delivery. The chapter only covered a simplified methodology for the sampling and analysis of samples collected during the storm events. This appendix therefore provides a detailed account of the methodology employed.

C.1 Storm sampling methodology

Samples were collected using an ISCO 6712 Portable Autosampler (Teledyne ISCO, 2010) from the sampling location detailed in Figure C-1. The sampler was configured with 24 1 litre Polypropylene bottles, with two bottles filled per sample as per analytical requirements. The sampler was triggered remotely via GPRS at the onset of a rainfall event rather than being linked to a rain gauge or river level monitor directly. The reason for this was to limit the sampler triggering during periods where no pesticides are likely to have been applied. Rainfall was therefore monitored using a Detectronic remote GPRS tipping bucket rain gauge (0.2mm bucket size, ± 1% accuracy at 26 mm hr^{-1} rainfall intensity (Detectronic, 2015)). The use of such a gauge allowed for real time rainfall data to be used in making decisions on when to trigger the sampler. Initially the sampler was configured to take a sample every 2 hours over a 24 hour period. It was soon realised however that this setup often missed the peak and descending limb of the hydrograph and hence the sampler was reconfigured to collect a sample every 4 hours over a 48 hour period.

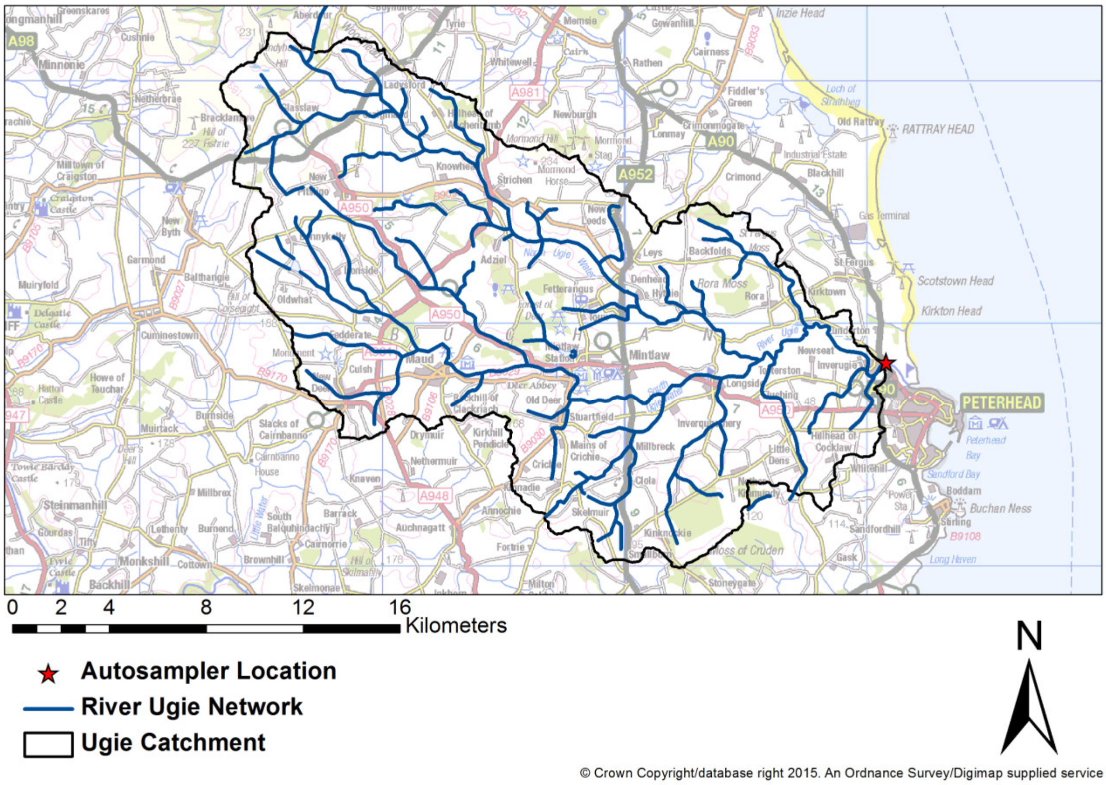

Figure C-1 - Location of the autosampler field site within the River Ugie catchment

Upon triggering samples were retrieved from the sampler within 48 hours and the samples divided into a number of different bottle configurations for analysis. Each sample was transferred into the following bottles for analysis:

- 2 x 500ml glass duran bottles treated with sodium thiosulphate
- 2 x 40ml amber glass vials treated with sodium thiosulphate
- 500ml clear plastic bottle

The plastic autosampler bottles were rinsed with deionised water and field blanks were prepared (with deionised water) following rinsing to make sure no pesticide residue was left in the rinsed autosampler bottles (methodology similar to Tediosi et al., 2012). All of the field blanks analysed were below the limits of detection for all pesticides.

C.2 Laboratory analysis

All samples were analysed in Scottish Water's UKAS accredited laboratory by professional laboratory staff. The total suite of pesticide analysed for are detailed in Table C-1 along with the concentration ranges capable with the analysis.

Table C-1 - Suite of pesticides analysed for and achievable concentration ranges (µg l^{-1})

Pesticide	Concentration range (µg l^{-1})
Monuron	0.003-0.200
Chlorotoluron	0.003-0.200
Monolinuron	0.005-0.200
Diuron	0.005-0.200
Isoproturon	0.003-0.200
Linuron	0.011-0.200
Chloroxuron	0.005-0.200
Carbofuran	0.003-0.200
Methiocarb	0.003-0.200
Cyproconazole	0.004-0.200
Epoxyconazole	0.004-0.200
Propiconazole	0.004-0.200
Tebuconazole	0.003-0.200
Simazine	0.003-0.200
Atrazine	0.004-0.200
Propazine	0.002-0.200
Trietazine	0.005-0.200
Quinmerac	0.006-0.200
Chloridazon	0.004-0.200
Metazachlor	0.002-0.200
Clopyralid	0.012-0.200

Dicamba	0.008-0.200
Bentazone	0.004-0.200
Bromoxynil	0.005-0.200
2,4-D	0.003-0.200
MCPA	0.004-0.200
Ioxynil	0.004-0.200
Dichloroprop	0.004-0.200
Mecoprop	0.003-0.200
Triclopyr	0.015-0.200
2,4-DB	0.004-0.200
MCPB	0.005-0.200
Metaldehyde	0.006-0.200

All substances were analysed using liquid chromatography-mass spectrometry using an Agilent 1200 high performance liquid chromatographer and an Agilent 6410 Triple Quad Mass Spectrometer. The exception is metaldehyde which is analysed using a Perkin Elmer Clarus gas chromatrograhy-mass spectrometry system. No tests were conducted for chemical sorption to the autosampler plastic bottles as all blank samples were below the limits of detection and therefore sorption to the plastic bottles was deemed negligible. The analysis assumed that limited transformation of the substances when the samples are in storage in the field takes place.

Tediosi A, Whelan MJ, Rushton KR, Thompson TRE, Gandolfi C, Pullan SP, 2012. Measurement and conceptual modelling of herbicide transport to field drains in a heavy clay soil with implications for catchment-scale water quality management. Sci Total Environ 438, 103–112

Appendix D Agronomist interview methodology and results

This appendix details the methodology, ethics information, questionnaire and answers used in Chapter 5 of the thesis to obtained detailed pesticide and nutrient management information about the River Ugie catchment.

D.1 Questionnaire Methodology

The development of the CaRPoW framework and associated models highlighted the need for specific information on crop types, pesticide use and fertiliser management in the River Ugie catchment.

The need for such information includes:

- Obtaining knowledge of specific crop rotations in the catchment.
- Having knowledge of specific pesticide preferences in the catchment for specific crops so that source potential values can be properly assigned to certain land uses.
- From the perspective of Scottish Water to get a better understanding of the uses of the 6 pesticides observed in high concentrations from monitoring data.
- Understanding fertiliser management in the catchment to determine if there are any specific preferences in the catchment or whether the catchment follows rules outlined in the literature (e.g. SAC crop guidance).

Previous work has demonstrated the value of obtaining such information from agronomy experts for the purposes of catchment management research (e.g. Dolan et al., 2014).

The methodology adopted to obtain such information has been adapted from previous work by Dolan et al. (2014). The Dolan et al. (2014) study was conducted in the Anglian region and the main driver was to ascertain the agronomic drivers of pesticide use. The present study, although similar, has a narrower focus and is largely concerned with obtaining information for use in a water quality model. In Dolan et al. (2014) data acquisition was conducted over three stages:

1. Determining the current behaviour and strategies to cope with pests in the regions crops
2. Assess how changes in future pesticide legislation would impact of chemical usage, cultural behaviour and land use in the region
3. Validate responses to stage two in a wider internet questionnaire.

Stages one and two were conducted using a semi-structured face to face interview technique and stage three with an online questionnaire. In this investigation it was deemed unnecessary to conduct two sets of face to face interviews and an internet based questionnaire when the geographic size of the Ugie catchment is much smaller (less agronomists working in the catchment) and the focus of the investigation narrower.

Therefore a semi-structured questionnaire driven face to face interview methodology was deemed appropriate to obtain the required information. The questionnaire is shown in section D.3.3 with questions split into 4 parts:

5. Cropping practices
6. Pest Issues
7. Pesticide usage
8. Nutrient management

The first section includes questions relating to cropping practices in the catchment and the second relates to specific pest issues for the crops outlined in part one and the methods of dealing with them. Part three specifically deals with the 6 pesticides highlighted as problematic in Scottish Water's monitoring data, questions relate to the uses of each and potential alternatives. The final section relates to fertiliser application for the crop identified in section one.

To gauge the number of agronomists operating in the River Ugie catchment the author attended a meeting arranged with agronomists as part of Scottish Water's Sustainable Land Management Incentive Scheme. A short presentation was given outlining the information requirements after which agronomists were asked to express an interest in taking part in the study.

The questionnaire driven interview was first of all tested in a pilot with one of the agronomists who expressed an interest in the initial meeting. Feedback was requested from the participant and amendments made to the questionnaire

All interviews were conducted face to face at the offices of the participants. Participants were asked to sign a consent form, a copy of which is included in section D.3.2. The interviews started with the author outlining the purpose of the study and the uses of the information acquired. The interview was recording for transcription at a later date. Although there was a structure to the interview the author used their judgement to ask follow up questions to certain answers and tangents to the questions were allowed if they were relevant to the purposes of the study.

Dolan, T., Parsons, D.J., Howsam, P., Whelan, M.J., Varga, L., 2014. Identifying Adaptation Options and Constraints: The Role of Agronomist Knowledge in Catchment Management Strategy. Water Resour. Manag. 28, 511–526.

D.2 Ethics sign off

The following details the consent form signed by all participants in the questionnaire.

- **PARTICIPANT CONSENT FORM**

Participant number: ____________

Date: ____________

I, ____ (please print your name in block capitals) confirm that I agreed to participate in the "***Determining Crop, Pest, Pesticide and Fertiliser Usage Information in the River Ugie Catchment for Use in a Catchment Management Model project***" which forms part of the STREAM EngD project "***The characterisation of catchment scale multiple pollutant processes to inform water industry catchment management***", which has been described to me as:

- This study aims to collate information using an interview driven questionnaire on the cropping, pesticide and nutrient management practices in the River Ugie Catchment.
- Data collected will be used to form the basis of inputs to a water quality model to determine risks to raw drinking water sources from land management activities.

I understand that all personal information that I provide will be treated with the strictest confidence and I have been provided with a participant number to ensure that all raw data remains anonymous.

I understand that although the information I provide will be used by Cranfield University and Scottish Water for research purposes, it will not be possible to identify any specific individual from the data reported as a result of this research.

I understand that the data collected will only be used for research purposes as part of the STREAM EngD project "***The characterisation of catchment scale multiple pollutant processes to inform water industry catchment management***". The results will be written up as a thesis/academic paper/sponsor report. I further understand that my raw data will be accessible only to the researcher and the supervising staff at Cranfield University. All data collected will be stored in accordance with the UK Data Protection Act (1998).

I understand that I am free to withdraw from this project at any stage during the session simply by informing a member of the research team, for whom contact details have been provided. I also understand that I can also withdraw my data for a period of up to 7 days from today, as after this time it will not be possible to identify my individual data from the aggregated results.

I confirm I have read and completely and fully understand the information provided on this form and therefore give my consent to taking part in this research.

Signature: ___________________________________ Date: _________________

Full name: ___________________________________ Contact number: _________________________

Address: ____________________________________ Email address: _________________________

If you have any questions about the research, or wish to withdraw your consent, please do not hesitate to ask to member of the research team via the contact details provided.

D.3 Questionnaire

The following details the questionnaire given to all participants

Determining Crop, Pest, Pesticide and Fertiliser Usage Information in the River Ugie Catchment for Use in a Catchment Management Model

Questionnaire to Agronomists

Before starting the questionnaire please complete a consent form

Part 1 – Cropping Practices

1. What area (in ha) of the Ugie Catchment do you provide cropping and pesticide advice for?

2. In terms of land area (in ha) what are the land uses and crop types that you cover?

3. In terms of profit what are the most dominant crops in the catchment that you cover?

4. What are the most common crop rotations that you are aware of in the catchment?

Part 2 – Pest Issues

1. Of the land uses and crops outlined in part 1 which ones do you provide management advice for (please expand on each):
    - Pests
    - Diseases
    - Weeds

2. Which of the following recommendations do you make for the above problems (please answer per land use crop type and expand on each if necessary):
    - Chemical
    - Cultural management
    - Integrated crop management

   If you make no recommendations, please answer why

3. Could you please rank the priority recommendations for each crop.

4. Are the management options crop specific, or do you have options that are suitable for a range of crops?

Part 3 – Pesticide Usage

Scottish Water have identified 6 difference substances in high concentrations in the River Ugie:

1. 2, 4-D
2. Chlorotoluron
3. CMPP
4. MCPA
5. Metaldehyde
6. Metazachlor

Please answer the following questions on each of the substances outlined above (please include the name of the pesticide in place of "pesticide x" in each question):

1. On which crop(s) is pesticide X used on?

2. For what reason is pesticide X used on these crops?

3. For each crop pesticide X is used on at what stage in the growth cycle of the crop (time of year) is the substance likely to be applied?

4. Do you recommend pesticide x for the reasons outlined in question 2? If yes please answer questions 5-9 and 12, if not please answer questions 10-12

Answer these questions if you answered yes to question 4

5. If you recommend pesticide x what are your reasons for doing so? For example:
    i. It is the only product available
    ii. It is the most cost effective product
    iii. It is part of a mix of substances used in a resistance management strategy
    iv. Other (please specify)

6. Do you recommend the use of pesticide x in conjunction with any other active substances in either a combined strategy or in a product that contains more than one active substance?

7. Are there any alternatives to pesticide x?

8. If so why do you not recommend these substances?
    i. Product is more expensive than pesticide x
    ii. Product is not as effective as pesticide x
    iii. Combination of the above
    iv. Other (please specify)

9. If pesticide x is recommended what advice do you provide for when it should not be applied e.g. when heavy rain is forecast or fields are saturated?

Answer these questions if you answered no to question 4

10. For what reasons do you not recommend the use of pesticide x?

11. What pesticide do you recommend using as an alternative to pesticide x?

Answer this question if you answered either yes or no to question 4

12. Do you have any further comments on pesticide x?

Part 4 – Nutrient Management in the Ugie

1. Do you provide advice on nutrient management for the crops outlined in part 1? (please identify which crops)

If yes please answer the remaining questions in part 4

2. For the land uses and crops identified in question 1 what fertiliser practices do you recommend? (e.g. inorganic fertiliser application, manure application etc.)

3. If inorganic fertilisers are recommended what are the most common types for each crop identified in question 1? (e.g. nitrate, phosphate, compound etc.)

4. How are decisions made on the application rate of fertilisers for each crop identified in question 1?

5. For each of the crops identified in question 1 at what period of the growth stage/approximate time of the year are the fertilisers outlined in question 2 applied?

6. When recommending fertiliser practices what advice do you provide for when fertilisers should not be applied e.g. when heavy rain is forecast or fields are saturated?

Thank you for answering the questionnaire.

D.4 Example questionnaire response

The following provides an example of the answers to the questionnaire provided a participant within the 'A Priori' questionnaire template.

<u>Participant A Responses in *'A Priori'* Template</u>

1. Cropping Practices

1. Catchment area
    - *60% of Ugie farmed area*
    - *Approximately 1000 spring hectares*

2. Area of land uses and crop types
    - *Approx 50% of that is combinable crop and the rest is grassland of some sort of another with a couple % of potatoes and swedes.*

3. Dominant crop types in terms of profit
    - *Majority of the catchment is mixed farms*
    - *Approx 6 dairy farmers*
    - *Of the beef farmers half might have suckler cows and most of them will be finishing beef cattle*
    - *Perhaps 30% would be purely arable*

4. Common crop rotations
    - *Split into two types of farms professional arable farmers who will largely follow an OSR – WW – SB – WB rotation*
    - *Wheat needs to follow a break crop (OSR). OSR follows winter barley because it has to be sewn in September.*
    - *People opt for 4 crop rotation because of problems with club root*
    - *The other type of farmer will be livestock who grow a bit of barley for feed (spring barley)*
    - *Occasionally there will be spring barley grown commercially for malt.*
    - *So all in all it is 4 crop rotation or spring barley*.

5. Crop sowing, emergence and harvest times
    - *Sowing – OSR before 7th Sept,, WB before 25th Sept, WW Sept/Oct and Spring Barley March/April*
    - *Harvest – WB first fortnight august, OSR last fortnight of August, SB September, Wheat mid-September, Oats second week September.*

2. Pest issues

1. Management advice for (including Chemical, Cultural Management and ICM)

1. Pests
    - *30,000 Geese in the Ugie eat wheat, winter barley and grass. Purely a scaring policy*
    - *Slugs – Heavier land helps slugs as fine seed beds prevent them moving, problem in OSR, Wheat and potatoes – Biggest controlling factor is moisture. Metaldehyde pellets put down.*
    - *Crane Fly – Damage in spring barley as they hatch in the spring – They lay their eggs in grass so problem is in grass fields that are ploughed for next crop in rotation. – Sprayed with Clopyrifos*
    - *Also issue with N.Ireland Crane Fly and Frit Fly that lay eggs in OSR and decimate WW. Sprayed with Clopryifos*
2. Diseases
    - *Worst diseases are the ones that like cold, damp conditions*
    - *OSR is sprayed for Leaf Spot – in spring this is light leaf spot followed by Sclerotinia.*
    - *In Wheat Septoria is the biggest issue which is rain splash spread – gets 3-4 sprays a year from March to July – extra spray in Scotland because harvested later – Azole Fungicides(prolenem metconizole, opus etc.)*
    - *For Barley Rinasporium is most common – controlled first thing in spring 2-3 sprays with Azole Fungicides (prolenem metconizole, opus etc.) – WB will have more sprays because it is there for more of the year.*
    - *Club root in OSR – Controlled by rotation*
3. Weeds
    - *Meadow grass is the main issue – used to be controlled by IPU and now CTU and PDM with some mixed with DFF. (Diflufenican)*
    - *Can be some issues with bromes but that's only with mintill – most farmers here plough.*
    - *Winer crops get a spray in autumn and then again in spring – Some will get CMPP if chick weed is a problem in OSR in March.*
    - *SB gets a sulphinide urea at a lot dosage together with CMPP – application varies per product some go on in Autumn some in spring. Used on 80-90% of barleys but low application rate.*
    - *50% of crops will be sprayed with glyphosate pre harvest to bring up and do away with any 'greens'.*
    - *Ploughing reduces the risk of grass weed growth*.

2. Priority Rank Recommendations
3. Crop specific or blanket management options?

3. Specific Pesticides

1. 2, 4-D
    1. Crop type
        - *Grassland and cereals*
    2. Reasons for use

- *Control rushes and ragwort*

3. Stage applied
    - *Can be at any time for rushes in grasslands but largely during the summer – Ragwort in april/may and August/September.*
    - *In Cereals may/june*
4. Do you recommend usage
    - *Yes*

    Answer if yes to 4
5. Reasons for recommendation
    - *Cheap*
6. In combination with other substances
    - *MCPA*
7. Alternatives
    - *MCPA*
8. Recommend alternatives
    - *Yes*
9. Advice for use in respect to water contamination
    - *Very soluble so with rushes you have to be careful as they grow in wetlands. But Rushes are also a sign of low pH.*

    Answer if no to 4
10. Reasons for not recommending
11. Which alternative

12. Further comments

2. Chlorotoluron
    1. Crop type
        - *Used extensively on cereals but is now finished*
    2. Reasons for use
        - *Control of meadow grass and other weeds*
    3. Stage applied
        - *Applied pre-emergence or early emergence.*
    4. Do you recommend usage
        - *Used to but now banned*

        Answer if yes to 4
    5. Reasons for recommendation
        - *Cheapest and most effective option*
    6. In combination with other substances
        - *Used with PDM and DFF*
    7. Alternatives
        - *PDM and DFF*
    8. Recommend alternatives
    9. Advice for use in respect to water contamination

        Answer if no to 4

10. Reasons for not recommending
11. Which alternative

12. Further comments

3. CMPP
    1. Crop type
        - *Base phenoxy herbicide for all spring crops.*
    2. Reasons for use
        - *Control of chick weed and other weeds.*
    3. Stage applied
        - *11-31 weeks so for spring crops mid-May to early June.*
    4. Do you recommend usage
        - *Yes*

      Answer if yes to 4
    5. Reasons for recommendation
        - *Cheap and covers a broad weed spectrum – does have weaknesses though that are covered by HBN or Starain.*
    6. In combination with other substances
        - *HBN and Starain where there are problems with fat hen weed.*
    7. Alternatives
        - *Sulphinile Urea*
    8. Recommend alternatives
    9. Advice for use in respect to water contamination
        - *Highly soluble so yes. Don't apply when there is likely to be a heavy dew*

      Answer if no to 4
    10. Reasons for not recommending
    11. Which alternative

    12. Further comments
4. MCPA
    1. Crop type
        - *Largely grasses but also cereals.*
    2. Reasons for use
        - *Control of weeds in Grasses and sometimes cereals*
    3. Stage applied
        - *Can be at any time for rushes in grasslands but largely during the summer – Ragwort in april/may and August/September.*
        - *For other grass weeds such as buttercups and nettles in June/July*
        - *In Cereals may/june*
    4. Do you recommend usage
        - *Yes*

      Answer if yes to 4
    5. Reasons for recommendation

- *Cheap*

6. In combination with other substances
    - *2, 4-D*
7. Alternatives
    - *2, 4-D*
8. Recommend alternatives
9. Advice for use in respect to water contamination
    - *Same as 2, 4-D, CMPP*

Answer if no to 4

10. Reasons for not recommending
11. Which alternative

12. Further comments

5. Metaldehyde
    1. Crop type
        - *OSR, Wheat and potatoes on heavy soils*
    2. Reasons for use
        - *Control of slugs*
    3. Stage applied
        - *Largely in the autumn depends on slug numbers although some people will apply them in a precautionary sense.*
    4. Do you recommend usage
        - *Yes*

    Answer if yes to 4

    5. Reasons for recommendation
        - *Most effective and cheapest available*
    6. In combination with other substances
        - *Not usually*
    7. Alternatives
        - *Ferric Phosphate*
    8. Recommend alternatives
        - *Only if part of stewardship scheme otherwise too expensive.*
    9. Advice for use in respect to water contamination
        - *Follow advice provided by VI and MSG but often advice doesn't get through to people applying from quad bikes etc. There is often not the appreciation of the impact of the pellets on water.*

    Answer if no to 4

    10. Reasons for not recommending
    11. Which alternative

    12. Further comments
6. Metazachlor
    1. Crop type

- *Winter OSR – 95% of OSR sprayed*

2. Reasons for use
   - *Effective for broad spectrum of weeds in OSR*
3. Stage applied
   - *Within 36 hours of being sewn so mid august to first week in sept.*
4. Do you recommend usage
   - *Yes*

   Answer if yes to 4
5. Reasons for recommendation
   - *Best available for weed spectrum*
6. In combination with other substances
7. Alternatives
   - *Butisan and propyzamide*
8. Recommend alternatives
   - *Propyzamide is used a lot down south to control black grass but this is not a problem in Scotland.*
9. Advice for use in respect to water contamination

   Answer if no to 4
10. Reasons for not recommending
11. Which alternative

12. Further comments

4. Nutrient Management

1. Nutrient advice for crops/land use in part 1
   - *Yes all of them*

   If yes answer remaining parts
2. Recommended fertiliser practices
   - *It really depends on the farm.*
   - *If they have livestock they will use their slurry*
   - *There is often trades and selling between farmers who have slurry and chicken muck.*
   - *Anything that slurry cannot provide is topped up with out of the bag fertiliser – this will be on a field by field basis though depending on the previous rotation, NVZ limits and timing limits. Winter cereals have big problems with being under the NZV limit because limits set too low.*
3. Common inorganic fertilisers
   - *More people having farms GPS mapped and basing phosphate and potash application on this.*
   - *Some people still variable spread phosphate but it's very expensive.*
   - *Most Scottish soils are acidic and naturally low in phosphate and lime so these are often toped up.*
   - *Nitrate levels are as per crop requirement and are rotationally driven.*

4. Application rate of fertilisers
    - *Variable*
5. Period of growth stage
    - *OSR, WB and WW top dress with N and sulphur, then a second and possibly third dose depending on previous rotation.*
    - *For SB the majority goes in the seed bed when its sown and then top dressed with 80-100 kg per hectare in total.*
    - *These are also limited by NVZ limits – can't put N after 1st sept for inorganic and 1st oct for organic fertiliser.*
6. Advice on when not applied
    - *Obviously dictated by NVZ and control on application to snow etc.*

Appendix E Example CaRPoW model outputs for each pollutant

This appendix provides examples of CaRPoW model outputs for each pollutant modelled.

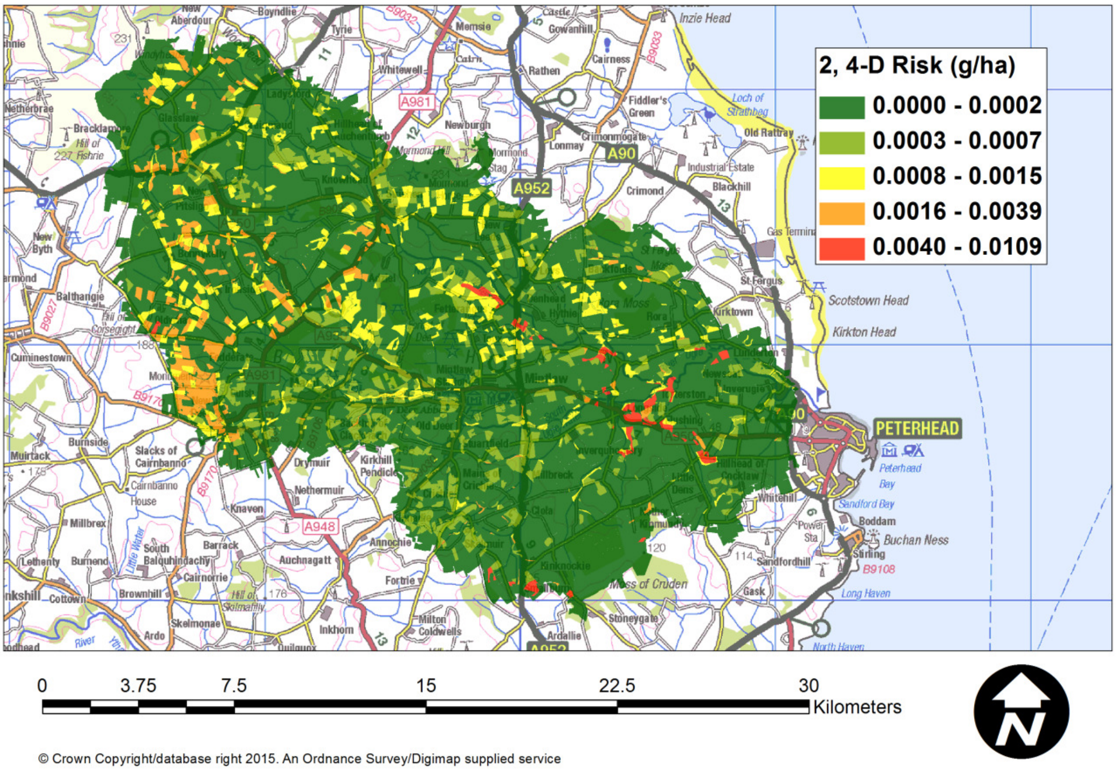

Figure E-1 - CaRPoW modelled 2, 4-D risk (dominant land use pattern 2008-2012)

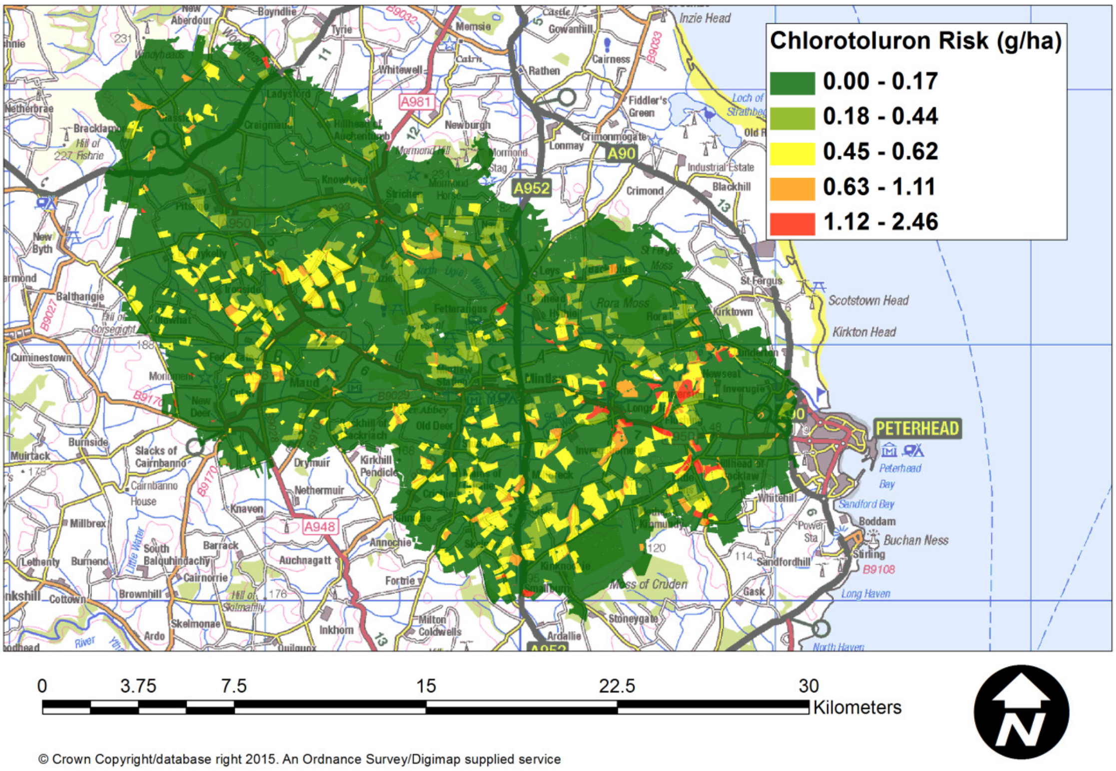

Figure E-2 - CaRPoW modelled chlorotoluron risk (dominant land use pattern 2008-2012)

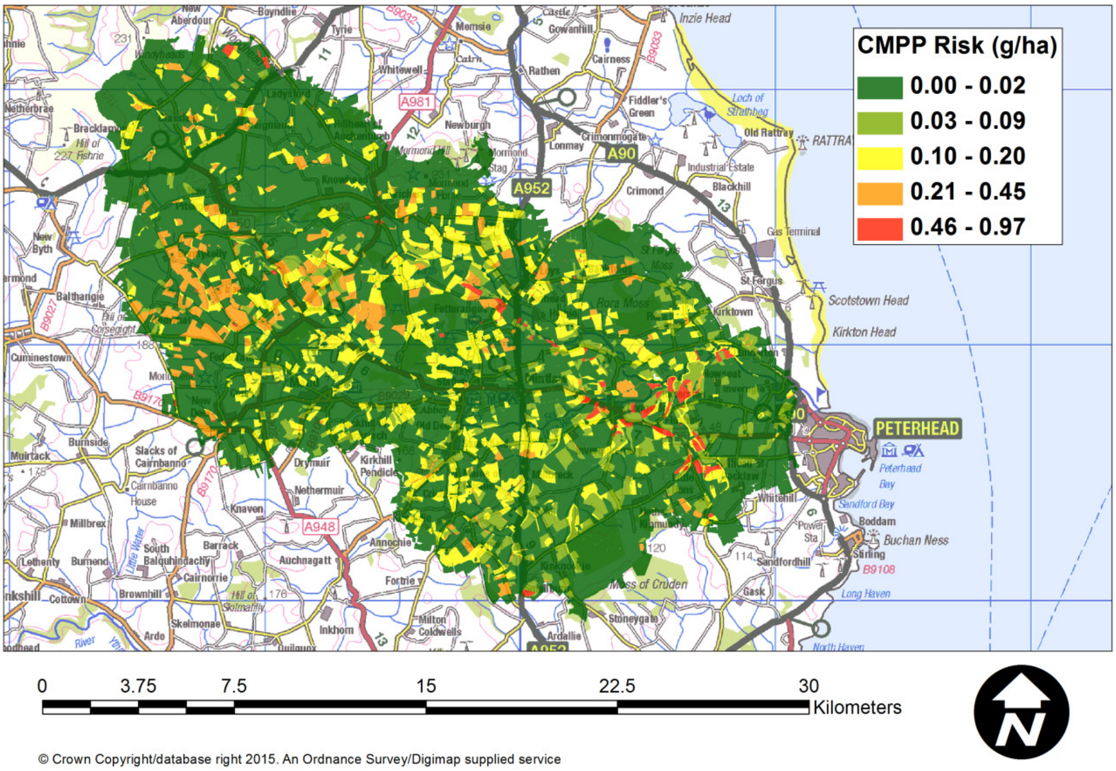

Figure E-3 - CaRPoW modelled CMPP risk (dominant land use pattern 2008-2012)

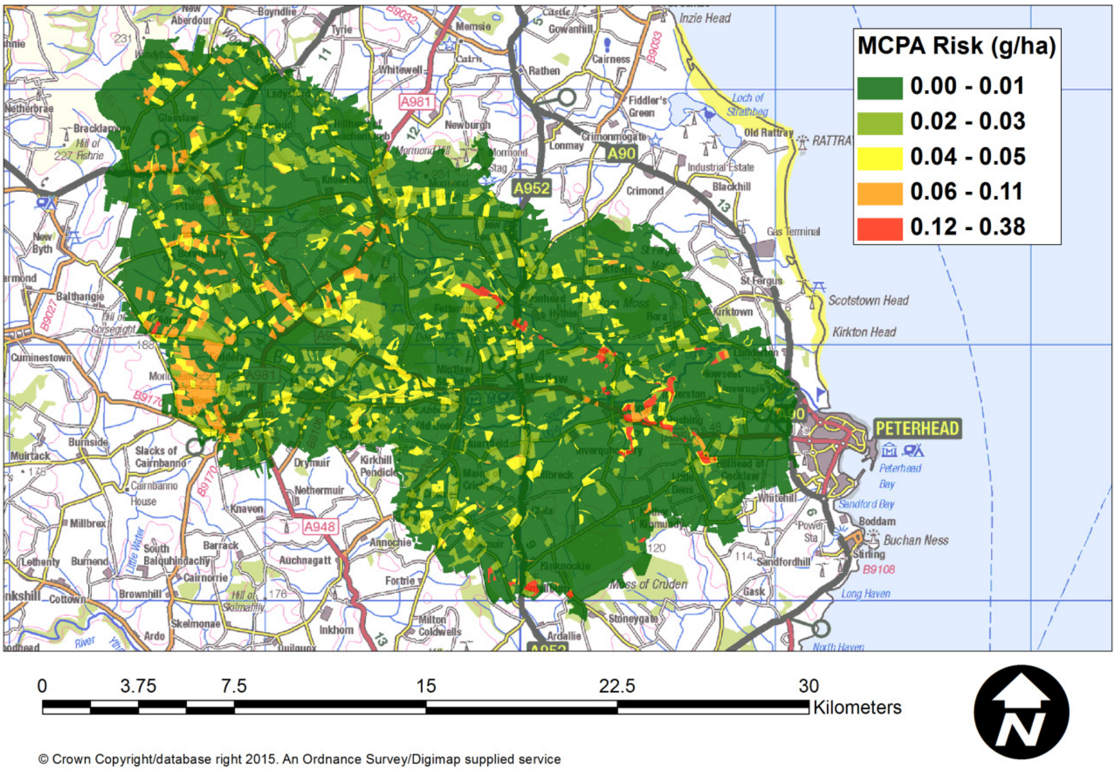

Figure E-4 - CaRPoW modelled MCPA risk (dominant land use pattern 2008-2012)

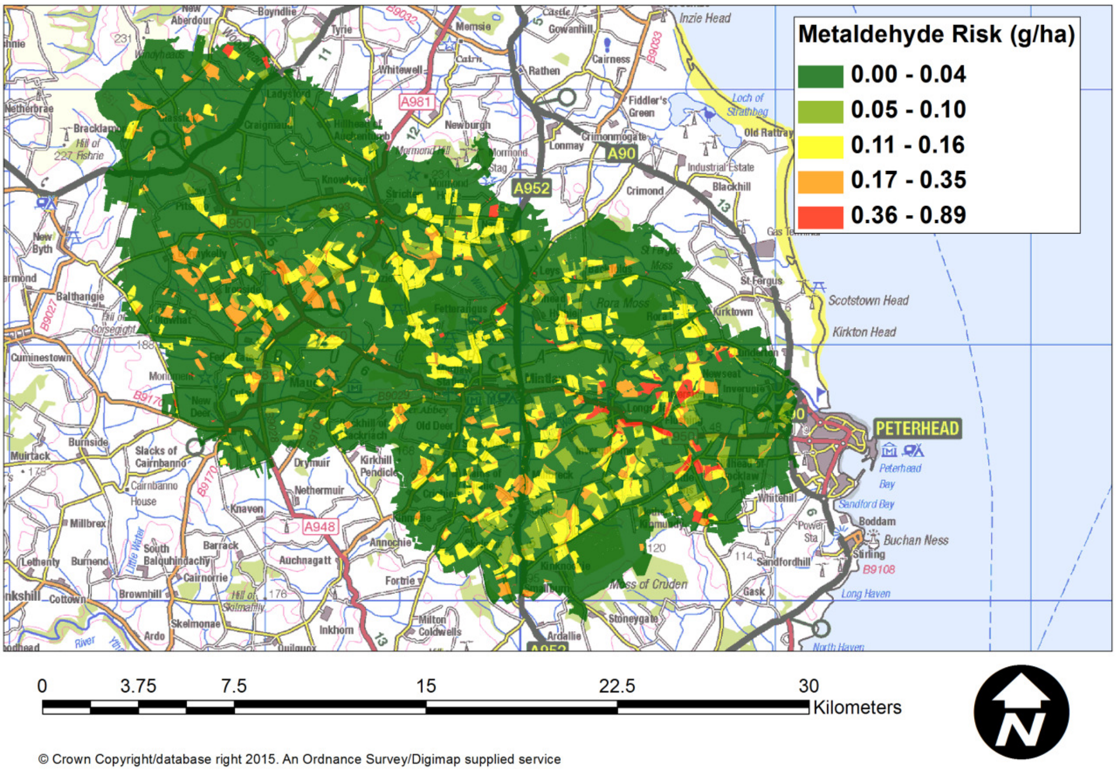

Figure E-5 - CaRPoW modelled metaldehyde risk (dominant land use pattern 2008-2012)

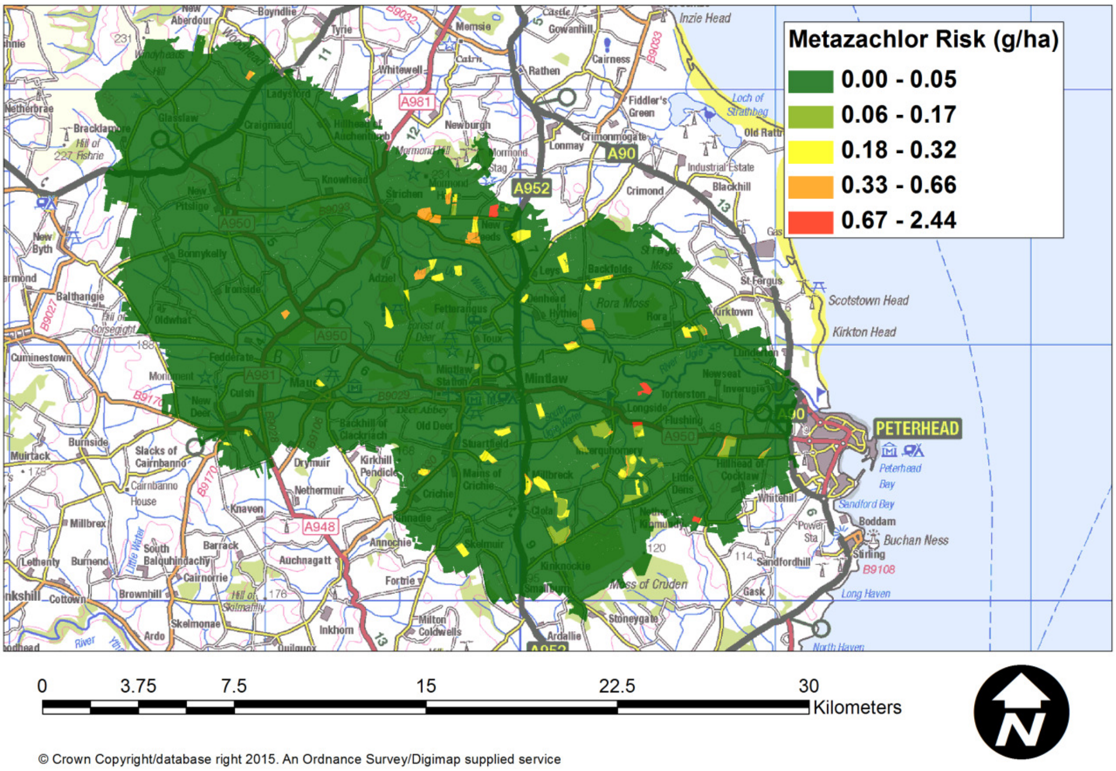

Figure E-6 - CaRPoW modelled metazachlor risk (dominant land use pattern 2008-2012)

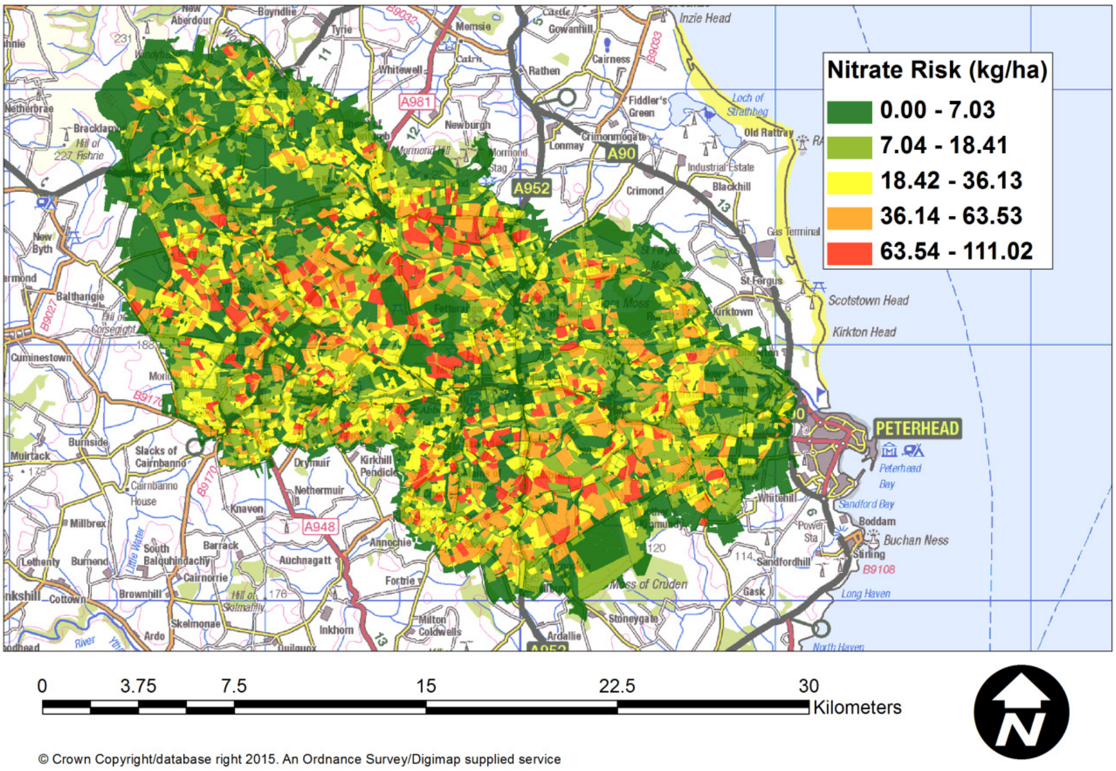

Figure E-7 - CaRPoW modelled nitrate risk (dominant land use pattern 2008-2012)

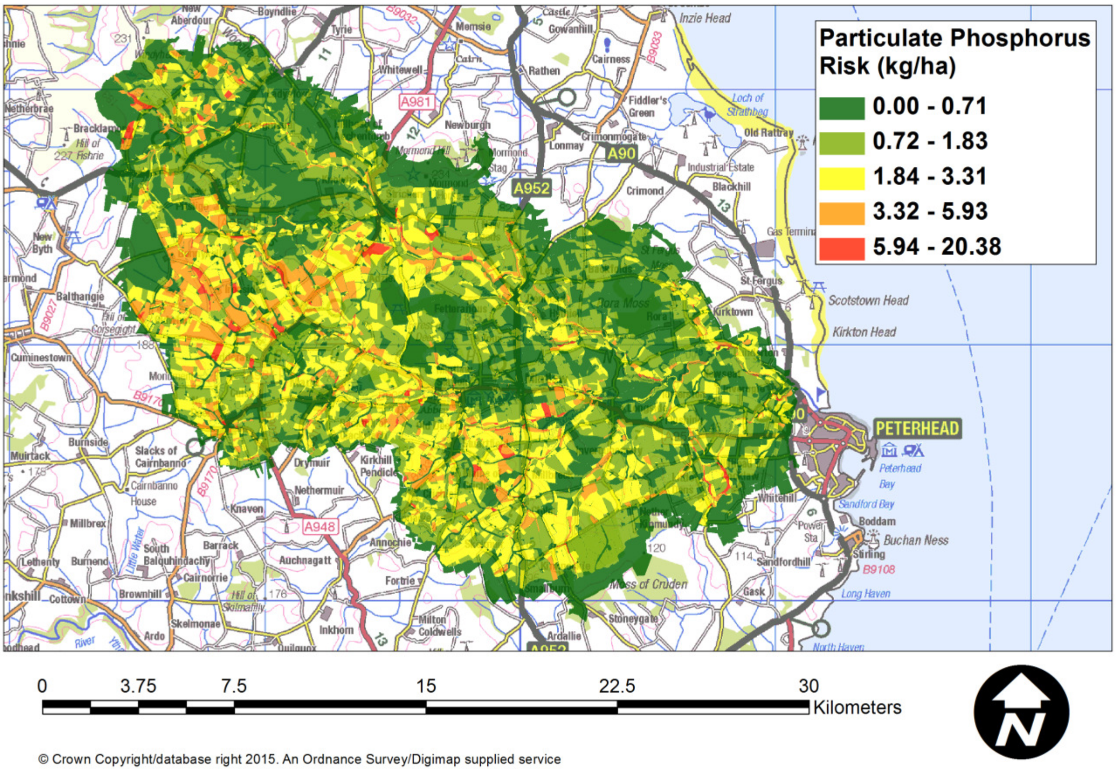

Figure E-8 - CaRPoW modelled particulate phosphorus risk (dominant land use pattern 2008-2012)

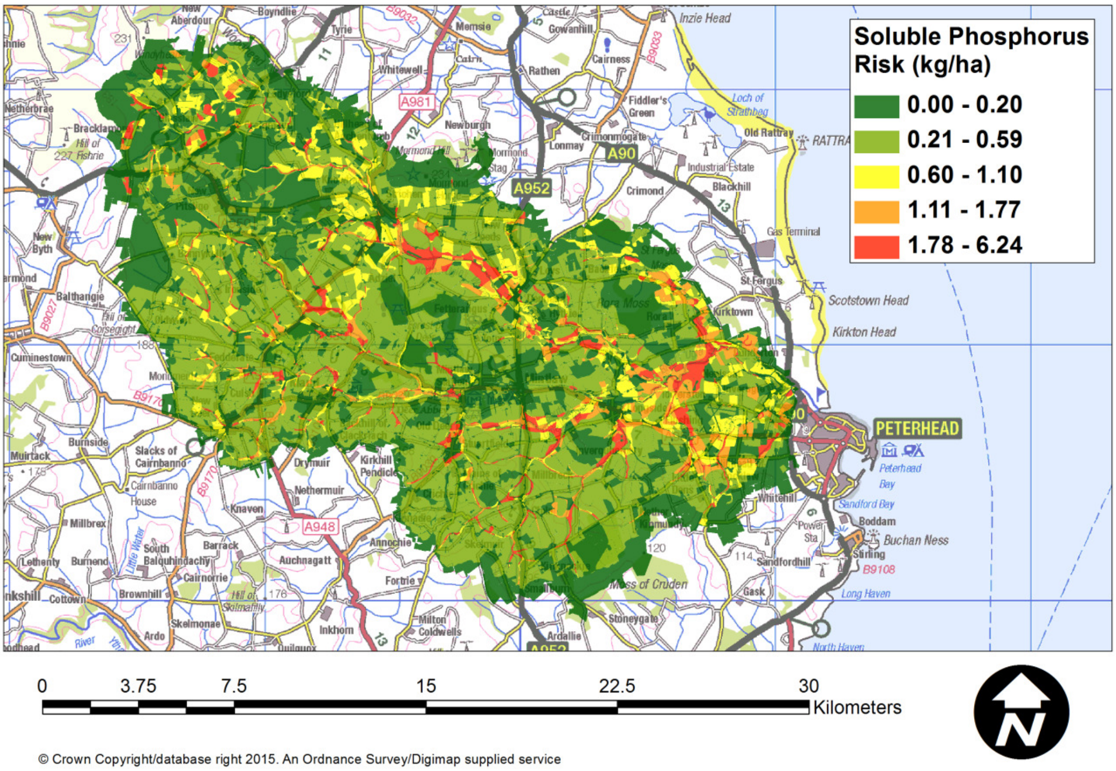

Figure E-9 - CaRPoW modelled soluble phosphorus risk (dominant land use pattern 2008-2012)

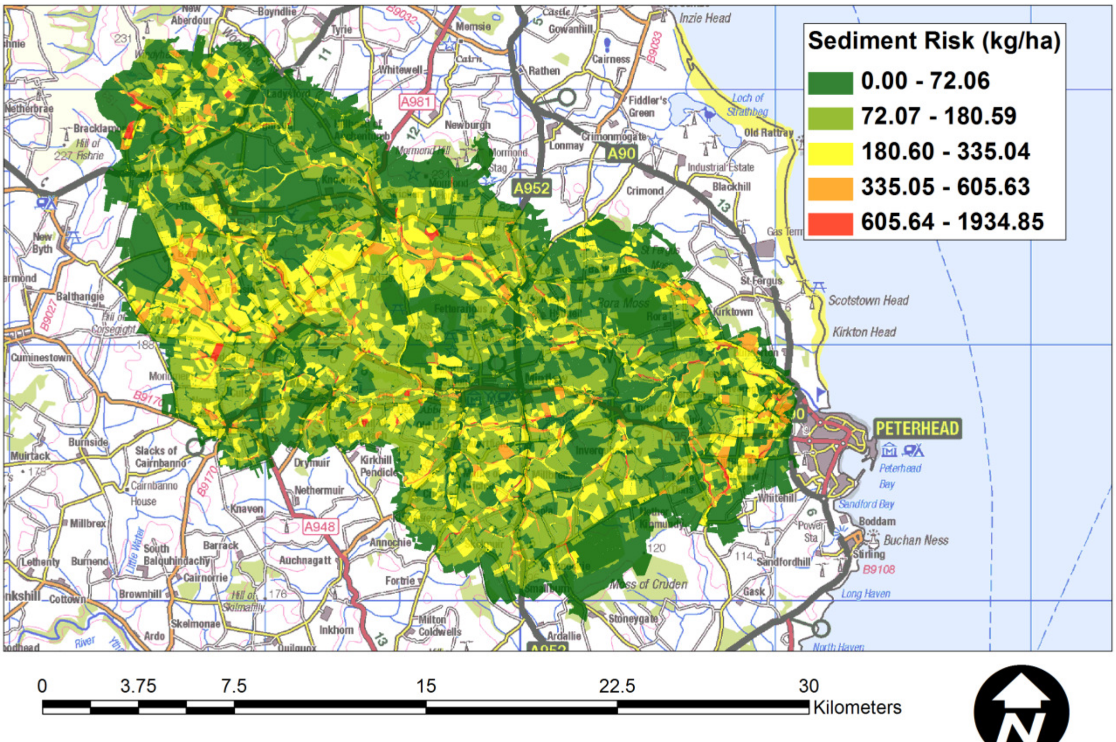

Figure E-10 – CaRPoW modelled sediment risk (dominant land use pattern 2008-2012)