Groundwater-surface water connectivity of heavily modified rivers, County Durham, UK

REBECCA SMITH

Groundwater-surface water connectivity of heavily modified rivers, County Durham, UK

Rebecca Smith

PhD Thesis

A thesis submitted in partial fulfilment of the requirements for the Degree of Doctor of Philosophy in the Department of Geography, Durham University

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Photos of the Twizell Burn and Herrington Burn taken throughout my PhD fieldwork (2015-2017).

Declaration

I confirm that no part of the material presented in this thesis has previously been submitted for a degree in this or any other university.

In all cases the words of others, where relevant, have been fully acknowledged.

Rebecca Smith

Durham University - 2019

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Groundwater and surface-water systems have long been considered fragmentally, lacking a holistic integrated understanding that is considered essential for sustainable catchment management. The high heterogeneity of local systems and the influence on water quality is typically unaccounted due to limited monitoring of hydrologic and hydraulic variables, particularly of minor aquifers. Often there is a dearth in understandings of the system characteristics, consequently impacting on wider catchment management. This thesis focuses specifically on water bodies in County Durham that are heavy modified attributing to their industrial past, with the current water quality being compromised by a multitude of historic and contemporary pressures. The research employs a combination of desk- and field-based approaches to investigate flow and solute patterns and processes operating at the groundwater-surface water interface.

The research demonstrates that through the collation of spatial data it is possible to assess the stream-aquifer connectivity by evaluating simple patterns in the landscape characteristics. In-turn challenging the local-scale connections and leading to subsequent investigations of the groundwater-surface water controls on water quality. Field-based investigations of the local systems highlight the integral role of near-stream sediments on the fate of flow and solutes from the surface and subsurface. Through the application of numerical modelling, flow pathways have been further interpreted, assessing the spatial and temporal interactions at the stream-aquifer interface in response to changing hydrological conditions. Findings indicate the likely role of the shallow groundwater having a detrimental effect on the cycling of flow, with dynamic responses reflecting variations in stream levels, thus highlighting the need to consider processes at the stream-aquifer interface that are typically overlooked. The findings of this research challenge the predominant targeted reductionist approaches to water management in systems of this sort, where the influence of the multitude of pressures pathways and their relation to the contemporary water quality has been overlooked. There is a need for practitioners to consider the freshwater systems over multiple dimensions and time to achieve sustainable water management.

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Statement of Copyright

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Acknowledgements

Aye, the PhD journey has been canny tough at times like, but wey I've made it!

The journey to this point would never have happened without the excellent supervision from Professors John Wainwright and Louise Bracken. Thank you for your patience, support, advice and guidance throughout my PhD. You have both always been there for me, whether it has been for a chat, to get me back on track, or to cheer me on. It has been an amazing privilege to work with you both.

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“Sometimes it seems the going is just too rough
And things go wrong no matter what I do
Now and then it seems that life is just too much
But you've got the love I need
To see me through”

You’ve Got the Love – Florence + the Machine (Lungs, 2009)

It is the love and support of my family, friends and colleagues that has got me through the PhD.

The encouraging words you have said, to never give up, and to believe in myself.

We are all different, but that is what makes us special and keeps the world interesting.

Be proud. Be you.

I wish to dedicate this thesis to my family and all those who have helped me along my way.

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"Heroes are made by the path they choose, not the powers they are graced with."

Iron Man

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Chapter 1 - Introduction

1.1. Background and motivation

There is a need to address water-quality issues, both in the present and in the foreseeable future (Wallace and Gregory 2002), considering the ever-increasing human and ecological demands for freshwater resources (Muller 2017). To meet such demands, it is imperative that water is of good quality. However, the quality of water, both at the surface and subsurface is increasingly threatened by pollution from historic industry (Younger *et al.* 2002, Potter *et al.* 2004, Gandy *et al.* 2007) as well as contemporary sources (Wheater and Evans 2009, Hering *et al.* 2015). The accumulation of pollutants and contaminants across surface-water (SW) and groundwater (GW) systems consequently results in a multitude of threats to freshwater resources attributing to the interactions and exchanges in flow and solutes across the streambed (Sophocleous 2002, Yu *et al.* 2006, Baldock *et al.* 2009, Kløve *et al.* 2011, Deb 2014, Harvey and Gooseff 2015, Johnson and Hallberg 2015).

Traditionally the monitoring and management of water quality has been broadly segregated between hydrologists and hydrogeologists, individually focusing on the SW and GW systems respectively (Macleod *et al.* 2007, Staes *et al.* 2008, Muller 2017). The understanding and management of pollution and contamination has typically been prioritised at the source or point of impact as part of a reductionist or '*command and control*' approach (Macleod *et al.* 2007, Staes *et al.* 2008, Heathwaite 2010, Li *et al.* 2016) overlooking the pathways and interactions from the source to receptor. Instead, addressing issues with a '*black-box*' or '*pipe-system*' focus (Figure 1-1) in either the surface or subsurface regardless of the exchanges within and between the systems (Bencala 1993, Bencala *et al.* 2011, Harvey and Gooseff 2015, Magliozzi *et al.* 2017). Consequently, the segregated understanding of water resources has, and most often remains to be resulting in conflicting management and solutions with priorities and procedures to address issues being dispersed amongst organisations and stakeholders (McDonnell 2008). The fragmented arrangement and subsequent mismanagement are despite the likely coupling and connectivity between the systems, whereby the deterioration or improvement of the SW having the potential to impact on the GW body, and vice-versa (Baldock *et* *al.*2009, Kløve *et al.* 2011, Figure 1-1). The stream needs to be considered as an integral part of the catchment system, as a conduit of inputs from the landscape with transport via flow paths downstream and across the streambed (Bencala 1993, Bencala *et al.* 2011, Figure 1-1).

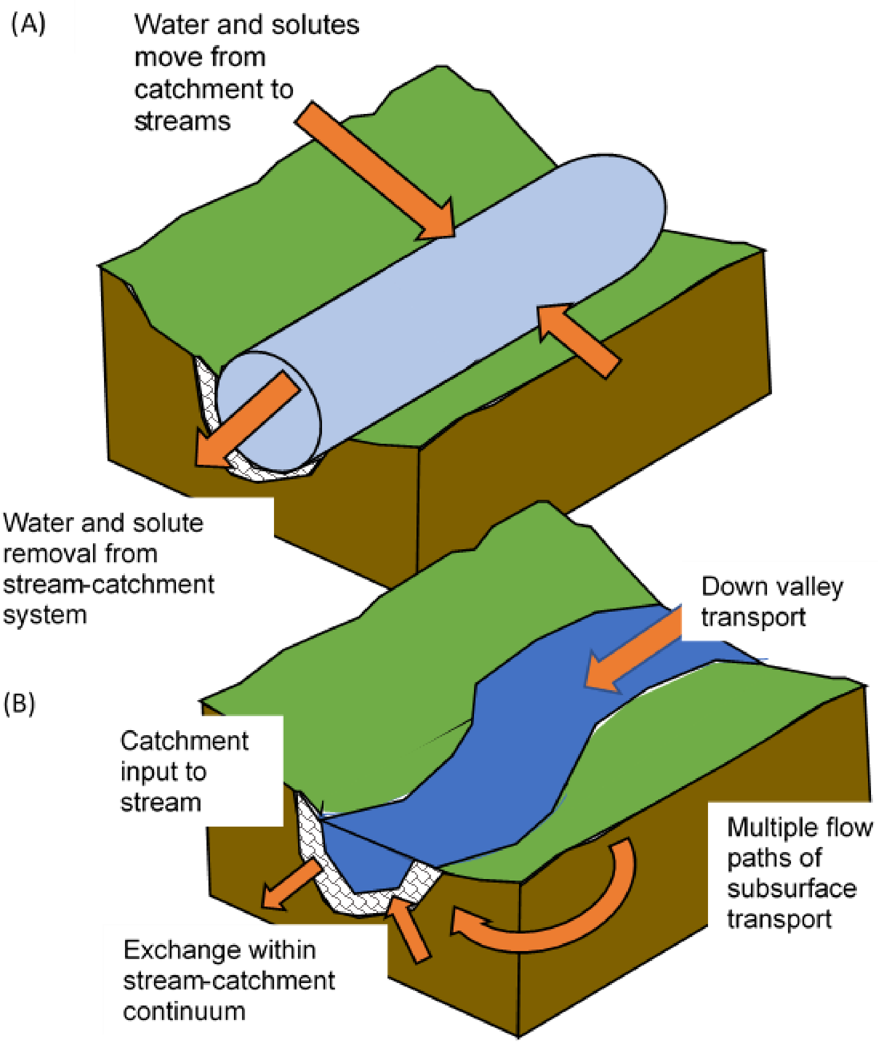

Figure 1-1: (A) The stream's function in a catchment considered as a pipe; (B) A contrasting view where the stream is an integral part of the catchment system (Source: adapted from Bencala 1993).

GW/SW interactions are widely acknowledged in research (Cardenas 2015). A continually growing body of literature are looking at the GW/SW exchanges and the myriad of processes spanning hydrological to ecological disciplines with the mixing of GW and SW within the streambed interface referred to as the hyporheic zone (Winter *et al.* 1998, Sophocleous 2002, Buss *et al.* 2009, Cardenas 2015, Figure 1-2). The hyporheic zone is characterised by the mixing of GW and SW, as well as biogeochemical activity attributing to fluxes in oxygen (O_2), nutrients or organic carbon (Brunke and Gonser 1997, Bencala 2000, Hannah *et al.* 2009, Wondzell 2011). The high reactivity of the near-stream sediments (Smith and Lerner 2008) with the mixing of GW and SW and biogeochemical activity creates potential environmental hotspots (McClain *et al.* 2003, Lautz and Fanelli 2008). Within these hotspots, the cycling and fate of dissolved nutrients and contaminants of GW or SW origin are potentially enhanced by hydrochemical or biogeochemical processes (Ibrahim 2012). The GW/SW interactions result in a mosaic of pathways operating across the surface-subsurface interface and are dependent on a range of spatial and temporal controls, namely the geomorphic and hydrogeologic features of a catchment, as well as hydrometeorology and geomorphology dynamics operating over short- to long-term scales (Tetzlaff et al 2007).

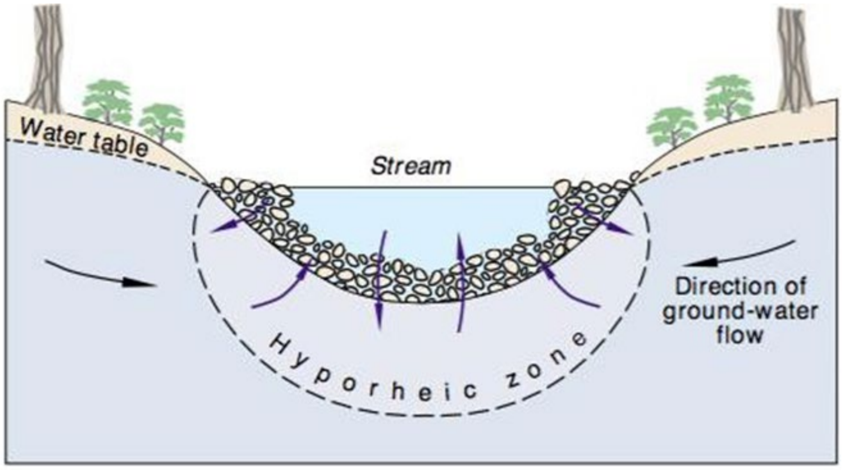

Figure 1-2: Hydrological interfaces: the stream, GW and hyporheic zone (Source: adapted from Winter et al. 1998).

Within academia there is a strong understanding of the GW/SW processes, and it is generally well documented that systems interact, with several comprehensive reviews on the stream-aquifer interactions (Cardenas 2015, Tanner and Hughes 2015). However, there is often a lack of direct data to quantify the individual processes or structural geological information to establish GW/SW connections of local systems (Tanner and Hughes 2015). There is growing emphasis to develop an understanding of such processes operating at the local scale and integrate these understandings into the larger scale patterns of GW/SW interactions and hyporheic pathways within the catchment boundaries (Harvey and Wagner 2000, Woessner 2000, Poole *et al.* 2008, Magliozzi *et al.* 2017). For effective water management there is a need to develop an understanding of the local-scale processes and link these understandings to the wider catchment, rather than assessing and managing the catchments broadly as closed systems with targeted efforts on specific pressures. The integrative understanding across the catchment is particularly relevant to the framing of recent legislative policy, including the European Union Water Framework Directive (2000/60/EC, CEC 2000, Wheater and Peach 2004, Skeffington *et al.* 2015). The intended holistic and integrated management of water resources at the catchment scale according to the WFD requires an improved assessment of the GW/SW interactions operating within catchments (Smith 2005).

1.1.1. Integrating GW/SW interactions into water management

The WFD focuses on assessing the status of GW and SW bodies at the river-basin (catchment) scale, while developing local networks of GW and SW monitoring sites (Teodosiu *et al.* 2003, Smith 2005). Promoting sustainable water management, the aim of WFD is for SW bodies to achieve ‘good’ ecological and chemical status, and GW bodies achieve ‘good’ quantitative and chemical status in accordance with the meeting of the defined objectives originally by 2015, and now 2027 (CEC 2000, DETR 2001, Schmedtje and Kremer 2011, Skeffington *et al.* 2015). Embedded within the principles of Integrated Catchment Management (ICM), the WFD is focussed on efforts to improve water quality at the catchment scale (Ferrier and Jenkins 2010, Rollason *et al.* 2018), with the intention of better managing the GW and SW systems, individually, and as one whole system (Alexander *et al.* 2007, Fenemor *et al.* 2011). The holistic and integrated management is prioritised given that the discharge of contaminated GW to an overlying stream may result in a significant decrease in the SW quality and therefore needs to be considered when defining the status of the attached GW body.

Acknowledging the management of water resources at the catchment scale with the promotion of the protection and enhancement of aquatic ecosystems as connected systems is a positive step towards sustainable water management. However, the intended goals are challenging to meet, with the need for an improved understanding of the connected aquatic and terrestrial systems (Biswas

2005, Smith *et al.* 2008, Conant *et al.* 2019). Current practices reflect a lack of integration, arguably attributable to the dearth of understandings, particularly of local systems, as well as lacking collaboration in the disciplines of water management (Falkenmark *et al.* 2007, Conant *et al.* 2019).

In this chapter, background to the research is presented, discussing the general relationships between streams and aquifers. Subsequently, a summary of the processes affecting the flow and solute fate at the GW/SW interface is presented, followed by a review of existing approaches to monitor GW/SW interactions. Finally, the aim and objectives of the research are developed through the identification of management issues within the study area of the River Wear catchment, County Durham, UK.

1.2. Current understanding of GW and SW interactions

1.2.1. General relationships between streams and aquifers

GW and SW systems have long been considered as separate entities in hydrological specialisations (Barthel 2014), given their different physical, chemical and biological properties (Kalbus *et al.* 2006). However, for an integrated and holistic focus it is crucial to understand the interactions between GW and SW systems with respect to activities which threaten the quality of water (Bertrand *et al.* 2014). Two main directions of flow exchange occur between the GW and SW systems, attributing to the loss of stream water to the subsurface (influent [losing] conditions), and the upwelling of GW to the surface (effluent [gaining] conditions) (Winter *et al.* 1998, Sophocleous 2002, Figure 1-3). Along a river reach there are spatial variations in these exchanges, whereby stretches of stream waters may either be gaining or losing water to GW flow, or otherwise a combination of both (Krause *et al.* 2014). Several factors determine the exchanges, including; the hydraulic conductivity of streambed deposits, streambed topography, GW gradient and stream curvature (e.g. Keery *et al.* 2007, Tetzlaff *et al.* 2007). Baseflow from GW sources can support stream when the stream levels are lower than the water table (Woessner 2017).

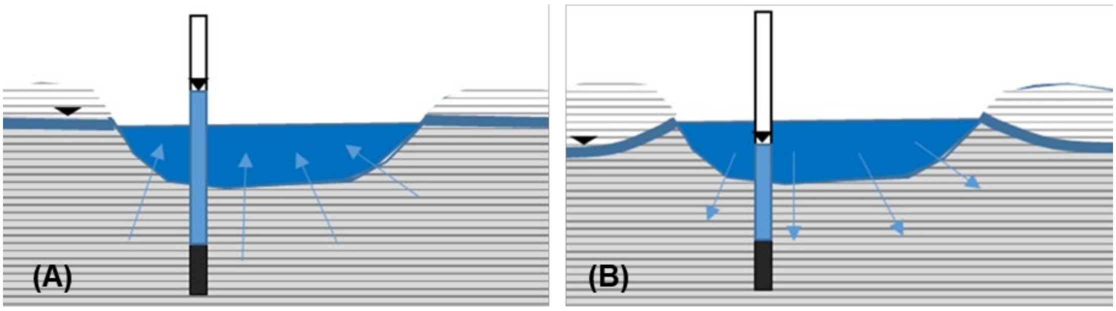

Figure 1-3: Schematic representation of (A) a gaining stream and (B) a losing stream (Source: adapted from Woessner 2017).

In the UK, it is typical for high heterogeneity of GW/SW exchanges, which are related to the sediment deposition and erosion of alluvial valleys, resulting in strong differences in the patterns of water exchange between streams and aquifers (Lawler *et al.* 2009, Tellam 2009). Where glacial deposits are present in the floodplains and channels creates preferential pathways resulting in discrete patterns of discharge of GW from the aquifer to the stream (Stanford and Ward 1988, Lawler *et al.* 2009). Where bedrock formations constrain channels, and are in direct contact with one-another, patterns of GW discharge are observed as point-discharges where rock is fractured, and diffuse discharge where there are inter-granular formations (Lawler *et al.* 2009, Tellam 2009).

1.2.2. Development of hyporheic exchange flows

The hydrological connectivity between the surface and subsurface allows the discharge and/or infiltration of water between streams and aquifers. Hyporheic exchange flows (HEFs) are superimposed on these processes, with the repeated infiltration of SW into the near-stream sediments and return to the SW along a reach (Harvey and Wagner 2000, Kasahara and Wondzell 2003). HEFs are driven by the saturated hydraulic conductivity of the streambed sediments, the spatial gradient of the energy head at the streambed, and the area of the cross-section where water exchanges occur (Tonina and Buffington 2009).

In-stream geomorphic features produce spatial changes in the streambed elevation and water depth causing HEFs to develop due to the change in head gradient of the stream (Kasahara and Wondzell 2003, Lawler *et al.* 2009, Tonina and Buffington 2009). Features such as riffles and pools are examples of features where the streambed topography strongly influences the water surface topography (Lawler *et al.* 2009, Tonina and Buffington 2009). The difference between the head of these geomorphic features and that of the water surface drives flow under the riffle and into the streambed and banks (Tellam 2009, Tonina and Buffington 2009, Figure 1-4). Similarly, where meanders are present, head gradients are created in the downstream direction, with the infiltration of flow into the bed and banks (Lawler *et al.* 2009). The presence of small obstacles including boulders and wood can also create changes in the head gradients on the streambed due to the irregular stream water topography (Tonina and Buffington 2009).

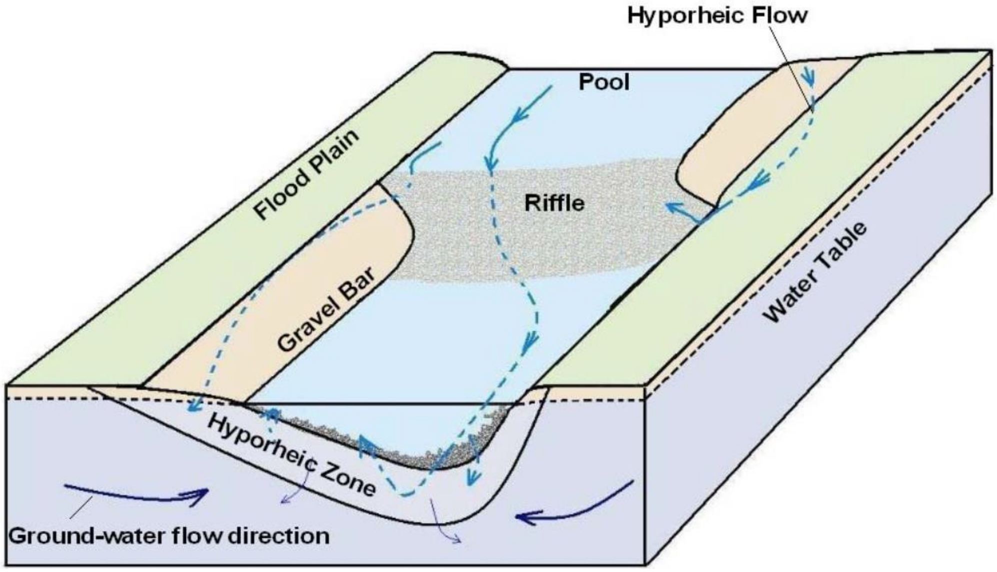

Figure 1-4: The hyporheic zone of a typical riffle-pool channel, showing hyporheic and GW flow (Source: from Tonina 2005 after Winter et al. 1998).

The vertical and lateral extension of HEFs is partially determined by the sediment characteristics of the streambed and floodplain. In areas of large alluvial deposits, e.g. lowland chalk areas of SE England, HEFs are often extended (Lawler *et al.* 2009, Allen *et al.* 2010). Whereas in upland parts of the UK, HEFs are most often restricted to the near streambed, close to the vicinity of the stream (Ibrahim 2012). Where there are patches of low-permeability sediment, HEF pathways can be potential diverted (Lawler *et al.* 2009).

1.2.3. Solute fate at the GW/SW interface

The development of HEFs supports fluxes of nutrients, organic carbon and dissolved oxidants to infiltrate into the near-stream sediment and mix with GW of contrasting hydrochemistry (Ibrahim 2012). The movements in flow are associated with the mixing of GW and SW in the hyporheic zone, resulting in the degradation, transformation, precipitation and sorption of solutes (Kalbus *et al.* 2006). Therefore, the loss and gain of water across the streambed are associated with movement of pollutants and contaminants derived from the surface and subsurface, spanning a range of sources which threaten the water quality of the respective systems. The fate of contaminants and nutrients is largely related to the near-stream sediment grain size and presence of organic carbon or minerals with a high absorption capacity, e.g. clay, iron (Fe) or manganese (Mn) oxyhydroxides (Smith 2008). Additionally, biotic activity can result in local changes to the reactivity of the streambed sediment, controlling the availability of organic matter, as well as influencing the precipitation or dissolution of the mineral phase (Hannah *et al.* 2009). During high flow events, the infiltration of fine sediments can have a similar effect, whereby the organic material alongside the disturbance of the streambed can impact on the mineral phase (Kaplan and Newbold 2000, Lawler *et al.* 2009). Spatial and temporal variations of the streambed reactivity mean that sorbed contaminants can be re-mobilised following the accumulation over time (Ibrahim 2012).

Besides the contrasting nutrient and organic carbon concentrations of the GW and SW, they have distinct redox conditions. Such conditions, coinciding with the mixing of GW and SW through the development of HEFs results in an environment within the hyporheic zone which can enhance the microbial activity (Brunke and Gonser 1997). The intensification of microbial activity can correspond with the enhancement of cycling, attenuation or release of nutrients and contaminants due to reactions occurring within the hyporheic zone (Boulton *et al.* 2010).

Biodegradation reactions occur under the influence of different redox potentials. The redox potentials indicate the dominant oxidant for respiration to occur in the system, and generally is oxygen, followed by nitrate (NO_3^-), Mn and Fe oxyhydroxides, sulphate (SO_4^{2-}) and carbon dioxide (CO_2) (Baker *et al.* 2000, Hannah *et al.* 2009, Pickup *et al.* 2009). Biodegraded organic contaminants have the potential to act as electron donors or acceptors (Chapman *et al.* 2007). In-turn these processes have the potential to decrease the concentration of organic contaminants and other soluble electron acceptors, e.g. SO_4^{2-}, coinciding with the release of other heavy metals or phosphate, associated with the organic matter or Mn and Fe oxyhydroxides (Gandy *et al.* 2007). Meanwhile chemolithotrophic microorganisms have the potential to oxidise a wide range of inorganic materials, e.g. Fe, nitrite (NO_2^-) and Ammonium (NH_4^+) (Pickup *et al.* 2009). Such activity can then lead to the production of NO_3^- (Storey *et al.* 2004) as well as the formation of oxyhydroxides, thus enhancing the streambed sediment reactivity (Gandy *et al.* 2007). At the GW/SW interface, biogeochemical processes vary both spatially and temporally. That is in addition to the variations in solute transit time, attributing to flow path length, head gradient and hydraulic conductivity of the sediment deposits (Hannah *et al.* 2009).

Developing an understanding of the movement of solutes is challenging, given that GW/SW exchanges can be highly variable even along small reaches, accounting to the bed heterogeneity and underlying geology (Cardenas *et al.* 2004, Heeren *et al.* 2010, Heeren *et al.* 2014, Aubeneau *et al.* 2015, Harvey and Gooseff 2015). GW/SW exchanges are recognised as a key mechanism determining the fate of nutrients (Dudley-Southern and Binley 2015) and have been extensively studied over the last 20 years (Kaandorp *et al.* 2018). In this time, studies have been conducted across a range of spatial and temporal scales (Brodie *et al.* 2007). A range of techniques exist spanning relatively simple and low-cost approaches to more recent technologically advanced techniques to investigate fluxes. However, the choice of which to utilise is typically based on the scale and rate of measurements. Commonly studies adopt a selection of methods (Ibrahim 2012), accounting for the multi-scale processes at the GW/SW interface.

1.2.4. Established GW/SW monitoring techniques

The monitoring of fluxes in flow and solutes is achievable through the application of a plethora of sampling techniques (Table 1-1). Sampling is often carried out along the stream channel, taking measurements to assess the hydrology and hydraulic characteristics. Field-sampling approaches at the surface are long established and typically comprise spot sampling, making use of, e.g. portable meters for the measurement of pH, electrical conductivity, and temperature

(Mayes *et al.* 2008, Banks and Palumbo-Roe 2010, Palumbo-Roe and Dearden 2013a). Water samples to characterise the water quality are typically by physio-chemical laboratory analysis, including the determination of pH, alkalinity/acidity, specific conductivity, hardness, and major anions and cations (e.g. Singh, 1988, Ibrahim *et al.* 2010). A core purpose of sampling is often to investigate the changes in loadings (e.g. Mayes *et al.* 2008), assessing contributions from surface runoff and GW sources. GW sampling is somewhat more restricted relative to SW sampling and dependent on the existence of monitoring boreholes (Brodie *et al.* 2007). When boreholes are available, they allow for the recording of GW levels and often the acquisition of water samples, although are frequently restricted to regional aquifers (Jones *et al.* 2000).

To account for temporal variations in water quality, studies resort to repeat sampling, with measurements obtained at different rainfall and hydrological flow regimes, to enable an understanding of the influences on contaminant concentrations and loadings. However, such methodologies are often costly and labour intensive. *In-situ* probes, samples and sensors partially alleviate the labour intensity with the ability to often collect high-resolution samples, e.g. temperature of the streambed (e.g. Bridge 2005). Numerical modelling approaches are growing in popularity to investigate processes by upscaling the understanding from point measurements (e.g. Niswonger and Fogg 2008), although are subject to potentially large datasets to parametrise the system studied. Typically, most studies looking at the stream-aquifer processes utilise a selection of approaches to capture the spatial and temporal variations (Brodie *et al.* 2007, Jankowski 2007, Buss *et al.* 2009).

Table 1-1: Examples of approaches used to investigate GW/SW fluxes in flow and solutes.

Approach	Description	Spatial Scale	Advantages	Limitations
Seepage measurements	Used to directly measure the seepage flux occurring at the stream-aquifer interface. An inverted open chamber comprising a bag is used to isolate an area of the streambed and the change in volume of water over time is measured (e.g. Lee 1977, Rosenberry et al. 2008, Rosenberry and Pitlick 2009).	Local	Able to directly measure seepage flux from the GW	Subject to measurements errors, and unsuitable for some gravel and heavy clay beds, and for use during high flows.
Field observations	Direct observations of the water, e.g. from springs at the stream bed, noting changes in water colour and odour (e.g. Thorne 1998, Buss et al. 2009).	Local, site-specific	Seepage hotspots can be identified quickly, with return visits possible to observe seasonal variations.	Seepage flux is not quantified, and dependent on the fieldworker's experience.
Ecological indicators	GW/SW discharges may be indicated by the vegetation and/or biota present. For example, where phreatophytic plants are present, indicates the water table is shallow (Seybold and McGlynn 2015).	Local, site-specific	Allows for a first-order assessment, aiding study site selection.	Localised and dependent on other factors, e.g. flow and seasonal changes.
Hydrogeological mapping	Involves the mapping of the underlying geology, stratigraphy, aquifer geometry and hydraulic properties (e.g. Stephens et al. 2019).	Intermediate to regional	Able to make a first-order assessment, inferring likely hotspots for GW/SW exchanges.	Hydrogeological data availability is limited often by the spatial and temporal resolution, with infrequent boreholes.
Geophysics and remote sensing	Using aerial/satellite imagery, changes in vegetation types and GW salinity can be mapped, which may be used as secondary indicators of GW discharge (e.g. Moridnejad et al. 2011, Rautio et al. 2018).	Local to regional	Increasing data available on open-source platforms, allowing for the mapping of landscape parameters, overcoming the need to conduct site surveys, which can be labour intensive.	Spatial resolution of datasets varies, depending on the location.

Hydrographic analysis	Using baseflow separation techniques and stream flow records in the form of time-series, it is possible for a baseflow hydrograph to be derived (e.g. Buss et al. 2009).	Intermediate to regional	Low cost, and where existing flow data is available, it can be carried out prior to fieldwork.	Only applicable where hydrological records are available, and only feasible as a method to gaining streams.
Hydrometric analysis	Makes use of Darcy's Law to estimate the hydraulic gradient between the GW and SW systems to assess the hydraulic conductivity between the aquifer and bed material (e.g. Käser et al. 2013, Byrne et al. 2018)	Local to regional	Through the installation of piezometers offers a basic insight into the seepage direction.	Point measurements only and reliant on hydraulic conductivity to be estimated to quantify seepage direction.
Hydrochemistry studies	Environmental tracers can be used to assess the stream-aquifer connectivity. Commonly used tracers include electrical conductivity and pH, major anions and cations (e.g. magnesium, chloride and sodium) (e.g. Fowler and Death 2001, Soulsby et al. 2005).	Local to regional	Provides an insight into the seepage flux and the ability to define, GW recharge and discharge.	Limited to gaining streams.
Artificial tracers	An artificial tracer is injected int the stream allowing for an insight into the GW flow paths and degree of hydraulic connectivity (e.g. Berryman 2007, Engelhardt et al. 2011, Clémence et al. 2017).	Local to intermediate	Direct evidence of water fluxes between the systems.	Tracers need to meet environmental regulatory controls, and there is potential for the degradation, precipitation or sorption of the tracers, thus affecting the performance. Limited to gaining streams.
Temperature studies	Seepage flux may also be estimated using heat, whereby temperate is measured in both the SW and GW. Surface temperatures typically are of a diurnal pattern according to seasonal trends, whilst groundwaters have very little variation (e.g. Hatch et al. 2006, Schmidt et al. 2006, Selker et al. 2006, Anibas et al. 2009, 2011, Kaandorp et al. 2019)	Local	Temperature measurements are simple to take, with advancements in technology enabling greater spatial and temporal coverage.	Measurements ae typically limited to small areas and need to be used alongside other monitoring techniques.
Numerical modelling	Using hydrological and hydraulic data, numerical models allow for the simulation of likely GW-SW movements (e.g. Guay et al. 2013)	Local to regional	Bridges the gap between field sampling which may be lacking in detail.	Dependent on the availability of data, with uncertainties associated.

1.3. EU Interreg TOPSOIL Project – UK-1 Pilot, Wear Catchment

This thesis contributes to a wider project examining the way in which we look at and think about the management of land and water across Europe. The EU Interreg North Sea Region TOPSOIL project is focusing on working on the improvement of water quality and quantity, while supporting environmental, financial and human benefits (TOPSOIL 2019a). Special interest is being paid to the to the development of methods to describe and manage the uppermost 30 m of the subsurface in order to improve climate resilience of the North Sea region (TOPSOIL 2019a). TOPSOIL wishes to develop novel approaches to maximise the transferability of solutions, enhancing the sharing of knowledge and experiences of partnership working (TOPSOIL 2019a). The project is focused on looking at the GW/SW connectivity and its implication for water resource protection and management in 16 pilot areas in the North Sea Region (TOPSOIL 2019b, Figure 1-5). In the UK, two pilot studies are being undertaken. UK-1 (Figure 1-5) looks specifically at the tributary catchments of the River Wear in County Durham, and this thesis supports the investigations in two of the four study areas.

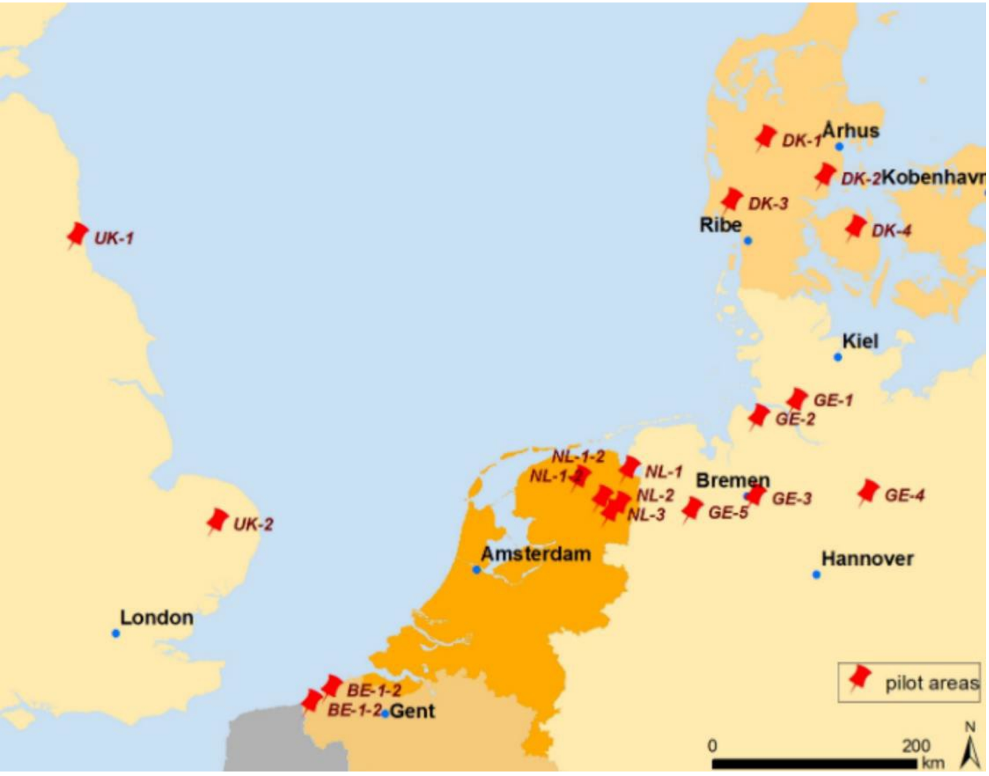

Figure 1-5: TOPSOIL pilot areas (TOPSOIL 2019b).

In the Wear catchment, the key drivers behind the TOPSOIL project are: i) the poor-quality status of the Magnesian Limestone GW body, ii) bad to moderate ecological status of the SW, iii) rebounding GW of the Coal Measures and iv) the influence of minor aquifer systems on the SW bodies. There is a need to account for the multitude of pressures that may contribute to poor-water quality which include increasing urbanisation, wastewater management, surface water flooding and climate change, besides historical industrial contamination, including landfill and significant water abstractions supplying mainly urban populations; all of which have typically been subject to fragmented management strategies.

Through collaboration between various organisations and stakeholders, including the Wear Rivers Trust, the Environment Agency, Northumbrian Water and Durham University, the interactions between the water bodies are to be investigated. The current understanding of the interactions at the interface between the GW and SW systems is limited at the local scale, with a poor understanding of the system characteristics and need to address water management at the catchment scale. The understanding and management of GW and SW is divided between practitioners in different disciplines, with data being held fragmentally between the organisations. Despite the recognition of the need to have a holistic understanding of the system to achieve more effective management and meet the requirements of the WFD, the links and implications are yet to be investigated with the specific catchments of interest. Ultimately, the intension of this doctoral research is to inform more joined up and holistic management interventions to protect water resources of interest encompassed within the scope of the TOPSOIL project. The findings of this research will feed into the interest areas of the TOPSOIL project, informing management in the Wear catchment, with emphasis on water quality.

1.3.1. Identifying water management issues in the Wear Catchment

Developments throughout the Wear catchment, including that of residential areas and industry has resulted in a multitude of pressures on the freshwater resources (TOPSOIL group, personal communication). Point and diffuse pollution from arising from contemporary and historic pressures are deterring the water quality of the GW and SW systems. There is a need to consider the attribution of pollution of the stream water, but also the possible interaction with GW and thus the likelihood of exchanges in the near-stream sediments with HEFs, considering the reappearance and remobilisation of pressures, including sorbed contaminants further downstream, beyond the source points.

Beyond the routine statutory sampling carried out by the Environment Agency to assess quantitative and qualitative status against the WFD objectives, the understanding of the water quality is limited, with GW insights restricted to selected boreholes (TOPSOIL Group, personal communication). The low economic importance of the local minor aquifers means that the hydrogeological importance of the aquifers and impact on the GW/SW interactions on attenuation of solutes is overlooked, however, it needs to be improved (TOPSOIL Group, personal communication). The improved understanding is essential to considering the future sustaining and management of the SW ecosystems and are currently under threat from a multitude of historic and contemporary pollution sources. Currently, stakeholders are focusing on individual issues, and consequently this is resulting in segregated mismanagement of the systems attributing to the fragmented understandings of the catchment systems. Additionally, there is a limited insight into the subsurface characteristics, thus further hindering understandings. There is a need to consider how connections exist within these catchments, from the surface to the subsurface, and the exchanges and interactions in flow and solutes which occur between them, providing the basis to the study of this thesis research. There is a need for a more comprehensive insight and understanding of the systems, supporting interdisciplinary and trans-disciplinary approaches to water resource management in the catchment.

1.4. Challenging GW/SW management practices through scientific research

Despite expansive research into hyporheic and GW processes, there is a lack of translation into water management practice due to disjointed and limited monitoring of water variables of the GW and SW hydrology and hydraulics, particularly at the local scale (Jones *et al.* 2000, Conant *et al.* 2019). The provision of basic hydrologic and hydraulic data is generally sufficient for major rivers and aquifers, however, the same is often rarely said for tributary streams and minor aquifer systems, with the characterisation of the physical, chemical and biological elements of the water usually limited by irregular or infrequent sampling (Jones *et al.* 2000, McDonnell 2008). Thus, the high heterogeneity in the movement of flow and solutes within these settings fails to be effectively captured. Therefore, such heterogeneities are overlooked, with catchment management essentially looking at easy to solve issues, masking the complexities. However, cross-scale interactions in the landscape really matter (Green and Sadedin 2005). There is a need to challenge the tendency in complex catchments to discount the scale and degree of natural patterns, processes and variability (Harris and Heathwaite 2012). Harris (2007) emphasises the need to consider the emergence of large-scale processes, in this case the catchment-water quality attributing from fine interactions. Therefore, while there is a need for the wider catchment, this then needs to be downscaled to encompass local processes, and then linked back up to the wider processes; something which needs to be addressed in current water management practices.

Currently, the understanding and management of water continues to prevail from individual sectors with targeted efforts as part of reductionist approaches rather than integrated approaches (Heathwaite 2010). The disaggregation between professional procedure and fragmented institutional roles is hindering the intended joined-up thinking and collaboration of water management in practice (Falkenmark 2004, Macleod *et al.* 2007, Staes *et al.* 2008). As a result, the focus of management continues most to be prioritised to individual pressures and drivers, and it is argued that the ICM principles of the WFD are neglected (Downs *et al.* 1991, Biswas 2005, Biswas 2008, McDonnell 2008). Thus, overlooking the processes and threats operating within the systems at various different spatial and temporal scales, with a prevailing one-dimensional insight into the systems, most often from the SW where it is relatively easier to describe and quantity and visualise the water relative to the GW bodies (Love *et al.* 2007, Bencala *et al.* 2011).

As a result of the lack of amalgamation in understandings, it is common practice to conceptualise systems to be either connected or disconnected at a broad scale, most often at a regional or catchment scale (Ransley *et al.* 2007). Typically, the focus of connections is between the SW and the major aquifers, despite the potential of more localised processes within catchments, including minor aquifer systems (Jones *et al.* 2000, McDonnell 2008, Environment Agency 2013, Abbott *et al.* 2017). Therefore, the management led on behalf of water companies and NGOs focus on addressing specific issues such as wastewater asset failure without any consideration of wider processes and coinciding issues (McDonnell 2008). Thus, emphasising the pipe-system focus, under the assumption that as the water passes from point A to B, and the pollutants disappear without a trace.

The need to look more closely at the GW and SW systems is prompted by historic and contemporary challenges with diffuse pollution being a problem (Heathwaite 2010). In heavily modified catchments there are a multitude of pressures acting on the systems, preventing the quality and quantity of the freshwater resources meeting human and ecological requirements, e.g. WFD objectives. Tackling multiple stressors that lead to diffuse pollution is essential for sustainable water management (Heathwaite 2010). However, as most environmental monitoring is focused on the statutory requirements, largely linked to point source measurements often results in major knowledge gaps of the GW and SW systems (Heathwaite 2010). There is a need to map the local-scale pressures to allow for targeted management (TOPSOIL Group, personal communication). Generally, there is a lack in the transfer of knowledge between science and practitioners (Lawrence *et al.* 2013).

Ultimately, current practice is simplifying the systems to be essentially two homogeneous compartments of water separated by the streambed, which is too basic. There is a need to look beyond the broad assumptions and examine the systems more closely, acknowledging that there are multiple historic and contemporary pressures and drivers, which in turn result in the movement of water within and between the systems, with exchanges and interactions occurring across spatial and temporal dimensions, including those at the GW/SW interface (Figure 1-6). However, such a holistic and integrated approach requires a collaborative effort, with the communication and sharing of knowledge and understandings between and across disciplines and organisations (Smith 2005, McDonnell 2008). That is in addition to the feeding through of scientific understandings into practice, which are arguably lacking (Grigg 2008), with the need for an interdisciplinary and trans-disciplinary approach to water management.

The tendency to discount the scale and degree of natural patterns and processes operating within catchment is inherent to the ignorance of looking at simplifying the complexities, and that the emergence of patterns from fine-scale interactions accumulate to larger processes (Harris 2007). The use of classification metrics to assess connectivity, often used in the support of management decisions overlook the complexities, with management prevailing from individual sectors, despite the overlooking of the complex patterns in GW flow paths (Fuchs *et al.* 2009). By looking at the finer scale processes in catchments and how they manifest is noted to be a key area to target efforts (Ryan *et al.* 2007), particularly with the need to sustain water resources, rather than have contradicting efforts and fragmented understandings.

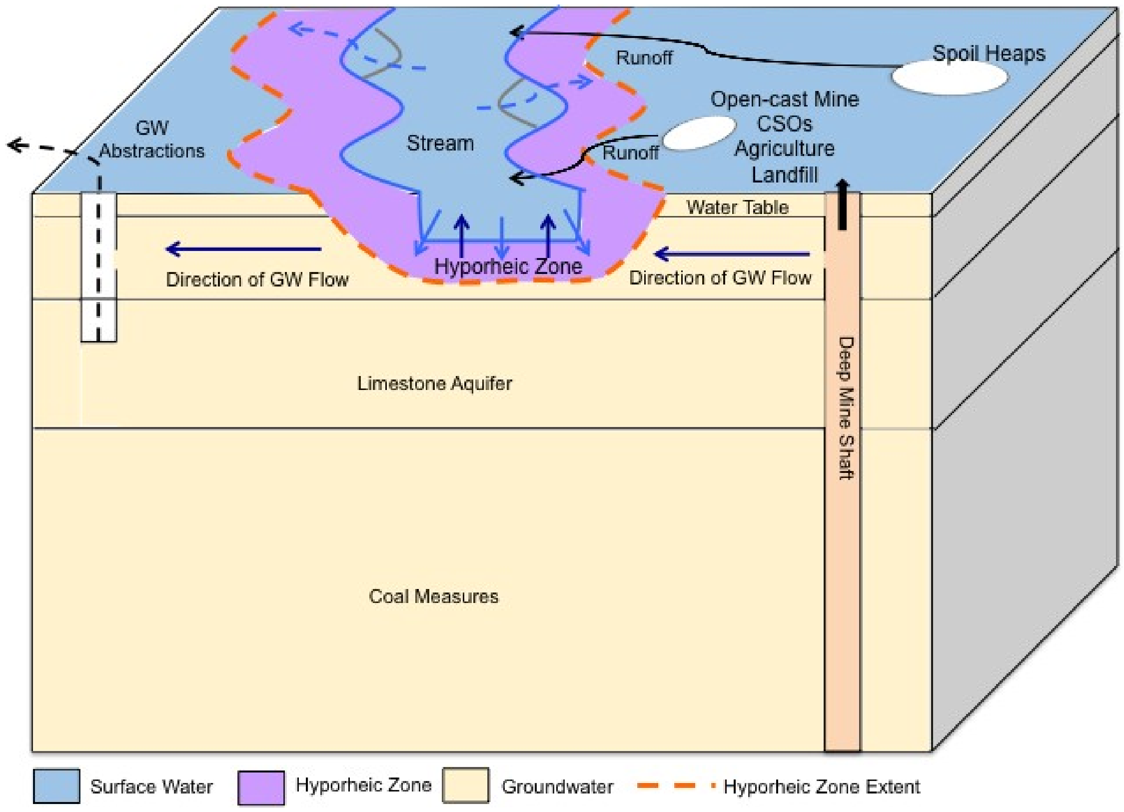

Figure 1-6: A simple conceptual diagram of GW, SW and hyporheic zone with examples of pollution sources in County Durham. Rebounding of major aquifers is not represented.

Considering the continued fragmentation associated with water resource management, the thesis seeks to investigate how the connectivity between GW and SW can be investigated to improve the understanding of GW/SW exchanges and interactions in tributary catchments that are heavily modified and under stress from multiple pollution sources. There is a need to improve the conceptual understanding, otherwise management will continue to address water issues with a closed systems approach (Niswonger and Fogg 2008). As a result, the stresses within and between the water systems will continue to be unaccounted, both spatially and temporally, consequently leading to unsustainable water management practices spanning the headwaters to downstream. To address water-related issues it is critical to address knowledge gaps (Wondzell 2015, Convino 2017), looking at the influences from the headwaters to downstream (Gomi *et al.* 2002, Leibowitz *et al.* 2018), as well as laterally and vertically across the streambed considering the GW and SW together (Wondzell 2015, Convino 2017, Figure 1-6). A key challenge facing river corridor investigations is the application of knowledge and understandings gained across the different disciplines, scales and orders of magnitude across the surface and subsurface systems (Harvey and Gooseff 2015, Larned *et al.* 2016). The first step is realising the complexity of the systems (Heathwaite 2010) – then it is a case of then breaking it down and looking at the system characteristics and then the pressures, and then how they link together.

Furthermore, the thesis looks to explore the current understanding of our water bodies and how water quality threats accumulate and disseminate in GW and SW systems. The focus is on developing an understanding of the GW and SW system connectivity where there is a lack of baseline monitoring. Such knowledge will, in-turn, enable an exploration of mechanisms by which interactions and exchanges in flow and solutes occur, with a key emphasis on the application of novel approaches to facilitate a spatial and temporal understanding. Specifically, the thesis seeks to explore the testing of the feasibility of using existing secondary data to inform assessment of water quality across the catchment where direct measurements of water variables are lacking. Subsequently leading onto field investigations from the conceptual understanding developed to assess the interactions and exchanges in flow and solutes, both in-stream and across the streambed. The research is undertaken at various scales, spanning the catchment to sub-reach scale, to point scales. Using the main findings from this research, this thesis will make recommendations as to how the water management in these stressed environments might be improved, working across disciplines and practices to achieve a more cohesive understanding of the systems. A key element is challenging how we look at two separate, yet connected environments, and move beyond the decoupling at the catchment scale, and thinking about the processes that are likely operating spatially and temporally along river reaches.

The research carried out in this thesis is on study catchments selected in the early stages of the TOPSOIL project as part of the UK-1 study. The catchments have been identified by water organisations and stakeholders with the need to address water quality. Including the failure to meet WFD objectives and limited understanding despite the strive for improvement of the environment, specifically the way we manage the water and the land in tandem as encompassed under the ICM principles and catchment-based approaches (CaBA, Deasy 2018).

1.5. Aims and objectives of the research

The aim of this thesis is to investigate the way in which GW/SW are connected and interact based on the application of a multi-method approach to assess the movement and fate of flow and solutes within, and between GW and SW systems in heavily modified streams of tributary catchments in the lower River Wear, County Durham. Throughout the thesis, the goal is to explore the use of novel approaches to conceptualise and characterise the connectivity and interactions between the GW and SW systems in situations where there is a fragmented understanding and thus subsequent decoupled management of the systems attributing the inadequacy of hydrologic and hydraulic data representative of the GW and SW systems.

To achieve this aim, the thesis has the following objectives:

Objective 1 – to assess the threats to GW and SW quality, identifying historic and contemporary sources through the application of desk- and field-based approaches, to give a primary assessment on the connectivity making use of reconnaissance walkover surveys and discussions with local water organisations and stakeholders.

Objective 2 - to assess the likely controls on the water movement, testing the feasibility of utilising existing data to conceptualise the characteristics and linkages between the GW and SW systems to provide an understanding of the connectivity when baseline monitoring is lacking. In-turn, this will involve reviewing existing integrated assessment approaches and understanding what is missing. They will result in a proposed framework/tool to facilitate an integrated assessment of the GW/SW system connectivity is to be recommended and introduced with the application to case study areas facing a multitude of on-going water quality threats.

Objective 3 – to undertake field sampling to determine the fluxes of water and solutes within the stream water and across the streambed, to further test the understanding of the GW/SW connectivity following on from the initial conceptualisation. By doing so, it is with the intention to assess the role of GW in the potential attenuation and release of flow and solutes and the likely consequent impact on the water quality of the overlying stream. Currently such interactions are overlooked and are currently viewed to be disconnected due to the neglected assessment of the superficial systems between the stream and major aquifers.

Objective 4 – to apply numerical modelling techniques to explore the system responses to changing hydrological conditions, interpreting the flow and solute patterns beyond the local-scale. Thereby extending the scope of the study and understanding beyond the spatial and temporal constraints of field sampling, upscaling the point-based understanding into the dynamics and processes operating in the wider systems.

Objective 5 – to make recommendations of how the management of GW and SW systems could be improved in working practice to enhance the water quality and fitting into the wider catchment priorities.

1.6. Research approach

Desk-surveys and field-visits were carried out along with discussions during early stage TOPSOIL meetings (late 2015) to assist in the selection of two case study catchments for which this thesis would focus on the local-scale GW/SW connectivity, linking to the understanding of current water-quality issues. The mapping of potential pollution sources during reconnaissance walkovers allowed for the identification of sites within the study areas to base subsequent investigations. The study areas were chosen because of the multitude of pressures acting on the current water quality, with subsequent failure in meeting the WFD objectives. The study area selection coincides with priorities from local practitioners, with research supporting the local-scale understanding, overcoming the limited insights. The research conducted for this thesis is on two of four study areas which the TOPSOIL group are focusing management on.

1.6.1. Study catchments

Study catchments were selected following discussions as part of the TOPSOIL project, with interlinking priorities and investigations into the water quality, including that from a regulatory and stakeholder perspective of the Environment Agency, Northumbrian Water, the Wear Rivers Trust and Durham University. The study catchments selected for this research are in the Lower River Wear catchment (length 96 km; catchment area 2280 km^2) and are the Twizell Burn (19 km^2) and Herrington Burn (13 km^2) (Figure 1-7). The streams form tributary catchments to the River Wear which rises in the Pennines and flows eastwards, discharging into the North Sea at Sunderland (Figure 1-7). Currently failing to achieve the WFD classification of ‘good’ status, the SW and GW of these catchment is currently impacted by historic and contemporary water pollution (TOPSOIL Group, personal communication), including those attributing to historic mining impacts.

The central and east parts of the Wear Catchment were extensively mined until the late 1900s via surface and deep coal abstractions (Figure 1-8). Coal mining operations have since ceased (Younger 1995). Mining has led to major physical modifications to the subsurface and of the stream channels, altering the flow paths and head gradients. Dewatering in the central areas of the Coal Measures outcrop continues, meanwhile beyond the radius of the dewatering pumps, the water table is fully recovered with uncontrolled mine water discharges (Younger 1993, 1995, Banks and Banks 2001). Predicting the rate and spatial variation in the GW rebound after the coal mine closures have been hindered by the lack of hydrogeological records, with GW investigations been most suited to the solution of operational problems (Sherwood and Younger 1994). The content of the GW discharges varies spatially. GW discharges are sometimes moderately mineralised and alkaline, with iron loadings resulting in thick iron ochre (Younger 1993). Although, with oxidative weathering and dissolution of sulphide minerals, especially pyrite means that surface discharges are often rich in iron, sulphate, aluminium and acidity (Gandy and Younger 2003).

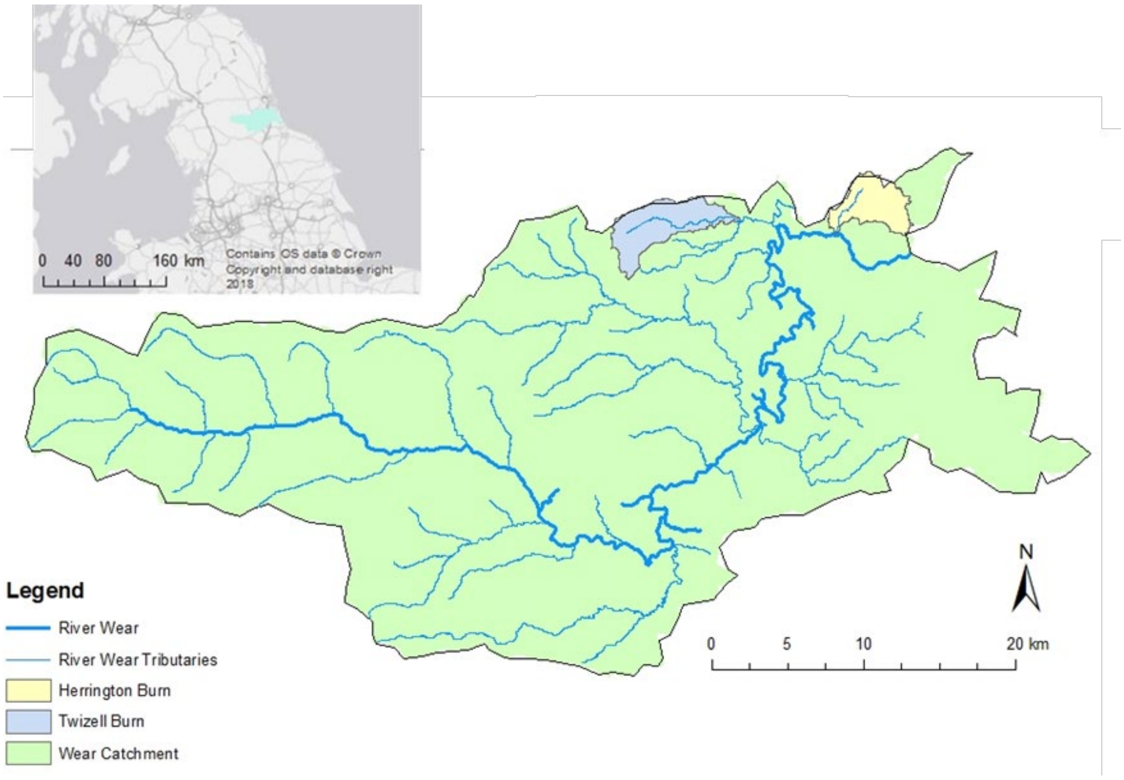

Figure 1-7: Thesis study areas in the River Wear catchment, County Durham, UK.

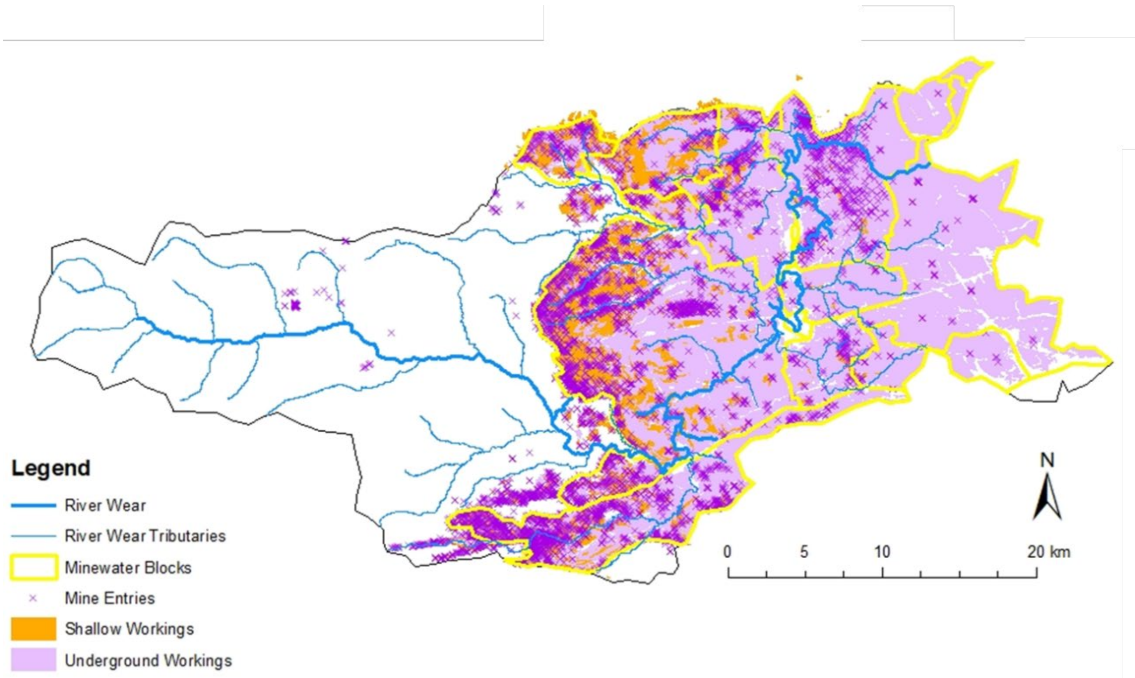

Figure 1-8: Coal mining extent in the Wear catchment (Coal Authority 2018).

Towards the east of the Wear catchment, a Magnesian Limestone outcrop overlies the Coal Measures supporting an aquifer used to support the provision of water to surrounding residential areas (Figure 1-9). Elsewhere the Coal Measures are constrained by superficial drift deposits (Figure 1-10). Minor aquifers are believed to be present throughout the superficial deposits, supporting baseflow to rivers (DEFRA 2019), and thus having the potential to impact on the water quality. The current approaches have led to belief that the aquifers have had no influence on the SW, however, there is a need to look at the minor systems. There is a need for investigations into the hydrochemical characteristics, which requires the delineation of the flowpaths and quantification of solutes from the identified pressures (TOPSOIL group, personal communication).

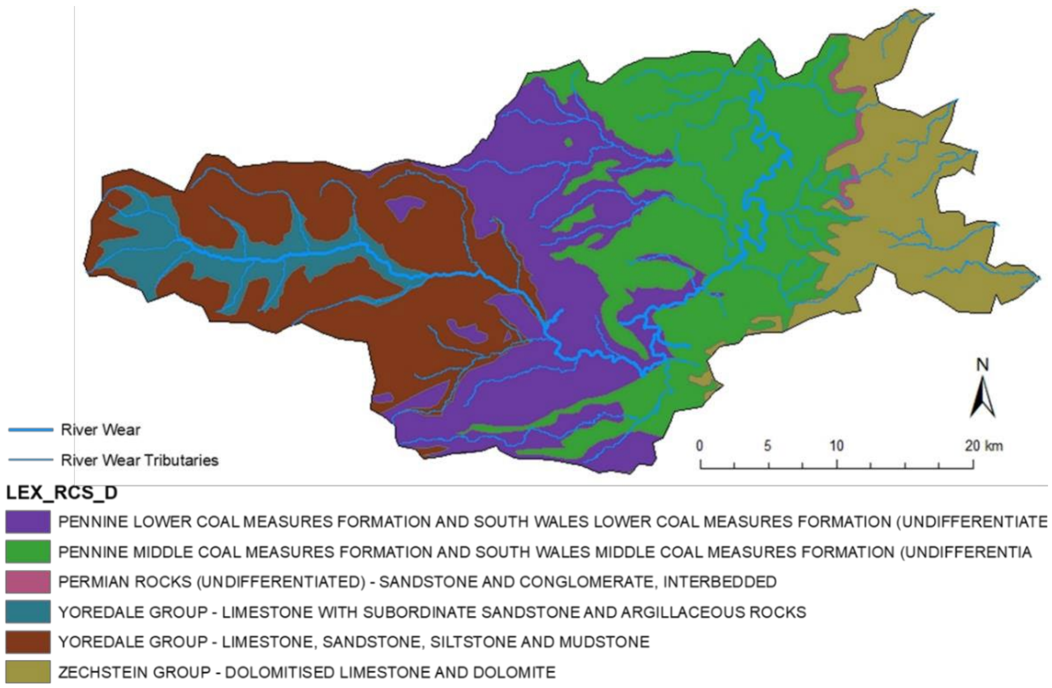

Figure 1-9: Bedrock geology of the Wear catchment 1:625k (Source: BGS 2010).

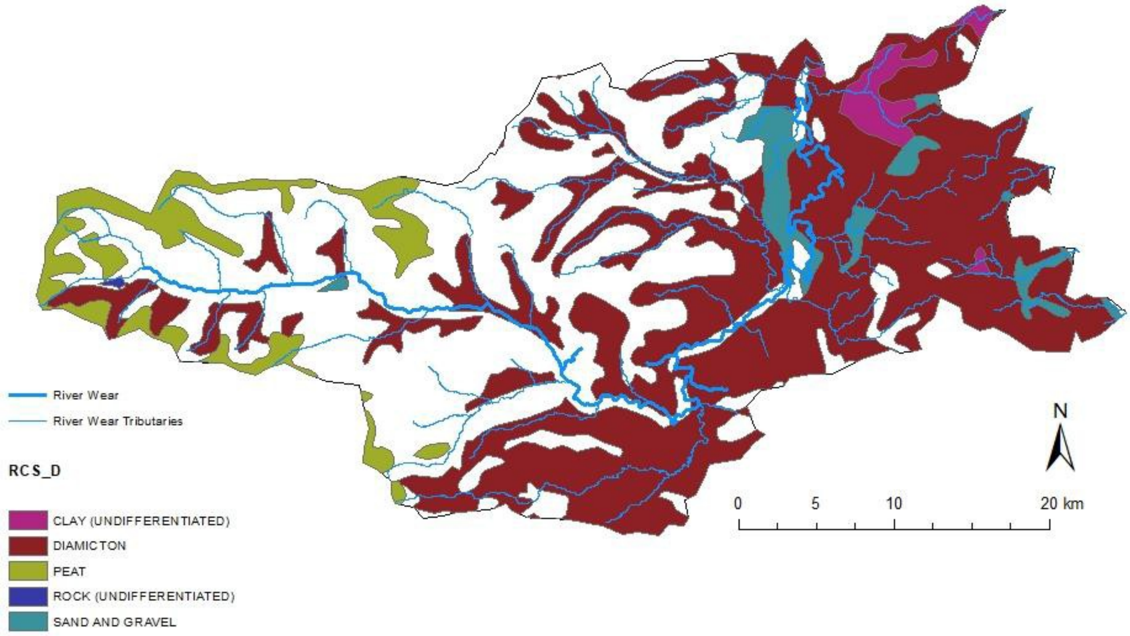

Figure 1-10: Superficial geology of the Wear catchment (Source: BGS 2010).

The research presented in the thesis covers three principle research areas:

1. Conceptualisation of GW/SW connectivity

The understanding of GW and SW systems is typically limited to the perspective of either the surface or subsurface, with the systems deemed connected or disconnected, typically at the regional or catchment scale. Whilst the systems appear entirely connected or disconnected at the larger scale, this is often based on a coarse resolution insight, neglecting the possibility of variations in the connectivity according to finer spatial and temporal scales, including those with minor aquifer formations. Establishing an understanding of the connectivity operating within the catchment is typically overlooked, especially given limited baseline studies with the main priority of sampling often for objective-based assessments, such as the WFD (Jones *et al.* 2000), without looking at the movement and interactions of flow and solutes beyond the sampling points.

The understanding of the system processes and dynamics over spatial and temporal scales is largely hindered by limited sampling, which is predominantly from the perspective of the SW, although often at infrequent sampling sites, and thus any potential changes in the chemistry, for example, go unaccounted, both throughout the system and across the streambed. Despite the anticipation for integration under ICM principles, the understanding of water quality across the entirety of the catchment is based on singular points without knowledge of the processes occurring, both downstream and across the streambed. Further to the limited monitoring, limited discussions between hydrologists and hydrogeologists managing the SW and GW systems respectively results in conflicting understandings, with the need for conceptual understanding of the system, supported with the collaboration of data and information (Grigg 2008).

2. Conceptualisation of GW/SW connectivity

Despite extensive research over the last 50 years into GW/SW exchanges, empirically driven understanding of such exchanges in the practice of water management is typically neglected, often due to the complexity of the systems, and limited tools and frameworks to implement and assess the connections in local-scale contexts (McDonnell 2008, Cardenas 2015, Kaandorp *et al.* 2018). Frequently, management decisions are based on a very limited, basic understandings, whereby the systems are considered as closed pipe systems, with water transport from A to B, irrespective of the changes along the route of the water (Bencala 1993, Bencala *et al.* 2011). Exploring ways to develop the understanding of GW/SW connectivity and exchanges supports intentions to develop integrated, holistic understandings.

However, at a local level, the focus is often prioritised to meeting targets as opposed to addressing the way in which the processes and interactions of drivers and threats are managed, lacking the quantification of the way in which threats disseminate and impact on the receiving water bodies, including those downstream. The fragmented prioritisation of addressing the different threats, such as effluent waste, results in the segmentation of the processes and drivers. With the focus on ensuring the achievement of statutory-based measures as opposed to capturing the processes and interactions. Such assessment often dictates the work of individual sectors, thus lacking the coherence between organisations. There is a need to look at the links between the processes and drivers themselves, as well as between them (Kaandorp *et al.* 2018), which dictates the threat at which pollution has on the systems.

3. Role of GW in the SW system

Driven by changes in legislation as to how GW and SW systems should be considered and thus managed, there is an ever-increasing emphasis on the understanding of the influence of the respective systems on one another. Whereby in addition to establishing an understanding of the connectivity, there is also a need to determine the impacts of the flow and solutes on the quality of the systems. However, the fragmentation between the organisations who manage the water systems can hinder the translation of the intended integration, which is largely attributable to the complex nature of the systems, coinciding with the lack of monitoring.

Although recent legislation theoretically strives for an integrated understanding of the GW and SW systems, established monitoring regimes do not reflect the integration, particularly beyond the constraints of major aquifers (Jones *et al.* 2000). Arguably the sampling is suited to the assessment according to the statutory frameworks, assessing against standards, but tends to fail to gain an insight into the systems under changing hydrological conditions, and between the GW and SW systems. Understanding the way in which GW and SW systems interact supports the achievement of working towards improved water quality, as we may be bettering the SW, however, this could be detrimental on the respective system without an understanding of it. Without integrative monitoring, or at least an insight into the system dynamics, we are essentially managing the systems as closed, disconnected systems, and this might not be true. There is a need to overcome the complexity and develop an improved understanding looking at the local systems and processes within the scope of the larger catchment systems.

The research presented in the thesis considers the intersection of the three themes outlined above, exploring current understanding and management of the freshwater systems, and seeks to quantify and evolve understanding, especially at the intersection across the two water systems and the interactions between them, both at spatial and temporal scales overlooked in routine assessments. The research adopts a multi-method approach (Table 1-2) to consider how we understand, investigate and manage water above and below the streambed, accounting to varies scales and pressures. In order to consider both the hydrology and hydrogeology of the SW and GW systems respectively, it is necessary to consider the interdisciplinary approaches, namely the methods used to assess the water movement and also the bringing together of already existing data and information with the aim of increasing the understanding of processes and interactions across the streambed, attempting to bridge the gap between research understandings and those adopted in practice.

The exact methods and data used at specific stages of the research are presented in the 'Methods' section of each of the Chapters 2-4. Here, a broad summary of the methods adopted throughout the research is presented below:

Table 1-2: Summary of the key approaches used throughout the research.

Approach	Description	Pros	Cons
Desk-based	Coinciding with walkover surveys, desktop analysis, e.g. using GIS allows for an insight into the system characteristics, making links between elements utilising existing datasets to derive information, looking across a range of spatial and often temporal dimensions, facilitating an assessment from the regional to catchment scales, and where data allows, local-scale assessments.	• Increasing amount of freely available data in the public domain	• Data resolution is often spatially and temporally limited depending on the site or study area • Sharing agreements need to be in place to allow for the dissemination of data held by organisations
Field measurements - including hydrochemical sampling, flowpath characterisation, and water and solute fluxes quantification	Establishing approaches to determine the hydrological changes and corresponding water chemistry through the obtaining of water samples through: i) SW spot sampling (grab-sampling); ii) SW quasi-continuous sampling and; iii) shallow pore-water sampling via piezometers. Allowing for a quantification of the chemistry as well as the fluxes in flow and solutes with hydraulic measurements.	• Capturing the system at a specific point in time	• Limited baseline data to draw comparisons for low order streams and minor aquifers • Laborious, requiring intensive and repeat surveys
Numerical modelling	To extend the spatial and temporal insight into the GW/SW system dynamics and processes, e.g. with changes in flow.	• Extend the understanding from existing data • Increasing number of off-the shelf models	• Parameterisation is challenging for heterogeneous systems • Simulation time increases with complexity • System representation is based on available data

1.7. Thesis structure

The thesis is structured using the following five chapters:

Chapter 2 presents an innovative approach, Integrated River Evaluation for Management (IREM), as a means of looking beyond the SW system, to evaluate how we explore GW/SW systems and the connectivity between them. Often tributary catchments have limited historical data, thus deterring the level of information which can be derived to understand the systems. IREM has been developed to test the feasibility of using existing data to provide a first-order assessment of the spatial and temporal dimensions. As a tool to investigate the GW/SW connections, IREM is applied to the Herrington Burn and Twizell Burn as a foundation for subsequent chapters.

Chapter 3 examines the role of the GW on the water quality of a reach of the Twizell Burn. The stream is representative of a complex, heavily modified system, which has limited insights beyond routine sampling led by the Environment Agency. The system response to changing hydrological conditions is investigated, exploring the buffering and propagation potential of the minor aquifer system, considering the local scale processes.

Chapter 4 seeks to extend the understanding of the system behaviour, upscaling the spatial patterns to investigate the response of the SW and shallow GW using numerical modelling approaches. Scenario-based simulations allow for an insight into the system dynamics and processes likely operating, dictating the hydraulic connections across the streambed in response to changing hydrological conditions, such an extreme rainfall events according to climate change scenarios. The purpose is to upscale the understanding from Chapter 3, linking it to the larger scale understanding developed in Chapter 2.

Chapter 5 draws together the key findings presented in Chapters 2-4, addressing the research aim, bringing the findings into the wider research context.

Chapter 6 contains the primary recommendations and conclusions of the research presented in the thesis.

The thesis is written in a journal-paper format, with the intention of Chapters 2-4 been published as stand-alone papers. In this way, the detailed literature and methods are presented in each chapter. Oral presentations of Chapters 2-4 have been presented to gain feedback (see below). Additionally, I have presented elements of each of the chapters at plenary stakeholder and partner TOPSOIL meetings, as well as quarterly international TOPSOIL meetings in Europe.

1.8. Summary

To summarise, the aim of this research is to determine the occurrence and spatial extent of water-quality issues looking to establish the interrelationships between GW and SW bodies. To do so, this research is interdisciplinary, working with, supporting and informing organisations and stakeholders with the shared interest in the GW and SW systems as part of the TOPSOIL project, which will facilitate data sharing and discussions, shaping the empirical data collection of this research. Ultimately, by investigating the interactions between surface and subsurface systems it is anticipated that this will support improved understandings of the catchments and lead to recommendations of effective and sustainable water resource management, moving beyond fragmented reactions.

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“Higher,

Further,

Faster!”

Carol Danvers (Captain Marvel, 2019)

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Chapter 2 - Integrated River Evaluation for Management (IREM): A novel approach to mapping groundwater-surface water connectivity

2.1. Introduction

In science and in practice, water resources have traditionally been monitored and managed from the perspective of either the surface or subsurface (Barthel 2014, Li *et al.* 2016), coinciding with separate problems and priorities of each, and addressed with fragmented policies and frameworks (Macleod *et al.* 2007, Staes *et al.* 2008). Recognised as an unsustainable approach, it is only within the last two decades that efforts to address and manage water resources have shifted towards more holistic and integrated approaches (Watson and Howe 2006, McDonnell 2008, Staes *et al.* 2008, Allen *et al.* 2010). Such approaches are commonly referred to as Integrated Catchment Management (ICM, Lerner and Zheng 2011), by which the hydrological catchment is used to organise the interventions of the landscape and hydrological processes to deal with water resource issues (Fenemor *et al.* 2011).

In recent years the application of ICM has grown, informing and shaping major policies, both nationally and internationally, including the WFD (2000/60/EC, CEC 2000, Smith 2005, Macleod *et al.* 2007, Pascual 2007). Legislation such as the WFD provides the opportunity to identify new innovative solutions for water management (Pascual 2007). However, most environmental monitoring is focused on the statutory requirements, largely linked to sites of point-source pollution or temporal measurements taken at fixed points leaving major knowledge gaps (Heathwaite 2010). The irregular and infrequent collection of water variables including hydrological and hydraulic data of the river and aquifer systems, particularly of minor formations, deters the ability to establish an understanding of the interactions according to the connectivity within and between the GW and SW systems (Heathwaite 2010). Thus, failing to capture the system characteristics and fine scales, specifically the localised patterns and processes of flow and solutes, and thus their role in the larger system processes is withheld by such sampling and knowledge gaps. There is a need to gather evidence to develop an understanding of the systems overcoming the shortfall in measurements, coinciding with the need for communication among those involved in water management (Holzkämper *et al.* 2012).

The starting premise of integrated approaches is understanding the system characteristics, and from this there is the need to link the channel and aquifers with the surrounding catchment, with an understanding of the associated natural flows of water, energy, biota and chemistry (Neal *et al.* 2000, Falkenmark *et al.* 2004, Ransley *et al.* 2007, McDonnell 2008, Rothwell *et al.* 2010). Such approaches require an amalgamation of knowledge and information, looking across various space and time scales, capturing the dynamics of the systems and processes across the surface and subsurface (McDonnell 2008). However, as many have argued, such as Biswas (2005) and Moss (2007, 2008), capturing the system dynamics and processes encompassed within the intended ICM framework is challenging to achieve, with the focus largely being on addressing and monitoring the symptoms of water quality. Additionally, it is difficult to implement the political and operational structures in the practice of water management to support the theoretical ideas, with various measurements set to be collected across various points throughout the systems by different practitioners. As a result, the sharing of data to derive information is often challenged by such structures and practices, meaning that data goes unused once it is used for its primary purpose, and the data is often not distributed (McDonnell 2008). Instead data and information are held by the individual or organisation and not used again, with understandings developed and held in the capacity of individuals. The integrated assessment of water quality across the GW and SW systems is reliant on the ability to pull together the available data to hand, assessing the connectivity, and in-turn the interactions and exchanges in flow and solutes. There is a need to somehow move aside the complexities associated with the high heterogeneity of heavily modified catchments if sustainable and effective management is to be achieved.

The aim of Chapter 2 is to look at how bringing spatial data together can inform us of the GW/SW connectivity by looking at links and patterns of the catchment characteristics to move towards thinking about GW/SW interactions at the catchment scale, and then onto consider the integral role of the local scale within catchment boundaries. By recognising and mapping the connections provides a basis for discussions between organisations and stakeholders. A review of the existing desk-based approaches to evaluate GW/SW connectivity is first presented. The application of approaches is then discussed in accordance with their usefulness in research and in practice with the assessment of connectivity. The feasibility of the application of these approaches is considered, particularly in relation to data availability and the output usefulness regarding the support of understanding local systems in favour of management decisions, e.g. water quality. Subsequent to this evaluation, gaps in current approaches are addressed, supporting the need for a revised framework to facilitate an integrated understanding of catchments. A proposed framework is introduced and tested using case study examples.

2.2. Integrated assessment of GW and SW quality within catchments

As ICM approaches have become more widely implemented, there has arguably been some recognised success in applying the principles (Rouillard and Spray 2017) in shaping the priorities and approaches in scientific research and in practice to manage water-resource issues (Macleod *et al.* 2007). However, ICM is predominantly focussed at the larger catchment scale (Rollason 2019), assessing the overall status of the water within the defined boundaries of the SW and GW bodies (Smith 2005). Singular issues are addressed at an organisation level (McDonnell 2008), rather than the much-needed focus on multiple pressures operating within the catchment boundaries (Heathwaite 2010). Addressing and solving a multitude of pressures is challenging, and currently lacking the amalgamated attention that ICM seeks to bring to water management linking the processes of the land and water. There is a need to consider the cross-scale interactions in landscape (Green and Sadedin 2005) overcoming the tendency to discount the natural patterns and processes and variability operating across various scales (Harris 2007, Harris and Heathwaite 2012). Most often, water managers are attempting to solve a multitude of problems without an improved understanding of the processes and pollution pathways operating within catchments. Consequently, they are lacking awareness of connections between systems as well as the pollution pressures and drivers and the links between them (Downs *et al.* 1991, Biswas 2008, Kaandorp *et al.* 2018).

Fragmented approaches frequently prevail due to the different types of data required and the level of useful information that can be derived from the available datasets to conceptualise the systems and processes operating by different practitioners involved in the water management (McDonnell 2008). With different actors at different levels of power and priorities, there is a need for a balance between the top-down governance with bottom-up approaches to water resource management such as those under the stakeholder-led CaBA (Deasy 2018). There is a need for more collaborative ways of working to develop a knowledgebase to support decision-making (McGonigle *et al.* 2012). Without such structures and approaches pressures on water quality are often audited, and little improvement in water quality is secured due to the lack of appropriate scientific methodologies and data to understand and access the full extent of problems across the wider catchment (Macleod *et al.* 2007). Therefore, water companies typically attend to anthropogenic pressures with end-of-pipe solutions, addressing the symptoms of issues (Moss 2007, Staes *et al.* 2008). Approaches prevail to manage the wider catchment and natural processes, with a lack of knowledge on the system processes and pathways (Ransley *et al.* 2007, Kaandorp *et al.* 2018).

Typically, the level of information provided by regulatory sampling is spatially and temporally restricted, with the intention being to support the somewhat rapid assessment against statutory measures, for instance the WFD (CEC 2000, Heathwaite 2010, Skeffington *et al.* 2015). The sampling fails to consider other elements and processes and is typically at annual cycles at fixed sampling points (Heathwaite 2010, Environment Agency 2019). The low intensity of the sampling means that often the processes and dynamics operating within catchments are overlooked, despite their fitting and influence into the wider catchment.

Across the surface and subsurface systems, threats accumulate, and it is with the multitude of threats that there is a need to conceptualise the links within and between the systems, considering the links between the pressures and drivers as a function of the catchment characteristics (e.g. Kaandorp *et al.* 2018). Ultimately, better management of pressures on water quality requires an integrated, conceptual understanding of the threats and systems, with a focus on the connections and interactions between them, specifically the landscape and the links with the SW and GW (Biswas 2004, Kaandorp *et al.* 2018). Thus, facilitating a more holistic risk characterisation for ICM, linking individual stakeholders' behaviour and decisions with catchment scale processes (Macleod *et al.* 2007). There is a need to consider the connectivity, from which the processes operating and driving the exchanges between the GW and SW systems can be considered, and the potential impacts on water quality for effective water resource management (Bracken *et al.* 2013).

2.3. GW/SW connectivity

Connectivity is described according to Wohl (2017) as the degree to which matter, and organisms can move in nature within spatially defined units. In streams, connectivity is typically thought of in terms of longitudinal, lateral and vertical dimensions, in which a channel is said to be connected or disconnected to the surrounding environment (Bencala *et al.* 2011, Wohl 2017). Connectivity between streams and the surrounding catchment has been intensively studied, with recent emphasis on the stream-subsurface connectivity, particularly in the last 50 years (Brunke and Gonser 1997, Sophocleous 2002, Fleckenstein *et al.* 2006, Bracken *et al.* 2013, Cardenas 2015). Conversely, GW/SW connections remain poorly understood when it comes to localised management, thus hindering the improvement of water quality. There is often a very broad understanding of the systems, for example, at the regional or catchment scales in accordance with defined spatial extent of water bodies, e.g. between the SW body and regional GW body. However, rarely does this understanding increase in resolution to that within the catchment boundaries. Primarily the short fall in the study resolution is because the systems are highly heterogeneous, complex and require an interdisciplinary focus, something that is not captured well under current legislative sampling, particularly where minor aquifers exist (Jones *et al.* 2000). Consequently, these difficulties result in the detailed understanding being poor due to the nature of any SW scale assessment often being cost prohibitive with limited obvious environmental benefit from a working practice perspective, balancing with other demands, e.g. water provision and regulation (Environment Agency NE, personal communication).

Research on hydrological connectivity has largely focused on the stream-catchment exchanges (Wohl *et al.* 2018), for example, linking to runoff and transport of solutes to streams, focusing on elements of linear pathways and processes. Hydrological connectivity can be very dynamic, particularly at the local scale with increasing variability in the parameters due to spatial and temporal heterogeneity (Rassam 2011, Blume and van Meerveld 2015).

Surface connectivity is often discussed in practice, particularly regarding flood management, whereas subsurface connectivity is more difficult to assess and has led to the development of a range of techniques to facilitate the assessment (Blume and van Meerveld 2015). While emphasis on connectivity continues to grow, it is with an ever-increasing focus on the stream-subsurface connectivity, linking the SW and GW systems, which is essential if we are to better understand the pressures depleting water quality and work towards more sustainable catchment management in accordance with WFD objectives (Fleckenstein *et al.* 2010). Such management should join the views and understanding of individual practitioners, including hydrologists and hydrogeologists, with the need for interdisciplinary and trans-disciplinary communication and involvement. Working across disciplines is essential given that the quality of the SW or GW can deter efforts given the interactions and exchanges between the systems (Sophocleous 2002, Kløve *et al.* 2011). Therefore, moving beyond traditional 'black-box' or 'pipe-system' analogies of the transport of flow and solutes along a stream (Bencala 1993, Bencala *et al.* 2011). There is a need to overcome this restricted focus if we are to achieve sustainable water management, challenging how the SW and GW systems are viewed.

The way in which GW is defined and considered has potential implications for the way that the systems are viewed and therefore the way they are managed in practice. Polices such as the WFD consider GW bodies as a distinct volume of water in an aquifer or aquifers (CEC 2000). The definition differs to the conventional definition of an aquifer, defined as a rock or sediment formation(s) that is saturated by water and permeable to transit water, e.g. to springs (Fetter 2018). GW which is of stream-water origin and held below the streambed in pores or voids for a given time and is often overlooked by top-down management despite its ability to transmit flow and solutes. The way that GW is perceived therefore has an impact on the management attention. The only focus of GW is often from the WFD assessment, therefore challenging the understanding.

Most often, less intensive sampling of GW results in the application of broad-scale understandings of the processes operating between the GW and SW along a whole river reach, rather than attempting to understand the behaviour more closely within a system. Consequently, streams are typically classified as gaining or losing to GW (Banks *et al.* 2011), despite the sub-reach and point-scale variations, which are omitted with coarse-resolution conceptual models (Wainwright *et al.* 2011). There is failure to link the local behaviour to that of the wider catchment, which limits the understanding of the interactions and exchanges along streams (Banks *et al.* 2011). Hence, often only the regional or wider catchment scale is considered of major rivers (e.g. Ransley *et al.* 2007; Environment Agency, personal communication).

As the degree of connectivity and subsequent interactions and exchanges in flow and solutes are highly variable and wide ranging between the GW and SW systems, the choice of approaches is by no means straightforward and is ultimately dependent on the available data and information required. Nevertheless, to facilitate an integrated understanding of riverine environments requires an understanding of the system characteristics, processes and associated drivers both above and below the streambed, as well as connectivity between the systems to determine the state of the GW and SW, and thus better manage the systems (Kaandorp *et al.* 2018). Developing an integrated understanding is twofold, with the need to look at the interactions between threats relative to the landscape structure (structural connectivity) as well as the functional connectivity, which broadly encompasses the way in which the structural units of the systems are linked to which they can collectively affect the hydrological processes, e.g. on the stream flow (Wainwright *et al.* 2011). In the following section, approaches to assess the connectivity using spatial datasets to derive information on the connectivity are discussed.

2.3.1. Relationships between catchment characteristics and water quality

To facilitate the communication and decision-making processes with ICM, new tools of addressing the GW/SW bodies has been necessary (Matthies *et al.* 2007). Such tools require the use of an array of datasets to derive information on the systems, relying on the collation of data across disciplines. The increasing availability of open source data has begun to ease the bottleneck problems of using secondary data held by other organisations (McDonnell 2008). However, when applying such tools, it is how the data is collated and information is derived as to the extent that it is useful in supporting the decision-making process for water management. Often, organisations and stakeholders are targeting the use of such tools to look at the data to support individual, specific problems, e.g. to assess the status of the assets, and not necessarily where or how the water and pollutants travel further, be that downstream or exchanged with GW held in the underlying aquifers. As well as the likely interactions between pressures and drivers (Kaandorp *et al.* 2018).

A key element to researching the riverine environment holistically requires an understanding of the water quality and the stressors, specifically the sources of the threats, e.g. point-source or diffuse pollution, and the drivers of the threats according to the landscape characteristics, e.g. the geology (Kaandorp *et al.* 2018). Research has demonstrated that it is possible to make relatively simple links between catchment characteristics, namely the geology (bedrock and superficial deposit: composition, permeability and thickness), topography, soil hydrology, stream flow, and land cover and even predict future likely changes of the water quality (e.g. Rothwell *et al.* 2010). By doing so, this approach enables an initial insight into the impact of the surrounding system on the water quality, looking at the stream water in accordance to the characteristics of the SW and GW environments, thus facilitating a first-order integrated assessment.

Water variables are often collected at the large scale as part of national initiatives, e.g. as part of the Land Ocean Interaction Study (LOIS) as discussed by Neal *et al.* (2000). Attempts to upscale the understandings using baseline data are outlined in recent work. Rothwell *et al.* (2010) demonstrated the application of the catchment-characteristic approach using Environment Agency monitoring data for North-West England. They undertook spatial analysis of the data in the Terrain Analysis System (TAS) (now known as Whitebox), a freely available package for spatial analysis (Lindsay 2005). Each of the respective catchment characteristics were assessed in turn to determine their relationship with water quality, with the intention of assessing the interaction and role of the respective stream water quality on the landscape (Rothwell *et al.*, 2010).

Whilst allowing for an understanding of the link between the source and point at which the samples have been obtained, the catchment characteristic approach does not consider the interactions between the threats or drivers and is simply looking at the patterns and likely controls on water quality on a factor-by-factor basis, overlaying the water quality data onto various spatial data in GIS. Rather than drawing linear relations between the water quality and characteristics, it has recently been highlighted in the work of Lintern *et al.* (2018) who suggest that there is a need to consider the interactions of the key factors which drive the water quality, focusing on those that control the source, transportation and evolution of the solutes, and how they act. However, such an approach is only viable where there are extensive sampling data available.

The need for integrated studies has resulted in a shifting focus more recently towards looking at the interactions between the stressors, and the role of respective systems on one another given the close coupling whereby poor status of the GW negatively impacts on the stream system (Kløve *et al.* 2011, Kaandorp *et al.* 2018). Research has focussed largely on the effect of stressors on the surface waters (e.g. Rothwell *et al.* 2010), and yet despite a wealth of research on GW/SW interactions (Woessner 2000, Sophocleous 2002), Kaandorp *et al.* (2018) provide evidence that the impact of multiple stressors on the integrated GW-SW systems is somewhat lacking, and therefore missing in terms of management decisions. Where the hydrological and hydraulic data is lacking for both the stream and aquifer, it is necessary to think beyond these constraints and think about how we can describe the systems to support decisions and management.

As part of an integrated assessment of the water quality, it is vital to understand the role of GW on the buffering and propagation of stressors within the SW system. To facilitate a holistic assessment, we should consider the combination of stressors, including the catchment characteristics, scale and management practices which determine the effect of GW drivers and states on the SW, with the impact of the GW state on the SW state occurring in relation to the degree of the connectivity across the streambed (Kaandorp *et al.* 2018). The degree of connectivity is often assumed on the basis of the characteristics of the surface and subsurface environments, such as the depth to the water table, land use/land cover and use of geological and hydrogeological maps (Buss *et al.* 2009). Although, the infrequent and limited monitoring restricts such an approach where water variables are not available to align with the secondary data. Therefore, alternative approaches are necessary.

2.3.2. Connectivity-index approaches

Jarvie *et al.* (2002) note the usefulness of spatial data to look at the empirical relationships between land characteristics and water quality. The increasing use of GIS to visualise and analyse spatial data has enhanced the ability to draw such relations. Considering the links between the land and water offers a basis to start and visualise the connections in the systems. Oyarzún *et al.* (2014) suggest several independent, but complementary approaches to assess the connections between GW and SW: the connectivity-index approach, as well as the use of hydrochemistry and water isotopic geochemistry. However, the latter two techniques require intensive field sampling, or the use of existing datasets, and are not discussed with the context of this chapter. Connectivity-index-based approaches, however, offer an initial screening assessment of the connectivity between the GW and SW systems through the consideration of several factors (Oyarzún *et al.* 2014).

Initially developed by Ransley *et al.* (2007) for the Australian Government, the connectivity-index approach was intended to be used as a screening tool to rapidly assess the hydrological connectivity between the surface and shallow GW of rivers. Data used include water-table depth, the river-channel sediments, the dominant geology, and the site geomorphology (Table 2-1). Each category is assigned specific scores to determine the connectivity and are then combined to give a ranking index for overall potential stream-aquifer connectivity (Figure 2-1; Ransley *et al.* 2007). This mapping method builds on existing techniques that used only depth to water as an indication of potential connection (Braaten and Gates 2002, Ransley *et al.* 2007). The approach provides information to designate the streams as being connected or disconnected and is therefore useful as a precursor to follow-up approaches, such as hydrographic analysis or numerical modelling.

The approach is useful as a first-order assessment of likely interactions across the streambed and provides a simple assessment of the connectivity. However, the approach is with limitations, particularly as the data is accumulated regardless of the resolution, thus failing to consider the connectivity at smaller scales and at dimensions, such as at the near-surface, or in response to changing hydrological conditions. The assigned metric value does not account for variations within a catchment, and in small catchments, only one value would be assigned; the use of classifications is therefore an issue of generalisations between different estimates, such that, they assume the same level of vulnerability regardless of the combination of the attributing factors. Additionally, the understanding is very much limited to the specific point, considering only one form of structural connectivity, which in the case of Ransley *et al.* (2007) it is the geomorphology. However, there is a need to assess the connectivity more holistically, therefore there is a need to consider the interactions between multiple structural characteristics of the environment and of the processes (Oyarzún *et al.* 2014).

Table 2-1: Connectivity index score table - water-table depth (dw), the river-channel sediments (rs), the dominant geology (ge), and the site geomorphology (gm) (Adapted from source: Ransley et al. 2007).

CI = (3)(dw) + (5)(rs) + (5)(ge) + (2)(gm)

Parameter	Class	Score
Water-table depth	<10 m	5
	10-20 m	3
	>20 m	0.5
Channel bed sediment	Sand/gravel	5
	Sandy loam/silty loam	3
	Silt clay loam	-1
	Clay	-4
Geology	Gravel/sand	5
	Clay/sand	3
	Clay	-4
Geomorphology	Erosional environment	5
	Depositional environment	1
	Hill top	0

2.3.3. Assessment of connectivity in practice

Where there is less intensive collection of hydrologic and hydraulic data challenges how we look at the system and quantify the connectivity with regards to management decisions. In the UK, assessing the risk of GW/SW interactions, approaches are very similar to those adopted in Australia, and have been used to develop GW vulnerability maps, providing an estimate of the aquifer designation (Carey *et al.* 2017). Produced in late 2017 by the Environment Agency, the aquifer designation maps are also based on index-based approaches, and used as a high-level screening tool to give practitioners an indication of whether a proposed development or activity is likely to be acceptable (e.g. located in an area of low vulnerability or over productive strata) or of potential concern (e.g. located in an area of high vulnerability on a principle aquifer) (Environment Agency, 2017). GW vulnerability is divided into three classes: high, medium or low. The classification of each 1-kilometre square depends on a calculated score, which considers the influence of each of the layers on pollutant loading and concentration of the water table (Figure 2-1). The score is dependent on a weighting factor and a calculated index score and is calculated as follows:

Vulnerability score = Weighting factor × Index score (summed for all layers)

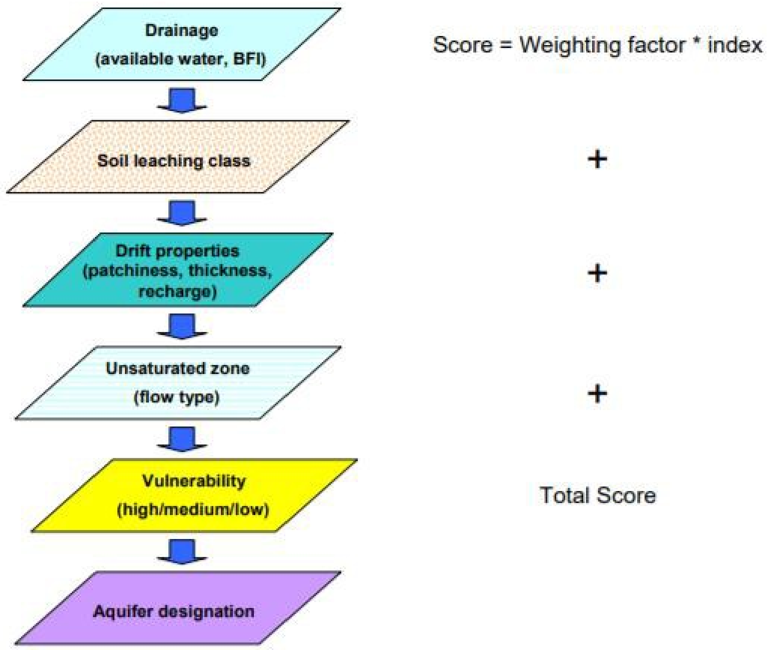

Figure 2-1: Data input into the groundwater vulnerability maps (Source: Carey et al.2017).

The greater the score, the lower the risk of a pollutant affecting the aquifer (greater protection = lower vulnerability). These scores are then converted to vulnerability indices (low, medium or high) using the score bands. The bands vary according to whether the receptor is bedrock or a superficial aquifer and were determined through expert judgement and sensitivity analysis. The final scoring was integrated into a GIS tool to calculate vulnerability on a 1-kilometre grid across England and Wales. These scores were then combined with the bedrock or superficial aquifer designation status to create the final GW vulnerability maps (Figure 2-2).

While proving a useful tool to water managers, the coarse resolution of the outputs means that the systems are generally declared either connected or disconnected on the basis of the low-high risk of exchanges with the surface water body. The combination of datasets used provides a useful precursor to the connectivity at the catchment scale, however, as noted previously, the lumping of the data to give a generalised estimate of the connectivity is of limited use, particularly as one factor could be more effective than the other, therefore skewing the connectivity estimate (Harris 2003). There is no effort to understand the connectivity at a localised, point-scale, looking at the longitudinal, lateral and vertical dimensions associated with the connectivity (Wohl 2017).

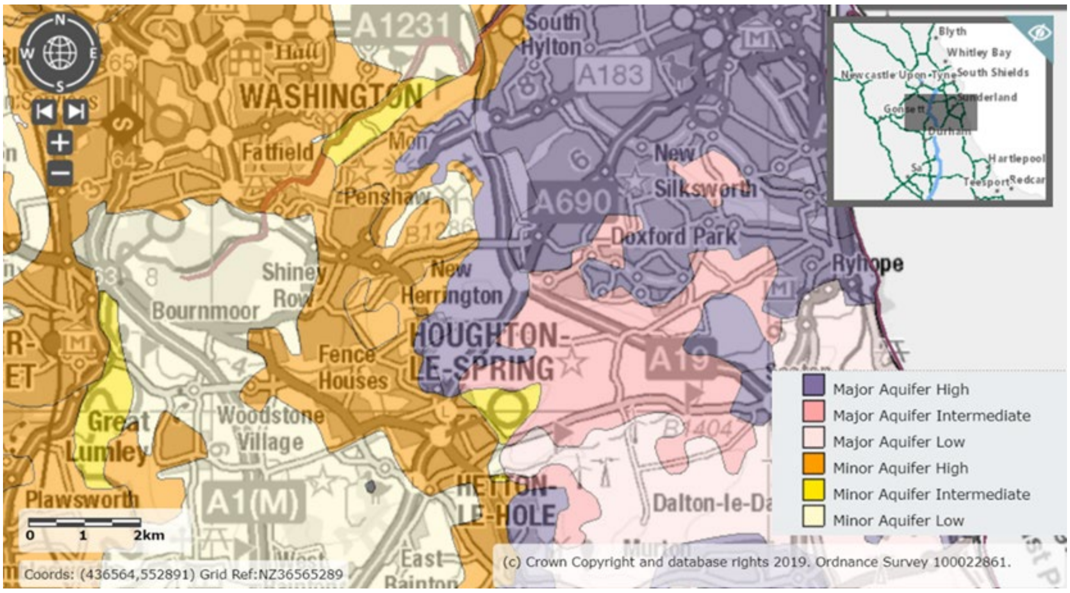

Figure 2-2: Screen-shot of GW-vulnerability map (Adapted from source: DEFRA 2019).

Therefore, in practice, a tool of this sort is useful as a primary basis for thinking about management interventions. However, as noted above, the connectivity of the GW and SW is restricted to a simplified loss/gain along a river reach, therefore the pollution pathways are often subject to a limited understanding. As a result, practitioners are lacking a holistic sense of awareness and thus limiting integration in management practices across catchments, resulting in the top-down priorities, and overlooking processes and pathways within the catchment that could help better manage threats.

In order to better understand the pathways and processes operating at the GW/SW interface, it is necessary to develop the conceptual understanding of the systems, looking at the multi-dimensions, beyond a coarse catchment resolution. For instance, through personal communication with the NE Environment Agency they confirm that a conceptual model of the Magnesian Limestone GW body was prepared in 2009. In this the EA examine the links between the structural units of the region in contact with the GW body, and assess the potential routes of water movement, to and from the surface water, using spatial data (Environment Agency NE, personal communication). There is no similar conceptualisation for elsewhere in the Wear catchment. There is a need to further develop a conceptual understanding, looking across the multiple dimensions, assessing the connectivity within catchments and along river reaches, incorporating elements of directionality, rather than assuming systems are entirely connected or disconnected, with gains/losses to the GW body.

2.3.4. Gaps in existing approaches

It is evident that for a holistic, integrated assessment of water quality that there is a need to consider the interactions between multiple stressors acting on the GW and SW systems. The influence of the threats on the respective systems is attributable to the degree of connectivity, from which the impact of the GW on the SW can be evaluated, be that a buffering or propagation potential of the incoming threat. Assessing the interaction of multiple stressors is somewhat more complex than looking at individual stresses relative to the surrounding catchment characteristics and requires more extensive water quality data records than those available in several catchments in the UK. While index-based approaches offer a first-order insight into the potential locations of GW/SW connectivity based on the structural units of the landscape they are somewhat limited. It is not possible to assume that classifications of the GW/SW connectivity are characteristic of the patterns and processes in specific catchments. There is a need to look at the connectivity more specifically. However, classification scores for the broad scale often this is the only understanding of the connectivity that exists on which to base management decisions. Although, the low spatial resolution (e.g. 1 km) means that potential pathways between the GW and SW systems are omitted, instead looking only at the bigger picture of dominant flow paths, and therefore overlooking any smaller disconnected ones which arise as the combination of structural units (Wainwright *et al.* 2011). Additionally, the functional connectivity between the structural units of the systems are unaccounted, and rarely are the data considered together. There is a need to look at the connections at multiple dimensions and time (see Figure 1-6) and use the understandings of connectivity for catchment management, something that is lacking (Heathwaite and Harris, 2011), with the support of discussions across and between disciplines.

While the index-based approaches utilise useful data, it is the way that it is brought together that is important, because an index score or classification does not facilitate an insight into the individual processes and links between drivers, and it cannot be assumed that the patterns and processes at the local scale are the same between catchments attribute to that same score of connectivity. The individual pieces of data in themselves can provide useful information about the surface and subsurface environments, it is a matter of exploring them individually and then together, constructing a more complex picture from simple links. There is a need to appreciate that when moving across scales within the catchment, from point to GW catchment scales that a low-resolution conceptual model may exhibit disconnectivity because one parameter becomes effective at a higher resolution. However, at a higher resolution the system may exhibit localised connectivity, which does not extend far enough to be evident at the coarse scale. As structural connectivity can emerge from a combination of different elements, and therefore, the lumping of the elements together is not so useful to assess for an integrated understanding. There is thus a need to look at the controlling elements in turn and bring the data together in a framework to make this assessment in more complex catchments.

2.4. Introducing the Integrated River Evaluation for Management Approach

If we are to work towards developing an integrated understanding of the systems, supporting management, there needs to be an improved understanding of the patterns and processes across multiple dimensions, and times if possible, beyond that of the catchment-unit scale. We need to find ways to amalgamate these data to inform understanding of SW GW interactions. Such an understanding is required to understand processes and pathways within the catchments to feed into management decisions in dealing with threats, which are often currently managed based on treating the GW and SW as decoupled systems.

IREM is proposed as a novel framework in which existing data can be brought together to assess linkages within catchments, and here I am looking to assess the hydrological connectivity within and between the GW and SW systems. In this approach I demonstrate the feasibility of using existing data to identify local links and pathways, where there is very limited simultaneous sampling of water quality. Bringing together such data supports the determination of the likely interactions in flow and solutes, in turn delineating the pollution pathways, which are largely unaccounted using current approaches. The IREM framework enables the consideration of multiple threats, both above and below the streambed moving away from the segmented viewpoints, with the aim of supporting further investigations and water management decisions.

The key objectives of IREM are to:

1. Identify and map the threats and drivers to the surface-water and GW systems, the former using walkover surveys and discrete water quality sampling, and the latter based on personal communication with regulating agencies, and map these using GIS;

2. To infer flow and solute pathways, looking at the multiple threats; and

3. Providing a framework to understand and look at the processes and water- quality issues.

2.4.1. IREM concept

IREM is proposed as a simple, first-order approach to provide an approximation of the characteristics and connectivity within catchments, providing a basis to then assess the likely GW/SW exchange pathways operating at the local reach and sub-reach scales. The novelty of IREM is that the approach is developed to utilise existing, freely available data, to assess the structural and functional connectivity within catchments, considering multiple spatial dimensions and time. The framework allows for the state of connectivity to be determined where intensive and simultaneous monitoring of the GW and SW has not been performed. As acknowledged previously, there is a range of existing data that can provide useful information about surface and subsurface environments, and here

I explore the collation of this data to develop a conceptual understanding of the systems. In practice these data, for instance, surface runoff and superficial deposit thickness are not typically brought together to investigate and conceptualise problems within catchments, instead there is typically a dependence on metric-based estimates, which offer limited insight, particularly when interested in smaller scale variations accounting to localised issues.

IREM allows for a holistic assessment of the system behaviour and connections required to deal with contemporary fluvial challenges, a key priority, moving beyond the fragmented view of the systems (Staes *et al.* 2008) to bring together data that helps to understand interactions between SW and GW that influence water quality (Figure 2-3). Where there are multiple threats to the water quality, a point-source attribution is inappropriate, as the threats themselves and the pathways intertwine resulting in diffuse pollution from a multitude of sources (Heathwaite 2010). Previously, attempts have just focused on the threats and local-scale assets, failing to demonstrate the ICM principles, which overlooks the multiple stressors affecting the water quality. There is a need to develop an understanding of the local links, moving towards understanding the processes and pathways likely operating within catchments to then challenge the current management of water-quality issues with a holsitc and integrated focus.

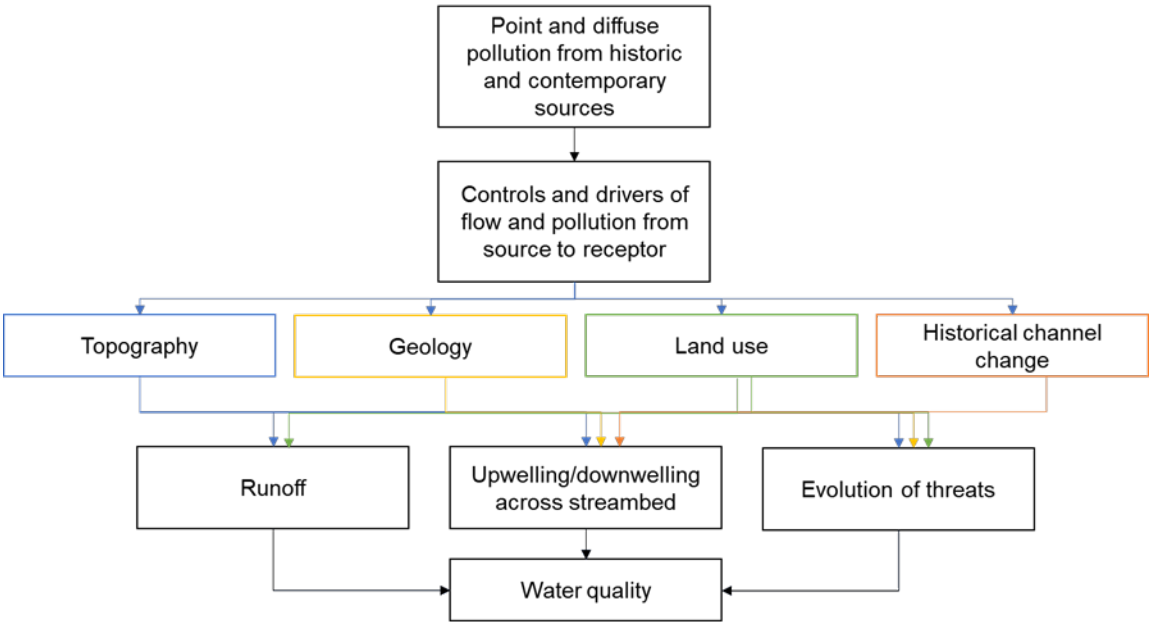

Figure 2-3: Data use in IREM, illustrating the links between elements/factors to derive patterns and pathways accounting to the overall conceptualisation of the catchment systems and resulting water quality.

2.4.2. The application of IREM

IREM is operationalised as a series of phases, in which elements come together to allow for an evaluation of the management of the rivers in question. The four key phases of IREM are outlined in the following sub-sections.

2.4.2.1. Phase 1 – Identification of threats

Overview: Data collection and collation to facilitate the identification of pollution threats towards water quality, identifying the pressures and drivers from which connects the pollution source to receptor, in this case, the channel and subsurface environments.

Within a GIS framework, existing spatial data are collated, allowing for visualisation and spatial analysis. Understanding the multiple threats to the system and water quality holistically requires a focus of the drivers and pressures, which are not typically routinely mapped across catchments. The former including factors such as the land use, land cover, discharge points, such as sewage treatment works and combined sewer overflows. Additional data mapped include topography, the channel evolution and geology, including the superficial deposit characteristics (e.g. the drift deposit thickness and composition) to consider the links between threats and the drivers between them (see Table 2-2 for the data used in IREM). In support of the identification of the threats to the SW, discrete water samples from the stream were obtained to provide a basis for understanding of the water (see Appendix A for grab-sampling procedure). Samples of GW are limited to boreholes, and are restrictive, mainly in minor aquifer systems.

Table 2-2: Data used in IREM, including details of the data source analysis.

Data	Source	Analysis	Type	Purpose of data
To understand pollution pressure and drivers				
Assets and consented discharges	Secondary (Environment Agency, Northumbrian Water)	NA	Secondary	Map threats to water quality
Spot samples for water quality	Field data	Laboratory analysis of anions and cations	Primary	Current standards of water quality, beyond regulatory sampling
Water table position	Secondary data (Coal Authority)	NA	Secondary	Water table position – current and future`
Walkover surveys	Field data	Supplementary notes	Primary	Validation of land cover, land use, point-source discharges
To understand pathways				
Land use/land cover	OS via EDINA Digimap	NA	Secondary	Characterise catchment
Topography	OS via EDINA Digimap (1 m LiDAR DTM)	Estimation of runoff pathways using hydrology tools in ArcMap	Secondary	Runoff pathway Estimation using D8 algorithm (O'Callaghan and Mark 1984) in the catchment calculated using a pit filling technique of the DEM (Wang *et al.* 2011).
Superficial deposit thickness and lithology	BGS via EDINA Digimap	Estimation of pathways based on thickness and lithology type	Secondary	Composite risk maps
Bedrock geology, faults	BGS via EDINA Digimap	Estimation of pathways	Secondary	Composite risk maps

2.4.2.2. Phase 2 – Structural connectivity

Overview: Development of composite indicators (i.e. risk maps), inferring patterns and processes and links between the systems based on the catchment characteristics, looking at the structure of the landscape.

Following the collection and collation of data in ArcMap, analysis of the data to infer pathways was performed, specifically the estimation of runoff pathways based on the topographical (DTM) data using the Hydrology Toolbox, as well as the generation of composite risk maps according to the superficial deposit thickness. Within ArcMap, the estimation of the runoff pathways is not without making several assumptions. Effectively the generation of the pathways is as a form of black-box modelling, because inputting the topography and getting an estimate of the flow path based on the smoothed, filled surface slope, thus overlooking, e.g. the soil storage capacity. Nevertheless, the output pathways are a useful proxy to delineate flow routes.

The composite risk map was prepared in accordance to the methodology discussed through personal communication with the North-East Environment Agency. The relative thickness of the superficial deposits was used as a primary indication of the risk, whereby those less than 5 m were deemed to associate with a very high risk of connectivity, less than 10 m high risk, and greater than 10 m low risk, similar to those used by the Environment Agency (Carey *et al.* 2017, Environment Agency NE, personal communication). The level of risk of connectivity is associated with the deposit thickness as a proxy value of the zone over which GW and SW would have to travel across the superficial deposits to reach the respective systems. That is with the assumption that the water table is not rebounded through the superficial layer, and that the deposits separate the shallow and deep GW.

2.4.2.3. Phase 3 – Conceptualisation of GW/SW connectivity

Overview: The third phase of the IREM approach involves the scaling down of the focus from the catchment scale and looking at the links between the structural units likely operating within the catchment boundaries, against the specific issues/threats identified. At this stage discussions between practitioners would be encouraged. The links are considered here as potential pathways for the transport of flow and solutes. For example, pathways may be inferred and delineated by the historical channel change or the presence of geological faults, thus looking above and below the surface.

2.4.2.4. Phase 4 – Revised understanding of GW/SW connectivity

Overview: The final phase of IREM focussed on discussing the new understanding to the catchment as an integrated holistic system to guide management, and what the results mean in practice.

The final phase of IREM involves evaluating the current understanding of the systems and management practices held by practitioners and stakeholders at present, and from this evaluating what the conceptual model developed in phase 3 of IREM brings to and challenges this current approach. It is about assessing what the collation of existing data can bring to the way in which we view and conceptualise the processes within catchments, and what this means for water quality.

2.5. IREM pilot test – Wear catchment

The application of IREM is demonstrated using two case study examples in the River Wear catchment: the Herrington Burn and Twizell Burn (Figure 2-4). The Herrington case is written up in detail to illustrate the application of IREM and how results have shaped water resource management. The Twizell case is presented as a short summary to demonstrate how IREM works across heavily modified tributary catchments with the need to address a multitude of pressures in complex settings. The application to the Twizell provides the baseline study for the subsequent research presented in Chapters 3 and 4, looking at the interactions and exchanges in flow and solutes. It was not possible to proceed with intensive sampling on the Herrington due to the nature of the streambed and selection of appropriate long-term sampling sites.

At present, water quality is managed in both catchments from a predominantly SW or GW perspective, despite the potential coupling with the respective system (Kløve *et al.* 2011). Through the application of IREM, pressures and the likely states of the GW and SW based on the connectivity between the systems will be identified, considering the four dimensions, spatially (x, y, z) and temporally, moving beyond the broad catchment-based understanding held at present. Both catchments are heavily modified, with historical mining and contemporary water quality issues attributed to effluent releases and misconnections, with the focus for management on end-of-pipe solutions, bearing little thought to the GW/SW interactions, which have not previously been accounted beyond that of the Magnesian Limestone carried out for the Environment Agency. The underlying GW is also heavily modified due to both historical coal mining and current mine water level control – a mitigation measure required to protect the rivers from pollution of iron from rising mine waters, now that the mines are closed (Personal communication with the Coal Authority via the Wear Rivers Trust).

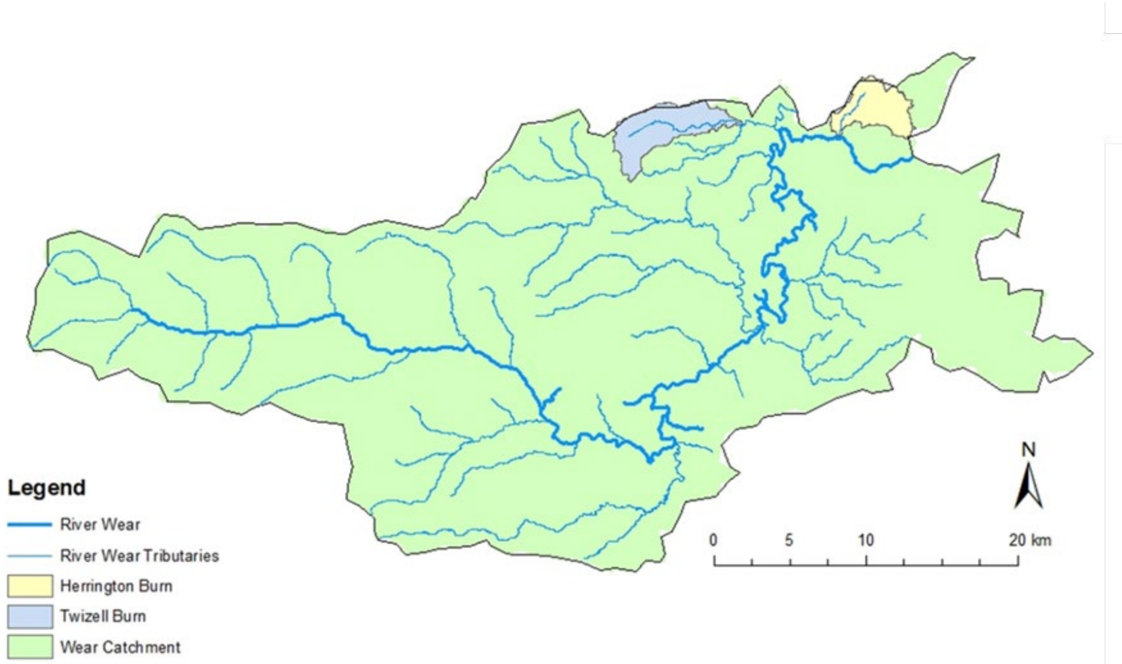

Figure 2-4: The Herrington Burn and Twizell Burn catchments relative to the River Wear, NE England.

2.5.1. Case study 1: Herrington Burn

The Herrington Burn (catchment area: 13 km^2) is a heavily modified tributary of the River Wear (Figure 2-6; Figure 2-5). Underlain by the Pennine Middle Coal Measures and Magnesian Limestone (Environment Agency 2019b, 2019c, Figure 2-5), the GW is classified 'poor' according to the WFD (Environment Agency 2019b), and the overlying SW as 'moderate' (Environment Agency 2019d). There is an objective to move the assessment of the Magnesian Limestone and stream-water quality to 'good' by 2027 (Environment Agency 2019b, 2019d). There is no similar objective for the Coal Measures, that is despite the extensive coal and metal mining waste effluents, with GW quality set to remain of poor quality (Environment Agency 2019c). There is a need to extend the understanding of GW/SW interactions, particularly in the area of the Coal Measures (Figure 2-5), with the potential detrimental effect of GW on the connected SW.

Water quality is a key challenge in the Herrington, especially regarding elevated nitrate concentrations in GW abstractions through the Magnesian Limestone at the borehole marked on Figure 2-5 (Northumbrian Water, personal communication). Currently, efforts are reductionist, targeting the impact at the receptor, in this case, the abstraction borehole, whereby prior to pumping as drinking water, the abstracted GW is blended to lower the nitrate levels for safe consumption. However, great costs are associated with the decontamination of the abstracted water. The reduction of such costs calls for more effective management with an exploration of potential sources and pathways of nitrate. Practitioners at the Environment Agency and Northumbrian Water initially believed that the nitrate source was attributable to the downwelling of poor-quality SW. Limited sampling and conceptualisation of the catchment inhibits the understanding and addressing of problems, such as that of the borehole. There is a need to conceptually understand the connectivity before it is possible to start thinking about the water movements and why the water at the borehole is contaminated, identifying potential pathways within the catchment, thus accounting for the local-scale characteristics, assisting in the addressing of a specific problem.

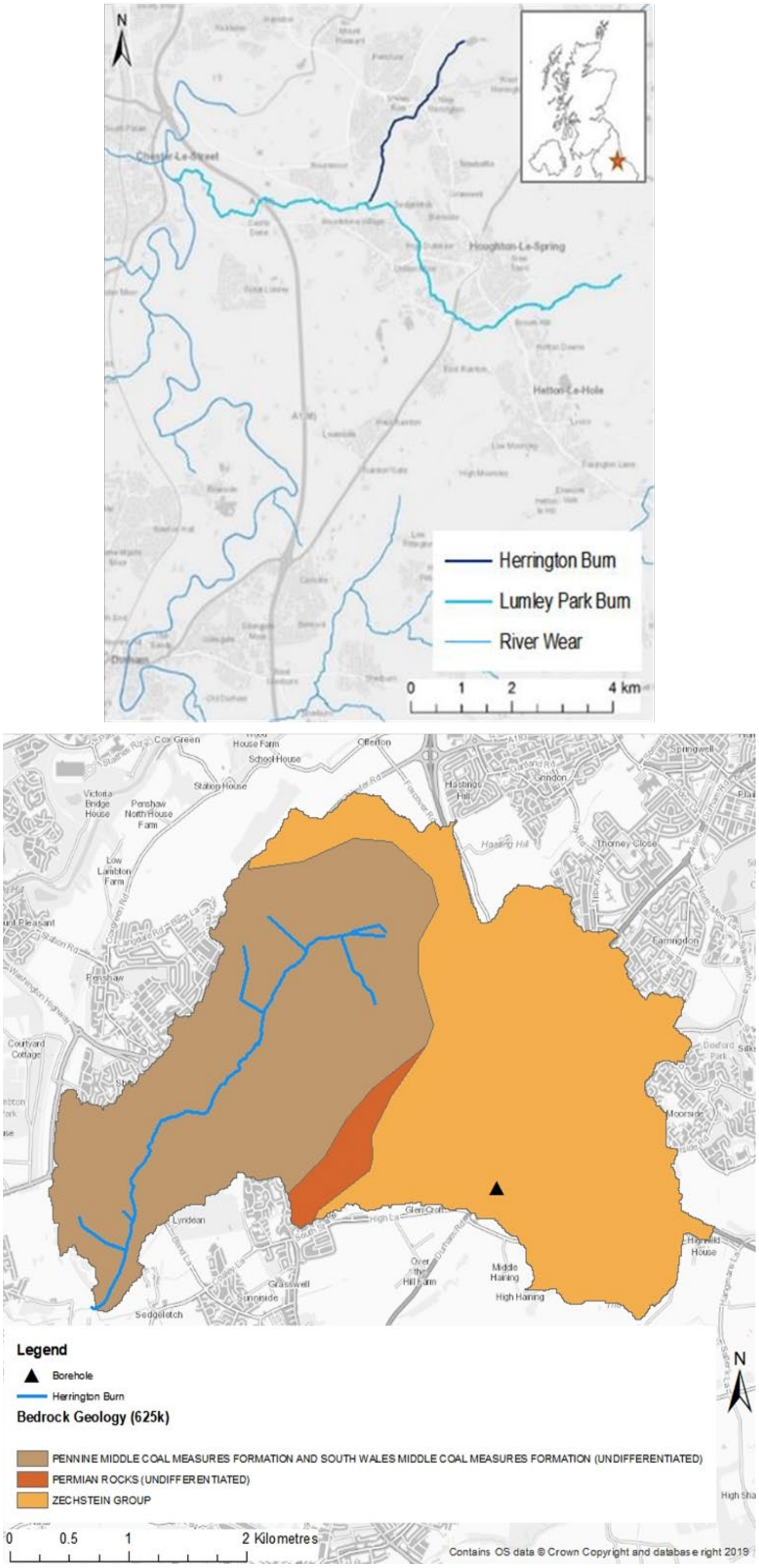

Figure 2-5: The Herrington Burn, tributary to the Lumley Park Burn and River Wear. Lower– borehole location and bedrock geology 1:625k (source: BGS 2010).

2.5.1.1. Identification of water quality threats/stresses

Threats within the SW catchment boundary of the Herrington are broadly encompassed as historical and contemporary sources attributing to surface coal mining and waste-water effluent releases respectively (Figure 2-6). Whilst some effluent releases are consented, others are intermittent from combined sewer overflows (CSOs) and outfalls, with releases most likely during storm events (Northumbrian Water, personal communication). There is the added pressure from redevelopment in the catchment, with expanding residential areas in the middle and lower Herrington, however, the impacts are not explored in the scope of this study. Consequently, a multitude of threats are present, from which pollutants can enter the stream from the landscape, including diffuse pressures from the surface, including those from worked coal mines and associated spoil heaps (Figure 2-6), besides from contemporary land use (Figure 2-7), e.g. animal grazing and pastoral farming.

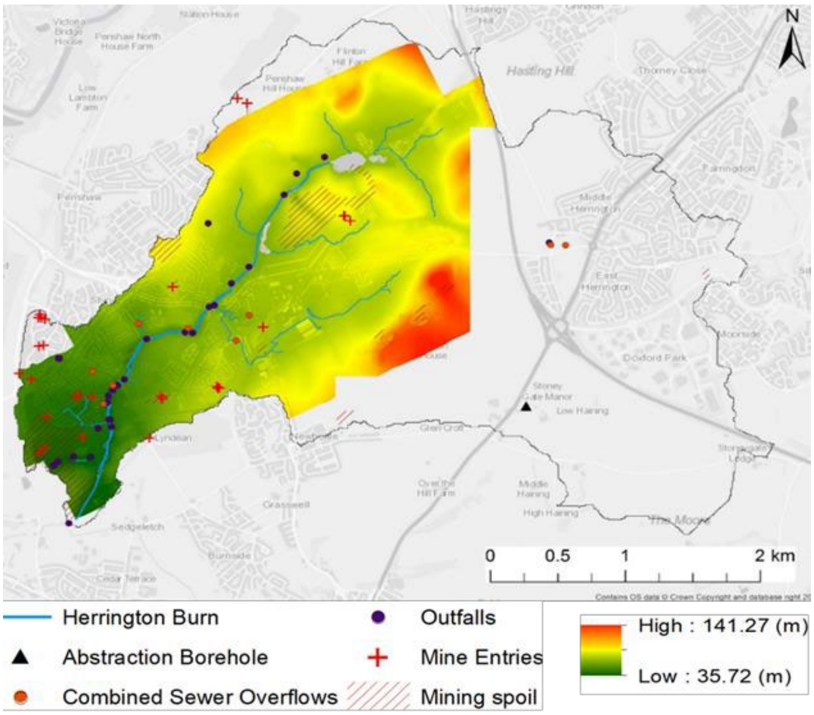

Figure 2-6: SW network, showing mining and effluent threats (Source: Coal Authority 2018, Northumbrian Water, personal communication), with elevation (Data sourced from: Environment Agency 2015).

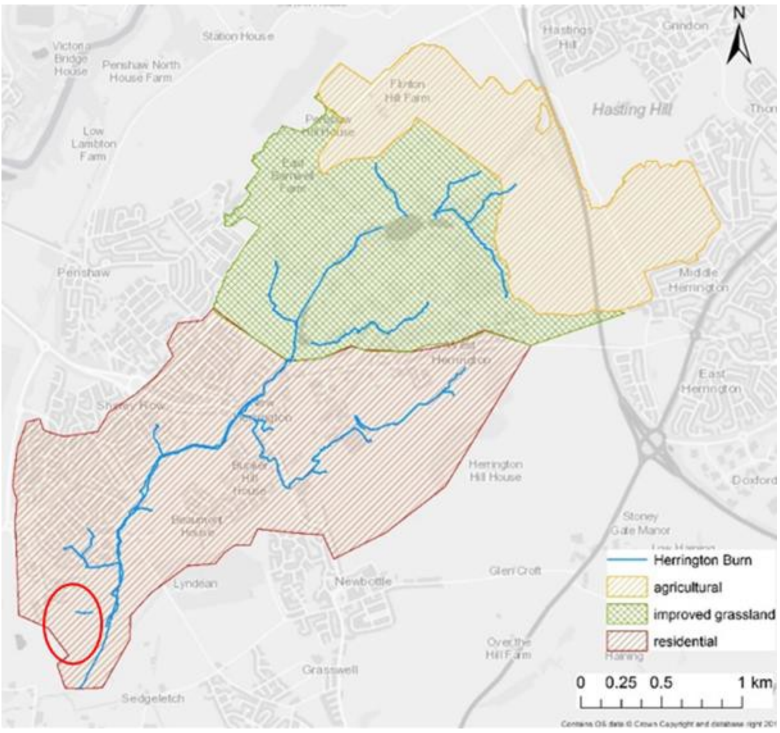

Figure 2-7: Simplified land cover map of the Herrington Burn catchment (adapted from source: NERC - CEH 2007). Marked is the continuing residential redevelopment at Elba Park.

SW quality is typified with localised spikes in sulphate and nitrate compounds, likely associated with the mining and effluent wastes respectively (Figure 2-8). Meanwhile GW monitoring of the abstractions from at the borehole (Figure 2-6) indicate elevated nitrate concentrations, around 80 mg/l – according to sampling conducted by Northumbrian Water (personal communication), The concentration is much higher than that in the stream. Initially practitioners suggested that the GW nitrate source was from the SW. Although, the quality of the stream water questions this (Figure 2-8), with the need to further consider the system characteristics.

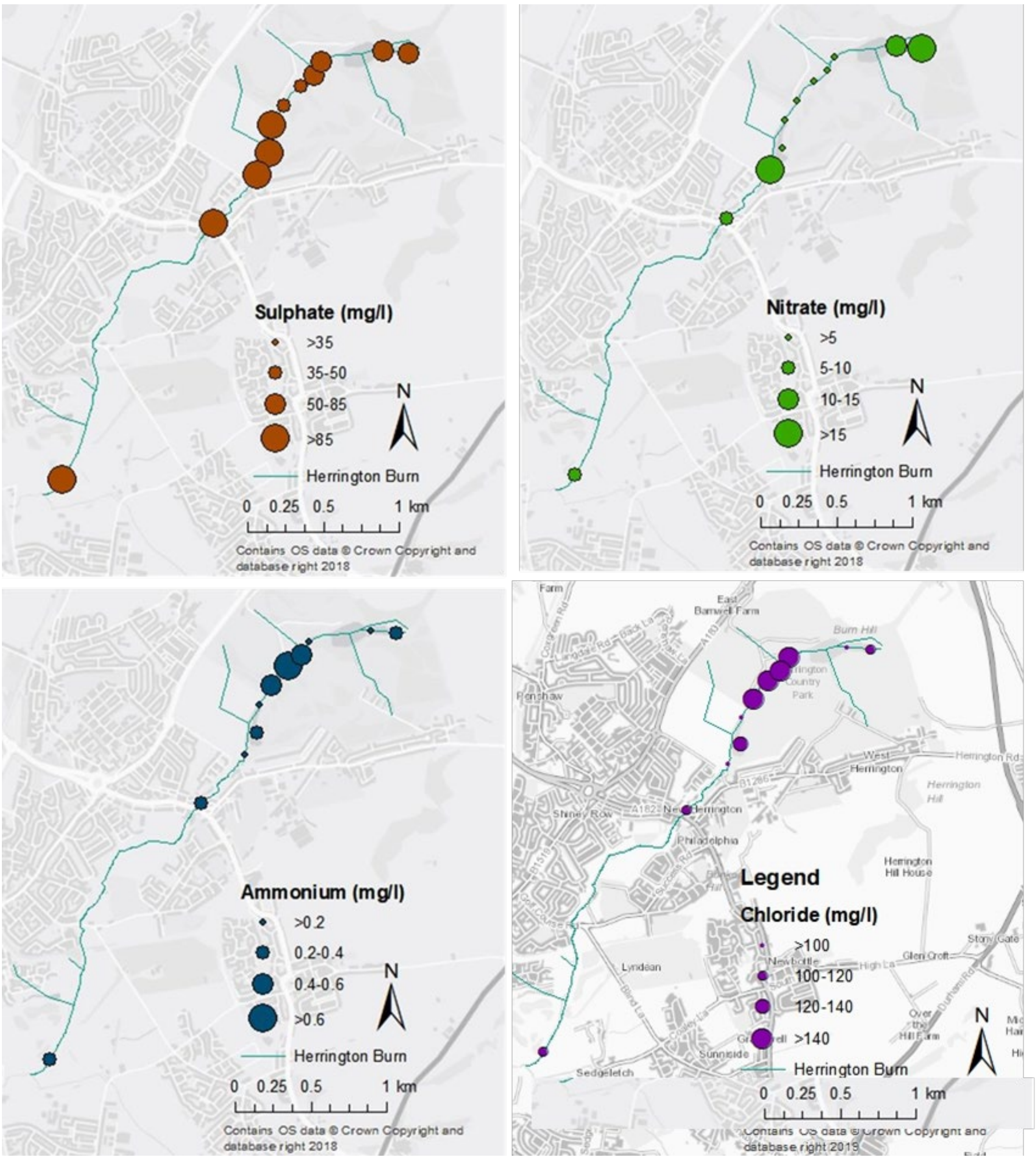

Figure 2-8: SW sampling locations during September/October 2016.

2.5.1.2. Structural connectivity

Initially the hydrological connectivity was assessed between the land and surface-water. Estimating the surface-stream runoff pathways using LiDAR DTM data and the ArcMap hydrological tools show several potential overland routes by which water enters the channel (Figure 2-6). Although they have not been validated during storm events, they are deemed potential routes through which the runoff could enter the channel as observed during walkover surveys. The stream is evidently well-connected to the surrounding hillslopes, with associated point-source releases, as well as sources of diffuse runoff, corresponding with localised chemical changes (Figure 2-8).

The presumption from practitioners was originally that the stream was losing to GW, hence the loss of pollutants to the ground; this has been the working hypothesis, which overlooks the more localised patterns along the reach, which may be caused by sub-reach variations in the superficial deposit thickness and permeability. The connectivity across the streambed was deemed to be a function of the thickness of the superficial deposits, the likelihood of exchange is summarised by a composite risk map (Figure 2-9). Where the superficial deposits are less than 1 m, GW/SW exchange were considered highly likely (Environment Agency NE, personal communication). Looking at Figure 2-9, the thickness of the superficial deposits in the Herrington headwaters', SW to GW losses appear likely (Figure 2-9). Thus, supporting the likelihood of loss of nitrates at the headwaters, with potential to enter the subsurface via discrete pathways, potentially entering the deeper strata via geological faults (Figure 2-9), or into the drainage network. Although such assumptions need to then be questioned with the addition of other data sources.

As the depth of the water table in the upper aquifer of the superficial deposits is unknown, with no sampling boreholes in the vicinity, although it is probable that given the relative thickness of the deposits that there is no attenuated, or perched water in the superficial system (Environment Agency NE, personal communication). Perching of water is more likely in the artificially modified land, such as the spoil heaps and landfill, not directly below the stream (Environment Agency NE and Northumbrian Water, personal communication, Figure 2-9).

Assuming the stream is essentially 'leaky', with permeable silts and clays (Figure 2-10) and that there is limited potential in the superficial deposits for perching of water it is highly probable that the stream-water leaks directly into the unsaturated zone below. The extent of the unsaturated zone is to a depth of 30 m below the streambed (Personal Communication with the Coal Authority via The Wear Rivers Trust), comprising bands of mudstones and sandstones, with geological faults lines intersecting the strata (Figure 2-10). Despite the potential of diffuse and direct pathways to the subsurface, via the superficial material and faults respectively (Lawler *et al.* 2009, Tellam 2009), the stream-water nitrate concertation is much too low (Environment Agency NE, personal communication). Further discussion with practitioners during the research and given the low nitrate concentrations in the SW, efforts were subsequently focussed beyond the channel, looking more closely at the subsurface.

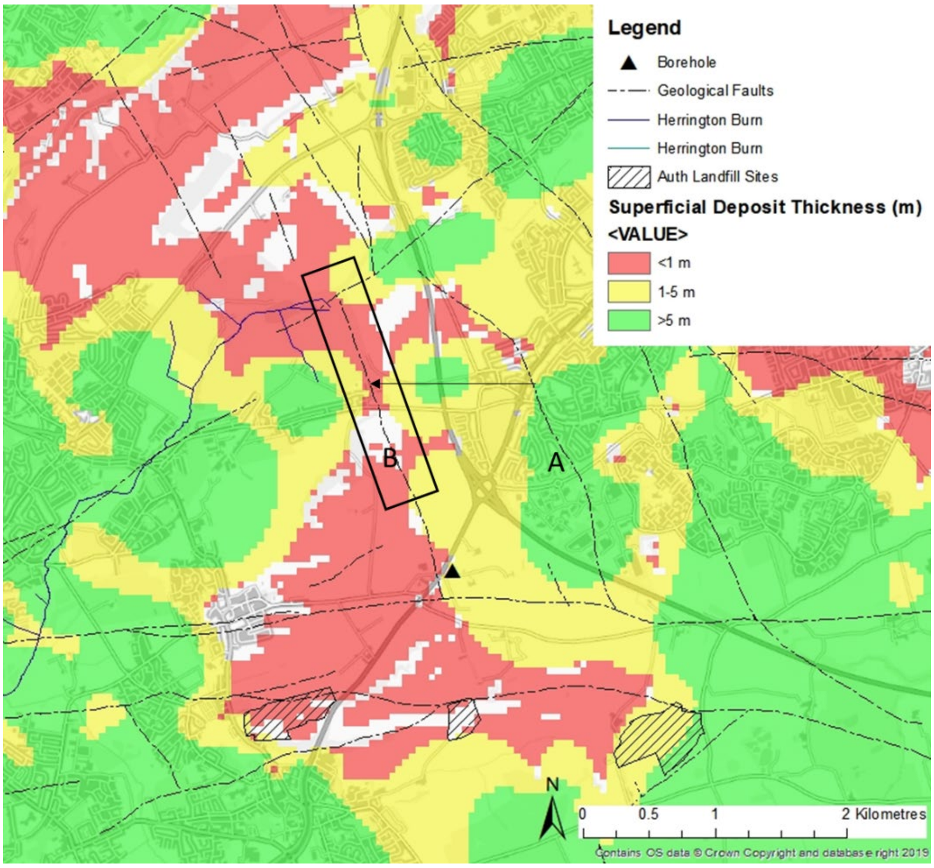

Figure 2-9: Superficial deposit thickness with inferred geological faults (Source: BGS 2013) and SW connection (A to B). Rectangle shows the hypothesised nitrate source zone.

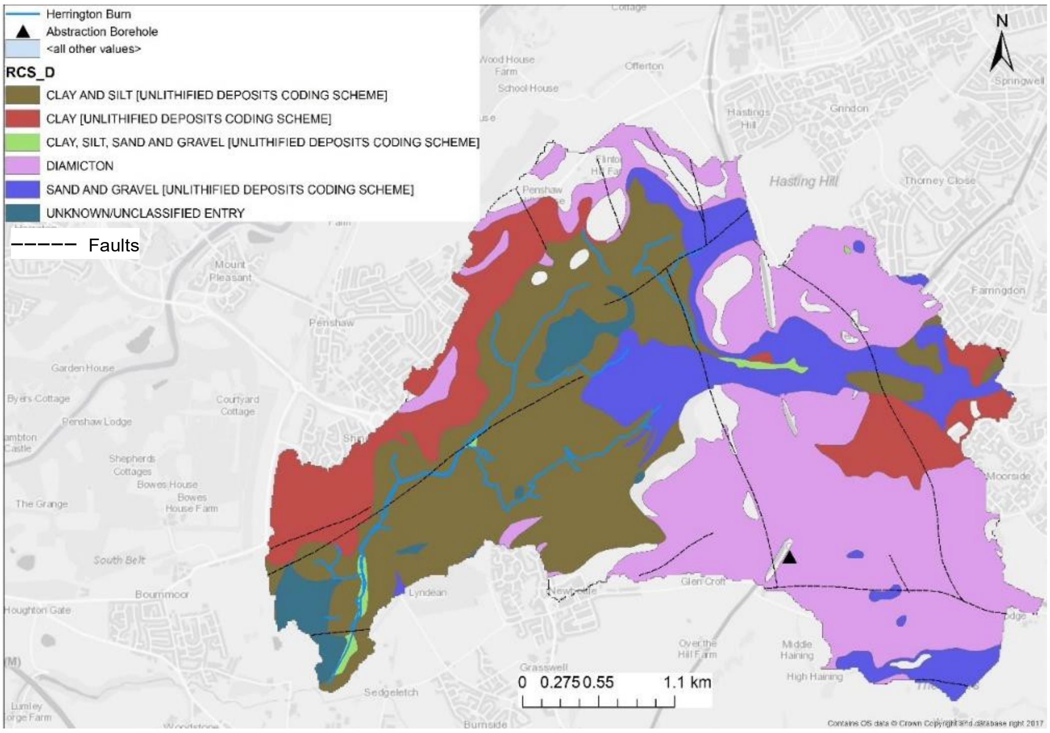

Figure 2-10: Superficial deposit composition and inferred geological fault lines (Source: BGS 2013).

Collating additional data with the composite risk map, the nitrate source was reconsidered, taking a closer look at the subsurface environment. It was subsequently hypothesised that nitrates could be either entering directly into the subsurface via the hillslopes, e.g. from landfill (Figure 2-9) and flowing towards the borehole via a geological fault (marked B – Figure 2-9). Or, that polluted water was directly entering the system via fault A (Figure 2-9) and flowing towards fault B, and onto towards the borehole. The A-B fault connection was also considered to be via the surface. It was found that under collation of the historical channel maps, that there is a historical path of the Herrington (Figure 2-11). Now culverted, water drains from agricultural fields into the drainage system via this path, thus potentially transmitting polluted water from the Herrington headwaters. In the headwaters, SW sampling was indicative of nitrate enrichment (Figure 2-8). However, subsequent interrogation of the drainage network led to discount any leaks in the system (Northumbrian Water, personal communication).

While the investigations in the Herrington continue, IREM has proved insightful in re-evaluating the landscape, stressing the need to consider the multiple spatial and temporal dimensions when focusing on water quality problems. The complexity of the issue is high, however, bringing data together has facilitated several avenues of investigation. As Figure 2-11 shows, the accumulation of data supports the hypothesising and testing of several ideas, of which would not have been considered without inferring connections in the landscape

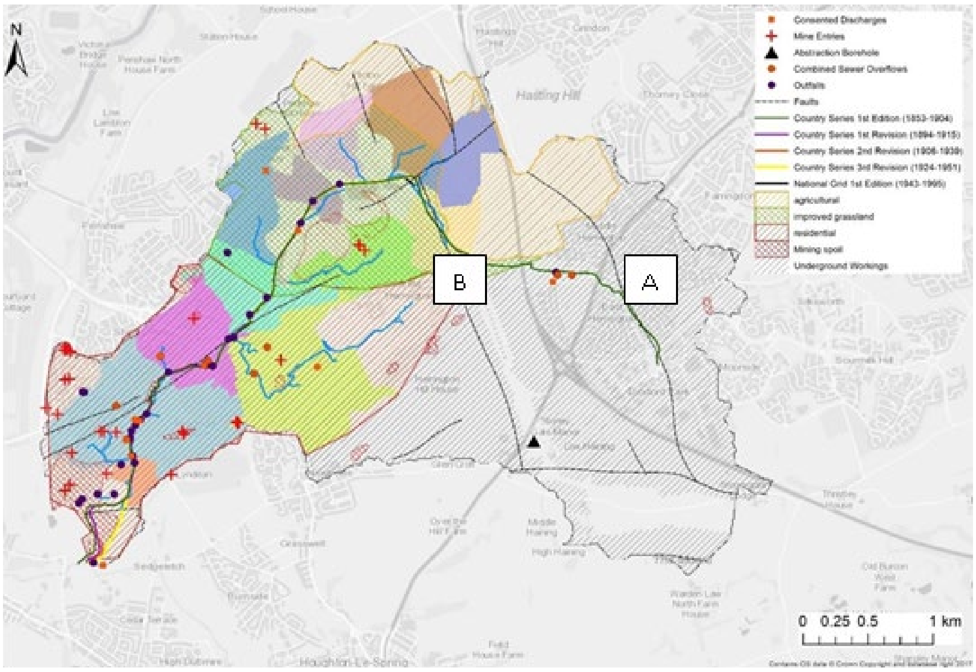

Figure 2-11: Historical Vs. contemporary path of the Herrington Burn (Source EDINA Digimap © Crown Copyright and Landmark Information Group Limited 2018. All rights reserved. [1853-1995].) with contemporary and historic threats (Source: Northumbrian Water, personal communication), land cover - 2007 (Source: NERC - CEH 2007), mine entries (Source: Coal Authority 2018) and geological faulting (Source: (BGS 2013) and source-areas contributing runoff to the channel.

2.5.1.3. Revised understanding of GW/SW connectivity in working practice

By bringing together data and assessing the links between factors influencing exchanges between surface and subsurface systems, a more complete conceptual understanding of the systems can be derived and hence facilitates a more robust assessment, e.g. of the nitrate source problem in the Herrington. While it was initially thought that the nitrate was sourcing from the stream-water, subsequent explorations initiated on these research findings have led to this theory being discounted. A series of other sources were investigated in follow-up to the enhanced insight into the connectivity. Specifically, the leakage from the urban drainage network at the head of the Herrington, runoff from landfill (based on the land-stream connectivity) and more recently to look more closely at potential damage to the borehole fabric. Site investigations are still on-going, with most recent efforts are focused bailing of water from the borehole for subsequent chemistry determination. From the testing, it appears that the source of nitrate is localised at around 50 mAOD (Northumbrian Water, personal communication).

Only by understanding the four dimensions together using the IREM approach was it possible to challenge previously held assumptions and explore small scale vertical dimensional changes within the systems; if the vertical component of the system was constant would have meant such important findings would have previously been overlooked. Comparing data over a period, specifically historical information with current information, enables for a time dependent assessment to be undertaken.

2.5.2. Case study 2: Twizell Burn

A brief write-up of this case study is presented to illustrate the application of IREM to a second catchment: the Twizell Burn (catchment area: 19 km^2, Figure 2-4). Similar to the Herrington, the Twizell is currently failing to meet the WFD objectives (Environment Agency 2019a). The Twizell has been exclusively managed from the SW environment. Threats to the SW comprise effluent releases associated with residential areas (CSOs and releases from the sewage treatment works) and historic coal mining spoil heaps (Figure 2-13). GW quality is poor due to mining impacts, attributing to the mobilisation of concentrated oxidised pollutants from mine water rebound and the saturation of old coal workings. The National Coal Board (precursors to The Coal Authority) predicted iron-rich mine water would discharge to the River Wear and its tributaries, the extent and impact, however, remains unquantified (Groundwork NE & Cumbria 2015). Managed GW rebound through the Coal Measures has been achieved through pumping, thus effectively disconnecting the GW in the bedrock aquifer from the rivers. However, the role of perched GW in superficial deposits are now questioned as to the impact they have on the SW system (Environment Agency NE, personal communication). Practitioners have previously addressed the GW and SW systems of the Twizell to be disconnected, that is despite the heavy modifications. Discussions arising from the TOPSOIL partnerships have led to question the connectivity of the Twizell, moving from the focus of the GW and SW systems been closed from one-another.

2.5.2.1. Mapping of threats to water quality

A multitude of stressors are affecting the stream-water quality of the Twizell (Figure 2-12). While effluent releases from assets are largely addressed by the water company, additional diffuse source, including coal mining effluents are not dealt with, therefore there is a need to quantify the threats and start thinking about the pathways and impacts (Groundwork NE & Cumbria 2015). As with the Herrington, the understanding of the systems within the catchment boundaries are deterred with the focus of monitoring and management from a prevailing statutory perspective. Thus, calling for the mapping of the threats to water quality as the starting premise of an improved understanding of the systems. As with the Herrington, the connectivity of the systems across the multiple dimensions has been interrogated, looking at the that the connectivity between the systems.

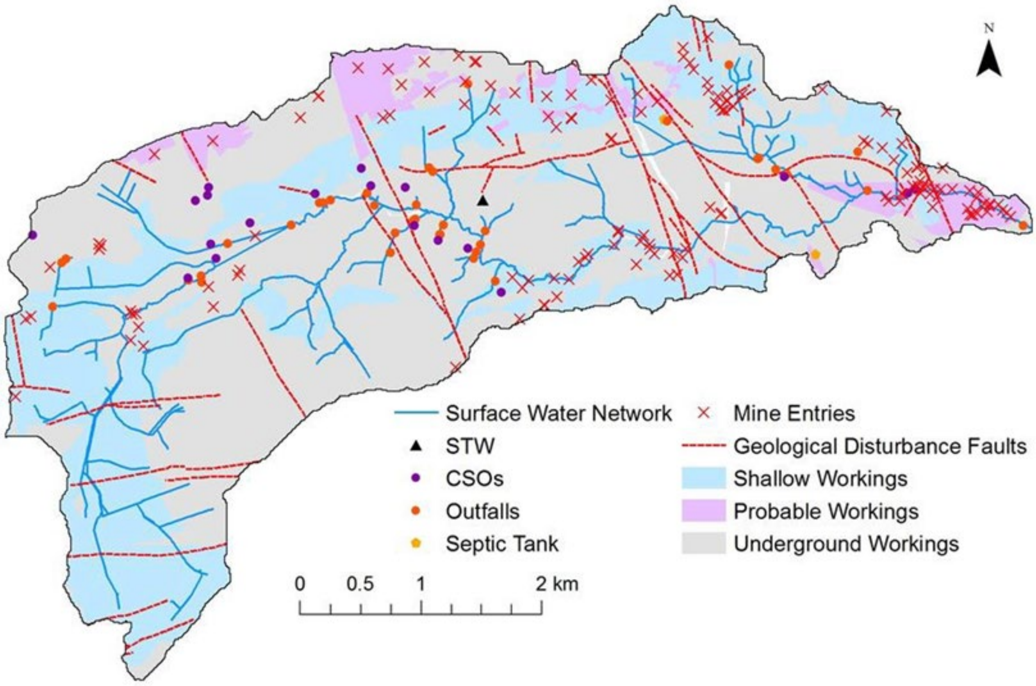

Figure 2-12: Threats to the Twizell Burn catchment, including historic and contemporary sources, e.g. sewage treatment work (STW) and combined sewer overflows (CSOs) (Source: Northumbrian Water; Coal Authority, 2018).

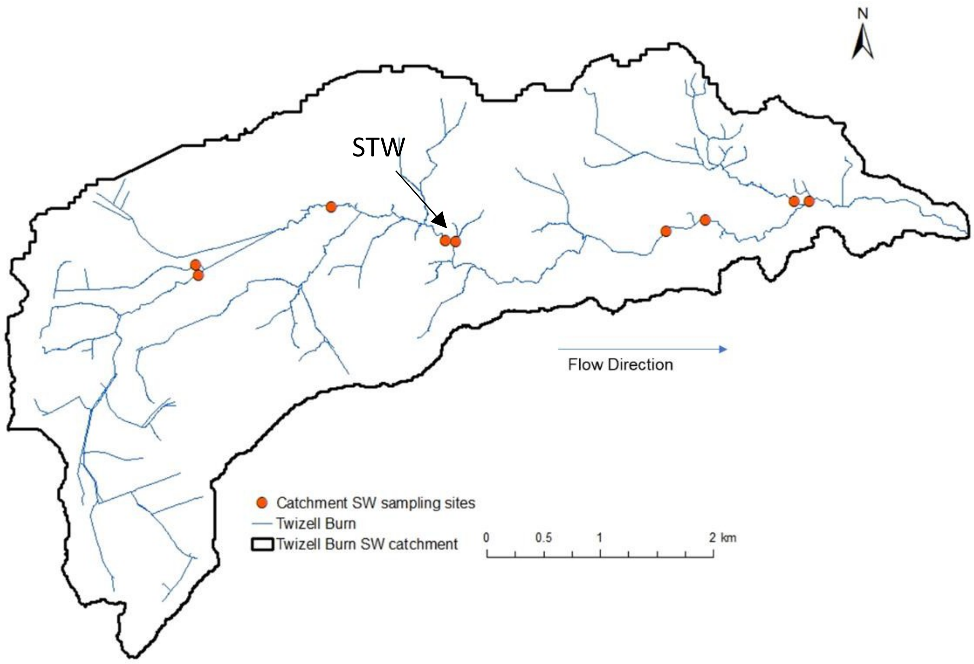

Figure 2-13: SW sampling points across the Twizell Burn catchment.

As part of the application of IREM, grab-samples of the SW were obtained across the catchment between September 2016 and September 2017 (Figure 2-14). The composition of the stream-water was variable, both spatially and temporally (Figure 2-14, Figure 2-15). The headwaters displayed elevated mining-related solutes, specifically SO_4^{2-} , Mn and Fe. Meanwhile, in the central parts, elevated nitrate compounds aligned with waste-water effluents, namely NO_3^- and NH_4^+ in proximity to the sewage treatment works (Figure 2-13, Figure 2-14). The concentrations of NO_3^- remained elevated further downstream, coinciding with an accumulation of mining-related effluents. With increasing flows, such as during February 2017, the dilution of mining-related solutes was evident with enhancement in nitrate-rich waters. From the sampling it is apparent that there is an accumulation of diffuse pollution sources. Efforts to address pollution have largely focused on point-sources, yet there is a growing need to consider the diffuse sources, and the accumulated threat to the freshwater systems, specifically considering how the threats operate and impact on the water quality.

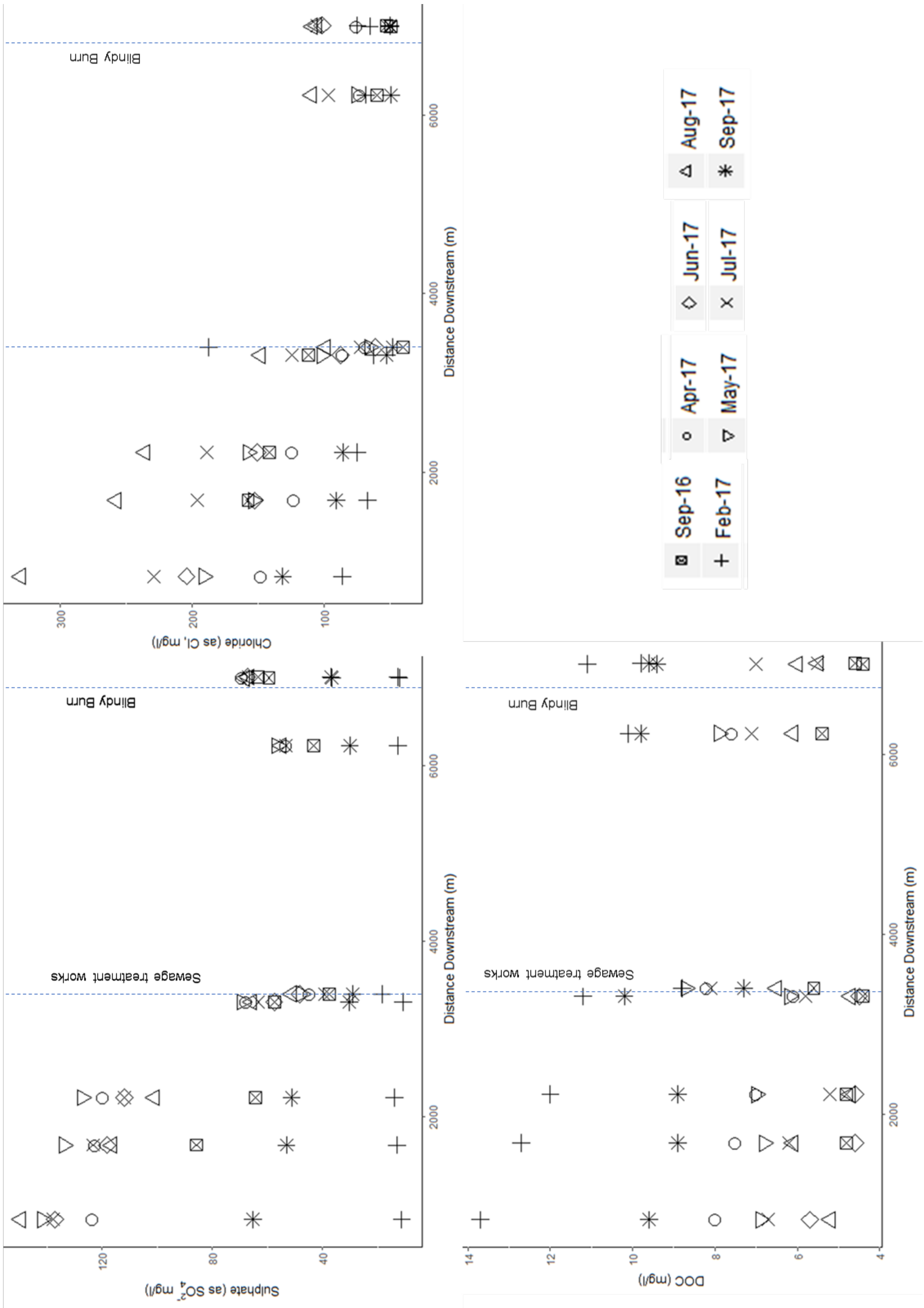

Figure 2-14: Ions sampled in the SW of the Twizell from Sept16 to Sept17.

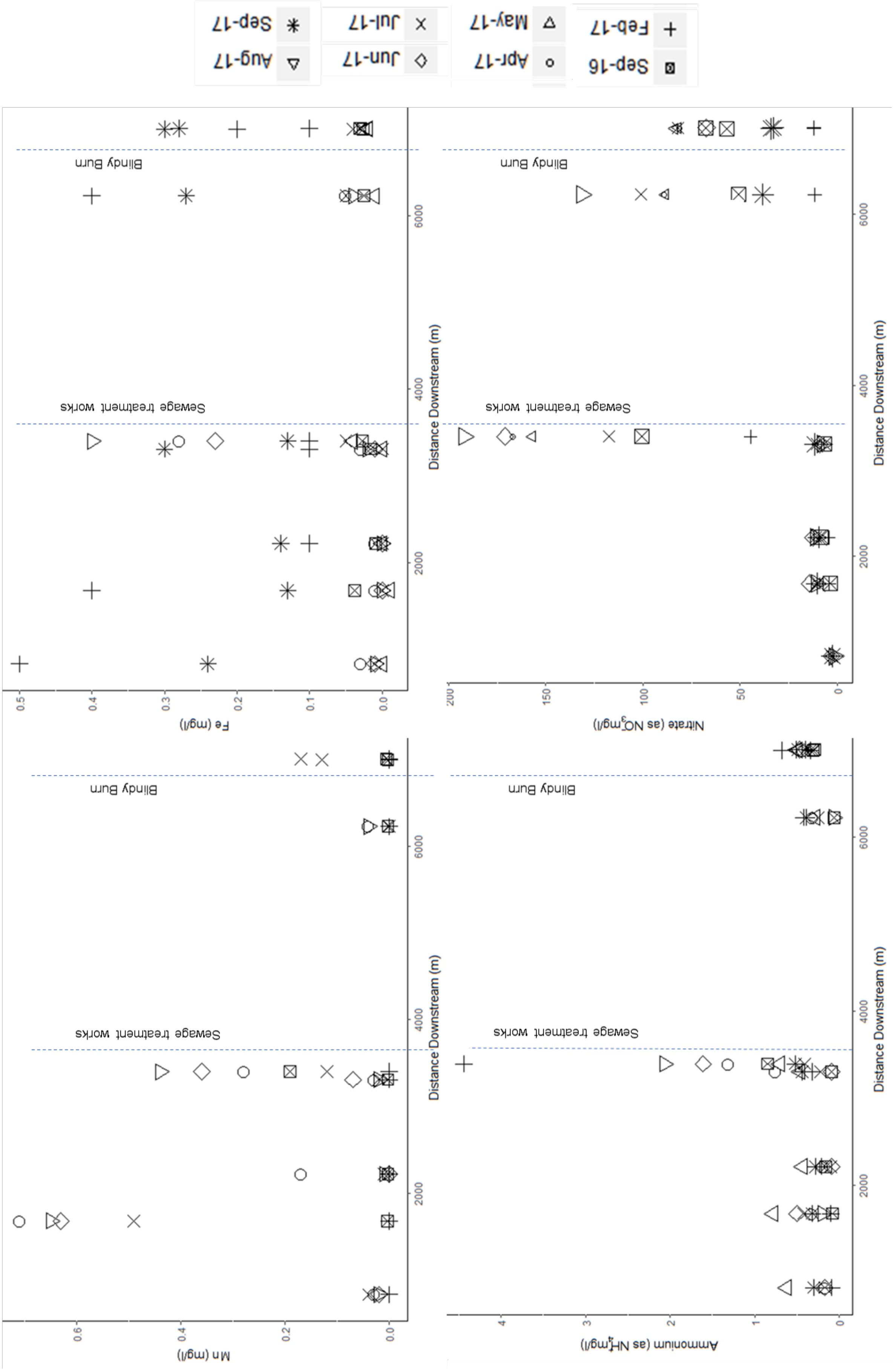

Figure 2-15: Ions and trace metals sampled in the SW of the Twizell from Sept16 to Sept 17.

Flow pathways from the point and diffuse sources of pollution are considered as a function of the hillslope runoff as well as those across the stream-subsurface interface. The Twizell is well-connected to the terrestrial landscape, with several small tributaries and inflows joining the main channel (Figure 2-16). In addition to the high heterogeneity of the superficial sediments with potential preferential pathways with the subsurface system based on the thin superficial deposits (Figure 2-16).

The superficial deposits are of variable thickness (Figure 2-16), comprising highly permeable gravel, sand and silts (BGS 2019, DEFRA 2019, Figure 2-17). The water table relative to the stream is also variable, in accordance with the pumping of the GW in the coal mining blocks (Coal Authority via the Wear Rivers Trust, Personal communication, Figure 2-16). It is thought that the Stanley mining block, the GW is connected to the stream, and in the Central Durham South mining block, there is an unsaturated zone (approximately 40 m depth) between the SW and GW systems (Personal communication with the Coal Authority via The Wear Rivers Trust).

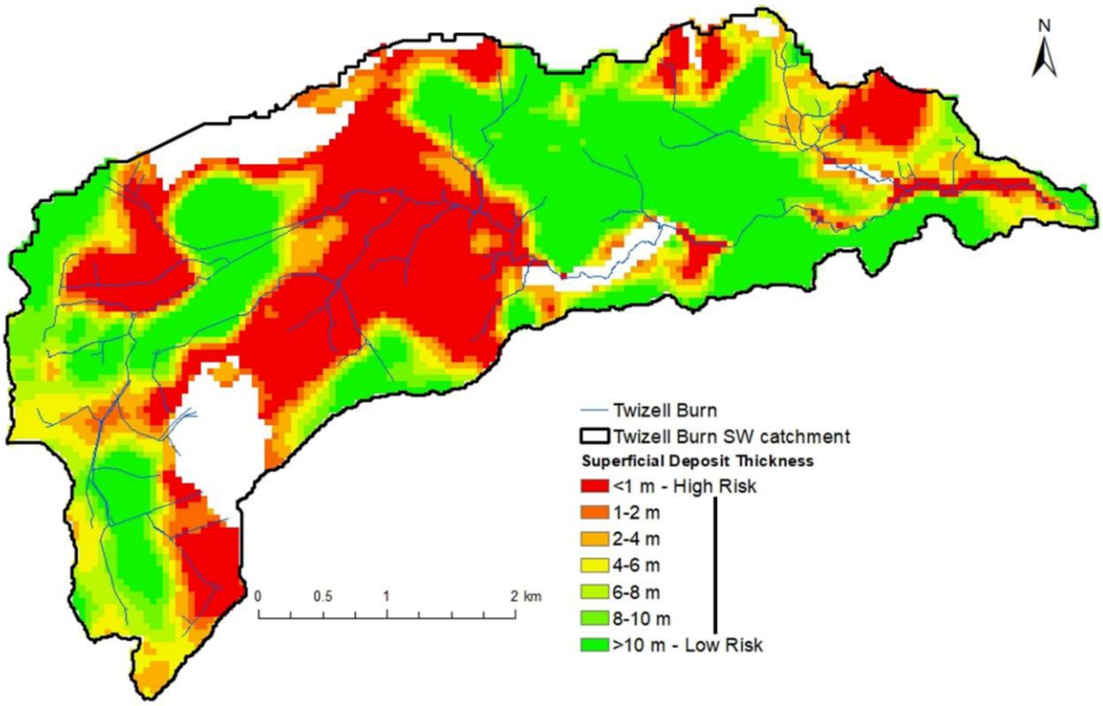

Figure 2-16: Composite risk map based on the superficial deposit thickness across the Twizell Burn catchment (Source: BGS 2013).

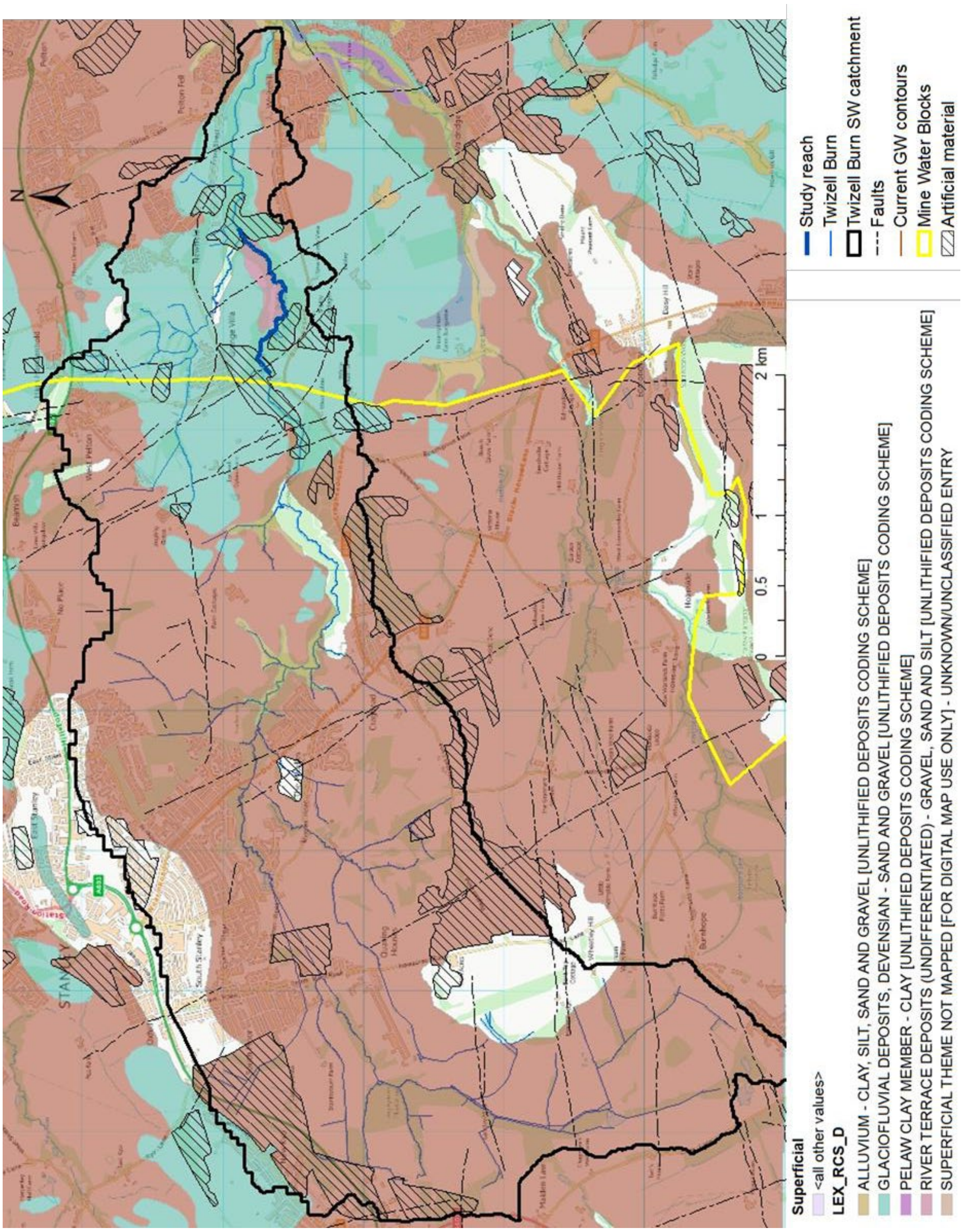

Figure 2-17: Mining blocks and superficial geology types (Source: BGS 2013, Coal Authority 2018).

Up until this investigation is was thought that the Twizell was entirely disconnected from the deep GW, however, this view has since shifted, and in-fact the presence of minor, perched water tables are now to be considered given the risk of connectivity (Figure 2-16). Perched water in the headwaters of the Twizell from the Stanley block and the perched water within the drift deposits underlying the stream reaches in the Central Durham South mining block are thought to be may be acting as a buffer/propagator to the identified threats, with the potential of discrete GW/SW movements. The thickness and composition of the superficial deposits suggests that there is a higher risk of connectivity with the stream-aquifer in the central and lower reaches (Figure 2-16; Figure 2-17).

2.6. Evaluating the IREM approach

The results of this study demonstrate the potential use of secondary spatial data as a way of exploring and developing a preliminary understanding of the connections between the terrestrial and aquatic systems where a paucity of monitoring data deters alternative approaches. By assessing the connections then allowed for thoughts to lead to the factors controlling and driving the evolution of water quality threats, which ultimately need to be better understood to facilitate more effective and sustainable management of water resources (Ivkovic *et al.* 2009, Bracken *et al.* 2013).

The application of IREM allows for a relatively simple, first-order approximation of the characteristics and connectivity compared to alternative, more technical and intensive approaches, as outlined e.g. by Oyarzún *et al.* (2014). IREM offers a useful insight into the system links and pathways, looking at simple patterns, such as those associated with the superficial deposits that may have the potential to support downwelling stream water, and links these observations with other factors, e.g. the thickness of the potential perching material. From such simple patterns, there is the opportunity to start informing how multiple threats impact on the water quality, above and below the streambed, complying a more complex picture from simple links between pressures and drivers (Harris 2007, Kluger 2008).

Recognising the links between controlling factors is essential element when working towards the ICM principles (Macleod *et al.* 2007, Kanndorp *et al.* 2018). Until now, the understanding has been that the stream environments have been closed to the GW, however, looking at the longitudinal, lateral and vertical, and temporal dimensions where relevant, and subsequent discussion with practitioners are indicative that the system connectivity is inherently complex and variable, requiring further investigations. Previously, such understandings of the connectivity having been omitted with high resolution screening studies (Wainwright *et al.* 2011). Applying IREM to the Herrington and Twizell catchments has proven insightful in terms of the next steps with management and research respectively.

The application of IREM has challenges the fragmented views of two heavily modified systems, faced with the complex water-quality issues attributing to a multitude of pressures. Decoupled views of the systems have hindered the understanding and thus likely the improvement of the water quality with procedures focusing on the end-point monitoring and dealing with the consequences rather than looking at the heterogeneity of the systems, accounting to four dimensions over space and time. While it is tempting to assume that systems are homogenous, which effectively simplifies the way the water movement and interactions, this is simplification is at the cost of mismanaging the issues the environment faces at the cost of putting stress on the water resources for humans, ecology and the environment. There is a need to recognise the complexity of systems. In both case studies it is evident that the systems are likely to be variably connected as a function of the catchment characteristics, for example, the geology and the permeability of sedimentary deposits. The understanding requires an insight based on several pieces of data to derive useful information, essentially by removing one could significantly alter the findings.

2.6.1. Further work

The GW/SW connectivity in the Herrington is complex and inherently important to consider in dealing with the drinking water abstractions. The findings of the application of IREM have led to the discounting of the original hypothesis that the source of nitrate at the borehole was from the stream environment. Consequently, leading to investigating and interrogating the drainage system, however, it was also discounted, given the relatively low nitrate levels compared to those sampled in the borehole. Most recently, at the time of writing, investigations to look at the borehole fabric continue, with no definitive source having yet been found. Without the application of an integrated approach such as IREM, the investigations were arguably at a stand-still, lacking coordination due to the missing of vital information, requiring the collaboration of data to make sense of a very complex system.

In the case of the Twizell, the GW/SW system is more intricate in that the managed rebounding GW and shallow GW of the superficial systems is likely acting as a buffer and/or propagator to the pollution arising from coal mining and contemporary sources, e.g. effluent releases, thus requires further investigation. Dissimilar to the Herrington which is receiving targeted efforts as part of on-going work on behalf of Northumbrian Water, the Twizell remains somewhat of a black-box system, with scattered efforts to address water quality at various points throughout the catchment, looking at asset failure, for example (Personal communication with Northumbrian Water). However, there is no wider scope to look at accounting the impacts of industry with the contemporary threats, thus leading for the thesis to carry forward looking specifically at the superficial system of the Twizell.

The primary investigations carried out in this chapter subsequently lead onto Chapter 3 – to look at the functional connectivity along the Twizell. In response to the changing hydrological conditions, the thesis investigates specifically the role of local scale processes of minor aquifers in the buffering/propagation potential of overlying streams, with the need to better understand local processes in the wide catchment understanding.

2.7. Conclusions

To summarise, using the existing spatial datasets has allowed for a more holistic understanding of the systems to be developed. Ultimately, IREM allows for a first-order insight when there are no other data available, such as the possibility of intensive field campaigns, which are costly and may ultimately target the wrong areas to address the challenges. IREM also encourages discussion between practitioners to support collaborative management, something which has traditionally been lacking in management decisions (Downs *et al.* 1991). However, while IREM allows a first-order approximation of the connectivity to be conceptualised, for it to be rolled out in practice further refinements are required, including the use of temporal data, such as flow and rainfall records to allow for changes over time to be factored into the understanding generated.

As demonstrated throughout this chapter, we need to start thinking about the catchment systems in a different way, not just as that the pollution enters at points, but from this, how the system is and interacts with the landscape and other features around it. Moving beyond the mismanagement of water resources requires a holistic and integrated understanding, and this is unachievable under the current protocol and procedures by which we currently attempt to understand the systems. Over recent years, the movement towards collating data to derive information and infer understandings to illustrate the GW/SW connectivity has grown. There is now the need to then look at what is happening in specific catchments of interest where water challenges prevail. There is evidently a need for multi- dimensional focus by starting to establish the movements in flow and solutes and what such processes attribute to the way in which they deal with pollutants and contaminants.

"I still believe in heroes"

Nick Fury (Avengers Assemble, 2012)

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Chapter 3 - Developing an integrated perspective on water chemistry between the stream and subsurface

3.1. Introduction

The work presented in this chapter builds on the findings of Chapter 2, which has led to consider the processes operating at the reach-scale GW/SW interface. The chapter considers the role of the minor aquifer system acting as a potential buffer and/or propagator to pollutants resulting from the historic coal mining, besides contemporary effluent wastes. Moving beyond the initial assessment of the GW/SW water connectivity, this chapter seeks to explore the mechanisms by which water moves across the streambed, in-turn assessing the interactions and exchanges in flow and solutes attributing to the dynamics and processes operating at the reach-scale within the Twizell Burn catchment.

The regulation of water quality has traditionally been undertaken from either a surface or subsurface perspective, with separate prioritisations and fragmented frameworks for managing each (Macleod *et al.* 2007, Staes *et al.* 2008, Li *et al.* 2016). Now deemed unsustainable, there is a growing focus on the need for integrative and adaptive solutions (Watson and Howe 2006, Staes *et al.* 2008, Schoeman *et al.* 2014). A key driver of integrative management is the WFD (CEC 2000), a novel approach based on policy, focusing on understanding and integrating all aspects of the water environment at the catchment-scale (Teodosiu *et al.* 2003, Voulvoulis *et al.* 2017, Varli *et al.* 2018). Promoting the protection and enhancement of SW and GW bodies, the aim of the WFD is to achieve the objective of ‘good’ status for all water bodies originally by 2015, and now 2027 (DETR 2001, Schmedtje and Kremer 2011). An integral element to the holistic integrated management is developing an understanding of the interactions between the water bodies. There is emphasis on the local-scale processes operating within the boundaries of the catchments, and thus developing a more complete understanding, leading to an improved whole-systems approach to water management.

GW/SW connectivity varies spatially and temporally in response to geomorphic and hydrogeologic features (Tetzlaff *et al.* 2007, Banks *et al.* 2011), including the geology, topography, climate, and the position of the stream-water body and water table with exchanges of the GW and SW occurring at the interface known as the hyporheic zone (Winter *et al.* 1998, Sophocleous 2002, Buss *et al.* 2009). Hyporheic flow paths are important drivers supporting the interconnection of surface and subsurface waters at certain locations (Malard *et al.* 2002, Tetzlaff *et al.* 2007), driving the exchanges and interactions of flow and solutes between the subsurface and stream-water systems with the mixing of stream water with deep GW and shallow GW of underlying aquifers.

Minor aquifers which form in the permeable superficial layers underlying the surface are often capable of supporting water supplies at the local scale, in some cases forming an important source of base flow to rivers (Environment Agency 2013). The vertical hydraulic conductivity of unconsolidated strata permits the loss and gain of stream-water and GW to and from the subsurface (Rains *et al.* 2006). Assessing GW/SW interactions with minor aquifers is challenging, notably because of the heterogeneity along the bed and banks, and complex flows and hydrochemistry associated with these settings, but monitoring is much less intensive in comparison to more productive formations (Jones *et al.* 2000, Ibrahim *et al.* 2010, Abbott *et al.* 2017). As a result, interconnections between the SW and shallow GW are often poorly understood (Niswonger and Fogg 2008, Conant *et al.* 2019), regardless of the contribution to the quality and quantity of water resources of the overlying stream-water, for example, through the provision of baseflow (Soulsby *et al.* 2001, Ivkovic *et al.* 2009, Lerner and Zheng 2011, Lee *et al.* 2018).

Emerging research has focussed on investigating the role and impact of minor aquifers on stream-water mainly using nested hierarchical approaches, often focusing on small scale, point features, such as riffles, pools and meanders (e.g. Soulsby *et al.* 2001, Malcolm *et al.* 2005, Käser *et al.* 2013), and nutrient dynamics (e.g. Dudley-Southern and Binley 2015). Yet in practice, despite the multiple threats to water quality, particularly in heavily modified tributary systems, the focus remains segmented, overlooking this stream-subsurface connectivity (McDonnell 2008). Most often the fragmented view of the SW and GW systems attributes to is a result of the lack of baseline studies and that there is no protocol to address and manage the minor superficial systems given that there is no provision of drinking water, for example, thus lack of need to prioritise from a management priority, hence lack of monitoring. However, as the GW/SW systems are likely connected, it is necessary to account to what is happening, given that a deteriorating GW system could impact greatly on the SW (Kløve *et al.* 2011), Therefore potentially impacting on the water quality of the stream, as also elsewhere in the catchment, or neighbouring water bodies. There is a need to challenge the mismanagement, especially where multiple threats are acting on the GW and SW systems. There is the need to understand the processes operating locally within catchments and link these to the wider catchment understanding to facilitate a holistic and integrated focus to water management.

3.2. Impact of minor aquifers on stream water

Despite challenging the success of integrative system management, isolated monitoring and management strategies remain under current legislation (Kalbus *et al.* 2006, Shepherd *et al.* 2006, Barthel 2014). Consequently, where a regional water table drops below and separates from the saturated zone associated with the streambed, it is assumed that water seeps only in the direction towards the water table below (McDonald and Harbaugh 1988, Winter *et al.* 1998) . Once this disconnection is assumed, it is thought that any further changes in the water table are negligible on the stream, causing no additional seepage loses (Niswonger and Fogg 2008). While this conventional view is held, the SW and GW are typically viewed and managed as ‘black-box’ or ‘pipe’ systems (Bencala 1993, Bencala *et al.* 2011), assuming they are closed from one another with the local or regional water table behaving independently of the stream (Niswonger and Fogg 2008). The tendency in practice has thus remained to address and manage issues with end-of-pipe solutions (Staes *et al.* 2008), decoupling the stream from the GW systems, assuming no interaction across the streambed.

However, such approaches do not consider the possibility of perched or mounded water supporting the formation of minor aquifers within the permeable strata underlying the streambed, which may diminish seepage loss and support gaining conditions in a stream (Soulsby *et al.* 2006, Niswonger and Fogg 2008). Often the downwelling stream water forms a saturated horizon within the porous medium, forming an inverted water table higher than the regional GW table (Leonhart 2005, Figure 3-1). The perched GW is often separated to the regional GW table by an unsaturated zone (Niswonger and Fogg 2008, Figure 3-1).

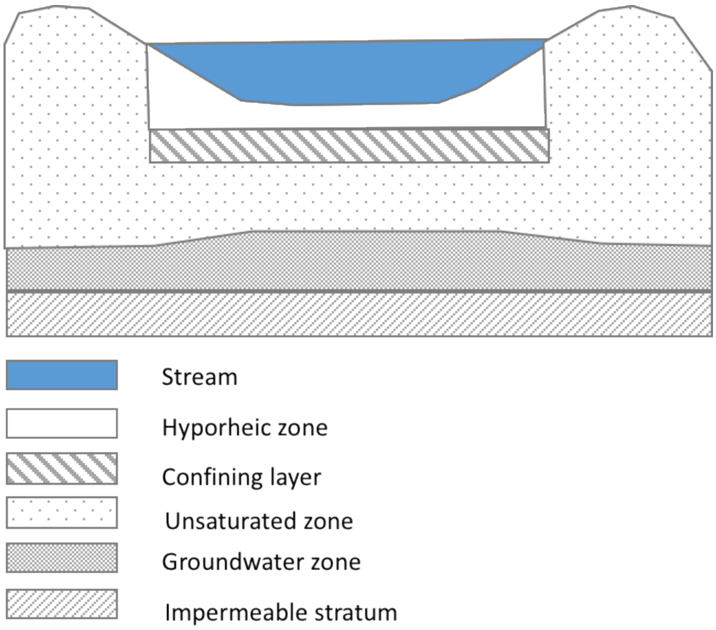

Figure 3-1: A perched hyporheic zone created only by infiltration of channel water beneath the stream bed (Source: Adapted from: Malard et al. 2001).

Where minor aquifers appear disconnected to the regional water table by an unsaturated zone, it has been common practice to manage the stream water quality entirely from the surface, decoupled from the GW system (Niswonger and Fogg 2008). However, this decoupling assumes that the exchanges between the stream water and the minor aquifer are negligible, and that there are no losses or influences with the major aquifer (McDonald and Harbaugh 1988, Winter *et al.* 1998), thus limiting the view exclusively to the stream water. Nevertheless, this simplified view inhibits an integrated understanding, because only managing catchments from the point-source threats at the surface, means that the integrative element of the management frameworks, such as the WFD, are lost, despite the potential exchanges between the GW and SW systems.

As acknowledged by Niswonger and Fogg (2008), few studies have been carried out which focus on the role of perched GW underlying streams on the water quality, and instead the focus of minor aquifer exchanges has been beyond the stream channel in the floodplain sediments, for example, on the surface-subsurface exchanges in the vadose zone (e.g. Orr 1999, Ascott *et al.* 2015, Ascott *et al.* 2016). Recent studies, for instance by Ibrahim *et al.* (2010), have focused on the conceptualisation of hyporheic flow paths in minor aquifers, looking at the interplay of geomorphic and hydrogeologic features at the reach scale. The understanding of these processes and interactions in systems in practice remains poorly addressed across tributary catchments, including those in County Durham. That is despite the multiple threats to the water quality in highly heterogeneous and complex systems. As discussed in Chapter 2, we need to consider the system in four-dimensions, with the lateral, longitudinal, vertical and temporal changes to develop an integrated perspective, and better manage water quality.

The aim of this chapter is to assess water quality beyond the one-dimensional focus to investigate the role of minor aquifer systems in heavily modified catchments and to assess the influence of shallow GW/SW exchanges on stream water quality. The focus is on deducing the flow interactions and solute exchanges in-stream and at the GW/SW interface of minor aquifers, influenced by changes in stream flow and geomorphic constraints. The existing understanding of these systems and interactions, which frames this work, is explained in the following section.

3.3. Assessing the near-surface exchanges between minor aquifers and stream water

GW/SW exchanges occur across a range of scales, along a continuum of hyporheic flow paths, whereby water that originates from the stream enters and leaves the subsurface several times along a reach (Woessner 2017). Hyporheic flow paths within minor aquifers can extend laterally at considerable distances from the stream, especially where high hydraulic conductivities exist (Tetzlaff *et al.* 2007). The identification of hyporheic flow paths is often difficult, especially where they are well-developed (Woessner 2000). Often, investigations of the flow paths and position of the hyporheic zone are informed by the reach- and channel-unit scale features (e.g. Ibrahim *et al.* (2010)). Also used are biogeochemical processes linked to organic matter in the riverbed which are interpreted from the distribution of relevant dissolved redox-sensitive species (dissolved organic carbon (DOC), O_2, NO^{3-}, SO_4^{2-}, Mn and Fe), as well as pH and alkalinity (Baker *et al.* 2000), and ecological gradients (Boulton *et al.* 2010).

Methods used to investigate the interactions between the stream and shallow GW are well-established and include point- to reach-scale approaches (Brodie *et al.* 2007) with varying complexity and costs associated, as outlined previously in

Chapter 1. Examples include: in-stream piezometers/shallow wells, seepage meters, floodplain monitoring wells, steam gauging, tests to determine the hydrologic properties of saturated sediments, tracer studies, mapping of head distributions and flow directions, sampling of biota and geochemical constituents, modelling water exchange locations and rates, and defining geochemical cycling and heat exchange (e.g. Brodie *et al.*, 2007; Woessner, 2017).

Exchanges have the potential to result in gains or losses of stream-water to and from the subsurface and are evident through changes in the stream discharge established through seepage metre measurements and differential flow gauging, for example (Brodie *et al.*, 2007). Fluxes in water are significant in that solutes are transported and exchanged within the hyporheic zone (Bencala *et al.* 2011, Krause *et al.* 2014, Freer *et al.* 2014). Solutes which originate from the surface or subsurface have the potential to cross the streambed, which in turn has implications for the ecology and nutrient dynamics of the respective systems (Boulton *et al.* 1998).

Within the hyporheic zone, hydrological, biological, and chemical changes are known to occur within the interface, which acts as a source and sink of pollutants (Kalbus *et al.* 2006, Lawrence *et al.* 2013). The hyporheic zone has previously been investigated in dealing with mining-derived pollutants (e.g. Gandy and Jarvis 2006) and nutrients (Dudley-Southern and Binley 2015). Consequently, such processes can result in the degradation, transformation, precipitation and sorption of elements present in the water (Kalbus *et al.* 2006). Now, GW/SW water exchanges are recognised as key mechanisms for the fate and transport of solutes, including nutrients between the GW and SW bodies (Dudley-Southern and Binley 2015). Therefore, an understanding of the connectivity is required to then determine the impacts on water quality, quantity and ecology (Brodie *et al.* 2007).

As minor superficial aquifers are often localised, there is a need to return the focus to the empirical understanding, at the intermediate scale, investigating the impact of the hyporheic flow paths and the subsequent impact on solutes as water flows through catchments, particularly at the reach scale (10 m – 1 km) (Bencala *et al.* 2011). Rather than continuing with the assumption that pollutants enter and leave the channel via inflows, approximating channels as a black box without looking at what processes are occurring within the reach, it is crucial to understand losses and gains to and from stream to the subsurface as a function of the minor aquifer system (Niswonger and Fogg 2008). The focus should be on the more localised changes in the solute chemistry across the streambed to develop integrated assessments of catchments, to then establish and quantify the stream-catchment connections and the solute transport and transformations (Bencala *et al.* 2011) feeding into the catchment-scale understanding, informing management under frameworks, e.g. the WFD.

The purpose of this chapter is to:

1. Quantitatively assess the role of the minor aquifer position through field sampling techniques;

2. Assess the chemistry of the SW and shallow GW, where possible sampling through a range of hydrological conditions to allow for an insight into the interactions with the stream flow, facilitating a first-order flow and chemical budget; and

3. Investigate the role of the minor aquifer as a source and sink of flow and solutes from multiple pressures.

3.4. Study area

3.4.1. Locations and SW resources

The study area is in the Twizell Burn (19 km^2), a tributary of the River Wear in County Durham, UK (Figure 3-2). The catchment is heavily modified; there are multiple threats to the water quality, including effluent discharges and historic pollution from the abandoned coal mines and contaminated land comprising waste spoil materials (Groundwork NE & Cumbria 2015; Personal communication within TOPSOIL Group; Figure 3-2). Previous understanding of the response and impacts to these perceived threats has been limited to regulatory spot sampling of the SW, assessing WFD compliance, with the extent of the historic industrial impact been largely unaccounted (Groundwork NE & Cumbria 2015) beyond that in the Twizell headwaters by Younger *et al.* (2002).

This study focusses on a 1.3 km reach of the Twizell (Figure 3-2). The reach was selected for an intensive monitoring campaign (April-July 2017) to assess spatial variations and the temporal controls on the water quality, including the role of the

GW/SW interactions, considering the flow and chemistry exchanges between the stream and shallow pore-water of the minor aquifer. GW/SW exchanges have not previously been considered in this catchment, albeit previous studies in the upper Wear catchment in the Rookhope Burn have explored metal mining and its impact on the hyporheic zone (Palumbo-Roe and Dearden 2013b). This research gap remains despite the extent of pollution and abandoned industry, and the anticipated impact on the SW, streambed and GW.

The reach is heavily modified, with adjusted channel form and artificial structures post-coal mining. The upper structure comprises a 150 m stepped weir (Figure 3-2) to divert the channel to allow for the dumping of mine wastes in the neighbouring farmland (Hartley and Wright 1988). Flowing through meandering sections with a series of riffle-pools, the reach lies downstream of the sewage treatment works and has extensive iron-ochre staining, supporting the need for an investigation into the impact of historic industry and contemporary threats. Following the conceptualisation in Chapter 2 using the IREM framework, this particular reach was selected on the basis of the separation from the regional water table due to the pumping to manage the rebounding GW post-mining of the Middle Coal Measures Formation, and that the complex superficial strata which are thought by practitioners to support a minor aquifer (DEFRA 2019; Personal Communication with Environment Agency NE and Northumbrian Water via TOPSOIL project meetings). The reach therefore provides an opportunity for developing an understanding of the GW/SW interactions and exchanges and the impact on stream-water quality, something which has not been previously considered for this catchment, and also where multiple pressures prevail to impact on the water quality. This assessment and understanding will better inform the current understanding of the water quality and thus the management of the water resources in catchments such as the Twizell with multiple threats to the water quality, which have been exclusively considered from the stream-water perspective.

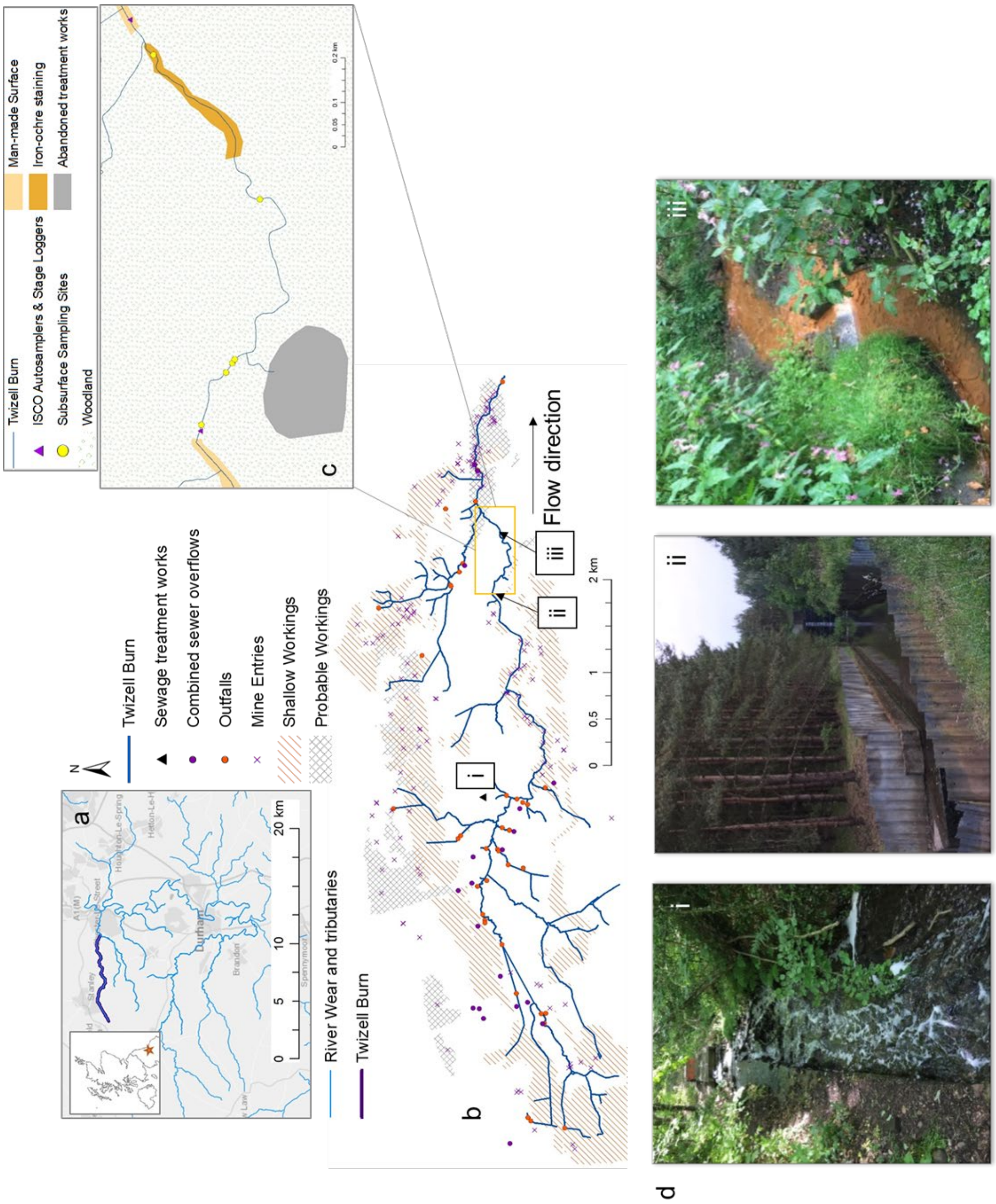

Figure 3-2:: (a) River Wear and Twizell Burn relative to the UK; (b) threats to the SW [Source: Northumbrian Water; Coal Authority 2018]; (c) reach-scale site showing threats and sampling sites; d) photos [i] sewage treatment works, [ii] stepped weir at upstream.

3.4.2. Geology and hydrogeology

The Twizell is underlain with highly permeable unconsolidated glaciofluvial superficial (drift) deposits formed during the Quaternary period, comprising coarse sand, silt, gravel and occasional clay deposits (BGS 2019; Figure 3-3). Superficial deposits are thought to support the formation of a minor aquifer, with the potential to sustain local water supply and baseflow (DEFRA 2019).

Underlying the superficial deposits are sedimentary bedrock, the Pennine Middle Coal Measures Formation comprising Mudstone, Sandstone and Siltstone (BGS Geology, 2018). Faulting of the bedrock strata is apparent upon review of geological records, although the inferred dip direction and water flows are unknown, thus require investigation beyond the scope of this study. Coals seams intersect the bedrock strata and have been extensively mined. Mining flourished in the catchment from the 1800s to late 1900s (Groundwork NE & Cumbria 2015).

Since the ceasing of mining, rebound of GW through the sedimentary bedrock has been managed through pumping (Personal communication Coal Authority via the Wear Rivers Trust). GW levels in the Stanley mining block are fully rebounded, while those of the Central Durham South mining block continue to be pumped south-east of the Twizell catchment at Kimblesworth. Following the ceasing of pumping in the future, the time of which is not yet documented, the Coal Authority expect that artesian conditions will arise. The deep GW within the Coal Measures is classified as having poor status, failing to meet the WFD objectives, and deemed unrecoverable given the lasting impacts and time necessary to clean-up to pre-industrial conditions (Environment Agency 2019c). The impact of deep GW on the stream-water is unknown. The scope of this study is to, however, challenge the current understanding and role of the shallow system, looking at the influence of the near-stream sediments to the stream-water quality.

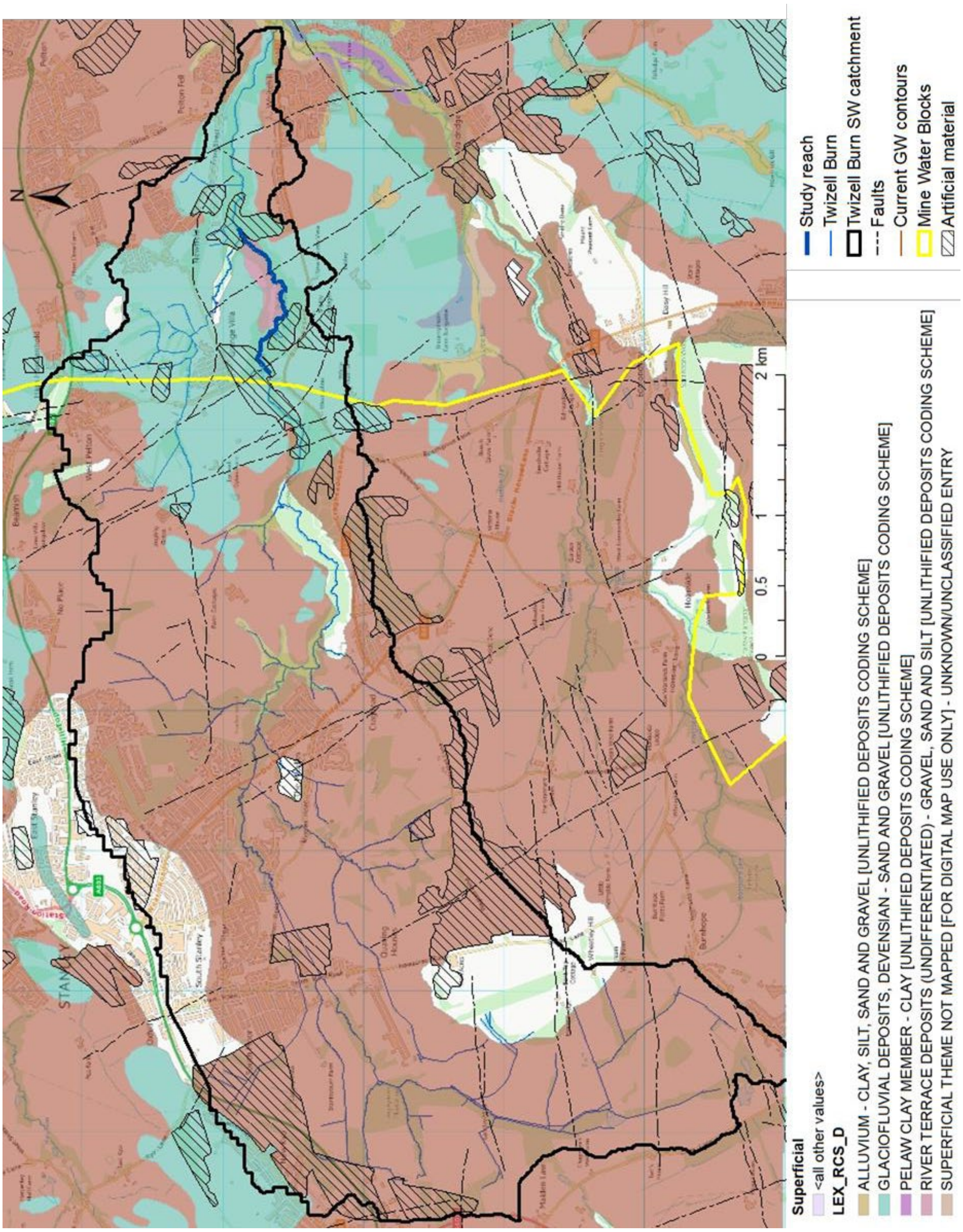

Figure 3-3: Coal mining blocks and superficial geology of the Twizell Burn and study reach (source: BGS, 2018 accessed via EDINA Digimap).

3.5. Methods

The methodology used is the second element in a hierarchical multi-scale approach, following the conceptualisation of GW/SW connectivity in Chapter 2, where geological and geomorphological information, such as the catchment characteristics, geological units and structures and changes in streambed have been investigated to assess the role of connectivity. This reach was subsequently identified as having potential GW/SW interaction of the near-stream sediment with a minor aquifer, and subject to an accumulation of multiple threats to the water quality, including those from coal mining and contemporary effluent releases. The study reach provided the opportune basis for this study, with the potential to investigate a complex subsurface, with rebounding deep GW that is currently managed by pumping to sustain mine-water rebound in the Central Durham South mining block (Personal communication with Coal Authority via the Wear Rivers Trust), and superficial layers supporting a minor aquifer system.

3.5.1. Stream flow

As the Twizell is ungauged, stage was monitored using VanWalt LevelSCOUT diver loggers (15-min frequency, March to July 2017), compensated for atmospheric pressure using a VanWalt BaroSCOUT logger (45-min frequency) (accuracy +/- 0.10% FS at 0-40°C). Stream flow was estimated using the velocity-area method, whereby velocity measurements were taken using a hand-held Valeport EM flow meter at cross-sections at various stream stages, developing a stage-discharge rating curve (Figure 3-4). Velocity measurements could not be collected at higher flows due to limited channel accessibility when the stage rose above ~0.35 m which made conditions too dangerous to enter the channel due to the velocity of the flow. Stage and discharge were monitored at either end of the reach (Figures 3-2). The purpose of this was two-fold, first to allow for the contributions to the steam to be established, and secondly, to determine the change, if any, in the GW to SW gains/losses over the reach during the sampling campaign, thus determining the connectivity status of the reach to the GW system. It was suspected that based on the likely high permeability of the underlying strata that the stream was losing to the subsurface.

The rating curves are thus interpolated and are extrapolated to facilitate the estimate of discharge outside of the observations (Figure 3-4), looking specifically at the use of a second-order polynomial and power-law trends (Braca 2008). The R2 values were around 0.9. Both the polynomial and power trend lines arguably fit reasonably to the data, despite the noise associated, particularly at the upstream site with a greater standard error relative to the downstream site (Figure 3-5; Figure 3-6). The choice of trend line fit to interpolate and extrapolate the data was nonetheless associated with some error, although with similar discharge estimates at the lower end of the curves, with greater uncertainty at the upper ends where flow gauging was not carried out.

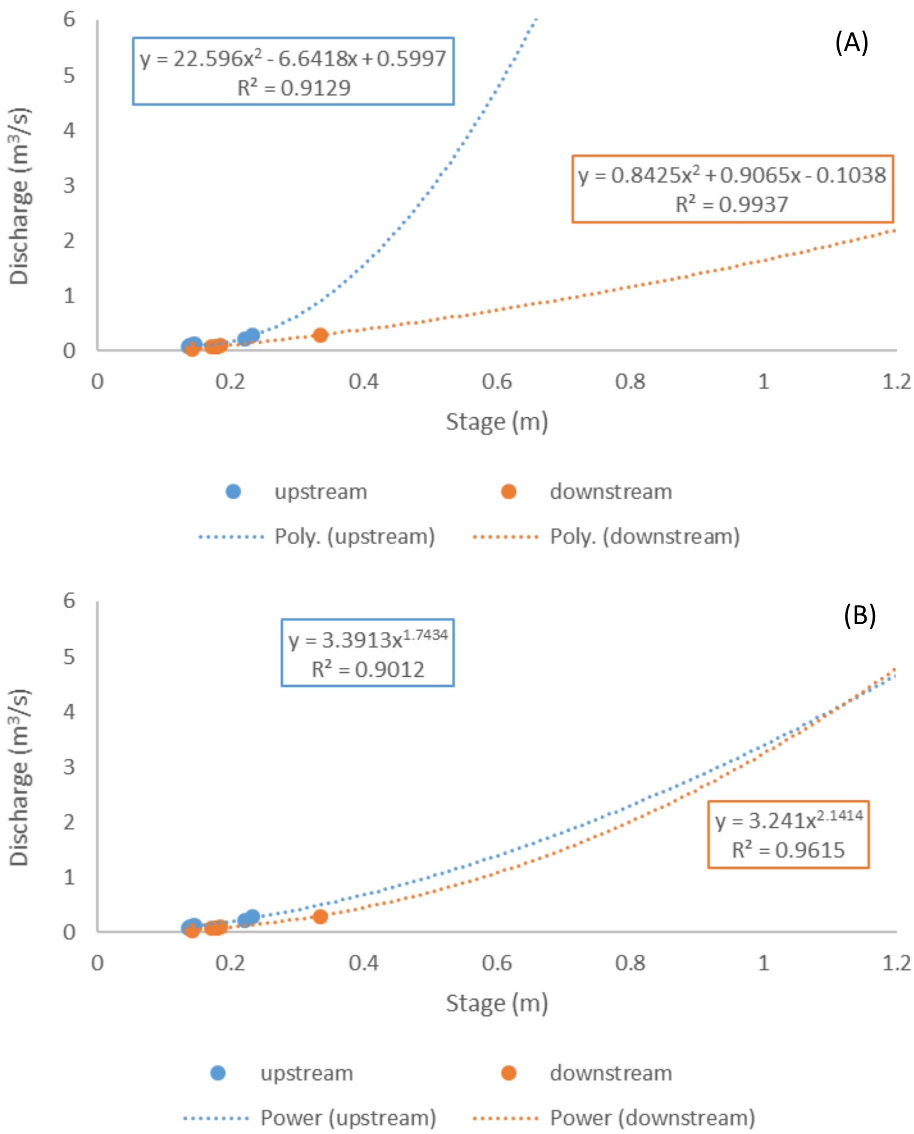

Figure 3-4: Stage-discharge rating curves for the upstream and downstream stage gauging sites: (A) power-law, and (B) second-order polynomial.

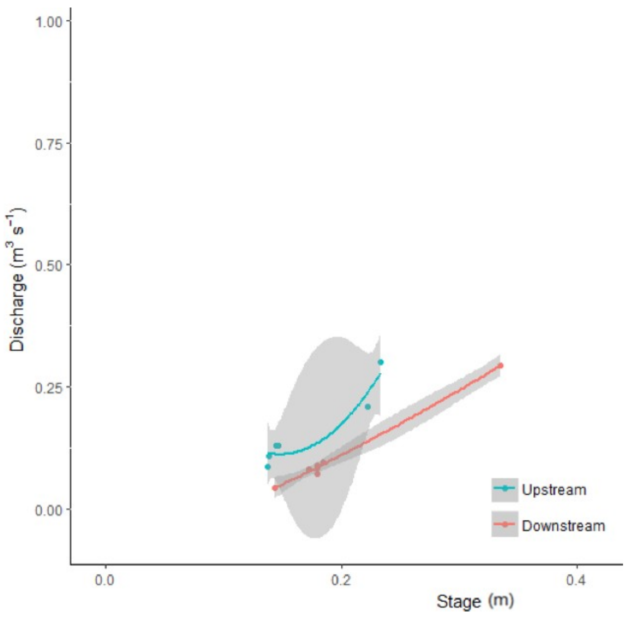

Figure 3-5: Standard error associated with interpolation of values using second-order polynomial.

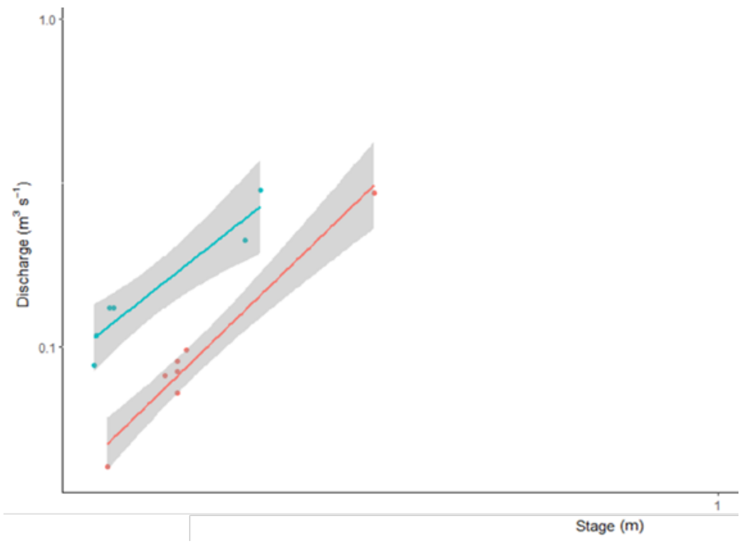

Figure 3-6: Standard error associated with interpolation of values using a power-law fit.

3.5.2. Design and implementation of mini-piezometers

A series of single mini piezometers were installed along the reach (Figure 3-7; Table 3-1). The piezometers were used to measure water depth and hydraulic heads, as well as hydraulic testing and collection of shallow subsurface pore-water samples for laboratory analysis. Piezometers were situated at intervals along the reach to assess the stream-aquifer interactions at the point-scale. Sites were selected based on the presence of channel-unit features such riffles, pools and run sections. Piezometers were constructed from one-metre lengths of 25 mm (ID) PVC piping, sealed at either end with rubber bungs, with a 0.3 m screen of drilled holes of 1 mm Ø following the design of e.g. Freeze and Cherry (1979), Lee and Cherry (1979), Ibrahim (2012) and Biddulph (2015). The design was relatively simple, with the screen length at least eight times the diameter (Watson 1993, Fetter 2018). The mid-point of the perforated sections represents a depth into the streambed sediments that was around 0.45 m below the streambed, facilitating an integrated sample of the pore-water across an interval of 0.3 m.

The piezometers are cheap and useful apparatus to take measurements, although prone to clogging and being swept downstream in high flows. The coarseness of the sand layers below the bed, and the constant back-filling due to the water flow, meant that the use of an auger was not a feasible method of installation. Instead, a fencepost driver and crowbar were used to break through the deposits and the piezometers installed using a direct-push method (after Woessner, 2017). The piezometers were installed in the bed to a maximum depth of 0.5 m. Practicalities associated with the installation of the piezometers meant that nesting was not possible, thus single, individual piezometers were used. Disturbed sediment was left to backfill around the piezometers, and they were left to settle for a minimum of two weeks allowing for natural hyporheic flow to recover (Ibrahim *et al.*, 2010). Initially, eight piezometers were installed, and were sampled to derive hydraulic parameter estimates and pore-water samples over the three-month spring-summer field campaign (Figure 3-7; Table 3-1). Later in the campaign, an additional four piezometers were installed (Figure 3-7; Table 3-1), replacing those damaged or swept away in high flows in May, and to sample additional sites along the reach (Figure 3-7), however, there were only sampled once in June 2017 (Table 3-1).

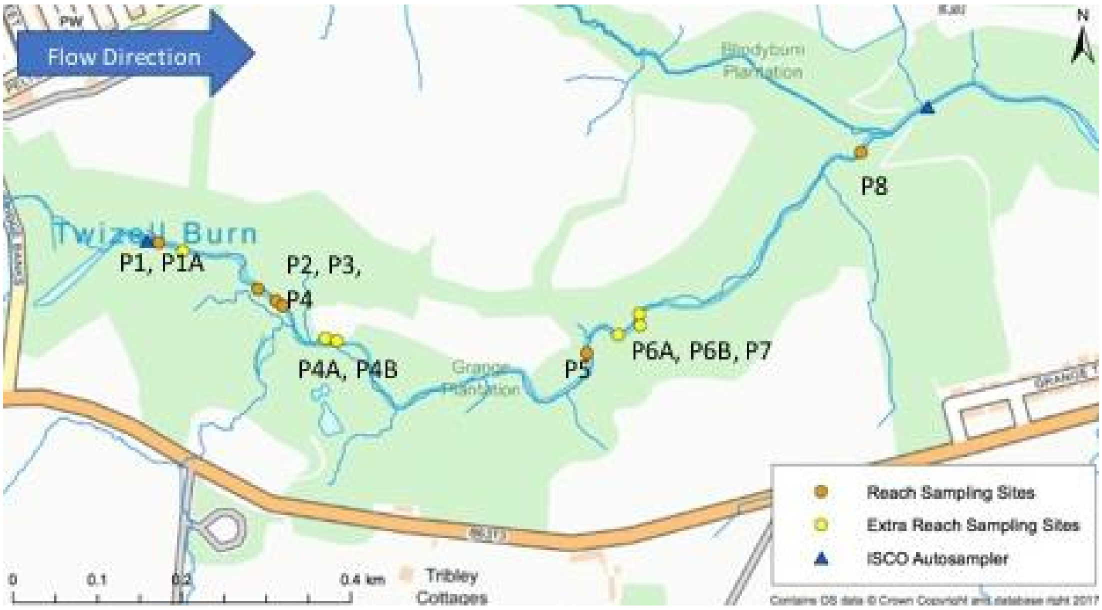

Figure 3-7: Reach sampling locations, showing the sites of piezometers and ISCO-3700 auto-samplers.

*Table 3-1: Piezometer locations and sampling dates (red: hydraulic and chemistry measurements; black: hydraulic measurements only) *these piezometers were vandalised, and so only sampled on two occasions.*

Site ID	Distance Downstream (m)	Times of Sampling	Description
P1	0	12/04, 25/04, 03/05, 16/05, 15/06, 01/07	Run
P1A	30	15/06, 01/07	Run
P2	145	12/04, 25/04, 03/05, 16/05, 15/06, 01/07	End of pool
P3	170	12/04, 25/04, 03/05, 16/05, 15/06, 01/07	Riffle
P4	180	12/04, 25/04, 03/05, 16/05, 15/06, 01/07	Riffle head
P4A	250	15/06, 01/07	Run
P4B	270	15/06, 01/07	Run
P5	680	12/04, 25/04, 03/05, 16/05, 15/06, 01/07	Run
P6	730	12/04 and 15/06*	Run
P6A	760	15/06, 01/07	Run
P6B	760	15/06, 01/07	Run
P7	770	12/04 and 15/06*	Run
P8	1140	12/04, 25/04, 03/05, 16/05, 15/06, 01/07	Upstream of the Blindy Burn

3.5.3. Streambed hydraulic gradients and fluxes

Vertical hydraulic gradients (VHGs) were measured as a first-order approximation of the direction of flow at verticals along the reach at the site of each of the piezometers. They were estimated using the following Equation (1) (Dahm *et al.* 2006, Ibrahim *et al.* 2010):

$$VHG\ (\%) = \frac{hs - hp}{L} \times 100 \tag{1}$$

Where:

hs is the difference between the top of the well and the stream stage (m);

hp is the difference between the top of the well to the water level inside (m);

L is the length of the piezometer buried beneath the stream bed (m).

A positive or negative gradient represents the upwelling or downwelling of riverbed flow relative to the streamflow respectively (Niswonger and Fogg 2008, Ibrahim *et al.* 2010). The water level inside the piezometer was left to stabilise prior to the measurement of the hydraulic head using a Solinst tape (Ibrahim *et al.*, 2010), and such measurements were taken prior to the collection of the pumping of the pore-water sample for laboratory analysis.

Vertical hydraulic conductivity (Kv), assumed to be 10% of the horizontal hydraulic conductivity (Kh – Equation 2), was used to estimate specific discharge corresponding to the upwelling and downwelling across the stream bed (Dahm *et al.* 2006, Ibrahim *et al.* 2010). At each piezometer, a minimum of three rising slug tests was performed, by adding water to the well and recording the time to draw-down (Woessner 2017). The results were then interpreted using the Hvorslev equation (following e.g. Ibr ahim *et al.* 2010):

$$K_h - \frac{r^2}{2\mathrm{L}(\mathrm{t2}-\mathrm{t1})}\ ln\frac{(L)}{(R)}\ ln\frac{(H1)}{(H2)} \tag{2}$$

Where:

Kh is the horizontal hydraulic conductivity [m/s]; r is the radius of the graduated tube[m];

L is the length of the screened section [m]; R is the radius of the screened section [m];

H1 and H2 are the respective draw-down ratios at time t1 and t2 [s].

Specific discharge was then calculated using the following Equation (3) (Dahm *et al.* 2006, Ibrahim *et al.* 2010):

$$q = K_v \frac{VHG(\%)}{100} \tag{3}$$

Where:

q is the vertical specific discharge [m/s];

Kv is the vertical hydraulic conductivity [m/s].

3.5.4. Analysis of water chemistry

3.5.4.1. *In-situ* measurements

Instantaneous estimates of the water chemistry were recorded in the field using a hand-held multi-parameter YSI probe, calibrated prior to each field visit. Readings included: temperature (°C), DO (mg/l and %), EC (as specific conductivity, mS/cm at 25ºC), pH, total dissolved solids (TDS, mg/l), pH and oxidation reduction potential (ORP, mV). For the collection of discrete grab samples of water, two 50 ml samples of water were collected using single-use polypropylene vials. Vials were pre-rinsed in sample water, filled and capped immediately. Samples were stored in a cool bag and transported to the laboratory, where on return they were refrigerated at 4ºC until filtering within 24 hours.

The shallow pore-water samples were collected following the hydraulic head measurement. Samples were obtained to assess the solutes and deduce chemical gradients relative to the stream-water. A Nalgene® hand-operated vacuum pump was used to withdraw pore-water samples from the piezometers into a Nalgene® filter flask. Sampling equipment was pre-rinsed in sample-water prior to collecting two 50 ml samples for YSI composition measurements and laboratory analysis. To minimise contamination between sites, those which were deemed more polluted were sampled last. Physical mixing of GW and stream-water inputs is interpreted using dissolved Cl- and Br- which are assumed to be conservative (Hem 1989, Ibrahim 2012) and measurements of pore-water electrical conductivity (EC), which approximates the sum of anions and cations in samples (Appelo and Postma 2005). Biogeochemical processes linked to the biodegradation of organic matter in the riverbed are interpreted from the distribution of relevant dissolved redox-sensitive species (dissolved organic carbon (DOC), O_2, NO_3^-, SO_4^{2-}, Mn and Fe), as well as pH and alkalinity (Baker *et al.* 2000). To characterize the hydrochemical differentiation between the stream and riverbed, the pore water is expressed as a ratio against a mean value or concentration of the parameter in the stream at the study reach and for the period of sampling. Absolute values are used for pH. Ratios greater than 1.0 indicate that the solute is more concentrated (or "enriched") in the riverbed pore water, relative to the stream; ratios smaller than 1.0 indicate that the solute is less concentrated (or "depleted") in the riverbed pore water, relative to the stream.

3.5.4.2. Laboratory analysis of samples

On return to the laboratory, samples were filtered through a 0.2 μm single-use filter (FisherbrandTM Polyvinylidene Fluoride Syringe Filter) to derive estimates of anions and cations via an ion chromatograph (Dionex), and 0.45 μm single-use filter (FisherbrandTM Polyvinylidene Fluoride Syringe Filter) to analyse for trace metals via ICP-OES and ICP-MS, and non-purgable dissolved organic carbon (DOC) by acid sparging and combustion (TOC-L). Method detection limits are presented in Table 3-2. Analytical precision was considered as to how close the analytical value of the concentration of a determinand, in this case, that of a certificated lab control sample, was to that of the method detection limit, which is the level at which a substance can be detected (Table 3-2). Analytical precision was taken as twice the standard deviation divided by their mean (Table 3-2). For quality assurance, field blanks, laboratory blanks and laboratory replicates were analysed for each round of chemical analysis. This was to ensure the standard of equipment washing, preparation and transport. Concentrations of major and trace elements were deemed minimal in the blanks, with levels lower than those of the reported data.

Table 3-2: Estimated quantification limits and analytical precision for laboratory analysis.

Substance	EQL (mg/l)	Analytical Precision (%)
Fluoride (as F)	0.01	1.02
Chloride (as Cl)	0.03	1.02
Bromide (as Br)	0.02	2.21
Sulphate (as S)	0.02	0.60
Phosphate (as P)	0.02	1.62
Nitrite (as N)	0.02	0.56
Nitrate (as N)	0.04	1.57
Sodium	0.05	0.98
Ammonium (as $NH4^+$)	0.02	1.04
Potassium	0.01	1.26
Magnesium	0.01	1.35
Calcium	0.05	1.33

Substance	EQL (mg/l)	Analytical Precision (%)	Substance	EQL (µg/l)	Analytical Precision (%)
Al	0.025	0.80	Li	1	3.00
B	0.025	0.70	Be	1	4.10
Ba	0.025	1.00	V	1	2.80
Fe	0.002	1.10	Cr	0.5	1.80
Mn	0.002	0.89	Co	1	2.40
Ni	0.002	1.19	Cu	1	1.40
S	0.5	1.43	Zn	2	2.00
P	0.025	1.41	As	1	1.70
			Sr	1	2.10
			Mo	2	1.10
			Cd	0.5	1.30
DOC	1.00	2.62	Pb	0.5	1.30

3.5.4.3. Evaluation of auto-samplers

The storage of water samples in the field and laboratory can impact on the sample quality, and there is a need to minimise the degradation and contamination of samples. It is often impractical to analyse a large number of samples immediately. However, minimising the contamination and degradation of samples is essential for assessing the health of the aquatic ecosystem (Aston 1980, Gardolinski *et al.* 2001). The most widely used methods of preservation are refrigeration, freezing, filtration and acidification to slow action of biotic processes (Avanzino and Kennedy 1993, Gardolinski *et al.* 2001). A rigorous cleaning protocol is also necessary to minimise contamination. Approaches include the use of sampling containers made of inert material such as HDPE (Nalgene®, (Gardolinski *et al.*

2001) and following correct handling and collection procedures, e.g. rinsing of the sampling vials in sample water prior to sample collection.

Deploying automatic samples for time series acquisition challenges the typical storage and filtration procedures. Typically, samples are stored unfiltered for several days, depending on the duration of sampling and ability to return to the site. To account for the potential degradation, it is recommended that the degradation is quantified (Gardolinski *et al.* 2001, Bieroza and Heathwaite 2016). In recent years technological advancements have led to an increase use of in-situ sampling and nutrient analysis, however, the uptake is costly and limited to sites.

When using automated sampling techniques, as in this study for quasi-continuous (time-series) sampling using ISCO autosamplers, the field storage is often supported using a refrigeration unit or using blocks of ice in the centre of the sampler base (e.g. Teledene ISCO 1998). However, the former is power supply dependent, and the latter only feasible for short periods of time. Whilst grab-samples could be collected and stored at the laboratory, the automated sampling could not be facilitated in such a way, and daily visits to collect the samples were unfeasible, with the inability to implement a refrigeration unit or ice. A concern was therefore whether that the quality of the samples would degrade, particularly anions, and unstable cations such as ammonium (as NH_4^+). To investigate the sample deterioration, a degradation experiment was conducted, focussing on the quality of ions in the samples over the duration of the experiment, comparing the relative changes in the concentrations of samples stored in the field, and in the laboratories where samples were stored outside and in the fridge. Those stored at the laboratory provided an idea of the time frame within which to filter the discrete samples.

In addition to the collection of discrete samples of the stream-water and pore-water, quasi-continuous sampling of the stream-water was undertaken with the intention of investigating the response and rate of changes in the hydrological conditions, specifically considering stream flow and runoff. At both ends of the reach, an ISCO 3700 auto-sampler was installed (Figure 3-7). Samples were pre-programmed to collect a series of discrete samples of the stream-water at a range of intervals, including daily and hourly samples to assess the hydrochemical response to changing flow corresponding with baseflow and storm conditions, to determine the stream-water response and transport rate of the incoming solutes from upstream and the changes over the reach. Autosampling is particularly useful to collect volumes of water without manual collection in the field, facilitating the understanding of nutrient dynamics in response to the hydrological conditions (Bieroza and Heathwaite 2015, 2016, Mellander *et al.* 2015). Although, limitations surrounding the sample storage are prevalent. As highlighted by Bieroza and Heathwaite (2016), fewer studies try to deal with the uncertainties associated with in-situ sampling, specifically associated with the limitations of storage transformations in unfiltered samples (Kotlash and Chessman 1998, Harmel *et al.* 2006, Bende-Michl and Hairsine 2010, McMillan *et al.* 2012). During baseflow conditions, nutrient export is limited, and in-stream processes become dominant, e.g. due to diel variations (Bieroza and Heathwaite 2016). The ability to detect the dynamics of the nutrient dynamics in response to such variations requires efficient and effective storage and analysis of samples.

To investigate the impact of various storage options and the subsequent impact on the sample characteristics, six, one-litre samples of stream water were collected (three from each site – upstream and downstream end of the reach where autosamplers were installed) and stored in three different ways:

1. In in the field in the ISCO base, with no lid – therefore subject to microbial degradation;
2. Outside, in a dark cool bag in the laboratory shed, with lid; and,
3. In the laboratory fridge, in a dark cool bag, with lid.

An initial sample was obtained from the large sample to form the baseline of the experiment, from which sub-samples in following days were collected, and the relative concentrations assessed.

Relative changes and coefficients of variation in the ion concentrations were calculated. As expected, samples taken from uncapped bottles were exposed to microbial decay, however, for the solutes of interest (Cl^-, SO_4^{2-} and NO_3^-), the relative change in the concentrations were minimal, and similar between the laboratory stored and field samples, with coefficients of variation <1.5% in those stored in the field for seven days, with refrigeration attributing to similar degradation (Figure 3-8). Considering the full set of data, some species were less stable, specifically NH_4^+ and PO_4^{3-}, where coefficients of variation were >30%

after seven days, and P was not recorded, given the rapid decay. These variables are therefore not used in the remainder of the study when discussing the temporal trends. The decay of trace metals and DOC was not considered in the degradation experiment; it was not possible to acidify samples in the field to evaluate trace metal degradation and DOC samples were not possible to analyse in the time-frame due to laboratory running schedules.

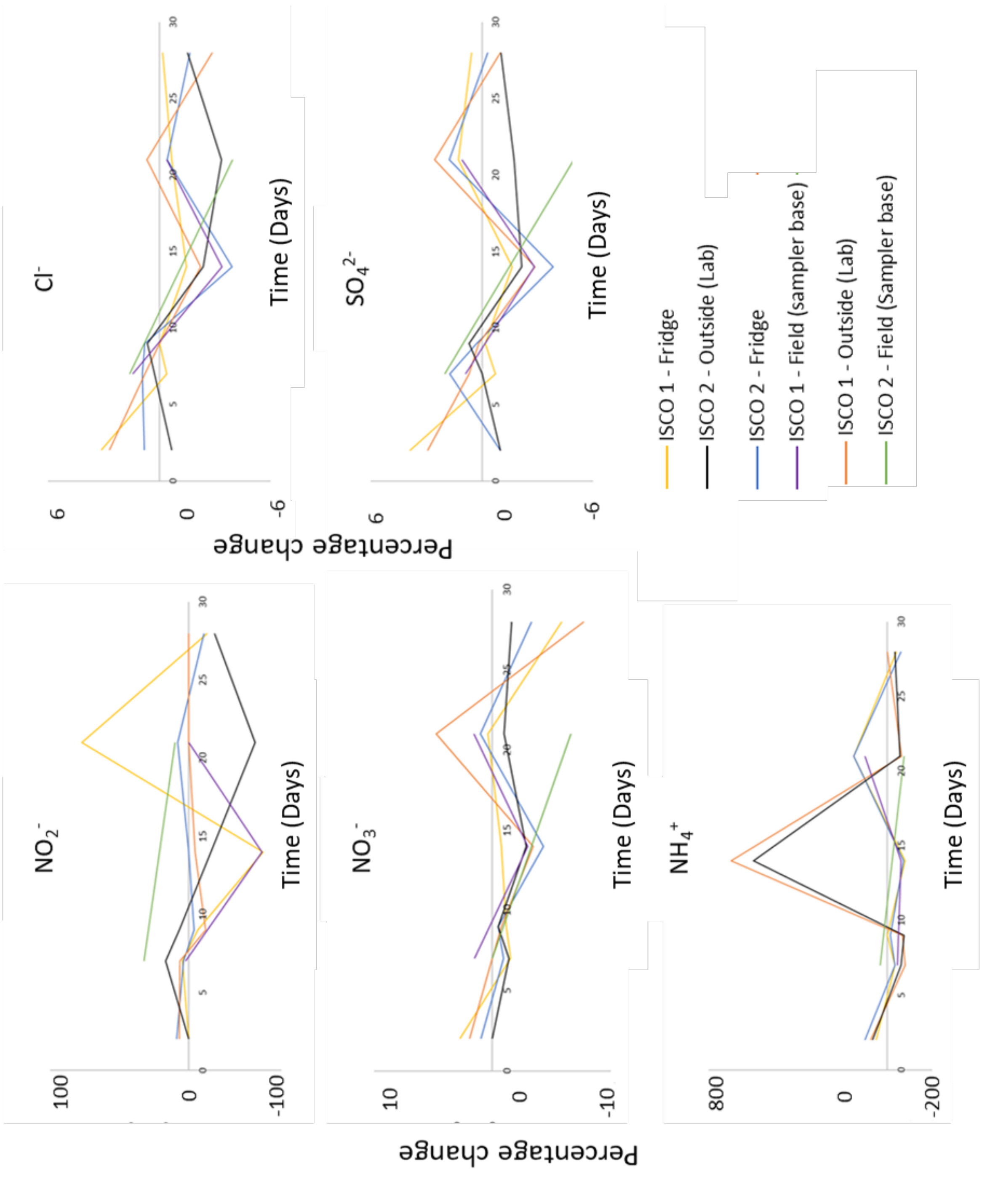

Figure 3-8: Percentage change in concentration according to the stated storage procedures outlined in the degradation experiment.

3.5.4.4. Events captured

Samples of the stream water and subsurface water were obtained over the sampling period (Figure 3-9). Autosamplers (ISCO-3700) enabled the collection of stream-water samples to determine the relationship between the chemistry and flow. ISCO samplers were programmed to collect samples on a daily, and hourly basis (Figure 3-9). The former enabled determination of the stream response to changes in flow on a daily basis with varying rainfall and pollution inputs, and the latter to assess the response and rate of change in surface-water chemistry to inputs during a flashy storm event on 27th May 2017, where stream levels rose by 0.5-0.75 m over a 15-minute period (Figure 3-9). Corresponding with the three-month auto-sampling regime, subsurface samples were collected at each of the piezometers, along with corresponding SW samples, allowing for first-order approximation into the role of the streambed in water chemistry, and changes along the reach, both in terms of the chemistry and the flow.

3.6. Results

3.6.1. Reach scale: hydrologic response

Quasi-continuous sampling over three phases facilitated an insight into the spatial and temporal responses of the SW to various changes in stream-water levels. Figure 3-9 shows the variations in discharge over the spring-summer sampling campaign. Periodic fluxes were observed and initially thought to be erroneous, however, they were found to be attributable to waste- water releases from the sewage treatment works 2.5 km upstream, contributing, on average, a twice-daily rise in stage, typically of 0.05 m (Figure 3-10). These fluxes lasted one-hour to pass from the upstream to the downstream gauge. Manual field measurements of the stream stage confirm flux occurrence, where gradual rises in the stream-water were observed on the morning of 16th May 2017 (Figure 3-10). Contributing flow from the adjoining tributaries was thought to be minimal, including that from the Blindy Burn, which is situated upstream of the lower gauging site on the Twizell (Figure 3-7). GW/SW flows were thought to be discrete.

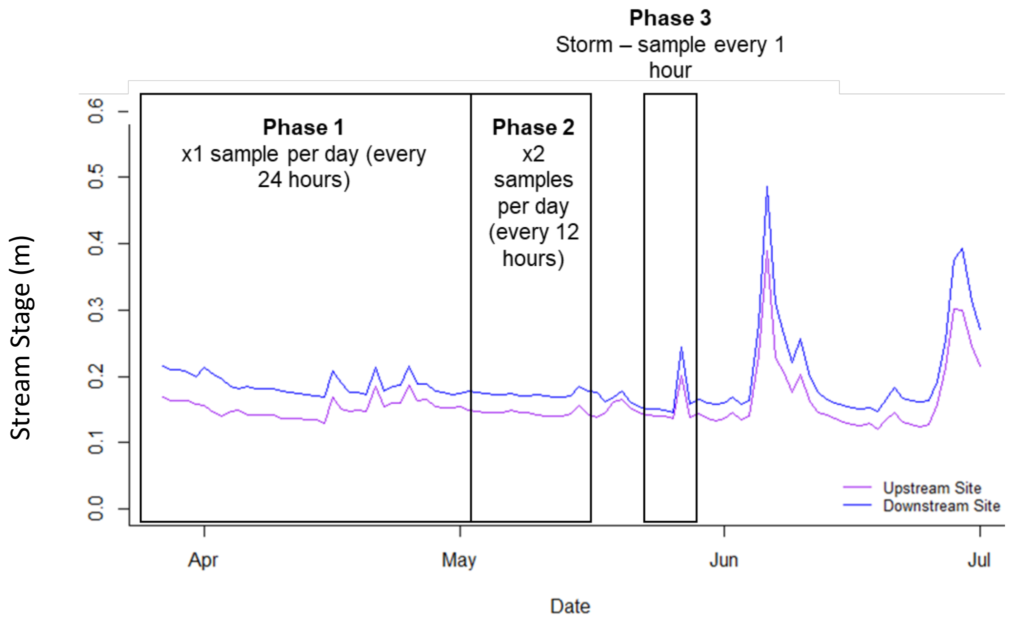

Figure 3-9: Sampling events during three-month intensive field monitoring campaign.

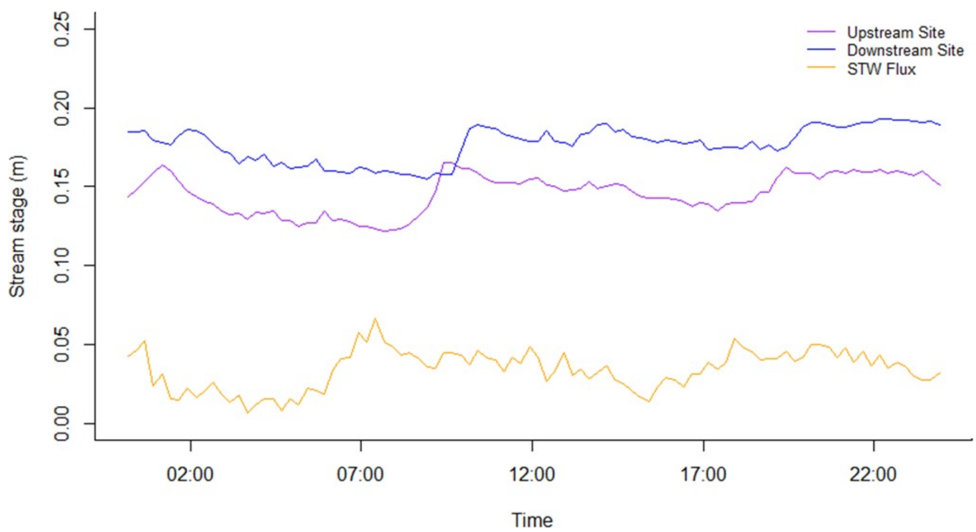

Figure 3-10: Discharge (15-min frequency) at either end of the study reach and corresponding flux from the sewage treatment works on 16th May 2017.

3.6.2. Point-scale: vertical hydraulic gradients and specific discharge estimates for single piezometers

For each of the piezometers, the corresponding vertical hydraulic gradients (VHGs) and specific discharges (q) are referred to as P1-P8 (Figure 3-11, Figure 3-12), denoting each of the sites (Figure 3-7). VHGs were variable, both positive and negative, inferring connectivity across the streambed, corresponding with discrete occurrences of upwelling and downwelling of stream- and pore-water respectively (Figure 3-11). At the reach-scale, VHGs typically ranged within +30% to -20% (Figure 3-11). More positive gradients were recorded during lower flow conditions, relative to higher flows, where the VHGs were generally weaker and more negative (Figure 3-13), hence appearing responsive to the pressure head (hydrostatic pressure) of the stream water. Where the stream head was raised, for instance during or following the onset of heavy rainfall, the piezometric heads appeared to respond, with the resulting VHGs indicating downwelling (e.g. 15/06/17; Figure 3-11) or indicating more neutral/very weak exchanges across the streambed, e.g. 01/07/17 (Figure 3-11, Figure 3-13). Besides the influence of the stream stage, geomorphic features also appeared to control the GW/SW exchanges, although to a lesser extent. With the measurements of the hydraulic heads there is anticipated to be associated error. Accounting for the error was a concern. To minimise human error, repeat measurements using a dip meter were obtained, however, with the associated water movement, error is likely to propagate, and therefore not entirely discounted.

Looking at the site-specific VHGs, the most, and consistently positive VHGs were at site P4, located at a riffle crest (Figure 3-12). This corresponded with weaker/negative VHGs at the riffle head, site P3. Otherwise VHGs were inherently more variable, as expected, likely influenced by the stream head, or a function of the underlying unconsolidated drift material beneath the streambed, resulting in non-consistent patterns of upwelling/downwelling as discussed in the conceptual model by Ibrahim *et al.* (2010).

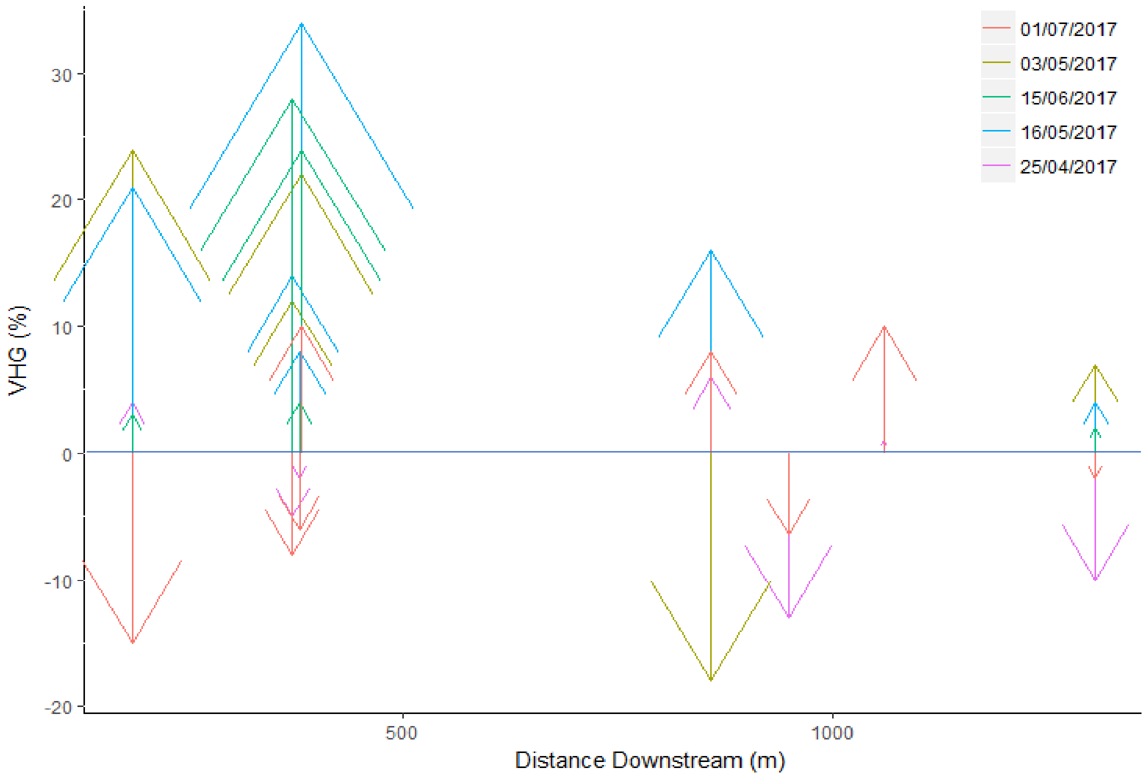

Figure 3-11: Intensity of VHGs – positive and negative VHGs respectively indicate upwelling and downwelling direction of streambed flow, relative to the stream.

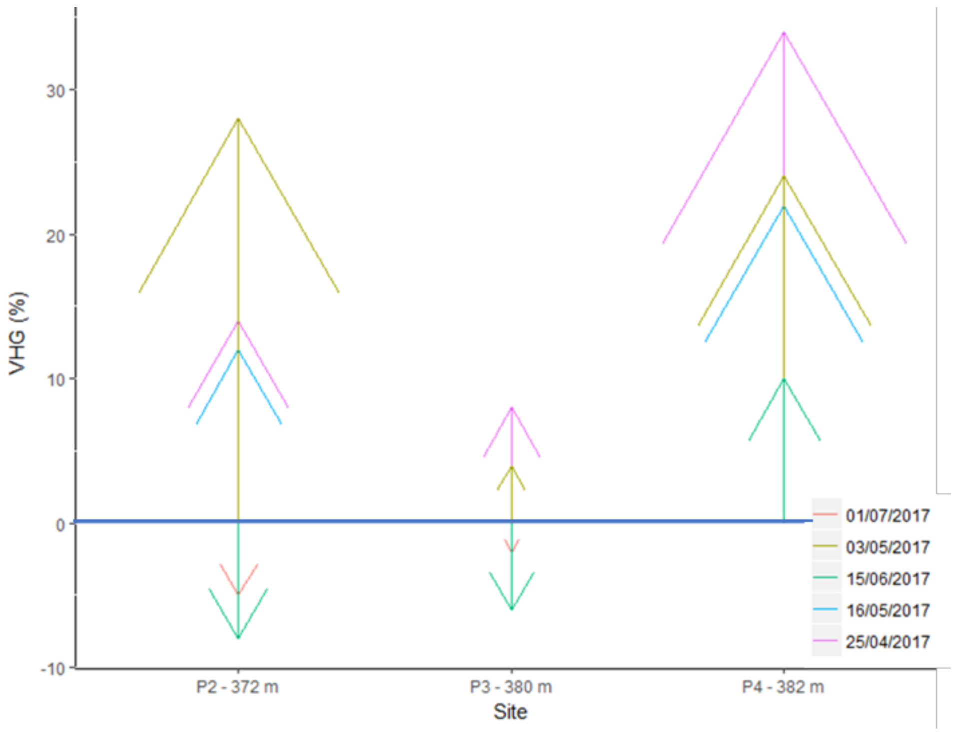

Figure 3-12: Intensity of VHGs at sites P2, P3 and P4 - positive and negative VHGs respectively indicate upwelling and downwelling direction of streambed flow, relative to the stream.

Estimates of the horizontal riverbed hydraulic conductivity (Kh) via falling head slug tests taken on 01/07/17 are shown in Table 3-3 and in relation to stream stage in Figure 3-13. Values of Kh varied along the reach and are similar to those observed for silt, sandy silts, and clayey sands (Fetter, 1994), indicative of high hydraulic conductivity; as expected of unconsolidated minor aquifer formations (Stanford and Ward 1988, Lawler *et al.* 2009, Ibrahim 2012). The subsequent specific discharges (qs) are also variable, fluctuating on a site-by-site basis, with average fluxes within the range of -5 to +4 m/day (Figure 3-13). There were no significant changes in the flow over the reach, suggesting no major gains or losses to, or from the deep GW, with a slight, but noticeable loss in stream-water, with inputs from runoff and inflows been minimal (Figure 3-9). Instead, site-specific fluxes are attributed to localised changes (e.g. Bencala *et al.* 2011), with deep GW upwelling/downwelling thought unlikely.

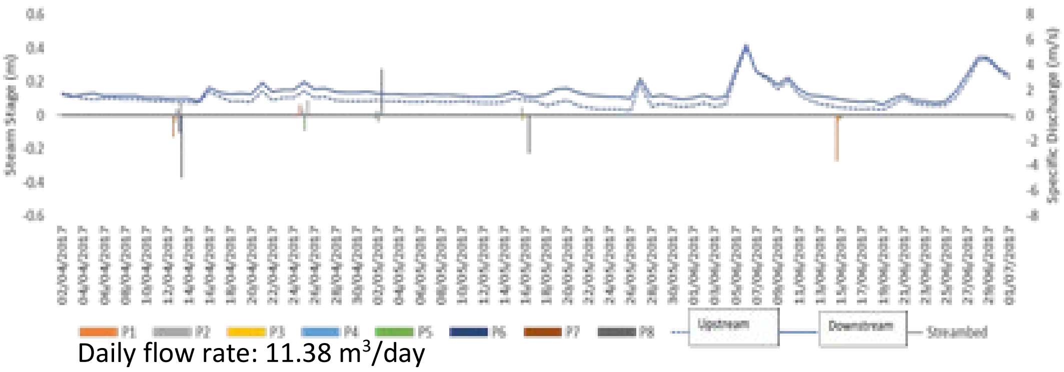

Figure 3-13: Stream discharge (15-min frequency) along the study reach with corresponding specific discharge measurements from piezometers.

Table 3-3: Sampling dates (red: hydraulic and chemistry measurements; black: hydraulic measurements only), with the screen depth and Kh estimates obtained on 01/07/17.

Date of sampling	Site	Screen depth (m)	K_h (m/s)	K_v (m/s)
12/04, 25/04, 03/05, 16/05, 15/06, 01/07	P1	0.45	0.00085	0.000085
15/06, 01/07	P1A	0.45	0.00085	0.000085
12/04, 25/04, 03/05,	P2	0.45	0.00021	0.000021
12/04, 25/04, 03/05,	P3	0.45	0.00019	0.000019
12/04, 25/04, 03/05,	P4	0.45	0.00019	0.0000019
15/06, 01/07	P4A	0.45	0.00057	0.000057
15/06, 01/07	P4B	0.45	0.00057	0.000057
12/04, 25/04, 03/05,	P5	0.45	0.00057	0.000057
12/04 and 15/06	P6	0.45	0.00085	0.000085
15/06, 01/07	P6A	0.45	0.00085	0.000085
15/06, 01/07	P6B	0.45	0.00085	0.000085
12/04 and 15/06	P7	0.45	0.00085	0.000085
12/04, 25/04, 03/05,	P8	0.45	0.00135	0.000135

N.B. – P6, P6A, P6B and P7 were in close proximity and therefore, the hydraulic conductivities were very similar.

3.6.3. Reach-scale: temporal patterns in water chemistry

Using quasi-continuous autosampling techniques to obtain daily time-series, it was possible to gain a first-order approximation of the changes in the stream-water chemistry as a function of hydrological flow variations, from which the loading and fluxes of flow and solutes could be assessed over the reach in the SW. An array of stream-water samples were collected over the spring-summer sampling campaign, with samples obtained at both ends of the study reach (Figure 3-7). Samples comprised 200 ml daily, twice daily and hourly samples. The stream-water was typically alkaline, with near-neutral pH values. Throughout the sampling period, the water temperature reflected the ambient air temperature, and was characteristic of oxidising conditions, with ORP values >50 mV. Based on the degrading quality relating to the storage of samples, conservative elements including Cl^-, B and EC, and stable non-conservative redox-sensitive species, including SO_4^{2-} and NO_3^- were analysed, and used to assess the likely impacts of mine-water pollution and waste-water effluent releases respectively. The remaining ions from the daily and twice-daily samples were deemed unstable from degradation analysis, whilst trace metals and DOC were not included in the analysis, first due to the unknown degradation in the field, the former as the samples were not acidified to preserve the metals, hence were likely to rapidly decay. Secondly, due to laboratory constraints which meant that the testing of the rate of degradation was not possible, these samples were discounted from the analysis. However, all species were considered from the storm sampling event (Phase 3 – Figure 3-9), given that the samples were collected, refrigerated and analysed within a 24-hour window.

3.6.3.1. SW sampling – Phase 1

Concentrations of conservative ions in the stream-water, specifically electrical conductivity (EC), bromide (Br) and chloride (Cl^-), were variable with the changes in discharge. Concentrations of B were generally too low to use as a conservative tracer. Cl^- loads appeared responsive to rises in flow corresponding with increasing concentrations at both sites (Figure 3-14). The loss in Cl^- corresponds with the observed loss in flow, with a net loss in the load indicating that there were no predominant influent conditions, e.g. from GW or tributaries, with minimal influence from the small adjoining tributary (Blindy Burn, Figure 3-7) near the downstream sampling site.

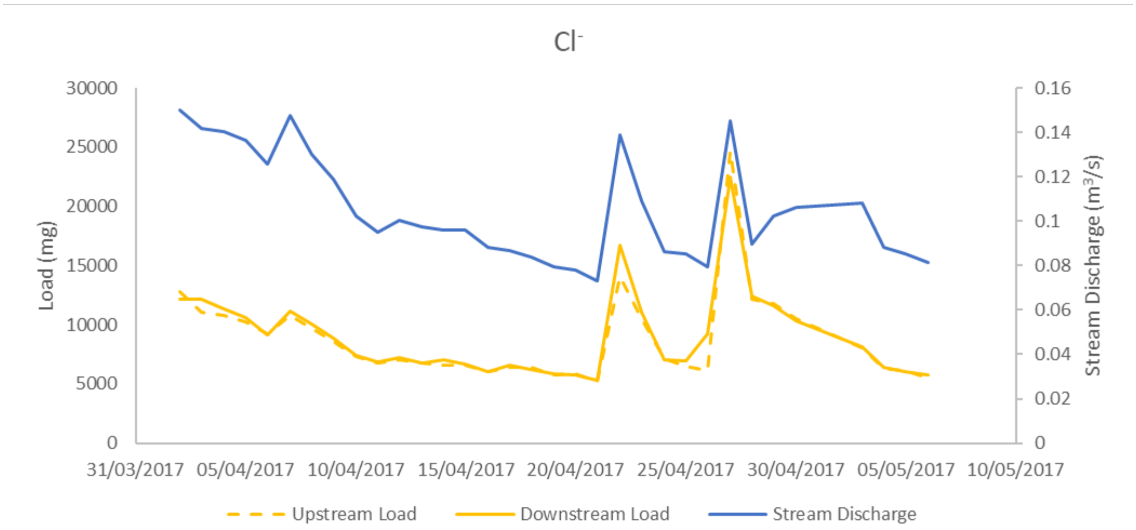

Figure 3-14: Load of Cl^- transported along the reach according to samples obtained once-daily (midnight) from 27/03/17 to 02/05/17.

Under prevailing effluent conditions, and relatively stable stream flow conditions (27/03/17 to 02/05/17 [Figure 3-9]), the load of SO_4^{2-} transported appeared to increase, with an average gain in load of 1850 mg/s transported over the reach (Figure 3-15). With the onset of more variable conditions, and relatively higher flows (Figure 3-15), there was an evident loss in SO_4^{2-} load, accounting to an average net loss of 2743.11 mg/s at the downstream end of the reach, likely corresponding with the dilution and subsequent loss of ions. Generally, the downstream end of the reach was more enriched, with greater loadings, thus suggesting discrete inflows from the subsurface via the superficial deposits.

Coinciding with this, the load of NO_3^- transported decreased over the reach, likely due to denitrification. Increases in the NO_3^- loadings were in accordance with relatively higher flows (Figure 3-16). Results therefore suggest that the system is responsive to changes in the flow, with a tandem of threats, alternating between mining and contemporary effluent-related sources in accordance with the stream-water conditions, with no gains or losses to the deep GW, and instead restricted to the shallow GW in the minor superficial aquifer.

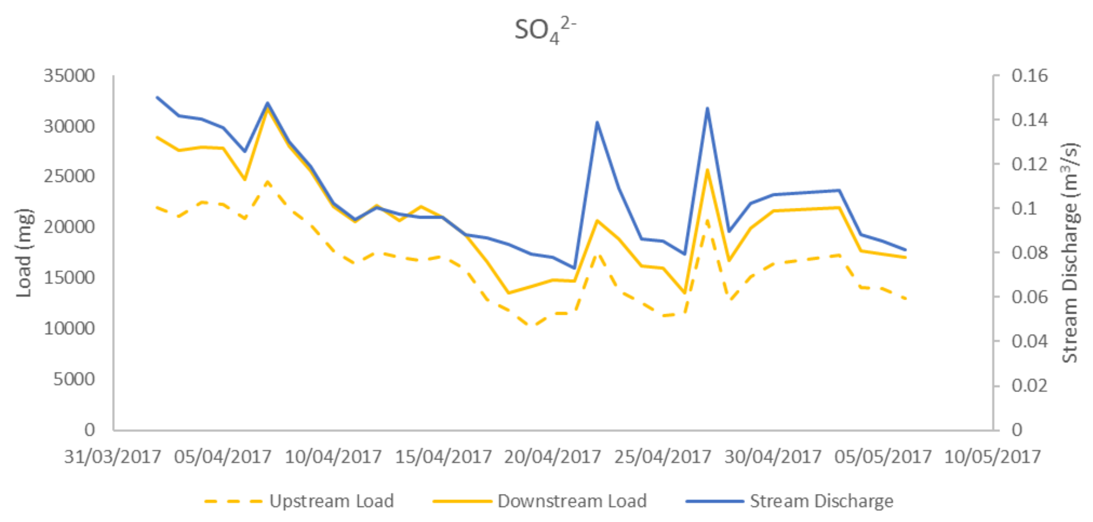

Figure 3-15: Load of SO_4^{2-} transported along the reach according to samples obtained once-daily (midnight) from 27/03/17 to 02/05/17.

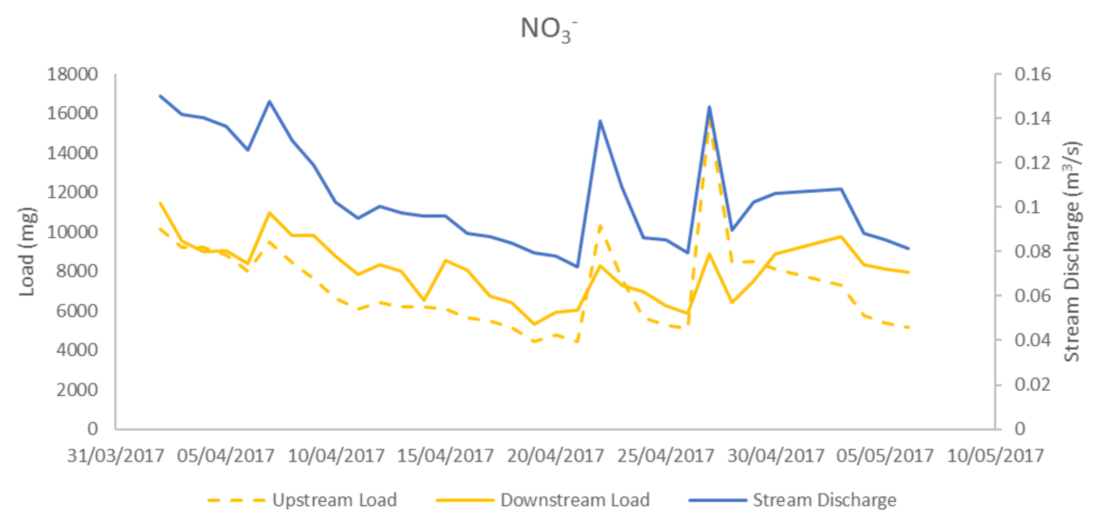

Figure 3-16: Load of NO_3^- transported along the reach according to samples obtained once-daily (midnight) from 27/03/17 to 02/05/17.

3.6.3.2. SW sampling – Phase 2

Subsequent sampling of the apparent mid-morning sewage treatment work flux was investigated with an additional stream-water sample collected at midday for two weeks (02/05/17 to 20/05/17) where there were no apparent fluctuations in stream stage, apart from those observed as a function of diel changes and the periodic releases from the sewage treatment works. Analysis of the chemistry indicated that changes were minimal and insignificant, with changes in discharge low (~0.07 m3/s). The nutrient loadings in the stream-water samples were not impacted by the flux; NO_3^- remained enriched in the upstream samples relative to those downstream.

3.6.3.3. SW sampling – Phase 3

In addition to the daily sampling, hourly samples obtained before, during and after a storm (Figure 3-17), allowed for the further understanding of the hydrochemistry response of the SW. The rainfall led to a rapid rise in the stage (Figure 3-9) and corresponded with the dilution of the solutes in the stream-water, indicated by the sudden fall in conservative and inorganic elements, including SO_4^{2-} and DOC, corresponding with dilution as marked by Cl^- (Figure 3-17). Under flood conditions, the nutrients were enriched, specifically NH_4^+ and NO_3^- (Figure 3-17). The response of the system was notable flashy, with the rapid change in the chemistry. Over the duration of the storm it is evident that the mining-related effluents were muted by elevated waste-water effluents.

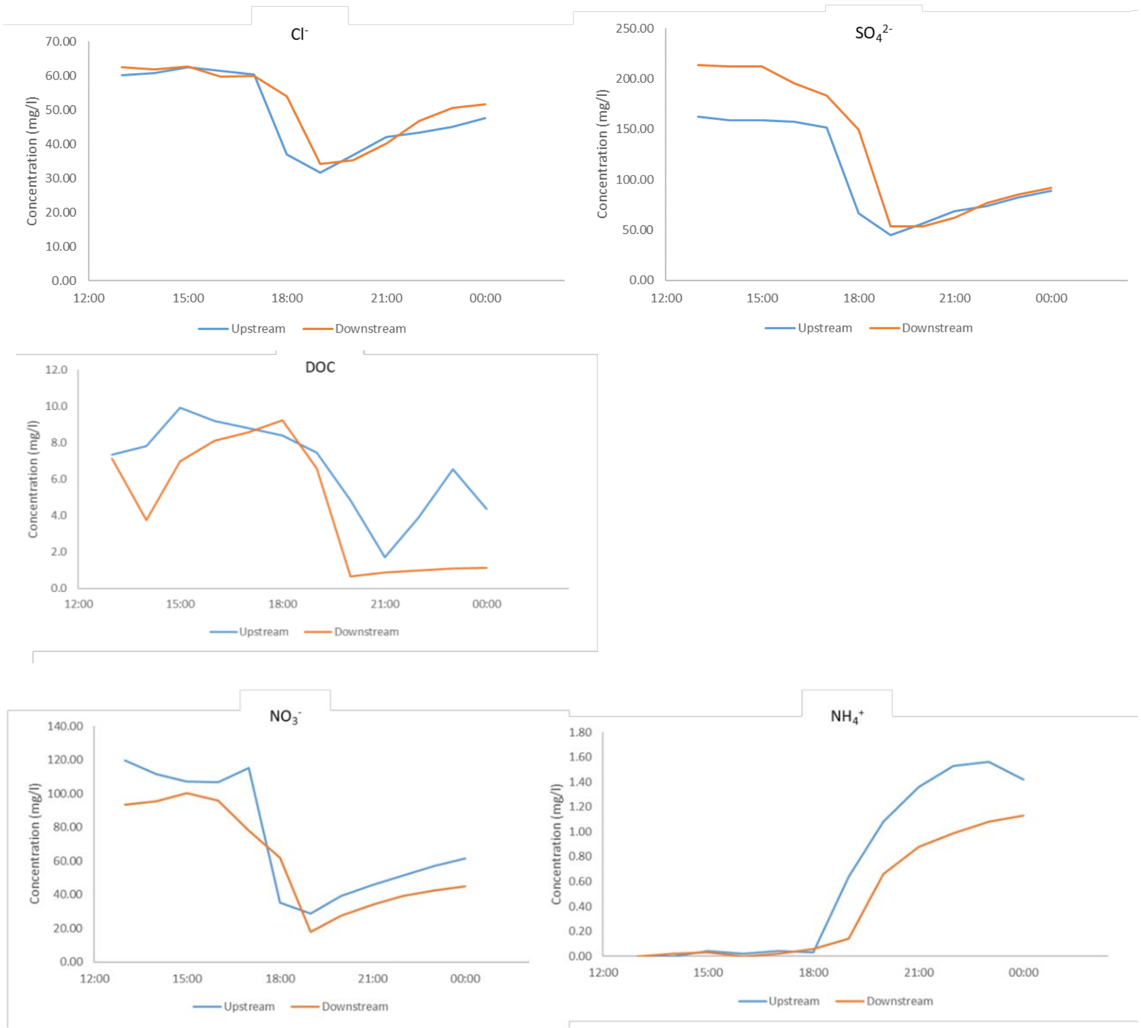

Figure 3-17: Load of solutes transported along the reach according to samples obtained hourly before, during and after the storm.

3.6.4. Stream-water chemistry

From the sampling it is apparent that the processes operating along the reach are highly heterogeneous and complex, with additions and losses in flow and solutes in the stream-water chemistry. It is evident from the reach-scale quasi-continuous sampling that changes in the effluent loadings are responsive to the stream discharge, with dilution of mining-derived solutes and corresponding nutrient enrichment during higher flows. Beyond the reach-scale patterns, localised discrete patterns of upwelling and downwelling of the SW to the subsurface has been understood based on the VHGs, marked with varying concentrations of solutes in the SW and shallow GW samples. Whilst it is challenging to assess the horizontal pathways and subsequent flow and solute movements occurring in the subsurface, the vertical patterns provide an insight into the system behaviour and potential hotspots in chemistry. Localised changes in the SW chemistry are likely attributable to surface leachates as well as upwelling from the subsurface. Conservative tracers, specifically Cl^- and Br provide a means of assessing such points, which are typically associated with the enrichment and dilution at the local scale (Ibrahim *et al.*, 2010).

On average, it was found that SO_4^{2-} was elevated at the downstream end of the reach relative to the upstream, corresponding with subsequent iron-ochre flushes/staining on the bed and banks of the channel, particularly at the lower stretch of the study reach. The raised concentrations are indicative of mining-derived solutes (e.g. Younger *et al.* 2002). The identification of the relative solute sources would require the use of isotopes, for example (Engelhardt *et al.* 2011), and would require further work beyond the scope of this research. Using the knowledge gained from walkover surveys conducted as part of the research, an outfall from the Alma colliery spoil at the upstream end of the reach (Figure 3-18) was considered as a key contributor of mining-related effluent (SO_4^{2-} > 450 mg/l and Mn > 0.9 mg/l).

Assessing the SO_4^{2-} to Br ratio, it would appear that SO_4^{2-} was considered to be acting non-conservatively, with localised points of enrichment in the stream water, dissimilar to those observed from the mining-spoil drainage outfall (Figure 3-19). Similarly, the enrichment in Mn over the reach, accounting to around 0.2 mg/l again were likely attributing to localised sources, with an elevated ratio of Mn to Br (Figure 3-19). The relative ratios of SO_4^{2-} and Mn showed no clear trends with Cl^- (Figure 3-20 and Figure 3-21). Concentrations of SO_4^{2-} and Mn were relatively smaller to those from the selected spoil heap outfall yet are important in highlighting the localised contributions to the stream-water chemistry.

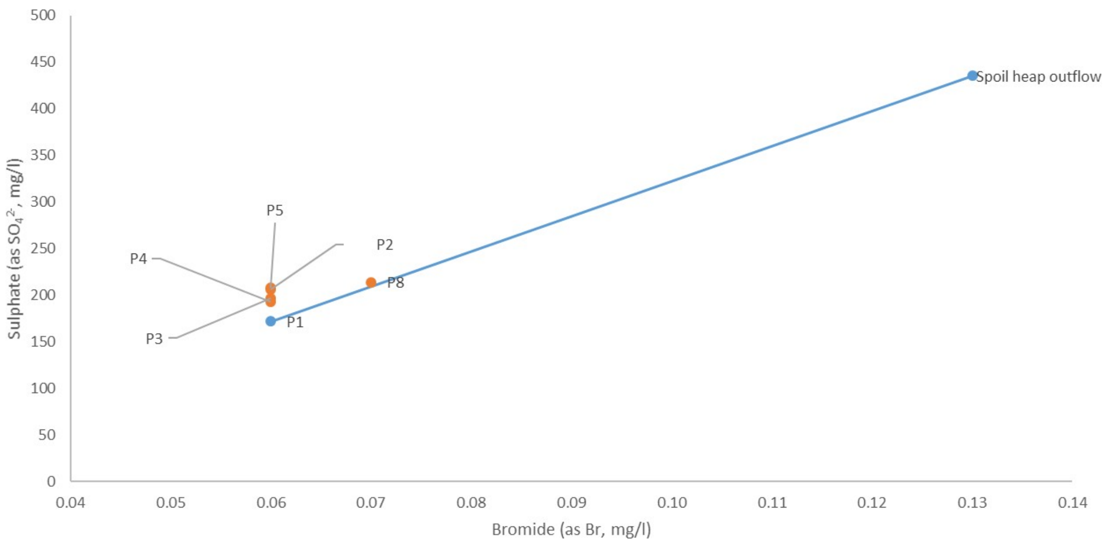

Figure 3-18: SO_4^{2-} and Br ratio for the piezometer SW samples, P1-P8.

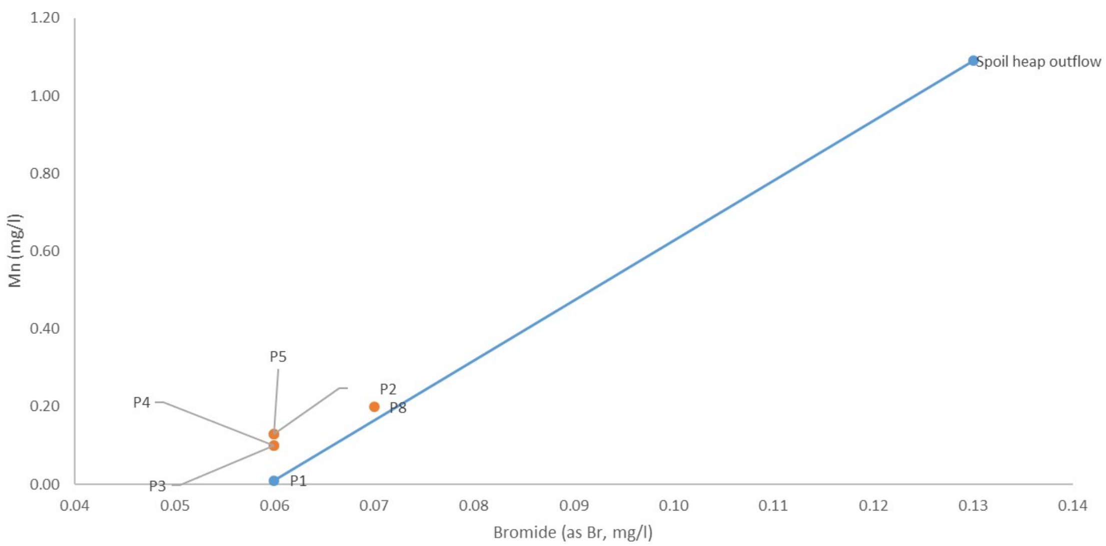

Figure 3-19: Mn and Br ratio for the piezometer SW samples, P1-P8.

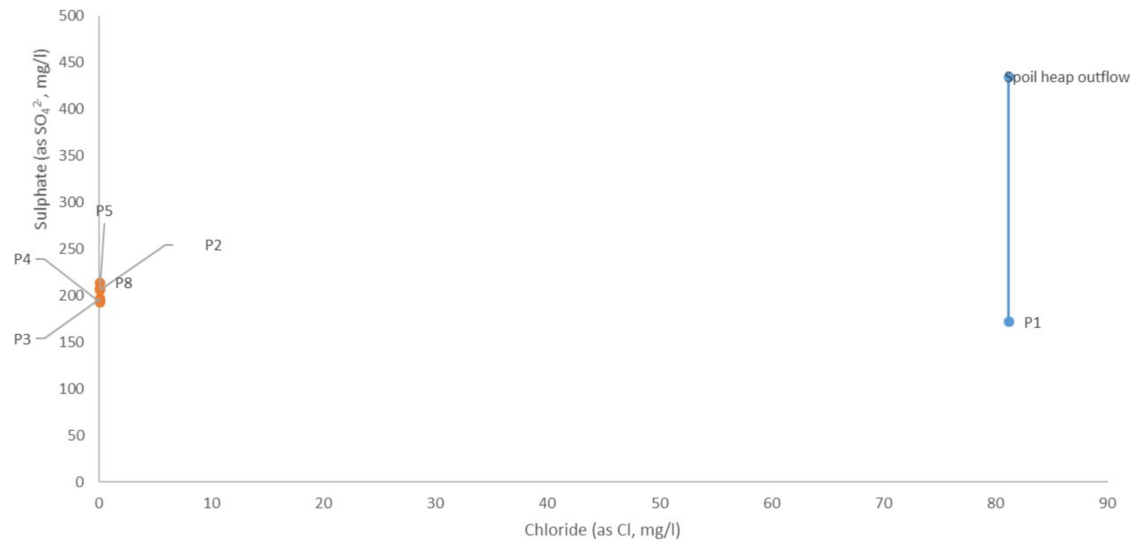

Figure 3-20: SO_4^{2-} and Cl^- ratio for the piezometer SW samples, P1-P8.

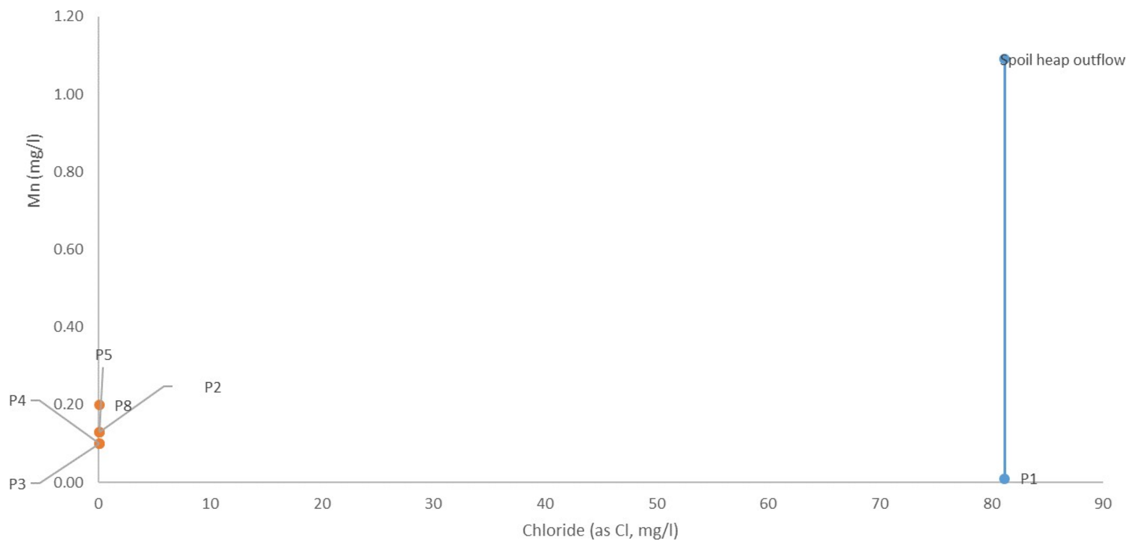

Figure 3-21: Mn and Cl^- ratio for the piezometer SW samples, P1-P8.

At the specific sites along the reach, comparing the solute concentrations in the SW and GW obtained from the piezometers, concentrations of solutes were indicative of the enrichment and depletion of mining-derived effluents, however, were behaving conservatively, with changes in concentrations operating by the same mechanisms, e.g. rise in stream levels. However, at some sites, specifically P1, P4 and P8 there was an enrichment of SO_4^{2-} and Mn, and at P3, an enrichment of NH_4^+ with the localised hot-spots suggesting solute propagation. At these named sites, the non-conservative nature of the solutes against Cl- and Br- suggest that the sources of SO_4^{2-}, and NH_4^+ at site P3, are from locations beyond the channel water, e.g. leaching from the banks, with pathways extending beyond the points sampled. Ultimately the exchanges between the stream and subsurface are much more complex than water moving up and down across the streambed, with pathways interacting in complex ways.

3.6.5. Pore-water chemistry

From the sampling of the piezometers it is possible to infer changes in the pore-water chemistry, relative to the stream-water (Table 3-4) to give an indication of the differences in chemistry across the streambed. The mean values used to normalise the pore-water samples are shown in Table 3-5 - absolute values of pH were used (mean values of other species were taken using the full reach of SW samples). Ratios of the concentrations between the stream and streambed were estimated, to determine the enrichment and depletion of species in the pore water (Table 3-6). Where stream-streambed ratios were greater or less than one respectively indicates the enrichment or depletion of species in the pore water relative to the stream water (Ibrahim *et al.* 2010).

At the reach-scale, the temperature of the GW was similar to the ambient conditions at the surface, with prevailing anaerobic (anoxic) conditions denoted by the DO (%) falling, during the sampling period, to a minimum of around 20%. Interchanging oxidation-reduction conditions during the sampling period were evident, both along the reach, and between the stream- and pore water, however, estimates of the reducing/oxidizing potential is limited without the collection of Fe and Mn (hydr)oxides (as done, e.g. in the work of Ibrahim 2012). Values of pH were generally consistent along the reach, and between the stream- and pore-water, with pH values of 6.6 to 7.9 associated with alkaline/near-neutral conditions. The subsurface chemistry appeared responsive to both the site characteristics and the stream stage at the time of sampling.

*Table 3-4: SW chemistry at piezometer sites (Figure 3-7) for sampling events: sample 2 (12/04/17)/sample 4 (16/05/17)/sample 6 (15/06/17) – NA (not sampled); * (not analysed).*

Site ID	DO (%)	EC (µS/cm)	pH	ORP (mV)	DOC (mg/l)
P1	108.6/114.3/102.8	0.94/0.94/0.88	7.68/7.90/7.21	0.7/50.7/13.4	7.0/7.3/5.1
P2	NA/107.6/97.2	NA/1.00/0.92	NA/7.18/6.97	NA/76.7/58.5	NA/6.2/5.4
P3	104.4/110.5/98.4	1.04/1.00/0.94	7.23/7.17/7.17	20.2/70.1/78.4	6.4/7.0/6.0
P4	104.5/107.8/97.5	1.04/1.00/0.94	7.16/7.16/7.19	13.7/73.2/73.9	6.2/7.1/6.0
P5	104.8/107.7/97.5	1.05/1.03/0.94	7.44/7.82/7.19	29.8/79.1/73.9	6.4/6.7/5.8
P6	106.5/NA/95.2	1.05/NA/0.94	7.49/NA/7.22	33.9/NA/54.0	5.8/NA/*
P7	104.2/NA/95.2	1.05/NA/0.94	7.47/NA/7.27	50.6/NA/60.6	6.4/NA/*
P8	102.4/*/94.5	1.05/*/0.95	7.62/*/7.39	27.6/8.2/95.2	6.3/6.2/5.0

Site ID	Fe (mg/l)	Mn (mg/l)	Zn (µg/l)	Chloride (mg/l)	SO_4^{2-} (mg/l)
P1	0.09/0.04/0.02	0.03/0.01/0.00	12.68/9.36/55.41	79.3/81.2/102.8	191.7/171.9/150.9
P2	NA/0.02/0.01	NA/0.13/0.06	NA/12.87/42.17	NA/80.7/101.7	NA/205.8/172.2
P3	0.03/0.03/0.01	0.19/0.10/0.05	15.11/13.34/61.72	76.0/82.0/96.7	208.2/196.8/171.6
P4	0.07/0.02/0.01	0.20/0.10/0.05	14.98/12.87/61.72	75.3/80.5/103.1	207.6/192.6/173.7
P5	0.02/0.02/0	0.14/0.13/0.04	6.77/12.68/38.4	76.2/82.1/102.5	206.4/207.6/172.8
P6	0.03/NA/*	0.18/NA/*	13.24/NA/*	76.2/NA/98.9	206.4/NA/172.5
P7	0.05/NA/*	0.17/NA/*	12.96/NA/*	77.0/NA/102.1	208.5/NA/160.5
P8	0.04/0.04/0.04	0.25/0.2/0.15	13.09/11.21/42.78	75.6/82.2/105.6	208.5/213.9/178.5

Table 3-5: Stream-water average composition from SW grab samples obtained along the reach at the piezometer sites (Figure 3-7).

Sample ID	DO (%)	SPC (µS/cm)	TDS	ORP (mV)	DOC (mg/l)
Sample 2 12/04/17	105.05	1.03	1.00	25.21	6.36
Sample 4 16/05/17	109.58	0.99	0.76	59.67	5.88
Sample 6 15/06/17	97.29	0.93	0.613	63.49	5.55

Sample ID	Fe (mg/l)	Mn (mg/l)	Zn (µg/l)	Sulphate (mg/l)	Nitrate (mg/l)
Sample 2 12/04/17	0.05	0.17	12.69	205.33	18.96
Sample 4 16/05/17	0.03	0.11	12.22	198.10	23.85
Sample 6 15/06/17	0.03	0.06	50.37	169.09	19.92

Table 3-6: Enrichment/depletion ratios of the GW chemistry relative to the SW averages (Table 3-5) for sampling events: sample 2 (12/04/17)/sample 4 (16/05/17)/sample 6 (15/06/17). Where SW/GW ratios greater or less than one respectively indicates enrichment (yellow) or depletion (blue) of species in pore water relative to stream water.

Site ID	DO (%)	EC	DOC	Fe
P1	0.36/0.39/0.24	1.17/1.31/1.63	0.99/0.97/0.52	0.21/NA/NA
P2	NA/0.43/0.84	NA/1.05/1.08 (µS/cm)	NA/*/0.69	NA/0.35/0
P3	0.48/0.54/0.29	0.63/1.19/0.98	1.16/*/1.16	0.64/0.35/0
P4	0.49/0.49/0.47	1.11/1.23/1.08	0.95/*/1.21	0.85/1.76/0
P5	0.47/0.49/0.64	0.98/1.03/0.90	1.05/*/0.67	0.42/0.35/0
P6**	NA	NA	NA	NA
P7**	NA	NA	NA	NA
P8	0.37/0.41/0.85	1.20/1.19/1.03	0.79/*/0.81	1.69/0/0

Site ID	Mn	Zn	Cl^-	SO_4^{2-}	NO_3^-
P1	1.63/7.70/24.51	3.12/0.77/1.46	1.04/1.10/0.99	1.54/1.86/3.09	0.80/0.75/0.41
P2	NA/0.36/2.22	NA/*/0.82	NA/1.12/0.95	NA/1.04/1.01	NA/0.81/0.56
P3	1.81/2.06/3.6	1.72/*/50.52	1.03/1.00/1.00	1.15/1.10/0	1.81/1.45/1.18
P4	8.93/10.84/24.69	1.63/*/1.06	0.86/1.36/0.90	1.39/1.51/0.90	0.59/0.65/0.86
P5	0.12/0.18/1.2	0.69/*/1.08	1.00/1.07/1.04	0.92/0.97/1.06	0.95/0.94/1.02
P6**	NA	NA	NA	NA	NA
P7**	NA	NA	NA	NA	NA
P8	8.81/9.49/36.51	1.13/*/1.56	0.86/1.04/0.93	1.44/1.41/1.01	0.49/0.58/0.57

N.B.: *denotes that samples were not analysed; **piezometers were damaged when sampling was due to be conducted; NA sites that were not sampled, e.g. due to damage of piezometer.

Conservative tracer (EC and Cl^-) patterns between the stream-water and pore-water displayed limited differentiation between the stream- and pore-water (Table 3-6). SW/GW ratios of these tracers were generally around one, reflecting the cycling of stream-water, and no additional deep GW fluxes (Table 3-6). Limited differentiation was generally the case, apart from at site P1, where EC was enriched and depletion coinciding with downwelling and upwelling (Figure 10; Table 6). Relative to run and pool sites, EC ratios in riffle sites (P4) fluctuated more, indicating both slight enrichment of EC in the streambed associated with the upwelling of pore-water (Table 3-6). Based on the similar composition of the conservative tracers in the stream- and pore-water, it was difficult to assess any definitive pathways of the hyporheic flow paths, and instead the enrichment and depletion of redox-sensitive species were assessed (Table 3-6).

Ratios of DOC between the streambed and surface generally showed limited differentiation during samples 2 and 4, with enrichment in DOC been more associated to sample 6, with depletion at run sites (P1, P2 and P5), however, dissimilar to riffle sites (P3 and P4) where concentrations indicated slight enrichment (Table 3-6). In all samples, O_2 (sampled as DO%) was depleted in the streambed, with most severe depletion in sample 6 corresponding with the loss of conservative species. The pH of the stream- and pore-water was similar (Table 3-6), with values indicating near-neutral pH.

The enrichment and depletion of redox-sensitive species was localised, varying site-by-site in accordance to the change in pressure head corresponding to the changes in stream stage. SO_4^{2-} was notably enriched at P1, particularly in sample 6. At other sites, SO_4^{2-} was also evidently enriched, including P3 and P8, but was relatively weak enrichment in comparison to P1, especially sample 6 (Table 3-6). Depletion of SO_4^{2-} - was evident in some instances, for example, during sample 2 at sites P2 and P5 (Table 3-6). Otherwise there was limited differentiation between the stream- and pore-water. Meanwhile, NO_3^- ratios marked both enrichment and depletion in the streambed (Table 3-6). The greatest depletion was associated with predominant downwelling across all samples at site P3, and pore-water depletion with predominant upwelling at site P4 (Table 3-6). However, the concentration ultimately depends what is in the stream-water at the time of sampling.

Concentrations of Mn were occasionally markedly enriched in the pore-water, coinciding with enrichment in SO_4^{2-}. In some instances, the enrichment in SO_4^{2-} and Mn corresponded with Zn enrichment, markedly observed during sample 6 at site P3, and lesser so at sites P1 and P8, although with slight enrichment (Table 3-6). Fe (total) concentrations were otherwise low, with Fe appearing to have precipitated on the streambed, observed during walkovers as bright-orange iron ochre staining (Figure 3-22).

3.7. Discussion

The monitoring network and sampling regime has enabled the investigation of the flow and solute fluxes, both in-stream and across the streambed, with the aim of making a first-order assessment of the influence of the minor aquifer formation and the likely impact of GW/SW exchanges on the stream-water quality. The findings and understandings are restricted to the events sampled over the three-month campaign and the sites where the sampling was performed. However, I was also able to consider the role of stream discharge and geomorphological changes on the resulting stream-water chemistry, looking beyond the one-dimensional understanding of the SW system upon which the WFD and management currently focus, assessing the potential system connectivity. Through reach- and point-scale sampling, the lateral, longitudinal, vertical and temporal changes in flow and solute fluxes have been broadly investigated, testing the following objectives for the Twizell: 1. to quantitatively assess the role of the minor aquifer position and contributions to stream-flow; and 2. to investigate the role of the minor aquifer as a source and sink of flow and solutes from multiple threats. Results suggest with water quality reflecting the proximity to these sources and changes in stream flow, with sampling providing a first-order insight into the complex nature of the subsurface and its likely impact on stream-water.

3.7.1. Threat variations according to stream-water hydrochemistry

In-stream solute concentrations vary in accordance with spatial and temporal changes, accounting to surface and subsurface contributions, such as land-use changes and hydrochemical processes linked to biotic activity (Ibrahim *et al.*, 2010). The variability in conservative solutes (EC and Cl^-) over the reach appears to reflect the stream stage at the time of sampling (Rice and Hornberger 1998). Fluctuations in EC and Cl^- are evident when looking at both the quasi-continuous sampling and discrete samples obtained along the reach at the piezometer sites. Between the upstream and downstream sampling sites of the reach, during relatively lower flows, the loss in load of conservative solutes (EC and Cl^-) was evident, with the high hydraulic conductivity of the unconsolidated superficial deposits, likely facilitating the loss to the underlying system (Tetzlaff *et al.* 2007). The exchanges are likely occurring between the stream-water and the minor aquifer, with no deep GW contributions, given that there were no spikes in conservative solutes and that GW flow pathways would likely exhibit dominant upwelling or downwelling, contributing to the stream flow. GW flow paths are more likely in constrained reaches with no superficial layering (Ibrahim *et al.* 2010). Whilst appearing disconnected to the deep GW, the role of the minor, perched aquifer system is nonetheless evidently interacting with the stream-water, with VHGs and specific discharges, potentially attributing to localised SO_4^{2-} loadings, corresponding with iron-ochre staining in the lower part of the reach.

Elevated nutrient loadings were particularly problematic during rapid-onset, high flow events such as during the spring storm sampled at the end of May 2017, where nutrient levels were 35-times and 50-times greater respectively at the upstream and downstream ends of reach at peak of the storm corresponding with reductions in SO_4^{2-} by half, likely due to dilution. Based on this observation, the historic and contemporary threats operate in tandem, with the impacts on the solutes present being a function of the lower and higher flows respectively. The solutes and loadings associated with the mining are therefore the priority for management interventions.

Discrete sampling of the stream water at the same time as the pore-water sampling did not reflect the SO_4^{2-} fluxes, which is likely due to the locations and timing of sampling, with the sampling not matching the quasi-continuous sampling, and the different time at which samples were collected, such as at midnight, which in turn were impacted potentially by the diel variability, as well as the inability to sample during high flows. The samples along the reach show little variation, with similar coefficients of variability for conservative and non-conservative solutes over the reach, suggesting the lack of surface and subsurface inputs over the reach. More detailed sampling is likely to be required to investigate the local-scale heterogeneity of the SO_4^{2-} in relation to the iron-ochre flushes (Holmes *et al.* 1994, Baker *et al.* 2000). Meanwhile, the quasi-continuous dataset reflects the spatial and temporal variability over a range of flow events. Assessing the mixing ratios of SO_4^{2-} to the conservative solutes, Cl^- and Br, indicate that it is non-conservative behaviour is indicative of upwelling along the reach, something which is to be further tested with numerical modelling approaches.

Overall, from the stream-water sampling is indicative that the SW system is responsive to the stream stage variation, with threats operating in tandem, which accounts for changes in solute concentrations, with changes in conservative (EC and Cl^-) and non-conservative solutes (SO_4^{2-} and NO_3^-). During relatively higher flows, the stream appears more vulnerable to the impact of effluent releases, with the dilution of SO_4^{2-} and disappearing of iron-ochre precipitates. During relatively lower flows, it appears that the mine-water is more problematic, with higher SO_4^{2-} and iron-ochre flushes, particularly in the lower half of the reach.

3.7.2. Interactions of the hyporheic flow paths and biogeochemical processes in the streambed

VHGs and specific discharge results support the contention that there is the development of a minor aquifer in the vicinity of the stream. Limited differentiation in the chemistry between the stream and streambed indicate high hydraulic conductivity, associated with upwelling and downwelling gradients. Similar patterns of EC, Cl^- and Br between the systems also support the high hydrological connectivity. Exchanges across the streambed are limited with increased flows, such as those observed during mid-June and early July 2017 (Figure 3-5). Low VHGs favour vertical hydrochemical differentiation of conservative and redox-sensitive species, for instance SO_4^{2-} and Mn. However, it is not known if these solutes coming from depth, i.e. below the piezometer depth sampled. These questions are investigated in Chapter 4.

Relative depletion of DOC, NO_3^-, SO_4^{2-} and O_2 in the shallow pore-water is indicative that solutes are introduced into the bed by infiltrating stream-water, with increased depletion of these species when the VHGs are positive or neutral. Essentially the stream-water is entering and leaving the subsurface along the reach, with the biogeochemical process operating within the hyporheic zone (Baker *et al.* 2000, Sophocleous 2002). Dynamic conditions were observed at some of the points sampled, whereby the streambed evidently retains Mn, for example at P1, P4, P3 and P8, particularly when the hydrological connectivity across the streambed reduces during relatively higher stream flow events. The enrichment of Mn is likely attributable to reducing conditions, coinciding with the depletion of O_2 and NO_3^- (Banks *et al.* 1997, Gandy *et al.* 2007). Where hyporheic flow paths are not evident, it is likely that the solutes are from beyond the sampled depth, or area, or from subsurface flow paths (Ibrahim *et al.* 2010). NO_3^- downwelling from the stream is more likely during high stream flows, as observed during sample 6, corresponding with effluent releases, with it been used in place of O_2 for biodegradation of organic material, with the possibility of denitrification occurring in these anoxic conditions in the presence of pyrite (Kaandorp *et al.* 2018), hence the accumulation of Mn. Otherwise N-species were depleted, indicating nitrification was not occurring, or occurring quickly (Duff and Triska 2000).

3.7.3. Shallow hyporheic zone

In this unconstrained reach, flow and solute exchanges are evident across the streambed and are complex, operating as a function of the stream flow and vertical hydraulic gradients, with inputs from historic and contemporary sources. VHGs typically ranged between +30 and -20 %, indicative of upwelling and downwelling, although were slightly higher in comparison to other studies for unconstrained reaches, for example (Ibrahim *et al.* 2010). Ratios of the solute concentrations between the stream and subsurface water confirm that enrichment and depletion is occurring, and it is proposed that the source of this water is most likely that from the stream, rather than solutes rising from the deep GW. Analysis of the research results has led to the working hypothesis that downwelling SW mixes with stagnant or low-flow water in the interface of the surface hyporheic zone (perched), as observed previously in the upper Wear catchment at Rookhope Burn by (Palumbo-Roe and Dearden 2013a). The composition of water in the hyporheic zone is dominated by SW and the temporal changes of the pore-water thus reflect those of the SW (Benner *et al.* 1995, Palumbo-Roe and Dearden 2013a), with hot-spots of enriched species, such as SO_4^{2-} and Mn occurring under changing conditions.

3.7.4. Monitoring implications for management

Following the monitoring of the flow and solute patterns, an initial insight into the system dynamics suggests that the minor aquifer in the vicinity of the stream is acting as a source and sink of flow and solutes, associated with effluent and mine-water discharges. Whilst results reflect the sampling events throughout the sampling campaign, the study has allowed an insight beyond that of the one-dimension of the stream-water, instead looking across spatial and temporal scales. Whereas previous regulatory sampling has been restrictive, with limited spatial and temporal sampling points, this study has evolved the understanding of the contemporary flows and chemistry to include GW/SW interactions. It is proposed that the spatial proximity to threats and variable stream-flow are key factors in controlling the SW quality. The role of the streambed then adds complexity and it appears that the hyporheic zone acts as a source and sink for pollutants, whereby they are attenuated, resulting in the enrichment of the pore-water, or degraded, occurring as a function of several processes, including the flow direction, oxidation-reduction potential, for example. Hence conceptualising the reach as a black box where the inputs and outputs in chemistry are a function of the flow along the stream alone is incorrect and not appropriate. The findings emphasise that local processes are key to evaluate when considering the larger, catchment-scale water movements, further supporting the need for hierarchal approaches as outlined by Magliozzi *et al.* (2017).

3.7.5. Further investigations

The findings from this study have provided a foundation for several areas of further exploration, which leads onto the next chapter in this thesis. The intention of Chapter 4 is to extend the understanding the reach scale results monitoring through the application of modelling. Specifically, looking at the likely responses to changes in stage, including flood conditions, which were not possible to sample and to further explore the spatial and temporal responses over the study reach, upscaling from point-sampling to further interpret flow patterns.

3.8. Conclusions

From the sampling it is evident that historic and contemporary threats negatively impact on the stream-water quality. To better understand and manage the impacts requires an investigation beyond the standard measurements, e.g. the WFD, assessing both spatial and temporal variations and likely drivers and controls, both above and below the streambed. The streambed interactions are complex, and not just a function of the hydraulic conductivity, or the upwelling/downwelling across the streambed, and here I have provided an insight from selected sites, which show the response to a limited, however, insightful range of events allowing for an investigation into the changes in stream flow and solute loadings. From the findings presented in Chapter 3, it is suggested that the streambed plays a key role in the cycling of the water chemistry. This study has relied on the use relatively of low-cost methods to give a first-order insight into the system dynamics, nevertheless demonstrating the importance of looking at the subsurface connectivity, which will be further explored in the next chapter.

"I would rather be a good man than a great king."

Thor (Thor: The Dark World, 2013)

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Chapter 4 – Using numerical modelling to understand the role and impact of groundwater-surface interactions on in-stream water quality

4.1. Introduction

Predominantly there has been a limited understanding of the links between drivers and how processes interact within and between the GW and SW systems, looking at water quality problems with a one-dimensional focus at limited points of the stream-water and subsurface environments. There is a need to better understand the connectivity and exchanges to enable more sustainable water management particularly in heavily modified tributary catchments, which are typically structurally heterogeneous, with modifications to the channel planform and deposition of man-made materials. Developing an integrated focus is not trivial, and as demonstrated in preceding chapters, in which utilising the existing data to derive information and linking it with field data is one way of achieving an understanding of the links within and between these relatively unexplored systems. In this chapter I remain focussed on the 1.3 km reach of Twizell Burn, and specifically consider the interactions and exchanges between the stream and shallow GW comprising a discontinuous minor aquifer with variably saturated unconsolidated superficial (drift) deposits (see Figure 3-7). The purpose of this chapter is to apply the understanding from the field sampling conducted in this research and upscale the insight beyond point measurements. The aim is to further challenge the understanding of the system behaviour over spatial dimensions and time, upscaling point-based system sampling of the hydrochemistry and hydraulics to investigate the flow and solute pathways, patterns and processes between the SW and GW systems.

Field sampling over an intensive three-month campaign (March-July 2017, see Chapter 3) indicates that the shallow GW system is interacting with the stream water, with the subsurface thought to be acting as a source and sink of flow and solutes, with attenuation in the near-stream sediment. Given the large vertical extent of the unsaturated zone of the fractured and faulted bedrock extending below the superficial system, connection of the stream with the deeper GW is thought to be unlikely (supported with personal discussions with the Environment Agency and Northumbrian Water), leading this research to scale the focus entirely on the shallow GW, near-stream pathways within a shallow hyporheic zone interactions attributing to the loss and return of stream water along the reach (Figure 4-1). The impacts of the stream and shallow GW system variability is reflected through the physio-chemical characteristics of the stream and shallow pore water, with the chemistry appearing responsive to the stream stage at the time of sampling and the bed geomorphology, with hydraulic head changes and subsequent variations in the flow and solutes. However, the insight into the system dynamics and processes operating within and across the streambed are restricted both spatially and temporally to specific sampling events and points along the reach. To extend the understanding, looking at the system behaviour in response to changing hydrological conditions, one such approach is through the application of numerical modelling to derive estimates of the hydraulic heads in the aquifer based on the data and information collated throughout this research to better inform and thus understand the system behaviour, further interpreting the flow patterns observed (Gooseff *et al.* 2006, Magliozzi *et al.* 2017). The research presented in this chapter is driven with the need to understand GW/SW connections and processes with the intention of better understanding and managing the water resources of a local scale, and how they fit into the wider system processes.

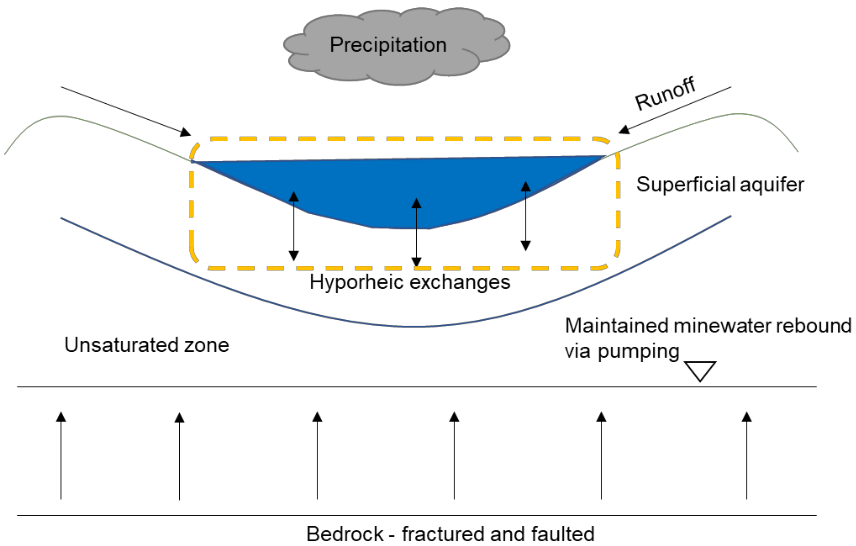

Figure 4-1: Conceptual cross-section of the Twizell Burn GW/SW systems, highlighting direct inputs into the systems and the shallow hyporheic exchanges within the minor aquifer.

The setting up and testing of a first-order numerical model, which has been implemented using the available spatial data, as well as primary field data collected in the spring-summer 2017 field sampling campaign will be used as an exercise to provide an upscaled understanding of the reach system. The intention is to investigate the system response to varying hydrological conditions, testing the response to observed events where it was not possible to sample, and scenario-based test simulations, such as with the onset of flooding as well as the likely extreme conditions with future climate change.

From the field sampling I have two main questions which require further investigation:

1. How do the hydraulic gradients across the streambed respond to changing hydrological conditions over space and time?

It is typical that with studies of this sort the nature of the sampling is at periodic intervals of weeks, or months. As a result, the sampling is demonstrative of a snapshot in time during which the samples are obtained, nevertheless this leaves a gap in the understanding between sampling events. Without the implementation of in-situ sampling apparatus, the ability to capture the hydrological response and associated chemical changes are not possible. Extending the insight into the system behaviour thus requires an extrapolation of the current understanding, which can be achieved through numerical modelling approaches (Gooseff *et al.* 2006). Modelling facilitates the possibility of estimating/representing the conditions, e.g. before and after storm events, looking at the trends over the reach and with time.

2. Are there any return fluxes (i.e. upwelling of GW/return of SW) along the reach, and if so, are they likely associated with the presence of iron-ochre flushes and staining as observed from the walkover surveys and sampling?

The possibility of sampling along the reach entirety would have required an extremely costly approach. The ability to identify return flows, however, requires the insight of the system at a higher spatial resolution than that achieved through the relatively small number of piezometers installed. Without continuous monitoring of the system, the system response is limited to the sites sampled, therefore, further upwelling and downwelling of GW/SW is likely missed. By upscaling the understanding from the piezometric measurements via numerical modelling offers a potential of identifying return flows based on the estimation of the hydraulic properties of the streambed material.

The research presented in this chapter:

1. Demonstrates the use of existing secondary data and field data to implement a numerical model approach representing the reach-scale system, with emphasis on linking together data and methods (see Magliozzi *et al.* 2017);

2. Tests the response and role of the near-surface, minor aquifer system in the cycling of water and solutes in response to changing hydrological conditions under observed and scenario-based events.

The following section outlines why there is a need to model GW/SW interactions and exchanges given the likelihood of the stream and shallow GW connectivity. Following on, the chapter outlines how the findings from Chapters 2 and 3 have been brought together with a focus on the collation of findings from the conceptualisations based on existing spatial data and subsequent field data.

4.2. Stream-aquifer exchanges

Stream-aquifer exchange is an important process in riparian systems (Sophocleous 2002), with the mixing of GW and SW in the near-surface environment referred to as the hyporheic zone (Winter *et al.* 1998, Brooks *et al.* 2015). Hyporheic flow paths extend from centimetres to kilometres in length and are nested within the GW flow system, beginning in the stream and returning to the channel often several times along a river reach (Kasahara and Wondzell 2003, Lautz and Siegel 2006, Boano *et al.* 2014). Hyporheic flows are increasingly recognised as a vital factor in controlling the transport and exchange of water and solutes along river reaches between aerobic (oxic) and anaerobic (anoxic) environments (Buss *et al.* 2009), with exchanges varying spatially and temporally relative to the system characteristics, such as the geologic heterogeneity and water table position (Fleckenstein *et al.* 2006, Krause *et al.* 2007). Emerging research continues to focus on the controls and rates of hyporheic exchanges, and the impacts on nutrient fluxes, in-turn assessing the fate and impact of flow and solute fluxes from catchment- to point-scales looking beyond the stream-water environment (Wöhling *et al.* 2018).

Understanding GW flows and hyporheic flows is largely based on field techniques, which include measurements of hydraulic gradients between the river and adjacent GW. Dilution tests using conservative solutes or heat tracers, pumping or slug tests, and mass balance approaches to determine losses and/or gains to GW from the SW are commonly applied approaches (Brodie *et al.* 2007, Rosenberry *et al.* 2008). Field techniques are covered in more depth in earlier chapters (see Chapters 1 and 3), and are therefore not further discussed here, apart from the emphasis that some techniques are more elaborate than others, with greater costs and labour intensity to yield results even over short study reaches (Wöhling *et al.* 2018). Consequently, GW/SW studies are often prioritised to sub-reach and point-scales, focusing on specific events and geomorphic features including riffle-pools and meanders; zones often associated with ecological impact assessments.

More extensive studies are instead typically reliant on baseline studies, the latter been problematic in tributary catchments given the lack of contemporary and historical datasets. Often studies are relatively short, with restricted time and space intervals they address, consequently meaning the drivers of the exchanges are often unexplored in response to the changing river levels or GW levels. Additionally, when focussed at the point-scale, studies often overlook the lateral and longitudinal responses between sampling points along reaches which means that studies often only consider the vertical gradients at a given point along the river reach, overlooking the wider system response, both spatially and temporally. Also, since high resolution approaches often require huge investment, the focus is typically on major aquifer systems, and those with a baseline dataset. Such approaches deter the understanding of smaller, yet important systems, specifically minor aquifers such as those comprising perched water tables in superficial formations beneath channels and hillslope, with the potential of discrete flow paths to the surface. The limited account of these systems is challenging the progression towards the intended sustainable catchment management and ICM principles associated with contemporary policy and frameworks such as the WFD and understanding and managing the water quality of low order headwater streams which are impacted by industry, looking beyond pristine streams which are often homogenous (Cardenas 2015). Beyond pristine headwater streams, those which are heavily modified and thus structural heterogeneous often have a more variable spatial and temporal turnover of nutrients. Thus, require a combination of laboratory, field and numerical modelling-based exercises to quantify the impacts in variability in the physical streambed at the stream reach and sub-catchment scales, looking beyond the wider catchment-scale focus (Magliozzi *et al.* 2017).

4.2.1. Stream-aquifer exchanges

Assessing and quantifying the impacts in variability along stream reaches and sub-catchment comprising minor aquifers is challenging with the lack of pre-existing field monitoring (Jones *et al.* 2000, Ibrahim *et al.* 2010). The state of connectivity between the streams and shallow GW systems is known to be highly variable (Brunner *et al.* 2009, Brunner *et al.* 2011), with the connectivity responding to changing hydrological conditions (Krause *et al.* 2014). Despite the likely influence, minor aquifer systems are often taken to be uninfluential on the stream water quality, and it is often assumed that they are impermeable and thus disconnected to the major aquifer, or overlying stream. Therefore, they are thought to have no impact on the stream or deeper GW systems (TOPSOIL group discussions). Such assumptions are evident in working practice, particularly in terms of management, with water managers dealing with the systems as compartments despite decades of research evidencing the streambed interactions occurring across several orders of magnitude. However, it is necessary to overcome this fragmentation due to the need for a holistic, integrated understanding of the systems, considering the impact and interactions of multiple threats acting on the systems simultaneously to better manage water quality.

Recent research continues to challenge the decoupling of the GW and SW systems, with an ever-increasing focus on delineating the flow pathways across the streambed in the hyporheic zone (Cardenas 2015). Despite the need to encompass the findings into working practices, the prevailing focus of management displays an unwillingness to adapt and move forward with the new understandings. Research thus needs to demonstrate what is happening in specific locations which are under threat from deteriorating water quality, and hence continue to result in the failure to achieve defined WFD objectives.

As demonstrated in the previous chapters, the Twizell Burn exhibits complex behaviour, and capturing the system dynamics and processes is by no means an easy procedure. Field monitoring captures the processes at given points and space, however, for a wider spatial and temporal understanding, numerical modelling is one such approach that can be applied. By doing so leads to question the current perception that the GW and SW systems are disconnected, and not homogeneous, accounting to the sediment lithology and thus hydraulic connectivity. Beyond the established field- and laboratory-based approaches to investigate the interactions, numerical modelling is increasingly used as a tool to derive a generalised understanding of the systems and variability of the impacts in combination with more traditional approaches (e.g. Niswonger and Fogg 2008, Krause, Boano, *et al.* 2014, Wilson *et al.* 2017).

In the following sections, established approaches used for the modelling of GW-SW interactions are outlined, with emphasis on bridging the gap between datasets to facilitate an understanding of interactions across the streambed. The application of the numerical models for the purpose of supporting GW-SW understanding are discussed, considering their suitability to look at shallow GW-SW exchanges at the near-stream environment, and the possibility of using such models with limited historical baseline data.

4.2.2. Bridging the gap between datasets and understanding interactions across the streambed

As previously mentioned, assessing the state of connectivity between the SW and GW requires large and dedicated field efforts (Wöhling *et al.* 2018). The systems are notoriously complex, with the direction of flow being influenced by several factors, ranging across regional to point scales. Field measurements offer only an insight into the variations over time and space, with the hydraulic head changes being highly variable, even over very short distances, in accordance with bed topography and pressure head attributing to the stream stage. Additionally, the heterogeneity of minor aquifer systems means that the pathways and exchanges are often intricate, based on the hydraulic properties of the bed material, thus heads vary largely even along short river reaches (Tetzlaff *et al.* 2007) making the mapping of the pathways and likely drivers particularly challenging, especially where the water table falls below the streambed. The lowered water table position results in the stream and the aquifer becoming variably saturated with the perching of water in unconstrained aquifers above the regional water table or water table of the major aquifer of the sedimentary bedrock. Although the lowered water table position is misleading because it implies a lack of feedback between the systems (Fleckenstein *et al.* 2010) and is often not the case (Bencala *et al.* 2011), with potential exchanges between the stream and minor aquifer, and with the major aquifer across the unsaturated zone. Often it is assumed that the whole reach is losing to the subsurface, however, localised head changes can occur, with heterogeneity in the characteristics in the streambed and floodplain (Lawler *et al.* 2009). It is the heterogeneity within catchments, and along streams that needs to be considered, to better establish an understanding of water quality.

In areas of high permeability, seepage losses can be high, even over relatively short reaches (Fleckenstein *et al.* 2006), thus resulting in the loss of solutes which have the potential to attenuate and react in the subsurface compartment comprising minor aquifer systems. The importance of these heterogeneities at the GW/SW interface have been highlighted in several recent studies (e.g. Fleckenstein *et al.* 2006; Ibrahim 2012). Whereas in the past such heterogeneities have been overlooked and assumed disconnected from the wider processes. The work of Brunner *et al.* (2011) has emphasised the need to focus on dealing with the impact of disconnection, hence this means looking at the minor, perched aquifer systems. This call has subsequently led to a recently emerging focus on the near-surface hyporheic exchanges, including those by (von Gunten *et al.* 2016), the latter focusing on gravel-bed rivers in New Zealand to name one such recent example.

While recent innovative field approaches allow for the assessment of hyporheic exchanges, the application to investigate the state of connection requires a large experimental field effort, with the likelihood of the connectivity been controlled by the nature of the river and GW levels, bed topography and hydraulic properties and GW pumping (Wöhling *et al.* 2018). Where the water table and/or hydraulic heads in the minor aquifer are highly variable, field efforts would need to be large to capture spatial and temporal variations at multiple sampling points. Due to difficulties with field measurements, the estimation of GW/SW exchanges is often complemented by numerical modelling (Fleckenstein *et al.* 2010). Numerical models are used to integrate field results of various types (surface and subsurface) and offer the potential to investigate the response of the systems and GW/SW exchanges under various scenarios. Several models are currently readily available as off-the-shelf tools, and include those which look at the GW exclusively, the GW/SW at the near-surface, stream and landscape, of which have differing levels of complexity, associated running time and input data requirements. Examples of such models are discussed in the following sections.

4.2.3. GW/SW numerical modelling approaches

Traditionally, the focus of modelling GW/SW exchanges has been on the stream-aquifer interactions at the regional or watershed scale, with a coarse representation of the stream-aquifer interface. This understanding has been attributing to a somewhat broad understanding that the hydraulic conditions are assumed to be homogeneous over large river reaches. Now, it is widely recognised that models need to consider the relatively local, smaller scale patterns and the dynamics of stream-aquifer exchanges at the near-surface (Dahl *et al.* 2007), such as those operating within catchment boundaries, specifically SW and GW boundaries.

Recent advances in the computational capabilities has led to the development of finer resolution models, enhancing the way in which systems are understood, including fully integrated models that simulate both saturated and unsaturated flow, as well as the SW, GW and the full coupling between them in a physical way (Brunner *et al.* 2010), which can be highly accurate (Wöhling *et al.* 2018). Although it is noteworthy that such models require high levels of data, and parameterisation can be extremely difficult, thus restricting their application beyond intensively monitored sites. At present there are several competing numerical models, each with associated pros and cons. Ultimately, the choice of model depends on the application of the model and inputs, which in turn are dependent on the data availability and simulation intensions. The ability to simulate the near-stream GW/SW interactions is a key aim of this chapter, and from reviewing the available software, MODFLOW (Harbaugh 2005, Harbaugh *et al.* 2017) offers a possibility of potential solution, with the ability of simulating heads and drawdowns of the water table, providing estimates of the system behaviour. Noting, however, that this research is not a modelling-based exercise, but instead part of a multi-method approach to investigate the GW/SW of tributary streams, thus modelling is used a tool to extend the current system understanding as established from the previous chapters.

4.2.4. MODFLOW

The research presented here uses MODFLOW, the United States Geological Survey (USGS) modular hydrologic model (McDonald and Harbaugh 1988, Harbaugh 2005, Niswonger *et al.* 2011). MODFLOW is an open-access finite-difference GW code (Harbaugh and McDonald 1984). MODFLOW was chosen because of the ability to simulate the near-stream environment making use of direct measurements and parameter estimates to represent the GW and SW environments (Harbaugh 2005). MODFLOW is considered an international standard for simulating and predicting GW conditions and GW/SW interactions, with numerous options to represent the GW flow (Harbaugh 2005). Originally developed and released solely as a GW-flow simulation code when first published in 1984, MODFLOW's modular structure has provided a robust framework for integration of additional simulation capabilities that build on and enhance its original scope. The family of MODFLOW-related programs now includes capabilities to simulate coupled GW/SW systems, solute transport, variable-density flow (including saltwater), aquifer-system compaction and land subsidence, parameter estimation, and GW management. MODFLOW is most often used to simulate GW/SW interactions (Furman 2008), with system stresses represented through the addition of a series of packages, e.g. river and stream flow routing (McDonald and Harbaugh 1988).

MODFLOW can distinguish between hydraulically connected and disconnected states and generally constitutes a good compromise between fully coupled models and conceptual models (Wöhling *et al.* 2018). Although, several assumptions are often required to be made. For example, rivers are always assumed entirely connected or disconnected to the underlying system (Brunner *et al.* 2010). Ultimately, the complexity of the model implemented using MODFLOW is variable, depending on the data availability and resolution of the outputs, which comes at a cost of parameterisation, calibration and simulation running times. There are several variants of MODFLOW, the choice ultimately depending of the level of user experience and model complexity. Beyond the capability to simulate and predict the fluxes in water, additional packages are supported, allowing for particle tracking and analysis (Harbaugh 2005, Pollock 2016).

Over the last 25 years, several versions of MODFLOW have been developed and revised (Hunt and Feinstein 2012). Early versions of MODFLOW were inflexible in the way that the unconfined finite-difference aquifer cells were handled when the water table drops below the bottom of the cells, resulting in cells remaining as ‘dry cells’ for the remainder of the simulation (Hunt and Feinstein 2012). MODFLOW is notoriously known for its inability to handle wet-dry problems robustly (Painter *et al.* 2008), and has led to the solving of GW flow problems using a Newton-Raphson solution rather than a Picard method, as used in previous versions of MODFLOW, e.g. MODFLOW-2005 (see Harbaugh 2005, Niswonger *et al.* 2011, Hunt and Feinstein 2012), where the re-wetting of dry cells results in numerically unstable models, preventing model convergence (Doherty 2001, Painter *et al.* 2008). MODFLOW-NWT uses the upstream weighting (UPW) package as a way of calculating intercell conductance (Painter and Seth 2003) and is considered as a powerful and sophisticated open-source software for research and practitioners to simulate the GW/SW environment (Hunt and Feinstein 2012). However, as with any numerical modelling there are the unavoidable challenges associated, e.g. with parameterisation, with the need of making often several assumptions, and the overall ability to reproduce simulated conditions which are representative of observations from the field. Nonetheless, numerical modelling is often the only way to investigate relatively unexplored systems, providing an insight into heterogeneous systems.

4.3. Approaches and methodology

The approach adopted in this chapter is outlined in Figure 4-2, which details the steps taken to develop a numerical model to represent and simulate the near-stream environment.

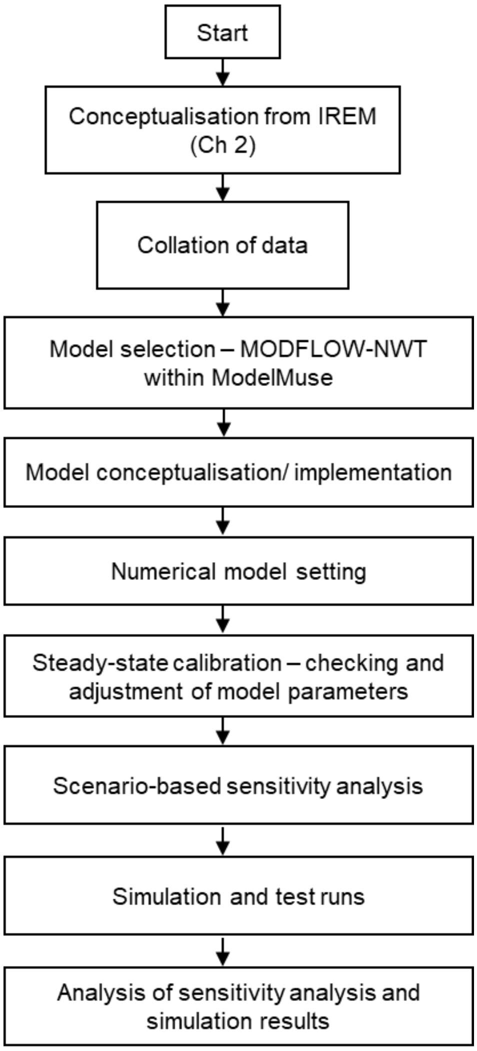

Figure 4-2: Steps taken to develop a numerical model representing the Twizell Burn reach using MODFLOW-NWT.

4.3.1. Study reach

The study reach is in the lower Twizell Burn (catchment area: 19 km^2), a heavily modified catchment with poor water quality attributing to historic coal mining and contemporary effluent releases from wastewater assets (Figure 4-3). GW rebound continues post-mining following the cessation of draining of the deep coal mining blocks (Personal communication with Coal Authority via the Wear Rivers Trust). Rebound has fully occurred in the neighbouring Stanley minewater block, meanwhile, along the study reach, in the Central Durham South minewater block, rebound is currently managed through pumping of water in the Middle Coal Measures, with GW levels maintained by the Coal Authority. Besides the impact from the deep coal mining, remnants of waste spoil materials from the surface mining are evident throughout the catchment, with iron ochre staining on the bed and banks of the channel.

In this chapter, the focus remains on the 1.3 km reach of the Twizell between Grange Villa and the Blindy Burn confluence (Figure 4-3). The stream and surrounding floodplain have been heavily modified, with artificial ground comprising mining spoil and concrete, stepped weir and culvert structures constructed following the coal mine abandonment allowing for the dumping of mining waste in neighbouring land (Hartley and Wright 1988). There is an accumulation of the threats along this reach as it is situated downstream of the sewage treatment works as well as inflows from reclaimed land comprising mining spoil. The stream-water quality has been managed exclusively from a SW perspective, yet with no monitoring downstream of the Grange Villa steps. A key focus has been addressing phosphates from the wastewater assets and sewage treatment works (Personal communication with Northumbrian Water). This focus has been sustained, despite the rebounding mine water from the coal measures in the upstream section (Stanley Mining Block), and inputs from open cast mining spoil sites. It has been assumed that the streambed is disconnected to the deep GW, however, the role of the shallow GW in the superficial layer remains questionable. Previous understanding and management have overlooked the potential role of the shallow hyporheic zone having an influence on the source and fate of solutes present in the system. The variability of the physical structure of the system, which is thought to be heterogeneous requires an assessment of the impacts to the SW quality.

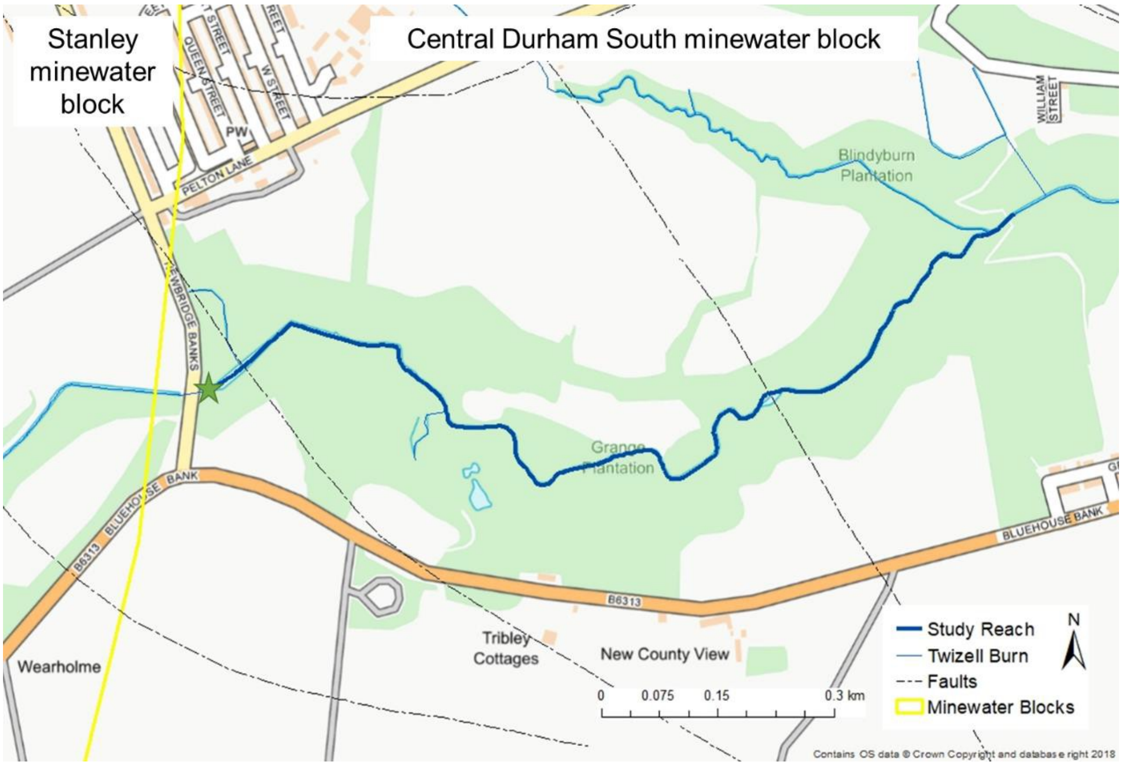

Figure 4-3: Study reach showing the geological faults (direction/dip unknown, Source: BGS 2013), with coal minewater blocks (Source: Coal Authority 2018) – star marks the Grange Villa stepped weir.

4.3.2. Application of MODFLOW-NWT: model implementation

In this chapter, MODFLOW-NWT is used as part of a numerical modelling exercise to quantify the impacts of variability in the physical streambed on the cycling of water, and with it, solutes from historical and contemporary effluent releases. In the following sections, the model implementation is discussed, considering the ability to represent and capture both the dynamics and processes operating within the systems as a function of the elevation, hydraulic conductivity and storage coefficients. Following on from the initial model set-up, parameterisation of the model is based on the use of primary field and secondary datasets utilising inverse modelling techniques to calibrate the model. Steady-state (stationery) calibration is performed based on the representation of head observations and simulations, followed by the testing of the model under observed events, leading onto scenario-based runs to investigate the model sensitivity as well as considering the likely system response to extreme events, attributing to changes in precipitation, including likely climate change scenarios.

4.3.3. Representing the near-stream GW/SW system

A shallow 3D GW/SW model was set-up using MODFLOW-NWT within the Graphical User Interface (GUI) ModelMuse (Winston, 2009) to assist with the delineation of the model domain, aquifer layers and setting of cell values using data imported from ArcGIS, including shapefiles and ASCII files representing,

e.g. the hydraulic conductivity and streambed features such as riffle-pools. The intention of the model was to represent the shallow GW system, looking at the near-surface GW/SW environment, specifically the exchanges along the study reach, making use of the hydraulic head and hydraulic conductivity measurements obtained in the field. The ‘Upstream Weighting package’ (UPW) was selected to represent the GW flow, allowing for an assessment of the flow between cells representing the systems, with the ability to set cell values using a combination of direct measurements and parameter estimates, e.g. hydraulic conductivity (Kx and Kz). Using the UPW package, aquifer layers are defined as confined or convertible. In this instance, the model layers by default were set as convertible, which means the flow package automatically assigns the layer as confined or unconfined depending on the elevation of the water table in the simulation. Throughout the model, the units of the measurements are set to metres for length.

4.3.3.1. Geology

The Twizell is underlain by variable thickness superficial (drift) deposits, comprising unconsolidated river terrace and glaciofluvial gravel, sand and silt (BGS 2019), which are evidently capable of supporting the perched of water, as concluded in Chapter 3. Beyond the broad-scale classifications of the superficial geology, analysis of the borehole fabric reveals that the upper parts of the superficial strata are heavily modified, and comprise man-made materials, for example colliery waste discarded from the coal abstractions. Boreholes drilled prior to the construction of the Grange Villa stepped weir provide a small insight into the superficial geology. Borehole depths extend up to a maximum of 30 m, with the majority available under public access via the BGS Onshore Geology Index (BGS 2019). Since there are no available borehole records exist to interrogate geology along the channel, the decision was made to assume that the floodplain area consisting of river terrace deposits were homogeneously comprising sand, silt and gravel, inferred from 1:50,000 BGS geology maps (Figure 4-4). Characterising the geology is notably challenging given the sparsity of available borehole records. Originally it was intended that a solid model of the geology was to be generated using Rockworks16 (RockWare Incorporated 2018), which could then be connected to the ModelMuse to delineate the aquifer layers (Harbaugh 2005). However, given the ‘block-like’ appearance of the generated geology, the initial proposal added little value to the understanding. Thus, the geology is assumed characteristic of sand, silt and gravel, with the localised hydraulic properties derived from the field sampling and published sources are instead used to characterise the system in the model set-up.

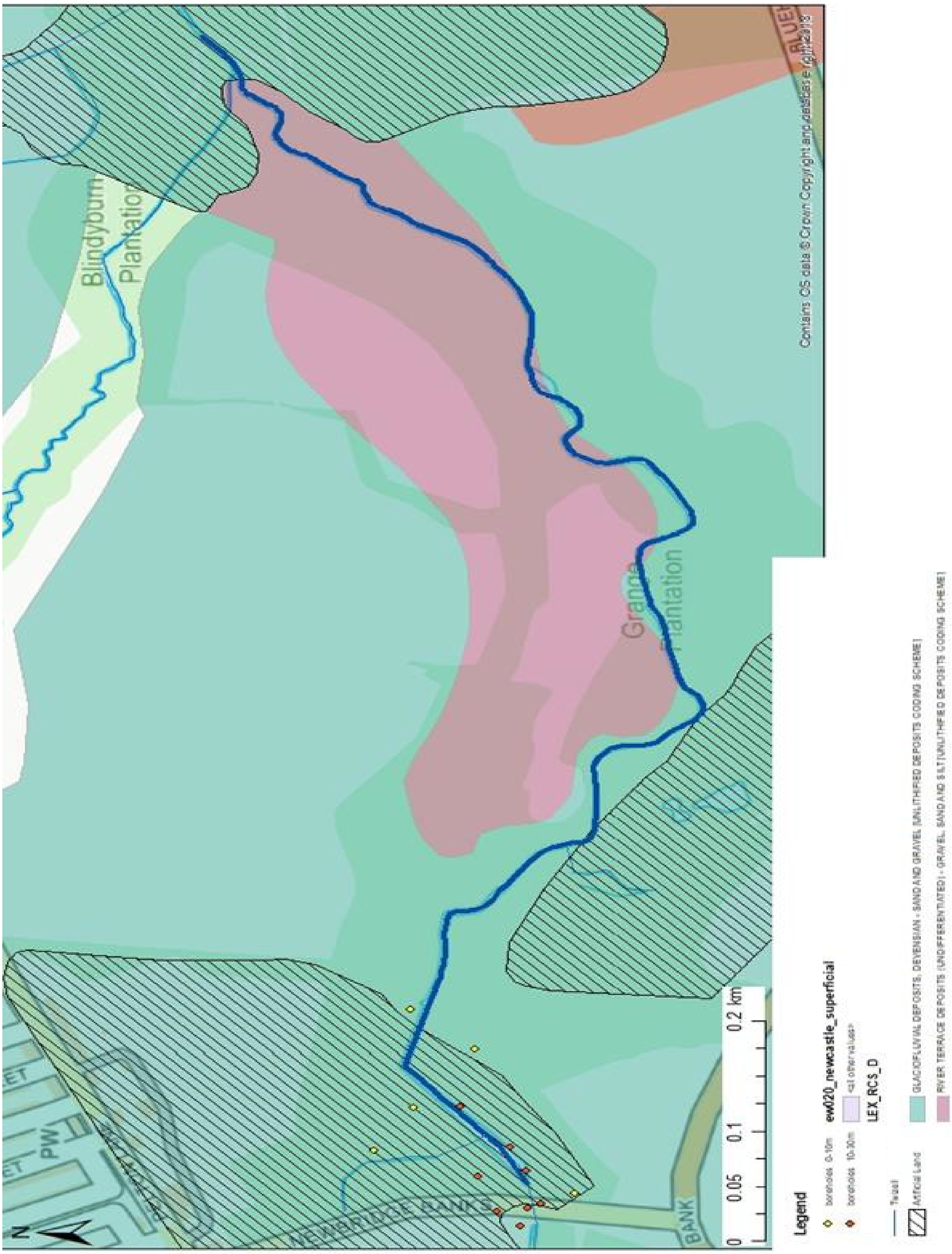

Figure 4-4: Superficial lithology according to the BGS 1:10,000 scale geology maps (Source: BGS 2013).

4.3.3.2. Spatial discretisation of the model domain

A plan view of the model domain is shown in Figure 4-5. For the purposes of simulation, only the channel and floodplain areas were defined to be 'active' as variable head cells. Beyond the floodplain, there was great uncertainty regarding the water table position and thus the support of the heads and given the lack of measurements and likelihood of been less influential on the channel processes, the remaining cells were set to be 'inactive', thus with the focus entirely on the channel processes, looking at the influences of the bedform and stream discharge on the hyporheic exchange flows. Sampling sites (as used in Chapter 3) are shown in Figure 4-5, where the piezometers were installed to obtain samples of the shallow GW and estimate the hydraulic properties of the bed material. Only five sites were selected based on the remaining sites having no hydraulic measurements, due to damage via high flows or vandalism.

The influence of external boundaries on the model domain is uncertain, and therefore the representation is based on the current understanding of the catchment. The western boundary of the model is located at the edge of the Central Durham South coal block, which adjoins the Stanley mining block. The connection between the blocks is unknown, meaning the impact of the rebounding water in the upstream block may or may not bear an influence on the downstream block, which is currently managed through pumping (Personal communication with the Coal Authority via the Wear Rivers Trust). Additionally, the flow direction and rate along the bedrock faults is unknown, although assumed permeable. Hence, for the initial model set-up and simulations for this research the boundary between the blocks is assumed to be a no-flow edge as is that of fault line (Figure 4-3). Thus, the focus of the model presented in this research is exclusively on the minor superficial aquifer system, comprising the unconsolidated glacial drift material underlying the streambed, which appears to have an influence on the accumulation of flow and solutes, as observed during the field sampling campaign. The eastern boundary of the model is drawn at the point of the downstream flow gauging site, approximately 1.3 km from the upstream gauging site. Here, the superficial deposits are around 4 m thinner along the streambed relative to the most upstream point sampled. The northern and southern boundaries are considered as no-flux boundaries. The intention of the modelling presented in this chapter is with the aim of producing reasonable estimates of the heads in the superficial system, and thus while it would be possible to produce a relatively complex representation of the system, considering multiple elements and avenues of the points noted above, would require extensive efforts beyond the scope of this study as part of a model-based exercise.

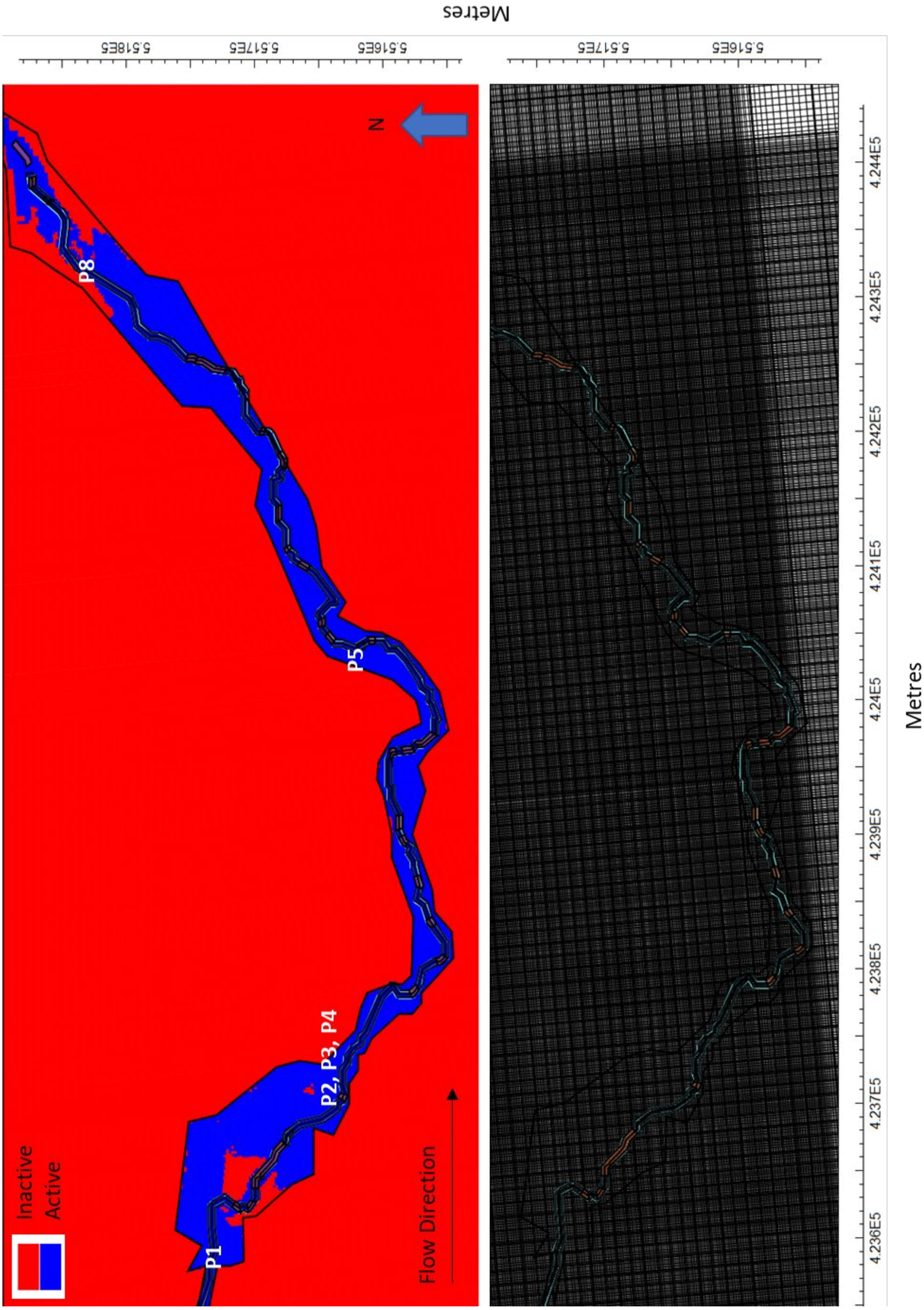

Figure 4-5: Representation of the model domain, with the red and blue shading representing the active and inactive cells respectively. Piezometer sampling sites from which the hydraulic properties are estimated from field sampling are denoted P1-8.

4.3.3.3. Representing the GW and SW systems

Model top and channel - The top elevation of the model is represented by a high-resolution 1 m composite LiDAR DTM (2010-2016) (accessed via Environment Agency 2015), which was interpolated at the central nodes of the MODFLOW computational grid cells. The channel representation according to the grid cells is challenging, particularly as the channel cuts across cells diagonally and it is not possible to discretise the channel horizontally resulting in a uniform exchange flux under the river (Brunner *et al.* 2010). It is acknowledged that because a river can only be tied to one grid cell, there is often a mismatch between the channel width and cell width (Brunner *et al.* 2010). With the need to capture the heterogeneity of the bed topography to represent the system dynamics therefore requires the use of finer grid cells than those representative of the width of the channel, for example 4 m, thus focusing on the centre of channel where the piezometric measurements were obtained.

Grid cells and aquifer layers - In MODFLOW, the system is represented by a discretised domain consisting of an array of nodes and associated finite difference blocks, represented as grid cells. Figure 4-5 shows the spatial discretization scheme in ModelMuse with a mesh of cells and nodes at which hydraulic heads are calculated. The nodal grid forms the framework of the numerical model, with cell values assigned at the centre of each cell according to direct measurements and parameters. Hydrostratigraphic units can be represented by one or more model layers representing the aquifer systems. The thickness of each model cell and the width of each column and row may be variable. As noted, the top elevation of the model domain is derived from a high-resolution LiDAR image, a 1 m DTM, to represent the dynamic nature of the bed geomorphology and grain size distribution. Below the model top, the model comprised two layers (Figure 4-6), representing the unconsolidated superficial material and sedimentary bedrock systems respectively. In order to avoid dry model cells, a coarse vertical discretisation of the aquifer is often used, therefore assuming that the hydraulic head does not vary vertically (Brunner *et al.* 2010). The first layer, the superficial aquifer, is representative of the superficial drift thickness (BGS 2013) relative to the elevation of the surface. The second layer, the bedrock, is somewhat more challenging to define, where the bottom of the model domain is set at 0 m AOD, with the base of the bedrock layer been unknown. Given that there is no available data of the hydraulic properties of the bedrock, it is assumed homogenous. The upper portion of the bedrock that is unsaturated, although assumed permeable with the presence of faults and fractures, with the hydraulic properties defined through the use of parameter estimates (e.g. Fetter 1994).

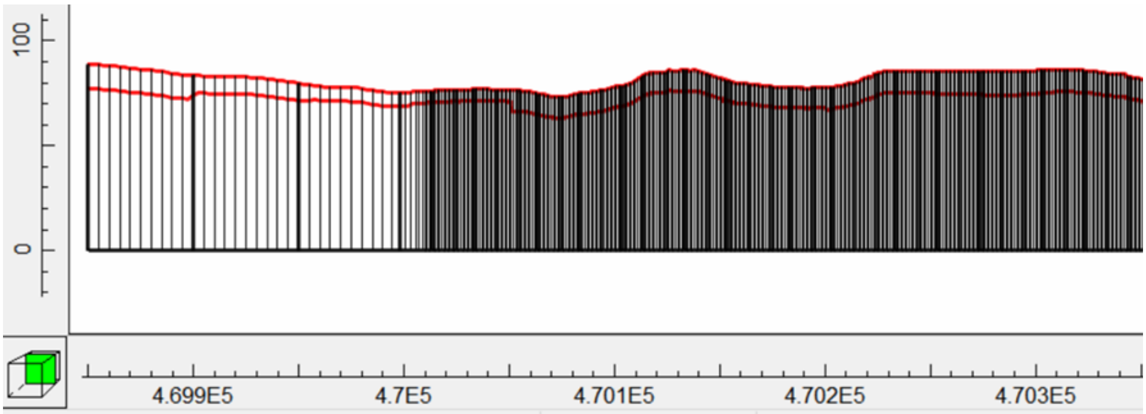

Figure 4-6: Screen-shot from ModelMuse showing the discretisation of the aquifer layers, the upper layer representing the superficial system with thickness according to the advanced superficial thickness model (BGS 2010c), with the lower, the bedrock extending to 0 m AOD.

4.3.3.4. Internal boundary conditions

In MODFLOW, the representation of water fluxes is based on a series of boundary conditions, considering the movement of water between the cells within and between the SW and GW systems. The boundary conditions are defined using a series of packages, requiring the estimation of the specified head, specified fluxes and head-dependent fluxes. As the aim of this research is to focus on storm-based events, occurring over relatively short time-scales relative to those with the deep GW, the fluxes considered were those between the stream and the superficial system, thus a combination of specified head and head-dependent fluxes, and beyond the channel considering aquifer recharge as a function of effective rainfall. Evaporation and evapotranspiration were not considered, given the focus of the modelling exercises on storm-based events.

The model implementation is based on several assumptions made regarding the flow into and out of the systems. The upper superficial layer is presumed to be variably saturated, with a dynamic water table as evidenced from the field monitoring, which appears to be responsive to the pressure head of the stream, as well as the bed morphology, e.g. riffles, pools and run sections. The vertical and horizontal extent of the saturation is uncertain given the piezometric sampling having been limited to a maximum of eight points along the reach. Meanwhile, the sedimentary bedrock layer is assumed homogenous, with the water table maintained under the current GW pumping regime and assumed at a specified head according to the GW contours, as discussed with the Coal Authority (via the Wear Rivers Trust, personal communication). The unsaturated zone between the stream and water table is assumed permeable, given the presence of fractures and faults. The north and south model edges were deemed no-flow boundaries, with no measurements of the water table depth beyond those obtained in the channel, thus assuming no fluxes from the surrounding land represented within the boundaries of the model domain (Figure 4-5).

To enable the solving of the GW flow equations, the model requires a set of initial and boundary conditions, the latter accounting to with a combination of specified head (e.g. time-variant head), specified flux (e.g. recharge) and head-dependent fluxes (e.g. with overlying rivers and streams) (Collins 1961, Coelho *et al.* 2017). With the lack of baseline monitoring, defining the location and numerical representation is critical, with the mathematical representation of the physical features determining the ability of the model to make reasonable and accurate predictions (Reilly 2001). Determination of the representative boundary conditions is an essential step of numerical modelling, although the selection of conditions should not be trivial, the choice is ultimately dependent on the knowledge of the simulated system. As there was no pre-existing knowledge of the system that could be used to represent the boundary conditions, I developed my study focusing on the evaluation of the effects of a combination of two boundary conditions, specifically the 'constant-head boundary' (CHD) and 'river' (RIV) package on numerical hydrological simulations of the unconfined superficial aquifer, looking at the average and extreme responses to changing hydrological conditions. The representation of the system is therefore based on the current understanding and data, with the system representation as a 'best-fit' combination of the according to the elevation, particle size and morphology of the channel to replicate observed conditions through inverse modelling techniques.

Specified Heads: The water-table position beyond the sampling points is unknown, and therefore the initial heads are based on linear interpolation from the field sampling at the piezometers as presented in Chapter 3. Based on field sampling, the water table is thought to be shallow, and near to the streambed, typically expected of lowland streams (Ibrahim 2012). Constant head boundaries (CHD package) at either end of the study reach were implemented, assuming that at either end of the study reach, where the streambed is lined with concrete, with the downstream (western) boundary been drawn at the location of the artificial section (Figure 4-3). Constant head boundaries were applied to represent the edge conditions at either end of the reach, with the reference head as the model top, assuming saturation of the concrete lined sections. The heads at either end of the reach were held constant throughout the stress periods.

Underlying the superficial layer is a sedimentary bedrock sequence. Based on the current pumping regime, the head in the Coal Measures is at 20 m AOD, and thus represented by a specified head (CHD package), with the assumption that the water table (head position) is otherwise thought to be constant, both spatial and temporally within the model domain. The unsaturated zone is not considered to bear influence, with the properties, specifically the characteristics and role of the faulting/fracturing in water movement being unknown.

Stream representation: The Twizell flows eastwards, with contributions from tributaries deemed minimal. Using the RIV package (a head-dependant flux boundary) the stream is represented, however, assuming no routing of the water downstream and that the stream stage is a kinematic wave, where the water is routed through the system, and the stage is parallel to the elevation of the model top, in this case, the streambed. In the RIV package, the user specifies two elevations. One represents the elevation of the bottom of the riverbed. The other represents the head in the river. If the head in the cell connected to the river drops below the bottom of the riverbed, water enters the GW system from the stream at a flux or a constant rate. If the head is above the bottom of the stream, water will either leave or enter the GW system depending on whether the head is above or below the head in the stream. A conductance term, which is multiplied by the streambed thickness (m) and vertical hydraulic conductivity is used to determine the flux of water between the systems according to the respective head positions. The streambed thickness is input as a global variable into the model.

Note, that a detailed parametrization of the stream geometry is possible, although impractical, given the associated high experimental costs. Therefore, for the reach entirety, based on the sensitivity to the parameterisation the streambed thickness is assumed 0.35 m.

To derive estimates of stage along the channel, the US Army Corp software, HEC-RAS (U.S Army Corps of Engineers 2010) was used to simulate water depths for each of the grid cells. The time-step of the model was set at 15-minute intervals, with 2D model outputs, from which the floodplain could be delineated (Figure 4-7). The 1 m LiDAR DTM was used and estimates of the channel parameters determined, including slope and channel roughness according to Manning's n, estimated using Chow (1959). Depths were simulated based on the incoming flow at the upstream point of the reach (Figure 4-5), with the resulting depths a function of the slope and roughness as the effective flow is routed through the model for various event sizes. The flow estimates were made using the stage-discharge rating curve as presented in Chapter 3. It is therefore likely that based on the standard error associated with the interpolation and extrapolation of flow estimates that this in turn feeds into the depth estimates (see Figure 3-5 and Figure 3-6). Simulated depths were validated against those observed at the stilling wells and piezometer sites along the channel and deemed reasonable to proceed with the modelling simulations. As there is no established, long-term monitoring of the shallow GW system, the recharge of the shallow aquifer system is unaccounted. Nevertheless, with the onset of rainfall, it is inevitable that there will be runoff from the surface.

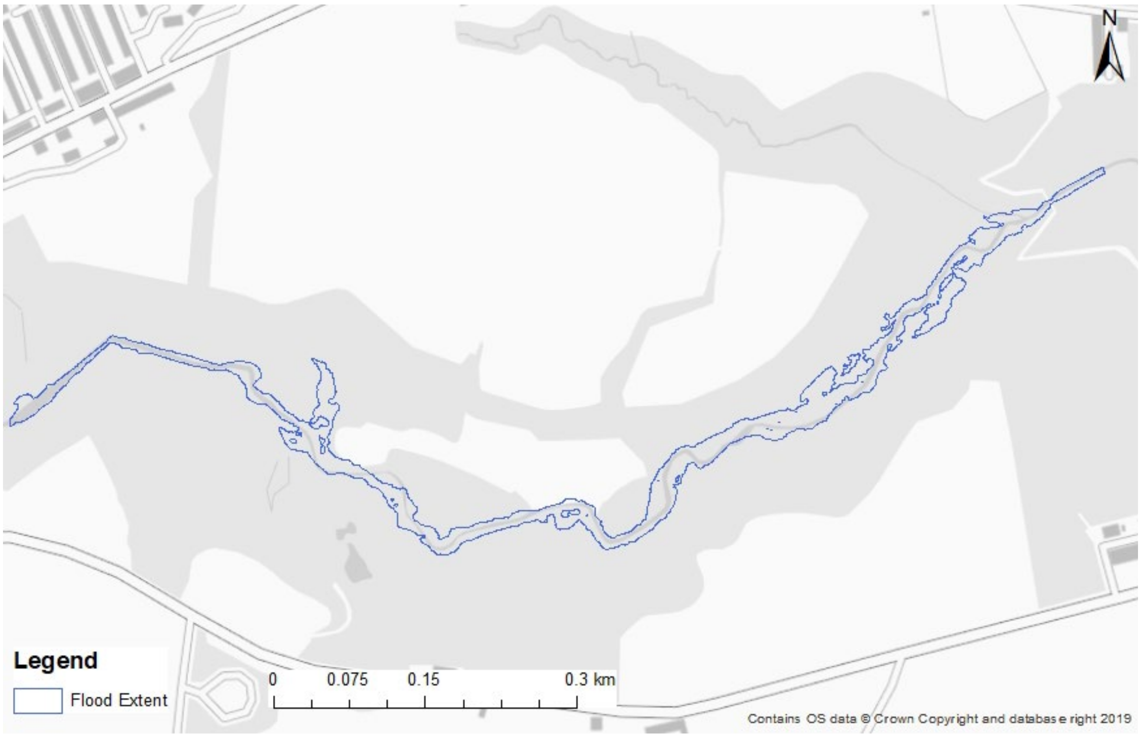

Figure 4-7: Floodplain extent for 1-in-100-year event using HEC-RAS.

4.3.4. Model parameterization

The parametrization of the model was based on the best-estimate of the initial head conditions and hydraulic properties of the superficial and bedrock systems. The initial heads were taken from the piezometric head measurements (Figure 4-6). Interpolating the heads along the channel through the application of the inverse distance weighting (IDW) techniques in ArcMap facilitated an initial value of the heads along the channel and floodplain. Where heads were lower than the base of the superficial layer bottom, the cells were set as 'inactive', as they were effectively dry, which would have resulted in subsequent issues with the model simulations. Estimates of the hydraulic conductivity were a combination of field measurements made at the piezometers and published records, from which representative values for the unconsolidated materials and sedimentary rocks were selected (e.g Domenico and Schwartz 1990, Fetter 1994), where measurements were not obtained, such as beyond the channel in the floodplain area.

Along the channel, horizontal (Kx) and vertical (Kz = Kx/10) hydraulic conductivity estimates were obtained via falling-head slug tests. Similar to the initial head estimation, using these conductivity estimates, the IDW technique was applied to generate estimates of the hydraulic conductivity along the subsequent unsampled parts of the reach (Figure 4-6). It was assumed that the estimates of hydraulic conductivity were reflective of the streambed material. Additionally, riffle and pool features were considered to have varying hydraulic conductivities, with riffles expected to have conductivities favouring downwelling at the riffle head and upwelling at the riffle tail. Estimates of the riffle-pool hydraulic conductivities were a combination of field measurements and published values. Parameterization of the riffle-pools was performed via co-kriging of the riffle-pool conductivities with locations of the features in ArcMap.

Estimates of the hydraulic conductivity of the underlying geology are according to previous studies (e.g. Domenico and Schwartz 1990, Fetter 1994). For unconsolidated drift material, the hydraulic conductivity (m/s, horizontal – Kx and vertical, Kz = Kx/10) are typically within the range of $9x10^{-7}$ and $6x10^{-3}$ m/s (Domenico and Schwartz 1990). The hydraulic conductivity of the sedimentary bedrock material comprising mudstones and sandstones is typically in the range of 3×10^{-10} to 6×10^{-6} m/s (Domenico and Schwartz 1990). Regarding the streambed conductivity, the values were trial-and-error in the calibration process, with the streambed conductivity having not been measured directly in the field and would require very extensive field efforts beyond the scope of this study.

Parameters included in the model set-up:

- Stream stage
- GW levels
- Hydraulic conductivity of the bed material

4.3.5. Model calibration

Model calibration general involves adjustments initial values and parameters to minimize the discrepancy between model simulations and observed data through inverse modelling techniques. Calibration is achieved by altering the horizontal and vertical hydraulic conductivities in the case of stationery (steady-state) calibration and checking the output simulated heads relative to observed heads in MODFLOW using the ‘head observation’ (HOB) package (Barnett *et al.* 2012, Wöhling *et al.* 2018). Model calibration is an iterative process, and is a balance between simplicity and complexity, and can be achieved through manual trial-and-error or automated procedures (Barnett *et al.* 2012). During trial-and-error calibration it involves changing a model parameter by a small amount and establishing how model predictions are affected by that change. It rests on the ability of the modeller, after each run, to identify and consider the differences in the predicted heads visually and statistically, the latter using the HOB package, with the ability to look at residual changes and error, e.g. root mean square error (Barnett *et al.* 2012). Alternatively, calibration can be achieved via automated parameter estimation codes such as PEST (Anderson and Woessner 1992). With the use of observed hydraulic parameters from the field sampling, it was decided that trial-and-error calibration would be preferred, with these estimates considered the suitable to represent the system. The trial-and-error method is adopted as it incorporates site-specific knowledge and ensures a gained insight into the behaviour of the model during the calibration period (Hassan *et al.* 2014, Bakar 2015)

During the calibration procedure, it is difficult to obtain exact model parameter values due to the different sources of uncertainty in the model (Bakar 2015). Sources of uncertainty enter the model from a range of sources, including the representation of the boundary conditions and observation data (Wu and Zhang 1994). Based on the only available data to calibrate the model been that from the piezometer measurements there was a considerate uncertainty, especially without the possibility of a transient calibration, thus reducing the confidence of predictions. Nevertheless, based on this being a first-order modelling approach to represent the dynamics and processes occurring at the GW/SW interface, the model was intended to allow for a general understanding of the time and spatial scales (Barnett *et al.* 2012). It is therefore emphasised that the model is worthwhile to gain an understanding which could not otherwise be achieved, linking the local processes to the wider system. However, it is with a lower degree of confidence in its ability to represent the system given the standard of calibration (Barnett *et al.* 2012). Measures to assess the calibration were the root mean square error (RMSE) and percentage discrepancy to assess the observed and simulated heads, and water budget respectively. A percent discrepancy less than 1% is deemed acceptable (Anderson and Woessner 1992) and applied in this study.

4.4. Results and discussion

4.4.1. Steady-state model calibration

Steady-state calibration was performed with the model assumed to be representative of average conditions with no stresses acting on the systems, with observed heads from 13/04/17 used to assess the simulated heads (Figure 4-8). As no historical measurements were available for the Twizell and relying entirely on the field measurements means that calibration is somewhat challenging. However, as noted above, this does not imply that the modelling is not worthwhile, it simply means that the simulated conditions are associated with a lower degree of confidence (Barnett *et al.* 2012), especially when stresses are applied. Nevertheless, the model allows for a gain in the general understanding of time and spatial scale changes of a system which has been unexplored until now, thus any advancement is better than none at all (Barnett *et al.* 2012).

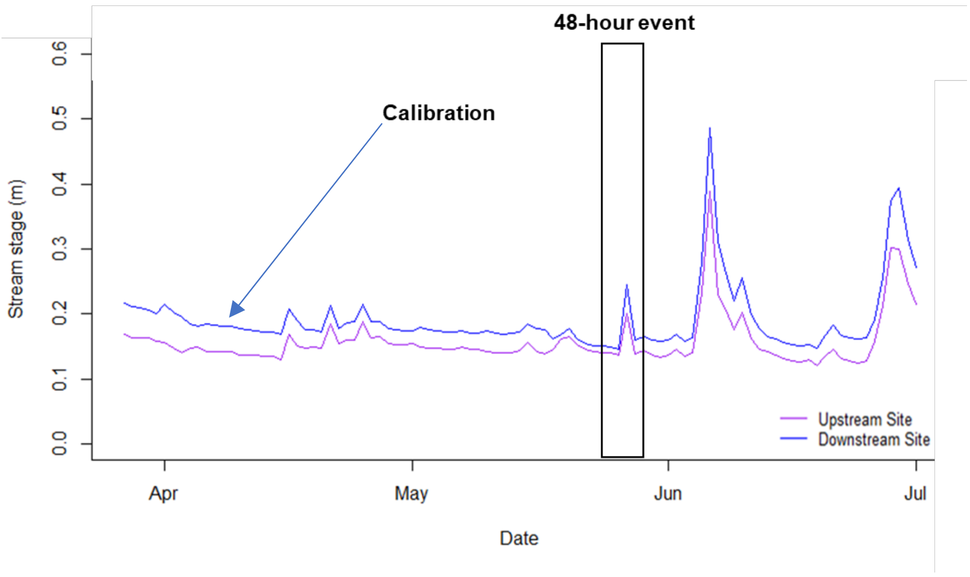

Figure 4-8: Observed stream stage (April-July 2017) at either end of the study reach (Figure 4-3), showing the calibration period and 48-hour scenario-based event.

The initial simulation under steady-state conditions comprised of direct measurements and parameter estimates of the horizontal hydraulic conductivity (Figure 4-9). The floodplain was denoted to have a value of 0.00016 m/s, representative of a homogenous sand and gravel system (Domenico and Schwartz 1990), and the riffle and pools of 3.6 and 0.0042 m/s respectively. The bedrock aquifer was set with a hydraulic conductivity of 1.8e-4 m/s, typical of sandstone formations (Domenico and Schwartz 1990) with the heads specified according to the GW contours and therefore maintained throughout the simulation. As the focus was on the near-stream, the bedrock was considered of little influence, with no need to consider the head flux given that the water table is maintained through pumping and unlikely to bear any short-term influence on the stream environment, thus GW upwelling from the bedrock aquifer was unexplored in this instance.

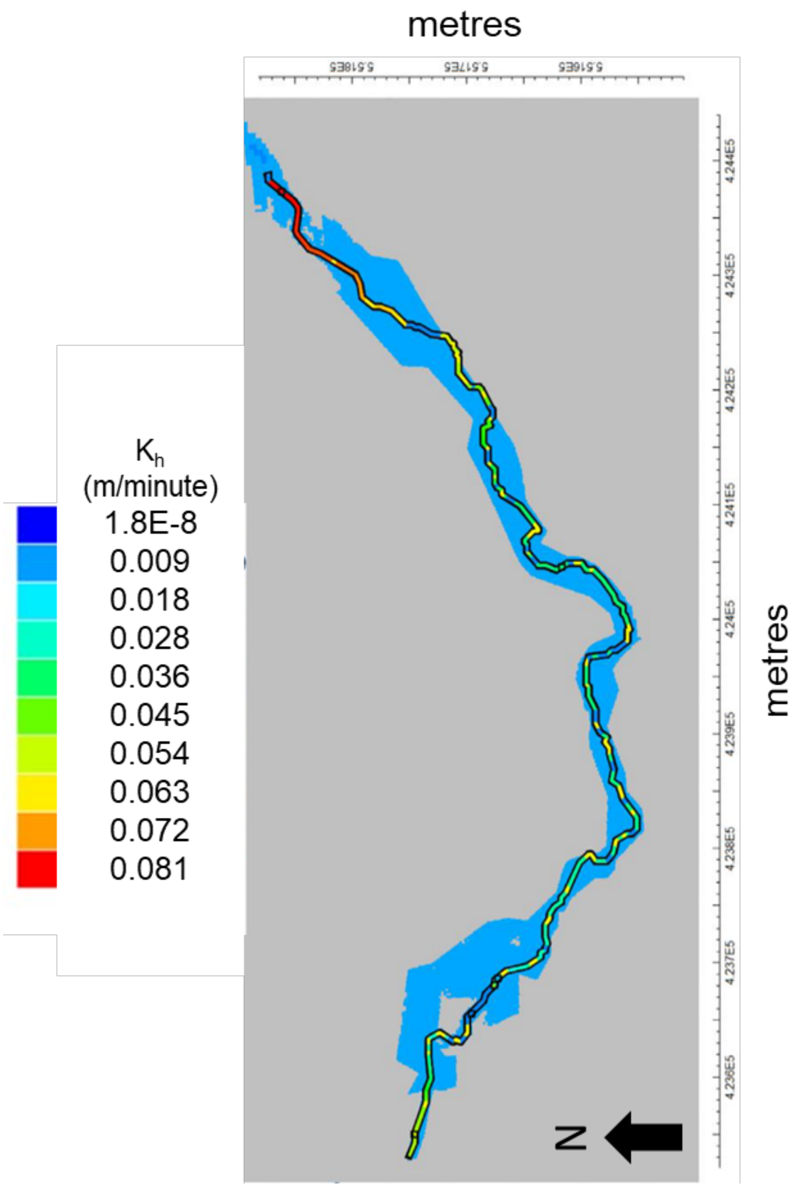

Figure 4-9: Horizontal hydraulic conductivity in m/minute for the channel and floodplain area.

Based on the conditions, predicted heads were reasonable, with an RMSE of 0.12. Heads simulated at the piezometers varied, although were reasonable given the noise and uncertainties in the system, with the model conditions according to the best understanding of the system (Figure 4-10; Table 4-1). The simulated values at each of the piezometer sites is, however, an interpolation of the surrounding heads, thus resulting in an over- or under-estimation of the heads. Because the calibration was limited to the piezometer sites, the uncertainty increases with distance from the sampled sites.

The observed and predicted heads at the piezometer sites are shown in Figure 4-10 and Table 4-1. The simulation of the vertical hydraulic gradients (VHGs) relative to the stream stage were estimated (Table 4-1). The VHGs were representative of the upwelling and downwelling direction of flow, although of a magnitude less in most cases. Sites P2 and P8 were considered intensive to changes in the horizontal hydraulic connectivity, and therefore, resulted in simulations which were higher than the observed heads, and thus near-neutral VHGs as opposed to the observed downwelling (Table 4-1). The cause of the higher value is attributable to the surrounding cell influence; however, further measurements would be needed to increase the certainty of the cause.

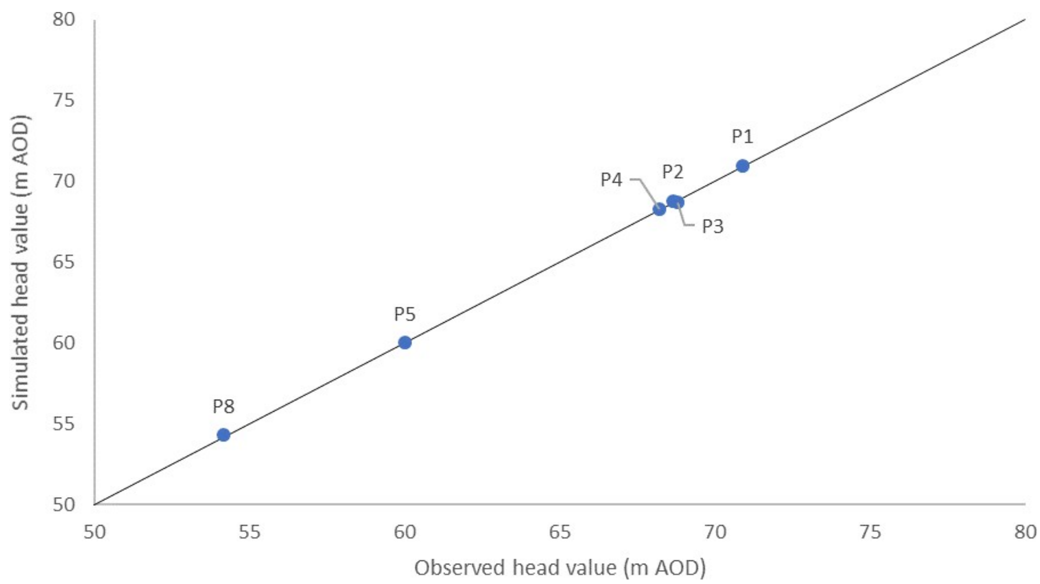

Figure 4-10: Observed and simulated values of the hydraulic heads at the piezometer sites under steady-state conditions with relative fit to 1:1 line.

Table 4-1: Observed and simulated values of the hydraulic heads and vertical hydraulic gradients (VHGs) at the piezometer sites under steady-state conditions, with residual errors.

Piezometer	Observed Head (m AOD)	Simulated Head (m AOD)	Observed VHG (%)	Simulated VHG (%)
P1	70.90	70.96	-23	-15
P2	68.64	68.81	-34	2
P3	68.80	68.79	-27	-27
P4	68.21	68.32	26	56
P5	60.00	60.02	9	2
P8	54.17	54.35	-43	3

4.4.2. Sensitivity analysis of the steady-state model results

Sensitivity of the model was analysed by examining the response of the hydraulic heads to changes in the model representation and parameters. The former referring to the bed topography and grid cell size, and the latter referring to the horizontal hydraulic conductivity (Kx), which also impacts on the vertical hydraulic conductivity (Kz) and riverbed fluxes; and the representation of the system. While it is possible to test the sensitivity of the model to variations in the river flux, the inability to directly measuring this parameter would likely result in great uncertainty, and therefore is evaluated as a function of the hydraulic conductivity of the streambed material and streambed thickness.

4.3.3.5. System representation

The model implementation is based on the ability of representing the dynamics and processes of GW/SW flow. With regards to the dynamics, the ability to simulate the observed patterns based on the bed topography requires considering the scale of the grid cells to capture enough detail of the local-scale changes in elevation. To represent both the stream stage at that point and thus the relative hydraulic heads according to the bed-scale features, specifically riffles, pools and run sections. Calibration of the model was based 1 m2 grid cells, which was a compromise between capturing the local scale head changes, against the ability to represent the system over a larger spatial scale (Brunner *et* *al.*, 2010). Either the grid cell exceeds the width of the channel, thus losing the ability to simulate the heads, given the loss of the resolution of the local scale bed topography at the metre-scale. Alternatively, the width of the channel simulate is reduced to focus on the central part of the channel, as done in this research, looking at the local-scale changes, requiring the use of a grid cell finer than that of the channel width. With an increase in the grid cell size, resulted in an increasing residual error, largely attributable to the piezometers, P2 and P8. Thus, suggesting that the residual error associated with the representation of the heads at these sites was likely due to sub-metre changes in the bed topography, as opposed to been sensitive to the horizontal hydraulic conductivity, which when altered, resulted in minimal changes to the head simulated at these sites, with changes to fourth-order scale changes. It was a balance between capturing the dynamics at the piezometer sites with the ability to represent the likely processes operating beyond these systems across time and space.

4.3.3.6. Horizontal hydraulic conductivity

Rather than a full-scale sensitivity analysis, the parameters values were altered by known amount, and the impact on the simulated heads assessed as a function of the residual and RMSE change (Figure 4-11). Varying the horizontal hydraulic conductivity impacted also on the vertical hydraulic conductivity (Kz = Kx/10). The varying of the hydraulic conductivity parameter allowed a first-order approximation of the sensitivity to be established from the estimated hydraulic measurements made both in the field and from published data. Since there was only one estimate of the conductivity for each piezometer, it was not possible to assess the confidence intervals. Values of the horizontal hydraulic conductivity were varied for the surrounding floodplain, the riffles and pools and at the individual piezometer sites. Figure 4-11 shows the resulting RSME for the changing of the conductivity values by an order of 50% in the floodplain, riffles and pools. In the case of the floodplain, the RSME change is linear, with an increase in the conductivity accounting to a slight reduction in overall error (Figure 4-10). Changes to the riffle and pool conductivities resulted in non-linear changes to the simulated heads (Figure 4-11). The impact of the hydraulic conductivity changes of the floodplain, and channel features on the heads was small (Table 4-2).

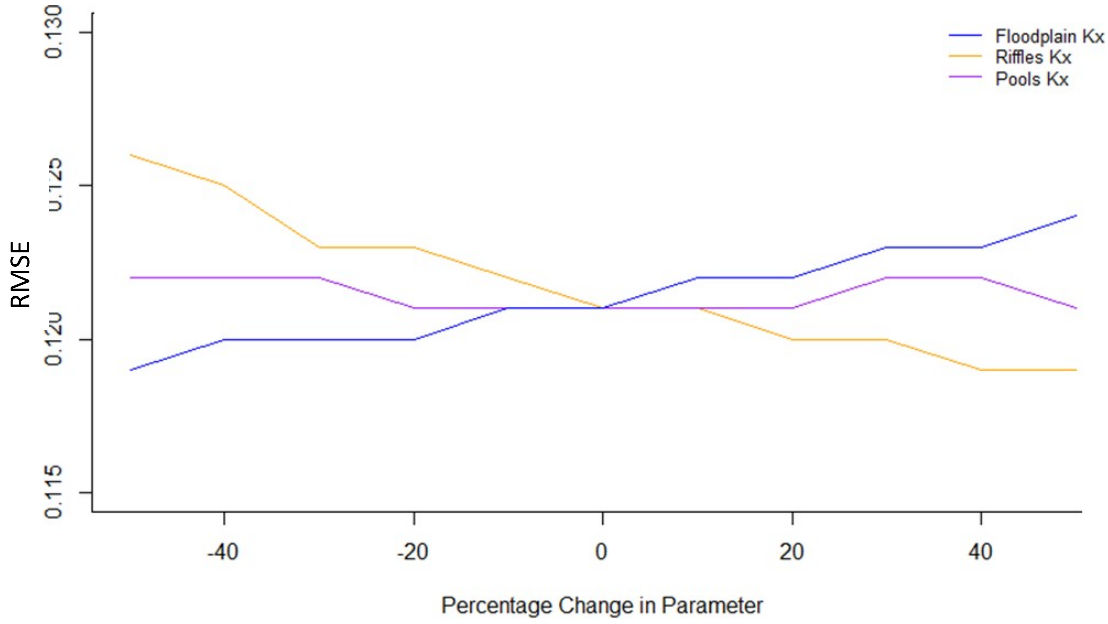

Figure 4-11: RMSE according to percentage change in horizontal hydraulic conductivity (Kx).

Table 4-2: RMSE at piezometer sites accounting to percentage change in parameter values.

	Piezometer Site (Pn) with simulated head values (m AOD)					
% change in parameter value	**P1**	**P2**	**P3**	**P4**	**P5**	**P8**
50	70.961	68.812	68.799	68.312	60.017	54.352
0	70.963	68.816	68.792	68.316	60.021	54.353
-50	70.966	68.818	68.786	68.319	60.025	54.353

Therefore, the insensitive to changes in the conductivity variations is indicative that the heads are responsive to other factors, e.g. the bed topography and stream stage. Working with the model implemented is therefore with uncertainties, unknowns and noise in the data, something that is inevitable in the modelling process. While the model is useful as a tool to gain generalised understandings of the streambed exchanges across space and time, it is with a lower degree of confidence than systems with historical baseline data. Small changes in the residual error suggests that the modelled hydraulic heads are likely sensitive to other factors not considered in the model set-up (Bear and Cheng 2010). Therefore, it would be necessary to investigate the system beyond this research in order to develop and improve the simulation ability and thus prediction capabilities of the model.

4.4.3. Model testing – challenging the current understanding of GW/SW system behaviour

Following model calibration, the ability of the model to simulate heads beyond those observed was tested, looking at the system behaviour under average conditions, specifically assessing the hydraulic heads and the VHGs along the study reach. In-turn it was possible to evaluate the model performance in its ability to represent the system at the measured points. Subsequent to this analysis, the model was tested in its ability to simulate the system behaviour in response to changing hydrological conditions, challenging how we understand the GW/SW system over space and time through transient simulations, looking at:

1. An observed 48-hour event looking to assess the changes in stream stage in response to the observed mid-morning flux from the sewage treatment works (as discussed in chapter 3), followed by a localised storm attributing to bankfull conditions;

2. Design flood events representative of 1-in-100-year rainfall event generated using the FSR/FEH rainfall-runoff method (Kjeldsen 2007); and

3. Climate change scenarios – based on the UKCP09 Weather Generator outputs for 2030s medium emissions scenario (Hadley Centre for Climate Prediction and Research 2017).

4.4.3.1. Model performance under average conditions

In response to the first of the defined research questions at the start of the chapter to assess the hydraulic gradients over space, the resulting VHGs delineated from the simulated heads along the reach are shown in Figure 4-12. As expected, upwelling and downwelling is variable along the reach, with localised changes reflecting the bed geomorphology in the presence of riffles and pools, associated with downwelling at the riffle head, and upwelling at the riffle tail. The VHG patterns reflect those observed in the field, specifically at sites P3 and P4, representative of a riffle and pool respectively (Figure 4-12). Beyond the measured points at the piezometers the uncertainty in the validity of the VHGs patterns grows, given that there are based on the estimations of the conditions at few points along the reach. Nevertheless, the trends provide insight into the system dynamics and processes operating which have not been accounted for previously.

The upper portion of the reach, it appears that SW is lost to the GW system at a greater rate relative to that in the lower section, which appears to have greater gains in flow marked by the upwelling from the subsurface relative to upstream (Figure 4-12). It is in the lower section where the iron flushes were observed under what I considered from my experience to be representative of normal flow conditions. With such conditions, iron-ochre was observed to stain the bed and banks. The findings from the modelling support the assertion that the iron flushes are attributing to the upwelling of water rich in metals, which precipitate on the bed of the channel due to an increase in the partial pressure. These processes result in an oxygen-rich, aerobic environment in the stream resulting in the precipitation of metals, hence the ochre staining, and the enrichment of sulphates in the stream water as observed from the SW sampling discussed in chapter 3. Ultimately, such patterns of upwelling and downwelling are expected, it is likely that some of the variations and trends were unaccounted given that every factor/condition(s) operating was not unlikely to be captured in the model set-up. However, based on the steady- state representation of the system with no external or internal stresses, it is evident that the hydraulic heads in the superficial system are representative of a combination of localised losses and gains to and from the stream water (Figure 4-12).

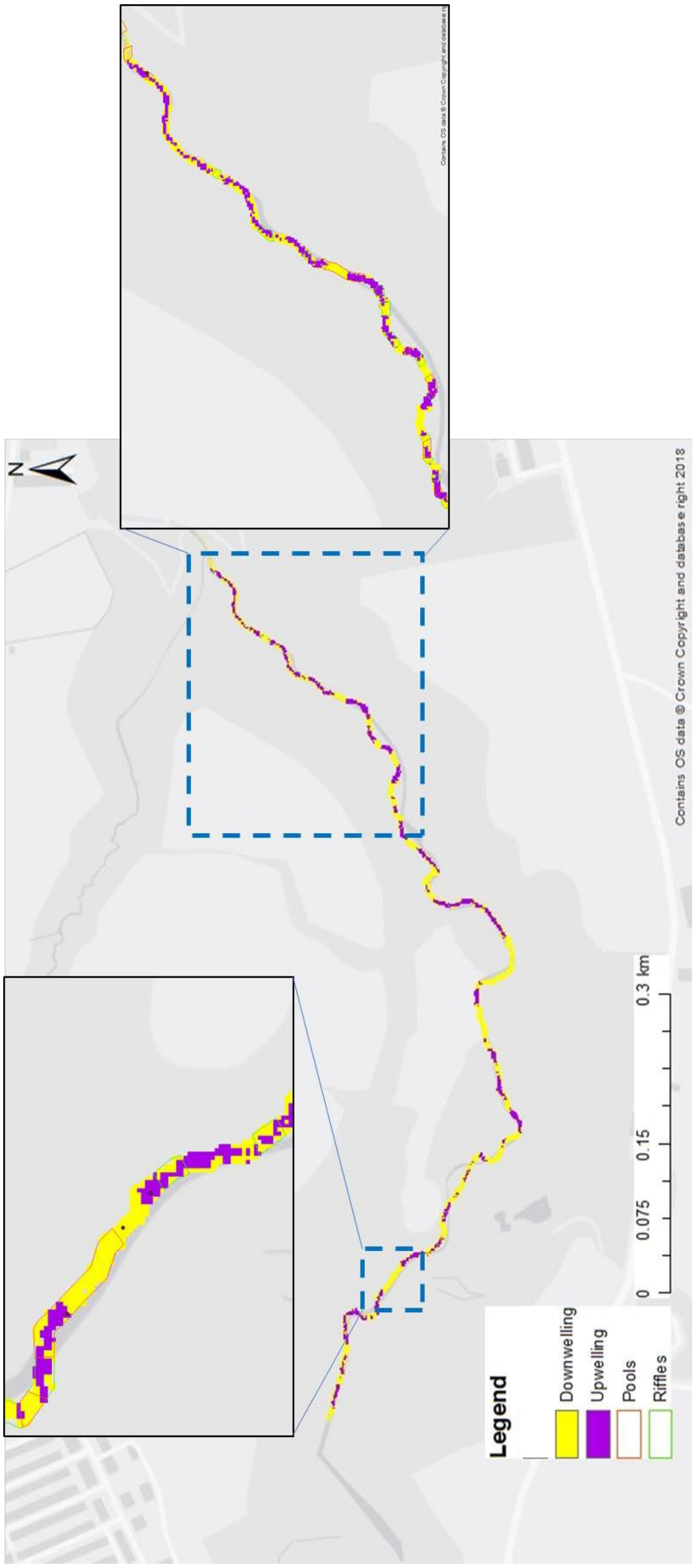

Figure 4-12: GW/SW patterns along the channel representative of average steady-state conditions. Zoom-in windows show the upwelling and downwelling associated with (a) the riffle-pool sequence observed by the piezometers P3 and P4 (left); and (b)the iron-ochre upwelling sub-reach (right).

In Chapter 3, it was hypothesised that the superficial system is acting as a near-stream buffer and propagator to solutes from the SW and GW systems. Whilst it is not possible to determine the time at which solutes are held in the bed material, or the lag time response in accordance to the upwelling and downwelling of flow, it is likely that the iron flushes observed along the lower half of the study reach is attributing to the upwelling of the shallow GW (Figure 4-12). The upwelling of sulphate and metal-rich (e.g. manganese) water from the subsurface accounts to the reduction in partial pressure, where in the presence of relatively higher oxidised water compared to the superficial system results in the dissolution of the metal solutes in the water, hence the iron-ochre staining on the bed . The source of the mining wastes is unknown, with tracing requiring the use of isotopes, for example (Engelhardt *et al.* 2011), and would require further investigations beyond the scope of this research. Nevertheless, based on these findings, the upwelling of mining water is therefore the likely source of the iron-ochre on the bed, as well as the enrichment and load increase of sulphate as observed during the field sampling over the reach. As outlined in Chapter 3, at the time of sampling the enrichment in sulphate was not in correspondence with the chloride:sulphate ratio, which lead to question localised sources attributing to upwelling along the streambed, thus the mobilisation of sorbed elements and return flows from the subsurface.

During average, baseflow conditions, the water quality of stream is likely impacted by the mining-derived solutes, associated with the aesthetical impacts of the system. With increasing discharge, it was highlighted in Chapter 3 that there was an effective tandem-effect, where dilution of the mining-derived solutes, e.g. sulphate, and reduced GW upwelling coincides with the enrichment of nutrients likely attributing to effluent releases from upstream of the reach. The understanding of the system response to these changing hydrological conditions was not measured at the piezometer sites, thus the system response was further explored with the modelling exercises.

4.4.3.2. System response to changing hydrological conditions

Beyond the average conditions, the response of the system to changing hydrological conditions was tested in response to a small flux (around 0.05 m3/s) representative of that observed from the sewage treatment works (Figure 4-13). Followed by a localised storm event which was representative of bankfull conditions (Figure 4-13) measured via stage gauging on 27/05/17 to 28/05/17. The storm peak illustrated the ‘flashy’ flood response of the catchment, with a rise in stage of around 0.6 m over a 15-minute interval. For the running of the transient simulation, the storage conditions of the aquifers were assumed homogenous, with estimates of the specific yield and specific storage from published sources (Domenico and Schwartz 1990).

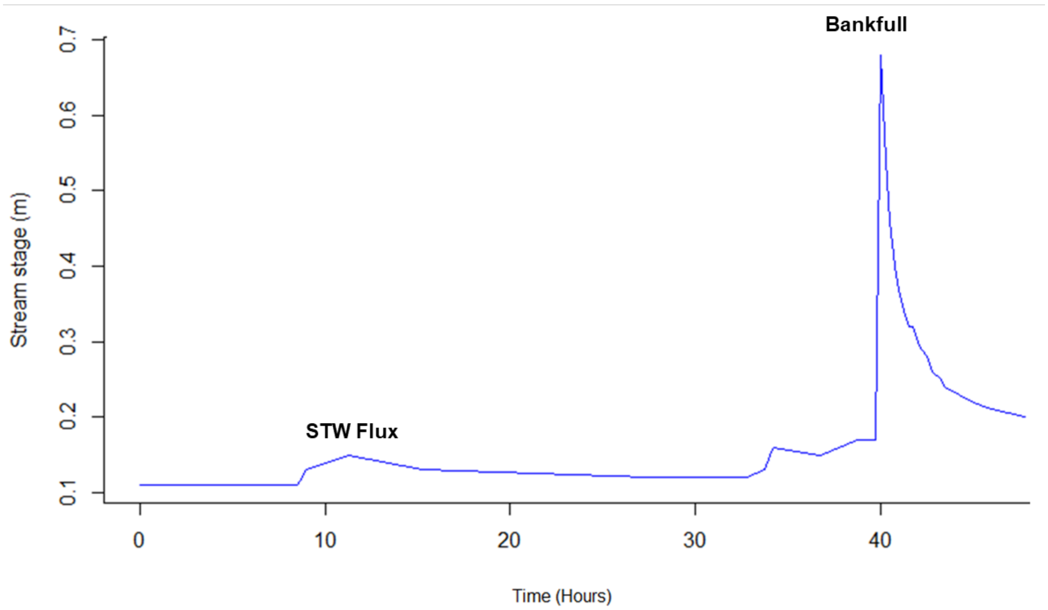

Figure 4-13: 48-hour event, with a flux from the sewage treatment works and a localised storm event between 27/05/17 and 28/05/17.

As discussed in Chapter 3, the flux from the sewage works resulted in a minimal change in the water chemistry, nevertheless it is interesting to see the response of the system to a relatively small increase in flow. Figure 4-13 shows the VHGs every 100 m along the study reach, from which it is indicative that the general increase in the heads is in response to the slight rise in stream stage. Measurements at the piezometer sites would be required before and after the sewage works flux to validate this finding. Meanwhile, at bankfull conditions, the majority of positive VHGs denoting upwelling become weakened and more negative indicating downwelling (Figure 4-14). Increased downwelling is expected in response to the rise in stream stage, accounting to the greater distance between the stream stage and water table of the superficial system, thus influencing downwelling given the sediment permeability. Under such conditions, the downwelling and trapping of water in the superficial layer results in the accumulation of solutes held in pore water. For example, manganese and sulphates, which were found to be greatly enriched post-storm events, corresponding with the loss of iron flushes at the surface, as outlined in Chapter 3.

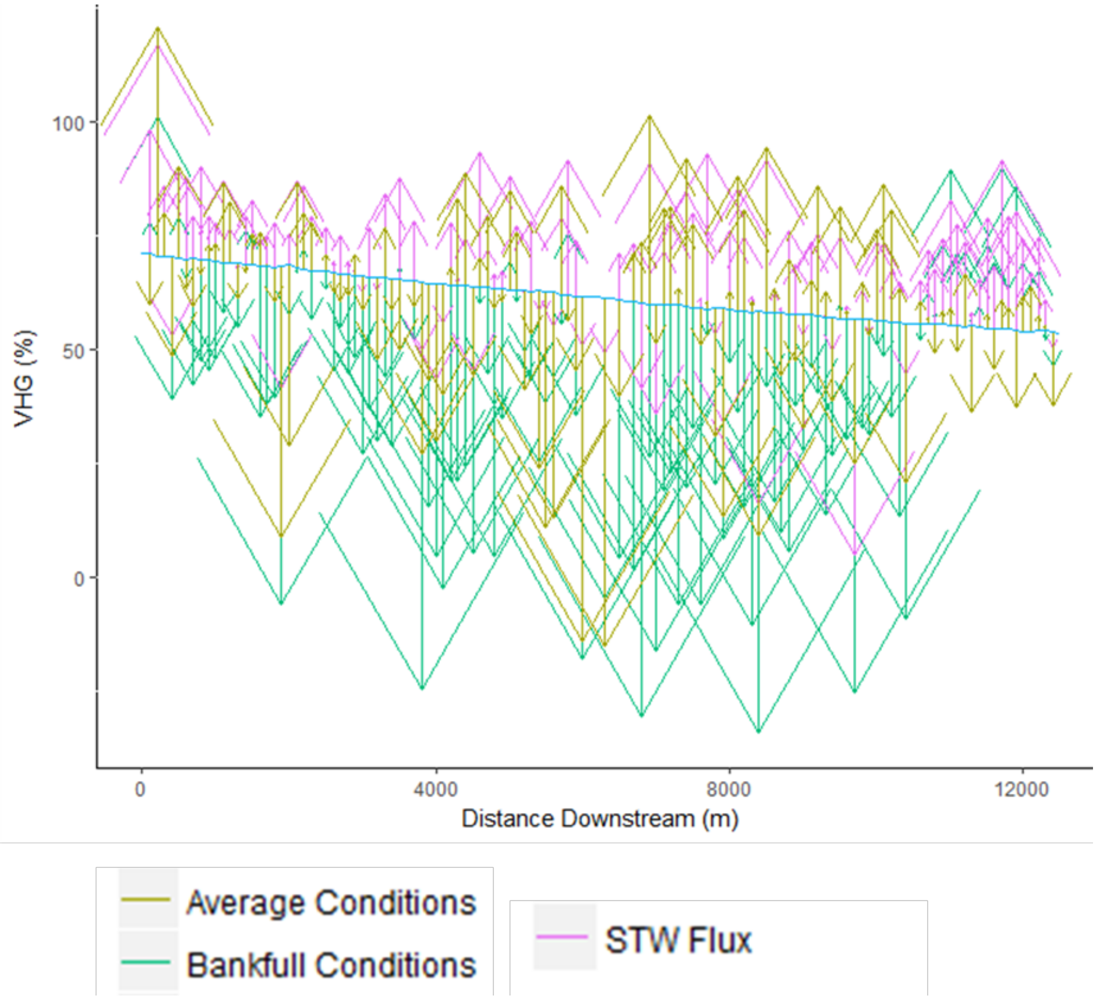

Figure 4-14: Intensity of VHGs every 100 m along the study reach under average conditions, as well as following a flux from the STW, and at bankfull conditions – positive indicates upwelling and negative indicates downwelling respective to the streambed topography (blue line).

4.4.3.3. Model testing under design scenarios

Extending the focus beyond the sampled events, using the FSR/FEH rainfall-runoff method (Kjeldsen 2007), design events were generated to represent hydrological conditions to explore and challenge the understanding of the system behaviour in response to more extreme events. An event representative of a 1-in-100-year event was generated, and subsequently routed through the model as a transient simulation. Figure 4-15 shows the hydrograph generated for the 100-

year event. As the FSR/FEH method generates hydrographs for the full catchment using the FEH catchment descriptors, it was necessary to scale the output hydrograph to the model domain area. At the start of the simulated storm, stage was similar to that under the average conditions, rising over the duration of the storm to a peak of 3.5 m. It is with the assumption that this change in stage would occur uniformly over the reach.

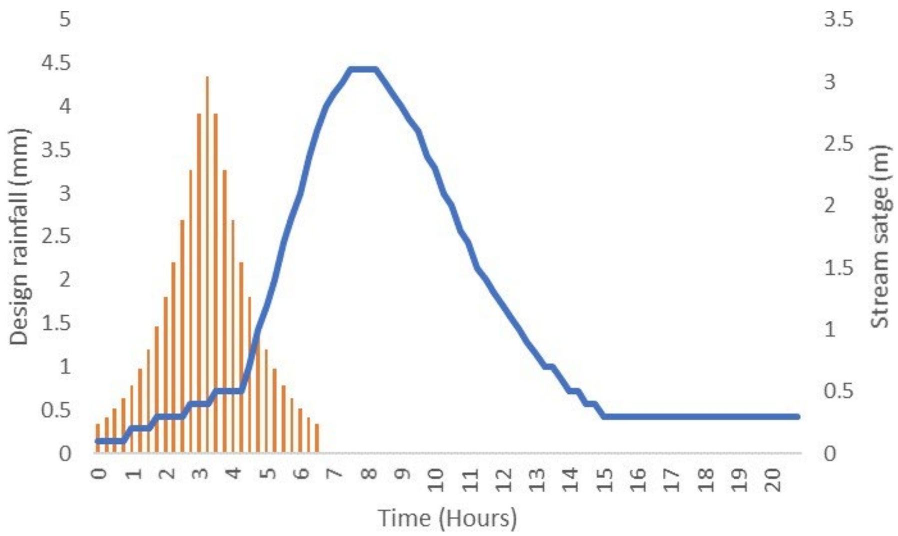

Figure 4-15: Hydrographs generated using the FSR/FEH rainfall-runoff method representative of a 1-in-100-year event.

Over the duration of the 100-year design event, the heads generated over time appeared responsive to the stage changes with a 2-4 m change in head across the piezometer sites (Figure 4-16). As stage returned to near-average conditions, the heads fells, although remaining elevated relative to the initial positions (Figure 4-16).

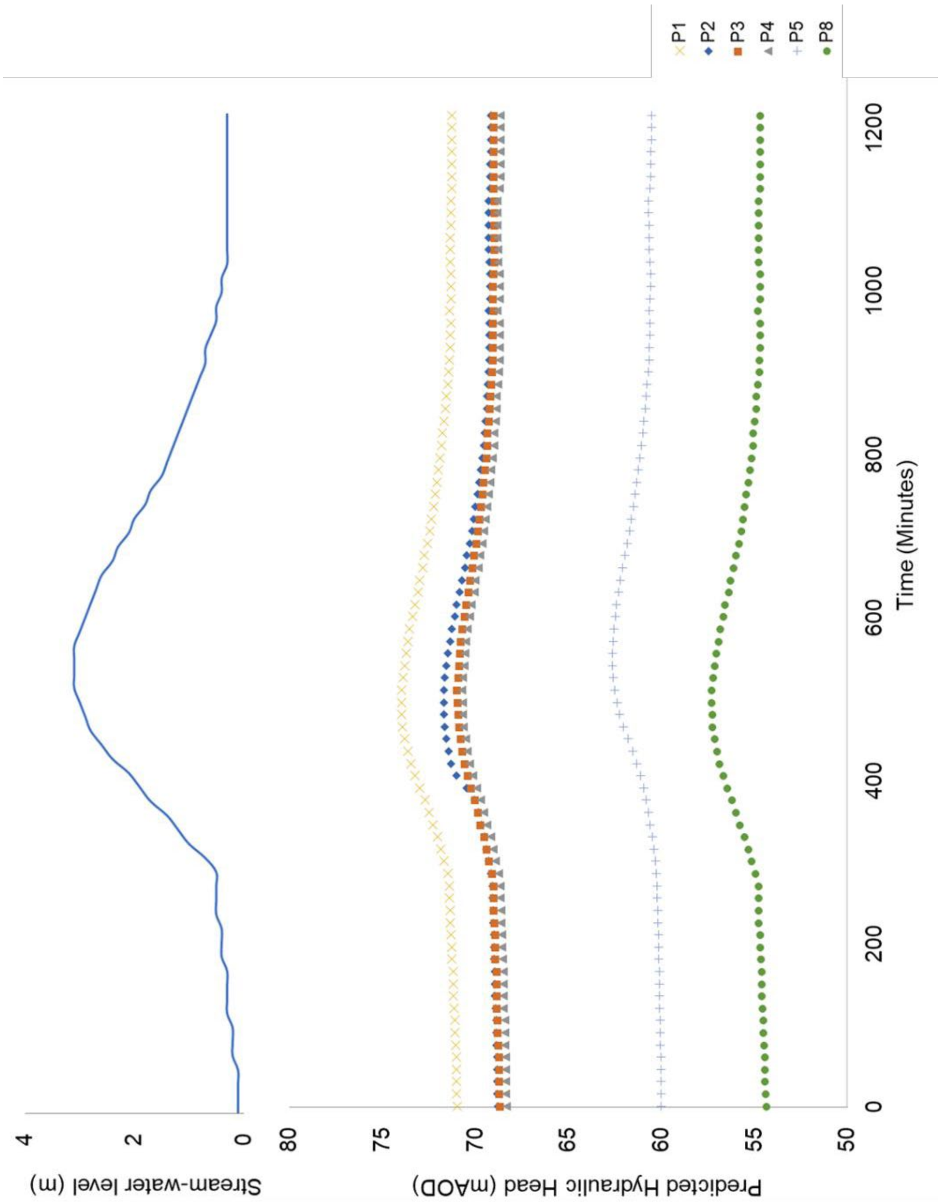

Figure 4-16: Heads simulated at piezometer sites P1-P5 and P8 during a design 100-year event.

Under average conditions (Figure 4-17) the upwelling and downwelling along the reach suggests that there is a movement of water from the surface to the subsurface and back again, likely coinciding with the precipitation of metal oxides on the bed attributing the partial pressure change as sulphide and metal rich waters move from the anaerobic subsurface to the surface (Buss *et al.* 2009). As the stage rises, downwelling from the stream to the subsurface is enhanced (Figure 4-17), coinciding with the loss of metal oxides from the bed, and enrichment of manganese and zinc in the bed, for example, as discussed in

Chapter 3. At the peak of the storm, and shortly after, it is likely that there is no movement of water across the streambed interface attributing to the saturation of the bed material. It would be necessary to then also consider the losses beyond the channel via the banks and floodplain to further assess the transport and cycling of flow and solutes. With conditions nearing return to those of average conditions at the end of the storm simulation, the VHGs appear to gradual return to those observed at the start of the storm, although with generally enhanced upwelling along the reach as the heads exceed the stream stage (Figure 4-17). In which the riffle-pools start to then predominate the upwelling and downwelling patters with the return of the upwelling along reach with the iron-ochre flushes (Figure 4-17).

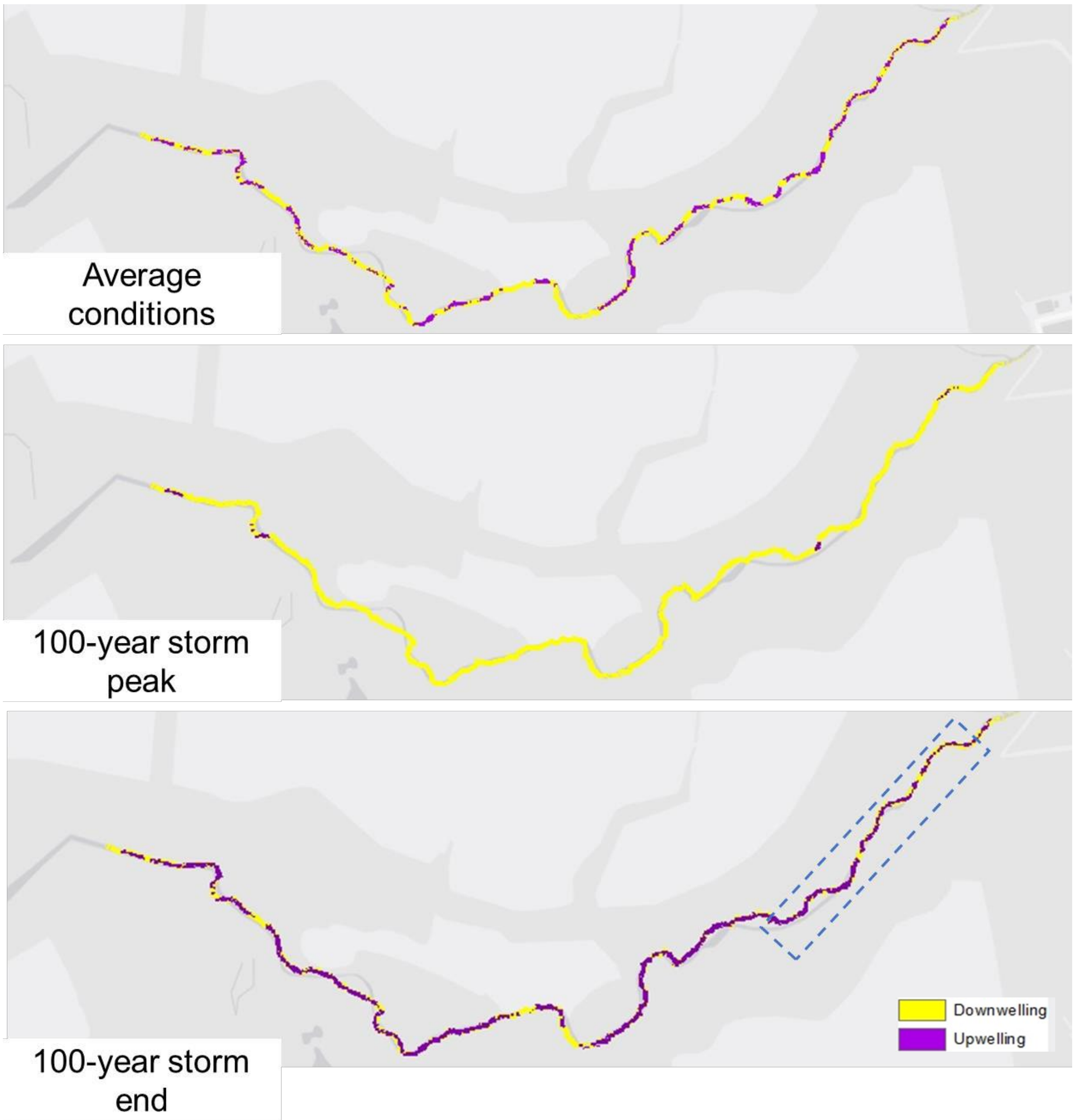

Figure 4-17: Upwelling and downwelling of GW respective to the SW over the streambed according to a 100-year design storm event, at the peak of the storm, and at the end of the storm.

4.4.3.4. Model testing under climate change scenarios

Daily rainfall time series generated at a 5 km resolution using the UKCP09 Weather Generator under a medium emissions scenario for the 2030s (CESER 2016, Research 2017) were used to investigate the system response to 1-in-100-year flood events according to future climate change projections. A total of 1000 scenarios were generated. The recurrence intervals of the 100-year events were assessed using the method of moments, assuming the maximum values fit a Gumbel distribution, from which the location and scale parameters were calculated using the mean and standard deviation. The cumulative averages of the location and scale parameters were calculated for each of the scenarios and are shown to converge within the 95% confidence intervals at around the point of 300 scenario runs (Figure 4-18).

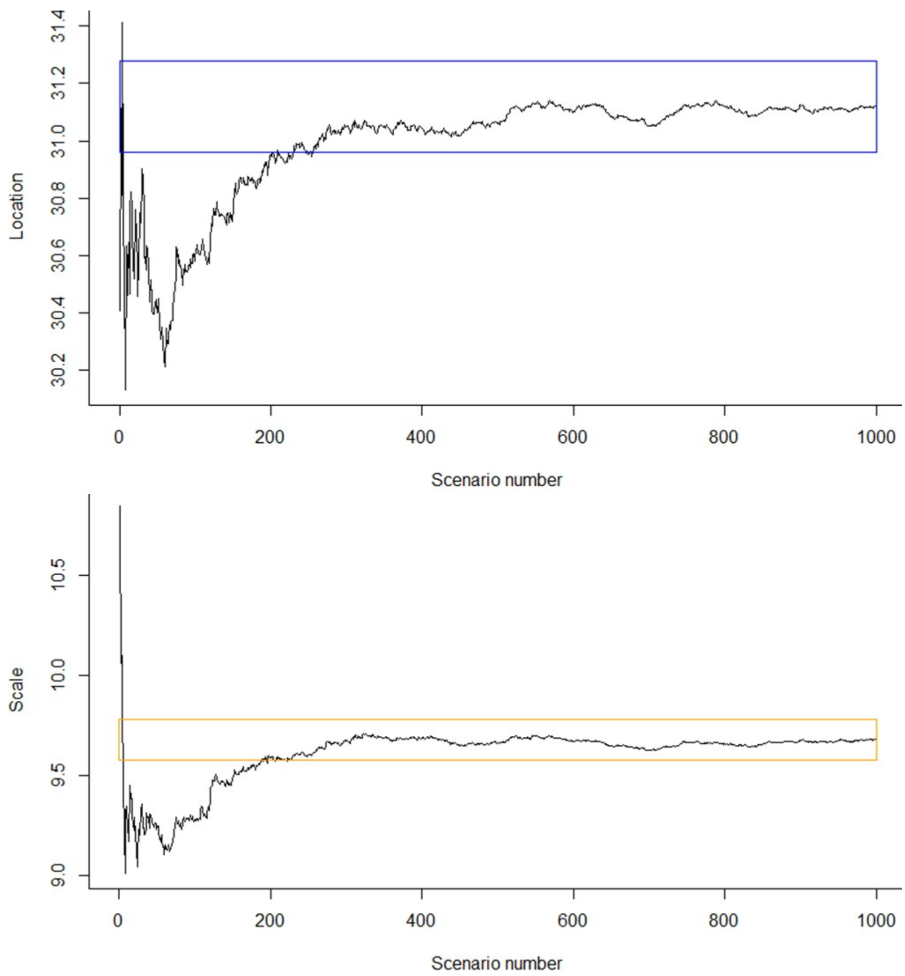

Figure 4-18: Cumulative averages of the location and scale parameters estimated for the 1000 scenarios for the 2030s, shown with 95% confidence intervals.

Based on the convergence, a total of 300 event-based simulations were completed. Scaling the simulated rainfall to that of the FSR/FEH rainfall-runoff 100-year event hydrograph (see section 4.4.3.3.) a series of stream-stage time-series were generated and ran through MODFLOW-NWT. The model simulations were based on the same initial and boundary conditions as used in earlier simulations, albeit varying the stream stage, producing simulations of hydraulic head changes. Over the duration of each design 100-year events, the simulated heads at each of the monitored piezometers sites were variable, with heads varying over 4 m between the minimum and maximum simulated heads (Figure 4-19). Head changes associated with higher rainfall events were around two-order of magnitude greater relative to those associated with comparable lower rainfall (Figure 4-19).

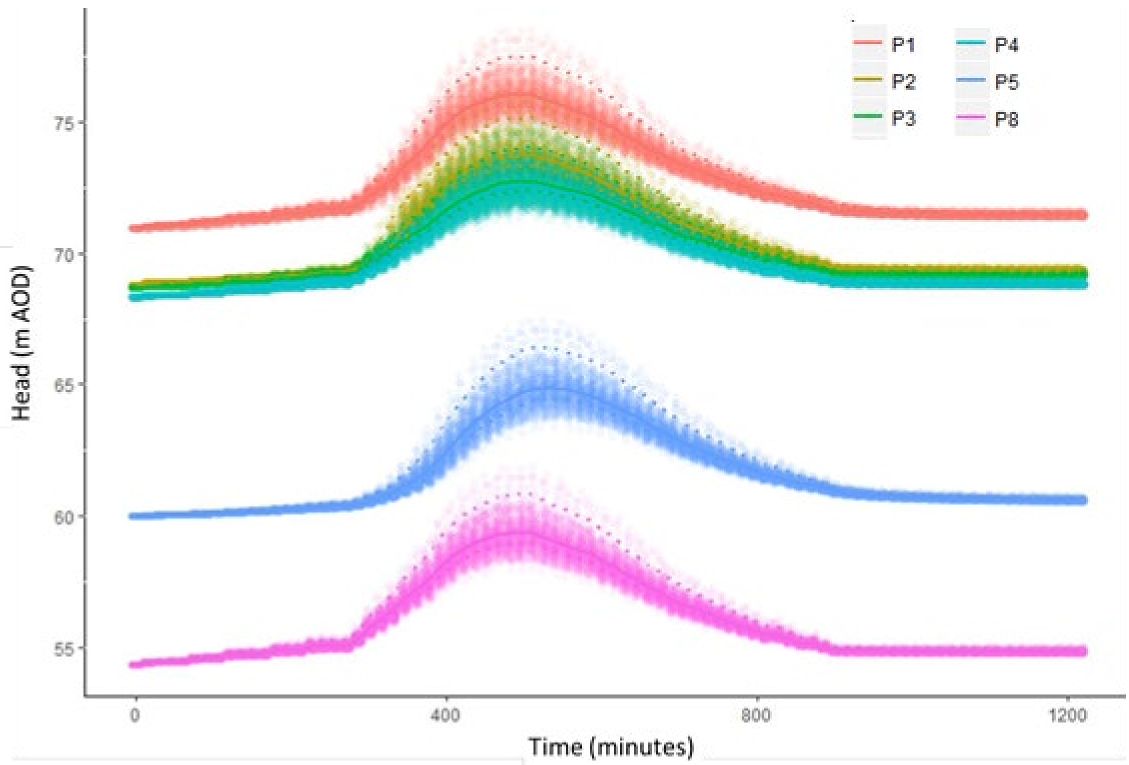

Figure 4-19: Hydraulic heads at the piezometer sites (P1-P8) within the 95% confidence interval as shown by the dotted lines.

Upscaling these findings along the channel reach, it is likely that in response to a 100-year rainfall event representative of the rainfall according to average climate change conditions in the 2030s, that at storm peak, the stream stage would be expected to rise by around 5 m, accounting exclusively to downwelling conditions along the reach (Figure 4-20). According to the simulations, downwelling conditions prevail with a fall in stream stage, although corresponding patterns of upwelling of GW are observed too (Figure 4-20). Such patterns of upwelling and downwelling are indicative that return flows of SW are likely occurring attributing from the saturation of the streambed. Relative to the initial conditions, the upwelling of GW post-storm is on average twice as strong, therefore providing a greater potential of solute movement over the streambed, particularly in the second half of the reach where the iron-ochre flushes have been observed. The response of the system post-storm under such conditions corresponds with exaggerated and more dynamic conditions relative to those observed under present-day conditions. The enhanced upwelling has potential to therefore transport greater flow and solutes to the stream, and thus deterring the SW quality.

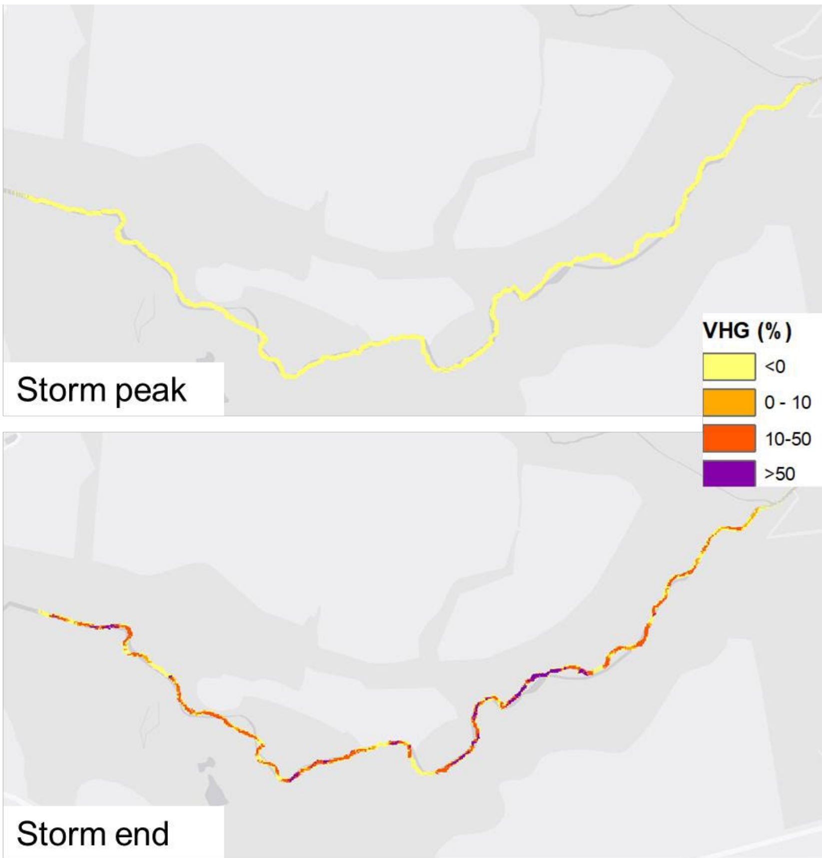

Figure 4-20: VHGs estimated according to an average 100-year storm event according to the 2030s UKCP09 rainfall scenario.

Looking at the extreme end of the climate scenarios, assuming the maximum rainfall were to occur for a 100-year event, corresponding with a maximum rise in stage to 8 m, the system response is greatly similar along the reach (Figure 4-21). As expected, the storm peak corresponds with predominant downwelling. However, the return to normal conditions is somewhat more gradual, and would likely take significantly longer relative to those under lesser extreme rainfall events. Figure 4-21 shows the simulated VHGs for such an event at the storm peak and following a fall in stage to less than 1 m. Such an occurrence could likely enhance the attenuation potential of the subsurface, although further investigations would be necessary.

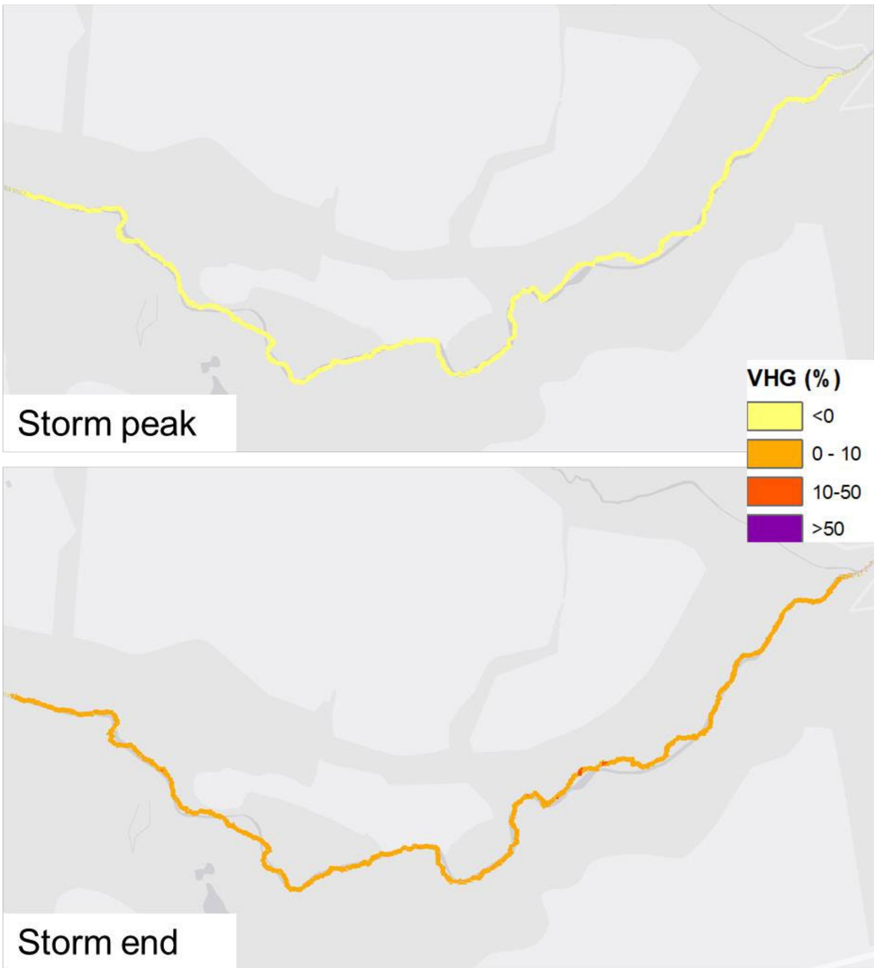

Figure 4-21: VHGs estimated according to an extreme 100-year storm event according to the 2030s UKCP09 rainfall scenario.

4.5. Concluding remarks: Challenging the current GW assumptions

The implementation of a numerical modelling approach has allowed an upscaled understanding of the general processes operating across time and space between the GW and SW systems. Hydraulic head changes are responsive to the changes in stage, with the extent of upwelling and downwelling operating as a function of the location and degree of change in stage. The simulated system responses are not without large uncertainties; however, they are insightful, particularly when thinking about the system response following the onset of large rainfall events which were impossible to sample the piezometers throughout the field sampling campaign. Returning to the two original research questions, the hydraulic gradients are responsive to changing hydrological conditions, and the iron-ochre flushes are likely attributing to return flows, although further testing, e.g. via isotopic analysis would be required to confirm this source.

Under average, baseflow conditions, the gains and losses to and from the stream are inherently variable along the reach likely owing to the bed characteristics. Gains and losses to the stream are supportive of the patterns observed in Chapter 3. Increasing discharge through the system attributes to the enhancement in the downwelling and associated loss of stream water to the subsurface, resulting in solute enrichment, e.g. manganese. Implying the understanding from the modelling to how we have otherwise understood this system. While it is evident that under baseflow conditions, the stream is impacted by the mining-derived solutes, which are lost from the subsurface. Meanwhile, during storm events, the subsurface becomes effectively cut-off from the stream with reduced vertical upwelling, and as a result solute concentration are likely to become enriched.

The Twizell is nevertheless a complex system, with dynamic changes in the water fluxes and chemistry. Traditionally assumed disconnected to the subsurface, this is unlikely to be the case, particularly here with reference to the shallow, near stream GW/SW system. It is important to consider and challenge how we look at these systems, as without coordinated joined-up understandings and management, the impacts can be further detrimental. For instance, as observed post-storm events throughout field sampling, the sulphide and metals are highly enriched in the streambed. If after a storm this is true, then when the upwelling of these enriched waters rises, coinciding with phosphate-rich waters from upstream could potentially result in the mobilisation of the entrained phosphate (Smolders and Roelofs 1993), leading to significant issues downstream. Such a concern has been pointed-out by Northumbrian Water; however, this is the first time that we have looked at the role of the streambed in having an attenuating and release potential.

Ultimately, the modelling is a useful exercise for challenging how the way we look at and think about the GW systems and the interaction with stream-water across various spatial and temporal scales. Modelling suggests that the hydraulic heads of the superficial system are responsive to changes in stream stage, with various patterns and dynamic changes in the upwelling and downwelling as a function of the bed geomorphology, but also the conditions. In this chapter I have looked at the response of the system to changing hydrological conditions as a result of periodic releases from the sewage treatment works and rainfall events of various orders of magnitude. With reference to the Twizell, where field sampling only provided a snapshot of the dynamics and processes, modelling has facilitated an assessment beyond these constraints. Without the application of modelling as a tool to better understand these systems, the prevalent understanding of the cycling and exchanges in flow and solutes would be continued from a one-dimensional focus, with a reliance on limited monitoring. Ultimately, there is a need to look beyond such limits and gain a fuller understanding of the system dynamics and processes, linking together the local- and larger-scale processes (Magliozzi *et al.* 2017).

“I can’t control their fear, only my own.”

Scarlet Witch (Captain America: Civil War, 2016)

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Chapter 5 - Discussion

This chapter draws together the key findings presented in Chapters 2-4, addressing the original research aim by evaluating the connectivity and processes operating at the GW/SW interface of heavily modified rivers in County Durham. The development and application of methods to conceptualise and capture the system dynamics and processes has been demonstrated via a combination of desk- and field-based approaches. In doing so I express the need for water resource practitioners to consider local-scale GW/SW interactions as an integral part of the wider catchment management approaches, moving beyond the focus of the systems as decoupled and disconnected.

5.1. Key research findings

5.1.1. Developing an integrated understanding of GW/SW systems

The shift towards developing a holistic integrated understanding is emphasised by overarching policy frameworks such as the WFD, as well as individual challenges in catchments, which are typically addressed with fragmented reactions within and across disciplines (Cosgrove and Loucks 2015). That is despite the likelihood of interactions between the systems (Kløve *et al.* 2011). There are several notable attempts discussed throughout research and in practice which endeavour to establish a more holistic understanding of the system characteristics and in-turn the GW/SW connectivity (e.g. Ransley *et al.* 2007). However, limited and infrequent data collection and baseline studies tend to inhibit the application of several of these approaches in their application to more complex catchments (Conant *et al.* 2019), particularly those as considered in this research which have been heavily modified.

The high heterogeneity of the system characteristics and multiple pollution pressures are typically unaccounted in heavily modified systems, with a paucity in the understandings. The need to between understand such systems to achieve more effective water management requires a focus of the wider systems, as well as the local processes operating within the catchment boundaries (Magliozzi *et al.* 2017). There is great emphasis on looking across multiple dimensions, moving from the wider understanding to more specific processes, and upscaling them back to develop a holistic integrated focus (Magliozzi *et al.* 2017). While such investigations are challenging, especially with the dearth of understandings in practice, it is nonetheless essential to start and develop an improved understanding of the system characteristics, particularly where poor water quality is key to address. There is a need to move from reductionist approaches to water management (Heathwaite 2010), considering the links in the landscape (Bencala *et al.* 2011, Kaandorp *et al.* 2018). While emphasis on these areas has been recognised, approaches are somewhat limited to more complex systems such as those in this study.

While classification/index-based approaches are useful for a broad assessment, the inability to compare and consider specific pathways limits their subsequent application to further consider the mechanisms by which pollution pressures impact on the water quality (Harris 2003). Instead such approaches generally allow for a broad assessment of the connected or disconnected state of whole catchments, thus limiting their usefulness in the application to smaller areas, and those which are heavily modified, facing a multitude of threats to water quality. With emphasis on the need to consider the links between pressures and drivers in-light of deteriorating water quality the work by Kaandorp *et al.* (2018) begun to show ways of linking the pressures and drivers and the likely connectivity between systems. However, there is also prominence on the need to consider the larger system, but also within it the mechanisms by which the systems interact (Magliozzi *et al.* 2017). Therefore, this thesis presented the application of methods to assess the larger scale links, and from this work towards assessing the role of local processes.

Chapter 2 took on board the need to establish an improved understanding of the catchment characteristics and likely connections between the systems. The chapter explored ways of developing an integrated understanding of GW and SW at the catchment-scale, focusing on the conceptualisation of connectivity within and between the systems, looking across the streambed and surrounding landscape within the catchment boundaries using existing spatial data. Chapter 2 primarily focussed on developing an improved understanding of the characteristics of catchments, utilising existing spatial datasets as part of a proposed framework. The aim was to demonstrate and test the feasibility of using the data available at present.

Chapter 2 introduced the concept and application of a tool of which I termed 'Integrated River Evaluation for Management' (IREM). IREM looked to establish a combined understanding of the GW and SW systems, with the basis of the approach been to collate existing spatial data on the catchment characteristics. The intention of the research was to show how collating often relatively sparse spatial data, e.g. superficial deposit thickness combined with additional datasets and empirical field sampling provides the ability to build up a complex picture of the likely links within and between the systems, emerging from the assessment of a series of simple inferences (Harris 2007, Kluger 2008). By mapping the pressures alongside the characteristics and inferring links between them enables for a more complete conceptual understanding of the systems within the catchment boundaries. The IREM approach is one way to move beyond assumptions that the systems are disconnected and instead begin to think about how the systems are connected within the catchment boundaries, based on their specific characteristics.

Connections were assessed according to the pathways between the hillslopes and water bodies, for instance, by looking at the geology composition, including the thickness and permeability. Looking exclusively at the surface provides only part of the understanding of the systems, it is necessary to expand the understanding below the surface, looking at the lateral and vertical dimensions. IREM demonstrated that by assessing the patterns and links across multiple dimensions is essential to proceed and think about the challenges within catchment boundaries. By mapping known water-quality pressures against the catchment characteristics it is possible to start and think about the potential flow pathways and processes, considering the stream water as an integral part of the connections between the SW and GW systems. Whereas reductionist approaches have tended to focus on masking such pathways (Heathwaite 2010), IREM challenged the understanding, looking beyond the point source attribution, thinking about how flow and solutes moves, rather than assuming it is encapsulated in either the surface or subsurface.

It was through the application of IREM that I was first able to begin to visualise the likely connections in the landscape of the study areas, namely the Herrington Burn and Twizell Burn. Initial mapping of the water-quality pressures was insightful. Most often this is not done in practice, with practitioners focusing on individual pressures, e.g. asset failure/compliance. To then map the drivers of the likely connections between the pressures and the links to the GW and SW systems challenged the current perceptions towards the systems. Flow pathways within and between the systems are largely unexplored in practice, with interactions across the surface-subsurface interface been discounted due to the dearth of understandings and masked by the complexity of the systems.

In its application to the study catchments, IREM was utilised in the producing of simple links and maps of the data it is possible to develop improved understandings, supporting discussions amongst practitioners addressing current water-quality issues in the Herrington and Twizell catchments. Not only did the composite maps produced allow for the communication with non-academic audiences, they also allowed for an evaluation of the likely threats to the water quality, alleviating the paradigm lock between science and practice, which has been a key step to progression in water management (Falkenmark 2004). Discussions were scoped from the outputs of IREM between practitioners and are arguably leading to more structured approaches - as personally observed during subsequent meetings with participants of the TOPSOIL group. Breaking down the barriers between institutions and stakeholders is somewhat challenging, with contrasting ideas as to how best approach and manage issues. Throughout this research, it is apparent that part of alleviating this challenge is about how data is used to communicate, and IREM did that. This was achieved through the use of maps to clearly communicate the story, and displaying a more complete set of data, rather than taking elements as practitioners have evidently done in the past. With the IREM approach is was effectively about mapping out a story, from the pressures, to the drivers and how they likely operate over space and time. Bringing the elements together, something that had not been achieved in the Wear catchment to date. From the application of IREM to the case study areas, it is emphasised that there needs to a focus across the multiple dimensions and time.

Following the application of IREM to the Herrington and Twizell, practitioners have started to question the current understanding of the systems, in-turn reconsidering their approaches and management practices. Discussions between practitioners have since taken place and continue with the shaping the next steps in thinking about how to investigate and address issues such as the abstraction challenge at the Herrington. Through the application of a relatively simple approach as IREM has led to more complex findings, including those continued at the Herrington by Northumbrian Water, and in this research. The remainder of the thesis focused on the Twizell where the likely connectivity between the stream and near-stream sediment was further explored in relation to the water chemistry attributing to historic and contemporary pollution pressures. The research led to demonstrate how it is possible to move beyond initial conceptualisations, with the need to then look also at the mechanisms by which flow, and solutes move in catchments. In heavily modified and stressed systems such as the Twizell, fragmented reactions typically fail to consider the complexity. There is a need to develop an insight of the multi-scale processes operating, looking across multi-dimensions in space and time (Magliozzi *et al.* 2017).

5.1.2. Near-stream GW/SW interactions and exchanges

Alongside SW, the coinciding GW quality is an integral element to consider for effective water management. Encompassing the local-scale processes into the wider catchment understanding is now encouraged, however, is challenging where there are limited baseline studies. For catchments such as the Twizell, GW/SW processes are therefore overlooked, instead focusing on specific sites as part of reductionist approaches (Heathwaite 2010). A reach of the Twizell was selected given the heavily modifications to the channel planform and accumulation of water pressures from the historic mining legacy besides contemporary effluent releases from upstream sources. The research looked to investigate the movement of flow and solutes across spatial dimensions, as well as assess the processes operating, looking beyond the pristine sites in which understandings are typically established (Cardenas 2015).

In Chapter 3 I reported the use of relatively low-cost field approaches to investigate the interactions and exchanges in flow and solutes during an intensive field sampling campaign over the spring-summer 2017 of the Twizell. The Twizell is an example of a catchment that is threatened by multiple pollution pressures yet given the high heterogeneity and complexity of the systems, as hindered by infrequent quantification of the flow and solutes, is typically treated as a black-box system, with reductionist approaches to water management. The sampling challenged the perception that the stream was effectively decoupled with the underlying subsurface. A view held in practice, and thus hindering effective management.

Sampling across the surface and subsurface over a range of time periods provided an insight into potential flow and solute pathways via the obtaining of discrete grab samples and quasi-continuous time-series of the SW. Sampling of the SW at the reach scale was indicative of the impact of pollutants on the SW chemistry in accordance to mining and waste-water effluents. The hydrochemistry of the SW reflected the impacts, with elevated nutrients during high flow events. While upwelling of GW to the stream was unlikely from the Coal Measures, given that there we no significant changes in stream flow over the reach, discrete pathways between the stream and superficial system were evident from the piezometric sampling.

The stream-water chemistry is likely impacted by returning stream water in addition to hillslope runoff entering the channel via riparian and subsurface flow paths. Through sampling of the shallow GW, the enrichment of solutes in the subsurface was evident, particularly SO_4^{2-} and Mn, coinciding with the downwelling of SW. Enrichment of solutes is indicative of the biogeochemical reactions occurring in the shallow sediments, with HEFs mixing oxidised SW with reduced GW. The accumulation of solutes in the subsurface implies that at the local scale, the subsurface is acting as a potential source and sink of solutes, with the dynamics and processes of the flow exchanges and solutes apparent to be operating as a function of the stream-water levels and bed geomorphology. The complex patterns and heterogeneity along the reach makes interpretation and thus management challenging. However, it is key that such patterns and processes are identified, from which the role of local-scale processes can be accounted in the wider management scheme. By assuming that the water quality in the subsurface has little influence on the stream-water quality is an over-simplification. The local-scale patterns and processes are essential in the wider understanding of the system. A small reach may only have been investigated but it adds to the knowledge that spatial and temporal dimensions cannot be overlooked.

A schematic conceptualisation of the processes identified along the study reach are shown in Figure 5-1. The superficial deposits are thought to be acting as a shallow hyporheic zone, with the attenuation of mining-derived pollutants. The downwelling of SW coincides with the enrichment of SO_4^{2-} and Mn in the pore water and the precipitation of iron-oxides along the bed of the channel. Further downstream, upwelling is thought to be occurring. This upwelling is potentially return flows of the downwelling surface water from upstream. The movement of water and solutes into the unsaturated zone is likely, however, inconclusive from this study. Additionally, the influence of the rebounding GW through the water quality along the reach is unknown.

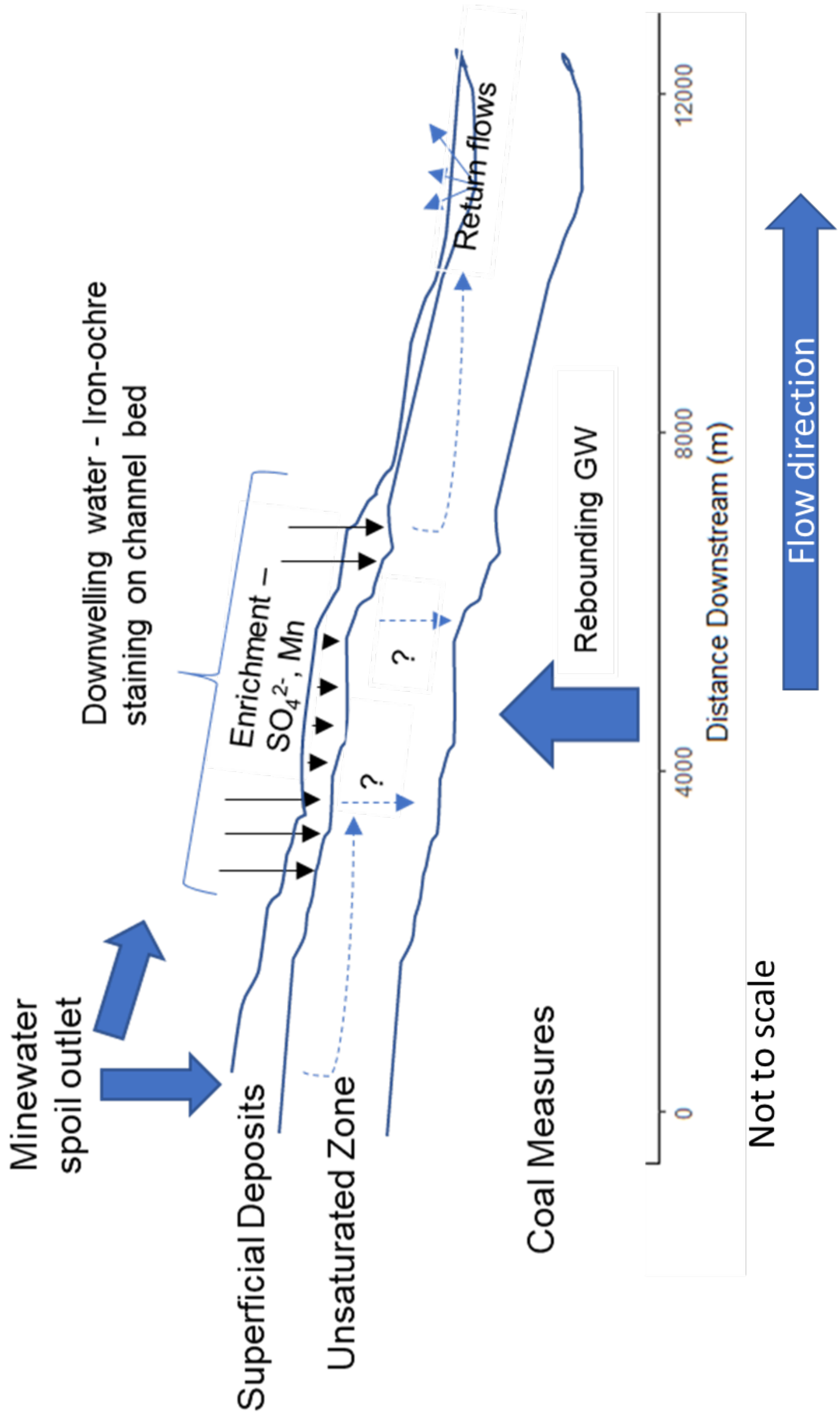

Figure 5-1: Schematic diagram of flow pathways along the Twizell Burn study reach.

5.1.3. Spatial and temporal variations in GW/SW behaviour and responses

In Chapter 4, the implication of changing hydrological conditions on the GW/SW interactions, specifically accounting to the movement in the hydraulic heads of the minor aquifer were investigated through numerical modelling simulations. In doing-so, the spatial and temporal GW/SW responses were further interpreted for the Twizell, bringing together the conceptual connectivity of the wider catchment, with an understanding of localised processes with the and the field measurements, interpreting the processes and dynamics of the systems beyond the localised understandings, and into the wider catchment response. Such links are largely missing in research and practice (Magliozzi *et al.* 2017), and this work showed one way that the link between local and wider patterns and processes could be achieved using modelling to bridge the gap between understandings.

The dynamic nature of the shallow water table position in the superficial deposits was evidently responsive to changes in stream-water levels. The simulation of hydraulic head patterns and associated vertical hydraulic gradients denoting upwelling and downwelling across the streambed under a range of scenarios were insightful, revealing that the high level of connectivity between the shallow GW and SW is something that should not be overlooked. Relatively small changes in stream levels accounted to little variation in the flow and hydrochemistry of the stream and subsurface, with the bed geomorphology and hydrogeology of the underlying superficial sediments driving any exchanges, with discrete flow pathways. Small fluxes in stream levels such as those observed during field sampling from the sewage treatment works had little impact on these discrete flows. Meanwhile, under flood conditions and extreme event scenarios, the system dynamics were greatly enhanced. The enhanced downwelling and subsequent upwelling of the GW highlight the integral behaviour of the interactions between the GW and SW systems.

Findings highlight that it is the cycling of the solutes with the movement of flows that determine the quality of the overlying systems, not only in the vicinity, but upstream and downstream. Localised exchanges in the flow and solutes do not just impact on the vicinity, and therefore an understanding of the local processes is central to the way in which water is effectively managed. This research only looked at a singular reach, however, further investigations beyond would be necessary to explore additional links. Ultimately, the stream should not be considered as a closed system, and instead as an integral part of the catchment (Bencala 1993, Bencala *et al.* 2011). As demonstrated in this work, despite the challenging systems, connections should not be overlooked when it comes to management decisions.

5.2. Reimagining water-resource management

Collectively, the findings of this research support that the stream-water quality is inherently intertwined to the characteristics and processes operating above and below the streambed, resulting in a complex and dynamic situation. To facilitate a more effective approach to managing the water quality requires the way in which we investigate and describe the water and systems to reflect this integration. An understanding of the larger system is essential, with the mapping of the pressures to water quality, not at least because then the source attribution can be considered, but to then also start and think about how pressures may impact and interact elsewhere in the catchment. The need to then look at the larger- and local-scale processes operating is emphasised greatly throughout literature (e.g. Ryan *et al.*, 2007).

The understanding of GW/SW processes has largely been at the more pristine sites (Cardenas 2015). While studies on the role of the hyporheic zone on the cycling of pollutants are evident, they often focus only on the role of singular pressures (e.g. Palumbo-Roe and Dearden, 2013). Looking at multiple pressures is with difficulties, however, these catchments, such as those in County Durham cannot be overlooked. These findings of this research have opened an alternative perspective on tributary catchments that were lacking an insight beyond the stream and has led practitioners to re-think current problems and approaches.

A whole systems approach, as envisioned by ICM requires the connections within and between the surface and subsurface systems to be mapped. Incidentally the high heterogeneity of catchments makes the connections likely complex. Making simple inferences, such as demonstrated with the use of IREM are essential to facilitate discussions between practitioners, without them the problems are likely to prevail. Trying to envision and manage the systems via top-down approaches overlooks the smaller processes. The fragmentation within and across disciplines with a vested interest in managing the water resources can be alleviated by stepping back from the complexity and looking at the simple patterns to begin with.

The thesis has demonstrated a new understanding of these tributary systems in the Wear Catchment, considering the local-scale changes and water quality, which has otherwise been limited to routine sampling and high-resolution screening studies. The research and findings presented feed into the wider efforts coordinated as part of the TOPSOIL project. Through the presentation at local partner meetings as well as international plenary meetings, the need for the integrated thinking is evident, requiring the need to bridge together the scientific findings into working practice. However, a key concern is that with the GW/SW studies across the pilot studies within the TOPSOIL project is the dealing with uncertainty. Specifically, when communicating to stakeholders who often prefer a definite answer or solution. Recent discussions during a plenary TOPSOIL project meeting in March 2019 highlighted that the uncertainty is something that must be demonstrated to stakeholders, and that uncertainty is something that cannot be avoided as we are dealing with unknown systems, especially since the GW is not easy to imagine or picture given it is below the surface. In the past, the uncertainty has associated with the ignorance to the subsurface systems, and this work has challenged this, addressing the need as to how to develop collaboration in water management (Conant *et al.* 2019).

5.3. Recommendation for catchment management

The research findings support the need to look more closely at the GW and SW systems, challenging how we currently monitor and thus manage them. Looking beyond the case study examples, there is potential to apply the same principles and procedures to address the freshwater resources elsewhere in the Wear catchment, and beyond. The need is underlined by the increasing pressure on water resources to meet human and ecological demands. The examples used in the thesis demonstrate that the stream systems are often extremely complex, and it should not be assumed that they are homogeneous. Each catchment is likely to be different, but it is about applying similar principles and approaches in bringing data together to start and think about these catchments in an alternative way, with the intention of instigating more sustainable, integrated and holistic management. In-turn demonstrating the use of existing and new data, assessing the roles of the SW and GW, and ultimately how threats operate within catchments, moving beyond looking at the wider catchment response, something that ICM approaches are currently missing (Biswas, 2005; Rollason *et al.* 2018). There is a need to link the local-scale processes into the larger catchment understanding.

The development of conceptual understandings of catchments, investigating the potential pathways of flows and solutes is at the minimum required to start and achieve the intended integration. Besides the conceptualisation, there needs to be an appreciation for the spatial and temporal variations in water quality. Routine sampling at present fails to achieve this, however, the interactions between the GW and SW are dynamic, and to better manage we need to enhance the understanding. Additionally, it is necessary to consider the role of multiple threats to the water quality. Focusing on specific issues is beneficial at the point of source or impact, but those managing the systems from an organisational to an informal level need to consider the upstream and downstream, and well as vertical movements.

"Whatever happens tomorrow you must promise me one thing. That you will stay who you are. Not a perfect soldier, but a good man."

Dr Erskine (Captain America: The First Avenger, 2011)

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Chapter 6 – Conclusions and recommendation for further work

This thesis has presented research which addresses GW/SW connectivity of tributary catchments with the need to address the poor-quality freshwater bodies with an integrated and holistic approach. In doing so the research explores the impacts of multiple threats acting on the systems attributing to the interactions and exchanges of flow and solutes across the streambed interface. In tributary catchments, despite the deteriorating water quality, and growing emphasis from policy and frameworks for interdisciplinary focus on addressing water quality, fragmentation and mismanagement of GW and SW continues to prevail. Such gaps in understanding are attributing to limited process knowledge and segmented procedures in addressing water quality issues.

The unexplored connections between the GW and SW systems has implications for their management, thus hindering any attempt at the surface or subsurface because efforts can be detrimental on each other. Therefore, management at one point in the system has the potential to deter efforts further downstream, as well as beyond the catchment. Developing conceptual understandings of the systems supports the potential of this communication and requires the integration of data, demonstrated through the IREM approach and subsequent investigations, with assessment across four dimensions (x, y, z and t), looking beyond the singular dimension of the SW or GW systems being connected or disconnected. From these conceptualisations, there is a need to capture the local-scale changes and examine processes operating within the catchment boundaries, specifically the movement in flow and solutes within and between the GW and SW systems. Linking the local-scale processes back to the wider system is essential, otherwise fragmented understanding prevail. Through the application of numerical modelling exercises, it was demonstrated that the patterns and processes could be linked.

6.1. Principal conclusions from the research

The research has found that:

1. Despite a shift in policy and frameworks to assess and shape how we manage water quality at the catchment scale, we need to start thinking about the systems in a different way, not just as that the pollution enters the stream channel via point and diffuse sources, but also how the GW and SW systems interact with the landscape and other features around it. Moving beyond the mismanagement of water resources requires a holistic and integrated understanding, and this is unachievable under the current protocol and procedures by which we currently attempt to understand the systems. Sustainable GW/SW management requires considering the connections between drivers and factors likely influencing the movement of flow and solutes. Considering subsurface connectivity as well as landscape connectivity is vital in making advancements in the addressing of water quality. Looking beyond the focus of the stream system, however, requires the integration of data and information, to then step beyond and target efforts to investigate the sources which threaten the water quality. It is then about taking this knowledge and disseminating it to stakeholders who can then make re-informed decisions on ways to manage the water quality.

2. From the sampling conducted in this research it is evident that historic and contemporary threats impact on the stream-water quality. To better evaluate the impacts requires an investigation beyond the routine measurements, assessing both spatial and temporal variations and likely drivers and controls, both above and below the streambed. Do-make evaluations simply ignore the historic dimensions in favour of instrumental data (which are often very limited). Most legislation is based on data that cannot possibly be obtained from instrumental records, and so it is to then question how we better use the available data. In data sparse situations, it is most feasible to accumulate the existing secondary data and then move forward with empirical investigations, rather than collecting data as done under routine sampling which is not linked to the already existing data.

3. The streambed interactions are complex. A combination of factors adds to the high heterogeneity, with the propagation of factors within the channel, catchment, and beyond, including the likelihood of extreme rainfall events. This study has relied on the use relatively of low-cost methods to give a first-order insight into the system dynamics. Due to the low-cost nature of the techniques applied thus enables for a much greater coverage capturing detail across the wider system, e.g. catchment scale, both spatially and temporally which can be more useful than an expensive approach which then lacks coverage. The replicability of intensive approaches is unfeasible. Nevertheless, demonstrating the importance of looking at the subsurface connectivity, which is partly responsible for the SW quality.

4. Traditionally, decisions as to how water resources are managed are based on a snap-shot insight into the systems. While field sampling is a useful approach to quantifying the water chemistry, it needs to be linked with other approaches, specifically laboratory work, existing data and modelling to extend the understanding providing a generalised understanding of the systems. Customarily, the prevalent understanding of the cycling and exchanges in flow and solutes would be continued from stream-system focus looking at the system at a given time and place, with a reliance on limited monitoring. However, there is a need to look beyond such limits and gain a fuller understanding of the system dynamics and processes and work with the available resources and supplement additional findings to them.

Ultimately, the impact of the fragmented views of the GW and SW systems from stakeholders has resulted in a disparate focus on different issues. Traditionally such an approach was accepted, however, emphasis from international policy, e.g. the WFD seek to move beyond these. Not only is there a lack of cohesion in the holistic investigation of how water and solutes move across the streambed, but it comes also from the lack of disciplinary connectivity. The shift requires coordinated efforts to gain an understanding of the systems, with collaboration between those responsible for managing the resources. Projects such as TOPSOIL are providing a platform to facilitate such a movement, yet it remains particularly challenging to implement, and has some way to go. In practice, through EU projects like TOPSOIL have been going on for decades, so the question is, why are they not any further forward in addressing the connections between disciplines? It is likely because they are not re-evaluating the systems and attempting to break-down the complexities. As ultimately this has implications for the learning process and understanding.

6.2. What the findings of this research mean for management

The traditional assumption that the GW and SW systems are disconnected has been held for some time. However, over the last 25 years, the shift in research to look at the GW/SW interface has highlighted the potential in changing how we should think about and manage water resources. There is the need to avoid targeted, black-box approaches. To facilitate the development of an integrated understanding is by no-means straight-forward and is associated with high costs if high resolution methods are chosen, for example, the use of in-situ recording devices. Regardless of the elaborate nature of selected methods, there is a growing pressure to address the GW/SW interactions, with complex interpretations of the systems possible to derive from simple analysis, as demonstrated in this research. With regards to management, this research has demonstrated that is feasible to look beyond the fragmented views of the SW system, from which it is possible through innovative approaches to start and gain a general understanding of the system dynamics and processes. As demonstrated at the study catchments, the way in which we start and think about how water moves through a system, and where it attenuates, for instance can start and lead to new intentions as to how we should this about issues.

One of the greatest challenges facing the integrated evaluation of water systems is the visualisation of the GW environment, which is difficult due to the lack of data available. However, it is then a matter of how we chose to work around these challenges. Using the available data resources, it is possible to derive information, which then supports subsequent investigations. Despite the lack of baseline water quality data, it is still possible to make links between factors, inferring potential flow routes, which can then be tested.

6.2.1. What the findings of this research mean for management in the Wear catchment

In the Wear Catchment, the limited insights and assessments of large- and local-scale processes within the catchment boundaries has hindered progress for sustainable management. Stepping aside from approaches that mask the threats to water quality, it is evidently needed that processes and pathways within and between the surface and subsurface systems need to be explored. In-turn looking at the interactions between the pollution pressures, considering both the historic and contemporary effluents. Such explorations require the need to step-back from the complexities of the systems and start by evaluating simple links in the landscape characteristics. Simple patterns and links can then be explored, as done at the Twizell reach, from which it has been demonstrated as to how the local processes likely fit into the wider system. The accumulation of threats in the Twizell appeared to intertwine, however, required an insight across the spatial and temporal dimensions to develop a greater understanding as to how water-quality issues are impacting on the system.

6.3. Recommendations for further research

In order to extend this research, the following areas for further research are suggested:

1. To test the IREM approach in other catchments, including those of the TOPSOIL UK-1 project, and elsewhere to allow for developments in the tool, including as a communication tool to stakeholders;

2. To assess the upwelling and downwelling mechanisms in other heavily modified catchments, which are structurally heterogeneous, allowing to compare the mechanisms of GW/SW exchanges, looking beyond pristine environments and looking at the role of multiple pressures to water quality; and

3. To increase the ability to calibrate and thus simulate the heads changes via numerical modelling requires larger integrated monitoring, beyond the routine sampling of the SW, e.g. the use of ground penetrating radar (GPR) and/or the drilling of boreholes, as well as interpolation of the faults to further determine direct GW flowpaths.

6.4. Summary

The findings of this research support that GW/SW systems need to be considered holistically to allow for more sustainable management of water resources, with evidence of the interactions of flow and solutes across the streambed. They will support management within County Durham, within the Wear Catchment, and inform of how we should conceptualise and better derive information from available data resources to support in the decision-making process in other tributary catchments. The ability to make such assessments and monitor water quality beyond limited points in the catchment is reliant on the collaborations and workings of stakeholders responsible for managing the water resources, with scientific findings informing working practice.

"…Love yourself, forgive yourself…

Go on a journey…"

Delilah – The Odyssey (Chapter 8) - Florence + the Machine (How Big, How Blue, How Beautiful, 2015)

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Appendices

Appendix A: SW grab-sampling procedure.

Secondary data was supplemented by instantaneous estimates of the water chemistry recorded in the field using a hand-held multi-parameter YSI probe, calibrated prior to each field visit. Readings included: temperature (°C), DO (mg/l and %), EC (as specific conductivity, mS/cm at 25ºC), pH, total dissolved solids (TDS, mg/l), pH and oxidation reduction potential (ORP, mV). For the collection of discrete grab samples of water, two 50 ml samples of water were collected using single-use polypropylene vials. Vials were pre-rinsed in sample water, filled and capped immediately. Samples were stored in a cool bag and transported to the laboratory, where on return they were refrigerated at 4ºC until filtering within 24 hours.

On return to the laboratory, samples were filtered through a 0.2 µm single-use filter (FisherbrandTM Polyvinylidene Fluoride Syringe Filter) to derive estimates of anions and cations via an ion chromatograph (Dionex), and 0.45 µm single-use filter (FisherbrandTM Polyvinylidene Fluoride Syringe Filter) to analyse for trace metals via ICP-OES and ICP-MS, and non-purgable dissolved organic carbon (DOC) by acid sparging and combustion (TOC-L). Method detection limits are presented in the Appendix A.

Table A: Estimated quantification limits and analytical precision for laboratory analysis.

Substance	EQL (mg/l)	Analytical Precision (%)
Fluoride (as F)	0.01	1.02
Chloride (as Cl)	0.03	1.02
Bromide (as Br)	0.02	2.21
Sulphate (as S)	0.02	0.60
Phosphate (as P)	0.02	1.62
Nitrite (as N)	0.02	0.56
Nitrate (as N)	0.04	1.57
Sodium	0.05	0.98
Ammonium (as $NH4^+$)	0.02	1.04
Potassium	0.01	1.26
Magnesium	0.01	1.35
Calcium	0.05	1.33

Substance	EQL (mg/l)	Analytical Precision (%)	Substance	EQL (µg/l)	Analytical Precision (%)
Al	0.025	0.80	Li	1	3.00
B	0.025	0.70	Be	1	4.10
Ba	0.025	1.00	V	1	2.80
Fe	0.002	1.10	Cr	0.5	1.80
Mn	0.002	0.89	Co	1	2.40
Ni	0.002	1.19	Cu	1	1.40
S	0.5	1.43	Zn	2	2.00
P	0.025	1.41	As	1	1.70
			Sr	1	2.10
			Mo	2	1.10
			Cd	0.5	1.30
DOC	1.00	2.62	Pb	0.5	1.30

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