In-stream and hyporheic water quality of the River Esk, North Yorkshire: implications for Freshwater Pearl Mussel habitats

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Declaration

This thesis is the result of my own work and has not been submitted for consideration in any other examination. Material from the work of other authors, which is referred to in the thesis, is acknowledged in the text.

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Abstract

River systems and their catchments are important for ecological, social and economic reasons. However, the increased and changing usage of these natural environments and resources for anthropogenic benefit have led to degradation in water quality, which has led to severe declines in aquatic species populations and their suitable habitats, as well as presenting health concerns with regards to drinking water standards. As a result of this, the Water Framework Directive (2000/60/EC) has been introduced, which is an EU legislation that requires “good ecological status” of freshwaters by 2015, providing a driver for management and conservation for UK river systems. One example of declines in species populations are freshwater pearl mussels (*Margaritifera margaritifera*), which are under extreme threat of extinction. Combining species revival with water quality improvements provides a method for testing effectiveness of implemented measures. This study analyses water quality, hydrological characteristics and hyporheic zone chemistry of the River Esk, North Yorkshire, through a variety of spatial and temporal scales. Changing water quality through storm events showed that general water quality of the Esk is of little concern, however, higher flows bring acidification to the upper part of the network, which presents a serious threat to freshwater pearl mussel survival. The hyporheic zone displayed interesting results in that chemical concentrations were far higher, whilst dissolved oxygen levels and redox potential were lower. Nitrate values were also lower, suggesting that reducing conditions were supporting oxygen-demanding chemical reactions such as denitrification, creating undesirable habitats for aquatic invertebrates. This study concludes that there is a lack of vertical connectivity between the channel and zones of interaction.

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1. Introduction

1.1 Context

Rivers provide habitats for both aquatic and terrestrial organisms, attenuate floodwaters, provide a means for anthropogenic transport and recreation, generate hydro-electricity, as well as being a source of water for agriculture, drinking and industrial cooling (Perry & Vanderklein, 1996). The imbalance between natural and anthropogenic usage of these systems has become far greater in recent years, changing the characteristics of river water quality, quantity and dynamics. Diffuse and point-source pollution from anthropogenic activity has become a major problem, due to increased solute and sediment inputs from industrial, agricultural and domestic sources (Baker, 2003; Edwards & Withers, 2008), leaving detrimental effects on ecosystems.

Improving water quality, as well as restoring natural conditions in the environment, is of increasingly greater importance. With the introduction of regional, national and European legislation such as the Water Framework Directive (WFD: 2000/60/EC), and the recognition that irreversible damage is being inflicted upon river systems and our environment, it is ever more vital that research into water quality progresses. However, the inherent 'black box' nature of catchment science and their site-specific characteristics make it difficult to conceptualise into a holistic understanding (Baker, 2003; Bracken & Croke, 2007; Tetzlaff *et al*., 2008).

One aspect of hydrology and catchment science is the chemical response to changing discharge during a flood. Intensive storm sampling can highlight the complexities of solute behaviour during storm events, and the large degree of inter- and intra-catchment variability (Walling & Webb, 1986). When looking at the changing chemistry of a stream it may be possible to infer the processes acting in the catchment that control flow pathways, residence times, land use effects and connectivity (Kirchner *et al*., 2000), or vice versa.

The effects of water pollution on species diversity and abundance are an aspect of river research that is of extreme importance (Hilton *et al*., 2006). Aquatic species are highly vulnerable to environmental changes, with many coming under threat of extinction due to human-induced pollution and habitat degradation (Weijters *et al*., 2009). The freshwater pearl mussel (*Margaritifera margaritifera*) is an example of a keystone species that has become close to extinction due to anthropogenically-induced changes (Hastie *et al*., 2000; Cosgrove & Hastie, 2001; Geist & Auerswald, 2007), and they are listed under a number of conservation legislations to try and improve their situation. More research is needed on the links between water quality and aquatic habitats, alongside the effects of land use and environmental change.

1.2 Aims & Objectives

The aim of this research is to assess the spatio-temporal characteristics of water quality of the River Esk, in order to gain a better understanding of its response to inputs of diffuse pollution at different scales, and the impact on in-stream habitats. This overarching aim will be explored using the following objectives:

1. To gather information on water quality and hydrological behaviour of the Esk during differing water stages.
2. To analyse the changes in water quality spatially downstream during storm events.
3. To analyse at-a-site changes in water quality during storm events.
4. To analyse monthly, catchment-wide water quality over a period of 6 months.
5. To analyse preliminary findings of water quality from the hyporheic zone (HZ) and compare this with simultaneous characteristics of the channel water.
6. To analyse the data so that possible reasons for the decline in freshwater pearl mussels can be evaluated.

The results obtained will be used to infer possible reasons for failures in revival of freshwater pearl mussels, and locations that could lead to their success.

1.3 Thesis Structure

This chapter has provided a broad overview of the study in question; it has also given the objectives and overall aim for the following thesis. In the following chapter, background information on the topics involved will be explored further, through discussion of key literature and scientific understanding. Chapter 3 describes the broad study area, including the individual sampling sites within it, before explaining the methodology used for data collection and analysis. Chapters 4 to 6 then presents the results, categorised into spatial trends, temporal trends and findings from the HZ. Chapter 7 discusses these results and their implications: conclusions are presented in Chapter 8.

2. Background Research

2.1 Water Quality

Water quality is a general term for the chemical composition of natural waters (Novotny, 2003: 25); it is studied for a variety of reasons, including hydrological, ecological and sociological with regards to health and drinking water (Perry & Vanderklein, 1996; Kumari *et al*., 2012). A clean, natural river is desirable to all those who use it; however, rivers are used for a great variety of activities, including habitats, food, electricity, mechanical power, waste disposal and recreation. The combination of these activities make it extremely difficult to keep the water quality stable, and it will almost always result in degradation (Perry & Vanderklein, 1996: 2).

Water quality is affected by a combination of natural and anthropogenic factors, and their contributions may change over space and time (Baker, 2003). Overall, it depends on interactions between soils and their underlying geology, topography, rainfall, anthropogenic sources and catchment hydrology (Rothwell *et al*., 2010). Changes in the chemical composition of rivers can result in pollution, which occurs when nutrients, sediment or organic material are added to the system that exceed a given quantity for good water quality where aquatic equilibrium can be maintained (Novotny, 2003: 25). These can reach the water through point sources or as diffuse pollution (Hooda *et al*., 2000). It is vital that the processes affecting stream chemistry in catchments are determined, particularly those under intensive agricultural and anthropogenic pressure, so that effective management can be implemented (Rothwell *et al*., 2010).

Point-source pollution originates from an easily identifiable area, for example a drainage pipe or a septic tank (Edwards & Withers, 2008); they are often predictable and periodic in their delivery to river systems. This problem has been significantly reduced, due to legislative focus on improving areas with significant point sources of pollution (Heathwaite *et al*., 2005), for example through the 1989 Water Act in the UK (Hooda *et al*., 2000). Less attention has been paid to the effects of diffuse pollution and ways to reduce it, which will now be discussed (Heathwaite *et al*., 2005).

Diffuse pollution is harder to measure (Baker, 2003), and varies between catchments depending on soil type, climate, topography, hydrology, land use and management (Heathwaite *et al*., 2005). It can be widespread and intermittent; therefore controlling it is complicated (Howden *et al*., 2009). Diffuse pollution is a particular problem in agricultural areas, where an increasing amount of fertilizer, pesticides and animal manure are being applied to fields due to an increase in demand for food production (Hooda *et al*., 2000; Jarvie *et al*., 2008). Nutrients can also be transported from slurry overspills, runoff from farmyards and bank degradation due to cattle using the streams as water sources (Jarvie *et al*., 2008). This increase has led to nutrient enrichment in soils, posing a greater risk of enrichment in waterways. During and after rainfall events, a catchment is likely to be better connected and more efficient at transportation (e.g. Lane *et al*., 2003; Bracken & Croke, 2007; Tetzlaff *et al*., 2007), both on the surface with runoff carrying these nutrients to the river at an accelerated pace, and in the groundwater, producing faster seepage through the hillslopes and floodplains (Edwards & Withers, 2008). These processes will be likely to have adverse effects on the ecology and hydrology of the streams.

2.1.1 Degradation of Water Quality

Nutrient enrichment from point-source and diffuse pollution in water can have detrimental effects on the ecosystem. It is generally accepted that rises in nutrient concentrations, particularly diffusely, are a result of agricultural intensification, expansion and specialisation (Howden *et al*., 2011a). In the UK, the main problems in waterways are nitrate, phosphate and sedimentation (Hilton *et al*., 2006).

A major problem with increased nitrate and phosphate is *eutrophication* (Heathwaite *et al*., 2005; Howden *et al*., 2009). Eutrophication is the enhanced growth of algae and other plant life, which decreases the availability of oxygen, light and space in the channel, degrading habitats and reducing survival rates of aquatic organisms (Monteagudo *et al*., 2012). Nutrient-rich waters can have other damaging effects on aquatic ecosystems and the growth and survival of organisms that live within them. For example, Belanger (1991) discovered that Asiatic clams in the Vermillion River, Louisiana, were found to grow to a much smaller size or not at all in areas of low dissolved oxygen.

In a lake environment it is relatively easy to see the importance that nutrients play in eutrophication, due to longer residence times. However, in a river environment residence times are much shorter, other variables need to be factored in and understood in terms of their importance (Hutchins, 2012). Some river catchments rely predominantly on groundwater sources to sustain flows, which have a long catchment response time compared to those which are more reliant on surface runoff (Howden *et al*., 2009; Howden *et al*., 2011a). This poses further difficulties to those working to reverse damaging effects. Without a clear understanding of solute travel times it is difficult to link cause and effect, and hard to predict future trends with confidence (Howden *et al*., 2011a).

Overland flow also contributes a large amount of suspended fine sediment, which can cause *sedimentation* in rivers, filling the gaps between the gravels in the bed. Fine sedimentation is a serious problem in many rivers, as it can have disastrous effects on salmon populations and other freshwater species such as mussels (Eastaugh *et al*., 2008; Sear *et al*., 2008). Salmonid eggs depend on a sediment-free environment for survival, so that they receive well-oxygenated flows and do not suffocate (Chapman, 1988; Zimmerman & Lapointe, 2005).

2.1.2 Water Quality Management

Introduction of legislation in recent years has driven scientific research towards effective mitigation of diffuse pollution and its effects. Due to the heterogeneity of river catchments, it is difficult to develop a set of general methods to follow; therefore it is important that any measures taken to reduce pollution are developed from specific issues. Measures need to be integrated with landowners and farmers, so that it is a long-term response that is both understood and undertaken with conviction. Separating authority over river management into catchments rather than geographical regions is a big step towards this, as it allows individual catchment management plans (Hering *et al*., 2010).

It is important to understand the behaviour of a catchment before any mitigation measures are taken; monitoring catchments can provide data for both short-term and long-term analysis. It can highlight both subtle and obvious changes in chemistry in relation to other parameters, and reactions to enhanced variables compared to baseflow conditions, both spatially across a catchment and temporally at varying locations along a channel. It was the analysis of long-term records of nitrate concentrations that first identified then problematic rises, after high concentrations were seen during the drought of 1975-6 (Burt *et al*., 2009).

2.1.3 Nitrate

Nitrate is one of the most problematic of water pollutants (Howden & Burt, 2008; Howden *et al*., 2011a); efforts to reduce nitrate loading in rivers has been recognised in the Nitrates Directive (91/676/EC) and the WFD (Hutchins, 2012), which will be explained in Section 2.2. In the early 1990s, areas of agricultural land in England and Wales were designated as "Nitrate Vulnerable Zones" (NVZs), with the aim to reduce nitrogen transfer; as of 2009, 70% of the land of England and Wales were NVZs (Howden *et al*., 2011a). The Nitrates Directive deals exclusively with pollution resulting from agricultural activities (Jackson *et al*., 2008). However, groundwater and channel water quality responses to nitrate are likely to follow for many years or decades after loads were applied (Howden *et al*., 2011a), making it hard to judge the effectiveness of mitigation measures.

Increases in nitrate may also be due to an increase in population in the green-belt areas, thus more sewage treatment works and more water abstraction, allowing less dilution (Howden *et al*., 2009). Estimates suggest that human activity alone has doubled the rate at which biologically available nitrogen enters the biosphere compared to pre-industrial levels (Burt *et al*., 2009).

Nitrogen in freshwater exists in a variety of forms: nitrite (NO_2), ammonium (NH_4), organic nitrogen and nitrate (NO_3) (Johnes & Burt, 1993). The relative abundance of each form depends on the environmental conditions present in a particular place, and the geochemical processes acting throughout the catchment. Organic nitrogen compounds in soils are insoluble and therefore move little through the catchment; however, they can release ammonium ions, which can be further transformed to nitrate through mineralisation and nitrification (Burt & Trudgill, 1993). Nitrate is highly soluble and therefore easily moved through the catchment with water in runoff and shallow subsurface flow. With an increase in catchment moisture there is a potential for loss of nitrates through denitrification in deeper soils and groundwater, due to increasingly anaerobic conditions (Vinten & Smith 1993; Burt & Trudgill, 1993).

When a catchment has had low moisture for a prolonged period of time, nitrate can build up in the soil, both from plant roots and nitrification in higher levels of oxygen. As a catchment wets up, these soluble nitrate ions will be leached from the soil and carried to the river network (Vinten & Smith, 1993). Freezing and thawing of a catchment can have similar effects on the nitrate concentrations carried to the stream. Freezing will kill soil biomass, providing a large source of matter for decomposition; as thawing takes place, the warmer temperatures will allow for chemical reactions (Vinten & Smith, 1993).

Ammonium is a nitrogenous compound that is toxic in the environment, and is produced during mineralisation from organic nitrogen (Heathwaite, 1993), as well as through dissimilatory reduction of nitrate to ammonium (DRNA) (Korom, 1992). Any detection of ammonium is poisonous, and with repeated levels can be detrimental to the growth and survival of freshwater flora and fauna (Randall & Tsui, 2002). Sustained levels may indicate the lack of nitrification and thus oxygen levels in the streambed.

2.1.4 Phosphate

Transfer of phosphorus to groundwater and thus to rivers are generally assumed to be negligible due to high potential for absorption and retention; however, relatively high concentrations have been observed in some groundwater bodies (Holman *et al*., 2010). In pristine rivers, annual loads of phosphorus are extremely low, since it is not abundantly available from most natural geologies (Mainstone & Parr, 2002).

Phosphorus has a high affinity with particulate matter, and so will often enter the channel through surface run-off of sediment; much higher concentrations are seen when excreta is washed into streams soon after application (Mainstone & Parr, 2002). Once in the river, it is biologically and chemically active, undergoing various transformations between particulate and dissolved phases between the sediment and water column, and biotic and abiotic environment (Mainstone & Parr, 2002). Elevated levels of phosphorus in rivers can increase eutrophication; accelerating growth rates of plant communities, as well as altering species composition through different conditions, it encourages algal growth, thus reducing light and oxygen and therefore reduces root depth of aquatic plants, making them more susceptible to being ripped out during high flows (Mainstone & Parr, 2002).

In the UK, monitored groundwater phosphorus concentrations have so far been compared to the EU drinking water standard (2.2 mg l^{-1}), and have not been identified as a concern (Holman *et al*., 2010). However, if the standard is based around ecological sustainability, this may be more of an issue. Natural levels of phosphorus in UK upland rivers are very low (below 0.01 mg l^{-1}); accumulation within the system may result in higher levels downstream in large rivers, but no more than 0.03 mg l^{-1} (Mainstone & Parr, 2002); this would mean that an elevated concentration of phosphorus in a river would highlight a significant concern.

2.1.5 Other Water Quality Parameters

It is important to analyse various parameters when looking at water quality so that comparisons can be made between them (Razmkhah *et al*., 2010), for example: pH, major anions and cations, conductivity and suspended sediment concentrations. If significantly higher levels of chemicals are observed when compared to previous long-term levels, then this would raise concerns as to where the source of the chemical is and why it is being released into waterways.

Water temperature and dissolved oxygen are both fundamentally important to the biological health of rivers, and therefore to the delivery of the WFD (Williams & Boorman, 2012). Water pollution is created by the breakdown of organic matter, resulting in low oxygen concentrations (Hilton *et al*., 2006); so dissolved oxygen is an important indicator of river health (Abowei, 2010).

2.2 Water Framework Directive (2000/60/EC)

The study of water quality and revival of species such as the freshwater pearl mussel (*M. margaritifera*) is relevant in the UK, as it ties in with the WFD. This is one of the most important pieces of current legislation in the EU (Allan *et al*., 2006); it aims to achieve "good ecological status" of all surface, ground and coastal waters by 2015 (Kallis & Butler, 2001; Peterson *et al*., 2009). Overall, it aims to improve, protect and prevent any further deterioration in water quality across the European Member States (Allan *et al*., 2006). The Framework was passed in June 2000, after 12 years of proposals (Kallis & Butler, 2001), and is regarded as highly ambitious (Peterson *et al*., 2009), by some even as over-ambitious with the given timescale (Hering *et al*., 2010). It is revolutionary, as it allows the member states to take control of their own water bodies, giving them the responsibility to meet the standards (Peterson *et al*., 2009).

The WFD has received a great deal of criticism, not only for its ambitious timescale, but also for its methods of quantitative measurement. "Good status" is defined as "slight deviation from reference conditions" (Hering *et al*., 2010), which means that scientists need to somehow determine these reference conditions for each river basin. It has also been pointed out that aquatic ecosystems that have been degraded over the last century cannot be fully restored in only 15 years (Hering *et al*., 2010). Despite this, the WFD has achieved a great deal in the last 12 years; many sampling and analysis procedures have been standardised across Europe, and extensive monitoring programmes have been implemented. It has also revolutionized water management, by dividing responsibility across hydrological catchments, rather than administrative borders (Hering *et al*., 2010).

In the UK, the EA characterise ecological status of rivers based on reference conditions, following a set of criteria that separates status into high, good, moderate, poor and bad (EA, 2013). The higher the deviation from the reference conditions, the lower the status of the surface water body. Reference conditions combine ecological, biological and chemical data (EA, 2013). The River Esk has been divided into three sections, two in the headlands and the third comprising most of the main channel (EA, 2011). From its source in Westerdale Moor to Baysdale Beck, the water quality is considered by the environment agency (EA) to be of a “moderate” status. From Baysdale beck to Sleddale beck is “good status” and Sleddale Beck to Ruswarp much further downstream is also classified as “good status”. The failure of the upper reach to have “good status” is due to an absence of Salmon and low densities of Brown Trout (EA, 2011), as well as incidences of acidification (Evans *et al*. in press). However, the “good status” of the main channel does not take into account the densities of other species, such as Freshwater Pearl Mussels, of which there are very few.

2.3 Connectivity

Before the 1980s, rivers were viewed separately from their surrounding landscapes, with little thought as to how they may interact. In the last few decades, rivers have been studied using more holistic approaches. In 1980, Vannote *et al*. described the ‘river continuum concept’, looking at a river as a continuous longitudinal gradient, with some lateral connections with the riparian zones. It mainly suggested that variables upstream affected those downstream (Thorp *et al*., 2006). This was developed further by Ward (1989), who recognised an even greater complexity, viewing the river as more than a single entity, but part of a complex set of interactions in a landscape not only laterally and longitudinally, but vertically and temporally too (Thorp *et al*., 2006).

These holistic views have been radically developed in the last few years, most influentially being the concept of connectivity. Connectivity has been recognized for both ecology and hydrology (e.g. Tischendorf & Fahrig, 2000; Bracken & Croke, 2007; Tetzlaff *et al*., 2007; Michaelides & Chappell, 2009) for its importance in understanding the behaviour of drainage basins. The pathways and timings that water takes to reach a channel and flow downstream depend on the connectivity of the catchment, which are heterogeneous in both landscape characteristics and spatio-temporal responses (McDonnell *et al*., 2007). Hydrological connectivity is defined simply as “the passage of water from one part of the landscape to another” (Bracken & Croke, 2007: 1749), but this includes the positions, timings and volumes of water and sediment at any point in time. In ecological terms, it is the “water-mediated transfer of matter, energy and/or organisms within or between elements of the hydrologic cycle” (Pringle, 2001: 981).

Understanding and development of this concept into a quantifiable method, could lead to the possibility of determining sources of nutrients and sediment that are contributing negatively to water quality through diffuse pollution. If an area is too well connected with the channel, then water can carry matter in high volumes at a fast speed, if this becomes a problem then the solution lies in decoupling the landscape from the channel and slowing connections down. However, in reality, a catchment is a ‘black box’; the inputs and the outputs are easily observed, but not so easily the processes in between (Bracken & Croke, 2007). This makes it difficult to judge the effectiveness of measures taken, or where indeed to begin.

It is important to understand that connectivity varies spatially and temporally through a catchment: temporally depending on moisture in the soil, weather conditions and land use, and spatially depending on how coupled the landscape is with the channel, distances to the channel and topography and geology of the landscape. With this in mind it is easier to comprehend how water quality can vary through space and time in an individual channel, and more solid suggestions can be sought as to how to address the problems.

2.4 Hyporheic Zone

Over the last three decades, there has been increasing recognition that the interactions between ground water and surface water in rivers has a greater significance than originally thought (Findlay, 1995; Malcolm *et al.*, 2004). They had traditionally been viewed as separate entities that were in different scientific fields (Brunke & Gonser, 1997; Boulton *et al.*, 1998). The zones of interaction have been coined the “riparian” and “hyporheic” zones (Orghidan, 1959 in White, 1993). The riparian zone is the region adjacent to the channel, whilst the hyporheic zone (HZ) is the deeper region extending below the flowing channel (Figure 2.1) (Wondzell, 2011). Riparian studies are extensive and growing in number (see Burt et al., 2010), however, less is known about the HZ. The HZ is defined by White (1993) as the “saturated interstitial areas beneath the streambed and into to the stream banks that contain some proportion of channel water”. Despite this definition, there is still no single, conceptual framework that provides universal boundaries and methods for researching the area (White, 1993).

The HZ can be considered as a “black box” aspect of hydrology, as it cannot be directly observed and is difficult to sample. For this reason, early research on this area involved the combination of biology and chemistry. Methods involved looking at the distributions

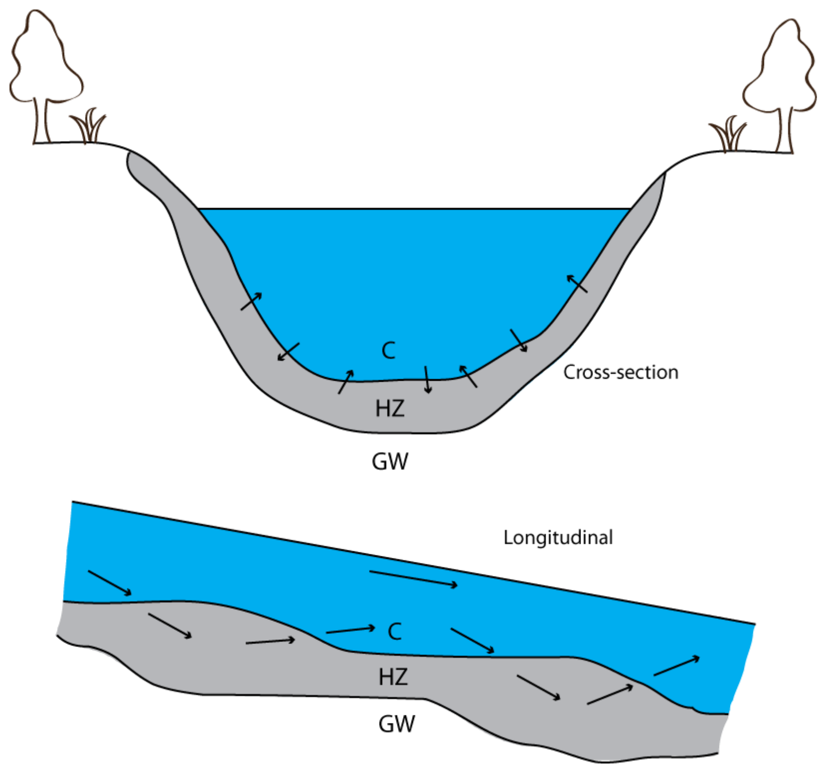


Figure 2.1. A diagram to show the movement of water between the hyporheic zone and the channel.

of groundwater (*hypogean*) and channel water (*epigean*) invertebrates, as well as looking at patterns in solute concentrations (e.g. Orghidan, 1959; Schwoerbel, 1961 in White, 1993; Boulton *et al*., 2010). Williams and Hynes (1976) refined this method and collectively termed the invertebrates from these regions as the “hyporheos”.

Danielopol (1989) questioned the validity of studying the HZ solely through distributions of mobile organisms, so hydrological methods were introduced. Models have been developed to try and explain the hyporheic boundaries; cross-sectional models consider the layout of permeable layers surrounding the channel, whereas longitudinal models present the HZ with relation to stream hydraulics, showing the forces that channel water imparts on the bed at different slopes, depths, directions and porosities (White, 1993) (Figure 2.1). Downwelling of water from the channel is thought to occur at the head of a riffle, when slope and depth decrease, then upwelling of interstitial water occurs at the tail, as depth increases and pressure is released (White, 1993).

There are two main methods for sampling water from the HZ (Scarsbrook & Halliday, 2002), the first being standpipe coring. This involves pushing a hard pipe into the bed that has small, perforated holes around the bottom; water is then slowly withdrawn from the bed through the tube using a vacuum pump (Soulsby *et al*., 2001). Shallow wells are often fitted to the outside of them to ensure no water from the channel mixes with the hyporheic water (Valett *et al*., 1990). The second method is the installation of permanent mini-piezometers beneath the bed, which can be placed at specific depths (Franken *et al*., 2001; Hlavacova *et al*., 2005). However, neither method is totally reliable**,** so developments need to be made (Palmer, 1993).

Much of the literature surrounding hyporheic research has focused on the survival of salmonid eggs in redds constructed in gravel-bed rivers (Soulsby *et al*., 2001). The recognition that water quality in the HZ is quite different to that of the channel has a great deal of significance with relation to the survival of organisms that live there for a portion of their lives, but are not specific to the underground regions. The HZ is a highly dynamic region, with spatially and temporally varying conditions depending on the influence of surface water or groundwater and their specific water quality (Soulsby *et al*., 2001). There is a clearly definable difference between the two water regions; water in a healthy channel is typically clean, well aerated through turbulence, has variable discharge, short residence times and changing physiochemical conditions (Boulton *et al*., 1998). In contrast, groundwater has long residence times in the surrounding catchment, with chemically reducing conditions that can decrease dissolved oxygen levels in the HZ, bring high chemical concentrations and lower the temperature (Soulsby *et al*., 2001; Malcolm *et al*., 2004), which can be highly detrimental to the survival of some organisms.

Human activities can affect the HZ considerably; most river restoration focuses on surface systems and their longitudinal and lateral connections, with the vertical dimension being largely ignored (Ward *et al*., 2001; Boulton, 2007), but a healthy HZ is vital to stream health (Boulton *et al*., 2010). When a population of invertebrates has been thriving in a river for a long period of time, their sudden decline would raise a number of questions with regard to the changing catchment conditions; for example a change in land use, leading to pollution of the waters flowing through the catchment and into the channel through the HZ.

2.5 Freshwater Pearl Mussels

The Freshwater Pearl Mussel is a slow-growing invertebrate that can live for over 100 years, and has a complex life cycle (Bauer, 1992). A single female mussel produces several million larvae per year (Young & Williams, 1983); these larvae, known as glochidia, then attach themselves to the gills of host fish (Trout and Salmon), where they remain for up to 10 months (Bauer, 1992; Geist *et al*., 2006). Host fish are lured to the mussels when the adults expose their mantle flesh, increasing the ease with which glochidia can attach to their gills (Abram, 2011). After this, they drop off into the riverbed as juvenile mussels, where they spend 5 years buried beneath the substrate before maturing into adults (Geist, 2010) (Figure 2.2). This is thought to be the most critical stage in their lives, as they are the most vulnerable to environmental conditions (Skinner *et al*., 2003).

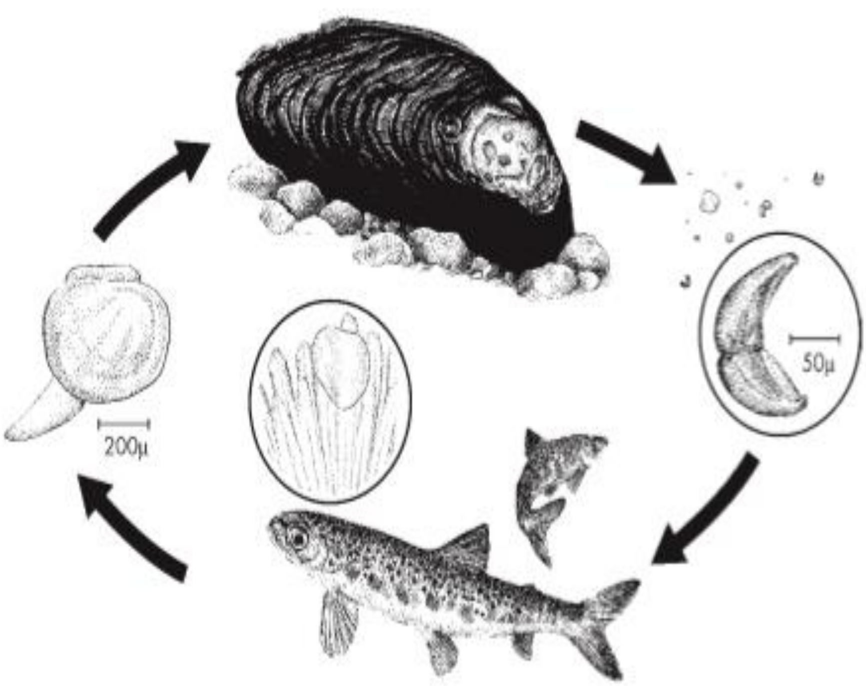


Figure 2.2. The life cycle of a Freshwater Pearl Mussel (*Margaritifera margaritifera*).
From: Skinner *et al*., 2003

Freshwater Pearl Mussels form an important driver in this project. They are long-living invertebrates that can be found in rivers, originally spanning a huge area, from the Arctic and regions in western Russia, through northern Europe to the east coast of North America (Bauer, 1987; Geist *et al*., 2006). Unfortunately, in the last 50-100 years, the previously large populations of pearl mussels have declined dramatically (Hastie *et al*., 2001), and few populations are showing any sign of recovery, implying that they are under severe threat of extinction (Fowles *et al*., 2010). In central Europe, populations have declined by over 95% (Bauer, 1986), and England and Wales only have tiny populations across 30 rivers (Fowles *et al*., 2010).

There are various reasons that are thought to have led to their decline, including: pollution, flow modification, over-exploitation, invasion of exotic species, a decline in fish stocks and habitat degradation (Cosgrove & Hastie, 2001). The need for conservation has been recognized in the UK under The Wildlife and Countryside Act of 1981, where they are listed in Schedule 5. This makes it an offence to knowingly harm, kill or take a mussel from its habitat (Boon *et al*., 1992; Hastie *et al*., 2003). They are also listed in Appendix III of the Bern Convention and Annex V of the European Habitats Directive, as well as being part of the Biodiversity Action Plan in the UK as a "priority species", in need of development and implementation of a survival plan (Hastie *et al*., 2003). For many years the mussels were fished intensively for their pearls; however, it is now illegal in most countries (Cosgrove & Hastie, 2001). This has minimized species exploitation and should no longer be a major problem, despite the long-lasting damage it has already created**.** Captive breeding programmes have been introduced in England and Wales to try and restore populations (Fowles *et al*., 2010), but this is difficult and labour-intensive (Preston *et al*., 2007).

Freshwater Pearl Mussels require clean rivers that are low in nutrients and lime (Geist *et al*., 2006). They also depend on good quality substratum that is relatively stable and has a well aerated flow through it (Geist & Auerswald, 2007). The current main concern for revival of Pearl Mussel populations is that there is a lack of juvenile recruitment (Geist, 2010); whether there is a single reason for this is unknown, but it is recognized that future research should focus on the habitat requirements for juveniles during their post-parasitic phase of life in the substratum (Geist, 2010). It was thought that a reason for mussel population declines was due to fine sedimentation; however, all mussels have internal osmoregulators, enabling them to maintain their water, pH and salinity levels, as well as filtering out sediment (Abram, 2011). It is therefore possible that the problem relates to other aspects of water quality, such as nutrient, conductivity and oxygen levels.

It is important that the species is protected not only for its own sake, but also because it is beneficial to its environment. It is thought that they increase the longevity of their host species (Ziuganov, 2005). When a Salmon has spawned, it stops feeding and undergoes phenoptosis, which is effectively a programmed death. It is a natural way of regulating populations and providing food for invertebrates, which are in turn eaten by salmon juveniles. It is not related to energy loss, but is a biochemical process that produces steroid hormones (Skulachev, 2012). It has been observed that when glochidia are attached to the gills of the Salmon, the process is stopped and their life can be extended by up to 13 years, spawning another 2-6 times. The mussels can regulate the Salmon lifespan to ensure they have a place to grow; in return they reduce the territorial behaviour of Salmon so that many can live in the same area without stress. The hypothalamus is overexcited after spawning, but the symbiosis with glochidia seems to inhibit its activity and support the optimal level of hormones, therefore stopping the triggering of senescence in fish (Ziuganov, 2005). This would mean a higher number of fish stocks in the river, and therefore a greater chance of survival for glochidia.

Research has suggested that a decline in recruitment is probably not due to a lack of population or fertility. Bauer (1987) suggested that fecundity, age and population size had no relationship, and that when a population of Pearl Mussels is low, some mussels morph into the opposite sex, allowing the glochidia to be fertilized. In unpolluted rivers, mortality of Freshwater Pearl Mussels is extremely low, with few natural predators (Bauer, 1987); this suggests that the probable reason for a lack of juvenile mussel recruitment and thus population revival is due to unsuitable habitat conditions due to pollution and human modifications.

Available host fish populations may also be a factor, which varies from river to river (Geist, 2010). Climate change could have major effects on this requirement, as drier, warmer summers could mean earlier reproduction, stopping synchronicity with host fish and reducing chances of reproductive success for mussels. Another issue with warm, dry summers is that suitable habitats may become scarcer, due to warm, shallow waters.

Climate change may also mean a higher frequency of major floods, increasing scour on the substrate. This could also be advantageous, as harmful material and pollution build up would be flushed out, along with excess sediment (Hastie *et al*., 2003). Rising sea level may also affect mussels, as freshwater species cannot survive in saltwater; those living in downstream, estuarine regions of rivers may become immersed in saline water with the onset of higher tides (Hastie *et al*., 2003). Schemes designed to reduce these effects of climate change for humans, such as dams and flood prevention engineering may also affect them (Strayer, 2006).

This project focuses on the water quality of the River Esk in the North York Moors National Park (NYMNP). In 2008, the Esk Pearl Mussel and Salmon Recovery Project was initiated to try and revive and conserve the species. In the Esk itself, it was thought that there are no more than 114 individuals still in the channel, over a distance of 10 km, based on a survey in 1999 (Killeen, 1999; 2009). However, this number comes with a degree of uncertainty, as different numbers have been found in different surveys, the most recent of which in 2008 found 727 live mussels, with an estimation of 1000-1500 overall (NYMNPA, 2008). These mussels were predominantly thought to be an age of 60+, and the lack of juveniles suggests that recruitment may not have taken place for several decades. If nothing is done to help the population, then they will be extinct in the Esk in the next 25 years (NYMNPA, 2008).

Table 2.1. Water quality objectives for freshwater pearl mussels from Oliver (2000) and Bauer (1988). Taken from: Young (2005).

Specific Attribute	**Target (Oliver, 2000)**	**Target (Bauer, 1988)**
Nitrate	<1.0 mg/l	<0.5 mg/l
Phosphate	<0.03 mg/l	<0.03 mg/l
pH	6.5-7.2	N/A
Conductivity	<100 µs/cm	<70 µs/cm
Calcium	<10 mg/l Ca CO_3	2 mg/l
BOD	<1.3 mg/l	1.4mg/l
Dissolved oxygen	90-110% saturation	N/A

Water quality objectives for Freshwater Pearl Mussel habitats have been proposed by Oliver (2000) and Bauer (1988) in Table 2.1. Mussel mortality is found with increasing nitrate values, with natural mortality levels observed only at sites where concentration was above 0.5 mg/l (Young, 2005), and Bauer (1988) found that values of calcium and conductivity were higher in rivers that held only adult mussels. It is known that unnaturally high levels of nutrients, conductivity, phosphates, BOD, metals and pesticides are detrimental, as well as high or low pH. Interstitial water chemistry is of crucial importance to juvenile mussels, but little work has been carried out on the parameters that influence the survival and distribution of them. Careful and realistic studies are urgently needed to set water quality objectives for mussels and to quantify effects of excessive nutrient levels (Young, 2005).

2.5.1 Freshwater Pearl Mussels in the Hyporheic Zone

There have been very few studies on the interstitial water quality of rivers when researching ways to revive populations of freshwater pearl mussels (e.g. Buddenseik *et al*., 1993), and identifying reasons for their initial decline (Young, 2005). Freshwater Pearl Mussel glochidia attach themselves to the gills of host fish during mid to late summer (Bauer, 1992), meaning that they will drop off as juveniles in early to mid summer of the following year. Flows during this time of year are generally expected to be low, and it is during this flow pattern that groundwater is of significant importance to the HZ (Wondzell, 2011) due to a reduction in hydraulic pressure from the channel and changes in depth. This is a crucial period of time for the invertebrates, and if the groundwater is of poor quality, with a reduction in stream flow to push through the gravels, then they are unlikely to survive. It is important therefore to not focus entirely on the quality and behaviour of the channel water, and to divert some attention to the water from the surrounding catchment that is entering the channel and influencing the hyporheos, before mixing with stream flow.

2.6 Summary

The above sections have highlighted the importance of rivers and the problems that are created from degradation of water quality, in particular eutrophication and sedimentation. The largest drivers of water pollution are nitrate, phosphate and fine sediment, which can be increased substantially from natural levels by agricultural fertilisers and animal waste, as well as industrial emissions and urban waste. Advances in catchment science have been aided by the introduction of legislation, the biggest of which being the WFD, which aims to improve the water quality and ecological status of all EU freshwaters by 2015. The connectivity between catchments and rivers has been recognized, particularly with regard to the influence of the zones of interaction: the hyporheic and riparian zones. These zones can heavily influence water quality, particularly in the interstitial waters where there are many aquatic species. Freshwater pearl mussels are an important example, as they are under severe threat of extinction due to habitat degradation. Reasons for this, as well as possible solutions to their survival need to be found.

3. Methodology

3.1 Study Area

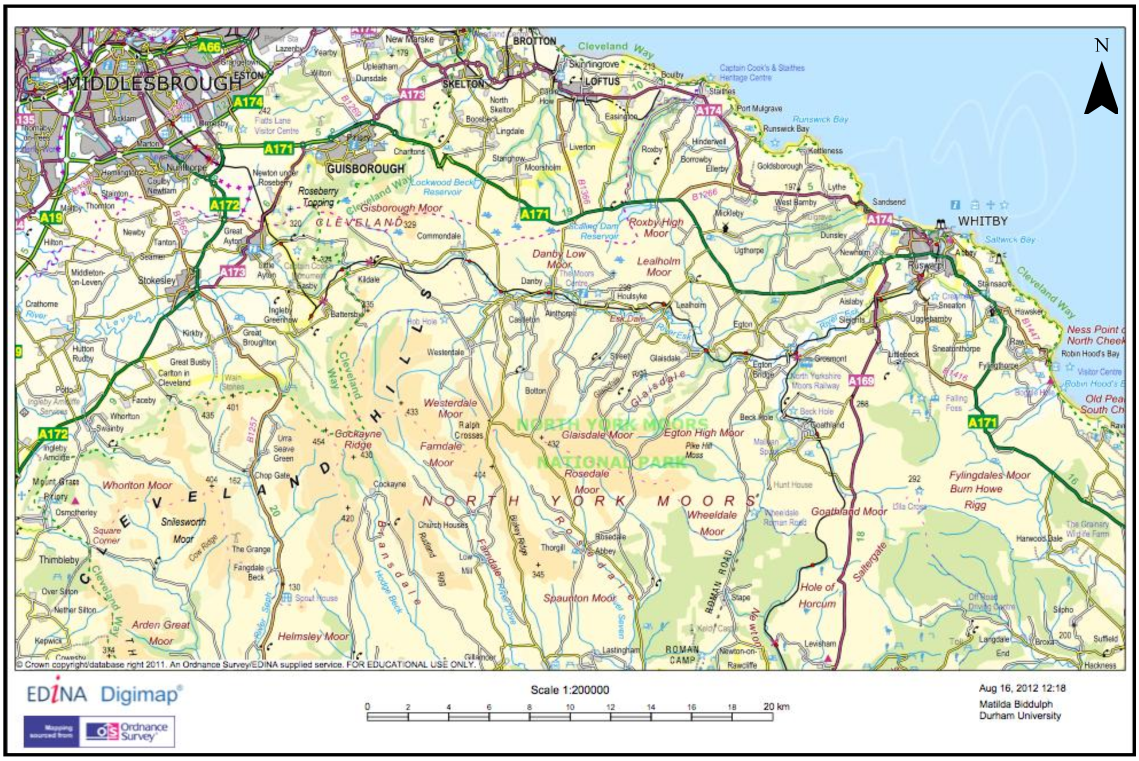


Figure 3.1. A map showing the extent and surrounding area of the River Esk in the North York Moors. Taken from Edina Digimap on August 16th 2012.

This project was based on the River Esk, a small river running through the North York Moors National Park in North Yorkshire (Figure 3.1). The Esk's source is on Westerdale Moor, 42 km from the sea at an altitude of between 300-400 m, before flowing east to meet the North Sea at Whitby, draining an area of 362 km^2 (EA, 2011). The average rainfall in the catchment is 950 mm (EA, 2010), which is a relatively dry climate for an upland environment, contrasting with the Lake District which receives an annual average of >2,000 mm (Hammond, 2005). The low rainfall levels may be explained by the low altitude of the moorland and its easterly location in the rain shadow of the Pennines (Simmons, 1969). The population of the catchment is small at around 83,000 (EA, 2010), with an increase during summer months due to tourism. Less than 5% of the catchment is urban, with many small villages and towns scattered around the river (EA, 2010). The predominant land use along the river is pasture and arable agriculture (EA, 2011).

The North York Moors has the largest area of heather moorland in England, covering 1436 km^2 (Evans *et al*. in press) and is a highly valued catchment for nature conservation. Large areas are designated Special Areas of Conservation (SAC) and Special Protection Areas (SPA), and there are 17 Sites of Special Scientific Interest (SSSI) (EA, 2010). They are developed over sandstones and shales (Simmons, 1969; Innes & Simmons, 2000). The upland plateau of moorland is underlain with Jurassic sandstones, and surrounding areas are generally shales and ironstones, with well-buffered limestones and clays present at lower elevations in the southern parts of the moors. Moorland soils are acidic, occupied by blanket peat, while lower valleys contain more alkaline pelosols, brown earths and stagnogleys (Evans *et al*. in press).

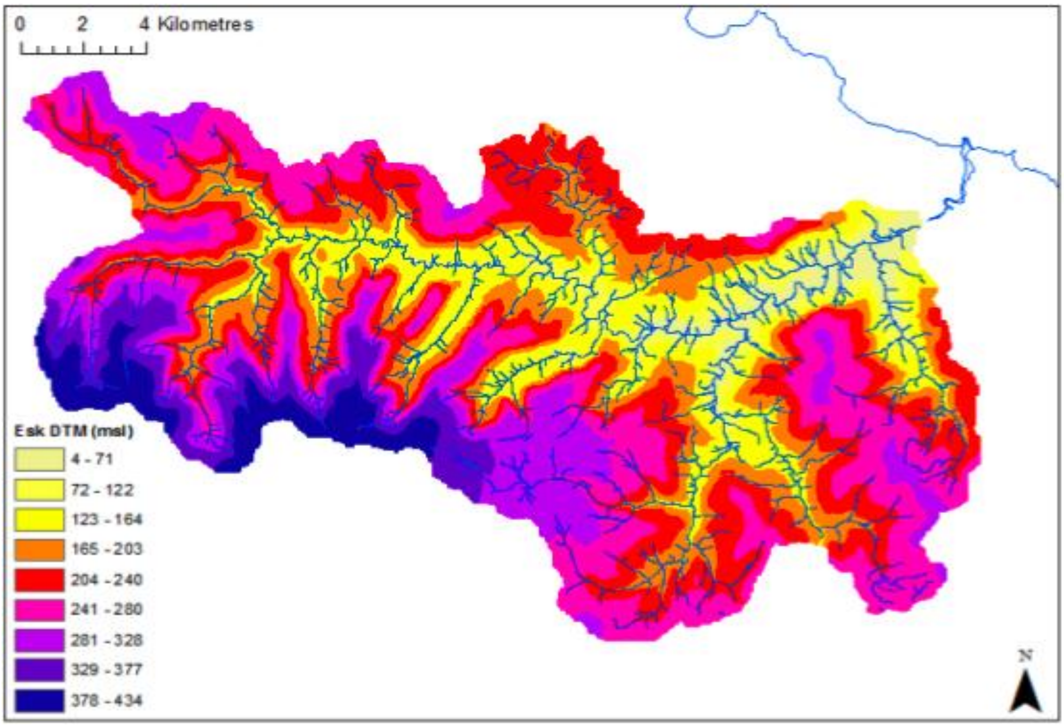


Figure 3.2. A topographical DTM of the River Esk catchment.

The River Esk is a major Salmon and Sea Trout river, with a 237 km length of it protected under the European Freshwater Fish Directive (EA, 2010). It also supports five species listed as threatened or in decline in the UK Biodiversity Action Plan: Otter, Water Vole, Kingfisher, Dipper and Freshwater Pearl Mussel (Evans *et al*. in press). The channel flows through a narrow valley, which often leads to flashy floods after prolonged or heavy rainfall (EA, 2011). Water quality of the river is generally good, according to a 2005 "General Quality Assessment" by the Environment Agency (NYMNPA, 2006), but headwaters suffer from acidification from the peat moorlands, as well as the introduction of nutrients from intermittent farm slurries (EA, 2011). The ecological status of the river is shown in Figure 3.3.

The major problems affecting the Esk are nutrient enrichment from agriculture and acidification from upland peats and acid rain from nearby industry. The moors are close to industrial areas and downwind of several coal-fired power stations, steel works and chemical plants (Evans *et al*. in press); this, combined with the low rainfall levels, brings high concentrations of SO_4^{2-}. Efforts to reduce the overall effects of acidification are being seen in the rapid restoration of vegetation over bare peatland (Hammond, 2005), better wildfire management and improvements to air pollution (Clark *et al*., 2010). Various improvements are being made to the catchment to restore habitats degraded by agriculture, including the fencing off of 27 km of riverbank, to prevent livestock trampling and reduce the introduction of silt into the channel. Foresters are working to reduce silt introduction from forest management practices in the uplands (EA, 2011). Despite this, the protected species on the UK Biodiversity Action Plan are still in decline.

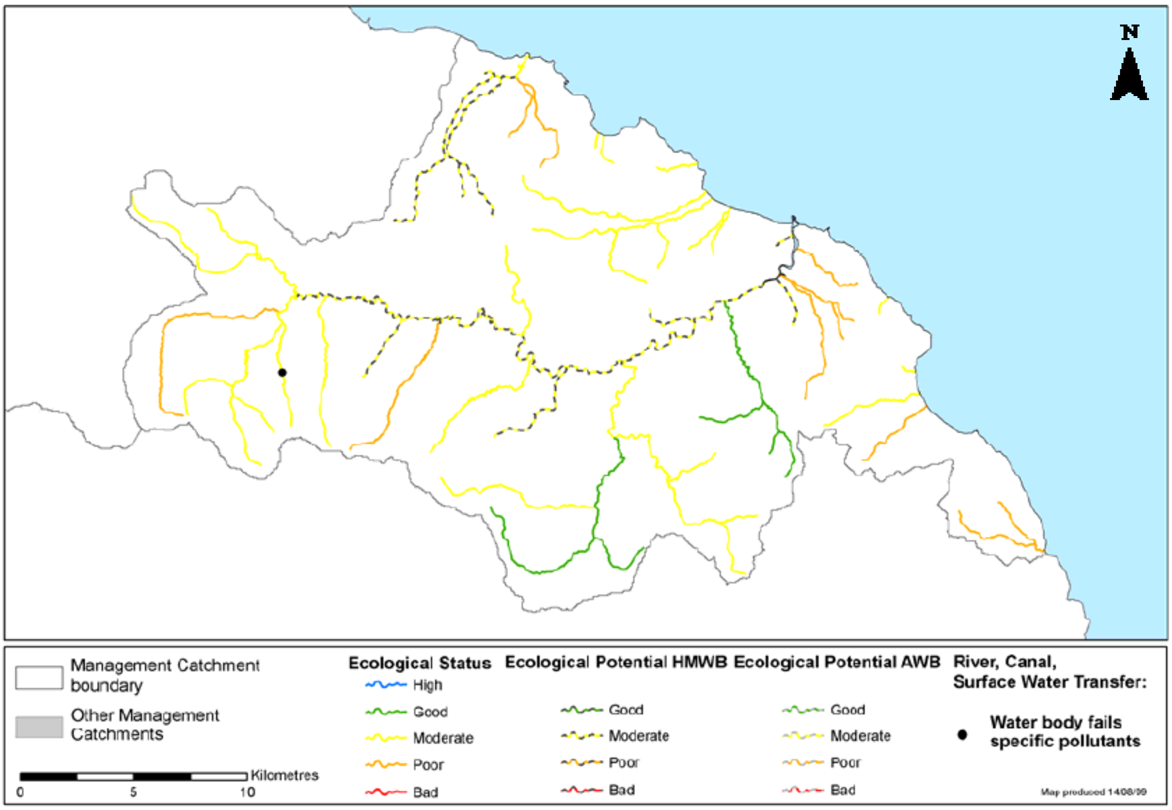


Figure 3.3. A map showing the ecological status of the River Esk after a survey was taken in 2005. Environment Agency, 2009.

3.2 Site Locations

The specific sites that are being studied within the catchment cover a majority of the main channel, from the upland reaches in Westerdale, downstream to Grosmont, including tributaries to the north and south of the channel. There are 19 overall and these are listed in Table 3.1 below, and shown on a map in Figure 3.4.

Table 3.1. Showing the 19 sampling sites. Site type denotes what form of sampling was done. Temporal being the location of the autosamplers to measure temporal changes in water quality. HZ being a site where there is also equipment set up to measure from the hyporheic zone.

Site Number	Site Name	Esk, Headwater Tributary or Tributary	Site Type
1	Lower Sleddale Beck	Headwater Tributary	Spatial, HZ
2	Upper Sleddale Beck	Headwater Tributary	Spatial
3	Baysdale Beck	Headwater Tributary	Spatial
4	Upper Esk	Esk	Spatial, HZ
5	Tower Beck	Headwater Tributary	Spatial, HZ
6	Castleton	Esk	Spatial, HZ
7	Danby Beck	Tributary	Spatial, HZ
8	Upper Toad Beck	Tributary	Spatial
9	Lower Toad Beck	Tributary	Spatial
10	Danby	Esk	Temporal, Spatial, HZ
11	Little Fryup Beck	Tributary	Spatial
12	Houlsyke	Esk	Spatial, HZ
13	Lower Great Fryup Beck	Tributary	Spatial
14	Upper Great Fryup Beck	Tributary	Spatial
15	Lealholm	Esk	Temporal, Spatial, HZ
16	Upper Stonegate Beck	Tributary	Spatial
17	Lower Stonegate Beck	Tributary	Spatial
18	Egton Bridge	Esk	Spatial
19	Grosmont	Esk	Temporal, Spatial

The sites along the Esk itself were chosen to gain a representative view of the changes along the channel. The downstream limit was taken to be at Grosmont, as this is where the final autosampler was set up. The downstream limit for FWPM is thought to be Glaisdale (NYMNPA, 2008), which is why there are more sites upstream of this than downstream. The tributary samples were taken predominantly from the confluence with the main channel; this was to ensure that the water chemistry entering the Esk was not altered by smaller tributaries feeding into the main tributary, that sampling did not pick up. Some tributaries had two sites, upper and lower; to see if any major differences occurred in their sub-catchments.

Table 3.2. Showing the dates of spatial surveys with parameters measured and weather conditions for each.

Spatial Survey	Weather	pH	Cond.	DO	SSC	Redox	Nutrients	HZ
23/01	Sunny, dry	✓	✓	-	✓	-	✓	-
22/02	Misty, windy, wet	✓	✓	✓	✓	-	✓	-
11/03	Sunny, windy, dry	-	-	-	-	-	-	✓
20/03	Sunny, windy, dry	✓	✓	✓	✓	-	✓	✓
13/04 (partial)	Dry, previous rain	✓	✓	✓	✓	-	✓	✓
25/04	Wet	✓	✓	✓	✓	✓	✓	✓
23/05	Dry	✓	✓	✓	✓	✓	✓	✓
25/06	Dry, previous rain, Flood	✓	✓	✓	✓	✓	✓	-

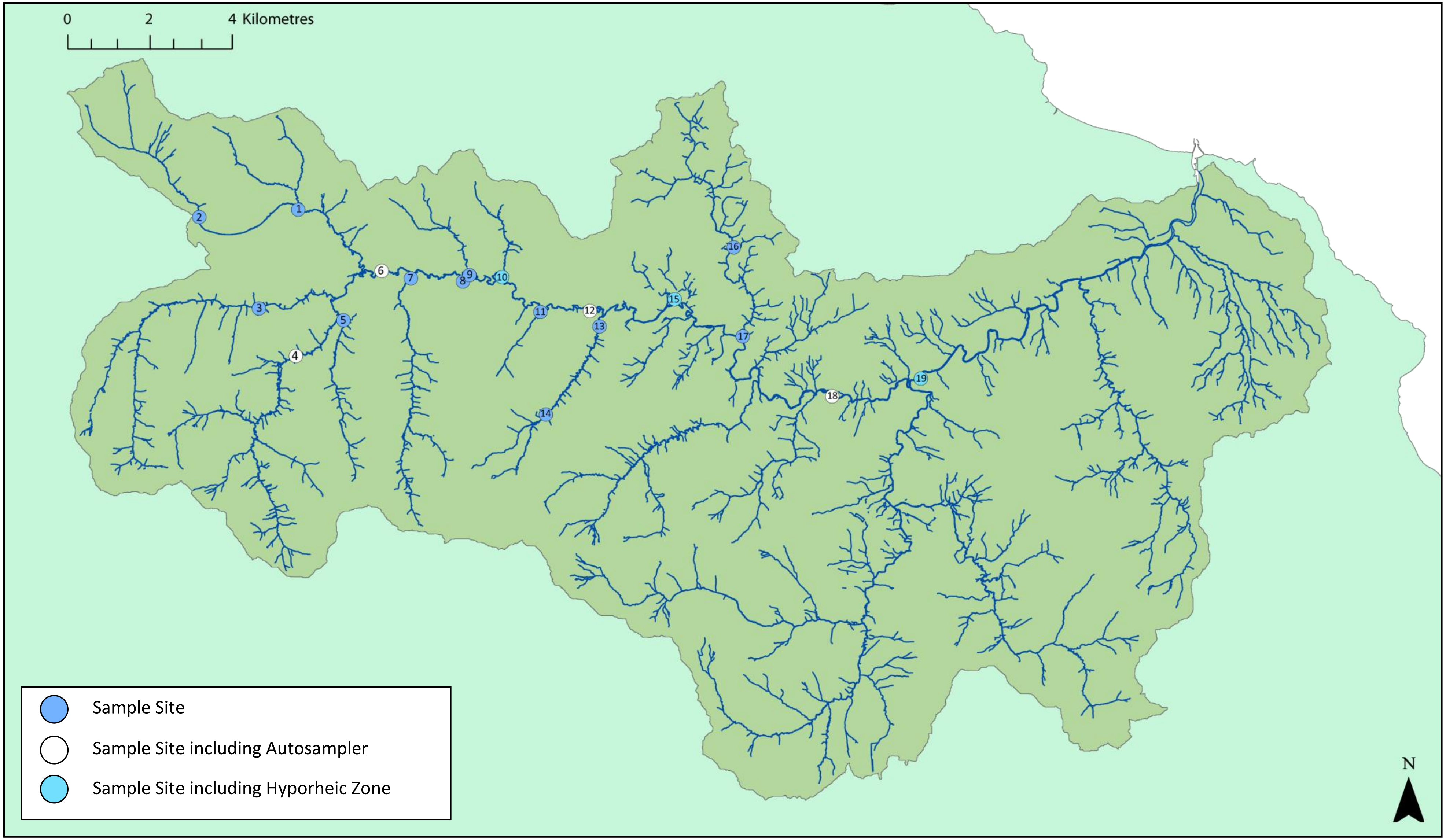


Figure 3.4. A map of the River Esk catchment, showing the 19 sampling sites for this project. See Table 3.1 for site names.

3.3 Methods

Methods for this project are divided between field methods and laboratory methods. There are three separate methods within the field and three in the laboratories.

3.3.1 Monthly Spatial Survey

A spatial survey was taken monthly between January 2012 and July 2012 to gain a detailed seasonal picture of the general water chemistry and suspended sediment concentration. Over a period of approximately six hours, 19 samples of river water were taken extending from the upper headwaters, downstream to Grosmont (Table 3.1; Figure 3.4). There are 7 samples from the main channel, and 12 samples from the major tributaries feeding into it. Samples were taken with a 1-litre bottle in relatively fast flowing water. Bottles were rinsed in the channel beforehand, and taken standing downstream of the sample collection point. Care was taken not to disturb the bed sediments, which could give an inaccurate representation of the channel water. These samples were then taken back to the laboratories in Durham the same day and stored in the fridge to prevent bacterial growth.

Simultaneously a YSI multi-parameter probe was used to measure pH, Electrical Conductivity (µS/cm), Dissolved Oxygen (mg l^{-1}), Temperature (^{o}C) and Redox (mV). The probe was held in the channel until all readings had stabilised, which took approximately 5 minutes. All parameters were calibrated in the laboratory prior to use. A cage was fitted around the probes so that it could be used in the rougher, faster-flowing areas rather than just in the slow flowing pools. Both the suspended sediment and water chemistry were later analysed relative to the river stage of the Esk, to see if variations in discharge effect quality.

3.3.2 High-Frequency Sampling

Monthly monitoring of the river channel was used to give a 6-month seasonal dataset across the entire catchment; however, it was also important to look at how the river responded to varying parameters and different time scales.

Sites 10, 15 and 19 were selected as permanent sites along the Esk (Table 3.1; Figure 3.4). These sites were chosen because they cover the upstream and downstream extent of the current population of Freshwater Pearl Mussels, as well as Lealholm being an area with a large number of mussels (Killeen, 2006). These three sites were also part of the monthly spatial survey. Automatic samplers (ISCO 6712) were installed to obtain samples at a higher frequency. These samplers can be programmed to sample a specified volume, at a specified time or time interval, or at a specified river level; this is useful as it can show the differing characteristics of the river.

This method was followed as the automatic sampling stations are readily available, and it is the easiest way of obtaining samples over 24-hours or longer periods of time, without being on site. For this investigation, the autosamplers were used in a variety of ways. Firstly to measure water quality during stormflow; when the river level rose to a specified height, it touched a float switch, which triggered the sampler to take 500 ml of water from the channel once an hour for 24 hours. Secondly, it was used to measure baseflow, but instead of using a float sensor, sampling began at a specified time. Baseflow was also taken with a time interval of 12 hours, so that a fortnightly dataset was created. These samples were taken to the labs to be analysed for SSC, anions and cations as described below, as well as measuring the pH and Conductivity.

River stage data, provided by the Environment Agency at Briggswath, Lealholm and Castleton, were used alongside the sample data, to gain an insight into the variations with discharge. The EA records the stage at these locations every 15 minutes, and so a detailed picture of the changes in stage has been collected.

3.3.3 Sampling from the Hyporheic Zone

Rivers with Salmon and Sea Trout spawning are generally of a good quality (Malcolm *et al*., 2004); however, as mentioned previously, the chemistry of the HZ may be extremely different to the surface water in the channel. This is due to the permanent lack of light and minimal exchange of aerated flow (Boulton *et al*., 1998; Malcolm *et al*., 2004). It also varies spatially with changes in channel morphology at varying scales, as well as temporally due to changes in water depths and water in the catchment (Malcolm *et al.*, 2004). For these reasons it is important to study this zone in a catchment, where prime habitats may have been degraded and unable to sustain suitable conditions for aquatic organisms.

Figure 3.5. Equipment installed in the riverbed to sample from the hyporheic zone.

Six sites were selected for investigating the HZ of the River Esk (Table 3.1): 1, 4, 5, 6, 7, 10, 12 and 15. Sites 1 to 7 upstream do not have any mussels in the area, but it is important to look at the quality of the water entering the main channel where they are found. Sites 10, 12 and 15 are areas where mussels are known to be. A comparison can be made between the areas to see if there is a marked difference, as well as a comparison between channel water directly above the HZ and that below the bed. The samplers were all placed at the tail end of riffles, as this is where there will be the most influence from the HZ, as well as being a more preferable habitat for mussels than the deeper, slow-flowing pools. The head of a riffle will likely have a higher concentration of channel water in it, due to increases in hydraulic pressure forcing it through; by the tail of the riffle, upwelling from beneath the bed should be a higher influencing process where pressure is lower (Wondzell, 2006).

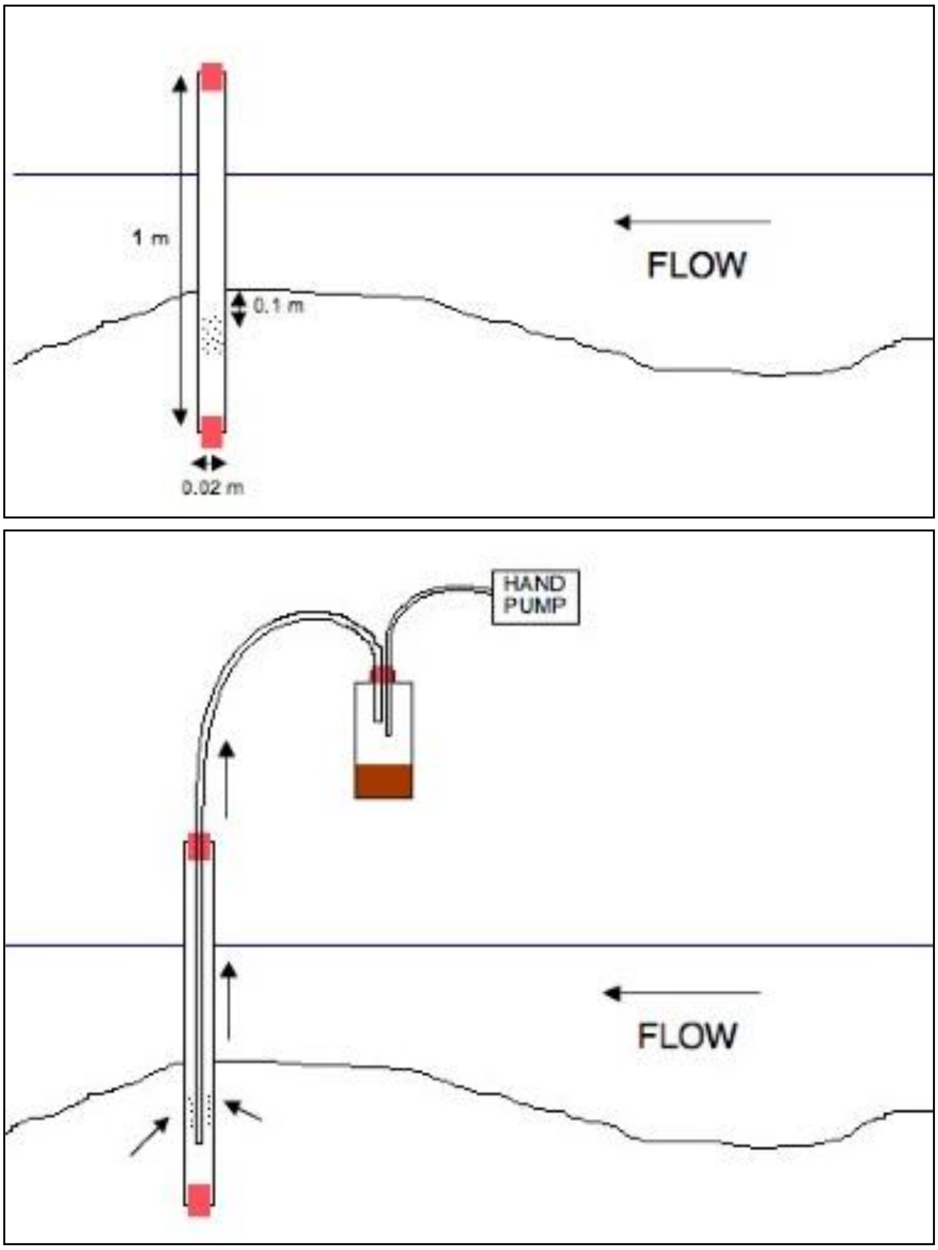


Figure 3.6. Equipment for sampling the hyporheic zone. Above shows the equipment when left alone in the channel. Below it shows the sampling procedure. The hand pump creates a vacuum and pulls water from beneath the bed, through the perforations and up the tube into the bottle.

Sampling equipment was designed and created that was relatively similar to those described in Soulsby *et al*. (2001). Wells were made from hard plastic tubes that are 1 m in length and 0.2 cm in diameter. Small, perforated holes were drilled around the circumference over a length of 20 cm, so that once placed in the riverbed they represent a depth from 10 cm below the bed to 30 cm deep. Augers were used to core out a small area of bed so that the tube could be slotted in, a bung was placed on the bottom of the tube so that it would not infill with sediment. When in place the equipment was left to settle for 2 weeks before samples were taken, so that natural conditions could be restored; any channel water that entered the tube during installation was pumped out until empty. When not in use, a bung is placed in the top, so that channel water cannot enter the tube. During sampling, a bung is put in place with a tube running through it down to the bottom of the well. This tube extends to a litre bottle, which is also attached to a vacuum pump (Figure 3.6). The vacuum pulls water through the perforations, up the tube and into the bottle. This process is repeated to ensure that the water being pulled up is actually from the HZ, and not residual channel water. This water is then tested for pH, DO, Conductivity and temperature, before being taken to the lab for anion and cation analysis.

3.3.4 Laboratory Analysis

All channel samples were stored in the fridge as soon as possible to reduce bacterial activity. They were also analysed as soon as possible after collection, usually the next day. Both spatial and temporal samples were taken to the lab to be tested for Suspended Sediment Concentration (SSC). Glass micro-fibre filter papers with a pore size of 1.2 µm were pre-weighed, before the samples were filtered through it into a Buchner flask using a vacuum pump. These filter papers were then dried at 105^{o}C overnight, before being cooled in a desiccator then re-weighed. The difference in weight was used with the sample volume to calculate the SSC in mg l^{-1}. The SSC will show the difference in concentrations with varying river levels and areas in the catchment, and can indicate the fine sediment levels in the channel.

From these filtered samplers, anion and cation analysis was carried out, this shows the different levels of chemicals in the water. If chemical levels are high, this can indicate bad water quality, which highlight areas in the catchment that need managing so that improvements can be made. Analysis was done by filtering 10 ml of the sample through a 0.2 µm pore size syringe filter; it is important that the pore size is this small, as bacteria are around 1.0 µm and can affect the overall water chemistry, as well as causing problems with the Dionex machine. The Dionex system measures anions using a DX500 operating system, and cations using an ICS 1000 system. The system monitors Fluoride, Chloride, Nitrate, Nitrite, Bromide, Sulphate, Phosphate, Sodium, Ammonium, Potassium, Magnesium and Calcium. Detection limits (Table 3.3) show the lower limits of concentrations that will show up on the system. Water samples from the autosamplers are also tested for pH and conductivity using pre-calibrated probes.

3.4 Summary

Table 3.3. Detection limits of chemical parameters for the Dionex system. Supressed conductivity detection is used. * means UV/vis detection has been used at 210 nm.

Anion/Cation	**Detection Limit (mg l^{-1})**
Fluoride (F)	0.01
Chloride (Cl)	0.03
Nitrite (N)	0.01
Bromide (Br)	0.02
Nitrate (N)	0.02
Phosphate (P)	0.02
Sulphate (S)	0.02
Nitrite (N)*	0.02
Nitrate (N)*	0.04
Sodium (Na)	0.05
Ammonium (NH_4^+)	0.02
Potassium (K)	0.01
Magnesium (Mg)	0.01
Calcium (Ca)	0.05

This chapter outlines the study area and specific site locations that are being used for this study, describing climate as well as topographical and geological characteristics of the region. It then describes the field and laboratory methods carried out in order to obtain relevant data for analysis. Field methods include a monthly spatial survey, higher frequency sampling at three sites, and sampling from the HZ; these are then analysed for specific parameters in the laboratory.

4. Changes in water quality during baseflow and stormflow

This chapter explores the differences in water quality from samples taken when the catchment was in two very different states of wetness. On 23/05/12 the river had very low flows and low antecedent moisture; contrastingly, on 25/06/12 the river levels were high. The high flows sampled were at the recessional stage of the flood after a very sharp peak during the previous night, rising by 0.85 m in 8 hours. There are 19 sites (see Figure 3.5 and Table 3.1), however, lower Stonegate Beck could not be sampled on 25/06/12 due to issues with safety and access. The smaller circles on the maps in this chapter depict water quality during low flows, whilst the larger circles represent the higher flow. Table 4.1 gives a summary of Esk characteristics alongside other river studies, for a comparison in nutrient levels. Table 4.2 gives a summary of the low, mean and high concentrations, observed over 6 monthly spatial surveys. The flood means are the averages taken from the high-resolution stormflow data from autosamplers at Danby, Lealholm and Grosmont. Only parameters that show values above the detection limits or significant variations are discussed here.

4.1 Spatial Maps

4.1.1 SSC

Figure 4.1 shows the SSC. The suspended sediment around the catchment is low during baseflow, all below 10 mg l^{-1}. It is likely that little or no sediment is being introduced to the channel from overland flow, with the principal sources of water being from groundwater. Low flows mean lower velocities of water in the channel, and therefore less energy to entrain and maintain sediment in suspension.

Sampling in higher flows displays a variation across the catchment. Measurements were taken on the falling limb of the flood hydrograph, so it is therefore possible that much of the available sediment in the catchment had been exhausted, and already conveyed downstream. Figure 4.1 shows that headwater tributaries still have very low concentrations, but a clear increase is seen with distance down the main channel, with the higher concentrations found at Egton Bridge and Grosmont. Egton Bridge and

Table 4.1. Mean water quality values for different river catchments. For the Esk, FM: stormflow average, M: catchment average.

		Concentration (mg l^{-1})											Catchment Information		
		NO_3	NH_4	P	Fl	Cl	S	Na	Mg	Ca	K	pH	Type	Area (km^2)	Data
1. River Esk (This study)	FM	0.65	0.04	0.01	0.09	14.35	3.61	9.90	2.23	7.68	1.53	7.0	Moorland and lowland agriculture.	362	FM: Monthly sampling of 48-hour storm events December 2011-June 2012. M: mean values of catchment over 6 monthly samples.
	M	1.07	0.01	n.a.	0.12	18.27	5.17	12.13	3.77	13.28	1.61	7.1			
2. River Dye (Reid *et al*., 1981)		0.19	0.13	0.01	-	6.12	2.25	5.18	1.14	3.09	0.44	6.5	Granite and moorland	41.2	Mean composition of weekly samples over a year (1977-1978)
3. Newmills Burn (Soulsby *et al*., 2001)		4.93	0.09	0.02	-	39.58	27.83	20.73	-	15.97	2.52	7.3	Small tributary of River Don	12	Mean chemistry between January and June 1999
4. River Taw (Jarvie *et al*., 2008)		4.00	0.07	-	-	14.80	12.70	8.70	2.20	8.30	1.10	7.1	Acidic upland, weather granite and lowland clay	71	Weekly spot sampling at Pecketsford Bridge between 1st September 2003 and 1st April 2005.
5. River Kennet (Neal *et al*., 2008)		8.48	0.03	-	0.10	20.90	26.30	7.17	1.83	-	1.73	7.5	Major tributary of the Thames. Chalk and clays.	118	Weekly sampling September 2003-October 2005 from Clatford.
6. River Frome (Bowes *et al*., 2011)		5.90	0.06	-	-	25.00	19.00	13.3	3.20	93.00	2.20	8.1	Agricultural, underlain with chalk.	414	Sampling between 2000-2009
7. River Eden (Murphy, 2012)		8.66	0.05	0.05	-	-	-	-	-	-	-	-	Rural sub-catchment	12.5	Mean of 15 minute concentration data between 2nd February to 21st May 2012.
8. River Wye (Jarvie *et al*., 2003)		4.77	0.08	0.15	-	-	-	-	-	-	-	-	Heterogeneous catchment	4136	EA data between 1991 and 2000.

Grosmont flow through some very steep valley sides, with tarmac roads and urban areas; any runoff will entrain available sediment and carry it easily to the channel. There is also farmland in the area, which would provide loose material in the fields. It may be that the tributaries have low suspended sediment concentration because they do not have sufficient velocities.

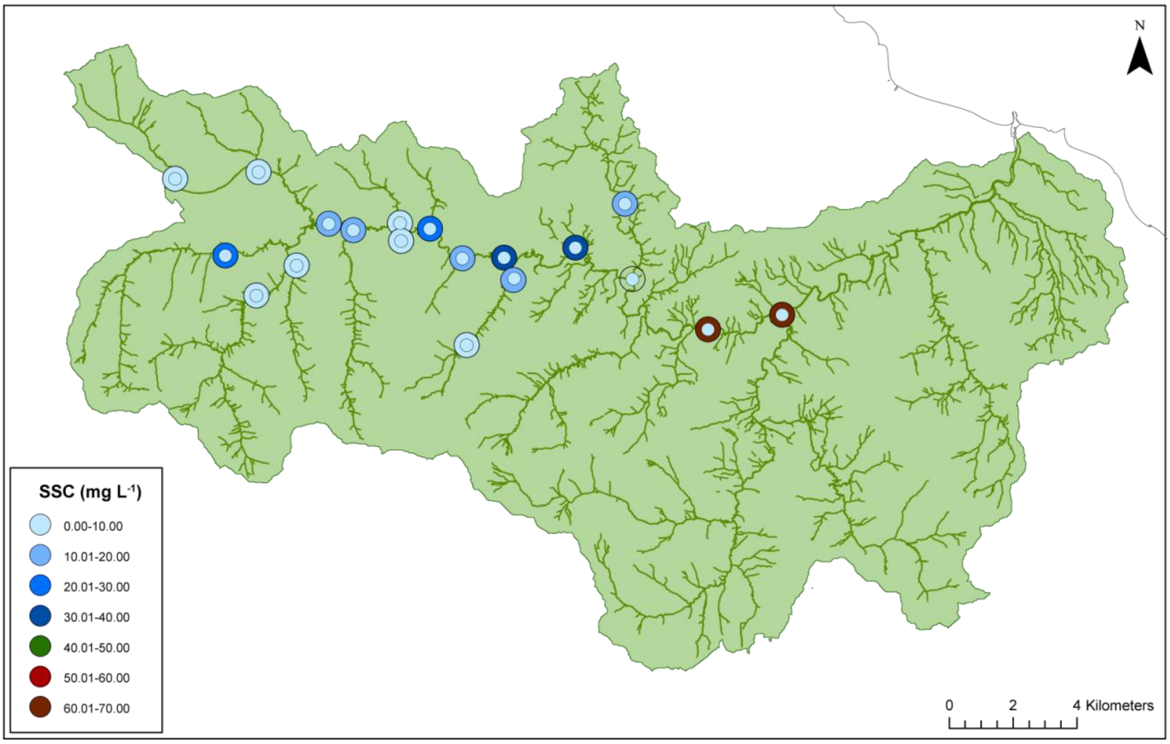


Figure 4.1. A map showing the suspended sediment concentration of the River Esk at 19 sites on 23/05 during baseflow (smaller) and 25/06 during high flow (larger). The large circle with no colour fill is a site with no data for that storm, and applies to all maps in this section.

4.1.2 Dissolved Oxygen and Redox

During baseflow, dissolved oxygen generally increased downstream, with concentrations of 10.71 mg l^{-1} in Baysdale Beck and 12.55 mg l^{-1} at Grosmont (Figure 4.2). In higher flows most sites were between 11.01 and 12.00 mg l^{-1}, with the exception of upper Toad Beck with only 9.00 mg l^{-1}. Sites downstream such as Egton Bridge and Grosmont decreased in concentration (Figure 4.2). Oxygen content varies with temperature, salinity, turbulence, atmospheric pressure and rates of photosynthesis (Chapman & Kimstach, 1996). Concentrations in unpolluted streams are usually around 10 mg l^{-1}, but anything below 5 mg l^{-1} can be detrimental to aquatic life (Chapman & Kimstach, 1996). Therefore these values of dissolved oxygen are not of concern to the aquatic life within the Esk.

Table 4.2. showing the low, mean, flood mean and high values found for the River Esk in this study. High sites are those with consistently high values that may be a cause for concern. Storm conc. Denotes the behaviour of the parameter with increase in flow.

	Low	Mean	Flood Mean	High	High Sites	Storm Conc.	Notes
SSC ($mg\ l^{-1}$)	0.31	7.50	-	76.36	-	Increase	Increases downstream, low headwaters.
Redox (mV)	2.3	89.4	-	254.6	DB	Increase	Extremely low in baseflow at DB and LTB
Dissolved Oxygen ($mg\ l^{-1}$)	9.00	13.02	-	16.30	UTB	No significant change	UTB is consistently lower.
Cond. (µS)	38.0	133.0	-	324.0	TB, LFB	Decrease	-
pH	4.4	7.1	7.0	8.2	-	Decrease	A low of 4.4 at BB during flood
Magnesium ($mg\ l^{-1}$)	1.18	3.77	2.23	8.64	TB, LFB, SB	Decrease	-
Chloride ($mg\ l^{-1}$)	5.92	18.27	14.35	37.92	DB, TB, LFB, SB	Decrease	-
Sodium ($mg\ l^{-1}$)	5.21	12.13	9.90	20.19	TB, LFB, SB	Decrease	-
Sulphate ($mg\ l^{-1}$)	2.11	5.17	3.61	10.71	DB, TB, LFB, GFB	Decrease	Low headwater concentrations
Fluoride ($mg\ l^{-1}$)	0.03	0.12	0.09	0.33	TB, LFB, GFB	Decrease	-
Nitrate ($mg\ l^{-1}$)	0.05	1.07	0.65	3.76	TB, LFB	Decrease	Low headwater concentrations
Calcium ($mg\ l^{-1}$)	2.45	13.28	7.68	34.51	TB, LFB, SB	Decrease	-
Ammonium ($mg\ l^{-1}$)	n.a.	0.01	0.04	0.33	DB	Increase	-
Potassium ($mg\ l^{-1}$)	0.41	1.61	1.53	3.87	DB, TB, LFB	Variation	TB, LFB, uGFB increase. The rest decrease or stay the same.

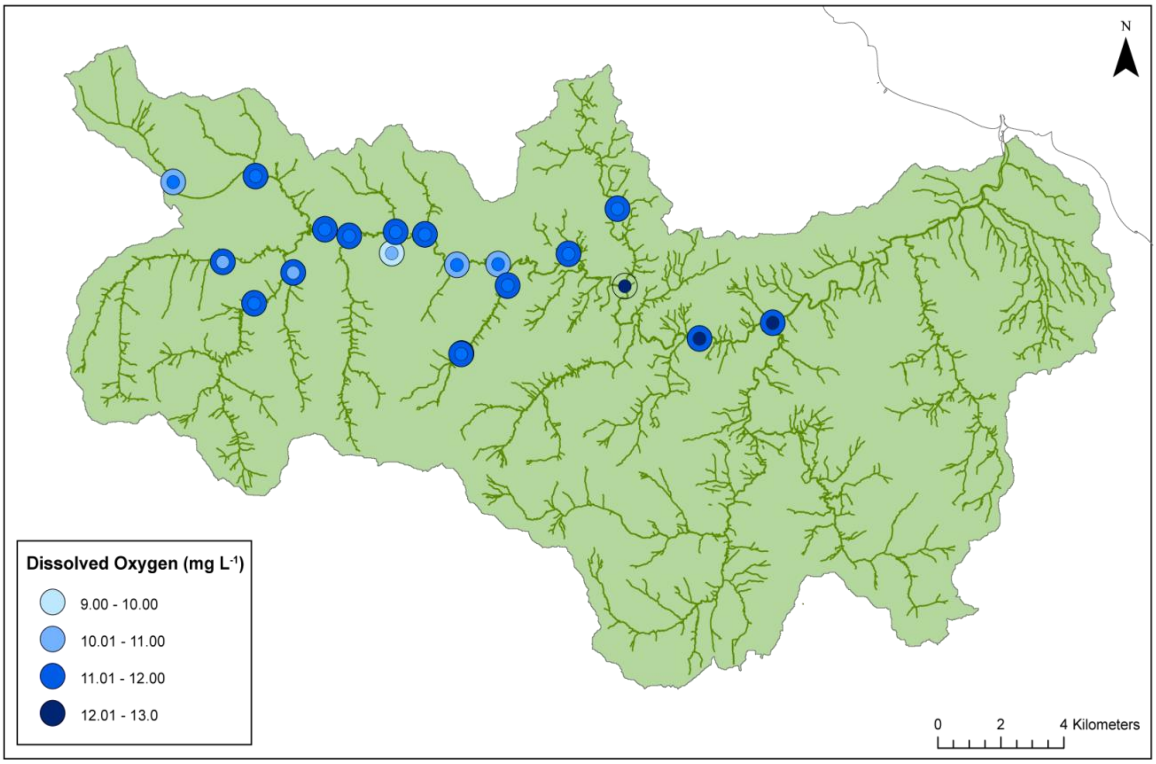


Figure 4.2. A map showing the dissolved oxygen concentration of the River Esk at 19 sites on 23/05 during baseflow (smaller) and 25/06 during high flow (larger).

During baseflow, redox remained below 80.00 mV but above 0 mV (Figure 4.3). During stormflow, the redox increased in all sites, with the highest readings found in upper Sleddale Beck with 232.5 mV, Baysdale Beck with 254.6 mV, lower Toad Beck with 252.2 mV and Lealholm with 236.4 mV. The site that did not substantially increase was Little Fryup Beck. A low or negative value of redox potential means that there is a greater potential for reducing and oxidising conditions in the water, potentially reducing levels of dissolved oxygen and creating more anoxic conditions; an unfavourable habitat condition. As dissolved oxygen increases, so too does the value of redox. In natural waters, values can range from - 500 mV to + 700 mV, and in waters containing dissolved oxygen it usually ranges from + 100 to + 500 mV (Chapman & Kimstach, 1996). A high potential for reduction in the channel could lead to the formation of toxic compounds such as ammonia, which is poisonous to aquatic life.

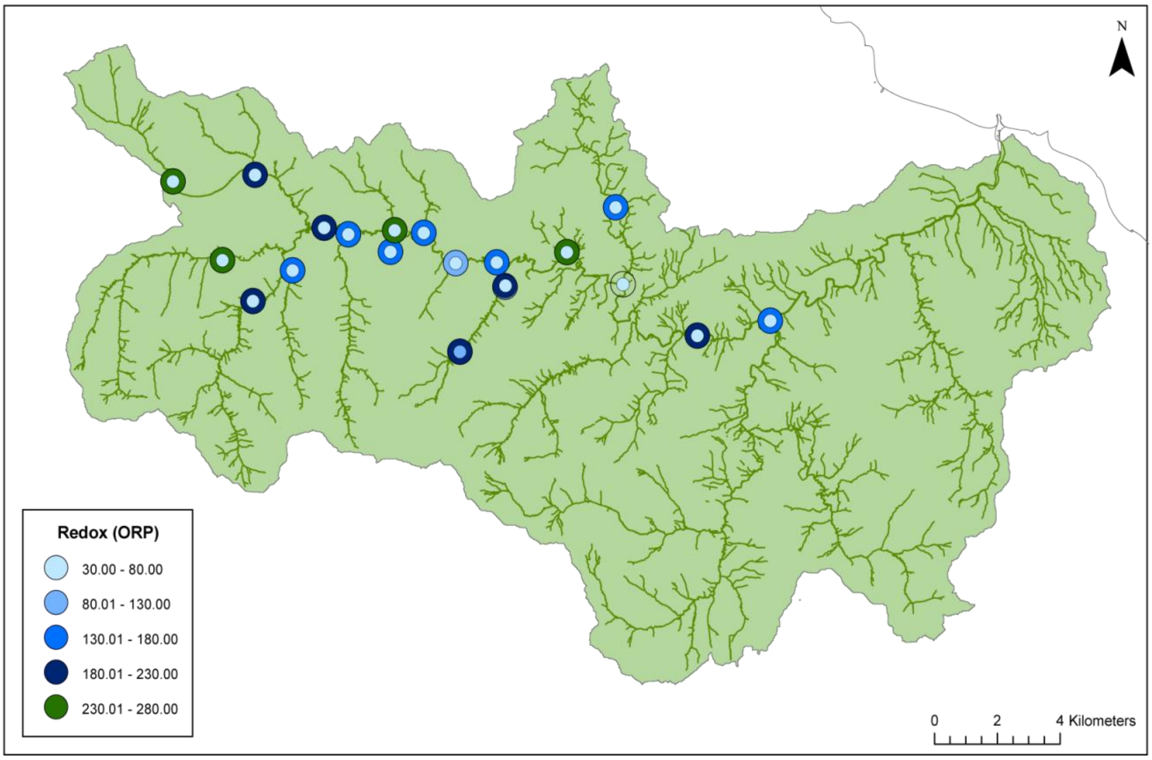


Figure 4.3. A map showing the redox potential of the River Esk at 19 sites on 23/05 during baseflow (smaller) and 25/06 during high flow (larger).

4.1.3 Conductivity

During baseflow the headwater conductivity was generally between 60.0 µS and 100.0 µS (Figure 4.4). Conductivity increased gradually with distance downstream, reaching 137.0 µS at Grosmont. The tributaries had higher conductivity, with Toad Beck at 215.0 µS, Little Fryup Beck at 185.0 µS and Lower Stonegate Beck at 190.0 µS. Great Fryup Beck also had relatively high conductivity with 142.0 µS at the lower site. During high flows the conductivity in the headwaters decreased to below 60.0 µS, a pattern followed by all the sites except Toad Beck, which remained high (Figure 4.4).

Conductivity in freshwaters is usually between 10 to 1,000 µS cm^{-1} (Chapman & Kimstach, 1996), and these values are at the lower end of this range, indicating that the Esk is relatively solute-poor. It may be that conductivity increased during the onset of the higher flows, but the volume of dissolved material in the water had been somewhat exhausted by this time. It may also be that the water had diluted the conductivity. Toad Beck is a very small, slow flowing tributary with a high amount of vegetation and fine sediment; it is surrounded by roads and farmland so would be expected to have a high volume of solutes carried towards it during runoff.

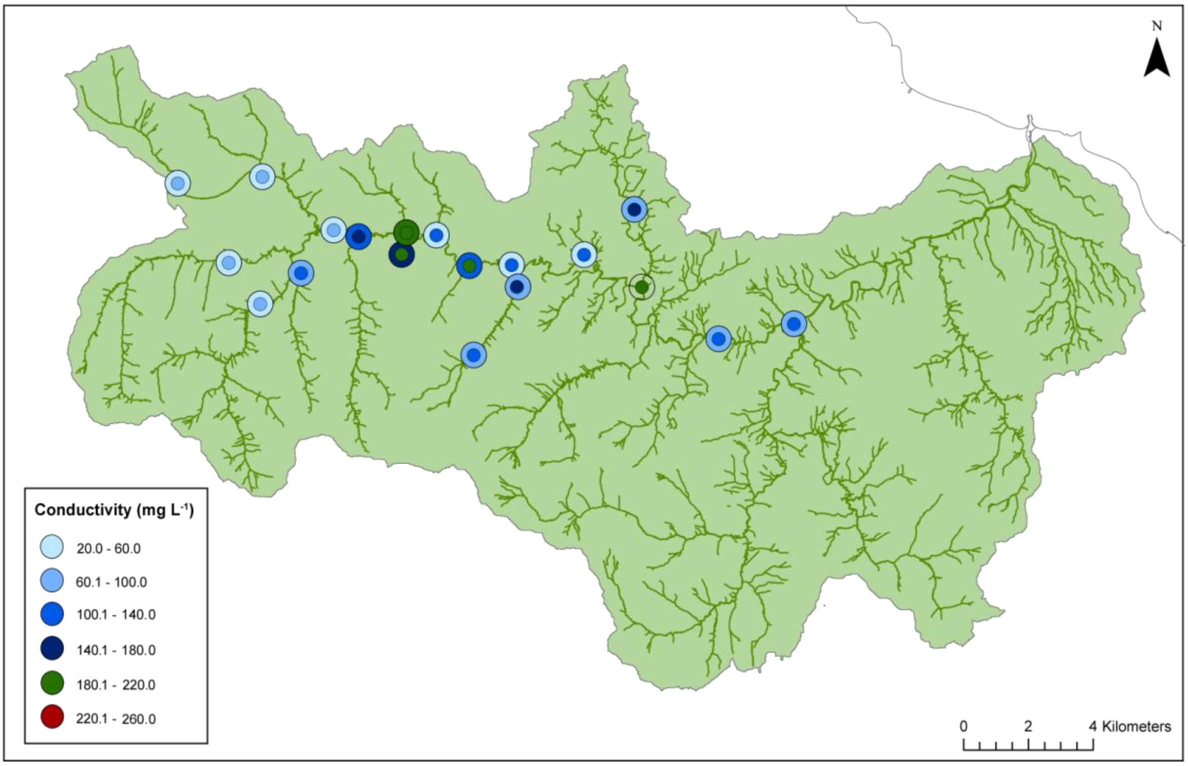


Figure 4.4. A map showing the conductivity of the River Esk at 19 sites on 23/05 during baseflow (smaller) and 25/06 during high flow (larger).

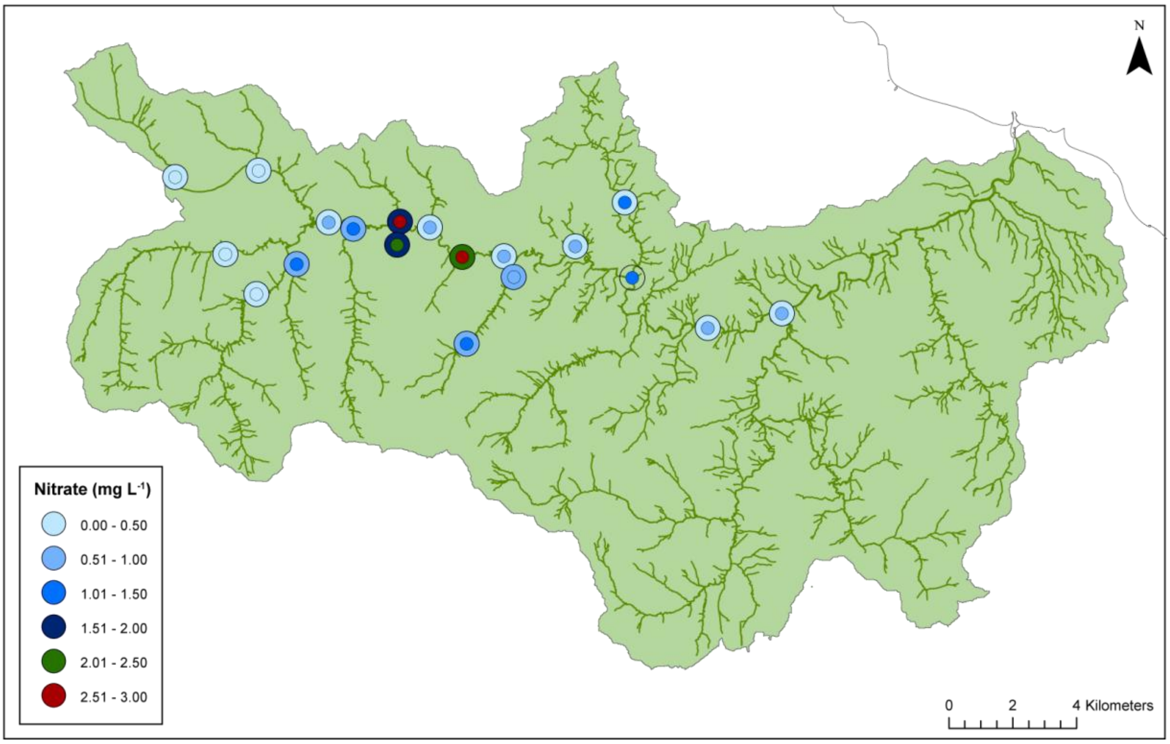


Figure 4.5. A map showing the nitrate concentration of the River Esk at 19 sites on 23/05 during baseflow (smaller) and 25/06 during high flow (larger).

4.1.4 Nutrients

4.1.4.1 Nitrate

During baseflow all headwaters had a concentration below 0.50 mg l^{-1}, except Tower Beck, which had 1.20 mg l^{-1} (Figure 4.5). The main channel sites were all below 1.00 mg l^{-1} and most tributaries were between 1.01 and 1.50 mg l^{-1}, with the exception of upper and lower Toad Beck, which had high relative concentrations of 2.05 and 2.83 mg l^{-1} respectively, as well as Little Fryup Beck with 2.63 mg l^{-1}.

During higher flows, all concentrations decreased to below 1.00 mg l^{-1}, again with the exception of Toad Beck and Little Fryup Beck. The Nitrates Directive (91/676/EC) refers to nitrate pollution resulting from agricultural activity; it considers surface and groundwaters to be polluted when levels are above 11.3 mg l^{-1}, therefore the nitrate levels in the Esk show little significance, also when in reference to Table 4.1 (Jackson *et al*., 2008).

4.1.4.2 Chloride

Figure 4.6 shows the chloride concentrations. During baseflow, the main channel Esk sites are all between 15.01 and 20.00 mg l^{-1}; the headwater tributaries have below 15.00 mg l^{-1}, with the exception of Lower Sleddale Beck at 16.95 mg l^{-1}. The tributaries are higher with 25.64 and 32.48 mg l^{-1} in upper and lower Toad Beck; concentrations are also high in Danby Beck, Little Fryup Beck and Stonegate Beck.

During stormflow the concentrations generally decrease, particularly at Egton Bridge and Grosmont, which more than halve in concentration. The headwaters decrease to below 10.00 mg l^{-1} and the tributaries all decrease but remain high. Chapman and Kimstach (1996) state that concentrations in pristine freshwaters should be below 10 mg l^{-1}, so these are relatively high values.

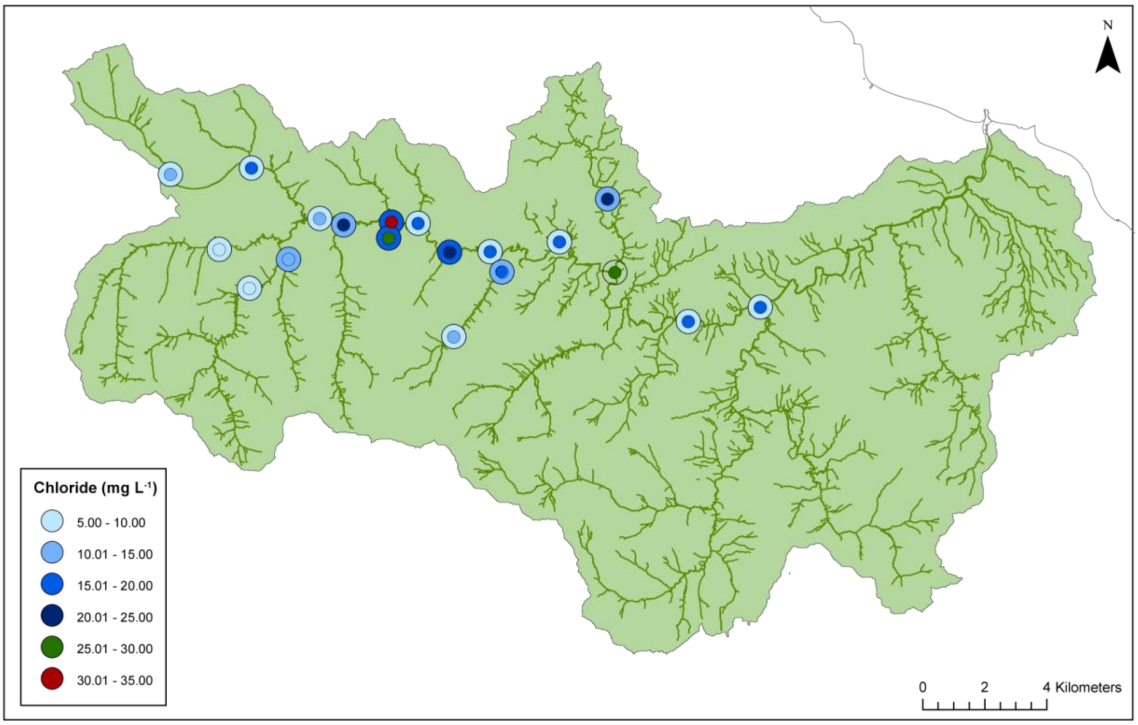


Figure 4.6. A map showing the chloride concentration of the River Esk at 19 sites on 23/05 during baseflow (smaller) and 25/06 during high flow (larger).

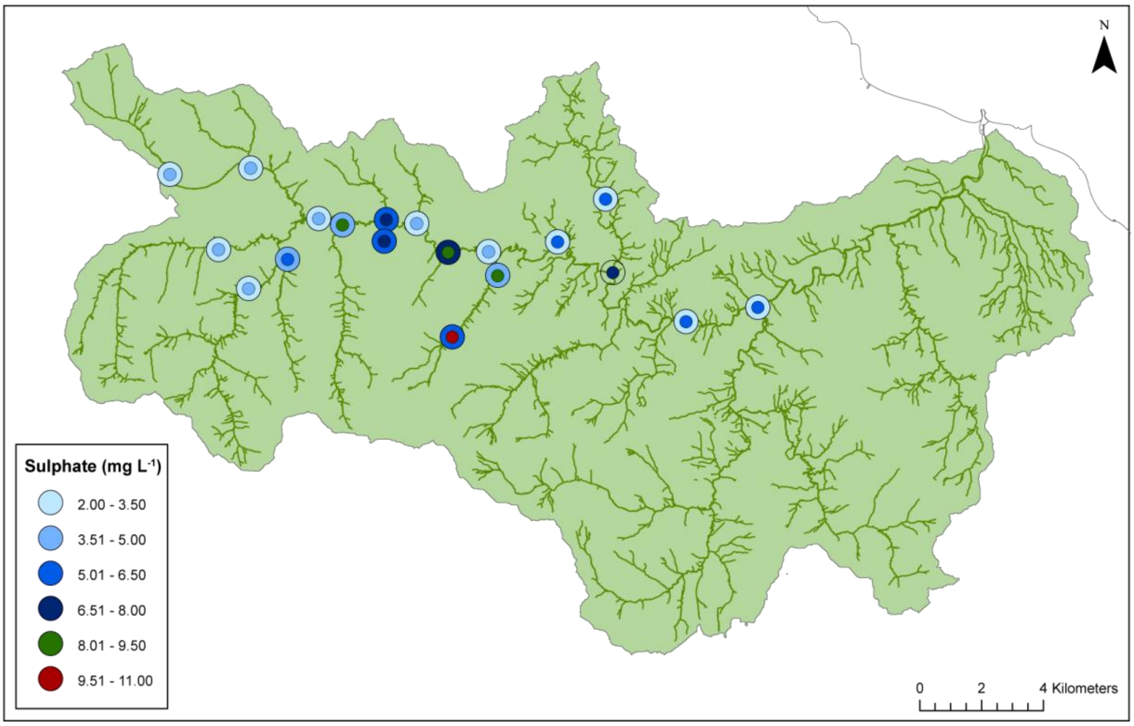


Figure 4.7. A map showing the sulphate concentration of the River Esk at 19 sites on 23/05 during baseflow (smaller) and 25/06 during high flow (larger).

4.1.4.3 Sulphate

During baseflow, headwaters were below 5.00 mg l^{-1}, with a slight increase downstream to 6.04 mg l^{-1} at Grosmont (Figure 4.7). The tributaries were all high, particularly upper Great Fryup Beck with 9.83 mg l^{-1}, which remained high at the lower site with 8.95 mg l^{-1}. During stormflow, all concentrations decreased, mainly to below 3.50 mg l^{-1}. The previously high tributaries decreased to between 6.51 and 8.00 mg l^{-1}.

4.1.4.4 Nutrient Summary

It is difficult to infer the behaviour of nutrients during the onset of high flow. However, the higher concentrations during baseflow reflect the undiluted nature of the water, particularly that at Toad Beck and other major tributaries, many of which are located adjacent to agricultural fields or roads. During baseflow the major water input will be from groundwater leaching into the channel from the riparian and hyporheic zones, bringing highly concentrated, hypoxic, old water, influenced by both the chemicals deposited above ground as well as the mineralisation occurring below it (Glover & Johnson, 1974; Burt & Trudgill, 1993). In higher flows, runoff and near surface throughflow dominate; bringing new water to the channel that may initially be concentrated from loose ground material and accumulated nutrients, but subsequently will be less concentrated than groundwater due to lower residence times in the catchment (Glover & Johnson, 1974).

When antecedent moisture in the catchment is low, the soil surface and upper subsurface will contain readily transportable soluble material, particularly if there has been a lack of precipitation for a long period of time; the longer this dry period lasts, the greater the intensity of flush concentrations will be when the soils are rewetted (Vinten & Smith, 1993). These solutes are then transported to the river via runoff or shallow throughflow, increasing the concentration input further as the catchment connectivity increases to new source areas (Walling & Foster, 1975; House & Warwick, 1998; Bracken & Croke, 2007; Tetzlaff *et al*., 2007). As the storm progresses there will be an exhaustion effect of solute availability, which may come a while after the peak in stage. This exhaustion effect is probably what is being observed for the higher flow concentrations of these maps.

The relatively high concentrations of chloride in the Esk could be due to a number of reasons (Table 4.1; Figure 4.6). Road salts are a large contributor to levels of chloride in catchments, as it is a direct application in a small area (Smart *et al*., 2001). The Esk catchment is characterised by steep roads that are extremely icy in the winter months, so there are high volumes of available salt that can enter the soils. Chlorides are also present in agricultural fertilisers, which may be leached form the soils into the channel. Also significant is the hydrogen chloride (HCl) released during waste incineration and coal combustion from nearby industry. The proximity of the Esk to the coast will bring saline water into the catchment, through precipitation of aerosols and therefore deposition of sea salts (Smart *et al*., 2001).

4.1.5 pH

During baseflow, all locations had a pH between 6.1 and 7.0 (Figure 4.8). On 25/06/12 samples were taken from the channel water that showed unusual conditions with regards to low pH levels, when compared to the average taken from the catchment over the 6 months. The headwater tributaries were particularly low, all below 6.0 with 4.4 observed at Baysdale Beck and 4.8 at lower Sleddale Beck; Castleton and upper Great Fryup Beck were also below 6.0. The pH increased downstream, with 7.3 at Grosmont. The main tributaries were generally of a higher pH, with the exceptions of Great Fryup Beck and Stonegate Beck (Figure 4.8).

pH values in natural freshwaters usually range between 6.0 and 8.5 (Chapman & Kimstach, 1996), so some of the values found here are quite acidic. A reason for this could be found from acidic deposition of industrial emissions. Another explanation could be that large amounts of catchment water had flowed over or through the acidic blanket peat of the moorlands, which can cause considerable water quality changes (Hobbs, 1986; Evans *et al*., in press).

The unusually high presence of ammonium in the water during this sampling period is interesting, as it was previously undetectable in most sampling months (Figure 4.9b). Values of 0.10 mg l^{-1} and 0.08 mg l^{-1} were found in Toad Beck, with pH values of 6.9 and

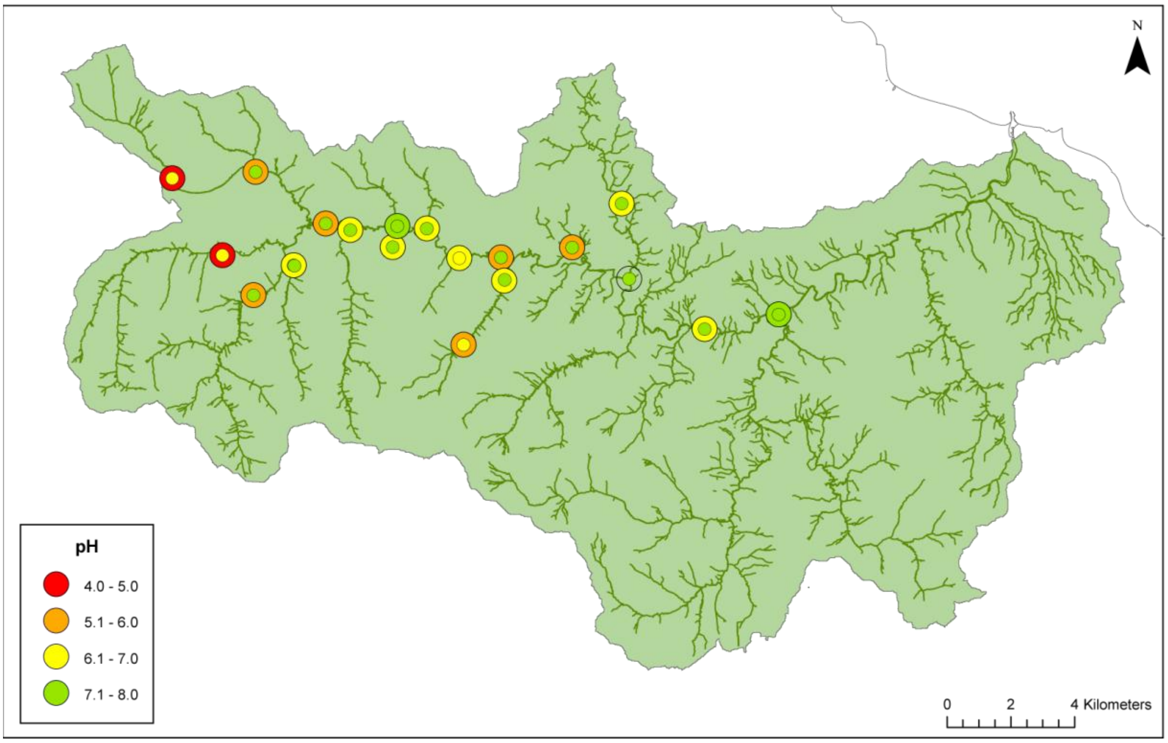


Figure 4.8.A map showing the pH of the River Esk at 19 sites on 23/05 during baseflow (smaller) and 25/06 during high flow (larger).

7.5 respectively (Figure 4.9a), this could pose serious problems to the aquatic life in the stream, as with increases in pH (generally >8.0), ammonium (NH_4) is converted to the more toxic form of ammonia (NH_3) (Heathwaite, 1993). The same applies to Little Fryup Beck, where a concentration of 0.07 mg l^{-1} and a pH of 6.9 were recorded. In unpolluted waters the concentration of ammonia compounds is usually less than 0.1 mg l^{-1} (Chapman & Kimstach, 1996); concentrations as high as 1.43 mg l^{-1} have been recorded in this study (Lealholm 10/05/12 06:00), which poses a serious concern for the toxicity of the river environment.

There had been a flood event two days before this one, leaving the catchment relatively saturated; this would explain the flashy nature of this event, displaying an immediate rise and fall of stage (Figure 4.8). The catchment response is likely to be caused by saturation-excess overland flow. The proximity of the headwaters to steep slopes and moorland would expose them to any water quality characteristics from the catchment before dilution can occur from the main channel. Oversaturation of soils can lead to reduced aeration and therefore more hypoxic conditions. This could explain why more elevated values of parameters are found in the headwaters than the main channel.

Chloride is considered to be a mobile anion; mobile anions have a direct effect on hydrogen concentrations in soils, as they facilitate the movement of cations from soil to channel. Therefore, inputs of chloride into soils reduce its capacity to retain hydrogen, leading to temporary streamwater acidification during storm events (Bishop *et al*., 1990; Smart *et al*., 2001). This is due to an increase in chloride concentrations and an increase in near surface through flow. It is assumed that these acid flushes are more significant in near-coastal streams, such as the Esk (Smart *et al*., 2001). The chloride concentrations found in the Esk are generally quite high (Table 4.1; Figure 4.6), and this may explain why the pH in the Esk was particularly low during these higher flows.

Wigington *et al*. (1992) found that surface waters that are most susceptible to acidic deposition in Europe are most frequently found in catchments with forest and moorland vegetation, where infiltration capacity in soils is high. The upper Esk catchment is characterised by this vegetation, and will be exposed to deposition from industrial emissions and sea salt from coastal rainfall. Industrial emissions include sulphuric acid (H_2SO_4) and nitric acid (HNO_3), which lower the pH of precipitation (Driscoll *et al*., 2003), therefore increasing the acidity in the soils.

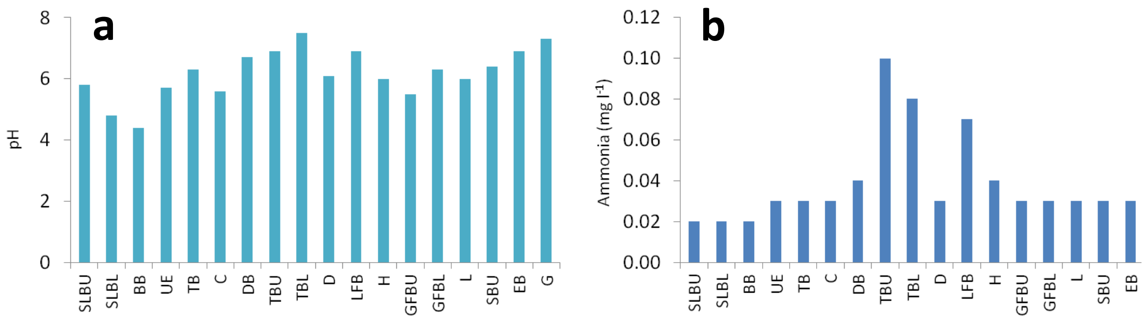


Figure 4.9. A set of graphs showing a) pH and b) ammonia concentrations across the catchment on 25/06.

During periods of baseflow, these rivers will be relatively alkaline, due to the contribution of waters from deeper soils, and this is shown in data for the Esk (Table 4.1; Figure 4.6). With the onset of rainfall and higher levels of shallow surface flow, water flowing to the channel will be more acidic due to the flushing of accumulated hydrogen ions in the soils from nitrification and atmospheric deposition (Wigington *et al*., 1992). Aquatic species, particularly fish and invertebrates, are highly susceptible to these acidic episodes, more so than a constant lowering of pH, due to the sudden changes in their habitats, offering little in the way of refuge or adaptation (Driscoll *et al*., 2003).

The neutrality of the water downstream may be due to a higher volume of water mixing from different sources, leading to a rising of pH from more alkaline sources. These sources may have been from the alkaline pelosols, brown earths and stagnogleys that make up the lower catchment (Evans *et al*., in press).

4.2 Summary

The nutrient, SSC and dissolved oxygen levels of the Esk from this study are not of high enough levels to pose a concern. The nutrient levels in baseflow were predominantly diluted in higher flow, and SSC increased only marginally, although this may be due to the late stage on the hydrograph that these samples were taken. Nutrient levels decreased in higher flows due to inputs of dilute rainfall from runoff through the catchment, whereas in baseflow concentrations were higher due to the higher significance of concentrated groundwater entering the channel (Figures 4.5 to 4.7). SSC increased downstream due to runoff carrying loose material from farmland and roads to the channel, as well as an increase in stream power to entrain and maintain suspension of particulate matter from within and adjacent to the channel (Figure 4.1).

Toad Beck, Little Fryup Beck and Stonegate Beck were sites with consistently high levels of nutrients, lower oxygen and redox levels and higher conductivity. These tributaries will be lowering the general water quality of the entire Esk drainage system and may be due to the land use surrounding these streams. Toad Beck displayed a low relative oxygen concentration of 9.00 mg l^{-1}.

In higher flows, headwaters display exceptionally low pH values (Figure 4.8 and 4.9). This may have gone unnoticed in previous studies as it may be episodic (in storm events), due to the leaching of acid deposition and mineralisation processes from upper soil horizons. Low rates of dilution in headwaters and lower overall volumes of discharge will reduce the likelihood of neutralisation, which is seen further down the catchment.

High levels of ammonium were detected in the high flows, which had previously been undetectable (Figure 4.9b). This observation, combined with low redox values and the possible saturation of the catchment due to antecedent rainfall, means that there is a probably a lack of nitrification due to lower oxygen levels in the soils and streambed. Low redox values show a high potential for reducing conditions (Figure 4.3), which may explain the high ammonium and low pH values. Redox values did increase slightly in higher flows.

5. Changes in water quality downstream

This chapter explores the changing water quality and stage of two storm events, one on 18/04/12 and the second on 10/05/12. The storms are very different in their behaviour and are both sampled over 48 hours. Tables 5.1 and 5.2 summarise the changing stage, SSC, conductivity, nitrate and potassium concentrations over the time period and the changes downstream by looking at characteristics at Danby, Lealholm and Grosmont. It must be noted that there was a lack of access to pressure transducers in this study to convert stage to discharge; therefore rating curves and suspended sediment load cannot be calculated.

5.1 Storm 1: 18th April 2012

5.1.1 Trends/Temporal Variations

Figure 5.1a shows the flood hydrograph for Danby, Lealholm and Grosmont; the two peaks at Danby are quite pronounced, showing a strong reaction to inputs of stormwater, rising to maximum stage in 12 hours and then 5.5 hours respectively. At Lealholm, further downstream, the peaks are dampened, reaching maximums in 14.5 and then 6 hours, showing a slightly slower reaction to inputs, either from the surrounding catchment or upstream from Danby, reaching peaks 2.5 hours and 1.5 hours later. At Grosmont it might be expected that peaks are even subtler, but this is not the case, potentially due to the presence of the Murk Esk, a major tributary upstream of the gauging station. Although the second peak is less pronounced, a peak is reached in only 9 hours, then only 2, both peaking before Lealholm. Upstream, at Danby, peaks are sharper and more pronounced due to the steeper landscape and a narrower channel, causing depth to increase faster than the downstream location of Lealholm, which is a braided reach of channel with a wide perimeter. Grosmont is a single stretch, far larger than that at Danby but narrower than Lealholm, hence the deeper waters. The Murk Esk tributary contributes considerable volumes of discharge to increase the stage downstream faster than the flood wave at Lealholm can catch up. The presence of roads very near to the sites helps to route any rainwater directly down to the channel, as well as any compacted farmland where infiltration is reduced due to a reduction of pore space.

Table 5.1. Summarising trends found in the flood of 18th April 2012.

Flood 1: 18th April		Danby	Lealholm	Grosmont
Peak 1		-	-	-
Start Time		13:00	14:00	15:00
Hours since previous rise		0	0	0
Start Stage (m)		0.23	0.29	0.74
Peak Stage (m)		1.89	1.31	2.08
Total rise in stage (m)		1.66	1.02	1.34
Duration (hours)		12	14.5	9
SSC (mg l^{-1})	At Start	10.57	8.33	33.49
	At Peak	844.91	348.06	400.87
Conductivity (µS)	At Start	114.2	129.3	141.3
	At Peak	98.8	92.1	105.1
Nitrate (mg l^{-1})	At Start	0.66	0.73	0.70
	At Peak	0.70	0.75	0.75
Potassium (mg l^{-1})	At Start	0.77	1.35	1.64
	At Peak	1.81	1.06	2.06
Peak 2		-	-	-
Start Time		11:45	14:30	13:00
Hours since previous rise		23	24.5	22
Start Stage (m)		0.70	0.72	1.35
Peak Stage (m)		1.10	0.81	1.45
Total rise in stage (m)		0.40	0.09	0.10
Duration (hours)		5.5	6	2
SSC (mg l^{-1})	At Start	182.78	94.44	117.83
	At Peak	287.96	85.83	99.78
Conductivity (µS)	At Start	88.5	108.7	106
	At Peak	99.6	102.5	107
Nitrate (mg l^{-1})	At Start	0.68	0.88	0.78
	At Peak	0.75	0.79	0.75
Potassium (mg l^{-1})	At Start	1.25	1.59	1.63
	At Peak	1.45	1.59	1.77

Figure 5.1b shows the changing SSC during the storm at the three sites. Danby shows four very sharp peaks throughout sampling, reaching 844.91 mg l^{-1} at its first peak before falling sharply again; it then rises again very slightly before falling to a trough, then rises to a larger peak of 1023.15 mg l^{-1}, falling rapidly before rising to two small, sharp peaks at the end of sampling. This behaviour is not mirrored downstream, with Lealholm only reaching one peak in SSC, of 409.44 mg l^{-1} at a similar time to Danby's first peak; it then falls and continues to gradually decrease. At Grosmont the behaviour is similar to that of Lealholm in that there is one major peak, but with a double crest. Concentrations of 500.00 mg l^{-1} are reached early on, before the upstream sites, before falling slightly then rising again soon after to 420.43 mg l^{-1}; after this the concentration decreases. When looking at the graph without the sudden rises towards the end of Danby's sampling, all sites along the river reach a relatively early peak, Danby simultaneously with stage, and downstream the peaks precede stage.

Figure 5.1c shows the conductivity. Danby and Lealholm follow a very similar pattern, rising to peaks 8 hours into sampling, before falling to a trough, Lealholm 2 hours ahead of Danby at this point but both after the stage peak; the conductivity then rises at both sites to a second, smaller peak, again with Lealholm peaking 2 hours ahead, both before the second peak in stage. Lealholm was consistently higher in conductivity than Danby. At Grosmont the pattern was not dissimilar, but with a seemingly earlier response; Conductivity reaches a peak 45 minutes before the peak at Lealholm, before falling, then rising to a second peak 2 hours before the trough in upstream conductivity. It then falls before gradually rising to a broad wave, whilst the upstream conductivity does the opposite.

Figure 5.1d shows the changing patterns of nitrate over the 48 hours. All sites display a subtle double peak across the period, the first peak being reached at Danby, with a concentration of 0.80 mg l^{-1} 2 hours before the peak in stage; it then falls to a trough on the falling limb of the hydrograph. After this the concentration increases to a peak with three high points, the highest of which is reached at the trough between the two stage peaks. At Lealholm the first peak is reached simultaneously with Danby, before falling to a trough 2 hours after Danby; the concentration rises to a peak with two high points, reached on the falling limb of the Lealholm hydrograph. At Grosmont, the peak is reached

5 hours after the upstream sites, and on the falling limb of the first stage peak, it then decreases and stabilises before rising to a second peak, again on the falling limb of the hydrograph and 5 hours after Lealholm.

The patterns in chloride concentration (Figure 5.1e) are similar across all 3 sites, with smaller variations within the overall trend. The overall trend is that they rise to a peak in concentration early, before the first peak in stage; the concentrations then fall to a trough on the falling limb of the stage peaks, before rising subtly to a smaller peak. At Danby the initial rise is very small, and peaks 2 hours before the peak in stage, the trough is simultaneous with Lealholm, before rising to a peak on the rising limb of the second peak. At Lealholm the peak is very sharp and much higher in concentration than the other two sites, with 20.92 mg l^{-1} compared to 14.48 mg l^{-1} at Danby; it reaches this peak very soon after the peak in stage, before falling sharply to a trough at the same time as Danby, the second peak is also similar to that of Danby. Grosmont falls initially but soon rises to a peak in a similar fashion to Danby, 45 minutes before falling jaggedly to a trough after the upstream sites. The second peak at Grosmont is reached quite a long time after the other two, on the falling limb of the hydrograph.

Figure 5.1f shows the potassium concentrations over the 48 hours, which are quite variable at all sites. At Danby the concentration begins low and rises to a peak of 1.94 mg l^{-1} before the peak in stage; it then drops jaggedly before a sharp dip on the rising limb of the second stage peak. At Lealholm the concentration also begins low, rising to a peak of 2.17 mg l^{-1} simultaneously with Danby, before falling sharply to coincide with the first peak in stage. Concentration of potassium then increases and remains relatively steady until another sudden drop to a low of 0.79 mg l^{-1} on the falling limb of the hydrograph. At Grosmont the pattern is similar, although the concentration begins high and decreases, rather than rising to a peak; after an early decline the concentration rises to a peak of 2.05 mg l^{-1} around the same time as the first peak in stage; it then drops sharply on the falling limb, 5 hours after the drop at Lealholm. It then follows a similar pattern to Lealholm before falling sharply again, this time 45 minutes before the fall at Lealholm. Potassium levels in natural waters are usually relatively low, generally less than 10 mg l^{-1}, due to the high resistivity of potassium-rich rocks to weathering; however, use in fertilisers and salts have increased levels in freshwaters (Chapman & Kimstach, 1996).

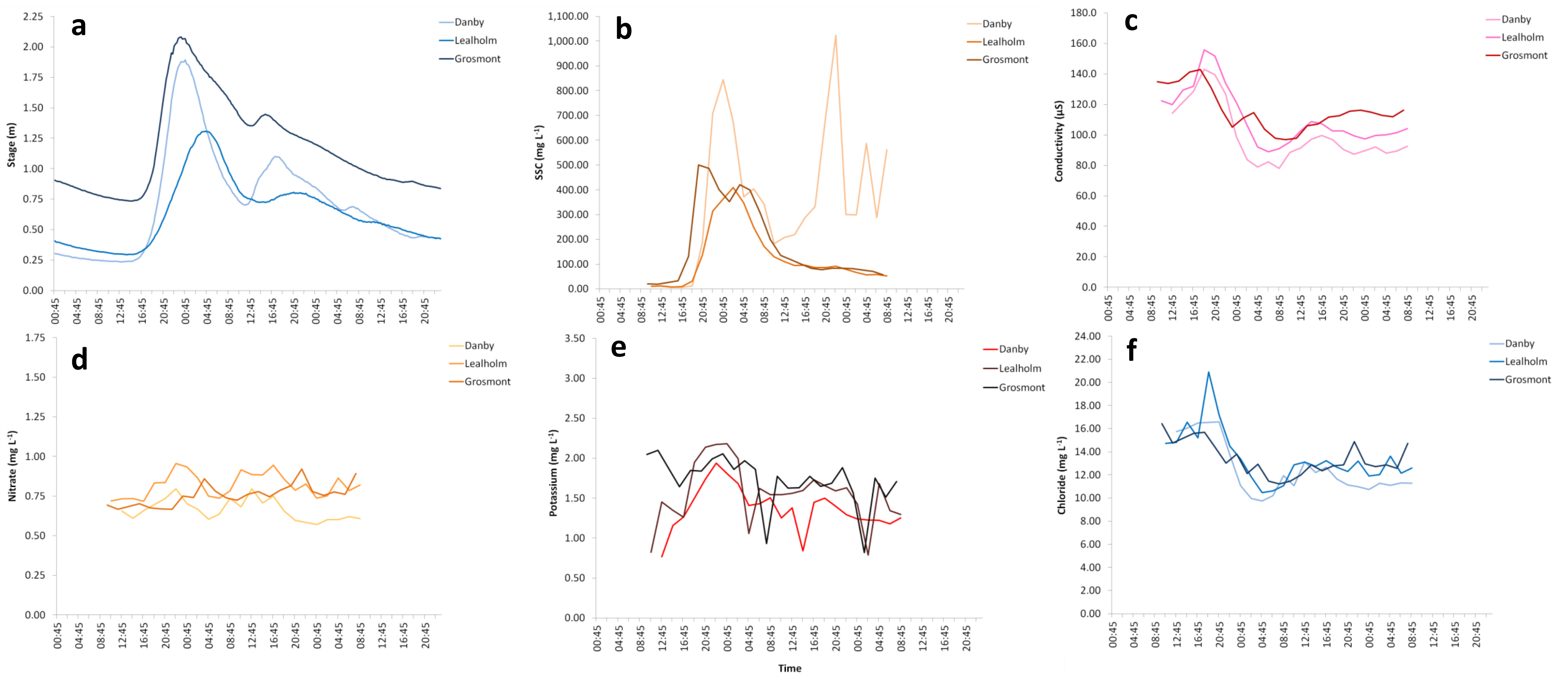


Figure 5.1. Showing the 48 hour hydrographs and chemographs of parameters over 48 hours on 18th April 2012. a) stage b) SSC c) conductivity d) nitrate e) potassium and f) chloride.

To summarise, the behaviour of the nutrients during this flood vary in time and magnitude. Most detectable parameters except potassium, nitrate, fluoride and ammonium followed a similar concentration pattern in response to river levels. They peaked twice, similar to stage at Danby and Lealholm, but came before the stage peaks, whereas at Grosmont the changes in concentration were subtler. There were similar levels of concentration across the whole reach. Concentrations were often seen to be increasing at Grosmont towards the end of sampling, as the river depth began decreasing. SSC peaks were simultaneous with stage initially, before signs of sediment exhaustion; Danby shows signs of sudden source availability that were not available before.

5.1.2 Trend Analysis

This is a relatively flashy flood, rising to a high peak quickly, before falling equally rapidly; a second rise in stage then creates a more gradual fall in stage at the end of the hydrograph. This suggests that the initial increase in channel depth is due to inputs from direct runoff from the catchment, shown in the quick removal of water downstream on the falling limb of the first peak (Figure 5.1a). The second peak is likely to also be a catchment input from further rainfall, but the slower decline in stage suggests that the channel is being supplemented with subsurface flow, preventing the river from returning to baseflow quicker. With this in mind, the water quality characteristics can be analysed.

By far the highest sediment concentration is found at Danby, and the downstream sites have a relatively similar value to one another. This suggests that there may be some major sediment sources around Danby that are readily carried to the channel, either regularly or as a one off event. Sampling takes place at a reach in the stream with steep, deep sides, which are likely to be susceptible to erosion. There are also some busy roads and a commercial moors centre nearby. Prolonged building works on a new overflow car park on a field adjacent to the stream, may have provided a large amount of sediment for the channel. Lealholm and Grosmont are surrounded by forest and grassland, which may explain why concentrations are lower. The later, sharp peaks at Danby, with an exceptionally high concentration may also fit with this explanation; as the catchment becomes wetted up and better connected, more sources of sediment may found that had not been previously, providing sediment for the channel. The trend is for SSC to be highest at the upstream site, but one would expect the overall sediment load to increase downstream, as discharge and catchment area increases.

As water flows through the catchment at the onset of a storm, the dominance of direct runoff will mean that any loose material, including sediment containing fertilisers, animal manure and road salt, will be carried with the water directly to the stream, bringing a sharp increase in the concentration of solutes. This will soon be diluted by the volume of water flowing into the channel. The lag between peak stage and the dilution of nutrients can be related to a flood wave; a flood wave refers to the faster velocity of water during a flood than that of mean water velocity in the channel. Velocity gradients both vertically and laterally in the channel due to bed and bank friction, create a non-uniform movement of water downstream. During high flows, flood water with a different concentration to that of the existing channel water would be moved downstream at a faster speed, therefore reaching a peak before dilution of concentrated baseflow occurs, creating a lag time (Glover & Johnson, 1974; Kurtenbach *et al*., 2006).

The change in significance of hydrological pathways towards subsurface flow after the first runoff-induced peak coincides with a smaller rise in concentrations. These nutrients have likely come from within the soil, or leached into it through infiltration, and may be older water, pushed through the catchment towards the channel by new water falling further up the hillslopes (Anderson & Burt, 1982). Potassium at Danby shows a more dramatic response in the form of its severe dips in concentration; the concentration begins like all the others, rising to a peak before the peak in stage, before a dilution on the falling limb. Potassium is known to react differently to other solutes during storm flow, perhaps due to its immobile characteristics when compared to nitrate, meaning more variable and less predictable patterns of movement through a catchment (Stott & Burt, 1997).

Antecedent moisture conditions of the catchment during this flood were likely to be relatively high, due to a number of small rainfall events in the week leading up to it. When antecedent moisture is high, soil saturation and connectivity of water moving through the catchment during previous storms are likely to have left a low availability of soluble material (Walling & Foster, 1975). At the onset of the storm, rapid runoff to the channel will induce an immediate dilution of solutes, leading to a trough on the chemograph falling almost simultaneously with the flood peak, rather than lagging behind it (Walling & Foster, 1975). During these conditions, runoff is likely to be saturation-excess overland flow, as rain falls onto already saturated land, implying that the dominant water source for this event would be “new” water, rather than “old” water from subsurface with a long residence time and possibly high concentrations of dissolved material (Pearce *et al.*, 1986; Kirchner *et al.*, 2000). Old water will likely be fed to the channel slowly and continuously in conditions of high moisture in the watershed, as it is pushed horizontally downslope to the channel, and vertically through soil horizons to groundwater. This will increase as catchment moisture increases, and explains why there is often a small rise in chemical concentrations a while after the trough is observed (Walling & Foster, 1975).

5.1.3 Hysteresis

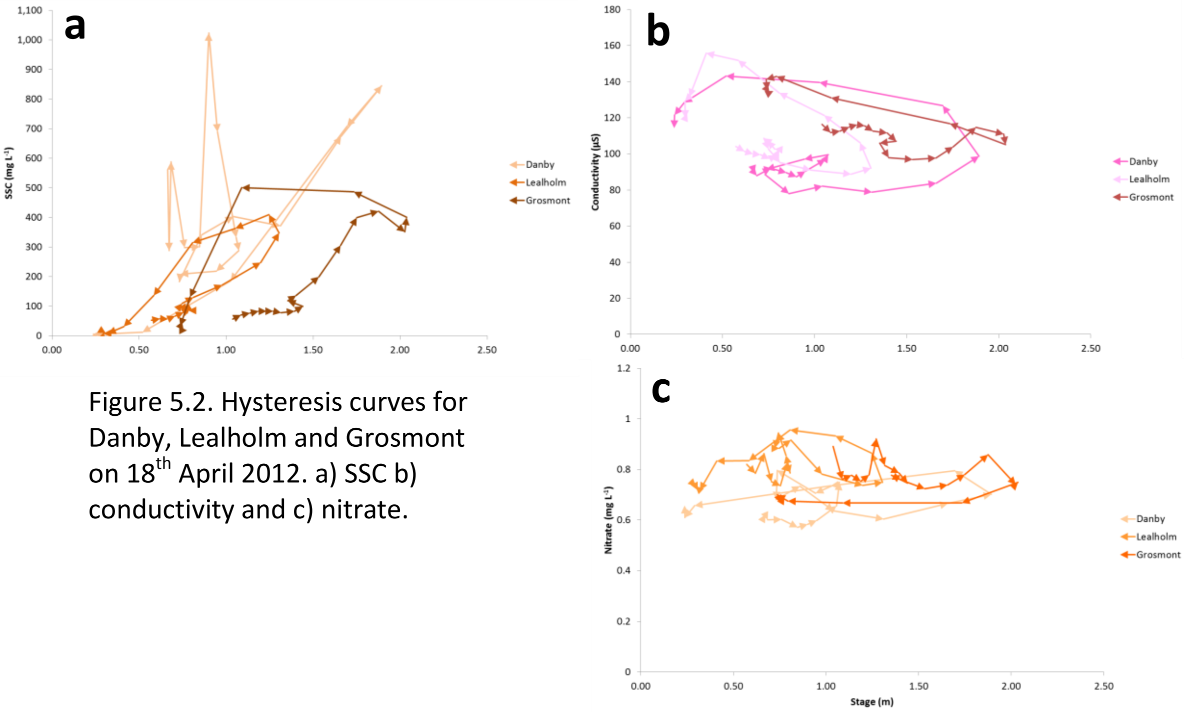


Figure 5.2. Hysteresis curves for Danby, Lealholm and Grosmont on 18th April 2012. a) SSC b) conductivity and c) nitrate.

The patterns observed above can be further analysed by looking at the hysteretic behaviour of SSC, nitrate and conductivity in the channel. Hysteresis loops indicate the differences in parameters in relation to certain discharges (House & Warwick, 1998), in this case differing river stage (Figure 5.2). The plotting of two variables produces loop trajectories that highlight either clockwise or anti-clockwise relationships (Bowes *et al.*, 2005); this evidence can then be used to deduce the sources of the solutes found (Klein, 1984; McDiffett *et al*., 1989). The behaviour of a particular catchment during storms can indicate land use, soils, geology and antecedent moisture conditions present (House & Warwick, 1998). By looking at the changing hysteresis downstream, changes in catchment characteristics can be attributed to certain behaviours. A clockwise loop indicates that higher concentrations are found on the rising limb of stage, whereas anti-clockwise contrasts with higher concentrations on the falling limbs (Bowes *et al*., 2005).

The dilution effect seen with rising discharge or stage, generally in an anti-clockwise trajectory, has been attributed to the dilution of solutes in concentrated baseflow by surface runoff (House & Warwick, 1998). If solutes are seen to increase with increasing discharge, then this suggests a contribution from sub-surface flow, with solutes being flushed out into the channel (House & Warwick, 1998), with lower concentrations seen later on, when sources have been exhausted. For sediment concentrations, an immediate increase with discharge indicates either resuspension of channel sediments, or localised sources adjacent to the channel (Klein, 1984); this is behaviour that is often seen in smaller catchments.

For the SSC in Storm 1 at Danby, there is no clearly defined hysteretic pattern, for it changes between anti-clockwise and clockwise throughout. Lealholm and Grosmont display clear anti-clockwise trajectories through the sampling period. Despite the fact that the concentration was behaving in an anti-clockwise trend, suspended sediment downstream increased rapidly with stage; at Lealholm concentrations then decreased as stage dropped, whereas Grosmont continued to increase slightly, before falling. The highest concentrations were seen at the very start of the falling limbs. This suggests that there may have been a lag in suspended sediment downstream, and that the majority of sediment supplied in this storm was being transported from upstream, rather than from the surrounding area or in-channel.

For the nitrate concentrations in Storm 1, Danby and Lealholm display two anti-clockwise trajectories, whereas at Grosmont the hysteresis is clockwise. For conductivity, all sites display anti-clockwise loops, with the exception of a slight clockwise change in the middle of sampling at Grosmont. Patterns of conductivity show clearly that dissolved solids increased as stage decreased and vice versa; this would be expected due to effects of dilution. However, at Grosmont the conductivity is predominantly anti-clockwise, whereas the nitrate shows a clear clockwise trajectory. This suggests that the initial increases in nitrate are due to runoff from surrounding agricultural land, but later on during the falling stages, nitrate supplies at Grosmont were lower than that upstream, either due to denitrification in the catchment or lack of supply from sub-surface flow. It may also be due to dilution from additional flow out of the Murk Esk. The contrast between nitrate and conductivity trajectories suggests that perhaps nitrate was coming from a different source to other nutrients.

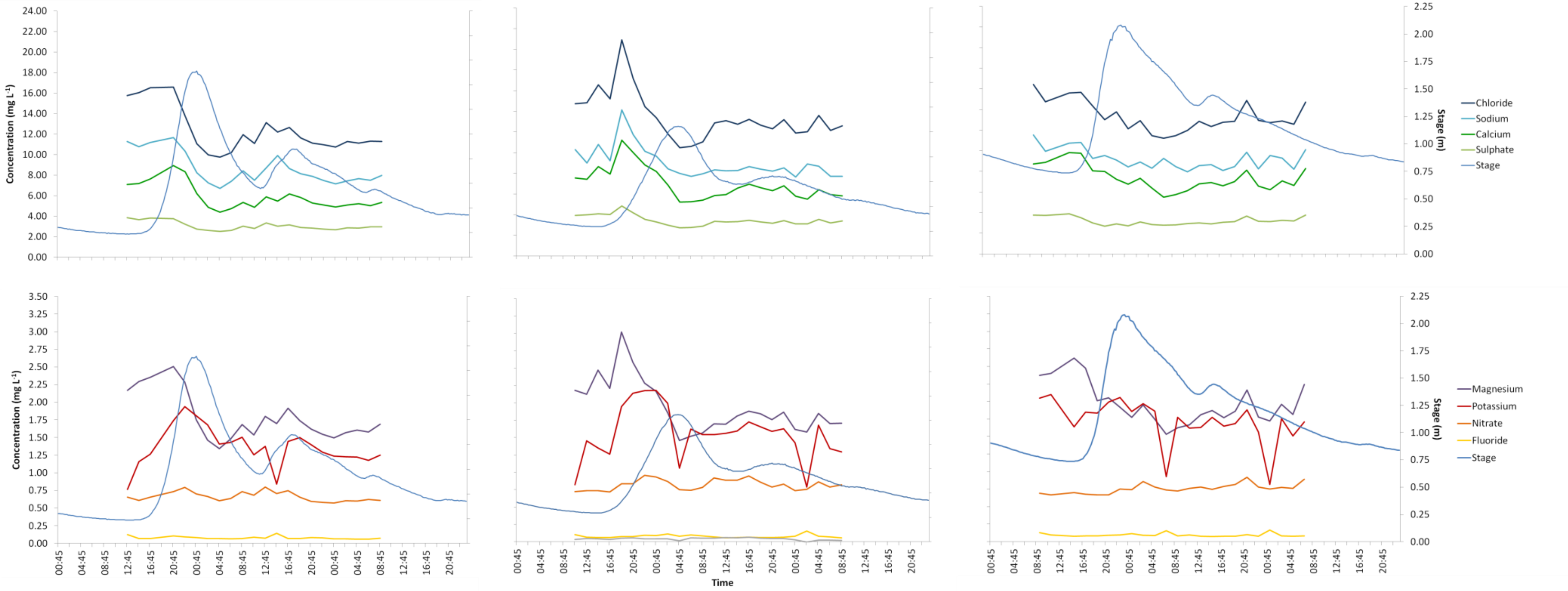


Figure 5.3. Graphs showing the downstream changes in parameters for 18th April 2012. Left graphs for Danby, middle for Lealholm and Right for Grosmont. Concentrations are in mg l^{-1} and stage is in metres.

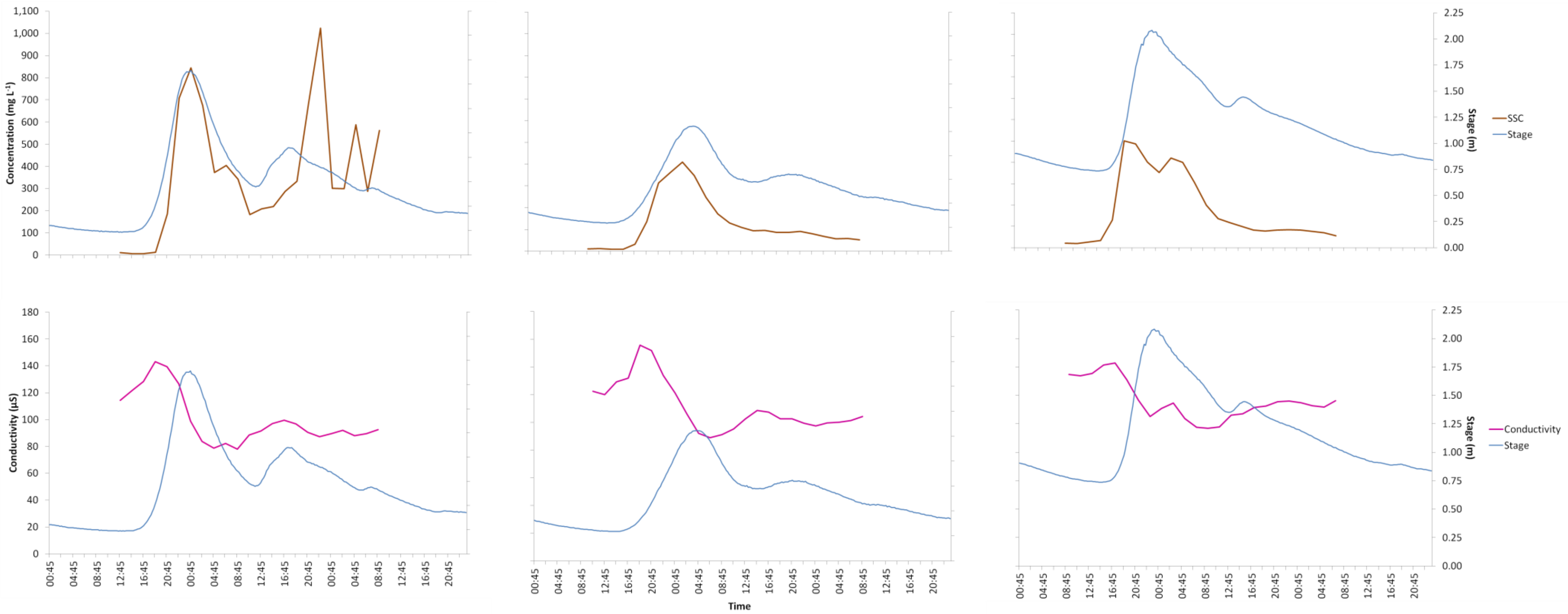


Figure 5.4. Graphs showing the downstream changes in parameters for 18th April 2012. Left graphs for Danby, middle for Lealholm and Right for Grosmont. Concentrations are in mg l^{-1} and stage is in metres.

5.2 Storm 2: 10th May 2012

Table 5.2. Summarising trends found in the flood of 10th May 2012.

Flood 1: 10th May		Danby	Lealholm	Grosmont
Peak 1				
Start Time		00:00	00:00	00:00
Hours since previous rise		0	0	0
Start Stage (m)		0.20	0.19	0.62
Peak Stage (m)		0.84	0.62	1.04
Total rise in stage (m)		0.64	0.43	0.42
Duration (hours)		9	12	13
SSC (mg l^{-1})	At Start	(05:15) 42.22	(06:00) 76.74	(03:00) 39.11
	At Peak	231.85	117.27	92.61
Conductivity (µS)	At Start	(05:15) 135.0	(06:00) 162.6	(03:00) 147.9
	At Peak	124.1	122.1	127.0
Nitrate (mg l^{-1})	At Start	(05:15) 0.69	(06:00) 1.15	(03:00) 0.85
	At Peak	0.95	1.13	1.22
Potassium (mg l^{-1})	At Start	(05:15)6.55	(06:00) 2.16	(03:00) 2.29
	At Peak	2.14	1.78	1.77
Peak 2				
Start Time		15:15	15:15	17:00
Hours since previous rise		15	15	17
Start Stage (m)		0.55	0.57	1.00
Peak Stage (m)		1.04	0.75	1.09
Total rise in stage (m)		0.49	0.18	0.09
Duration (hours)		5	8	3
SSC (mg l^{-1})	At Start	137.78	81.59	133.48
	At Peak	221.67	116.82	108.94
Conductivity (µS)	At Start	83.3	100.0	121.1
	At Peak	92.3	102.1	117.2
Nitrate (mg l^{-1})	At Start	0.47	0.70	1.06
	At Peak	0.63	0.75	1.07
Potassium (mg l^{-1})	At Start	1.75	1.66	1.99
	At Peak	1.59	1.65	1.94
Peak 3				
Start Time		09:15	12:00	14:30
Hours since previous rise		18	19	21.5
Start Stage (m)		0.44	0.46	0.83
Peak Stage (m)		0.86	0.65	0.98
Total rise in stage (m)		0.42	0.19	0.15
Duration (hours)		12	12.5	9
SSC (mg l^{-1})	At Start	161.48	28.14	30.43
	At Peak	95.00	51.90	46.17
Conductivity (µS)	At Start	87.9	102.3	115.6
	At Peak	84.6	94.3	114.9
Nitrate (mg l^{-1})	At Start	0.46	0.53	0.62
	At Peak	0.40	0.41	0.78
Potassium (mg l^{-1})	At Start	0.93	1.25	1.35
	At Peak	1.03	1.21	1.75

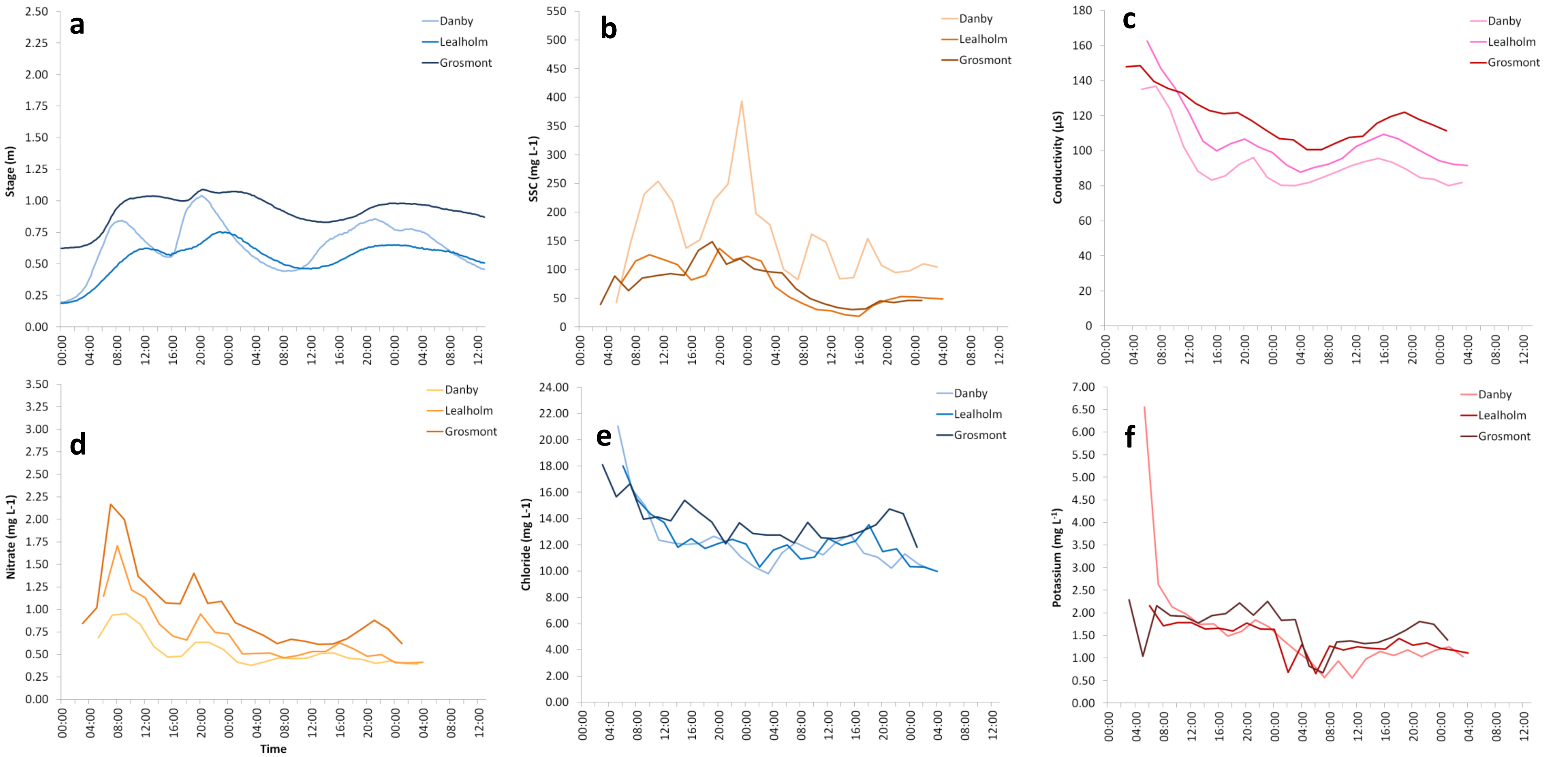


Figure 5.5. Showing the 48 hour hydrographs and chemographs of parameters over 48 hours on 10th May 2012. a) stage b) SSC c) conductivity d) nitrate e) potassium and f) chloride.

5.2.1 Trends

Figure 5.5a shows the flood hydrograph for Danby, Lealholm and Grosmont on 10/05/12. There are three visible peaks but these are much smaller and less pronounced than those on 18/04/12. The initial peak is reached at Danby after 9 hours, rising only 0.64 m, followed by a smaller rise of 0.49 m over 5 hours; these peaks are the most pronounced on the hydrograph, but the third rise of 0.42 m over 12 hours is far more gradual. At Lealholm the first rise of 0.43 m takes 12 hours, followed by 0.18 m over 8 hours and then 12.5 hours with a similar rise. At Grosmont it takes 13 hours, followed by a very smaller rise of 0.09 m over 3 hours, and then 9 hours. The peaks at Lealholm and Grosmont are subtle and gradual. The shape of the hydrograph requires a similar explanation to that of Storm 1, with the differences in rise sensitivity due to channel shape.

Figure 5.5b shows the SSC. Danby again displays four pronounced peaks, rising to its first of 253.52 mg l^{-1} before falling sharply then rising to its highest peak of 393.70 mg l^{-1}; both of these peaks are reached 3 hours after the peaks in stage. The SSC then falls before rising to two smaller peaks on the rising limb of the third peak. Contrastingly, Lealholm only shows two peaks in concentration and both come 2.5 to 3 hours before the peaks in stage, with much lower concentrations than those upstream. At Grosmont the concentration peaks slightly at the very beginning of sampling, before rising to a larger peak of 148.70 mg l^{-1}. As was seen in Storm 1, the SSC at Danby is significantly higher than further downstream, enhancing the suggestion that there is a large amount of readily transportable material around the site at Danby, or further upstream of it. There is a steep-sided weir shortly upstream of the site, which may aid the process of maintaining suspension through increased energy in the water. When Lealholm and Grosmont are continually decreasing after their last peaks, Danby sees two additional peaks, similar to the pattern found last time. This shows that the SSC at Danby responds well to changes in stage as the final rises in concentration are associated with final stage peaks on the hydrograph. Downstream the sites do not respond, signalling sediment exhaustion.

Figure 5.5c shows the potassium concentrations. There is more of a pattern seen in this flood than in Storm 1, with the exception of a very high start in concentration at Danby, with 6.55 mg l^{-1}. This high relative concentration is sampled on the rising limb of the first peak, but it drops rapidly to a trough in concentration by the rising limb of the second peak. It then rises slightly to a peak as the second stage peak begins to decline; the concentration then decreases to a low point, with a slight spike and fall as the river begins to rise again for the final peak, before gradually rising towards the end of sampling. At Lealholm the pattern is similar, although it does not begin with a high concentration; the spike and fall is replicated here but 4 hours before Danby, on the falling limb of Lealholm's second peak. Grosmont exhibits a sudden drop at the beginning of sampling, as the river begins to rise for the first peak; after this it remains relatively steady with small spikes before falling to a trough on the falling limb of the second peak, at the same time as Danby's low.

Figure 5.5d shows the conductivity. Danby and Lealholm again follow a similar pattern, falling to a low conductivity at the trough between two stage peaks, before rising again to a peak around the stage peak; it then falls again to a second trough on the falling limb of this peak, before rising again on the rising limb of the third stage peaks, finishing sampling with a decline. Grosmont is similar, but only displays one trough in conductivity, falling gradually from the start to a low 1 hour after Lealholm, on the falling limb of the second stage peak; the conductivity then increases to a peak on the rising limb of the thirds peak, before falling. The trough and peak on the graph show a clear succession downstream, with Danby reaching the extremes first, followed by Lealholm and then Grosmont.

Figure 5.5e shows nitrate concentrations. There is a very strong pattern shown between the upstream and downstream sites on this chemograph, displaying three peaks. All sites begin low and rise to a peak before the peaks in stage, within 2 hours of one another. The concentrations then fall to a trough, Danby and Grosmont in between their two stage peaks, Lealholm on the rising limb of its second peak. The concentrations then rise to a second, smaller peak within an hour of one another, Grosmont and Lealholm on the rising limb, Danby on the peak. The concentrations then decrease relatively steadily until a rise towards the end of sampling, Danby and Lealholm on the rising limb of the final peak and Grosmont on the peak.

Figure 5.5f shows the chloride concentrations. Danby and Lealholm follow a similar pattern once again, starting with high concentrations before falling to a trough to coincide with the stage trough between two peaks. Concentration then decreases further to another trough on the falling limb of the second stage peak, before rising to a peak further down the falling limb. This peak then declines before rising further to a peak on the rising limb of the final stage peak. After this, Lealholm continues to rise before falling towards the end of sampling. Grosmont displays five peaks in concentration, potentially displaying a continuous lag in concentration highs from further upstream.

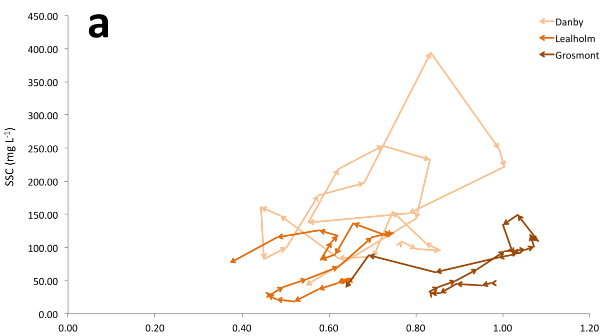
To summarise, nitrate concentrations during this storm event display a strong pattern with the changes in stage, reaching peaks before stage and troughs on the falling limb. Conductivity responds to only two of the rises in river levels, reaching peaks before stage and troughs after the stage peaks. Potassium displays an unusually high start upstream, after which the signal is less pronounced, with two visible peaks which are reached on the falling limb of the first peak and the rising limb of the third peak. Chloride patterns are not very clear, with small peaks and falls throughout.

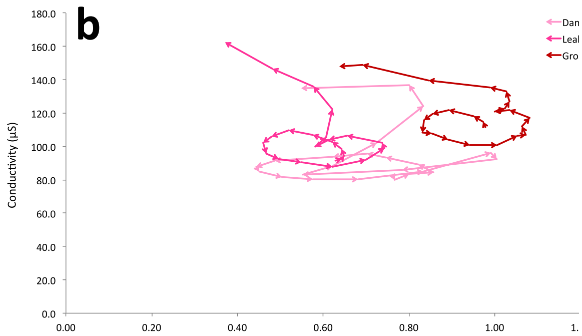
5.2.2 Trend Analysis

This flood has a small overall rise in stage; upstream displays three clear peaks, but as the water moves downstream the peaks become far more subtle, displaying what could be one long rise with three peaks within it. The sharper rises for the first two peaks suggest an influx of overland flow into the channel upstream of Danby, which are conveyed downstream to a more dampened effect. This could suggest that rainfall was perhaps not falling across the entire catchment, thus providing fewer water sources for the channel downstream. Alternatively, the rise upstream may not be reflected as well when the channel becomes wider downstream. The third peak on the hydrograph could suggest a contribution from subsurface flow.

The pattern of SSC during this event strengthens the theory of surface runoff for the initial stages of the storm, as sediment increases substantially at this time. The tailing off at Lealholm and Grosmont would then suggest that any additional water entering the stream may be from subsurface flow, with few sediment inputs; however, the sudden spikes from Danby suggest otherwise. A weir upstream of Danby could aid the resuspension of a large amount of sediment on the bed or from the channel banks where further downstream the channel could not. Nitrate reflects the increased runoff at the storm onset, with water flowing over farmland, bringing higher concentrations of nitrate to the channel in two waves. This then decreases, probably as supply has been exhausted and increased channel discharge dilutes the concentration; concentration then increases towards the end of sampling, suggesting leaching from subsurface flow. Potassium and Chloride display a different pattern to nitrate, decreasing as stage increases, reaching their lowest concentrations on the recession of the two initial stage peaks; this implies a classic dilution of concentration in the river. After this the concentrations increase gradually, suggesting an increase in the importance of groundwater sources.

5.2.3 Hysteresis





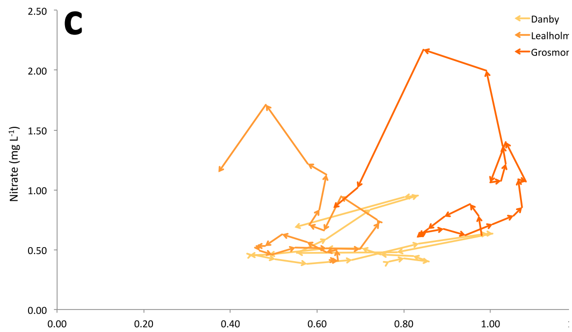


Figure 5.6. Hysteresis curves for Danby, Lealholm and Grosmont on 10th May 2012. a) SSC b) conductivity and c) nitrate.

The SSC for Storm 2 at Danby begins with a slight anti-clockwise direction (Figure 5.6a), before showing two expansive clockwise trajectories. Lealholm and Grosmont both display a constant switching between clockwise and anti-clockwise, beginning clockwise and ending anti-clockwise. At Danby, the slight anti-clockwise loop comes after a small increase in stage followed by a decrease; this may have caused resuspension of in-channel bed sediment, before the rise in stage again, which would have brought sediment from outside the channel. At Lealholm and Grosmont, the initial clockwise loops come as stage decreased, suggesting that a previous rise in stage that was not sampled would have brought high energy to entrain sediment, and with a decrease in stage, SSC decreased. As stage rose again the SSC did also, and continued to rise as stage dropped again, perhaps due to a lag from upstream sediment being delivered downstream.

Figure 5.6b shows that Conductivity follows a clear anti-clockwise trajectory in two loops at Lealholm and Grosmont, showing increased concentrations on the falling limbs of two peaks. Danby displays a slight clockwise loop between two anti-clockwise ones, with conductivity increasing with stage. The nitrate concentration at Danby also shows a switching of direction (Figure 5.6c), beginning anti-clockwise, before becoming clockwise with very little change in nitrate concentration, concentrations increase towards the end in an anti-clockwise loop. At Lealholm and Grosmont the trajectories are clearly anti-clockwise, with the biggest rises in concentration seen on the falling limb of the hydrograph. The clear anti-clockwise behaviour of the river in this storm strengthens the evidence that as stage increased in the channel, dilute runoff kept solute concentrations low, however, as stage decreased the concentration of nitrate, and the conductivity, increased rapidly, either from subsurface flow or loose material from the ground.

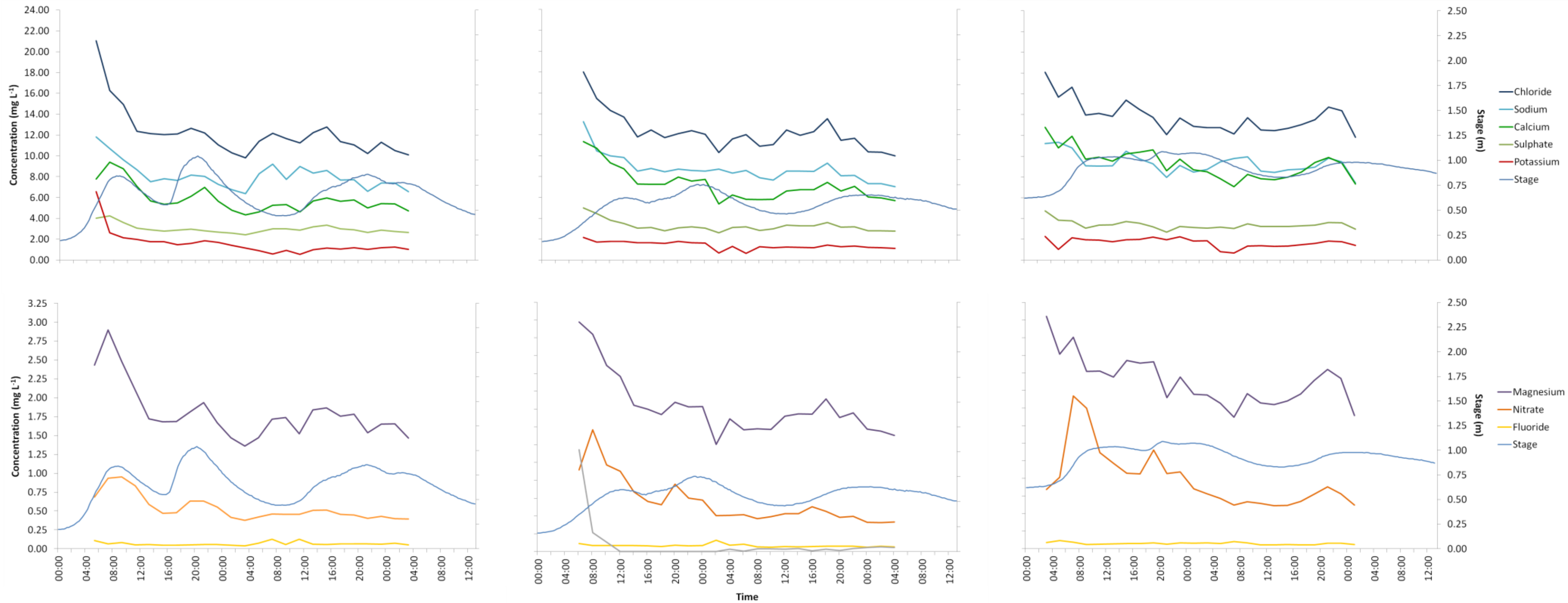


Figure 5.7. Graphs showing the downstream changes in parameters for 10th May 2012. Left graphs for Danby, middle for Lealholm and Right for Grosmont. Concentrations are in mg l^{-1} and stage is in metres.

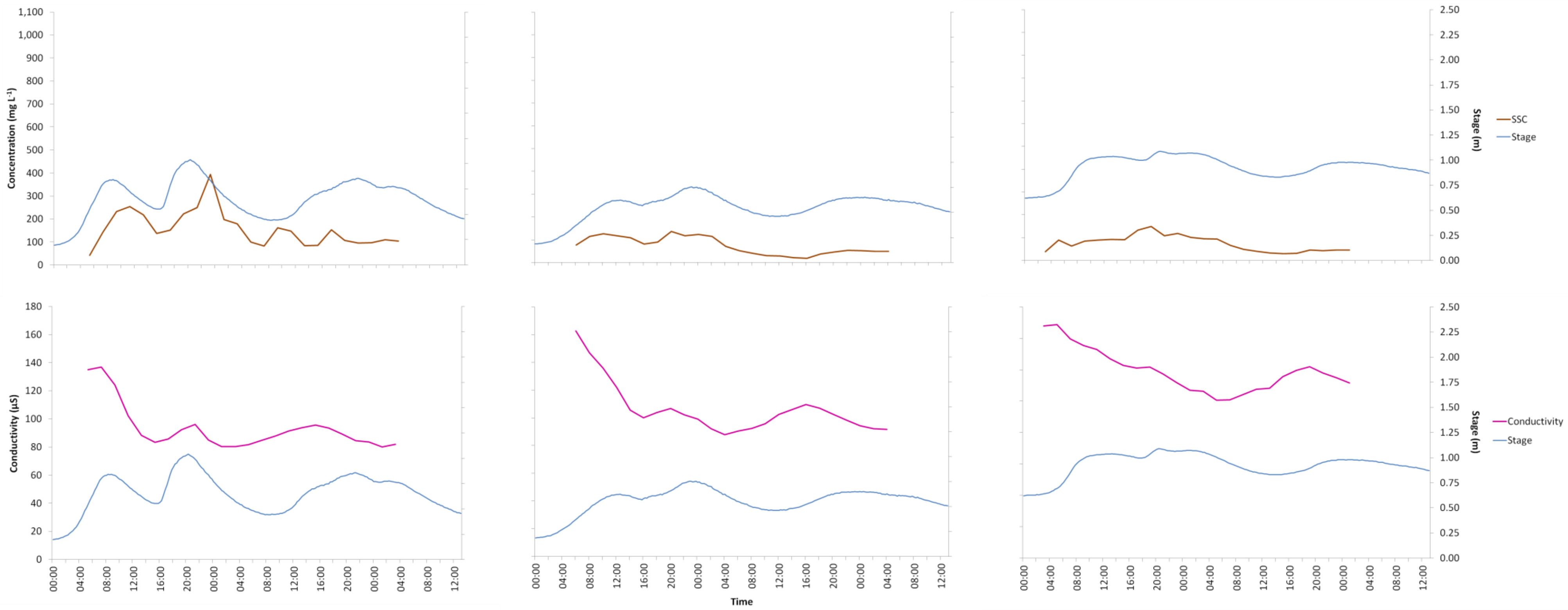


Figure 5.8. Graphs showing the downstream changes in parameters for 10th May 2012. Left graphs for Danby, middle for Lealholm and Right for Grosmont. Concentrations are in mg l^{-1} and stage is in metres.

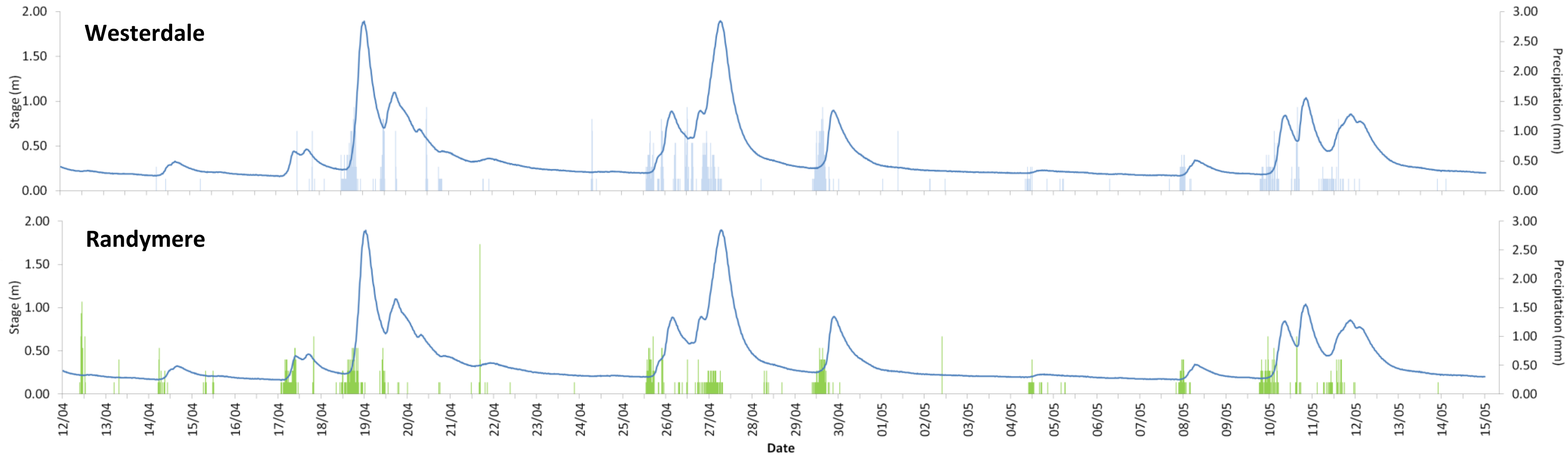


Figure 5.9. Precipitation levels from Westerdale logger and Randymere logger from Environment Agency data plotted with stage from 12/04 to 15/05. Data collected in mm every 15 minutes.

5.3 Comparison between Storm 1 and Storm 2

The two storms above have a number of characteristics that would suggest they are quite similar, for example the fast rise in stage at the beginning, particularly at the upstream site. However, the rise in Storm 2 was far less pronounced, rising only 0.64 m upstream, translating to 0.42 m at Grosmont, compared to a rise of 1.66 m at Danby and 1.34 m at Grosmont in Storm 1 over a similar time scale. Figure 5.9a shows the changing stage with rainfall, logged from a gauge at Scaling Dam Reservoir to the north of the field sites.

For Storm 1 there was a high volume of rainfall over a short period of time, falling 19.6 mm over 9 hours, and a further 11.8 mm over the remainder of the sampled storm event (Figure 5.9). The first peak in stage at Danby was reached 4 hours after the 9-hour rainfall event, and the second peak was reached 5 hours after 6.2 mm of further rainfall. The rainfall data from Westerdale logger do not show a substantial amount of rainfall in the week leading up to the storm, but data from Randymere Logger (Figure 5.9) showed that 26 mm of rain fell before it. For Storm 2, 12.2 mm of rain fell over 10 hours, followed by a further 14.4 mm over the rest of the event. The first peak in stage was reached 3 hours after the rainfall event, and the second was reached 4 hours after 6 mm more rain fell. The final peak was reached 4 hours after 7.8 mm fell. Based on Randymere logger, there was 10 mm of rain in the week leading up to the storm (Figure 5.9).

The high amount of antecedent rainfall for Storm 1 would mean that the catchment was relatively wetted up, with a high water table and low potential for infiltration at the onset of further rainfall. The high volume of precipitation over a short period of time on 18/04/12 would therefore lead to a fast rise in river levels, due to high amounts of direct runoff. Storm 2 has less antecedent precipitation; this combined with the lower rates of rainfall would explain why the peaks do not reach the heights of Storm 1.

In Storm 1 the nutrients show a distinctive rise and fall pattern, with the chemographs peaking in concentrations before or with the peaks in stage, and reaching lows on the falling limbs. This is indicative of a dilution effect from the flood wave lagging behind the concentration. There is a slight increase in their concentrations towards the end of sampling, which signifies contributions from subsurface flow. In Storm 2, there is less of a pattern, but peaks in concentration were generally before the stage peaks.

Ammonium was present at Lealholm during both floods, but not at the other sites; it was particularly high at the start of Storm 2, with 1.43 mg l^{-1}, before dropping to negligible levels again. There was an overall decrease in nitrate concentration in Storm 2, starting with peaks as high as 2.17 mg l^{-1} at Grosmont, but in Storm 1 levels remained similar, with the exception of small rises. In fact, these are patterns for most of the nutrients; showing an overall drop and continuing to do so at the end of sampling, whereas in Storm 1 the nutrients, although decreased overall, seem to have levelled out towards the end of sampling and were even beginning to increase again. Conductivity mirrored these patterns in both storms. It may be that in Storm 2 that the catchment was not wetted up enough to flush out further groundwater and subsurface flows, hence the continual decrease. The timing of the storm comes after a month of continuous storm events in April, perhaps exhausting the supply of nutrients in the catchment. In Storm 1, sufficient saturation in the catchment would allow a greater connectivity across the landscape, providing the channel with continuous groundwater supplies, increasing the channel concentrations as stage decreased.

SSC follows a similar pattern in both storms, with the peaks at Danby coming after the peaks in stage, whereas the peaks at Lealholm and Grosmont come before them. The concentration at Danby is considerably higher in both storms, with additional peaks when there are none downstream. The suspended sediment concentration is only a snapshot of the location at a particular time, rather than giving an indication of the overall load downstream. The SSC shown at Lealholm and Grosmont may represent the resuspension of bed sediments at the onset of higher flows, with a greater potential for entrainment. The same may be true and Danby, only with the addition of fine sediment sources that are not available downstream.

5.4 In depth study of all flood events and water quality at Danby

This section looks in detail at the way water quality changes over a time scale with relation to stage. By looking at 5 separate storm events, an idea of how the channel responds to different antecedent conditions can be assessed.

Table 5.3. Summary data for five different storm events at Danby in 2012.

Date	Peaks	Max. Stage (m)	Flood Duration (hours)	Sampling Duration (hours)	Max SSC (mg l^{-1})	Max NO_3 (mg l^{-1})	Max K (mg l^{-1})
18th April	3	1.89	199	48	1023.15	0.80	1.94
25th April	3	1.90	199	48	7365.82	1.30	6.12
10th May	3	1.04	121	48	393.70	0.95	6.55
8th June	2	1.55	171	24	554.81	0.83	1.64
22nd June	2	1.10	178	24	228.73	0.51	1.92

Figure 5.10a shows the trajectories of conductivity over five storm events at Danby. The general trend over the five storm events are for anti-clockwise trajectories; rising in conductivity on the falling limbs. Most events, particularly the storms with the highest stages on 18th April and 25th April, display a clear pattern throughout the event. However, the storm on 10th May shows a clockwise loop in between two anti-clockwise ones. Figure 5.10b shows the changing nitrate hysteresis at Danby. Nitrate displays a general trend of anti-clockwise trajectories; however again there is a clockwise loop in the middle of sampling on 10th May. The 8th June displays an anticlockwise loop as stage rose, followed by a clockwise loop as stage rose for a second time.

As the stage rises there will be a dilution of concentrated base flow in the channel, mainly from direct runoff of low concentrated precipitation. Nitrate almost always displayed its greatest rise in concentration on the recessional limb of the hydrographs, as runoff and discharge drop and concentrated subsurface flow reaches the channel. For the spring events and latest event of 22nd June, there is very little rise in concentration until this recessional limb; however, on 10thMay

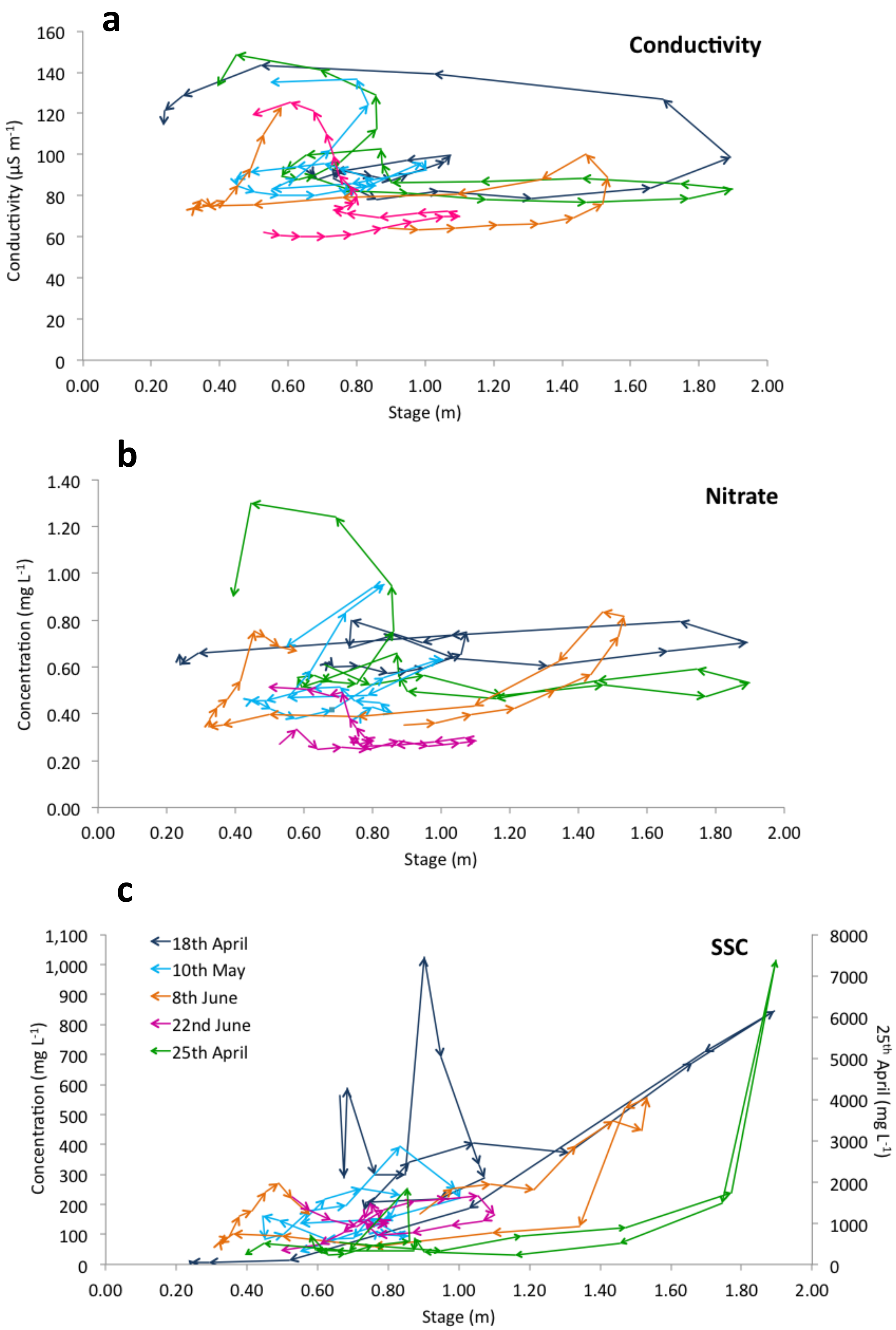


Figure 5.10. Hysteresis curves showing five floods at Danby for a) conductivity b) nitrate and c) SSC.

and 8th June there are initial rises with stage as well, suggesting that nitrate may have been plentiful on the surrounding fields at this time, when it was not during the others.

Figure 5.10c shows the changing SSC hysteresis signals at Danby. During the larger storms, SSC produced narrow, projected peaks that reached a maximum concentration with stage, for example the 18th April, 25th April and 8th June. In the smaller storms there are no obvious peaks, rather a smooth loop shape instead. On 18th and 25th April there are no clear patterns, but the remaining storms produce clockwise loops throughout the events. For smaller catchments such as the Esk, clockwise loops in these relationships are common (Klein, 1984), as an increase in discharge would bring greater velocities within the channel to entrain loose bed sediment, as well as bringing runoff through the catchment leading directly to the channel, picking up available material from the lower catchment in its pathway. These sediment sources would be likely to have been exhausted towards the end of the storm event, as well as the reduction in energy as discharge decreases. The larger spikes found in storms that reach a greater depth suggest a greater connectivity across the catchment; larger amounts of rainfall bring a greater chance of sediment being suspended, both within the channel and adjacent to it.

The larger spring storm events differ from the smaller summer events. The spring events at Danby bring greater levels of stage and greater variations in SSC. In addition to the greater volumes of rainfall, the supply of sediment may have been greater. The winter preceding these spring events was very dry; this would mean that little available material would have been removed until this point, providing plentiful supply in the area. The nitrate concentrations vary little until the very end of sampling, on the final recessional limb. In contrast the nitrate in the summer months varies greatly nearer the start of sampling, with the onset of runoff over surrounding land; however, lower rainfall brings lower levels of SSC. As mentioned above, this may be due to the short-term application of fertiliser on the agricultural land on 10th May and 8th June.

6. Water Chemistry in the Hyporheic Zone

The following chapter presents the findings from preliminary research on the HZ of the River Esk. It begins by presenting mean values found across the sampling period, but this will be discussed in more detail in Section 6.2, where comparisons are made between the channel and HZ during one specific time, to account for changes in catchment conditions. It will then look at the behaviour of dissolved oxygen and Redox during wet and dry periods.

6.1 Sampling Period Means

The table below summarises the average values for each site that were collected between March and June 2012. These averages are then compared with channel averages over the same time period.

Table 6.1. Mean values for hyporheic zone data. All in mg l^{-1} except Redox (mV)

Site	DO	Redox	NO_3	NH_4	Fl	Cl	Na	S	K	Mg	Ca
Upper Esk	8.65	37.5	0.30	0.02	0.19	11.52	9.92	4.18	0.82	2.20	7.63
Tower Beck	10.05	21.5	0.41	0.04	0.15	21.63	12.94	5.56	1.64	3.09	14.75
Sleddale Beck	8.25	-12.2	0.21	0.24	0.19	15.34	11.31	3.10	1.20	3.33	17.88
Castleton	n.a.	n.a.	0.33	n.a.	0.22	14.23	12.40	4.57	0.87	2.62	10.59
Danby Beck	11.55	15.0	1.08	0.15	0.26	25.02	15.62	7.87	2.23	4.09	17.69
Danby	n.a.	n.a.	0.49	n.a.	0.17	18.36	13.95	4.79	1.06	3.65	15.91
Houlsyke	n.a.	n.a.	0.38	0.02	0.42	32.45	21.32	4.99	1.70	3.86	16.95
Lealholm	10.44	55.9	0.52	0.01	0.39	18.33	15.89	5.30	1.33	3.95	13.91

Redox

Redox values are substantially lower in the HZ than in the channel (Figure 6.1). In the HZ, all average values are below 60.0 mV, and at lower Sleddale Beck it is -12.2 mV, compared to 89.8 mV in the channel. At Danby Beck the HZ has only 12.0 mV, compared to 69.3 mV in the channel. This is a pattern across all 5 sites, and shows that conditions in the HZ have a far greater potential for reducing conditions.

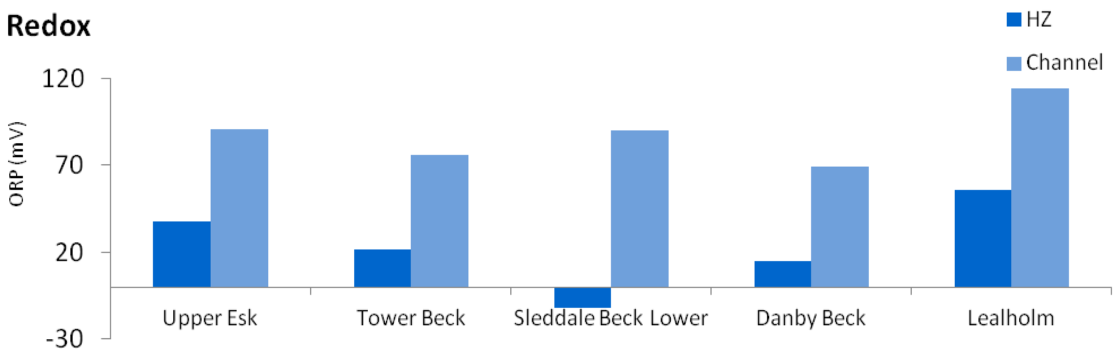


Figure 6.1. Average redox potential for five hyporheic zone sites taken between May and June 2012.

Fluoride

On average, fluoride values are higher in the HZ than in the channel (Figure 6.2). This is particularly true at Houlsyke and Lealholm. At Houlsyke the concentration in the channel is 0.11 mg l^{-1}, but in the HZ it is 0.42 mg l^{-1}. At Lealholm the channel is 0.12 mg l^{-1}, but in the HZ it is 0.39 mg l^{-1}. Fluoride levels will be analysed further in Section 6.2.

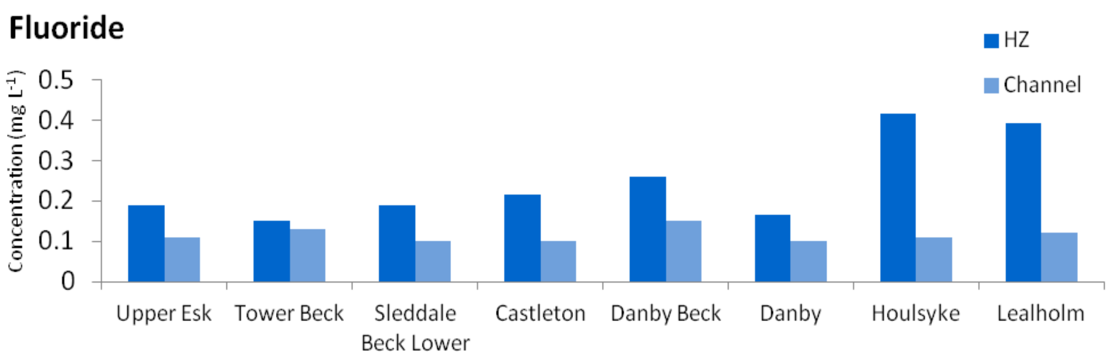


Figure 6.2. Average fluoride concentrations for five hyporheic zone sites taken between May and June 2012.

Calcium

Calcium concentrations are consistently higher in the HZ than in the channel (Figure 6.3). Particularly at Tower Beck, lower Sleddale Beck, Danby and Lealholm. At lower Sleddale Beck the channel has 7.02 mg l^{-1}, but the HZ has 17.88 mg l^{-1}. At Danby the HZ has 15.91 mg l^{-1}, and the channel only 10.47 mg l^{-1}.

Calcium levels in natural waters usually do not exceed 15 mg l^{-1}, unless in the presence of carbonate-rich rocks (Chapman & Kimstach, 1996). Freshwater pearl mussels require environments that are low in lime concentrations (Geist, 2010), so high calcium in the HZ sites could potentially be a reason for their decline. High calcium concentrations may be due to the underlying limestones in the south moorlands of the catchment (Evans *et al*. in press).

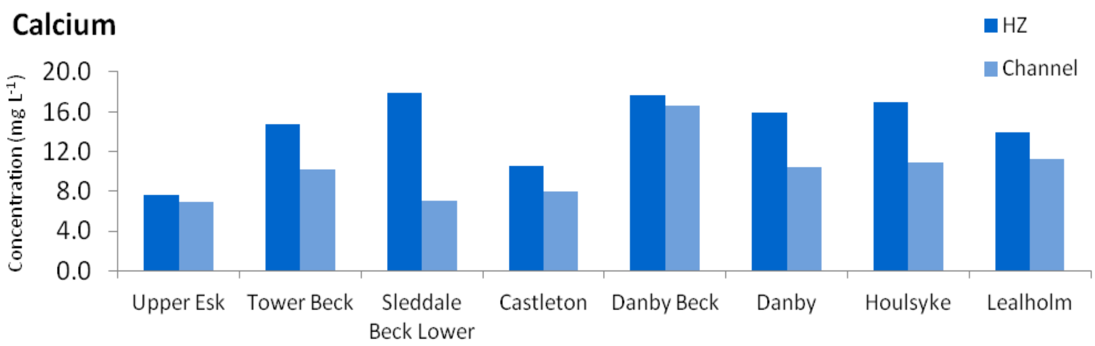


Figure 6.3. Average calcium concentrations for five hyporheic zone sites taken between May and June 2012.

Conductivity

The average conductivity of the HZ is always higher than in the channel from these results (Figure 6.4). In Houlsyke there is a very large difference, with 56.0 µS in the channel but 346.0 µS in the HZ. At Upper Esk and Danby Beck there are also noticeable differences.

Higher levels of conductivity in the HZ are likely to be due to a lower level of flow through the interstitial areas, reducing the rate of renewal. Groundwater with higher solute concentrations will prevail here, and conditions of lower oxygen, light and flow will encourage chemical reactions and reducing conditions.

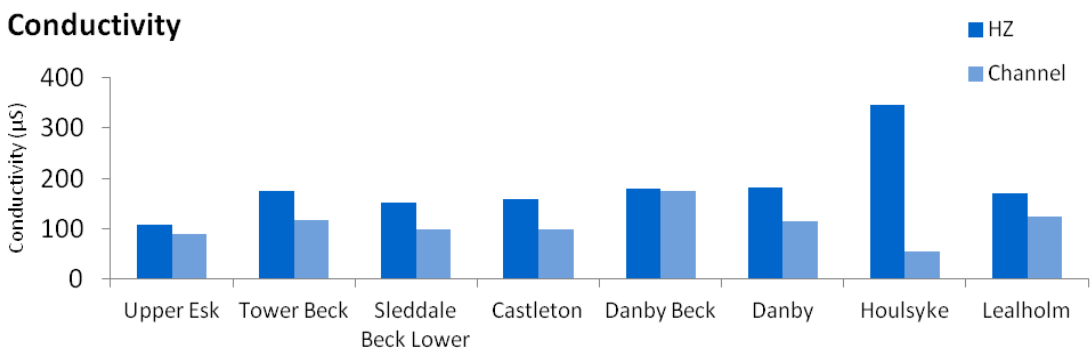


Figure 6.4. Average conductivity for five hyporheic zone sites taken between May and June 2012.

Summary

To summarise, conductivity and nutrient levels in the HZ are all higher than in the channel, with the exception of nitrate, which is lower. Redox values are all lower than in the channel. The averages above are taken from various time periods in varying levels of flow and antecedent conditions. Section 6.2 below will discuss the difference during one specific time period.

6.2 Differences in water quality between the channel and HZ during baseflow (23/05/12)

6.2.1 Dissolved Oxygen and Redox

Dissolved oxygen in the channel appears to increase downstream, with a low of 10.71 mg l^{-1} in Baysdale Beck, but 12.34 mg l^{-1} at Grosmont (Figure 6.5). Most sites had a value between 11.01 and 12.00 mg l^{-1}. The sites with HZ values to compare showed a marked difference. All sites except Lealholm were 8.00 mg l^{-1} or below, with a low of 6.93 mg l^{-1} at lower Sleddale Beck, compared to 11.22 mg l^{-1} in the channel.

Redox values in the channel sites were mainly between 30.0 and 80.0 mV (Figure 6.6). The HZ values were similar in Upper Esk, Tower Beck and Lealholm, but Sleddale Beck and Danby Beck were significantly lower. Lower Sleddale Beck had a value of -11.7 mV, against 50.7 mV in the channel. Danby Beck was 18.1 mV in the HZ, but 56.4 mV in the channel.

It is unsurprising that the levels of dissolved oxygen in the HZ are lower than in the channel water. As outlined in Chapter 2, the area beneath the riverbed receives very low flow velocities, as water is pushed through the gravel at differing pressure gradients. The low levels of light will also mean a lower concentration of oxygen due to lack of photosynthesis. Any organisms living there will immediately use the available oxygen, further lowering the oxygen concentration. Available oxygen will also be used during processes of nitrification and other biogeochemical processes. Oxygen levels in the HZ are not of a worrying level (cf. Chapman & Kimstach, 1996); however, the low redox levels present a concern due to high potential for reducing conditions.

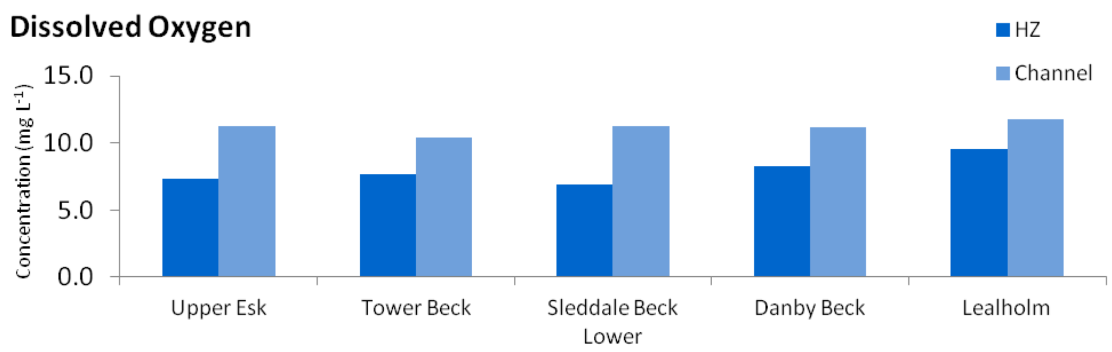


Figure 6.5 Dissolved oxygen concentrations for five hyporheic zone sites taken during baseflow on 23rd May 2012.

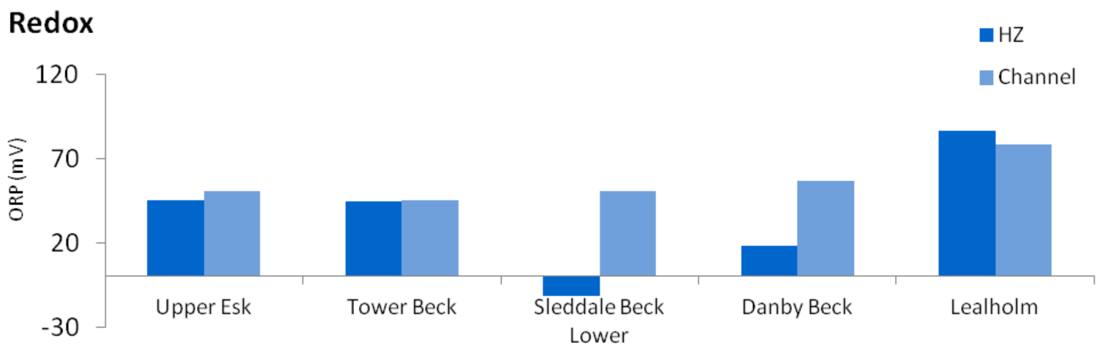


Figure 6.6. Redox potentials for five hyporheic zone sites taken during baseflow on 23rd May 2012.

Reducing conditions in the HZ will bring high nutrient concentrations, and potential for higher levels of toxic chemicals such as ammonium. Aquatic species such as the freshwater pearl mussel will then be continuously exposed to these conditions, therefore increasing the likelihood of mortality or stunted growth. The presence of low redox also gives an indication of the riverbed structure; lower rates of mixing between channel and interstitial waters will mean higher residence times of interstitial water. Freshwater pearl mussels and other aquatic species require a habitat with sufficient mixing and aeration through the gravels (Killeen, 2006), and a bed that is too compacted and choked with fines will be undesirable.

The redox values found in this study show an extreme contrast to those found in Killeen (2006), where every site sampled showed a value greater than 300 mV. These samples were taken between 2 and 8 cm below the bed, which is closer to the channel water than this study; however, even the channel water values do not exceed 300 mV, with an average of 89.4 mV. This poses a requirement for further redox testing, as the methods of testing between the two studies were quite different.

6.2.2 Nutrients

Fluoride

Fluoride is generally of similar values along the channel, but higher values are seen in the headwaters and tributaries, particularly Toad Beck, Little Fryup Beck and upper Great Fryup Beck (Figure 6.7a). The HZ values are higher than channel water; in Danby Beck the channel value is 0.14 mg l^{-1}, but in the HZ it is 0.36 mg l^{-1}. In the Lealholm channel it is 0.14 mg l^{-1} again, but in the HZ it is 0.26 mg l^{-1}.

Fluoride sources in a catchment are generally from rock mineral weathering and industrial emissions, but concentrations in natural waters are usually less than 0.1 mg l^{-1} (Chapman & Kimstach, 1996). In groundwaters the concentration is often higher, and high levels of fluoride can be toxic to animals, so the levels found in the HZ could have important implications to the survival of freshwater pearl mussels.

Nitrate

Nitrate values were low in headwaters and higher than the main channel in the tributaries (Figure 6.7b). Toad Beck and Little Fryup Beck were hotspots, with 2.83 mg l^{-1} in Toad Beck at the confluence with the channel; Little Fryup Beck had a value of 2.63 mg

l^{-1}. Lower Sleddale Beck and Danby Beck had similar values for HZ and channel, but Upper Esk, Tower Beck and Lealholm all showed a difference. The HZ values are all lower than the channel, with 1.20 mg l^{-1} in the Tower Beck channel, but 0.30 mg l^{-1} in the HZ; Upper Esk had 0.15 mg l^{-1} in the HZ and 0.46 mg l^{-1} in the channel, and finally Lealholm had 0.42 mg l^{-1} in the HZ and 0.80 mg l^{-1} in the channel.

These results suggest that nitrate in the channel comes predominantly from overland or shallow subsurface sources, and any nitrate in groundwater may be undergoing processes of denitrification. Denitrification occurs in anoxic or hypoxic conditions, suggesting that these processes had occurred in the soils before reaching the HZ (Rulik *et al*., 2000), as dissolved oxygen levels here are sufficient for sustained life (cf. Chapman & Kimstach, 1996). Rulik *et al*. (2000) found that the HZ of the River Sitka, Czech Republic, remained oxic even at 40 cm, and that nitrate was lowest at the downstream end of a riffle, where there is the lowest contribution of channel water, due to denitrification. Studies on a riffle in Speed River, Ontario also found that nitrate concentrations were higher in the channel then the groundwater (Storey, 2001; Storey *et al*., 2004).

<u>Ammonium</u>

In the channel, ammonium was undetectable, but in the HZ it was more visible (Figure 6.7c). It was particularly high in lower Sleddale Beck with a concentration of 0.33 mg l^{-1} and Danby Beck with 0.23 mg l^{-1}. As mentioned in Chapter 4, with a high pH, generally above 8.0, NH_4 is converted to NH_3, which is a far more toxic form of the compound to the aquatic environment (Heathwaite, 1993). In the HZ at Sleddale Beck and Danby Beck, the pH was 6.7 and 7.2 respectively; this may not be high enough to reach the predictions from Heathwaite (1993), but it is still high enough that this process may occur to some extent. This combined with low levels of nitrate show that there may not be sufficient dissolved oxygen for nitrification to occur, and low nitrate levels suggest conditions suitable for denitrification (Vinten & Smith 1993; Burt & Trudgill, 1993).

Despite these high levels of ammonium found in the HZ, they are not found in locations where freshwater pearl mussels have previously been thought to be abundant, if present at all. At Lealholm, a site considered to be the best habitat for freshwater pearl mussels

(Killeen, 2009), no ammonium was detected (Figure 6.7c). This may be due to higher flows and thus high pressures to force channel water through the HZs, bringing higher levels of oxygen and thus nitrification; this is reflected in the higher levels of nitrate found in the HZ here (Figure 6.7b). Interestingly, both nitrate and ammonium were high in Danby Beck (Figure 6.7b,c), but with one of the lowest redox values (Figure 6.6). Reducing conditions here will mean high rates of chemical transformations and differing stages of the nitrogen cycle.

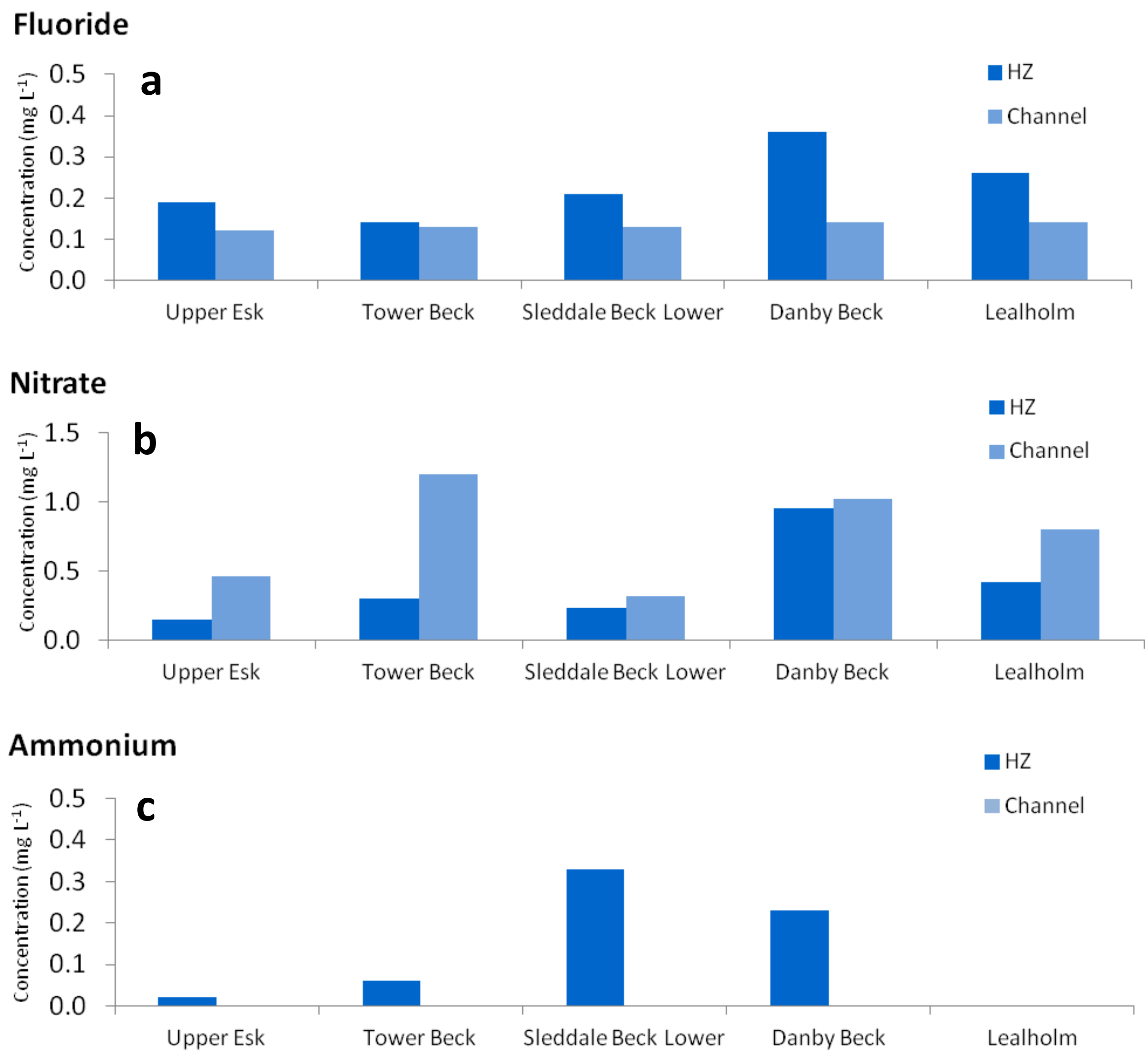


Figure 6.7. Concentrations of a) fluoride b) nitrate and c) ammonium from five hyporheic zone sites taken during baseflow on 23rd May 2012.

6.3 Redox and DO in the HZ during changing states of wetness

During baseflow, the DO in the HZ is low; lower Sleddale Beck, Upper Esk and Tower Beck are all below 8.00 mg l^{-1}, and Danby Beck and Lealholm are between 8.01 and 9.00 mg l^{-1} (Figure 6.8). During higher flows, the dissolved oxygen increases, reaching 14.8 mg l^{-1} at Danby Beck, and levels of between 12.00 and 13.00 mg l^{-1} for Tower Beck and Lealholm.

During baseflow, the redox levels are low, dipping below zero to a negative value of -11.7 mV at lower Sleddale Beck, and all others being positive values but below 80.0 mV. During higher flows the redox decreases further, with a low of -12.7 mV at lower Sleddale Beck and -1.9 mV at Tower Beck. The other sites are positive but below 30.0 mV.

The lower oxygen levels during baseflow would be due to a greater volume of groundwater than channel water. Lack of rainfall would mean less oxygenated water entering the channel and lower volumes of discharge would mean less hydraulic pressure to reach the interstitial areas. For these reasons, the concentrations would be expected to increase as they did in higher flows.

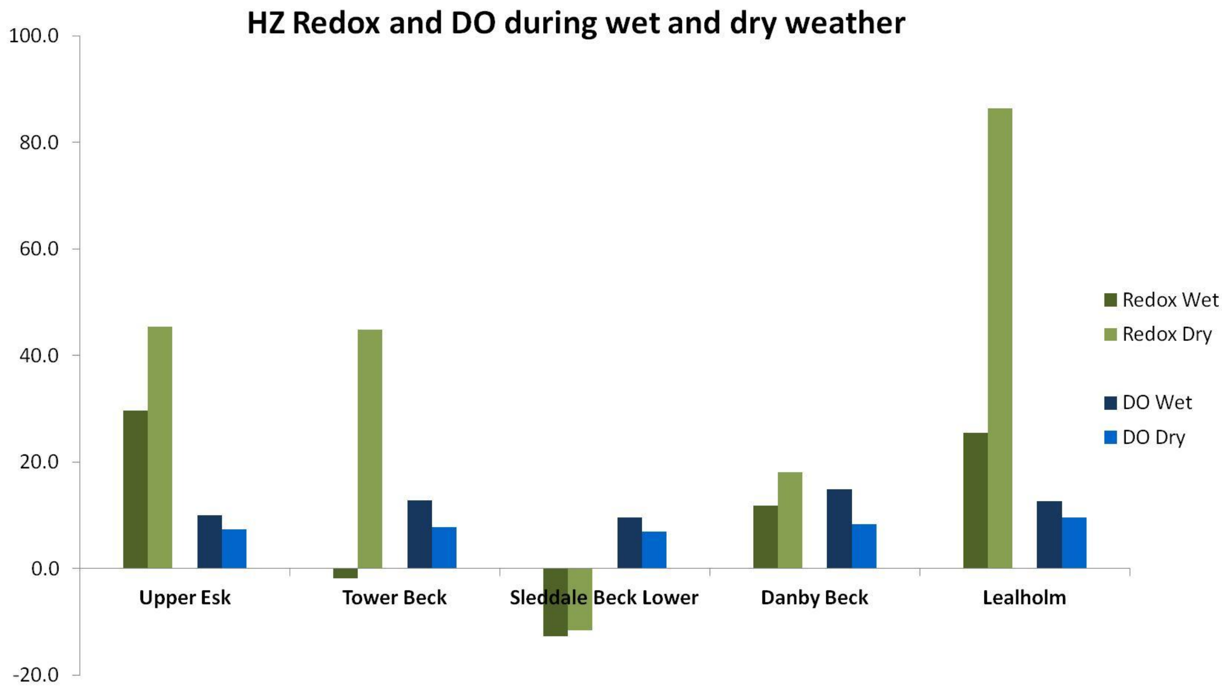


Figure 6.8. Comparisons between redox potential and dissolved oxygen during wet weather on 25th April and dry weather (baseflow) on 23rd May for the hyporheic zone at five sites.

Low redox potentials in baseflow would be expected for the same reasons as dissolved oxygen concentrations. However, with higher flows the redox did not increase, with the expected influx of less concentrated, oxygenated water. This suggests that the HZ was less influenced by the channel water, but more so by the greater volume of old water entering the HZ from groundwater sources, due to the rising of water tables and flushing of water through the catchment. Although oxygen concentrations are not of a particularly worrying level, redox values suggest a high potential for reducing conditions, which poses a concern with regards to toxic substances such as ammonium.

6.4 Summary

In summary, dissolved oxygen levels are generally lower than in the channel, but do not drop below 5 mg l^{-1}, which is the concentration proposed by Chapman and Kimstach (1996) as being problematic to aquatic life. In higher flows the concentrations of dissolved oxygen are yet higher, which is a positive sign for surface to sub-surface mixing.

However, redox potentials are extremely low, reaching negative values in some areas. In higher flows this redox potential decreases further, suggesting a greater importance of groundwater. These values pose concern for aquatic life, particularly for freshwater pearl mussels, as they require low nutrients and high levels of oxygen (Geist *et al*., 2006).

Nutrients are generally higher in the HZ, particularly fluoride and ammonium, which are toxic in high concentrations. Higher concentrations are not unexpected, but ammonium levels are a problem here as it suggests a lack of nitrification and thus a lack of surface to sub-surface mixing in the channel, a contradiction to the results from dissolved oxygen.

In contrast to other nutrients, nitrate is always lower in concentration, suggesting processes of denitrification either in the surrounding soils or the HZ itself. Denitrification occurs in anoxic conditions, so this, combined with the lower redox values and higher nutrient concentrations, suggests that dissolved oxygen in the HZ is not sufficient to sustain a desirable habitat and there is insufficient mixing with channel water.

7. Discussion

7.1 Spatial and temporal trends in water chemistry in the River Esk

From the results presenting in Chapters 4 to 6 a number of observations have been made about the characteristic processes that are acting in the River Esk catchment. An interesting discovery was the episodic acidification of the upper reaches during high flows; a combination of factors serves to explain the event, for example the high chloride inputs, industrial emissions and natural blanket peat of the moorland (Soulsby et al., 1995; 1997**)**. However, more research is needed on the frequency and severity of these acid flushes in the Esk, to deduce whether it could cause problems within the river habitats, and whether these events are more common than in previous decades. It may be that the acidification is a natural consequence of the geology and soils of the landscape, but it may also be due to increased anthropogenic effects of air pollution emissions or fertiliser application. It may be a more indirect effect of climate change, with an increase in saline precipitation reaching inland. Constant acidification events would have a marked effect on the aquatic ecosystem in the channel, in which case efforts to reduce chloride and other nutrient applications needs to be undertaken.

The responses of the channel to storm events found in this study suggest that the catchment has quite a high hydrological connectivity. Inputs of rainfall are followed rapidly by rises in stage (Figure 5.9), showing particular sensitivity to secondary inputs of precipitation through subsequent rises after initial peaks in stage. Evident inputs from groundwater are shown in more gradual slopes on the hydrograph, deduced from chemograph behaviour, again suggesting that connectivity is high, particularly when the catchment is wetted up. The nutrient response to these storms showed a classic dilution effect (Burt & Trudgill, 1993), with initial rises in concentrations due to loose material being carried by overland flow, seen before peaks in stage, followed by a dilution after exhaustion, on the falling limb of the hydrograph; this is then followed by a gradual rise from groundwater contribution. When antecedent conditions are higher, the hydrograph displays a flashier response, due to rapid overland flow rather than infiltration and therefore slower throughflow (e.g. Storm 1 in Figure 5.1a). Conversely when the catchment has been dry for a period of time, the hydrograph is less pronounced (e.g. Storm 2 in Figure 5.5a).

It is evident that agriculture is having an effect on the water quality of the Esk, particularly in Toad Beck and Stonegate Beck, where nutrient concentrations are consistently high, and the channel is surrounded by a large amount of farmland. However, most levels of nutrients are not of a high enough level to be of concern (Chapman & Kimstach, 1996). Nutrient levels are also quite low in comparison to studies on other rivers (Table 4.1). It is hard to compare levels of suspended sediment, as in this study only concentration was taken into account, rather than overall load. When comparing levels to Oliver (2000) in Table 2.1, mean nitrate levels during baseflow reach 1.07 mg l^{-1}, which is only slightly higher than the recommended <1.00 mg l^{-1} for optimum freshwater pearl mussel habitats. This level is particularly high in reference to Bauer (1988) in Table 2.1, who states that nitrate levels should be below 0.50 mg l^{-1} (Young, 2005). However, in the HZ nitrate levels are far lower than in the channel, with an average of 0.50 mg l^{-1}.

Despite the lower nitrate concentrations, other nutrient levels were often significantly higher in the HZ, particularly fluoride, ammonium and calcium. This shows that although hydrological connectivity from hillslope to channel appears to be high, connectivity between the channel and HZ is far less developed. Higher levels of groundwater than channel water in the HZ mean hypoxic and unfavourable habitat conditions. Redox values are of particular concern, due to the extremely low values found here, again highlighting the lack of vertical connectivity. It is here that reference levels by Oliver (2000) and Bauer (1988) present more of a concern, and strengthen the argument that riverbed conditions are not appropriate for aquatic survival.

7.2 Why are Mussels not recruiting in the main channel or tributaries?

These results have important implications for the conservation and revival of freshwater pearl mussels; previous research has found that they thrive in habitats that are low in nutrients and fine sediment, with high levels of oxygen (Geist *et al.*, 2006; Geist & Auerswald, 2007; Geist, 2010).

If the pH of certain areas of the Esk is consistently lower in times of high flows, as found on 25/06/12, then this will undoubtedly have a lasting effect on the growth and survival of Freshwater Pearl Mussels. Heming *et al*. (1988) found that when placed in water of pH 5.25, the mussels could easily maintain a gradient between the acidic water and their internal mantle fluid through neutralisation using their $CaCO_3$ reserves. However, continual depletion of calcium reserves, particularly in juveniles, will be detrimental during periods of valve growth, which is crucial for internal chemical regulation (Heming *et al*., 1988).

Simultaneously with these low pH values, high ammonium levels were also detected in the channel. Samples from the HZ were not collected at this time due to immersion of equipment; however, interstitial samples from the 23/05/12, when flows were low, detected high concentrations of ammonium, with 0.33 mg l^{-1} in Sleddale Beck and 0.23 mg l^{-1} in Danby Beck. These two sites have yielded high concentrations of ammonium in April as well. Ammonia (NH_3), as an un-ionised compound, is toxic to aquatic life, and freshwater pearl mussels are highly sensitive to it (Augspurger *et al*., 2003) as it can inhibit growth and decrease availability of oxygen. The predominant sources of ammonia in streams are threefold: the leaching and runoff of nitrate ions from the catchment, due to fertiliser application, animal excreta, industrial effluent and sewage outflows; a waste product of many plants and animals, and finally the product of organism decomposition (Vinten & Smith, 1993; Randall & Tsui, 2002). As pH increases, the levels of ammonium (NH_4) transforming to ammonia (NH_3) increases, which is far more toxic as it can enter the permeable membranes of aquatic life in this form (Heathwaite, 1993; Randall & Tsui, 2002). Any presence of this compound in the River Esk will be detrimental to the revival and survival of Freshwater Pearl Mussels.

Redox values recorded for the HZ were exceptionally low at some sites, reaching consistently negative potential at Sleddale Beck, very low values at Danby Beck and a negative reading at Tower Beck. Redox values in the stream itself were not particularly high in baseflow, increasing only in higher flows. Reducing conditions in the stream and substratum will have serious effects on the quality of the habitat and microhabitat for a Freshwater Pearl Mussel and other organisms, as it causes nutrients to transforms to more toxic compounds and reduces the level of available oxygen. Longer residence times will increase the volume of waste products that the aquatic species and plant life are producing, thus increasing the available chemicals and carbon dioxide for reactions. The better connected the HZ and channel water is, the better the conditions will be, as aerated flow will renew and refresh the waters.

Although many of the nutrients analysed for this study showed little difference between the channel water and interstitial waters, there were a number that showed a marked variation. Geist and Auerswald (2007) carried out a study whereby they compared channel and interstitial waters from streams with healthy populations of juvenile mussels, termed F streams, and streams with no juvenile recruitment (NF streams). They discovered that F streams were similar in concentrations, whereas NF streams were clearly varied, leading to the argument that studies of channel water quality for the survival of Freshwater Pearl Mussels were irrelevant (Geist & Auerswald, 2007). The parameters with substantial differences for the Esk are: dissolved oxygen, fluoride, calcium, redox potential and ammonium al differences. This is potentially due to processes acting in the catchment that are altering the water chemistry, either through inputs or biogeochemical processes. However, it may also be that the structure of the riverbed is not physically connected in a way that allows sufficient throughflow of water, thus leaving the water in the HZ with a longer residence time and higher potential for transformations in reducing conditions (Geist & Auerswald, 2007).

In order to determine the reasons for lack of juvenile mussel survival in the Esk, further research is needed on the quality of the HZ along the entire estimated 10 km reach (Killeen, 2006). Studies also need to be carried out on the quality of the riverbed structure, and thus the vertical connectivity of the water column. The results above suggest that discrepancies in certain parameters between the channel and interstitial areas are having a lasting detrimental effect on mussel survival during the juvenile life stages.

Persistently high concentrations of chemicals in the main tributaries, particularly Toad Beck, Little Fryup Beck and Stonegate Beck, but low concentrations of suspended sediment, leads to an assumption that fine sedimentation is unlikely to be an issue. Low nutrient concentrations in the main channel water, and relatively high oxygen concentrations means that water quality in the channel itself is of little concern. However, samples from the HZ of the channel show higher concentrations of nutrients, lower concentrations of dissolved oxygen and extremely low redox. Further investigation of these sites over a longer time scale would give a greater indication of the differences between the two zones. Higher nutrient concentrations in the channel when undiluted from runoff suggest that groundwater of high concentration is entering the stream via the HZ. However, lack of connectivity is leaving yet higher concentrations in the substratum, and this is a major problem for macroinvertebrate habitats. Consistently lower nitrate concentrations in the HZ may lead to an assumption that the more anoxic nature of groundwater in the HZ is causing higher rates of denitrification from NO_3 to N_2 or N_2O, or DRNA when ammonium is present (Korom, 1992; Burt & Trudgill, 1993; Heathwaite, 1993).

The water quality of the Esk is not of particular concern when based on the results from this study. However, disparities found between the channel quality and interstitial waters is of concern, as this is the zone in which Freshwater Pearl Mussels live. Despite efforts to improve catchment farming practices, diffuse pollution effects may be irreversible for years to come, due to the uncertain and variable residence times of groundwater. High levels of fertiliser chemicals may be in high abundance in groundwater, that had been applied decades before any conservation practices and laws were put in place (cf. Howden *et al*., 2011b). However, in the long term this will undoubtedly have a beneficial effect on the quality of the HZ, but it is a question of time, and whether it will be too late. For this reason, semi-artificial conservation of mussels is important, but only as a short-term strategy until habitats have been restored (Geist, 2010).

Changes in flow regime, and therefore changes to the structure of the riverbed, may also be important; long-term records of stage and precipitation are needed to see if any patterns can be deduced. Installation of weirs, for example upstream of Danby, will undoubtedly have an effect on the shear stresses acting on the bed and the hydraulic pressure gradients pushing through the sediment. This would also affect the connectivity of host fish along the channel, reducing their ability to reach further upstream, thus reducing the possibility for glochidia to survive to juvenile stages.

Populations of Salmon and Sea Trout have markedly decreased in recent decades (Killeen, 1999); they have continued to gradually increase in number in the past 15 years, recovering from extremely low levels (EA, 2011). A dispute over ownership of the tidal reach of the Esk is still unresolved, and so there are no regulations or controls on the amount of fishing (EA, 2011), leading to high levels of exploitation. Barriers to upstream fish migration are also a problem, as they reduce the extent of available habitats for both mussels and fish, a particular example is the Danby Mill Weir (EA, 2011). The River Esk is the only principal Salmon river in Yorkshire, and has conservation limits regarding spawning levels, and currently the Esk is considered 'at risk', as it does not reach the requirements for Salmon, whereas Sea Trout are considered as 'probably not at risk' (EA, 2011). Overall, the populations of host fish in the Esk are improving; however there is a still a way to go before they reach sustainable levels for freshwater pearl mussel survival.

7.3 Are there any locations along the channel that would make suitable sites for reintroduction of FWPM, based on findings.

By analysing the results from this study, it is possible to start looking at specific sites along the channel that would make suitable reintroduction sites than others, and better areas to focus on water quality improvements.

The headwater streams to the west of the catchment all display low nutrient concentrations compared to the rest of the channel network, which are ideal conditions for the Freshwater Pearl Mussel. Redox values were similar across the entire catchment during low flows, but in higher flows the higher redox values were found in the headwaters. This had the opposite effect in the HZ however, with redox reducing significantly in higher flows; although a steadfast comparison cannot be made, as these are two different events, two months apart. Smaller volumes of discharge in headwaters will mean a lower hydraulic connection with the interstitial waters, creating more of a gradient between the two zones. Of the headwaters, the Upper Esk site would be the most appropriate site, as redox conditions are not too dissimilar, sediment concentrations are low, dissolved oxygen levels are higher than sites around it and nutrient concentrations are also low. However, more research into conditions in this area during high flows are needed to gauge the behaviour of pH, and whether these low values found are a common occurrence or just one off events. Freshwater Pearl Mussels are able to adapt to short-term deficits in habitat requirements, but long-term exposure will not be suitable (Geist & Auerswald, 2007).

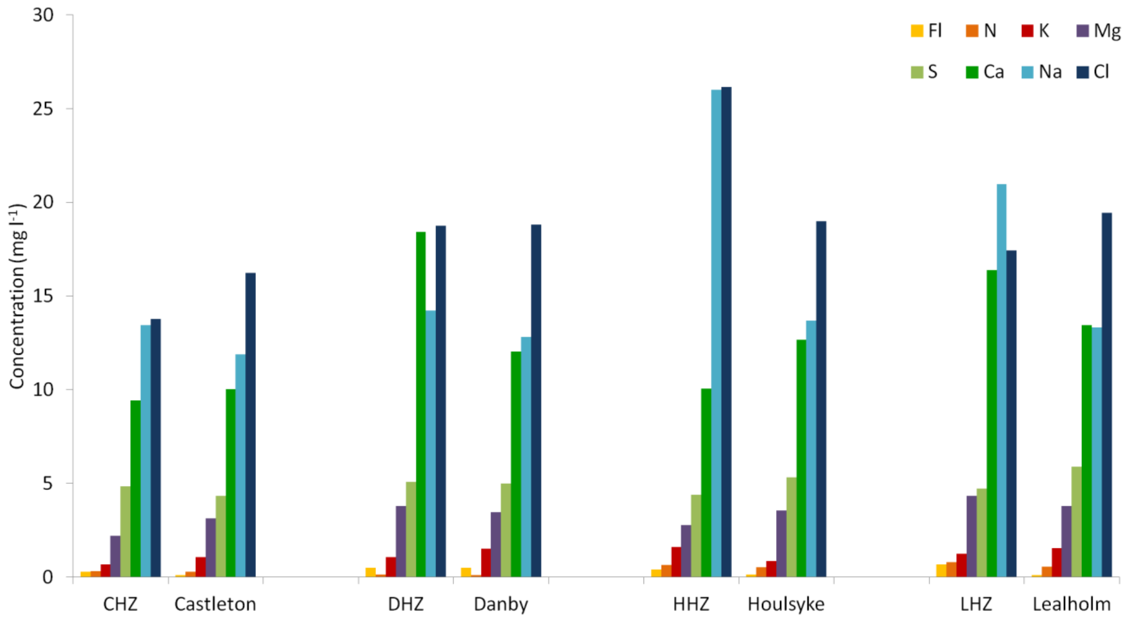


Figure 7.1. Values for parameters from the hyporheic zone and channel at four sites taken on 20th March 2012.

The major tributaries that were sampled for this study were repeatedly higher in nutrient concentrations than the other sites, particularly Toad Beck, Little Fryup Beck and often Stonegate Beck. There is a significant amount of farmland surrounding these becks, potentially providing the source to these high nutrient concentrations. There were no samples taken from the HZ for these tributaries, with the exception of Danby Beck, which proves to be a site with high conductivity, but lower nutrient concentrations than the other tributaries. The change of land use downstream from the headwaters shows a change from moorland and high amounts of forest vegetation, to agriculture and small urban areas with sewage effluent. These tributaries would not be a suitable location for Freshwater Pearl Mussels, although the lower reaches of Great Fryup Beck would be more favourable than others, despite the upstream reaches showing spikes of high concentration on occasion.

The main channel itself is where the remaining population of Freshwater Pearl Mussels are found, albeit smaller in number. Nutrient concentrations generally increased downstream, with the highest concentrations found at Egton Bridge and Grosmont; this is to be expected due to high volumes of discharge and larger catchment areas. Freshwater Pearl Mussels had previously thrived in the Esk, therefore reasons for this change must be due to a change in the river's behaviour or characteristics; it is unlikely to be due to channel water quality or sedimentation, and possibly it is due to interstitial water quality and a change in the channel's flow regime, leading to a change in gravel bed structure and therefore lack of vertical connectivity.

Figure 7.1 shows comparisons of parameters between the HZ and channel on 20th March 2012. The sites that show fewer disparities in concentrations would be more suitable than those with greater differences, as it would indicate a greater vertical connectivity. Castleton shows a similar picture for both interstitial and channel samples; however, a report from Killeen (2009) suggests that flows upstream of the Castleton site are far too strong for freshwater pearl mussels, but slightly downstream has good habitat potential (Figure 7.3). Although there were few samples taken for the HZ at Castleton, average nutrient values and conductivity are generally lower than other sites, and channel water is also of a higher quality, this shows high potential for a suitable habitat. Danby is also highlighted as a potential site for freshwater pearl mussels (Figure 7.3); it may not be as desirable as Castleton and Lealholm, as average nutrient values are generally higher.

The site at Lealholm has some of the highest redox and dissolved oxygen levels than those across the rest of the catchment; there were also particularly low nutrient concentrations and low SSC during baseflow. There was no ammonium detected in the HZ or indeed the channel across most of the sampling period, despite reaching 0.03 mg l^{-1} during a flood on 25th June. These conditions make a desirable habitat for the mussels, particularly with a low average nitrate concentration, and is recognised as a 'good pearl mussel habitat' by the Killeen (2009) report on reintroduction sites for the Esk. The braided stretch of river at Lealholm means that flows will be marginally lower than if it were one major channel, giving the mussels a certain degree of protection during flooding. The general water quality of the HZ here shows that there are some high levels of fluoride however, with an average of 0.39 mg l^{-1}. This may contribute a reason as to why juvenile mussels are not surviving here, as fluoride at this level could be toxic (Chapman & Kimstach, 1996).

The interstitial waters at Houlsyke had a very high conductivity, with the highest concentrations of fluoride, sodium and chloride; however the channel water was not particularly high relative to the other sites. The site flows through a farm with a small riparian strip to one side, but open farmland on the other, leaving the channel susceptible to both polluted runoff as well as leaching through subsurface flow and groundwaters. This would not be a suitable site for the introduction of Freshwater Pearl Mussel juveniles. Figure 7.2 shows the map made by the NYMNPA to highlight the site where habitats are suitable for juvenile mussel survival. Figure 7.3 suggests a stretch of channel through Houlsyke as a suitable habitat; from the results of this study, Houlsyke would be highly unsuitable for juvenile freshwater pearl mussels. This is highlighted in Figure 7.2, which shows the large differences between channel and HZ.

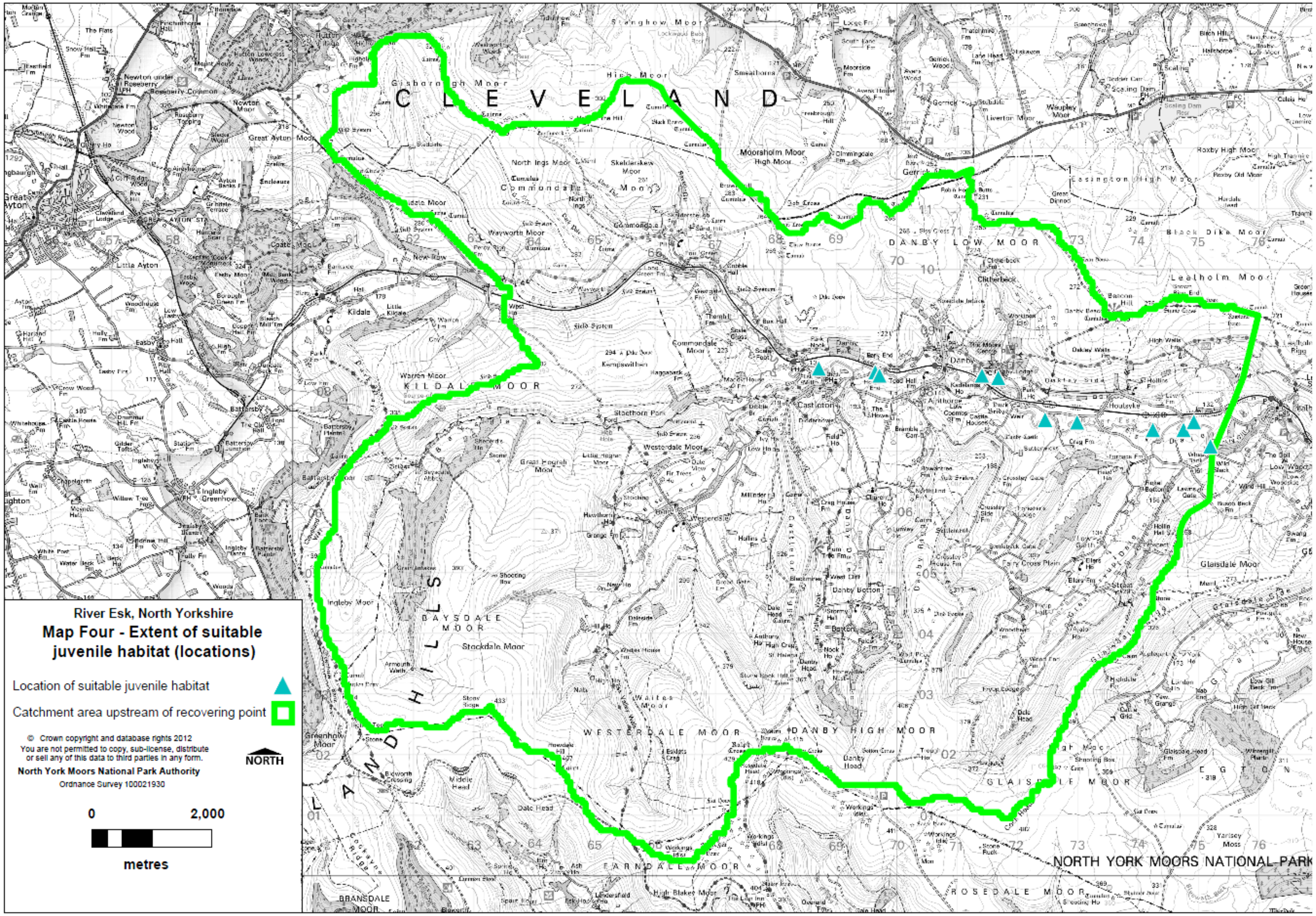
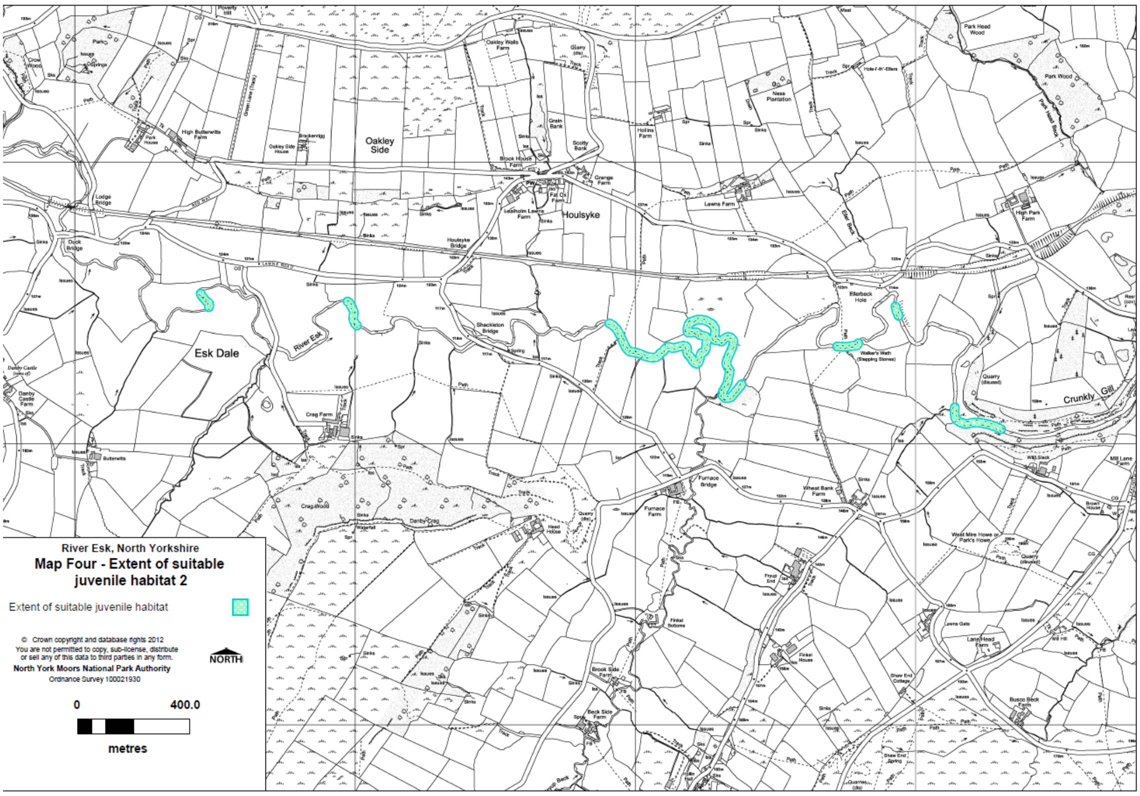


Figure 7.2. A map showing the suitable habitats for juveniles in the River Esk, created by NYMNPA (2012).



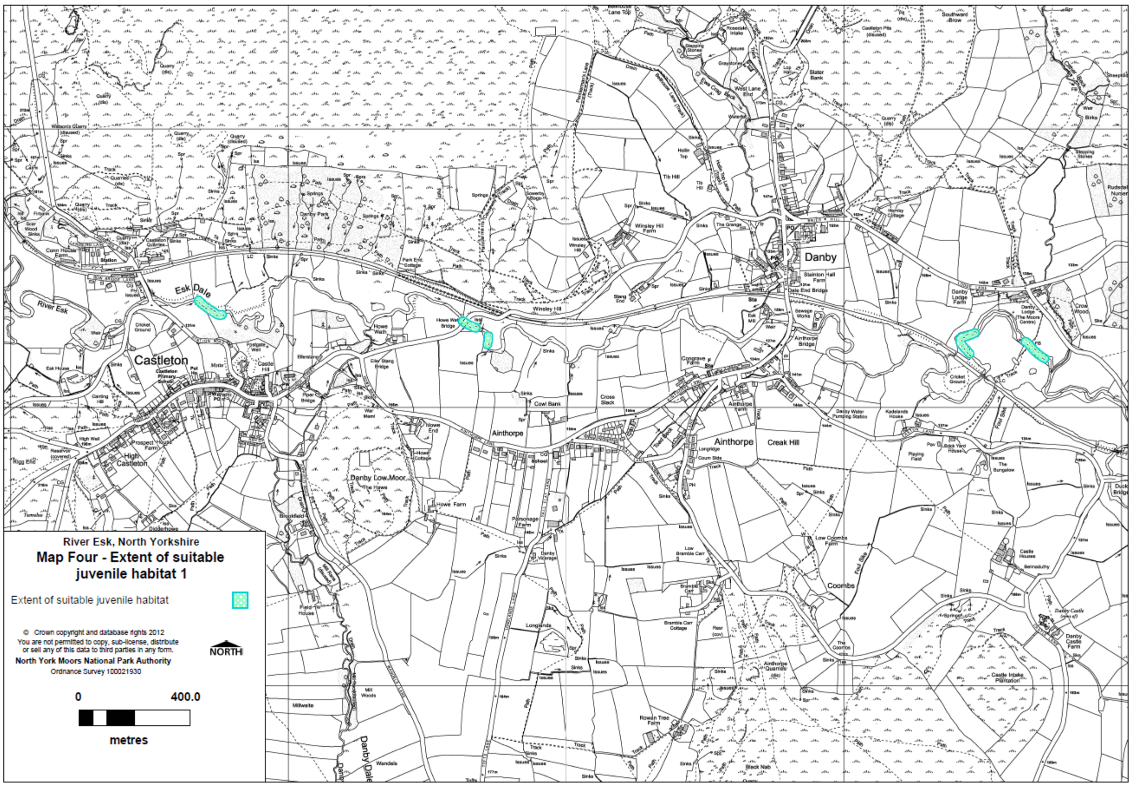


Figure 7.3. A closer view of the suitable habitats for juvenile mussels from Figure 7.0. NYMPA (2012).

8. Conclusion

8.1 Conclusions

To conclude this study a reflection on the objectives set in Chapter 1 must be addressed to assess whether the aim has been achieved. The aim of the study was to gain a better understanding of the Esk's response to inputs of diffuse pollution, and the subsequent impacts on in-stream habitats at different scales.

Information has been gathered on the water quality and hydrological behaviour of the Esk during a variety of storm events, which have in turn been analysed for their temporal changes, as well as spatial differences downstream. The following conclusions can be made:

- River response to changing inputs of rainfall depends largely on the antecedent moisture conditions. The catchment is relatively well connected, shown in the rapid response to changing stage in the channel in response to inputs of rainfall. These characteristics, along with anthropogenic control on nutrient/pollutant application, determine the behaviour of the channel water quality during a storm.
- During a storm, hydrograph shape and response reflects the shape and depth of the channel at each site; downstream the peaks often precede those upstream, due to inputs from large tributaries. Nutrient concentrations were relatively similar along the entire reach, but suspended sediment displays higher concentrations at the upstream site.

Monthly spatial surveys have enabled an analysis of catchment-wide water quality, providing snapshots of chemical concentrations, dissolved oxygen levels, redox and pH in a variety of land uses, from forested headwaters to lowland areas surrounded by agricultural fields and urban settlements. The following conclusions can be made:

- Headwaters are generally solute-poor and low in SSC. Main channel water quality increases in concentration with distance downstream, due to greater discharge and catchment contributing areas, but remains relatively low in concentrations overall. Main-stem tributaries had the poorest quality, particularly Toad Beck, Little Fryup Beck and Stonegate Beck, where consistently high levels of nutrients and extremely low redox levels were found. These results reflect land use, as tributaries are surrounded closely by agriculture, whereas headwaters are mainly forest and moorland.

- Monthly sampling has also revealed evidence for episodic acidification in the upper catchment. This poses a serious threat to freshwater pearl mussels and other aquatic species, particularly if it is a common occurrence.

Preliminary investigations have been conducted into the HZ, displaying a new vision into catchment processes and providing important discoveries into water quality that have not been captured previously. The results from the HZ have also been analysed in conjunction with simultaneous channel water measurements, to compare differences between the two environments and assess levels of connectivity between them. The following conclusions can be made:

- Nutrient concentrations are generally higher than channel water, and ammonium was present whereas in the channel it was not. An exception was nitrate, which was consistently lower in the HZ than the channel. Redox and dissolved oxygen levels were lower than the channel. Reducing conditions and low nitrate values suggest a combination of denitrification and DRNA.
- Results from the HZ highlight the unsuitability of certain sites whereas before they had been considered preferable, for example at Houlsyke. At the same time, some sites showed potential for mussel survival, for example at Castleton, where vertical connectivity between channel water and the HZ was high and water quality was of a relatively good standard.

These results have then been used to infer possible reasons for the failures in freshwater pearl mussel populations. At the end of this study, a number of conclusions can be reached:

- Freshwater pearl mussels are not recruiting successfully in the River Esk due to a combination of factors. Results from the HZ and channel water comparisons show that there is a lack of connectivity at some sites between the channel and channel bed. This may not have been true in the past when mussels thrived in the area. This could be due to changes in the flow behaviour, potentially as a result of weir installations and similar channel blockages.

- Lack of connectivity between the channel and HZ has implications for the redox, dissolved oxygen, nutrient concentration and pH of the interstitial zones, as without a constant throughflow of channel water, interstitial waters will have longer residence times, and become unsuitable for habitation. High levels of chloride, ammonium and fluoride found here will be highly detrimental to habitat suitability and species survival.

8.2 Limitations to the Study

This study was limited in a number of ways, most crucial of which was the short timescale in which sampling could be carried out. With a longer time period, annual data sets could have been created, to assess whether there is a clear seasonal change in the results found. Extended sampling of the HZ in summer months would also have been beneficial. Hyporheic sampling equipment often could not withstand the high flows during storm events, so lower discharges would have allowed for more frequent and abundant data collection, over a wider spatial range.

Pressure transducers and solar panels that had previously been installed at the autosampler sites were no longer functional. With the use of these pieces of equipment, continual stage data could have been collected at the specific locations, and discharge of the channel could have been calculated. Discharge data would have allowed for calculations of sediment load, as well as the analysis of rating curves.

Samples collected for the HZ were tested immediately after collection and every care was taken not to contaminate the samples; however, any changes in temperature may have caused slight changes to the composition of the water. The same is true for any other samples collected, which were stored in fridges and subsequently analysed as soon as possible after fieldwork, to prevent any bacterial growth from altering the chemistry.

Overall this study was limited by time, so it is crucial that more research is carried out in the area in future years, so that findings can be utilised to create effective and successful changes to the catchment.

8.3 Further Work

This study has introduced the importance of HZ water quality with regard to aquatic invertebrate conservation and revival. In order to progress these findings further, a more in-depth study is needed across a greater stretch of the River Esk, so that a catchment-wide image can be developed, particularly in areas where mussels have previously thrived. It is also important to look at the water quality of the HZ at varying depths below the riverbed, so that gradients of changes in water quality can be analysed.

Episodic acidification could be potentially fatal to freshwater pearl mussels, so analysis is needed on this over differing storm events and seasons. This would give a better understanding as to the frequency and magnitude of these events.

This study has been carried out with the assumption that juvenile mussel survival is the limiting life stage to their revival. However, more intensive, detailed studies are needed on the host fish population of the Esk. This way, a better understanding of the success of the glochidial life stage can be satisfied.

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