Investigating natural variability within headwater catchments in North Yorkshire, with regards to Margaritifera margaritifera conservation

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Investigating natural variability within headwater catchments in North Yorkshire, with regards to *Margaritifera margaritifera* conservation

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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 or other authors, which is referred to in the thesis, is acknowledged in the text.

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Abstract

Catchment management for water quality is an evolving process that requires social cohesion between a variety of stakeholders, effective management of land, coupled with a change in social behaviour, in order to effect a reduction in the flux of nutrients entering a river. Through creating a dynamic strategy which acknowledges the limitations of reducing nutrient concentrations entering a river, catchment managers are required to improve water quality according to the Water Framework Directive Legislation (2000/60/EC). Current catchment management processes have successfully reduced nutrient concentrations from point sources and are beginning to address nutrient concentrations associated with diffuse sources. In rural catchments, such as the one studied, diffuse pollution is influenced by land management practices, agricultural practices, and septic tank contributions. Highlighting the importance of adopting an integrated catchment management plan to address the headwaters within a catchment, this thesis has recognised the variations within water quality which can be overlooked by monthly spot sampling at a downstream location of a river catchment. Conservation efforts for the umbrella species *M. margaritifera* requires spatial and temporal investigations across a catchment to ensure successful relocation and recruitment. Hydrological connectivity plays an integral role within a catchment; new transportation routes can elevate nutrient concentrations, thus degrading water quality. Through investigating the different hydrological connections within a catchment, appropriate management practices can be identified. Spatial variations across the low-order tributaries of a catchment can have a significant influence on river water quality downstream. The catchment management practices, which go hand in hand with creating a healthy, self-regulating ecosystem, with minimal environmental degradation, must be aligned to these spatial variations in connectivity and pollution transport. This thesis investigates the spatial and temporal variability of water quality within three rural subcatchments of the River Esk in the North York Moors, in particular the influence of land use, differences in management practices and the importance of viewing the hydrological connectivity at different scales of a catchment. Fortnightly sampling using a YSI probe and anion and cation analysis was undertaken. The results of the research led to suggestions for addressing water quality variations across the headwater tributaries with the aim of improving the recruitment of the umbrella species *M. margaritifera* in the River Esk catchment.

Glossary of Terms

BOD – biological oxygen demand

Brash – material composed of wood to reduce the effect of bank scour

Buffer strips – an area of between 5-10m of fenced off land set aside by the farmer to allow the growth of coarser vegetation and trees

COD – chemical oxygen demand

Eutrophication – elevated levels of nitrates and phosphates from agricultural and urban runoff, which causes a bloom in algae plants and reduces the amount of light and dissolved oxygen available in a river

Glochidia – parasitic stage of the lifecycle of *M. margaritifera*

Poaching – stock (in the case of the Esk cattle or sheep) eroding the river bank and releasing a flux of sediment

Recruit – successful breeding of young Freshwater Pearl Mussels

STW – Sewage treatment works

Umbrella species – a flagship used to concentrate conservation efforts with the hope to improving an entire ecosystem

WTP – Wastewater treatment plant

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1. Introduction

1.1 Context

Rivers and their ecosystems are remarkably resilient in their ability to recover from physical and chemical disturbances (Gore & Douglas Shields, 1995). Rivers are self-regulating systems that have the ability to respond to environmental changes and have the ability to process nutrients in a water body. Geomorphological features such as riffle-pool sections can draw up groundwater, increasing flow and thus diluting nutrient concentrations. Changes in land use may degrade the overall health of rivers. As human activity, such as the intensification of agricultural practice, alters the landscape, the drainage network expands, re-connecting previously disconnected fields directly to a watercourse, resulting in elevated losses of sediment, nitrogen and phosphorus (Collins & Zhang, 2016; Foster *et al,* 2011; Johnes *et al*., 2007). Ditches are often installed to drain fields and improve their yield, creating direct pathways for runoff and stored nutrients to enter a watercourse, which in turn reduces the ability for a river to self-regulate.

Since the introduction of the Water Framework Directive (2000/60/EC) and Nitrates Directive (91/676/EEC), improving water quality has been a key driver of river restoration. A review of the success of the Water Framework Directive concluded that only 17% of water bodies had reached Good ecological status (Defra, 2015). Water quality is degraded by the input of organic effluents (Miserendino, *et al* 2008) which can impact aquatic and riverine ecosystems. Water quality can be defined as the degradation of physical, chemical or biological traits of a water body (EA 2016; Brooks *et al.,* 2013). Elevated nutrient concentrations are a major cause of waterbodies not achieving Good ecological status (EA, 2018). Phosphorus levels have increased from the 1950s to the 1990s, with the decrease in concentrations post 1990s associated with improvements of sewage treatment works (EA, 2017). Nitrate concentrations have seen two increases, the first during World War II as large areas of land were converted to agriculture and the second in the 1960s associated with greatly increased fertiliser use (Burt *et al,* 2011). The necessity to improve water quality and restore rivers to more natural conditions is beginning to be achieved through active catchment management. There has been a recent shift away from the 'black box' approach to river restoration; instead managers are adopting a more holistic, natural approach, attempting to create rivers which can adapt to climate change.

Legislation aimed at reducing point source pollution has brought the issue of diffuse pollution to the fore. In rural catchments, agriculture is increasingly blamed for contributing approximately 40% of diffuse pollution and thus the degradation of water bodies; however, it is only recently that the negative effect on water quality caused by septic tanks and sewage treatment works has been highlighted in rural catchments (Taylor *et al* 2016). Diffuse urban pollution provides a difficulty for regulation because source tracing and its episodic nature inhibit mitigation processes (Ellis & Mitchell 2006). As legislation and water body managers have realised the scale and issue of diffuse pollution, a new approach has begun to be adopted to remedy the effects. Catchment managers have started to consider the importance of spatial and temporal changes of nutrients in the context of a catchment, to effectively target diffuse pollution and thus improve waterbody status. Through investigating the natural variations within a catchment, Pinay (2009) postulates that catchment managers could address the problem of intrinsic limitation of nutrient removal in landscape structures; in this way tackling the impact of land use change on river flow could help understand the consequences of interdependency of element cycles and the cumulative effect of the long-term human impact on rivers.

Water quality has implications for biodiversity. Freshwater Pearl Mussels *(M. margaritifera)* are good indicators of the health of a river; they are considered to be an "umbrella" species due to harbouring certain characteristics which match those of flagship species (Geist 2007). The habitat requirements of adult and juvenile pearl mussels differ, due to the adult's resilience to changes in an ecosystem (Geist 2007); thus, rivers that can sustain an adult population may not be able to recruit juveniles due to degraded water quality. Fine sediment can limit oxygen supply in the interstitial zone (Geist 2007); therefore, reducing sediment supply by mitigating erosion should benefit juvenile recruitment. Negative effects of increased fine sediment deposition on *M. margaritifera* habitats have been reported by Bauer (1988), Buddensiek *et al* (1993) and Geist (1999a, b). *M. margaritifera require* good hyporheic zone exchange, high oxygen levels, and low nutrient concentrations in order to thrive (Bauer 1998, Buddensiek *et al* 1993, Geist 1999a). *M. margaritifera* can filter 50 litres of water a day (Cosgrove & Hastie 2001). Therefore, improving water quality and restoring rivers to a 'natural' state promotes recruitment and thus sustains a healthy river. More research is required to improve *M. margaritifera* habitats and restore populations to ensure natural recruitment of the species. Therefore, examining spatial and temporal trends in water quality with the hope to quantify changes at a catchment level will help with future conservation of *M. margaritifera.*

1.2 Aims and objectives

The overarching aim of this thesis is to develop the concept of integrated catchment management by examining water quality in three catchments with regards to *M. margaritifera* conservation to inform practices of management. The research is based in a rural catchment of the River Esk, in the North York Moors, where land drains, ditches, small tributaries, septic tanks and sewage treatment works can all affect the water quality. Findings will be embedded into current management practices. Objectives are as follows:

1. To examine water quality in three catchments (Danby Beck, Great Fryup Beck and Toad Beck) through undertaking various water quality analyses such as

conductivity, temperature, pH, dissolved oxygen (DO), anions and cations, chemical oxygen demand (COD) and biological oxygen demand (BOD).

2. To compare water quality in all three catchments investigating temporal and spatial changes to water quality in a catchment.

3. To provide solutions for addressing nutrient removal within a catchment context in the hope of conserving *M. margaritifera.*

1.3 Thesis structure

This chapter has provided the context for this study and outlined the aims and objectives. Chapter 2 provides a discussion of the literature that has shaped this study. Chapter 3 introduces the study site and outlines the methodology, including the types of analysis undertaken and the sample locations. Chapter 4 investigates the temporal variations of certain water quality parameters and provides reasons why they change. Chapter 5 discusses the spatial variations of water quality parameters, once again providing reasons for how and why they change. Chapter 6 compares point sources and diffuse sources and provides examples of how a diffuse source can become regarded as a point source as the catchment area of investigation increases. Chapter 7 discusses the results found in this thesis and their implications. Chapter 8 concludes the thesis offering limitations and suggestions for future work.

2. Literature review

2.1 Introduction

This section discusses relevant issues surrounding employing an integrated catchment approach to improve water quality for *M.* margaritifera. The literature discussed in this chapter underpins the aims and first objective stated in Chapter 1, but also provides a rationale for the data collected.

2.2 Integrated Catchment management

The greatest challenge of catchment management is to understand the science behind it (Newson, 1992). Changes in management approaches are associated with the ways in which we use our rivers (Downs & Gregory, 2004). Early anthropogenic interventions in river activity involved flow modifications for irrigation; later activities involved channel modifications to facilitate crossings. With navigation came large-scale structural modifications of rivers, such as dredging and the removal of woody debris. Rivers thus became re-aligned for construction of roads and railways and later for flood control. By the 19th century, engineered rivers were becoming the new norm, following the lead of channelization of rivers such as the Rhine. The 20th century saw more extensive lengths of rivers channelized as civilisation and agriculture spread to floodplains. The era of 'technology can fix it' was not without its challenges (Leopold, 1977): the primary reason for the failures in river management was that 'engineered rivers went against natural rules' such as the disconnection of the floodplain (Newson, 1992). As environmental awareness surged, the approach shifted from engineered to soft management, as Winkley (1972) describes, 'working with the river not against it.' The shift in approach was first undertaken to mitigate or enhance previous management, later to rehabilitate and restore rivers.

Three phases of management have been identified by Downs and Gregory (2004): (1) management of perennial water sources for local agriculture and domestic supplies; (2) embracing management for navigation, water power and local regulation of floods for irrigation and drainage; and (3) regulation by large structures (including channelization) as part of a complex basin and inter-basin development for power generation, water supply and/or flood control. Technological development was thus a driving factor for changes in management techniques. The 'quantitative revolution' in the 1960s provided managers with the ability to examine in detail the environmental impacts of management methods (Petts et al., 2000). This led to an improved understanding of river processes and the impact of anthropogenic activity (Downs & Gregory, 2004) and in turn, the emergence of catchment management.

Integrated catchment management involves non-structural (vegetative) and structural (engineering) practices (Gergersen *et al.,* 2007) and is a process through which people can develop a vision, agree shared values and behaviours, make informed decisions and act together to manage the natural resources of their catchment (Murray – Darling Basin Ministerial Council, 2001). The overarching focus is on how the varying activities affect the relationships among land, water and other natural resources within a catchment. It uses tools and techniques such as physical, regulatory, or economic means for responding to problems. Collaborating with individuals, stakeholders, and government bodies creates a cohesive, holistic approach to managing a catchment. In this way, integrated catchment management embraces the sentiment that good water management is essential for sustainable development (Smith, et al., 2015).

DEFRA (2013) states that adopting a catchment-based approach (CaBA) will promote the development of more appropriate River Basin Management Plans, driven by top-down legislation such as the WFD. CaBA partnerships drive cost-effective practical delivery on the ground, enhancing biodiversity, reducing flood risk and increasing resilience (CaBA, 2017). Demonstration Test Catchments, a new initiative testing the effectiveness of on-farm mitigation measures at reducing diffuse agricultural pollution whilst maintaining food production capacity, is being trialled in four catchments in England (Outram *et al,* 2014). It is hoped these catchments will provide evidence to characterise rural diffuse pollution problems (Collins *et al*., 2015). Additionally, the adoption of catchment sensitive farming is providing quantification of diffuse pollution from agriculture (Zhang *et al,* 2012). Working with NGOs, water companies, local authorities, landowners, angling clubs and academics, various stakeholders are informed at all levels to provide cohesive management practices benefitting all stakeholders.

As a result of changing management practices, the UK has seen a shift in the way in which rivers are managed, adopting an integrated concept, which provides a significant cost-benefit ratio of 1:8: every £1 provided from a catchment management funding stream attracts a further £8 of investment (CaBA, 2018). The driving force behind the shift in strategy stems from a reduction in the amount of funding available; thus, through working in partnership larger schemes can be implemented achieving greater improvement of water quality. Adopting an integrated catchment management approach can engage an array of stakeholders, bring about behavioural changes and thereby reduce the concentration of nutrients entering a river.

2.3 The role of hydrological connectivity

2.3.1 Key issues

Connectivity is crucial to our understanding of catchment behaviour (Lane *et al.,* 2003, McDonnell *et al.,* 2007, Pringle, 2003, Tetzlaff *et al.,* 2007). Understanding the land-water linkages is vital when studying the integrated biogeochemical cycles in a catchment (Steiglitz *et al.,* 2003). Bracken and Croke (2007) identified three 'types of connectivity: (1) landscape connectivity, which refers to the physical coupling of landforms (hillslope to channel) within a drainage basin;

(2) hydrological connectivity, which refers to the passage of water from one part of a landscape to another and is expected to generate some catchment runoff response; and (3) sedimentological connectivity, which refers to the physical transfer of sediments and attached pollutants through the drainage basin and may vary considerably with, amongst others factors, particle size.

Key issues within research on hydrological connectivity highlighted by Bracken *et al* (2013) are: (1) how patterns and processes at the hillslope scale determine water transfer at the catchment scale; (2) how management of hydrological connectivity can be applied across and between environments; (3) how the concept of hydrological connectivity works at different scales; and (4) understanding the role of spatial and temporal variability in input rainfall and how this influences functional controls of hydrological connectivity. Bracken *et al* (2013) suggest catchment managers must find new ways of thinking and working in hydrology; otherwise we may not exploit the full potential of the concept of hydrological connectivity. Shifting from viewing hydrological connectivity as a catchment property that either does or does not emerge, Ali and Roy (2009) argue that lateral, longitudinal and vertical catchment linkages should be thought of as a probability distribution both temporally and spatially. One important aspect about hydrological connectivity that is fundamental to the research presented here is how management should consider linkages between different areas within a catchment in a lateral, longitudinal and vertical way and how this may vary with season. Such an understanding could help improve the effectiveness of interventions.

The main pathways which connect a catchment are: surface runoff, interception, infiltration, percolation and groundwater flow (both shallow and deep). The ability of a pathway to connect across a catchment is reliant upon a number of variables including: soil type, compaction, rainfall, geology, pore size, land use and land management. As anthropogenic activity increases, land use becomes a significant control of nutrient pathways. Compaction, vegetation cover and soil porosity can reduce the amount of infiltration and percolation in a catchment (Slattery & Burt, 1997).

2.3.2 Connectivity management

Connectivity has proved a useful concept for catchment managers for identifying the non-linear relationship between on-site disturbances and off-site response (Bracken & Croke, 2007), although Pringle (2001) suggests such management has not yet been successfully achieved. This is because hydrological connectivity is rarely considered in practice and is often ignored until water quality and quantity issues arise. Furthermore, alterations to hydrological connectivity occur outside management boundaries (Pringle, 2000). A further reason why management of hydrological connectivity is difficult is because it is an emergent process, which occurs at the hillslope scale as a consequence of plot-scale interactions (Ali & Roy, 2009). Secondary controls of hydrological connectivity are: functions of disturbance, biological transformations and anthropogenic inputs of organic matter and nutrients (Steiglitz *et al.,* 2003).

The dynamic nature of hydrological connectivity has implications for sampling, as internal linkages vary over different time scales due to the changing availability of surface/subsurface water (Ali & Roy, 2009). One of the most popular approaches for investigating connectivity is sampling soil moisture connectivity (Ali & Roy, 2009); however, spatial soil moisture patterns do not always reflect the hydrological corrections being made, nor are they applicable across all catchments and environments (Bracken *et al.,* 2013). Nadeau and Rains (2007) confirm hydrological connectivity exists as a continuum, with hydrological connectivity between headwater rivers and downstream rivers existing somewhere in between tight linkages of continuum such as the relationship between rainfall and run off and weak linkages (Nadeau & Rains, 2007). The preferential state hypothesis suggests a catchment can have two characterisations: a wet state and a dry state; the dry hillslope region is unconnected with strong vertical flow and unorganised soil moisture spatial patterns (Grayson et al., 1997). The river continuum concept may have underplayed the lateral dimensions of a river ecosystem (Downs & Gregory, 2004) and Statzner and Higler (1985) believe it to be a simplification of reality, which highlights connectivity and a holistic approach.

The research discussed underlines the importance of integrating understandings of hydrological connectivity and water quality. Humans have more than doubled global land-based cycling of nitrogen (N) and phosphorus (P) and hence it can be difficult to determine the best scale at which to manage land and water resources. There is uncertainty about pollution sources, pathways and impacts, about the occurrence of spatially and temporally stochastic pollution events, adding to challenges for catchment management. The technical problems of catchment management are also cross-sectoral. For instance, legal authorities for water supply and protection many span multiple agencies and levels of government. Inter-agency communication and coordination is thus required. The absence of market incentives to reduce pollution motivates intervention by governmental and non-governmental entities. Even if a diffuse pollution source can be identified, the monitoring and enforcement costs associated with resolving the pollution source can be prohibitive and so action is not always taken.

2.4 Catchment variations

Headwater tributaries, including the three test catchments in the River Esk catchment studied here, receive quantities of water from numerous sources, including snowmelt and groundwater (Nadeau & Cable Rains, 2007). A review undertaken by Burt and Pinay (2005) demonstrated there is a large variability of nutrient fluxes from small (>10km^2) tributary basins, but little variability from the entire basin. This confirms a low signal-to-noise ratio in large basins, but high signal-to-noise in smaller tributaries (Strayer *et al,* 2003); the three subcatchments in the River Esk can be categorised as smaller tributaries in this regard. Additionally, Nadeau and Rains (2007) suggest the structure and function of headwater rivers are strongly controlled by local physical, chemical and biological conditions. Burt and Pinay (2005) suggest that the spatial arrangement of land cover continues to be significant at the intermediate scale, and thus spatial and temporal investigations are necessary. The relationship between land use conversion and ecological response is difficult to establish because of the large variation and distribution of land use within a catchment; major changes in land use may take decades to stabilise, ecological responses may lag behind physical habitat modifications, and little is known about the effectiveness of land management adaptions (Strayer *et al* 2003). Few studies have attempted to transfer reach- and plot-scale understanding of subsurface hydrological connectivity to the catchment scale between landscapes and streams (Caruso, 2015). Additionally, quantification of nutrient concentrations in small catchments are complicated by nutrient fluxes which occur at seasonal, event and inter-annual timescales (Gascuel-Odeoux *et al,* 2010; Moatar *et al* 2013; Thomas *et al* 2016a). Furthermore, the nutrient residence times can be of the order of decades within soil, unsaturated zones, and groundwater (Howden *et al* 2011; Kolbe *et al* 2016; Meter *et al* 2016; Sebilo *et al,* 2013).

An understanding of variance structure is necessary to scale predictions or implement effective interventions in dynamic landscapes (Haygarth *et al*. 2005, Lowe *et al.* 2006; Temnerud *et al.* 2010). Lateral fluxes are influential in stream networks, as delivery of nutrients from upstream environments is often a magnitude greater than in-stream production or removal (Brookshire *et al* 2009; Lefebvre *et al.* 2007). Despite the introduction of the WFD (2000), nutrient concentrations remain high, partly because of the difficulty associated with monitoring and predicting water quality in complex freshwater landscapes (Abbott *et al.* 2016; Isaak *et al.* 2014; Meter *et al* 2016). The WFD imposes thresholds of annual loads, an appealing strategy which combines smaller catchments within a larger river catchment (Howarth 2008; Reed & Harrison 2016). However, there is growing evidence that suggests a need to understand the source and sinks in headwater catchments to reduce downstream nutrient fluxes (Alexander *et al.* 2007; Bishops *et al.* 2008; Brookshire *et al.* 2009; Burt & Pinay 2005; McDonnell & Beven, 2014.) Amplitude and frequency of chemical variations within a catchment differ dependent upon scale. Nutrient loads in catchments greater than 100km^2 are deterministically associated with percentage of agricultural cover and associated nutrient inputs (Howarth, 2008; Jordan *et al.* 1997; Omernik *et al.* 1981), but nutrient loads vary widely despite similar land cover in drainage basins smaller than 20km^2 (Brookshire *et al.* 2009; Burt & Pinay 2005; Lefebrve *et al.* 2007; Schilling *et al.* 2013). Thus, the relationship between land cover and nutrient loads within a catchment requires spatial and temporal investigations for effective management to be achieved. Assuming spatial variability in water chemistry in a river network depends primarily on the extent and connectivity of upstream sources (Abbott, Zarnetske, Pinay *et al* 2018); quantifying the variations within a catchment can provide strategic targeting of nutrient sources.

2.5 Water quality

Adhering to current legislation in the United Kingdom is an integral part of creating and sustaining an integrated catchment management plan. The creation of the Water Framework Directive (WFD), adopted in 2000, introduced a comprehensive river basin management planning system to help protect and improve the ecological health of our rivers, lakes, estuaries, coastal and groundwaters (EA, 2015). It set out to restore water bodies to good ecological status by 2015 (Defra, 2016). River basin management plans are currently in their second cycle, after the initial phase finished in 2015. Reviews of the success of the legislation concluded further specific pollutants should be added to the Directive, and more stringent regulation should be implemented. The Shellfish Directive, a daughter directive of the WFD implemented in 2006, was specifically created to improve the protection of bivalve and gastropod molluscs. The River Esk is a shellfish watercourse because of the population of *M. margaritifera.*

Other relevant legislation such as the Habitats Directive and Birds Directive were implemented earlier, in 1992, with the aim to promote the maintenance of biodiversity to maintain or restore natural habitats and wild species (JNCC 2017). The North York Moors is heavily influenced by the Habitats and Bird Directive legislation, with areas designated as Special Areas of Conservation (SACs) and Special Protection Areas (SPAs). This legislation ensures that protected areas will not suffer from developments that can encroach or damage the environment or its species. Should a proposed development cause concern, assessments are required to assess potential damage and provide mitigation solutions.

Diffuse pollution has become a key cause of pollution in UK rivers, with increasing concentrations of nitrate and phosphate, organic matter, sediment and pesticides entering river systems from diffuse agricultural sources. As legislation continues to advance, diffuse pollution takes a more central role with approaches such as catchment sensitive farming and catchment-based management being more widely adopted. With recent developments in the political sector, the effects of Brexit on water legislation and environmental practices will be interesting to follow (Robins et al 2017). Implicit here is that improvements in our understanding of water quality should help improve catchment management.

The considerable anthropogenic nitrogen mobilisation due to agricultural waste water discharges, provides detrimental impacts on the aquatic environment (Lavelle *et al,* 2005).

However, the transfer of nitrogen and phosphorus to rivers across catchments is spatially and temporally variable (Outram *et al*., 2015). Once mobilised, nitrogen is involved in a sequence of transfers, transformations and environmental effects (Galloway and Cowling, 2002, Galloway *et al,* 2008) and thus the management of a single source is not always efficient (Oenema, 2011) so nitrogen needs to be managed in an integrated way;. Therefore, applying both the first law: nitrogen can be transformed into difference species; and the second law: since nitrogen has the natural tendency to dissipate, an integrated approach must be taken (Oenema, 2011). Such an integrated catchment management approach can take two forms: the first considers that vertical integration is linking source and impact (Oenema, 2011) and considers the upstream and downstream collective.ly The second is horizontal integration, in which nitrogen species, sources and emissions are combined in the management plan (Oenema, 2011).

2.6 Sources of pollution

2.6.1 Background to Diffuse pollution

There are various definitions of diffuse pollution. The Government's definition of diffuse pollution is: unplanned and unlicensed pollution from farming, old mine workings, homes and roads (Gov, 2012). Such a definition suggests diffuse pollution can be classified into agricultural and non-agricultural sources, with agricultural pollution attributing an estimated 33% and non-agricultural attributing an estimated 14% respectively, rivers across the UK that fail to meet WFD legislation (Gov, 2012). Using a slightly different definition, Campbell *et al* (2004) state diffuse pollution is the truly non-point source contamination, together with a myriad of individually minor point sources. Similarly, D'Arcy and Frost (2001) define diffuse pollution as non-point source pollution, such as sheet runoff or seepage into groundwater. For the purpose of this thesis, diffuse pollution is defined as 'sporadic pollution over a number of pathways entering a catchment'.

SEPA (1996) highlighted the importance of diffuse pollution as the scattered individual discharges that cannot be controlled, although Heathwaite *et al*. (1996) suggest that identifying the causality of diffuse pollution is difficult to prove. Diffuse pollution impacts are often associated with nutrient enrichment, contamination of sediments, and siltation (Campbell *et al.,* 2004). Toxic impacts can be intermittent and difficult to identify, made even more difficult through masking by gross pollution from the major point sources such as sewage and industrial effluent (Campbell *et al.,* 2004). In developing countries, diffuse pollution can cause harm to public health if basic sewerage networks aren't installed and seepage from both agricultural waste and human waste occur.

2.6.2 Diffuse pollution from agriculture

Agricultural diffuse water pollution remains a notable global pressure on water quality (Taylor *et al.,* 2016). It has long been recognised as a significant environmental issue at the catchment, regional and national scale (Johnes & Burt, 1991; Heathwaite *et al* 1996; Carpenter *et al,* 1998*;* Johnes *et al,* 2007; EA, 2007; McGonigle *et al,* 2012; Withers *et al,* 2014; Zhang *et al,* 2014). Agriculture accounts for around 70% of UK land areas (McGonigle *et al.,* 2012) and hence Campbell *et al* (2004) suggest that diffuse pollution is both an indirect and direct consequence of anthropogenic activities. Agricultural diffuse pollution is cited as a significant pressure in 40% of rivers and coastal water bodies (Taylor *et al.,* 2016), whilst the EA estimates that 33% of water course failures to adhere to WFD legislation are attributed to agricultural diffuse pollution issues (McGonigle *et al.,* 2012). In this way it is estimated that agriculture accounts for 61% of total nitrogen load and 28% of total phosphorus load within surface water bodies in the UK (Taylor *et al* 2016). Recent modelled cross-sector source apportionment for England and Wales suggests agricultural contributions of total nitrogen, total phosphorus and sediment are dominant in 53% of inland water bodies (Zhang *et al* 2016. Howden *et al* (2013) suggest that if the production of affordable food increases in importance on the political agenda, the challenge to reduce diffuse pollution from agriculture will become even greater.

Diffuse pollution arising from agricultural activity is thus a major concern within the aquatic environment (D'Arcy & Frost, 2001). However, implementing diffuse pollution controls is challenging due to its spatial and temporal contributing sources (Zhang *et al,* 2017). Pollutants from agricultural land can occur in a dissolved form or can be adsorbed on to particulate soil material. Distinguishing between land use decisions and pollution prevention activity is therefore important for catchment management (D'Arcy & Frost, 2001). D'Arcy and Frost (2001) believe continuous monitoring of catchments that have known diffuse pollution problems is required to quantify and evaluate best practice management.

A wide range of variables exist that can impact diffuse pollution which include; soil type, rainfall, microbial activity, and level of groundwater which can inhibit the ability to quantify where a pollutant occurs (O'Shea, 2002). Lag times between source and location of measurement or impact in a catchment can vary, reducing the ability to pinpoint a certain pollutant to a particular site. Pollutants can remain inactive or trapped in source pathways for years, thus reducing the damage created by a pollutant. Hence, managing diffuse pollution is complex and the mitigation measures necessary must be undertaken over years, often beyond terms of governments.

2.6.3. Point sources

Chapman (1992) defines a point source of pollution by suggesting it is a source that can be collected, treated or controlled. It therefore follows that a common characteristic of point source pollution is that it can be relatively easily measured and so most countries regulate such outputs (Campbell *et al.,* 2004). Point source pollution is historically thought to occur from industrial activity, human activity and sewage effluent, usually taking a direct path into a river occurring throughout the year.

2.7 Legislation for water quality

European legislation has undergone major developments since the 1980s, partly as a result of the privatisation of the water industry, and partly through evidence demonstrating the improvement of water quality from the 1960s, although no further signs of improvement have been evidenced (Heathwaite *et al*., 1996). Catchment management is directed by regulation and legislation. However, policy approaches for controlling agricultural pollution include the promotion of voluntary codes of good practice, incentivised schemes and regulation (Zhang *et al, 2017).* UK and EU legislation require cost-effective pollution control, as well as implementing best management practices (BMPs) to lower nitrogen and phosphorus in accordance with EU laws (Panagopoulus *et al.,* 2012). To reduce point source and diffuse pollution, management locations for Basin Management Plans (BMPs) must be identified. However, due to location and cost effectiveness, management locations tend to gravitate towards places of high pollutant sources. It follows that the detrimental impacts of agricultural diffuse pollution on downstream aquatic environment have increased water treatment costs (Mulholland & Dyer, 2010).

Regulation of farming practices became necessary to improve water quality. Post-war farming practices increased exponentially; the use of nitrogenous fertilisers tripled (Howden *et al* 2013), intense ploughing occurred and there was an increase in land drainage. As negative effects of intensive farming became evident in watercourses, regulation of farming practices began to be implemented. Nitrate Vulnerable Zones became mandatory in 1996, after voluntary measures from the Nitrate Sensitive Areas were established under the Nitrates Directive (Worrall *et al* 2009). Nitrate Sensitive Areas required nitrate concentration to be lower than 11.3mg/l (Defra, 2002a). Nitrate vulnerable zones were also designated in areas where agriculture provides 20% or more of the overall loading to surface waters (Defra, 2002a). Nitrate Vulnerable Zones have not been applied to the North York Moors catchment, due to lower nitrate concentrations and only small areas of agriculture. The Countryside Stewardship Scheme, introduced in 2016, aims to 'protect and enhance the natural environment, in particular the diversity of wildlife (biodiversity) and water quality (Countryside Stewardship, 2015). It is hoped that through this scheme, priority areas will be identified to meet environmental objectives (Zhang *et al,* 2017).

Howden *et al* (2013) suggest that, although in theory both criminal and common law can protect water users from acts of pollution, the difficulty begins when trying to pinpoint a specific incident to a particular landowner. The "polluter pays" principle should be able to convict people and businesses that cause damage to the environment; however, one would have to argue the person in question had foreseen the potential damage and continued to release the slurry, for instance, into an aquifer (Howden *et al.,* 2013). Current legislation, such as the Water Framework Directive, instead attempts to reduce the number of pollution incidents instead of punishing the offender after an incident (Howden *et al.,* 2013).

Diffuse pollution has become a key cause of pollution in UK rivers, with increasing concentrations of nitrate and phosphate, organic matter, sediment and pesticides entering river systems from diffuse agricultural sources. As legislation continues to advance, diffuse pollution takes a more central role with approaches such as catchment sensitive farming and catchment based management being more widely adopted.

2.8 Costs of treating water quality

O'Shea (2002) suggests that pollution arises because the cost of discharging pollution is not borne by the polluter. Costs associated with treating water quality can spiral into millions of pounds, depending on the type of pollution incident and what is included in the ecosystems services (POST PN478, 2014). For example, waste water from a mine releasing 330kg of iron ochre directly in Saltburn Gill, North Yorkshire, required a treatment plant costing between £8 and £13m over 25 years, £10m of which was funded by the EA, DEFRA and coal authority (Gov, 2015). In 2008 Jacobs suggested agricultural diffuse pollution has an annual cost of £238m in the UK whilst South West Water estimates 17% of its customers' bills are for water treatment costs (POST PN478, 2014).

Adopting preventative methods to inhibit pollution from entering a water system can be cost-effective. Using cost-benefit analysis, the cost of interventions to create buffer strips, rejuvenate and restore wetland areas can be a fraction of the cost of cleaning up a pollution incident. Morris and Camino (2011) suggest that if UK wetlands were increased by 10%, a benefit of an additional £292 per hectare per year for inland wetlands, and £1793 per hectare per year for coastal wetlands would be achieved. Furthermore, if inland wetlands provided water quality improvements, £263m of benefits would be generated (Morris & Camino 2011). If wetlands were used as natural flood management, by retaining water in an upper catchment, an aggregate value of £366m would be created (Morris & Camino 2011). Thus, by utilising natural resources to retain nutrients, or capture water, the costs of water management would reduce, whilst ecosystem biodiversity would increase.

2.9 Freshwater threats

Conflicts over freshwater use are increasing as humans develop new water-intensive technologies and demand for water increases, such as through increased abstraction licenses. Conflicts include: abstraction, navigation, dams, fishing, agriculture, ecosystem services, and habitats. These conflicts map onto the five major threats to global freshwater biodiversity that have been outlined as: overexploitation, water pollution, flow modification, destruction or degradation of habitat, and invasion by exotic species (Dudgeon *et al* 2006). Although water quality is improving, with significant reductions in point source pollution and industrialised pollution, threats from nutrient enrichment are growing (Dudgeon *et al* 2006).

In light of threats to freshwater, habitats thresholds for water chemistry have been suggested. For example, Bauer (1988), Oliver (2000) and Moorkens (2000) proposed thresholds for *M. margaritifera* which provide guidelines for water quality values (Table 2.1).

Specific Attribute	Threshold Value (Bauer, 1988)	Threshold Value (Moorkens, 2000)	Threshold Value (Oliver, 2000)
Ammonia		0.01mg/l	
BOD	1.4mg/l		<1.3mg/l
Calcium	2mg/l		
Conductivity	<70µs/cm	65µs/cm	<100µs/cm
Dissolved Oxygen		9-9.7 mg $O_2 l^{-1}$	90-110% saturation
Nitrate	<0.5mg/l	0.125mg/l	<1.0mg/l
pH	<7.5	6.5-7.6	6.5-7.2
Phosphate	<0.03mg/l	0.005mg/l	<0.03mg/l

Table 2.1 *M. margaritifera* thresholds as proposed by Bauer (1988), Moorkens (2000) and Oliver (2000) based on field and laboratory observations. Source Norbury (2015)

2.10 *M. margaritifera* Conservation

In the last century, *M. margaritifera* became extinct in wide parts of Central Europe (Buddensiek, 1995). Population losses of up to 90% in Central Europe have occurred in areas where *M. margaritifera* are surviving (Bauer *et al.,* 1980). Losses of 80% have been recorded in England and Wales (Young & Williams, 1983), many of which could be attributed to pearl fishing (Buddensiek, 1995) or declines in water quality through eutrophication and industrial pollution (Cosgrove *et al.,* 2000). The conservation of *M. margaritifera* has been recognised by legislation (Cosgrove *et al.,* 2000). Initial conservation practices focused on the effects of abiotic habitat factors on species (autecology) and on the complex relationship between species (synecology), hoping to provide detailed habitat requirements (Geist, 2010). Recent conservation has shown that ecological studies can benefit from combination with genetic studies; investigating genetic diversity can help suggest sustainable conservation strategies. Research has suggested that small isolated populations can suffer from the loss of genetic variability, which can contribute to inbreeding and rapid extinction (extinction vortex) (Geist, 2010.) The conservation of biodiversity with, and between, species remains the goal (Geist, 2010). Adapting an integrated conservation approach that identifies and sustains both ecological processes and evolutionary lineages will help aid the protection of freshwater pearl mussels (Geist, 2010). Similarly understanding mussel distribution and abundance is crucial for conservation (Strayer, 2008).

2.10.1 The contribution of the Freshwater Biological Association (FBA)

The Freshwater Biological Association (FBA) is currently leading a captive breeding project for the survival of freshwater pearl mussels. A partnership project between Natural England, EA, and FBA was set up in 2007 to create an 'ark' with the hope of successfully breeding juvenile pearl mussels and releasing them into nine English rivers. The ark is located near Lake Windermere, using water from the lake for the juvenile breeding. Water quality is closely monitored. The River Esk is part of this conservation program, specific aims are to successfully recruit young juveniles at the Ark facility, and relocate adult juveniles to sites along the River Esk where the quality of water is deemed appropriate for *M. margaritifera.*

The River Esk supports a population of approximately 1000 mussels, confined to a few kilometres upstream and downstream of Lealholm. It sustains an aged population with no signs of recruitment in the past 25 years (Kileen & Moorkens, 2015). Although the project officer on the River Esk had previously translocated 30 adult mussels to the FBA facility in 2007, the River Esk Project Officer at the National Park decided to translocate a further 20 mussels in May 2016, in the hope to increase the chance of breeding. Glochidia drop-off was unusually early, the fish were tested on the 1st August, confirming they had already released glochidia. By bringing forward the life cycle by 3 weeks, glochidia release was not missed. Subsequently 11,000 glochidia have been recorded, and are currently being monitored.

The River Irt in Cumbria has successfully bred juvenile mussels to the age of nine, and is therefore considering the options for relocation back into the Irt. Water quality is a key contributor to mortality rates in juvenile mussels; staff at the West Cumbria Rivers Trust are monitoring DO, pH, suspended sediment closely. Before relocation, the FBA created a flume in the laboratory to expose the juvenile mussels to differing rates of flow, to help acclimatise them to natural flow conditions. Understanding spatial and temporal variations in water quality is crucial before such relocation of pearl mussels is undertaken in the River Esk. Part of this is deciphering sources of point and diffuse pollution to enable appropriate mitigation to be undertaken.

2.10.2 The importance of continued research on *M. margaritifera*

Studies into sediment microhabitats of pearl mussel populations at sites with high rates of juvenile recruitment all showed low percentages of fine sediments, high redox potentials and no or only small differences in the chemistry of water taken from different depths of the interstitial zone and from the free water (Geist & Auerswald, 2007). Pollution had a significant effect on freshwater pearl mussels in England and Wales, whereas overfishing had a significant effect in Scotland (Young & Williams, 1983). Pollution may act indirectly by creating an unsuitable habitat for host salmonids therefore impacting freshwater pearl mussels (Young & Williams, 1983). Bauer (1987) found a positive relationship between mortality and nitrate concentration in the water. The relationship between fast growth and short lives requires growth information for target populations to be obtained to ensure conservation (Hastie *et al,* 2000). The literature discussed in this section has provided a deeper understanding of natural variations within a catchment and the necessity of investigating spatial and temporal trends of water quality in three headwater catchments. The next chapter introduces the methodology used in this research.

3. Methodology

3.1 Study area

Based in the North York Moors, this project focuses on the upper Esk catchment, specifically three sub-catchments; Toad Beck, Danby Beck and Great Fryup Beck. The River Esk (Figure 3.1) has a catchment drainage area of 362km^2 (EA, 2016) with the source on Westerdale Moor, flowing east to the mouth at Whitby. The river flows through a narrow valley incised into the soft shale beds of Jurassic bedrock that were deposited some 150-200 million years old (EA, 2016). Comprising mainly mud and sandstones, rainfall response and catchment runoff have significant impacts on river levels (EA, 2013); the steep valleys produce a rapid response which correlates to sharp peaks in the river hydrographs.

The moorland area is heathland, one of the largest in England (Evans *et al.,* 2014). Vast areas have been designated as a Special Area of Conservation (SAC) and Special Protection Area (SPA) for birds. Additionally, there are 17 Sites of Specific Scientific Interest (SSSI) encompassing a variety of habitats and geological features (EA, 2009). The upland area has a maximum elevation of 450m, with average rainfall of around 1000mm (Evans *et al.,* 2014). Moorland soils in the catchment are acidic, organic or organo-mineral, with the central plateau occupied by blanket peat (Evans *et al.,* 2014). The acidic nature of the uplands can cause spikes in DOC after flushing of the water table. The peat layer is shallow <1m depth, placing it close to the climatic limit for blanket peat formation in Great Britain (Clark *et al.,* 2010). The moorland area has been affected by historic land management, including: short rotation burning for grouse production, extensive sheep grazing, drainage and forest planting, and is sometimes susceptible to wildfires (NYMNPA, 2008a).

The River Esk is the main salmon and sea trout river in Yorkshire, with 237km of river protected under the European Freshwater Fish Directive (EA, 2009). However, fish stocks have been in decline since the 1960s (NYMPNA, 2001). The Esk supports five of the threatened/declining species listed on the UK Biodiversity Action Plan: otter, water vole, kingfisher, dipper and freshwater pearl mussel. A recent classification using the Water Framework Directive suggests that the majority of rivers in the Esk are classified as Good Ecological Status. However, *M. margaritifera* requires 'High Ecological Status', specifically low in nitrogen and phosphorus, close to the proposed freshwater pearl mussel's relocation spot. Great Fryup Beck Catchment is 14.297km^2 and is classified as 'Moderate', increasing from 'Poor' in the 2009 cycle of river basin management plans. Danby Beck catchment is 13.062km^2 and is classified as 'Good', previously 'Moderate'. Toad Beck falls under 'Esk from Sleddale Beck to Ruswarp' catchment, which has been

’Moderate’ for both cycles of monitoring; however, in 2009 the chemical element of the WFD (EA, 2009) failed, and in 2015 it was classified as ‘Good’.

The 2015 river basin management plan for the Humber catchments, where the River Esk is situated, suggests that 32% of water bodies are suffering from pollution in rural areas and 38% are suffering from pollution from waste water (DEFRA, 2015). Failures to adhere to water quality WFD legislation in the Esk catchment are caused by diffuse pollution from agriculture (EA, 2009). Differing approaches to land management have seen an increase in the amount of soils and sediments entering the rivers. Runoff containing phosphorus or nitrogen can cause excessive algal growth in a river. Sedimentation is a particularly important issue in the Esk, as it can smother spawning sites for fish and juvenile *M. margaritifera*. Water discolouration is a major issue in the upland parts of the catchment (Holden *et al.,* 2007) and chlorination of highly-coloured water releases trihalomethanes, which are potentially toxic and carcinogenic (Kneale & McDonald, 1999) are also issues. Mitchell and McDonald (1995) and Clausen (1980) found that drained catchments produced much more discoloured water than undrained catchments. Pollution from waste water, especially leakages from septic tanks, have been relatively overlooked by the EA in the catchment, although the release of nutrients can impact water quality.

Land use has a significant role in water quality; the dominant land use assertions can be quantified to help guide future management. Table 3.1 shows the percentage land cover for each study catchment, whilst Figure 3.2 shows the catchment land use. Danby Beck is dominated by improved grassland, with rough low-productivity grassland interspersed throughout the catchment. Toad Beck is the most modified of all three catchments; improved grassland is the dominant land use. Towards the mouth of Toad Beck, land use changes to built-up areas and gardens, and arable and horticulture. Great Fryup Beck is predominantly improved grassland, with a mixture of arable and horticulture, and rough low-productivity grassland towards the mouth of the Beck.

Table 3.1 Percentage land cover for each catchment (CEH, 2007)

Land Use	Toad (%)	Danby (%)	Great Fryup (%)
Acid Grassland		1.2	1.9
Arable and Horticulture	25.8	1.1	20.9
Bog		1.1	1.3
Dwarf Shrub Heath		9.9	4.9
Coniferous Woodland		1.1	0.1
Broad leaved, mixed and yew woodland		3.5	4.4
Improved grassland	53.2	67.8	52.4
Rough low-productivity grassland	12.9	12.7	12.9
Built up areas and gardens	8	1.1	0.6

Figure 3.1 River Esk catchment, located in the North York Moors National Park. The three tributaries studies are highlighted on the map.

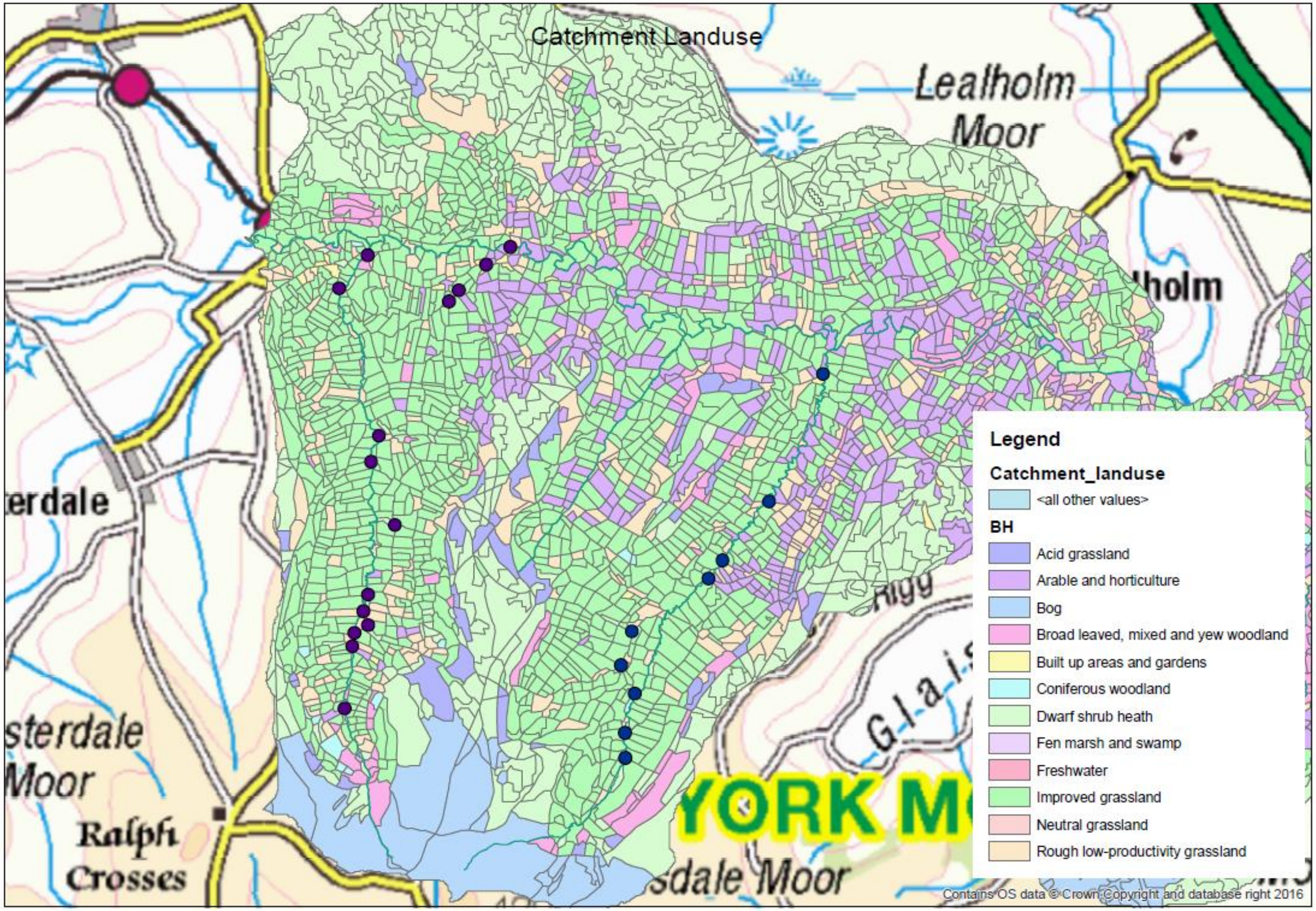

Figure 3.2 Catchment land use of the three tributaries in North Yorkshire, Great Fryup sampling points are highlighted with a dark blue marker, Danby Beck and Toad Beck are highlighted with a purple marker. (CEH, 2007)

3.2 Site Locations

Three tributaries were chosen for detailed field investigations. These three tributaries make up a sub-catchment close to the identified relocation of the freshwater pearl mussels (from a captive breeding programme). The three sub-catchments encompass a wide range of habitats, which means that the effectiveness of catchment management can be compared between these study sites. Analysing similar catchments with different management techniques can highlight the effectiveness of buffer strips and bank stabilisation efforts to reduce both pollutants and sediment. All three streams are considered flashy in nature (Norbury, 2015).

3.2.1 Toad Beck

Toad Beck was highlighted in Norbury (2015) and Balmford (2011) as a tributary with high sediment yields and high pollution. Despite its largely rural setting, Toad Beck was selected to represent an "urban" river catchment, stretching 1.3km, passing through the centre of Ainthorpe. Toad Beck has had significant channel modifications, including two culverts and a significantly straightened reach; the watercourse was modified through two fields to follow the field boundaries, reducing sinuosity. The source begins at a pond, surrounded by intensely improved pastureland, before descending past an intersection of a sewage network. It has two culverted sections, with numerous overland surface pipes, potentially transporting sewage effluent and waste. It enters the Esk upstream of Danby Sewage Treatment Works. Table 3.2 and Figure 3.3 shows the sample locations for Toad Beck.

Table 3.2 Sample locations and the type of sampling for Toad Beck

Site Number	Site Name	Type of Sampling
1	Mouth	YSI Probe, DOC, Anion and Cation, COD, BOD
2	Culvert	YSI Probe, DOC, Anion and Cation, COD, BOD
3	Fire station	YSI Probe, DOC, Anion and Cation, COD, BOD
4	Strait Lane	YSI Probe, DOC, Anion and Cation, COD, BOD
5	Pre-disturbance	YSI Probe

3.2.2 Danby Beck

Danby Beck was chosen to depict the effect of mitigation upon an area of intensely improved pasture. It is 7.7km long, starting on peat moorland. Many of the farms and dwellings it passes are not connected to the main sewerage network and rely upon septic tanks. The channel width is much wider than Toad Beck, and a riparian buffer strip stretches along the majority of the stream. There are two waste water treatment plants, Yorkshire Water and Botton Wastewater Treatment. Botton has three ponds, which filter waste water via reed beds and rocks. There is a generator/wind powered turbine which redistributes waste, bringing it to the surface ensuring aerobic reactions can occur. Yorkshire Water is required to reduce the amount of ammonia (and other chemicals) released into the environment according to Water Framework Directive legislation. Danby Beck was thus chosen to represent a rural catchment with significant mitigation measures and improvements. Table 3.3 and Figure 3.3 outline the locations for water quality sampling.

Danby Beck catchment has had a significant amount of mitigation: the installation of buffer strips, drinking bays and bank stabilisation. Management processes have attempted to revert it to a more 'natural' environment. By studying the quantity and diversity of water quality in this catchment, it provides empirical evidence for the success of the mitigation methods.

3.2.3 Great Fryup Beck

Great Fryup Beck was chosen to represent a rural catchment which contained limited or no improvements. Great Fryup Beck is 8.2km long, starting on peat moorland, draining an area of improved grassland. Little work has been done to mitigate erosion and drainage of farmland. It suffers from high levels of sediment yield due to poaching. Great Fryup Beck is important for showing the effect of sediment yield on the pollutants downstream and whether the flushing of peat moorlands has a great impact on pollutants. Some land owners on Great Fryup Beck refused access; thus the spatial data collection is slightly limited compared to Toad and Danby Beck. Sample locations are given in Table 3.4 and Figure 3.3.

Table 3.3 Sample locations and the type of sampling for Danby Beck

Site Number	Site Name	Type of Sampling
1	Mouth	YSI Probe, DOC, Anion and Cation, COD, BOD
2	Ashfield Road	YSI Probe, DOC, Anion and Cation, COD, BOD
3	Farm road bridge	YSI Probe, DOC, Anion and Cation, COD, BOD
4	Burtree Lane	YSI Probe, DOC, Anion and Cation, COD
5	Church Bridge	YSI Probe, DOC, Anion and Cation, COD
6	Tributary	YSI Probe
7	Drinking bay	YSI Probe, DOC, Anion and Cation, COD, BOD
8	Tributary	YSI Probe, DOC, Anion and Cation, COD
9	Wesleyan Chapel	YSI Probe, DOC, Anion and Cation, COD
10	Yorkshire Water d/s	YSI Probe, DOC, Anion and Cation, COD
11	Tributary	YSI Probe, DOC, Anion and Cation, COD
12	Yorkshire Water u/s	YSI Probe, DOC, Anion and Cation, COD
13	Botton Treatment Works u/s	YSI Probe, DOC, Anion and Cation, COD
14	Farm bridge	YSI Probe
15	Camphil Village Trust road bridge	YSI Probe, DOC, Anion and Cation, COD
16	Pipes	YSI Probe, DOC, Anion and Cation, COD
17	Pre-disturbance	YSI Probe

Table 3.4 Sample locations and type of sampling for Great Fryup Beck

Site Number	Site Name	Type of Sampling
1	Furnace Farm	YSI Probe, DOC, Anion and Cation, COD
2	Meander	YSI Probe, DOC, Anion and Cation, COD, BOD
3	Tributary	YSI Probe, DOC, Anion and Cation, COD
4	Foot Bridge	YSI Probe, DOC, Anion and Cation, COD
5	Village Hall	YSI Probe, DOC, Anion and Cation, COD
6	The Street road bridge	YSI Probe, DOC, Anion and Cation, COD
7	Farm road bridge	YSI Probe, DOC, Anion and Cation, COD
8	Tributary	YSI Probe, DOC, Anion and Cation, COD, BOD
9	Tributary	YSI Probe, DOC, Anion and Cation, COD, BOD
10	Meander	YSI Probe, DOC, Anion and Cation , COD, BOD
11	Iron Ore	YSI Probe, DOC, Anion and Cation, COD, BOD
12	Road bridge	YSI Probe, DOC, Anion and Cation, COD, BOD
13	Pre-disturbance	YSI Probe, DOC, Anion and Cation, COD, BOD

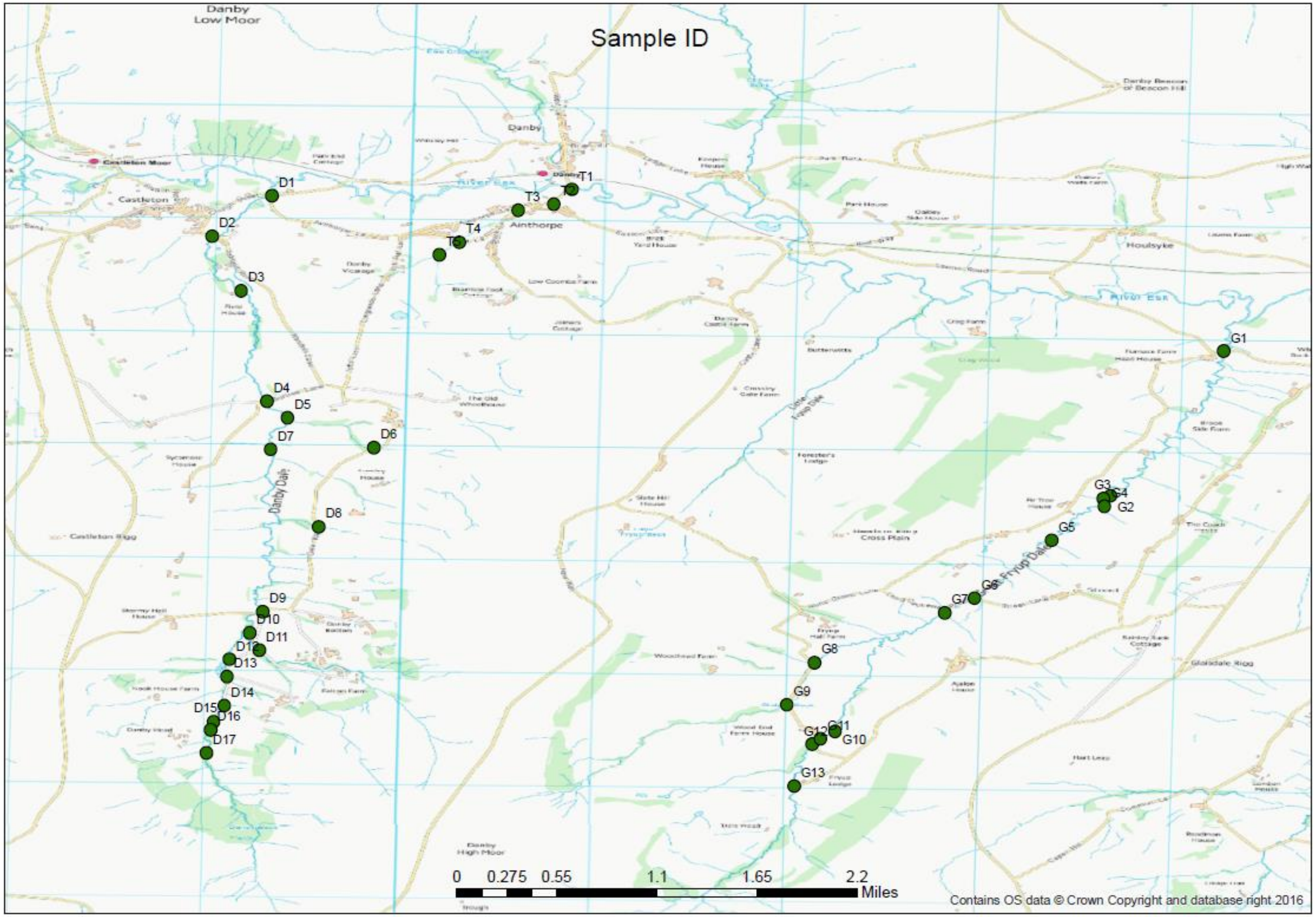

Figure 3.3 Sample locations for each of the three tributaries: Danby Beck (D1-D17), Toad Beck (T1-T5) and Great Fryup Beck (G1-G13).

3.3 Methods

3.3.1 Walkovers

An initial walkover was completed to identify key point source areas along all three tributaries. Using Yorkshire Water sewerage network maps of the three tributaries, 3 dwellings in Toad Beck, 23 dwellings in Danby and 46 dwellings in Great Fryup were estimated to be unconnected to the main sewage network. The walkover identified key types of pollutants and where they enter the river system (Figure 3.4).

3.3.2 Sampling - spatial

Fortnightly samples were taken from July – December to observe variations in water quality characteristics. Various attributes were sampled: anions and cations, COD and DOC were all measured. Manufacturing and sampling issues have led to COD being sampled less frequently than hoped. In September COD, DOC, anions and cations were measured fortnightly. Manufacturing issues at the factory have affected the analysis of COD as boxes of COD chemicals could not be sourced when required. BOD was measured in November; however, the quality control used to calibrate the chemical reaction using a known value of BOD failed, thus reducing the validity of the results.

3.3.3 Sampling - temporal

A YSI probe was used to measure spatial variation in the study tributaries of conductivity, dissolved oxygen, temperature and pH. YSI probes are hand-held devices which can measure a variety of parameters and give instantaneous results. Conductivity was measured in μs cm-1, dissolved oxygen was measured in % saturation and temperature was measured in degrees Celsius. Readings were taken fortnightly to record variations that may occur during high flows. The versatility of using a hand-held probe in the field allowed multiple locations to be measured.

3.3.4 Justification of methods

Laboratory and field methods were used to undertake water quality analysis across the study sites, which provided a wide variety of parameters for analysis. Adopting a spatial method of water quality analysis highlights potential pollution sources and failures in a catchment which would not be represented in spot sampling of the downstream tributary undertaken by the EA. Flow was not measured since temporal and seasonal variations in water quality parameters was beyond the scope of the current research. However, the influence of discharge on water quality was broadly captured through field notes and analysis of rainfall data rather than detailed measurement Periodic sampling of headwaters can provide valuable information about pollutant sources and inherent resilience in subcatchments (Pinay, 2017). Furthermore, building upon the research undertaken by Norbury (2015), Balmford (2011), Biddulph (2013) using similar water quality sampling techniques provides long-term monitoring opportunities and before and after studies, vital for *M. margaritifera* conservation.

Using a YSI probe, spatial variations along individual subcatchments were recorded and compared over time. The YSI probe provided an instantaneous baseline of data to which laboratory data could then be compared, which provided empirical evidence which can be used to determined potential relocation sites for *M. margaritifera*. At fortnightly intervals, changes in water quality were recorded.

Monitoring of DOC was chosen due to the vulnerability of *M. margaritifera* to variations in organic nutrients. COD analysis was chosen to highlight the natural variations within each catchment and thus the hydrological connectivity. Anion and cation analysis was undertaken to identify where specific pollutants are entering the system, therefore improving future management of the area. ArcGIS and Microsoft Excel were used to plot spatial and temporal data, adapting a traffic light system to show locations where concentrations were above the threshold for *M. margaritifera* (see Table 2.1).

Adapting the methods used in Norbury (2015) a traffic light system was chosen to visually represent changes in water quality both temporally and spatially. Similar to the WFD 'High', 'Good', 'Moderate' and 'Poor' classifications used nationally by the EA a traffic light system is one of the more practical methods used for interpreting water quality data. By using Moorkens (2000), Oliver (2000) and Bauer's (1988) proposed thresholds to create a scale for a number of parameters (see Table 2.1) the water quality results presented in Chapters 4 and 5 can be easily interpreted by project officers in the North York Moors National Park. Thresholds used for the data analysis are classified on those proposed by Moorkens (2000) Oliver (2000) and Bauer (1988), observations greater than the strictest threshold (shown in red) are not suitable for *M, margaritifera* populations. Thus, although a traffic light system is used, focus on reducing the number of observed data classified as the strictest threshold is paramount for improving water quality to a level sustainable for *M. margaritifera.*

Additionally, adopting a recognised way of presenting water quality data in 'bands' such as the WFD aforementioned project officers and EA catchment coordinators will be able to implement targeted measures to improve water quality.

3.4 Laboratory Analysis

3.4.1 COD analysis – SCA Method ISBN 0 117519154 (1986)

Chemical oxygen demand is a commonly-used indicator of water contamination, defined as the amount of oxygen required to oxidise all pollutants in a given volume of water (Jin & Tu, 1990, Pisarevsky *et al.,* 2005). High values of both COD and BOD are indicators of serious water pollution issues. Contamination from organic pollution can damage the ecosystem because of the uptake in oxygen from the decomposition of organic matter. Due to laboratory and manufacturing difficulties during the data analysis period, limited COD analysis was completed for this study. A brief overview of the method for COD analysis is provided.

COD analysis requires a sample to be oxidised by digesting with sulphuric acid and potassium dichromate in the presence of a mercury sulphate catalyst. A stock of 2000mg/l is made using 1.7g +- 0.005g of potassium hydrogen thalate per litre which can last for one week once it is pre-dried at 105^{o} C for one hour. Using one blank and six standards for calibration, including a quality control (a known standard used to calibrate results) of standard 4, the 20 samples could be analysed.

Once the sample is oxidised, there is a reduction of the chromium ion from Cr^{4+} to Cr^{3+}. This gives a quantitative colour change from orange to blue/green, which gives an indication of the concentration of the organic substances present. The colour change is measured at 590nm using an absorbance uv/vis spectrophotometer.

The samples are heated for two hours on a heating block at 150^{o} C, to speed up the reaction. Once cooled, the samples are filtered using a 0.2μm filter to reduce the interference. The samples are placed into a spectrophotometer and scanned with a correlation coefficient greater than 0.995. In between samples to reduce the risk of contamination, the cuvette is cleaned using de-ionised water and left to drip dry. This could dilute the next sample; however, the effect of dilution is minimal in comparison to the effect of tissue remnants left on the cuvette.

Table 3.5 Standards used for the COD analysis

Sample	**Mg/l**	**Ml**
Blank	0	0
Standard 1	10	0.5
Standard 2	25	1.25
Standard 3	50	2.5
Standard 4 (Quality Control)	75	3.75
Standard 5	100	5
Standard 6	250	7.5

3.4.2 Anion and cation analysis

River water samples require filtering at 0.45μm before they can be analysed using the Dionex. Once filtered, the samples are pipetted into 5ml bottles. The Dionex analyses both anions and cations. Water is used as an eluent for both the anion and cation suppressor. The eluent is mixed with an acid to create an acidic suppressor, and phosphorus is mixed into the eluent to create a basic anion suppressor. The eluents are pumped through a flow tube, where the sample is mixed. The reaction is based on electrical current causing an attraction between the positive and negative ions of the sample. In the anion analysis, Fluoride is the lowest ionic concentration and results for this appear first; to speed up the results for phosphate, the length of the Dionex column is increased. This process is duplicated for the cations.

Samples can require extra dilution if levels of pollutants are too high, in the case of Batch 5 (taken on 10/11/2016), sulphate, sodium and chloride levels were high and therefore the samples were diluted and retested.

One drawback to using a Dionex is the detection limits on nitrite, phosphate and ammonium, shown in Table 3.6. With regards to the *M. margaritifera*, some of the detection limits appear at the highest estimated range of 'safe' thresholds proposed by Bauer (1988), Moorkens (2000) and Oliver (2000) (Table 2.1). Therefore, it is difficult to distinguish the exact concentration of the pollutant. Although detection limits are often higher than the thresholds proposed (Bauer, 1988; Moorkens, 2000; Oliver 2000) previous studies on the River Esk have used a Dionex for analysis, thus continuing this methodology provides catchment managers with long term data sets that can be compared to assess whether management strategies are impacting on pollutants in the River Esk.

Table 3.6 Detection limits of compounds measured using a Dionex

Anion	Detection Limit Mg/l
Phosphate	0.02
Nitrate	0.02
Nitrite	0.01
Cations	
Ammonium	0.02
Calcium	0.05

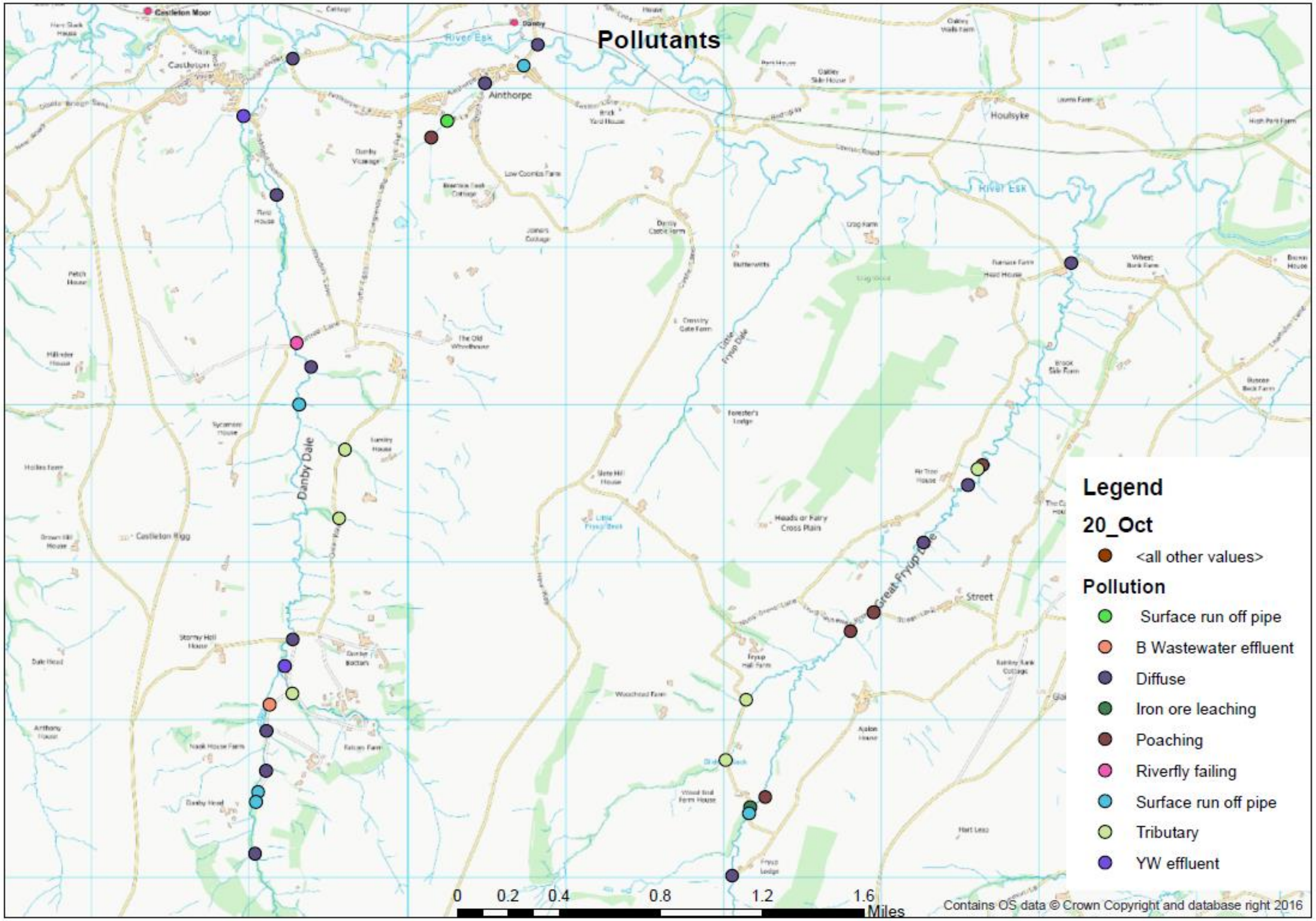

Figure 3.4 Types of pollutant at the sampling locations in the three tributaries

4. Results: Temporal variations in water quality at the catchment scale

4.1 Introduction

To obtain an understanding of water quality in a catchment, parameters were investigated over a period of 6 months. Data collection started in July (2016) and finished in November, ensuring summer and autumn water quality could be captured since summer months are inherently dominated by a growth in plant and animal life. The influx of nutrients into a water body will seriously affect the water quality. Furthermore, capturing autumnal water quality will ensure flood events, two of which were recorded during the data collection, to assess the impact of high flows on water quality. ArcGIS was used to plot dissolved oxygen, and conductivity using a traffic light system. Thresholds used were those suggested by Moorkens (2000) and Oliver (2000) and Bauer (1988). To sustain *M. margaritifera* DO and conductivity must fall into the classification coloured green. The thresholds proposed by Moorkens (2000) Oliver (2000) and Bauer (1988) were used in combination to create a colour coded scale. For management purposes understanding locations where conductivity, ammonium, phosphate, nitrate and nitrite exceed proposed thresholds is crucial. Since the current research is investigating whether the study catchments are suitable for FWPM relocation, using a traffic light system to expresses how often and more specifically where the average of water quality data collection is over the proposed threshold is used. This is deemed more useful for practitioners rather than undertaking detailed statistical analysis.

4.2 Dissolved Oxygen

Adapting thresholds set by Moorkens (2000) and Oliver (2000) a traffic light system was used to represent whether DO levels failed or met the criterion proposed in Table 2.1. Figures 4.1– 4.10 show the observed results. Dissolved oxygen content is an indication of the status of the water with respect to balance between oxygen-consuming and oxygen-producing processes (Hem 1970). To sustain fish populations it should be above 30% saturation (Dunk *et al.,* 2007).

DO mean for the sampling period is 90.83% for Toad Beck, 99.43% for Danby Beck and 93.82% for Great Fryup Beck. Standard deviation for DO is 17.42 for Toad Beck, 19.17 for Danby Beck and 11.95 for Great Fryup Beck. In the period of July to November dissolved oxygen levels fluctuate between 43% and 138% saturation. July and August show dissolved oxygen levels to fall below 90% saturation on some occasions, which both Moorkens (2000) and Oliver (2000) suggest to be the threshold for *M. margaritifera* recruitment and sustaining healthy populations. Readings taking during September, which suffered from low flows (judged subjectively from the observed state of the flow whilst collecting samples in the field and from rainfall records), saw the majority of readings of dissolved oxygen beneath 90%. Readings taken on the 26th September show Danby Beck obtaining levels of dissolved oxygen between 90-110%. October through to November saw most tributaries obtaining levels of dissolved oxygen above the recommended thresholds set by Moorkens (2000) and Oliver (2000) of 110%.

There is a noticeable trend of higher DO readings above 90% in the headwaters of both Danby Beck and Great Fryup Beck, which could be accounted for by reduced human impact. The highest percentage of DO saturation on Danby Beck of 137% was recorded in the headwaters. Readings of above 110% are considered by Moorkens (2000) and Oliver (2000) to be favourable for the recruitment of juvenile *M. margaritifera*.

There are occasions when the headwaters of Danby Beck have lower DO readings, such as on 26th September with a saturation of 65%. However, average Headwater readings are 92%. The lowest recording of DO on the 13th September of 78% was observed at the mouth, with average readings of 93%. Tributaries on Danby Beck have lower levels of DO; D11 has an average saturation of 98%. In November, Danby Beck tributaries have saturation levels of 88.5% and 93.8%.

Toad Beck has higher readings, between 80% and 122% towards the mouth of the tributary, and starts to obtain DO levels of higher than 110% towards the end of October. T4 has lower annual readings in comparison to other sample locations of DO with an average of 79%. T3 (between two culverts) has lower DO readings between 89% and 99%. Great Fryup Beck has higher DO saturation at the mouth with an average of 92%, in comparison to the headwaters which have an average of 89%. Great Fryup Beck has an outlier of G3 (a tributary), which has a DO range of 81% to 96%; it is a tributary which fluctuates between passing or failing thresholds suggested by Bauer (1988) and Moorkens (2000) and Oliver (2000).

In October and November, figures 4.7-4.11, Great Fryup is at, or above, Moorkens and Oliver's (2000) criterion with records of DO above 100% saturation. G3 is consistently failing to meet the DO threshold for *M. margaritifera*, with its highest DO saturation in October and November of 89%. G3's highest DO saturation is 96%, in July. This highlights the importance of localised point source pollutants, whilst demonstrating the need to consider data against proposed thresholds to ascertain whether these tributaries can sustain *M. margaritifera.* Even after the flood event of 8th November, Great Fryup's DO levels are still significantly lower with only 3 recordings above 100%, and one recording at G3 of 81%. Danby Beck exceeds 100% four times, with its lowest DO saturation of 88.5%; this could suggest less aeration along the tributary, or more pollutants entering the tributary and lowering the DO, using up oxygen in chemical reactions.

4.2.1 Dissolved Oxygen – monthly average for all tributaries

Figure 4.1 shows the average dissolved oxygen content for the duration of the sampling period on all three tributaries. Concentrations of DO lower than 100% saturation are concerning, levels below 50% are classified as Poor (UK TAG, 2008). Toad Beck has the lowest average of DO at 90.8%, compared to Great Fryup Beck at 94% and Danby Beck at 99%. Annual seasonal variations of DO were plotted, showing September DO to be the lowest, coinciding with low river flows and variations in water temperature. Danby Beck and Great Fryup Beck have higher dissolved oxygen readings, with the majority of annual readings over 90%. Toad Beck is considerably lower, especially in July and August, with its lowest reading of 43.5% dissolved oxygen. Danby Beck has the highest DO averages, with its highest reading of 127.5% in November. The averages across all three rivers converge during autumn which could be explained by temperature variations in the three valleys which effects weaken during autumn.

4.2.2 Dissolved Oxygen – sample average for individual tributaries

Toad Beck sample averages of DO decrease upstream to 79% with the exception of T5, which has an average saturation of 85%. The highest average reading is at T1 of 104%, which could suggest groundwater has entered the system and recharged the dissolved oxygen level. T4 is unusually low with an average reading of 79%. Danby Beck has a variable pattern of DO, with D1 average being marginally higher at 93%, and D17 at 92%. There are spikes in DO at D4 (115%), D8 (120%), D15 (104%) which could account for a lack of data skewing the averages. Great Fryup DO tends to fluctuate from the head to the source of the river. All of Great Fryup's sample averages are below 100%, with the exception of G13 (104.73%). G3 has the lowest average at 89.50%.

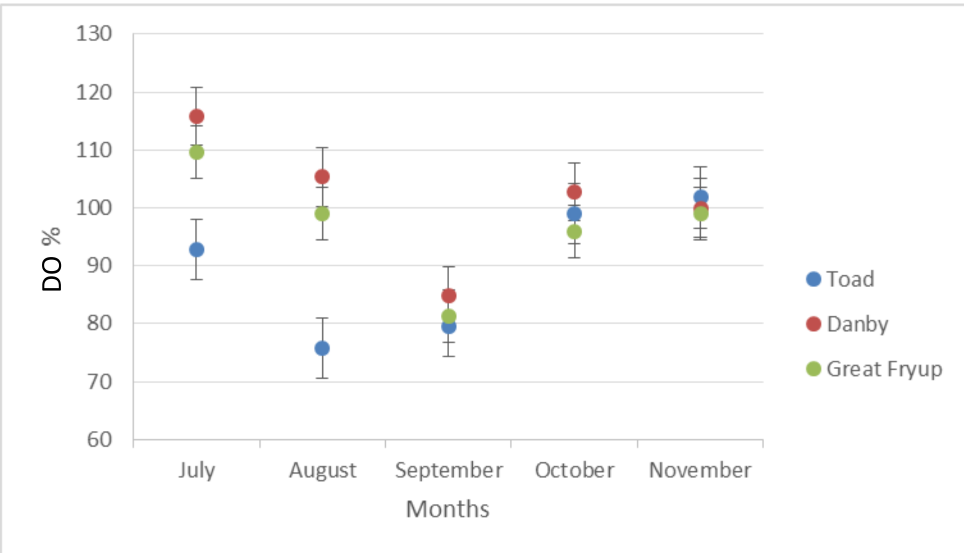

Figure 4.1 Mean monthly dissolved oxygen content measured for each of the three tributaries. Error bars represent one standard deviation of the mean.

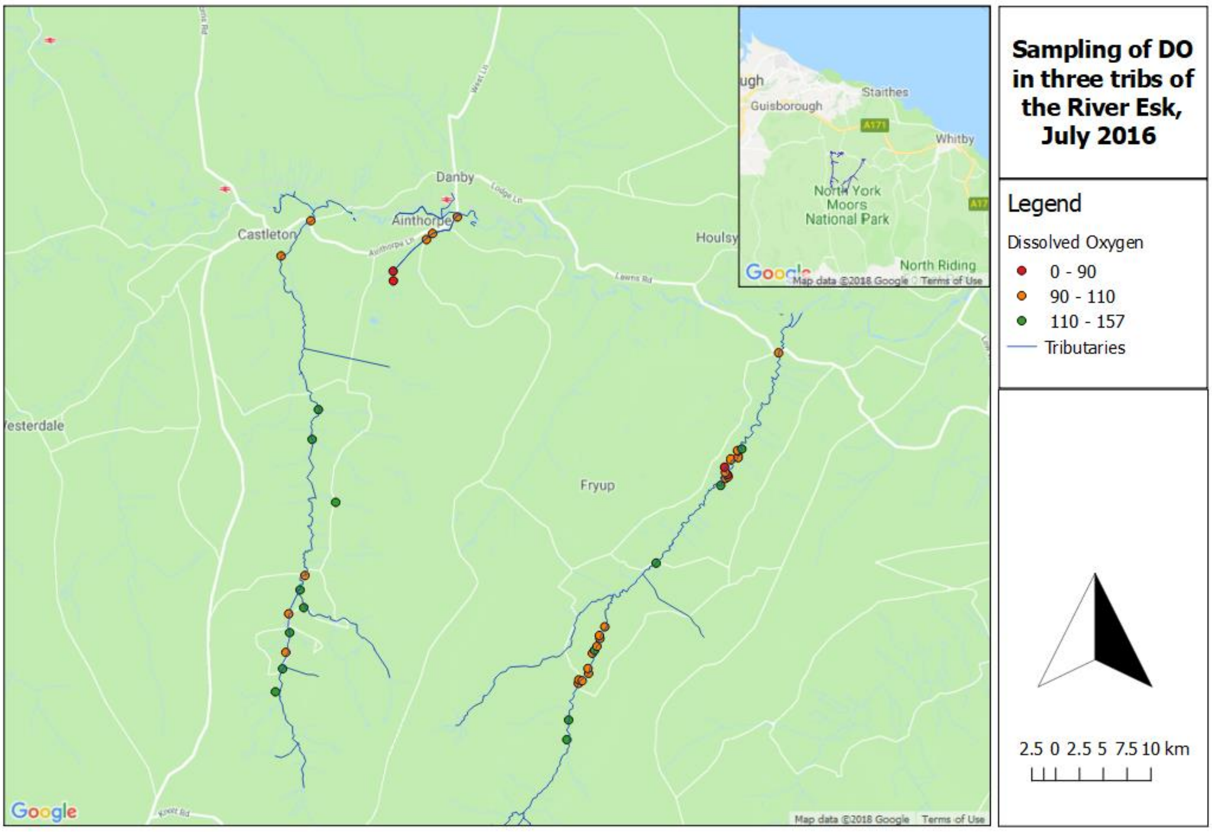

Figure 4.2 DO concentrations taken in July, data plotted using the threshold proposed by Oliver (2000) Moorkens (2000) and Bauer (1988)

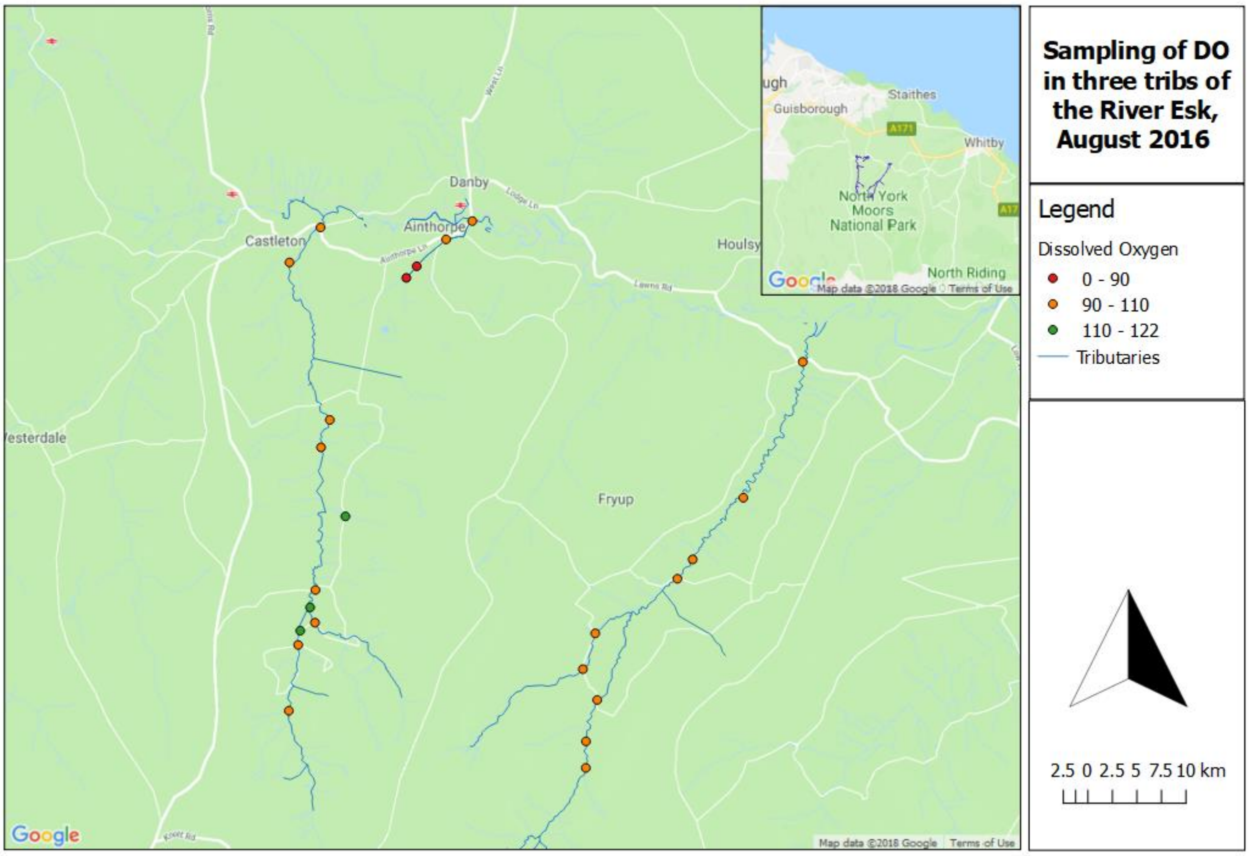

Figure 4.3 DO concentrations taken in August, data plotted using the thresholds proposed by Oliver (2000) Moorkens (2000) and Bauer (1988)

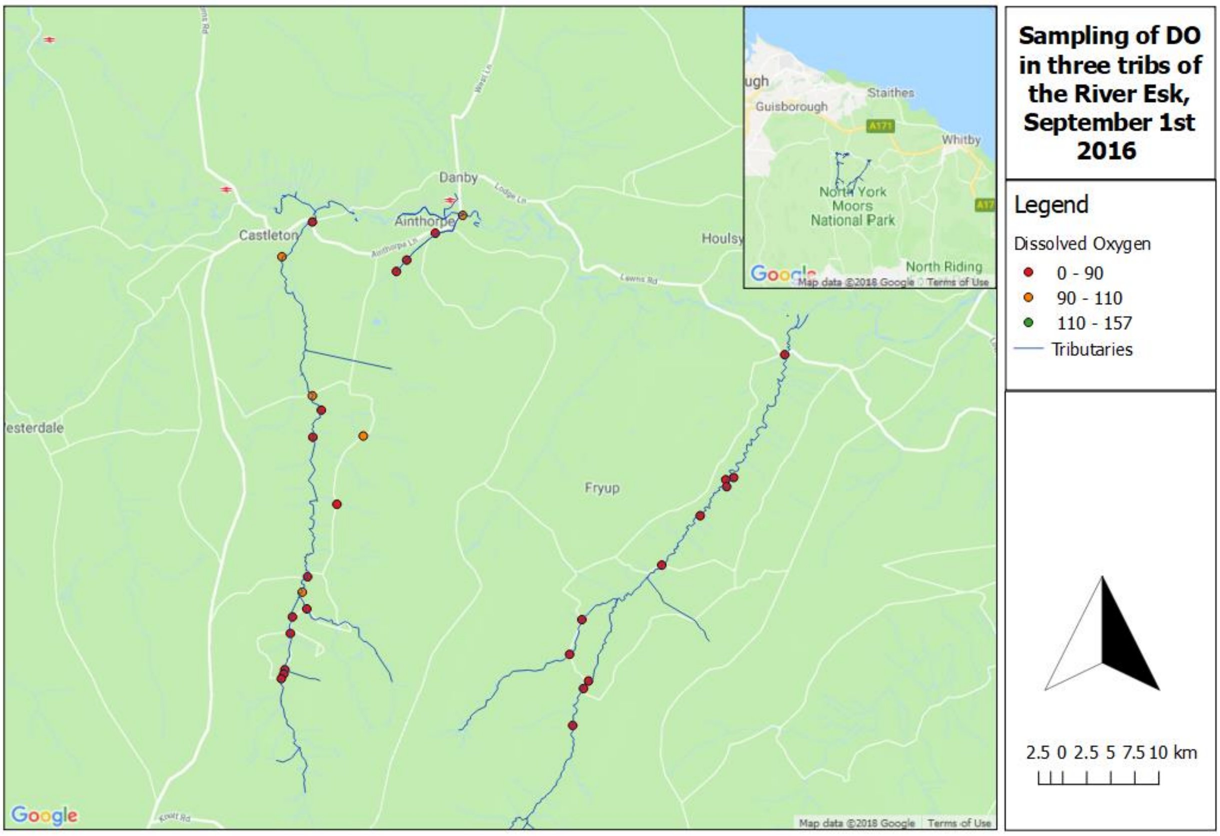

Figure 4.4 DO concentrations taken in September, data plotted using the thresholds proposed by Oliver (2000) Moorkens (2000) and Bauer (1988)

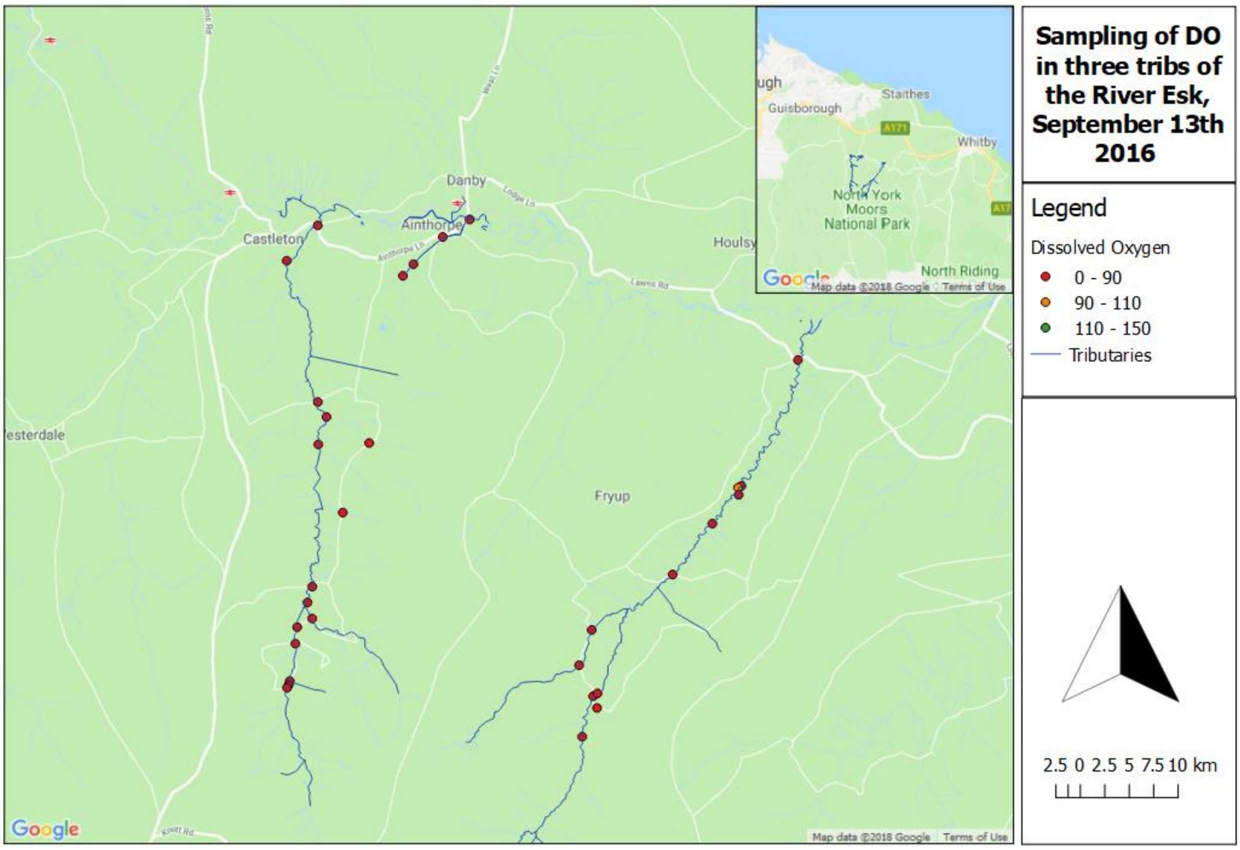

Figure 4.5 DO concentrations taken in September, using the thresholds proposed by Oliver (2000) Moorkens (2000) and Bauer (1988)

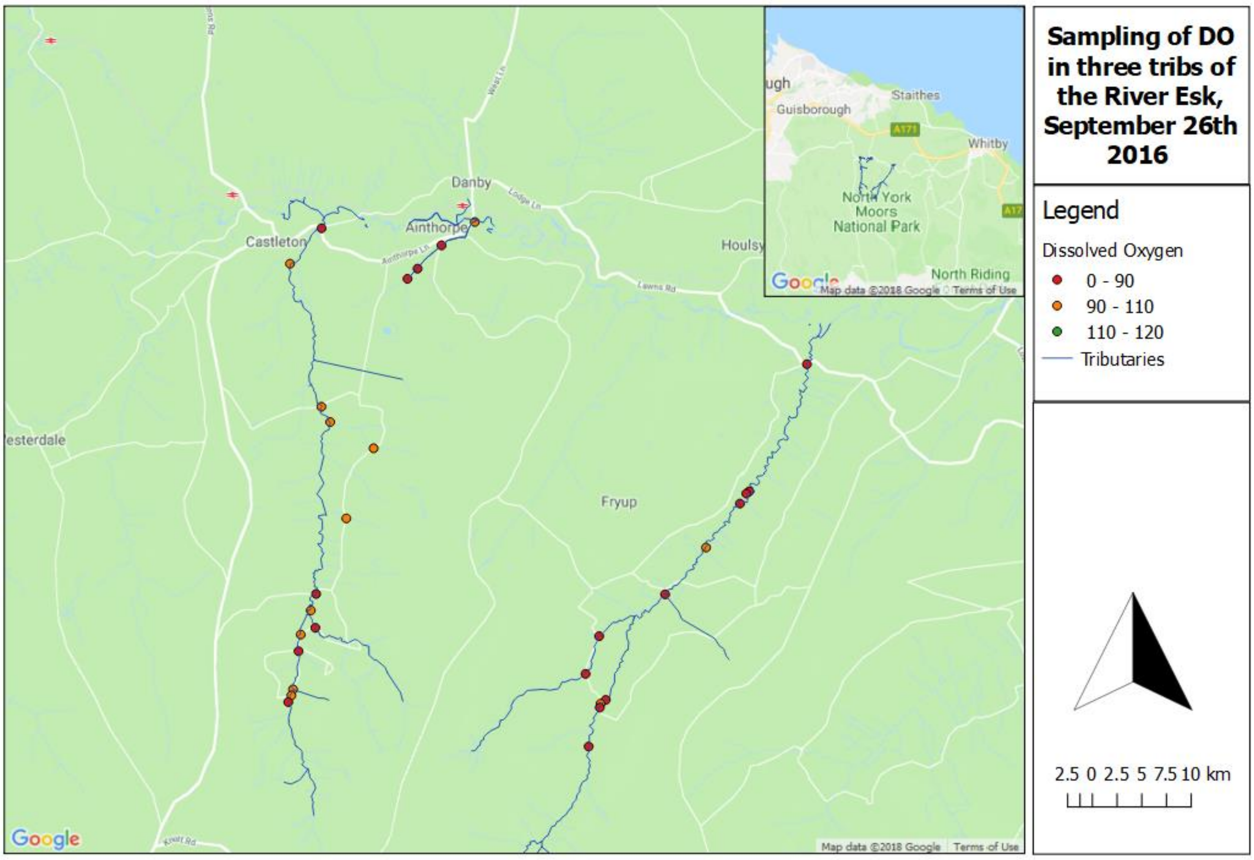

Figure 4.6 DO concentrations taken in September, data plotted using the thresholds proposed by Oliver (2000) Moorkens (2000) and Bauer (1988)

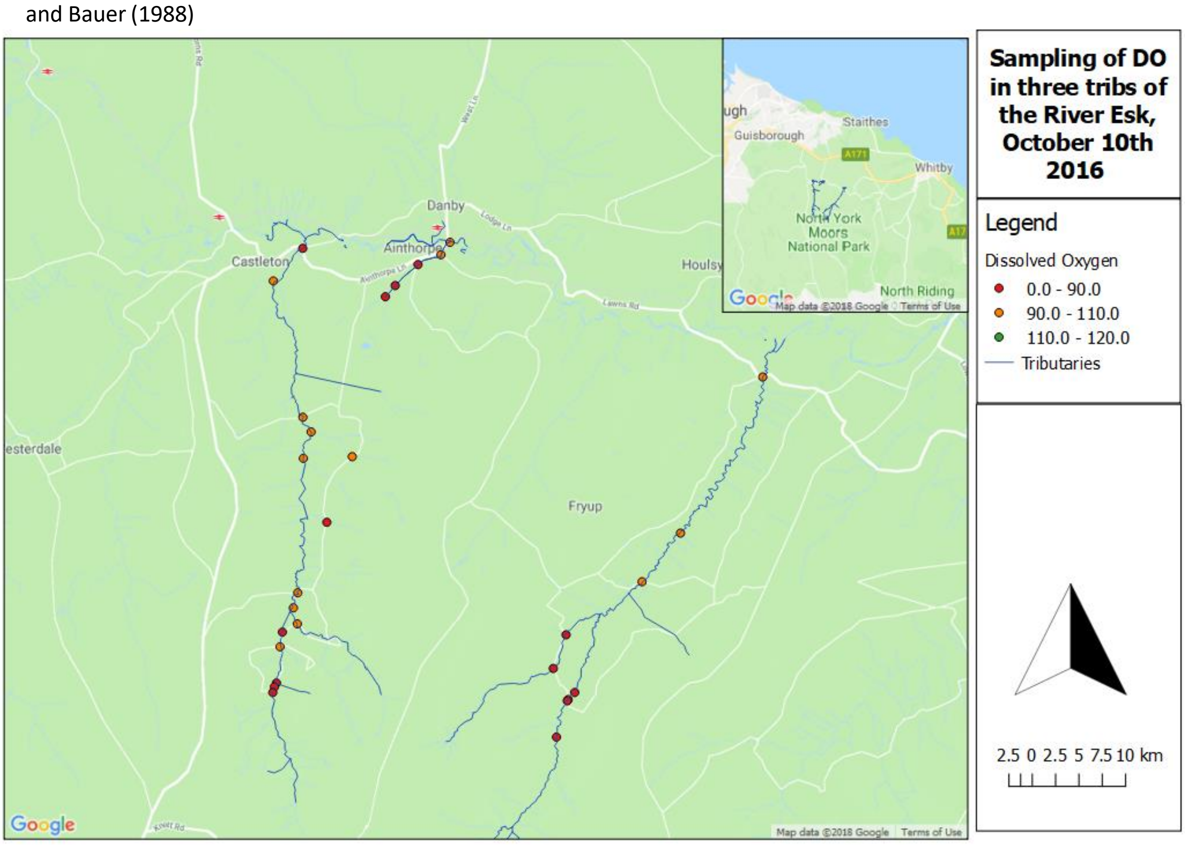

Figure 4.7 DO concentrations taken in October, data plotted using the thresholds proposed by Oliver (2000) Moorkens (2000) and Bauer (1988)

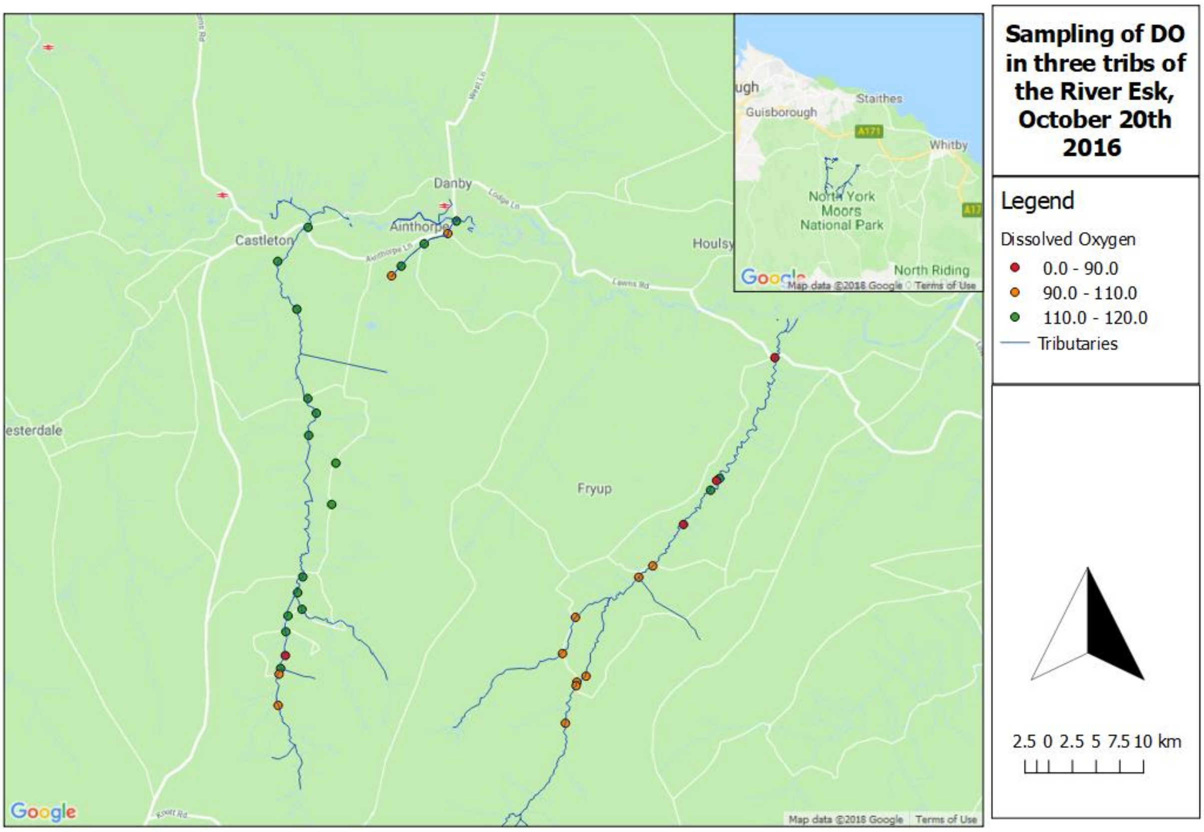

Figure 4.8 DO concentrations taken in October, data plotted using the thresholds proposed by Oliver (2000) Moorkens (2000) and Bauer (1988)

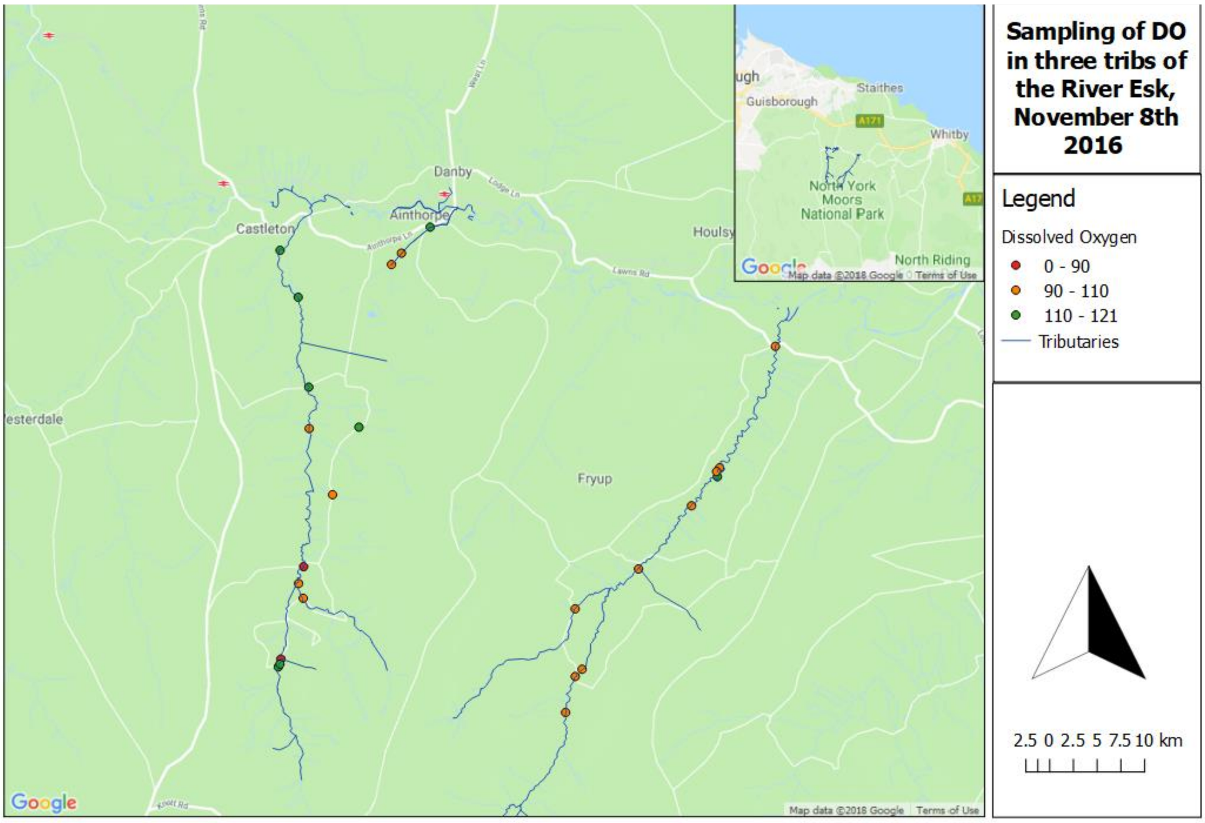

Figure 4.9 DO concentrations taken in November, data plotted using the thresholds proposed by Oliver (2000) Moorkens (2000) and Bauer (1988)

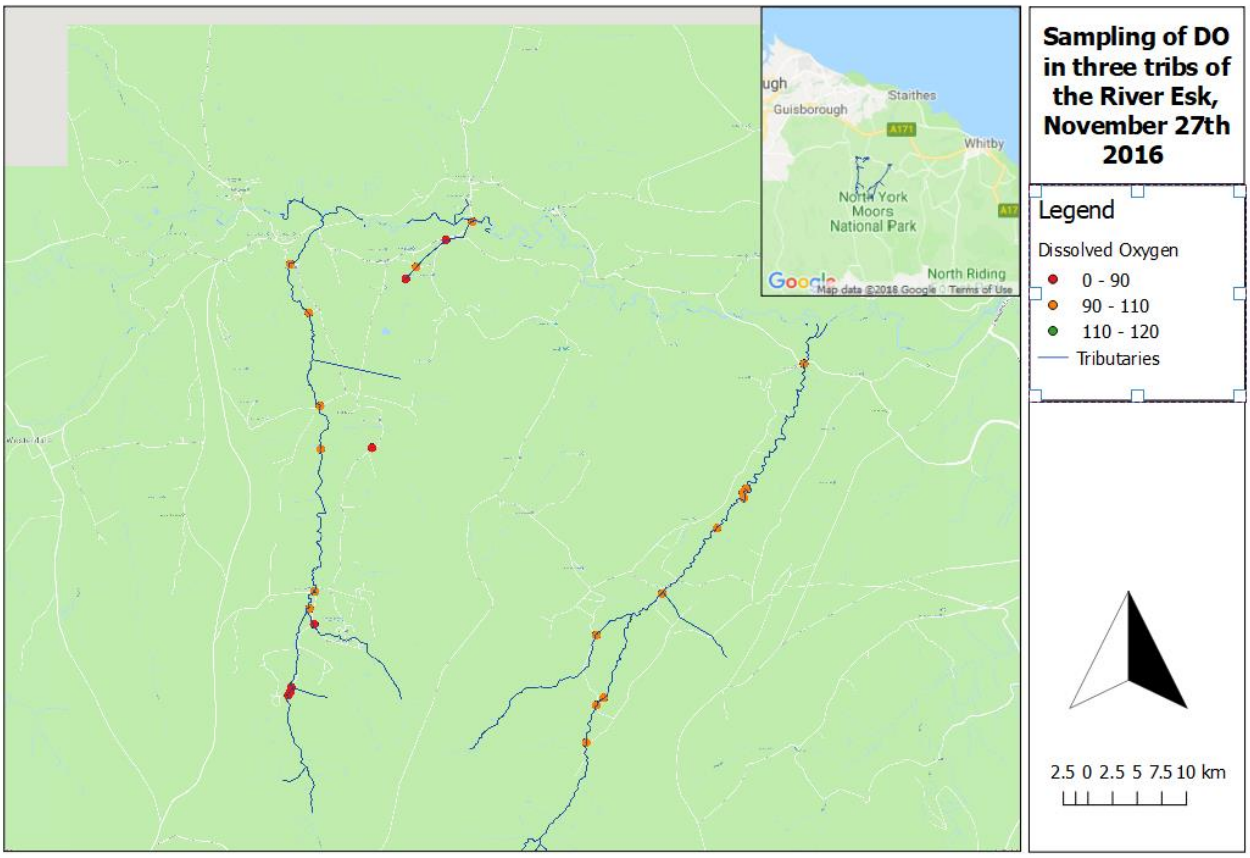

Figure 4.10 DO concentrations taken in November, data plotted using the thresholds proposed by Oliver (2000) Moorkens (2000) and Bauer (1988)

4.3 Conductivity

4.3.1 Conductivity – Seasonal Variations

Mean values for conductivity over the sampling period are 203 μs cm^{-1} for Toad Beck, 127 μs cm^{-1} for Danby Beck and 111 μs cm^{-1} for Great Fryup Beck. Standard deviation for the sampling period is 71 μs cm^{-1} for Toad Beck, 48 μs cm^{-1} for Danby Beck and 47 μs cm^{-1} for Great Fryup Beck. Between July and November conductivity decreases from 122 μs cm^{-1} to 88 μs cm^{-1} on Danby Beck. Similarly, Great Fryup Beck decreases from 129 μs cm^{-1} to 94 μs cm-1. Toad Beck shows an increase in conductivity from 151% to 193%. July through to October shows higher levels of conductivity with all tributaries having the majority of points over 100μs cm^{-1}. Figures 4.12 – 4.22 show conductivity observations. Occasionally, there are anomalies in this trend as shown on Great Fryup Beck at G3; similar trends are shown in minor tributaries on Danby Beck, for instance D8 which has a conductivity result of 256 μs cm^{-1}. As flow levels and 2 storm events occur in November, conductivity reduces to as low as 45μs cm on Danby Beck, which highlights the importance of dilution.

As flow rates increase in October and November, there is a shift in the number of sample locations which fall below 100 μs cm-1. The headwaters of both Danby Beck and Great Fryup Beck tend to be lower with 50 μs cm^{-1} and 60 μs cm^{-1} recording in November. Great Fryup Beck conductivity decreases to 48 μs cm^{-1} and 73 μs cm^{-1}. Danby Beck's headwaters are categorised as green (above 110 μs cm^{-1}) in both November surveys, and Great Fryup Beck categorised as green at the start of November. Toad Beck is consistently above the 100μs cm^{-1} threshold, with an overall average conductivity of 203 μs cm^{-1}. Occasionally tributaries draining into Danby and Great Fryup have a significantly lower conductivity reading such as G3 which has a conductivity of 35 μs cm^{-1} on 26th September and G8 with a conductivity of 77 μs cm^{-1}.

After the second storm event on the 22nd November, conductivity levels were recorded 5 days later and showed Danby Beck's upper catchment to be lower than 65μs cm^{-1}, and Great Fryup Becks upper catchment to be between 70-100μs cm^{-1}. Solute concentration is normally reduced during periods of storm runoff (Anderson and Burt 1982), which is shown by the low concentrations of 72 μs cm^{-1} at G12 – G14 on Great Fryup Beck. Similarly averages for Danby Beck post storm are 88 μs cm^{-1} and 94 μs cm^{-1} on Great Fryup Beck. Toad Beck has a lower average in November of 193 μs cm^{-1} compared to the highest average of 276 μs cm^{-1} in October.

Juvenile *M. margaritifera* can be smothered by fine sediment blocking the interstices reducing the exchange of oxygen, unlike adult *M. margaritifera* juveniles lived buried within the substrate.

4.3.2 Conductivity – monthly trends

Figure 4.11 shows the conductivity averages from July to November on all three tributaries. Conductivity is heavily dependent on flow rates, in theory with an increased input of water into a system, the transportation and influx of sediment into a system will increase. Toad Beck has the highest concentration of conductivity, with an average of 203.1µs cm^{-1}, compared to Danby 127.4 µs cm^{-1}, and Great Fryup 112.4µs cm^{-1}. Toad Beck is consistently above 150µs cm^{-1} and noticeably higher in October, which could be caused by higher flows. A noticeable spike in October is present for all three tributaries, which could be accounted for by low flows. November has some of the lowest recorded conductivity results, with an average of 94 µs cm^{-1} on Great Fryup Beck and 88 µs cm^{-1} on Danby Beck, which coincides with higher flows during a flood event. Contrasting to the converging autumn trend observed in dissolved oxygen, conductivity converges in the summer, which could reflect the reduced frequency of storm events eroding sediment and thus transporting dissolved ions, which elevate conductivity.

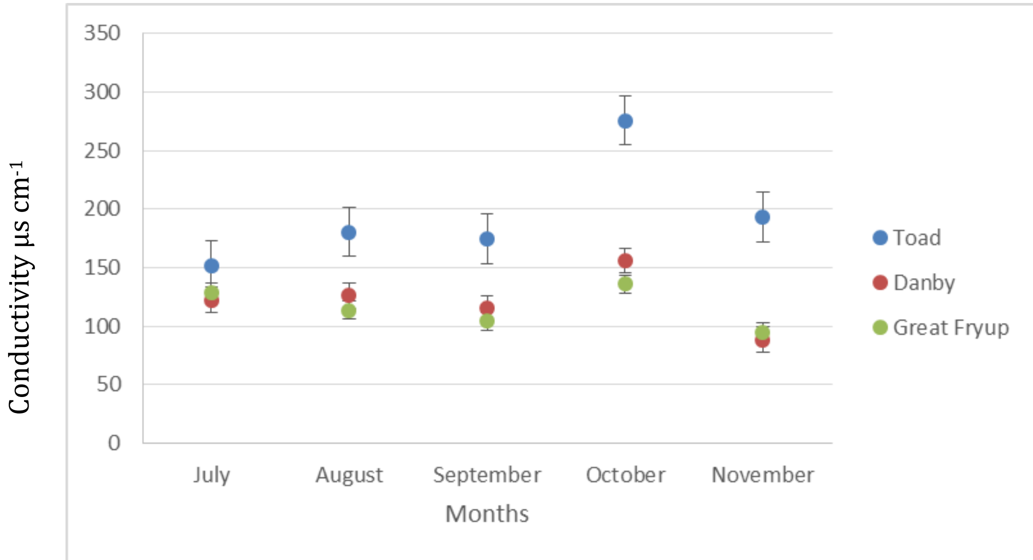

Figure 4.11 Average conductivity measured along each of the three tributaries during each month of the study, error bars are plotted.

4.3.3 Conductivity - average trends

Toad Beck conductivity increases downstream and peaks at T3 (212µs cm^{-1}). Highest recordings of conductivity occurred towards the end of October, with a high of 418µs cm^{-1} at T4. Danby Beck has an increasing trend downstream, with conductivity at D17 73µs cm^{-1}, compared to D1 at 180µs cm^{-1}. There is a noticeable spike at D8 at 256µs cm^{-1}, at the end of October; it should be noted that this was the only reading taken at this point, therefore averages can be skewed. Great Fryup Beck shows a similar increasing trend downstream, although G2 is lower than expected at 124.5µs cm^{-1}.

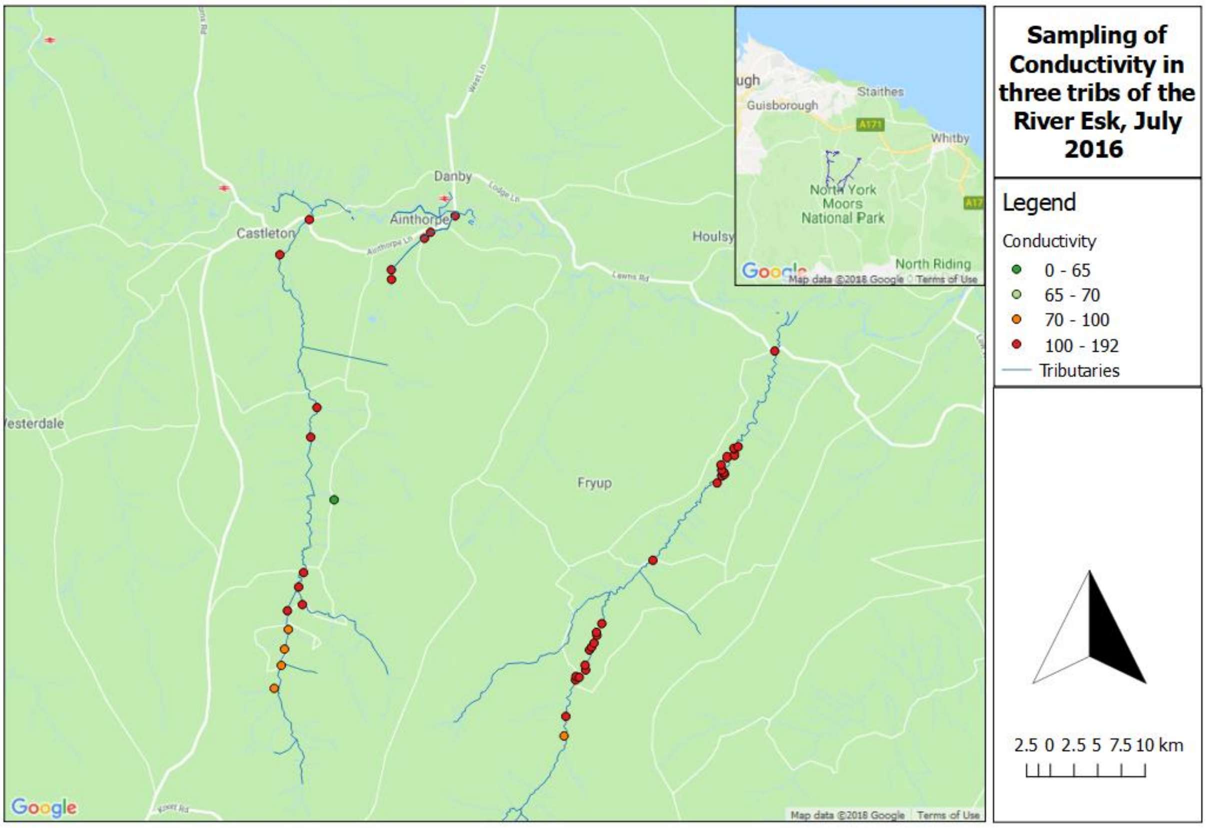

Figure 4.12 Conductivity observations taken in July, plotted against thresholds proposed by Oliver (2000) Moorkens (2000) and Bauer (1988)

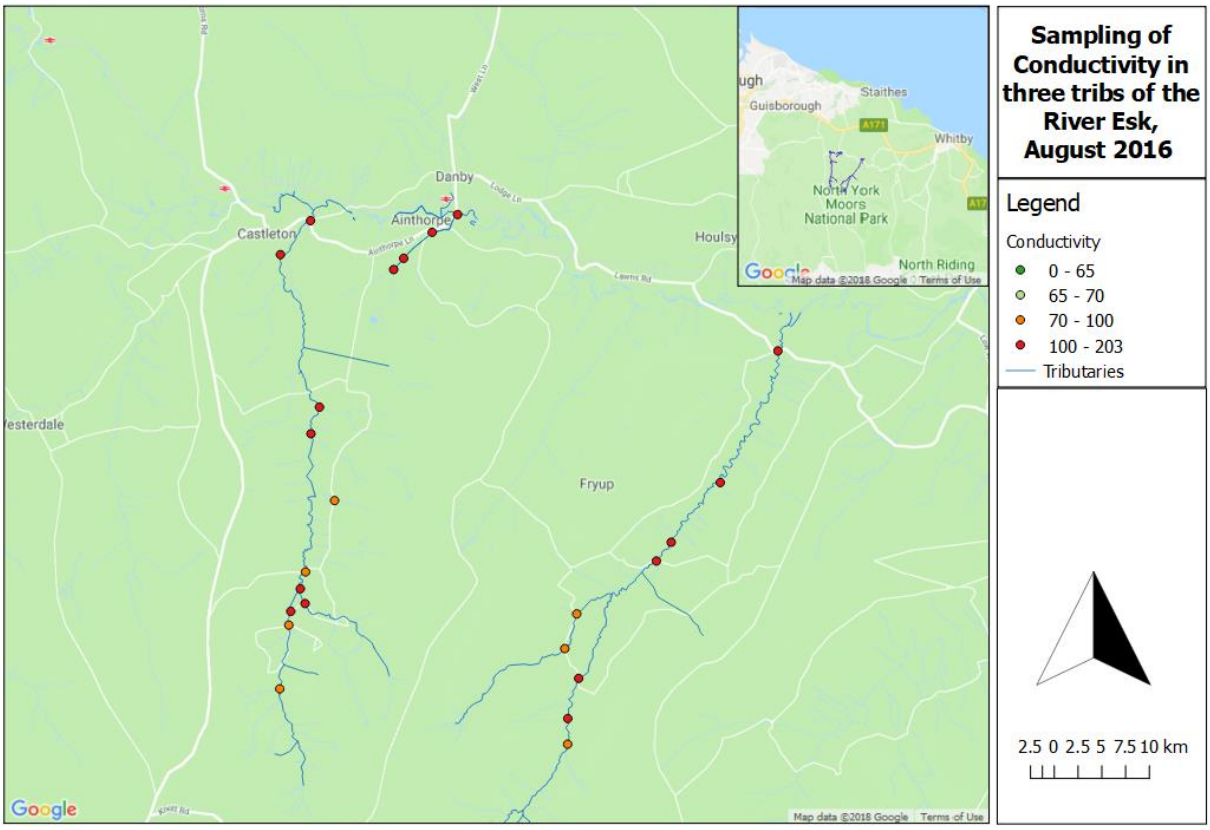

Figure 4.13 Conductivity observations taken in August, plotted against thresholds proposed by Oliver (2000) Moorkens (2000) and Bauer (1988)

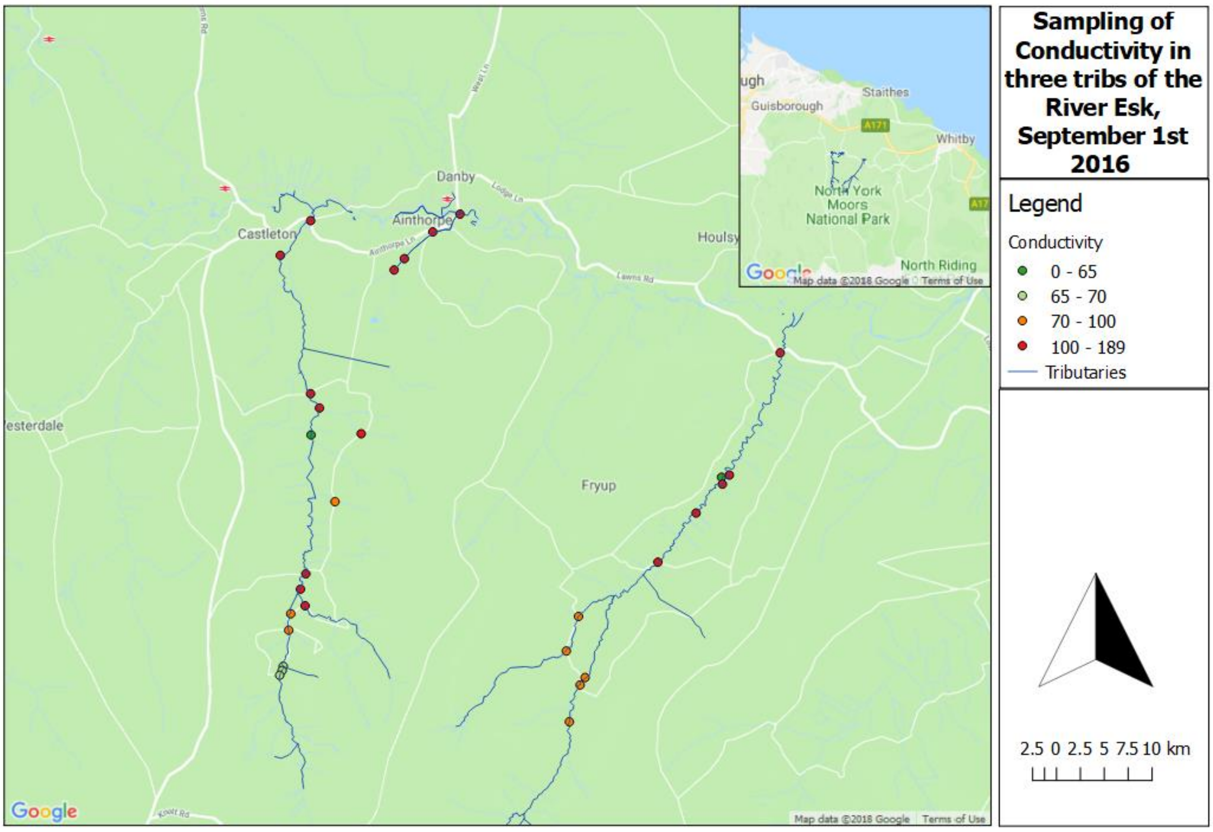

Figure 4.14 Conductivity observations taken in September, plotted against thresholds proposed by Oliver (2000) Moorkens (2000) and Bauer (1988)

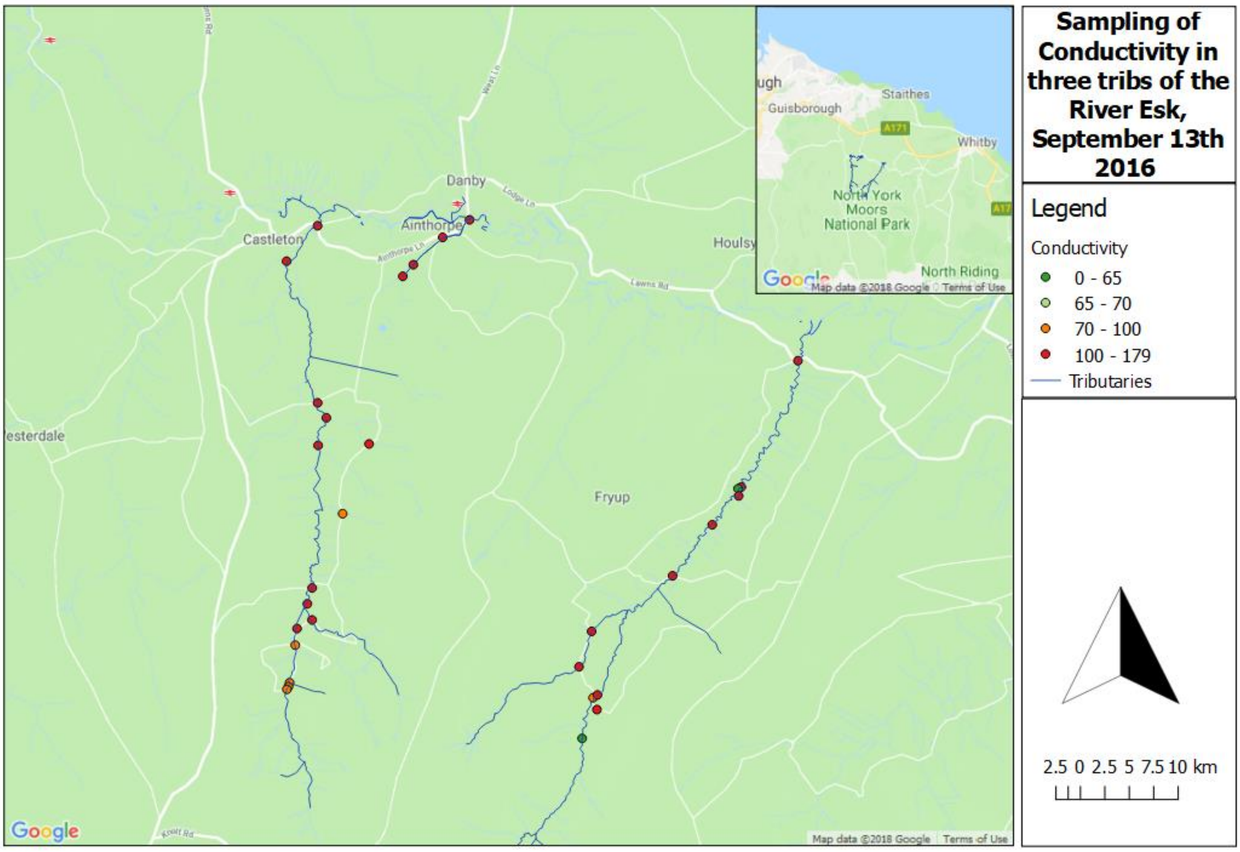

Figure 4.15 Conductivity observations taken in September, plotted against thresholds proposed by Oliver (2000) Moorkens (2000) and Bauer (1988)

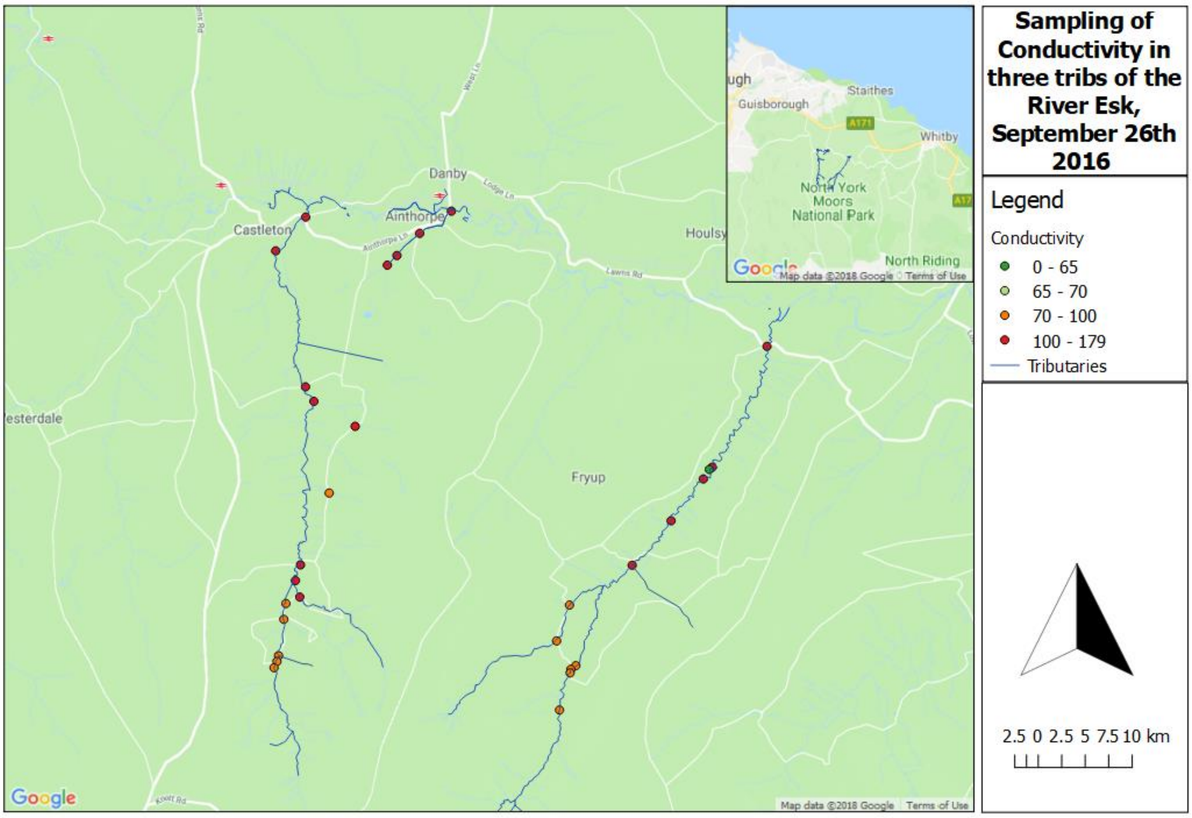

Figure 4.16 Conductivity observations taken in September, plotted against thresholds proposed by Oliver (2000) Moorkens (2000) and Bauer (1988)

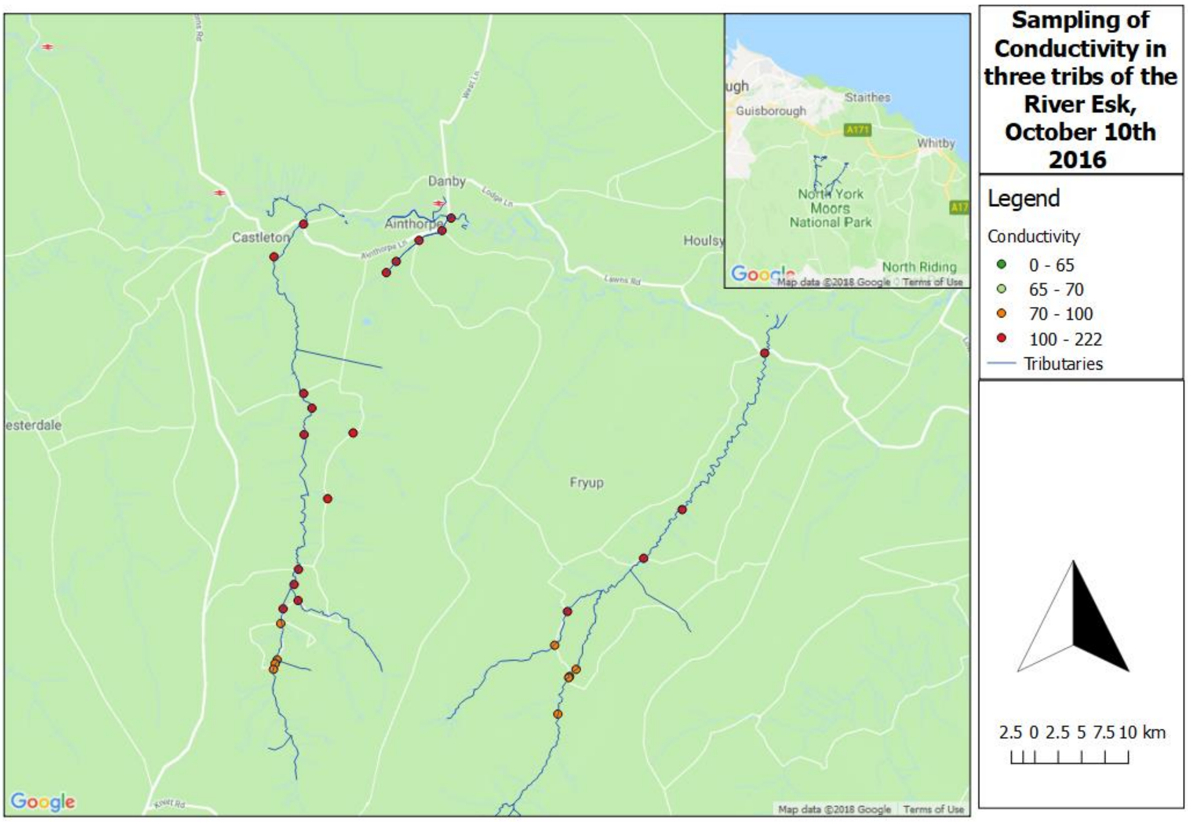

Figure 4.17 Conductivity observations taken in October, plotted against the thresholds proposed by Oliver (2000) Moorkens (2000) and Bauer (1988)

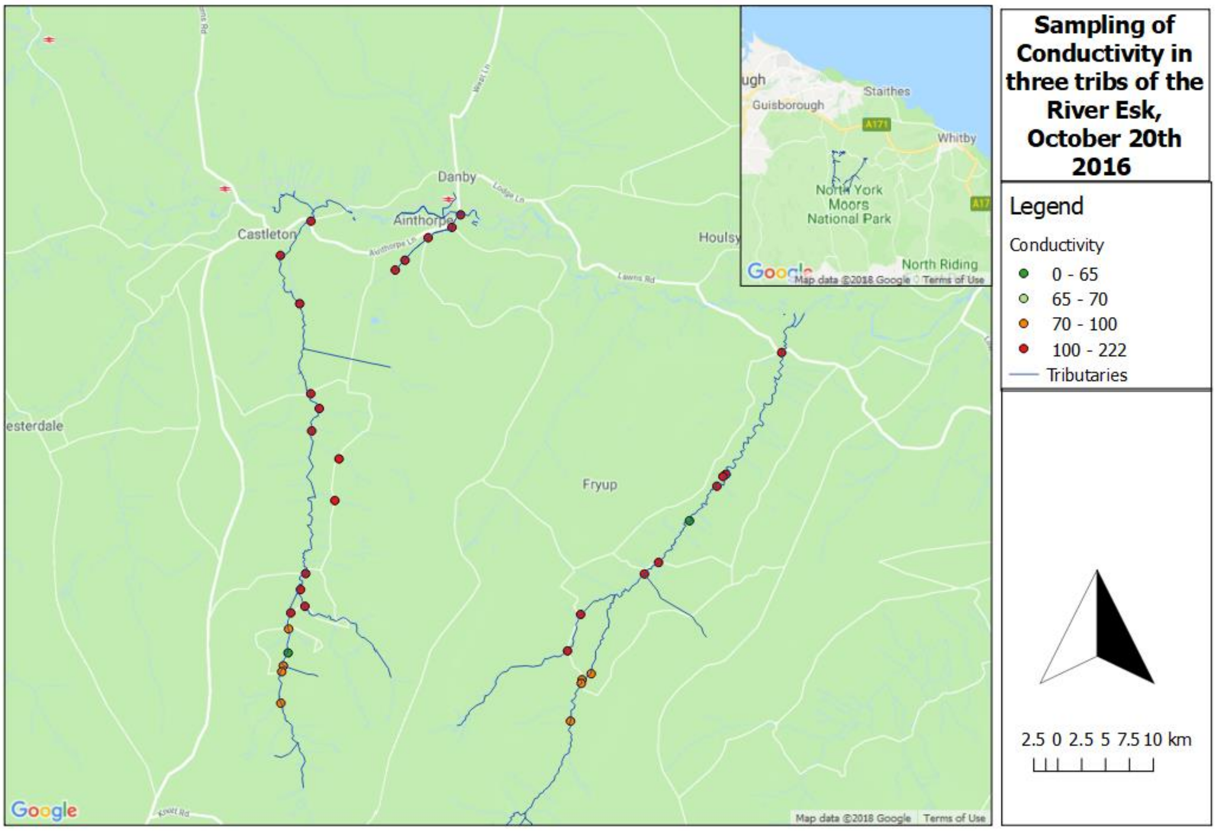

Figure 4.18 Conductivity observations taken in October, plotted against the thresholds proposed by Oliver (2000) Moorkens (2000) and Bauer (1988)

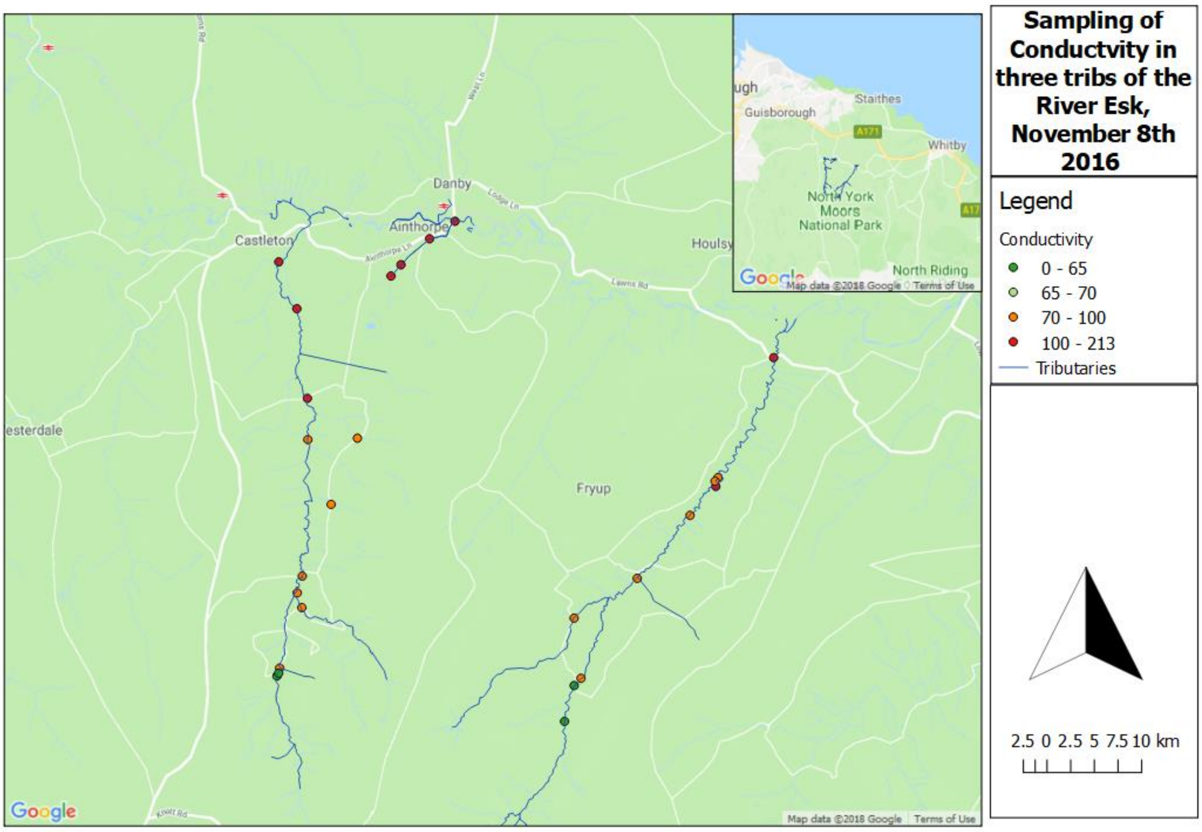

Figure 4.19 Conductivity observations taken in November, plotted against the thresholds proposed by Oliver (2000) Moorkens (2000) and Bauer (1988)

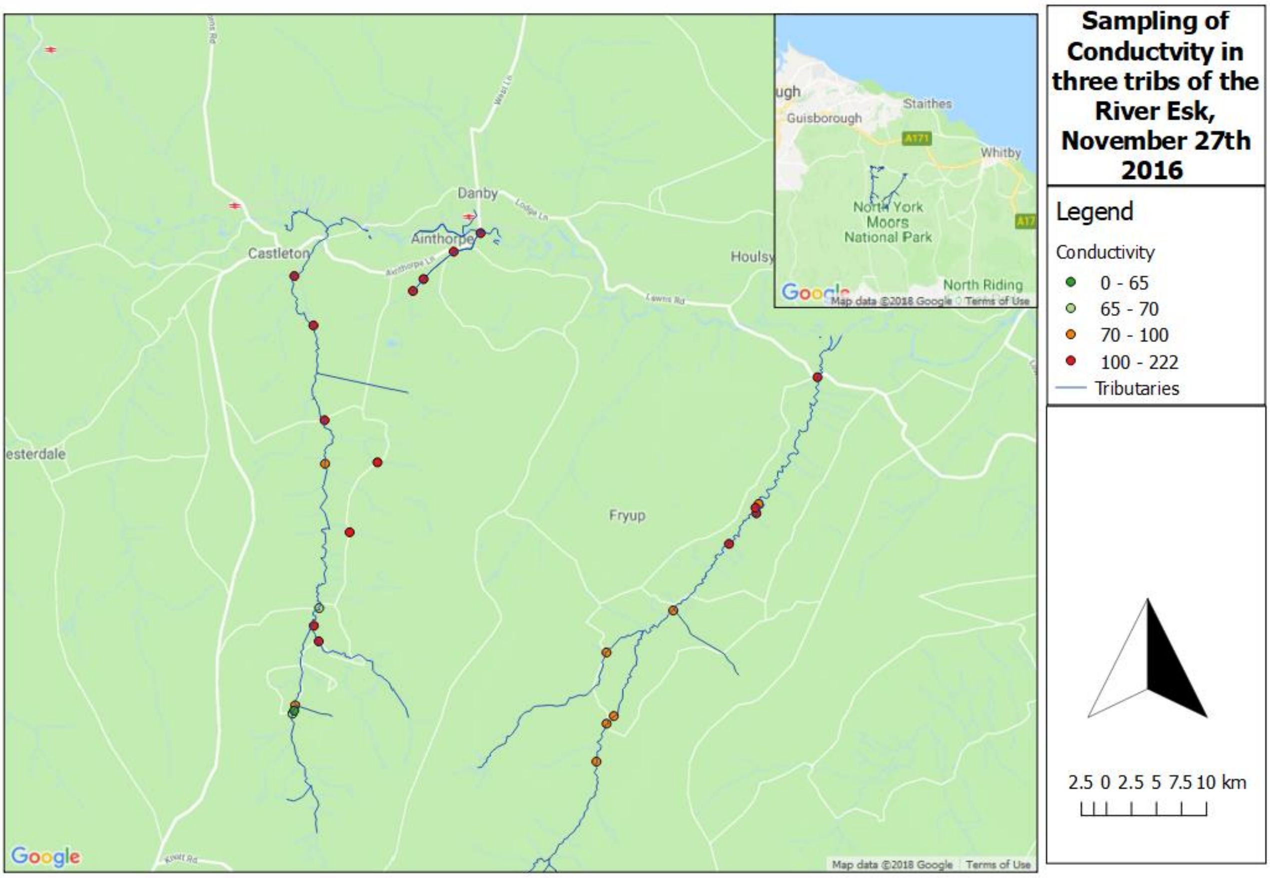

Figure 4.20 Conductivity observations taken in November, plotted against the thresholds proposed by Oliver (2000) Moorkens (2000) and Bauer (1988)

4.4 Temperature

Figure 4.21 shows the average monthly temperature for all three tributaries. Temperature has a clear negative trend from July to November ranging from 17 ° C to 6.4 ° C. July sees a wider spread of average temperatures, with Toad at 12.1 °C compared to 16.9 °C at Great Fryup. Great Fryup has a highest average temperature at 11.5 °C. The convergence of temperature in autumn could be associated with a reduction of seasonal fluctuations across the three rivers. Water Framework Directives suggest temperature should be lower than 21 °C for UK rivers (EA, 2009).

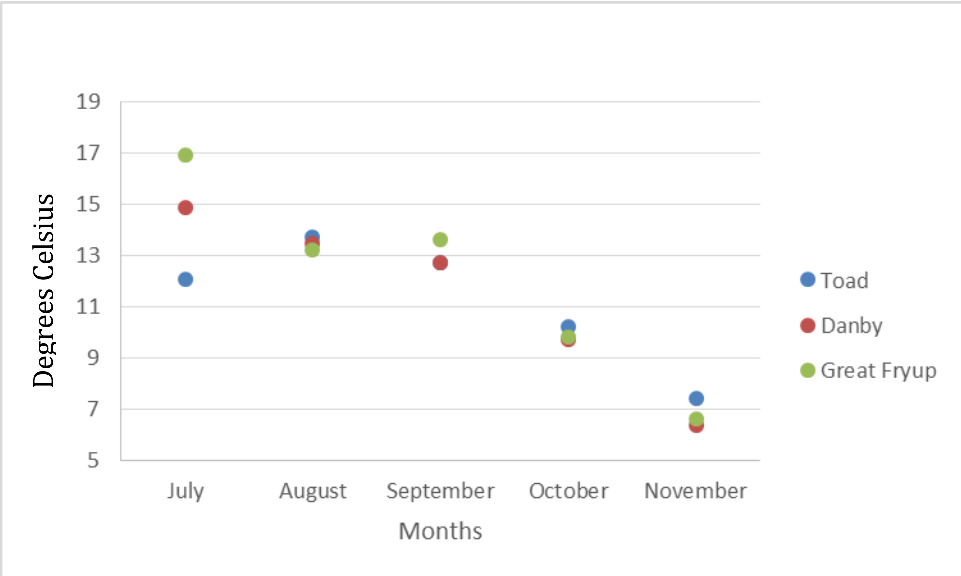

Figure 4.21 Monthly temperatures for all three tributaries

4.5 pH

Danby and Great Fryup Beck catchments are influenced by fluctuations in flow, altering the water table which causes the flushing of DOC, turning the water brown and increasing the acidity of the pH. The upper catchments of Danby and Great Fryup Beck have lower pH values, falling between 5.0 and 6.0. Danby Beck has a value of 5.0, whereas Toad has a value of 6.7 and Great Fryup Beck has a value of 5.4. Toad Beck is slightly acidic with all values falling between 6.0 and 7.0. Danby Beck clearly shows how pH values are affected by dilution downstream with a final value of 7.3. Great Fryup Beck is more acidic towards the upper catchment with values falling between 5.0 and 7.0. G12 has a slightly more neutral value of 6.2.

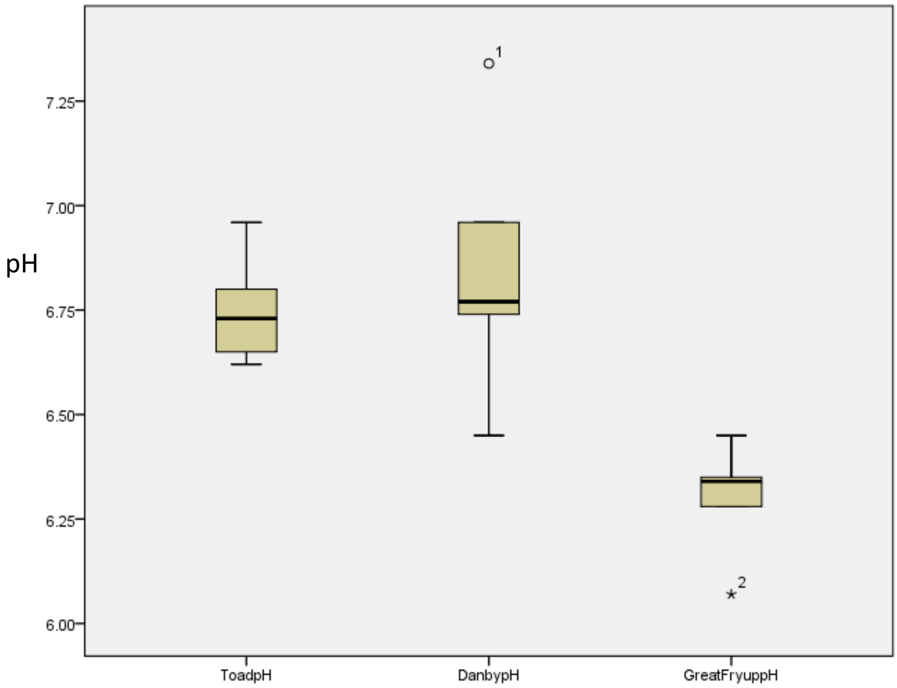

Figure 4.22 Box plot showing the range of pH values on each tributary, the circle and star markers represent outliers.

4.6 Spatial variations of pH

Figure 4.22 shows the variation of pH values on all three tributaries, values lower than 7.0 are acidic. pH values fall within a range of 6.0 to 7.3. Danby Beck is slightly more neutral than the other becks. Its median is weighted towards the minimum values. Great Fryup Beck is more acidic with a median of 6.4. Both Danby and Great Fryup Beck have outliers, at 7.3 and 6.1 respectively.

4.7 Summary

Temporal variations over a 6-month period can alter water quality significantly. DO, conductivity, temperature and pH are sensitive to climatological changes and differing flow levels. DO falls within the thresholds suggested by Moorkens (2000), Oliver (2000), Moorkens (2000) and Oliver (2000); however, if recruitment of *M. margaritifera* were to be successful, levels of DO would have to improve during the autumnal months. Similar conclusions can be drawn from levels of conductivity, it is a significant issue on all three tributaries, and mitigation to reduce levels is necessary. Temperature is within the guidelines suggested by the EA (2009); however, new threats from climate change could impact negatively. pH levels are within the guidelines of the WFD(UK TAG, 2008): it is clear that the headwaters of each tributary are slightly more acidic; however, *M. margaritifera* has been known to prefer slightly acidic conditions (Buddensiek *et al.,* 1994).

5. Results: Spatial Variations in Water Quality – causes and sources of diffuse pollution

5.1 Anions

Using the SPSS statistical package, box plots were created to show the range of anions and cations on all three catchments. Nitrate, chloride and sulphate are plotted on separate box plots. Anion concentrations fall within current water quality legislation; however, in relation to the specific requirements of *M. margaritifera* the levels are higher desired, although limited research into thresholds for anions and cations for *M. margaritifera* exist. Toad Beck has a much narrower variation between anions, which could be attributed to fewer sampling locations as Toad Beck is the smallest catchment. Alternatively, Toad Beck water quality could be influenced by one dominating factor: land use – specifically agriculture which is a significant control in the catchment. Fluoride levels on all three becks are above 0.15mg/l, Phosphate concentrations are lower on Danby and Great Fryup Beck with maximum concentrations of 0.16mg/l on Danby Beck and 0.1mg/l on Great Fryup Beck. Nitrite has a broader range on both Danby and Great Fryup Beck with mean values lower than 0.1mg/l on all three becks. Nitrate values are lower than 5mg/l, chloride values are between 15 and 30mg/l, sulphate values are between 5 and 15mg/l. Fluoride, nitrite, nitrate, phosphate and chloride will be discussed in further detail.

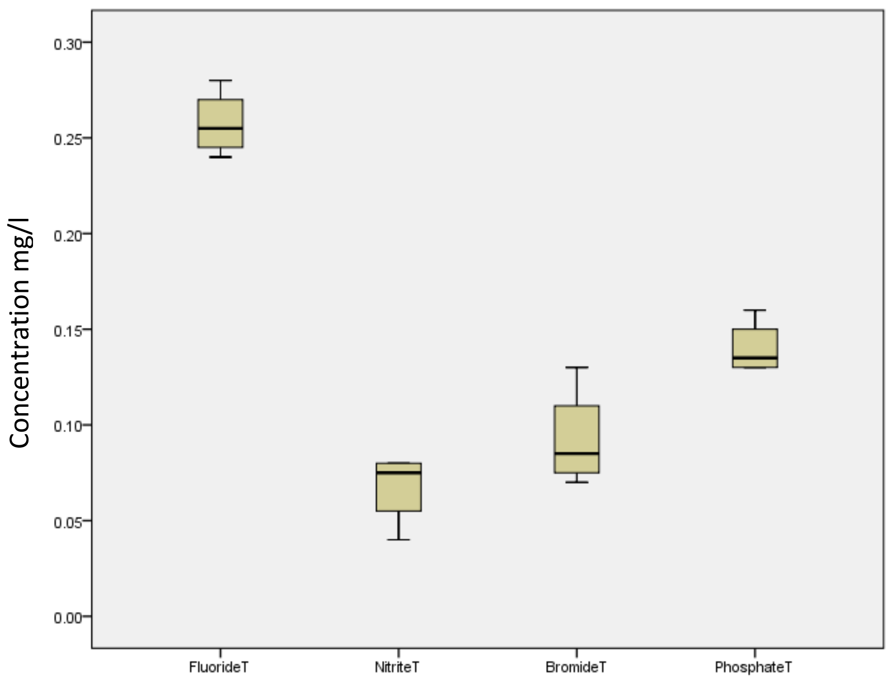

Figure 5.1 Anion concentrations Toad Beck

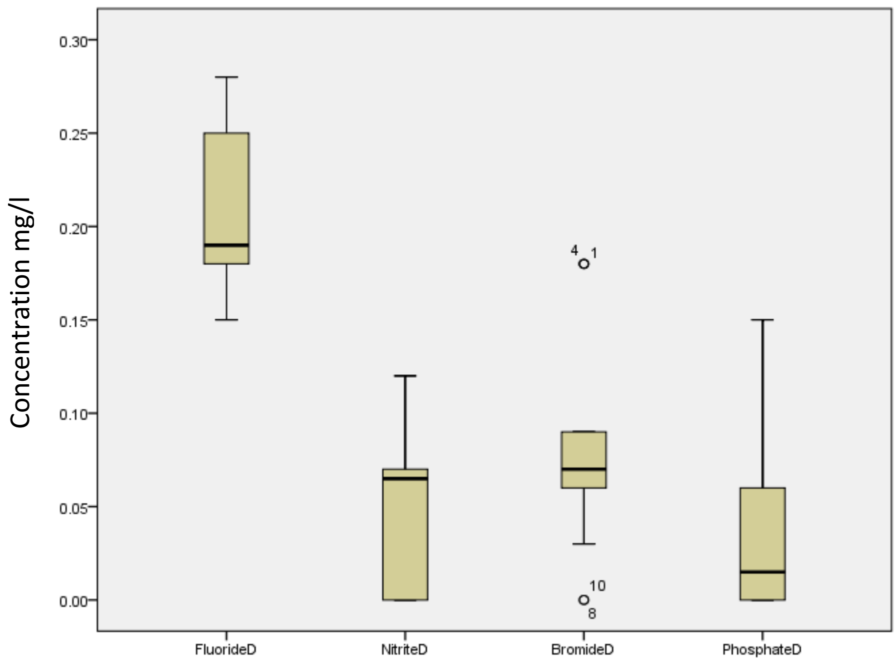

Figure 5.2 Anion concentrations Danby Beck, the circle markers for Bromide represent outliers.

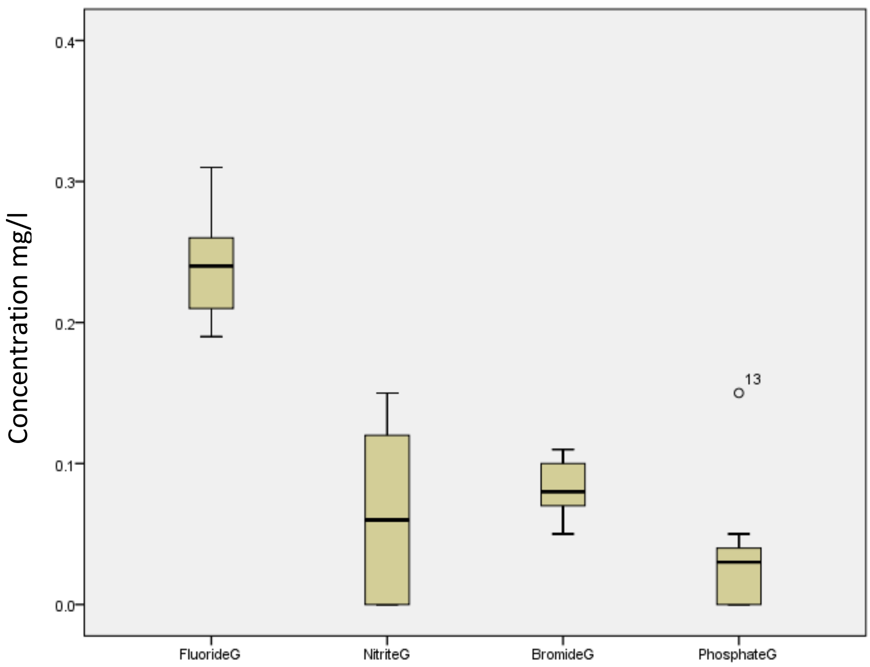

Figure 5.3 Anion concentrations Great Fryup Beck, the circle marker represents at outlier of Phosphate.

5.1.1 Phosphate

Figure 5.4 shows phosphate to be significantly higher on Toad Beck with concentrations between 0.13 and 0.16mg/l. Danby and Great Fryup Beck have multiple occasions where phosphate was not detected; however, there could be concentrations of 0.02mg/l or less within the catchment. Maximum phosphate concentrations of 0.04mg/l on Danby Beck are similar to the mean phosphate concentration of Great Fryup Beck.

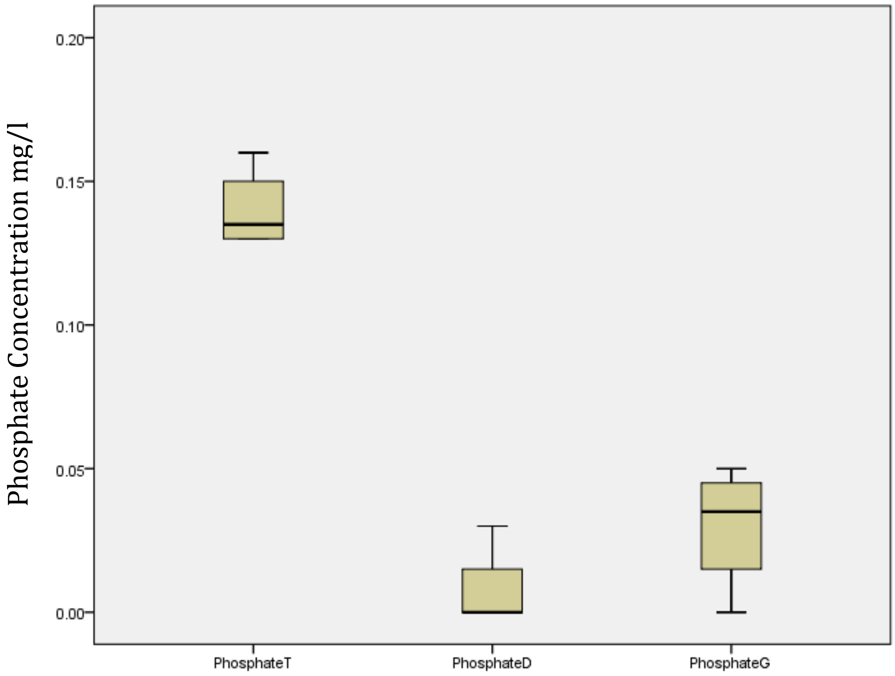

Figure 5.4 Phosphate concentrations on Toad Beck, Danby Beck and Great Fryup Beck

Using the strictest thresholds, the detection limit is too high in relation to proposed thresholds for conservation of freshwater pearl mussels. Phosphate is highest on Toad Beck, with an average concentration of 0.14mg/l. Great Fryup and Danby Beck have an average content of 0.03mg/l. Phosphate peaked at 0.21mg/l at T1, 0.15mg/l at D8, and 0.05mg/l at Great Fryup. Toad Beck has an increase in phosphate concentration downstream, with a slight decrease at T2. Danby Beck has a series of points where phosphate is undetected, especially upstream. D9 has a significant spike of 0.15mg/l, which is downstream of Yorkshire Sewage Treatment Works, which is to be expected. Prior to D9 there is an increase in phosphate concentration, from no trace of phosphate to 0.09mg/l, which suggests an increase in the amount of fertiliser applied to the soils in this subcatchment. Further downstream, past D8, phosphate concentration decreases to 0.03mg/l or no trace. Great Fryup has a significant amount of phosphate in the upper catchment at G13 with a concentration of 0.15mg/l. Excluding G13, there is a decreasing trend from 0.05mg/l to no trace of phosphate.

Phosphate concentrations on Toad Beck are heavily influenced by agriculture and thus are significantly higher with all sample locations registering concentrations above 0.12mg/l (Figure 5.5). A significant proportion of the catchment categorised as improved grassland with fields of re-seeded grassland and horticulture. Thus, pesticides and fertiliser are likely to be added to the surrounding fields to increase yield. The lack of riparian zones between the agriculture and beck increase the concentration of phosphate to concentrations of 0.16mg/l. Spikes observed in Danby Beck such as D10 and D12 (both 0.05mg/l) are attributed to effluent from STW and Botton WTP releasing higher concentrations of nutrients into the beck than what occurs naturally upstream (Figure 5.5). The spike seen at D8 of 0.05mg/l is a tributary which connects farm yards, septic tanks and previously disconnected areas of land directly to the watercourse, bringing increased supplies of nutrients. Spikes in phosphate concentration in the catchment such as G3 and G8, both with concentrations of 0.04mg/l, can be attributed to tributaries bringing higher concentration of nutrients into the beck. The spike at G10 to 0.04mg/l is a result of surface pipes entering the beck. G13 in theory should have a lower concentration of phosphate as it is the least affected by human activity at the head of the catchment; it has a concentration of 0.15mg/l, however there are a significant proportion of secondary tributaries draining the upland catchment, where sheep are present on the moors and lower fields which are categorised as improved grassland.

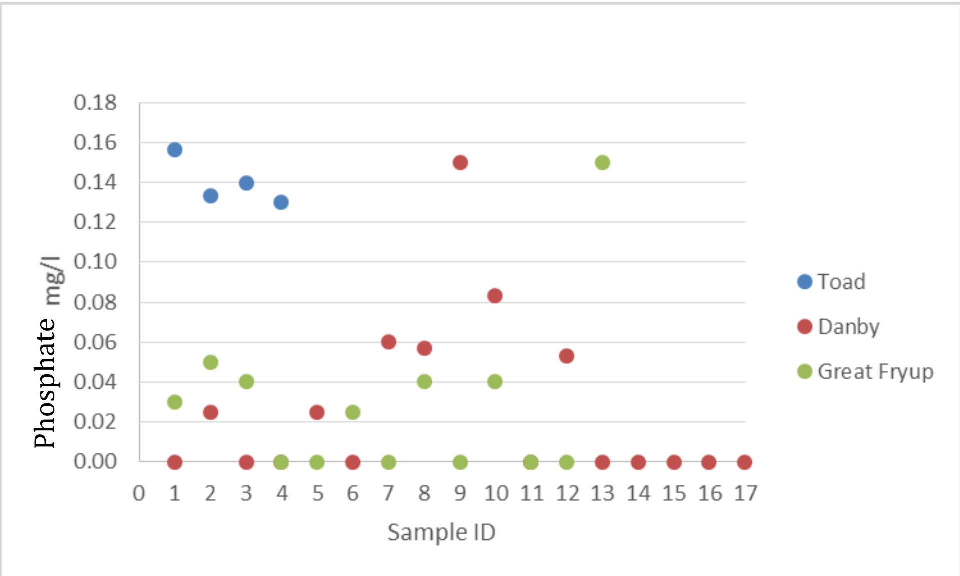

Figure 5.5 Phosphate average concentration on Toad Beck, Danby Beck and Great Fryup Beck

5.1.2 Nitrogen – Nitrate and Nitrite

Nitrogen sources include land drainage, plant and animal debris (Chapman 1992). Elevated levels of nitrate are caused by fertilisers applied to the land. Similarly, large quantities of stock concentrated in small areas can lead to increases in nitrogen. Heathwaite (1993) postulates nitrogen could be a controlling element in the eutrophication of water for two reasons: firstly, there tends to be higher concentrations of nitrogen than phosphorus; secondly, cyanobacteria have the ability to regulate nitrogen concentrations from the atmosphere, and therefore are not responsive to limitations in supply. Nitrate is expressed as NO_3-, nitrite expressed as NO_2- and ammonium as NH^4.

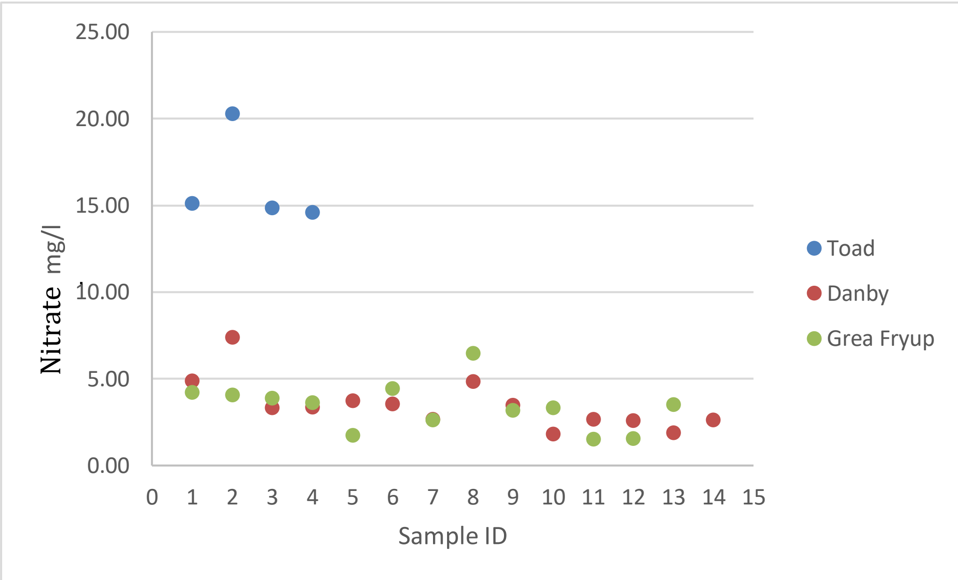

Figure 5.6 Average nitrate concentrations on Toad Beck, Danby Beck and Great Fryup Beck, Moorkens (2000) proposes a threshold of 0.125mg/l for *M. margaritifera.*

Nitrate thresholds (Table 2.1) according to Bauer (1988), Oliver (2000) and Moorkens (2000) are <0.5mg/l, <1.0mg/l and 0.125mg/l respectively. Toad Beck regularly exceeds the thresholds with an average of 16.21 mg/l, significantly higher than Danby at 3.48mg/l, and Great Fryup at 3.39mg/l (Figure 5.6). Toad Beck peaks at 20.28mg/l at T2 while concentrations increase downstream. Danby Beck shows an increasing trend downstream of nitrate concentration, with a peak at D8. Great Fryup has an increasing trend of nitrate downstream. There is a peak at G8 of 6.47mg/l.

Nitrite levels average at 0.06mg/l on all three becks (Figure 5.7). Toad Beck peaks at 0.25mg/l at T3 and T4. Toad Beck has a relatively consistent level of nitrate concentration present in the system, marginally decreasing downstream. Danby Beck peaks at 0.26mg/l at D8. There is no overall trend for nitrite. It shows a decrease downstream; however, there are locations such as D10 and D13 which are outliers to the decreasing trend, which have concentrations of 0.06mg/l. In some instances nitrite is not detected in the system. Great Fryup peaks at 0.12mg/l at G13.

Nitrite concentration decreases downstream on Great Fryup Beck with a noticeable spike at G5 of 0.20mg/l.

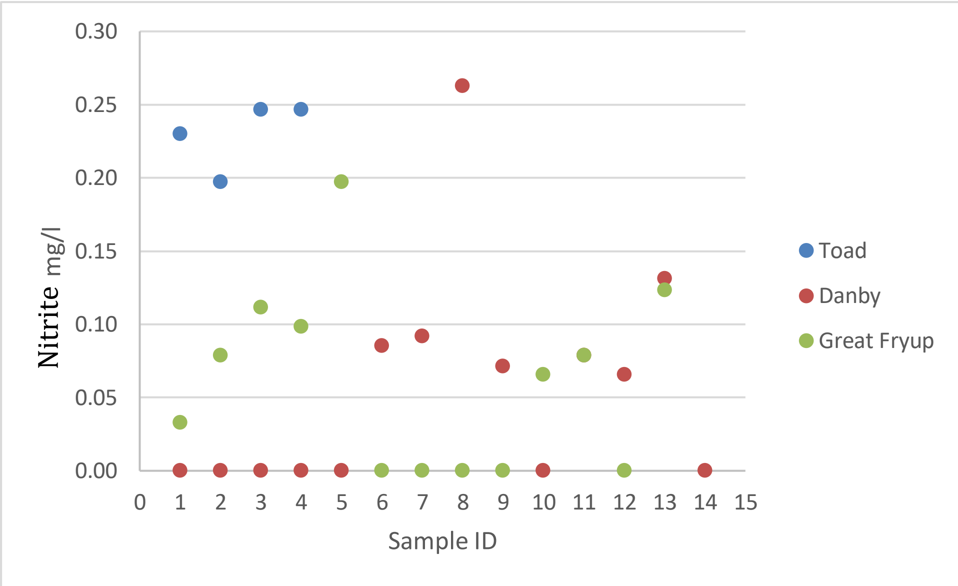

Figure 5.7 Nitrite average concentrations on Toad Beck, Danby Beck and Great Fryup Beck

Ammonification of nitrogen compounds produces NH_4^+, which is then oxidised during nitrification to create NO_3^-, before denitrification occurs to create NO_2^-. This is called denitrification. Therefore, a reduction in nitrate can be assumed and an elevation in nitrite is because of denitrification. Denitrification can influence aquatic production, by modifying the form of recycled nitrogen, and forcing ammonia into the denitrification sink (Kemp, 1988). The presence of NO_2^- in a river suggests reduced oxygen availability. When comparing the Nitrate graph to the Nitrite graph it is evident there are much higher concentrations of Nitrate. This is typical as nitrite begins to appear in low oxygen waters (Jorgensen *et al* 1984), and nitrate remains high in rivers even with denitrification processes. Nitrate occurs naturally in groundwaters as a result of soil leaching (Chapman 1992), therefore elevated levels of nitrate in comparison to nitrite is expected. It is suggested anthropogenic input of nitrate into a catchment is overwhelming and cannot be regulated via denitrification.

The elevated levels of nitrate observed on Toad Beck are attributed to surface pipes, and ditches increasing the runoff from agriculture and therefore increasing the supply of nitrate from fertiliser, soil leaching, groundwater and soil mineralisation. The spike observed at T2 of 20.28mg/l could be a result of an accumulation of arable and horticulture land use towards the middle of the catchment, combined with the influx of surface pipes draining gardens. Levels of nitrite on Toad Beck are lower than nitrate concentrations which could suggest denitrification is not an influential control on the catchment. The low concentration observed at T2 of 0.20mg/l is contrasting to the spike of nitrate. The consistent concentration observed on Danby Beck is a result of the installation of riparian buffer zones filtering the nitrate applied to the surrounding agricultural fields. Spikes in nitrate are attributed such as those at D9 can be attributed to the STW and Botton WTP. Nitrogen loads should remain equal across the year from a sewage outfall (Worrall & Burt 1998). Therefore, spikes in nitrogen correlated with changes in flow and thus dilution. The sporadic concentration of nitrite on Danby Beck suggests how local point source and geomorphological features such as pools can impact denitrification. Spikes in concentration of nitrate observed on Great Fryup Beck such as D8 are attributed to tributaries bringing in an influx of nutrients from agricultural fields, which is an example of when diffuse pollution can be categorised as point source, depending on the scale of analysis. The spikes of nitrite on Great Fryup Beck, which mirror the sporadic nature on Danby Beck, could also suggest local factors influence nitrite concentrations.

Nitrate concentration on the River Esk collected (EA, 2016) over a period of 16 years (missing data from 2009-2012) show a decreasing trend (Figure 5.8), the red line represents the threshold for *M. margaritifera*. When considering the Moorkens (2000) threshold value, nitrate concentrations remains too high for successful *M. margaritifera* populations. The decreasing trend in Nitrate could be a direct result of changes in legislation such as the creation of the WFD and changes in land use, such as the installation of buffer strips adjacent to the river channel.

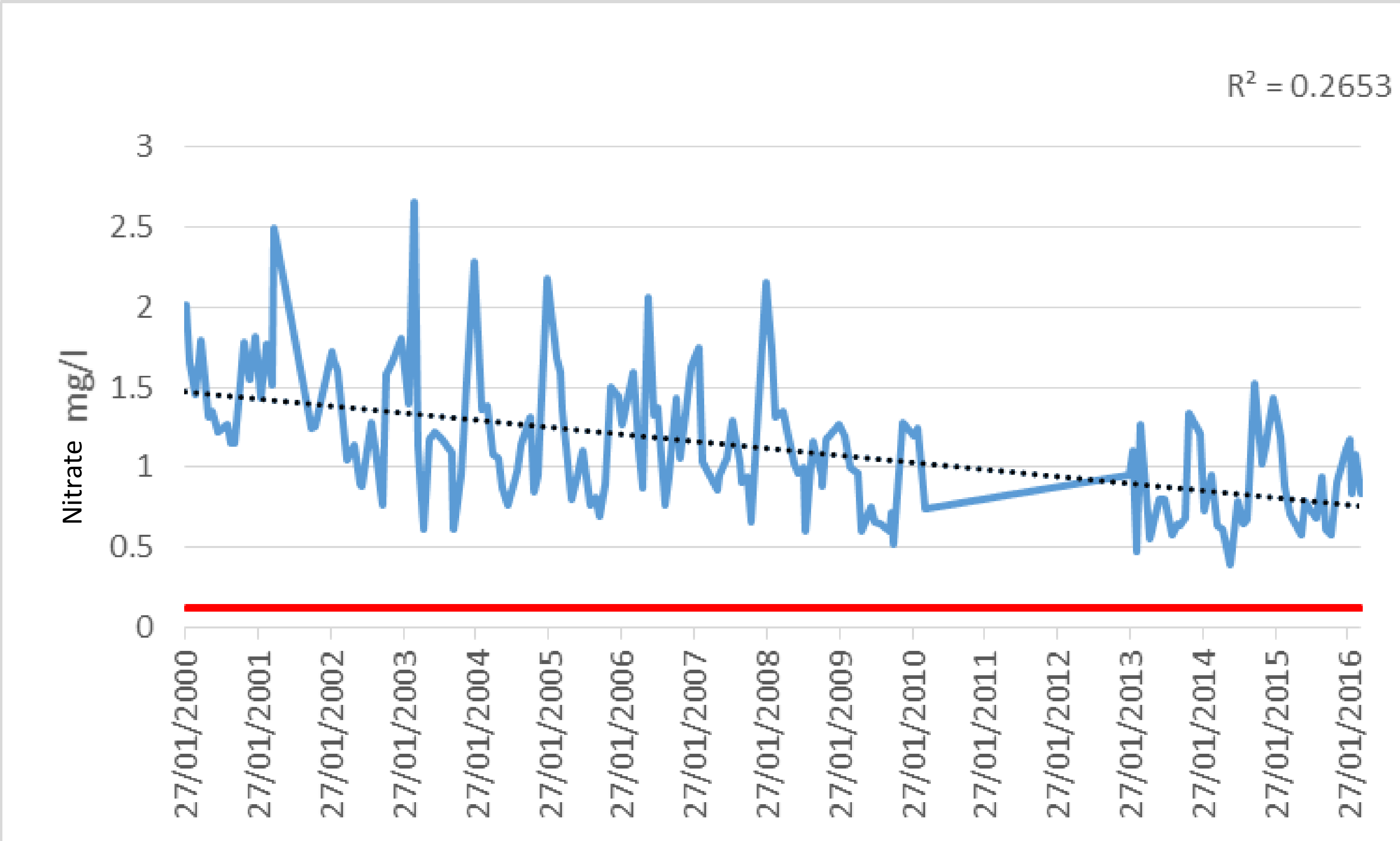

Figure 5.8 Nitrate concentration on River Esk (EA, 2016)

5.2 Cations

Cation concentration is significantly higher on Great Fryup Beck which could be attributed to a lack of mitigation and riparian zones (Figure 5.11). Danby Beck has a wide range for calcium, which could be influenced by tributaries and riffle pool sections diluting concentration (Figure 5.10). Calcium is higher on Toad Beck ranging from 21 to 27mg/l (Figure 5.11). Ammonium has the largest variation on Danby Beck with a much lower mean of 0.9mg/l (Figure 5.12). Calcium and ammonium will be discussed in further detail.

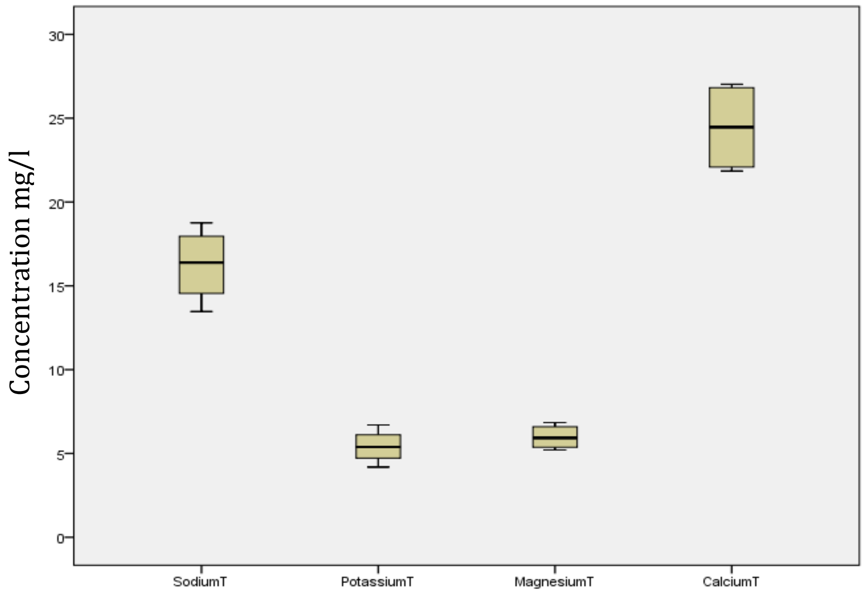

Figure 5.9 Cation concentrations on Toad Beck

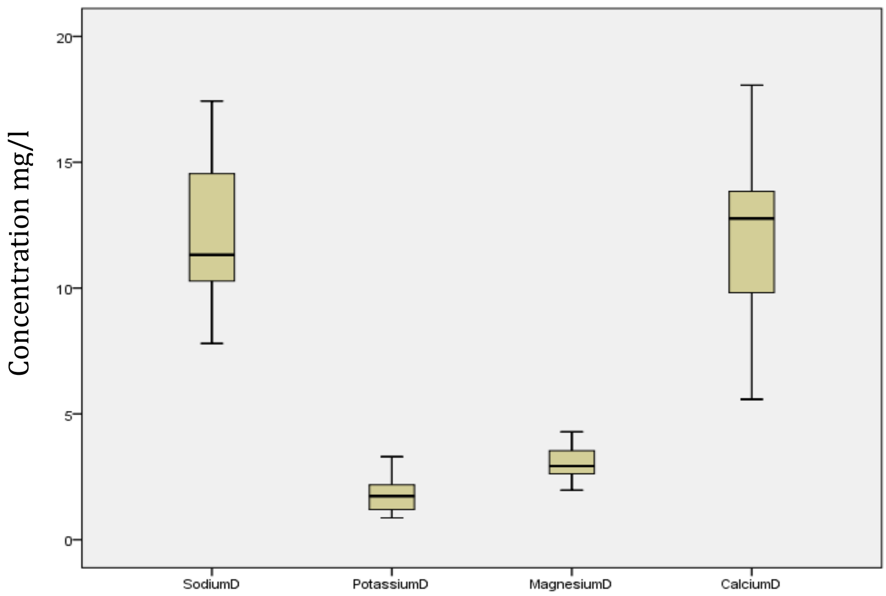

Figure 5.10 Cation concentrations on Danby Beck

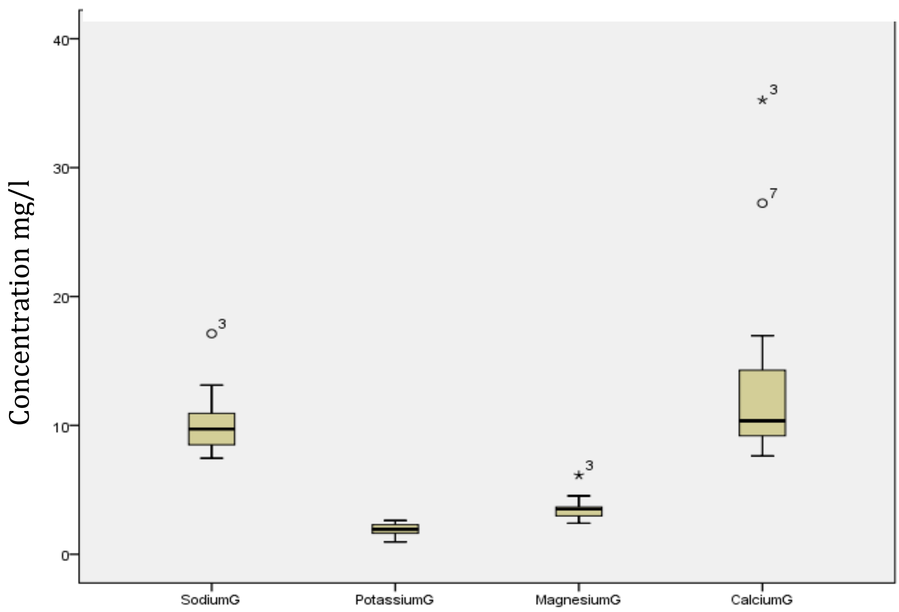

Figure 5.11 Cation concentrations on Great Fryup Beck, the circle and star markers for sodium, magnesium and calcium represent outliers.

5.2.1 Ammonium

Ammonium occurs naturally from the breakdown of nitrogenous organic and inorganic material, and excretion from biota (Chapman 1992). Ammonium is expressed as NH_4^+. Unpolluted waters contain less than 0.2mg/l.

Ammonium has the lowest mean and largest variation of concentration on Danby Beck between 0.03 and 0.18mg/l (Figure 5.12). Toad Beck has the highest mean and smallest spread of ammonium concentration. Great Fryup Beck has the highest maximum concentration of ammonium with an observed recording of 0.21mg/l.

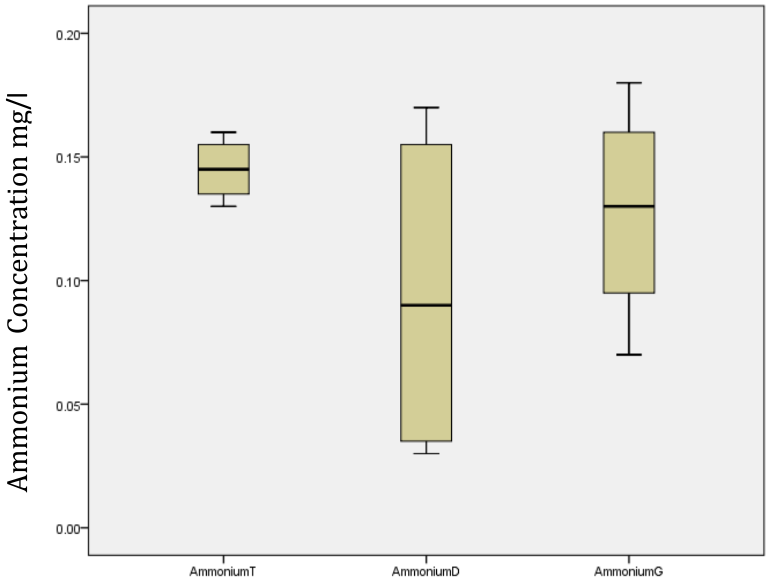

Figure 5.12 Ammonium concentrations on Toad Beck, Danby Beck and Great Fryup Beck

Annual average for ammonium in Toad Beck is 0.15mg/l the highest in all three catchments, in Danby it is 0.09mg/l and in Great Fryup Beck it is 0.14mg/l (Figure 5.13). Ammonium peaks at 0.23mg/l on Toad Beck at T2, T3 and T4. Toad Beck has an increasing concentration of ammonium downstream, with a highest average reading of 0.16mg/l at T2. Danby Beck ammonium concentration peaks at 0.35mg/l at D10. Danby Beck has a sporadic trend of ammonium concentration, which could indicate ammonia entering the system from point source locations. D8 has its highest annual peak of 0.18mg/l. Ammonium is not detectable at all locations, due to having a high detection limit of 0.02mg/l. D3 and D4 have slightly lower readings of ammonium with concentrations of 0.03mg/l and 0.04mg/l respectively. Great Fryup Beck has a maximum concentration of 0.36mg/l at G13. Great Fryup Beck average concentrations are consistently above 0.1mg/l, all except G3 which could be considered an outlier with an average concentration of 0.07mg/l. 0mg/l values are left to demonstrate traces of ammonium, however the detection limit on the analysis could not define the concentration.

Ammonium levels on Toad Beck increasing downstream to concentrations of 0.16mg/l are attributed to the population density, frequency of septic tanks and intensity of agriculture. The spike observed at T2 can be attributed to the influx of surface pipes in the culverted section increasing the concentration of nutrients. The sporadic pattern of ammonium on Danby Beck highlights the importance of diffuse pollution being categorised as point source pollution as there are clear spikes where tributaries, ditches and pipes, which in the context of a rural catchment are usually categorised as diffuse, are bringing elevated levels of ammonium. Great Fryup concentrations support this conclusion.

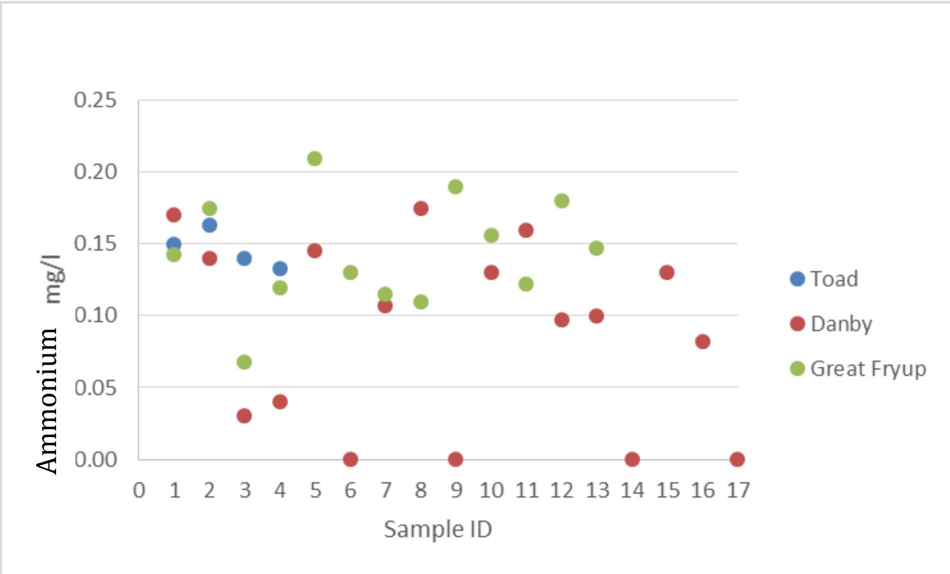

Figure 5.13 Ammonium average concentrations on Toad Beck, Danby Beck and Great Fryup Beck, Moorkens (2000) proposes a threshold of 0.01mg/l for *M. margaritifera.*

5.2.2 Calcium

Calcium sources are from dissolved rocks rich in calcium minerals (Chapman 1992). Concentration for typical water is less than 15mg/l unless limestone is present.

Great Fryup Beck has a large variation in calcium concentrations, with a maximum of 35.2mg/l, its mean is very similar to Danby Beck (Figure 5.14). Danby Beck has a small variation and similar mean to Great Fryup Beck which could suggest similar factors such as geology control calcium concentrations in both catchments. Toad Beck has a mean that is 10mg/l higher than Danby and Great Fryup Beck.

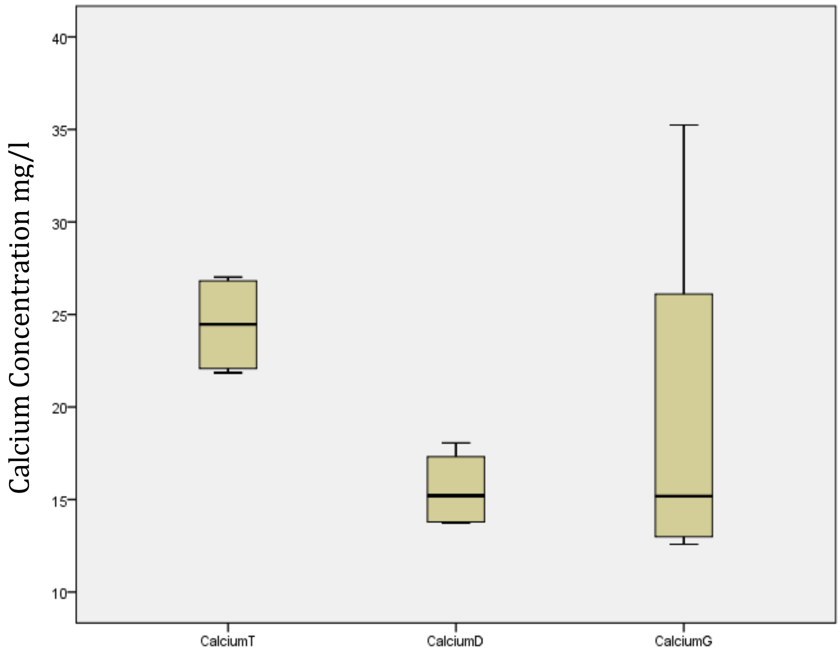

Figure 5.14 Calcium concentrations on Toad Beck, Danby Beck and Great Fryup Beck

Calcium concentration (Figure 5.15) is highest on Toad Beck with an annual average of 24.5mg/l, Danby Beck has an average of 10.1mg/l and Great Fryup Beck has a slightly higher concentration at 14.1mg/l. Toad Beck concentration peaks at 32.9mg/l at T4. Toad Beck calcium concentration increases downstream before decreasing to its lowest at T1 21.9mg/l. Danby Beck peaks at 19.4mg/l at D2. Danby Beck calcium concentration increases downstream, D9 and D11 are slightly higher than the trend at 17.4mg/l and 15.2mg/l respectively. Great Fryup Beck peaks at 47.4mg/l at G7. Great Fryup calcium concentration increases downstream, with two outliers at G7 and G3 with concentrations of 27.2mg/l and 35.2mg/l.

The bell-shaped curve observed on Toad Beck could be attributed to surface pipes, and runoff from roads. Consistent levels of calcium could be attributed to a steady supply of groundwater in both Danby and Great Fryup catchments, with spikes at G7 being attributed to runoff from rainwater however more data points are required to confirm this.

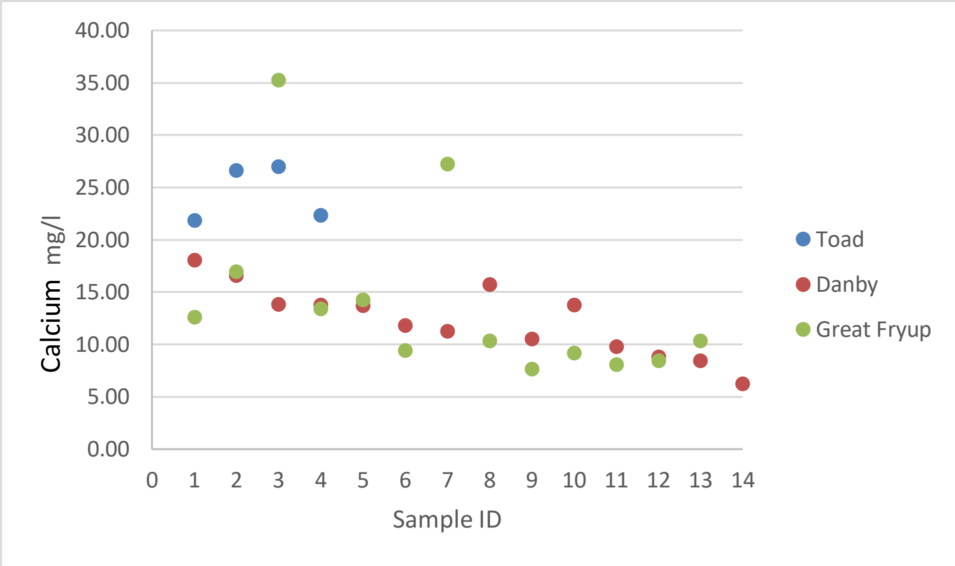

Figure 5.15 Calcium average concentrations on Toad Beck, Danby Beck and Great Fryup Beck

5.3 Dissolved Organic Carbon (DOC)

Burt and Worrall (2004) highlight that records of increasing DOC go back to 1971. Increases in dissolved organic carbon could be associated with changes in terrestrial carbon reserves impacted by climate change – rising temperatures increase the rate of oxidisation and increase the drawdown of the water table (Burt et al., 2004). Tranvik and Jansson (2002) suggest the prime variable for DOC concentrations is the proportion of a catchment which is a wetland. Tranvik and Jansson (2002) suggest DOC increases could be hydrological, increased precipitation creates a flushing of DOC. Increases in DOC have previously been attributed to increased precipitation; Tranvik and Jansson (2002) argue during a drier period with warmer temperatures, there is longer retention and thus increased DOC removal in lake processes, thus decreasing DOC present in a river system. Transport of DOC through a catchment is a significant factor for levels of DOC. New pathways created during a drought could bypass the acrotelm, where the reserves of labile carbon are stored. Increases in stored carbon post-drought conditions could see a higher than expected level of DOC entering the system (Burt et al., 2002).

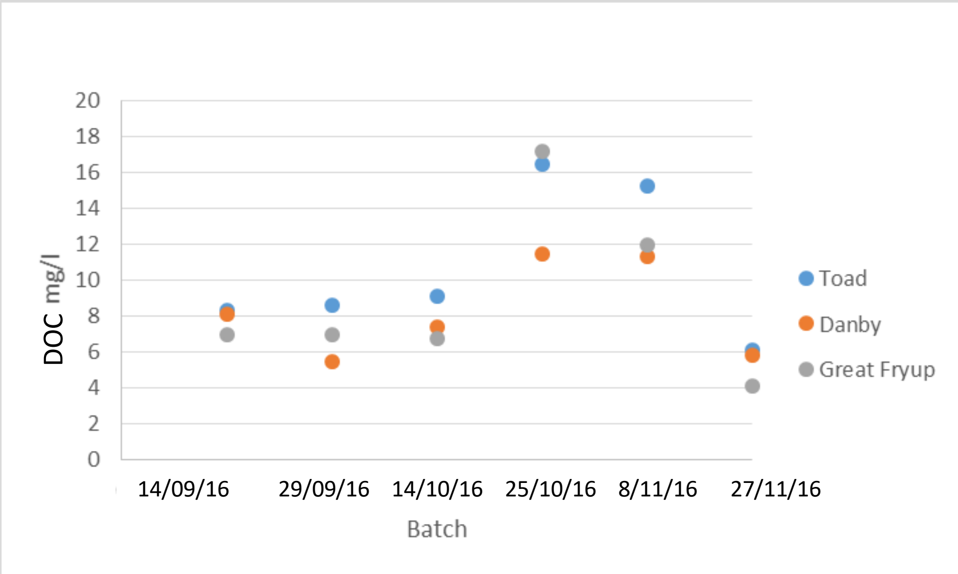

Figure 5.16 DOC concentrations on Toad Beck, Danby Beck and Great Fryup Beck

DOC was measured from September to November, which according to Burt and Worrall (2004) should record maximum DOC concentrations. Averages of the samples for each stream were calculated, showing Toad Beck to have the highest concentrations of DOC peaking at 17mg/l (Figure 5.16). Batch 4 has the highest concentration of DOC, with Toad Beck having an average of 16.4mg/l. DOC increases to peak at batch 4 on all three rivers to 17mg/l. Batch 4 samples were taken on the 20th October, 2 weeks before a flood event occurred. This explains the decreased levels of DOC found in batch 5 and 6 to 6mg/l. Two flood events occurred in November, the 8th November saw a moderate increase in river levels and velocity, whereas 22nd October saw a considerable increase in river levels and velocity. Danby Beck DOC levels were slightly elevated in batch 1 with a concentration of 8mg/l (Figure 5.16). DOC peaks at batch 4 with a concentration of 11.4mg/l. Batch 5 shows a minor decrease in DOC levels to 11.2mg/l. Great Fryup Beck DOC levels do not show as clear an increasing trend as the other becks. DOC levels fluctuate around the 6mg/l mark for the first three batches. Peak DOC occurs in batch 4 with a concentration of 17.1mg/l. Great Fryup Beck shows a clear decreasing trend after the flood events, this could suggest Great Fryup Beck has better connectivity links between the catchment and the peat moorland above. Highest concentrations of DOC are present in batch 4 before the flood events of November, two possible reasons for this are: firstly, as flow levels increase dilution can occur, therefore DOC concentrations could be lower post flood event; secondly, hydrological changes, such as wetting of the upland soils could relink pathways containing high levels of DOC and inputting them slowly into a system, through lateral and horizontal connections.

Using box plots, the spread of DOC values is clearly represented. Danby Beck has a much smaller range of DOC in comparison to Toad and Great Fryup Beck, with values falling between 4.29 and

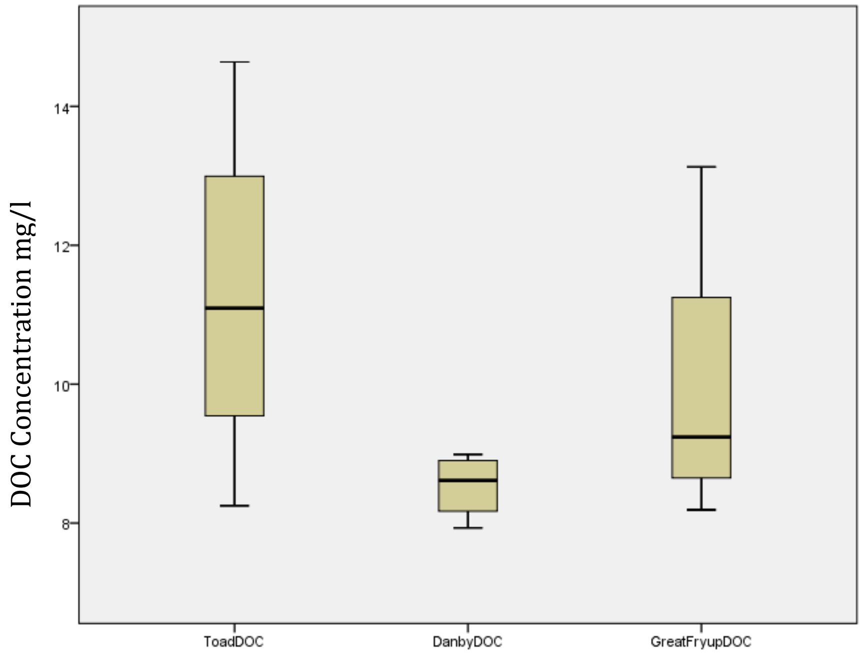

Figure 5.17 DOC concentrations on Toad Beck, Danby Beck and Great Fryup Beck

10.88 (Figure 5.17). The minimum values for all three rivers are quite similar. The upper quartile for Great Fryup Beck falls between 9 and 11, suggesting a weighting towards the upper quartile and maximum values.

5.4 Chemical oxygen demand (COD)

COD concentrations observed in surface waters range from 20mg/l to 200mg/l (Chapman 1992). COD concentrations were highest in batch 5, Toad Beck 59mg/l, Danby Beck 52.3mg/l and Great Fryup Beck 65mg/l (Figure 5.18). Great Fryup Beck had the highest and lowest concentration of COD. Batch 6 had the lowest concentrations of COD, samples were taken after a flood event, and therefore lower levels of COD were expected. COD concentrations were very similar in batch 3 and 6, on Danby Beck and Great Fryup Beck. Danby and Great Fryup Beck have very similar catchment controls, both being influenced by their connectivity to the moorland.

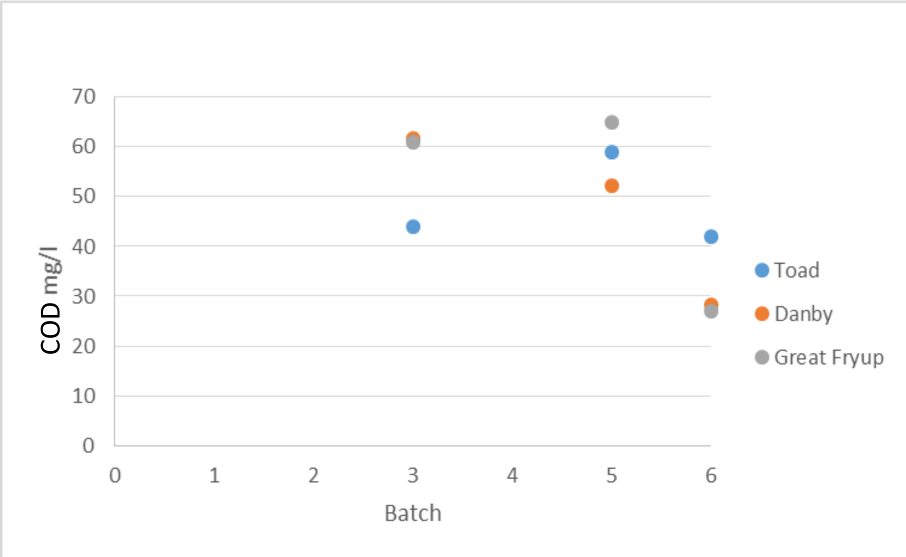

Figure 5.18 COD concentrations on Toad Beck, Danby Beck and Great Fryup Beck

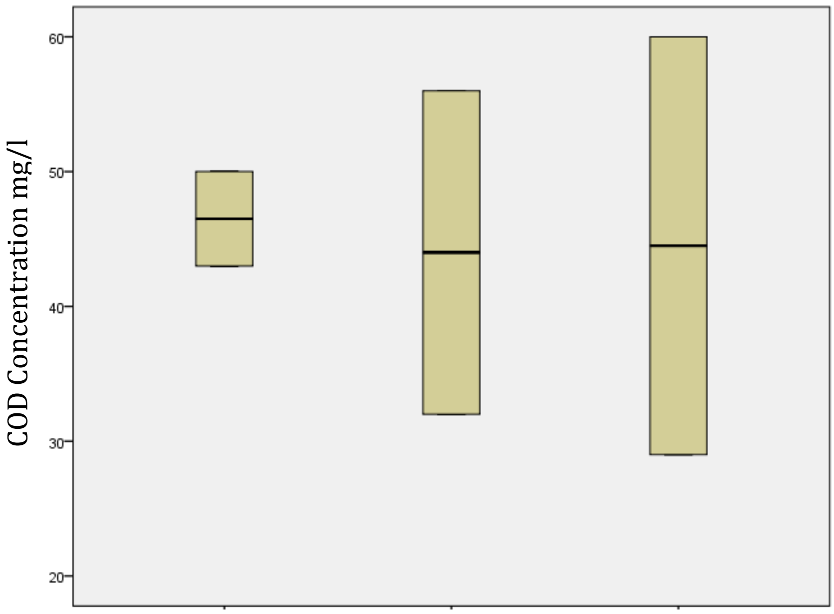

Figure 5.19 COD concentrations on Toad Beck, Danby Beck and Great Fryup Beck

The range of COD concentrations increases with river size (Figure 5.19). Great Fryup Beck which is the longest beck has a COD range of 4mg/l to 86mg/l. The median for Danby is 44mg/l and Great Fryup Beck is 45. The minimum and maximum values for all three rivers are incredibly close to the lower and upper quartile values making it difficult to isolate values.

Undertaking t tests (Table 5.1) on both COD and BOD results has shown no significant statistical difference between Danby Beck and Great Fryup Beck. Although Danby Beck has had river restoration techniques implemented in the catchment it has not significantly influenced the water quality relative to Great Fryup Beck were no restoration works have taken place.

Table 5.1 T test results from Danby Beck and Great Fryup Beck showing no statistical significance difference between water quality concentrations

Parameter	T test
COD	0.064
DOC	0.722

5.5 Biochemical oxygen demand (BOD)

Measurement of biochemical oxygen demand was attempted on all three rivers. The QC failed to fall within the expected limits. Although the QC failed, BOD readings were obtained, providing an estimate for BOD levels in the three rivers. Danby Beck has the highest concentration of BOD with a reading of 1.2mg/l, Great Fryup Beck has a BOD concentration of 1.1mg/l, and Toad Beck has a BOD concentration of 0.4mg/l (Figure 5.20).

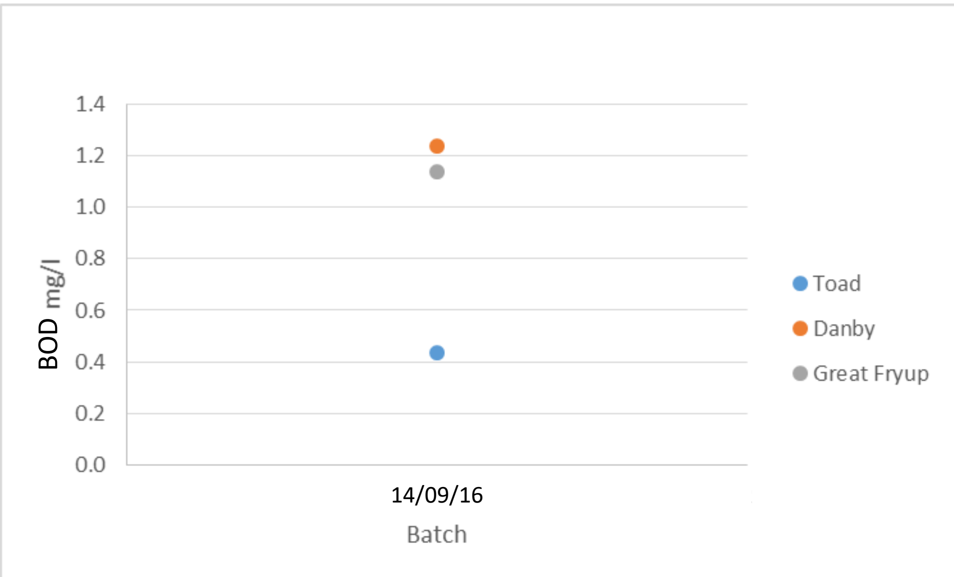

Figure 5.20 BOD concentrations on Toad Beck, Danby Beck and Great Fryup Beck

5.6 Point Sources

5.6.1 Yorkshire Water Sewage Treatment Works (STW)

Point-source locations are usually attributed to outflows from industrial municipalities and the discharge of pollutants through a pipe or ditch (Brooks et al 2014). Figure 5.27 highlights point sources in a section of Danby Beck. The Yorkshire STW releases secondary treated sewage directly into Danby Beck through a pipe. Treated sewage can still contain low levels of nutrients, within the guidelines of the WFD – usually up to 1mg/l for phosphorus (Kartashevsky *et al,* 2015), but with regards to *M. margaritifera* the water releases from a sewage treatment plant is still higher than the guidelines for the protection of *M. margaritifera.*

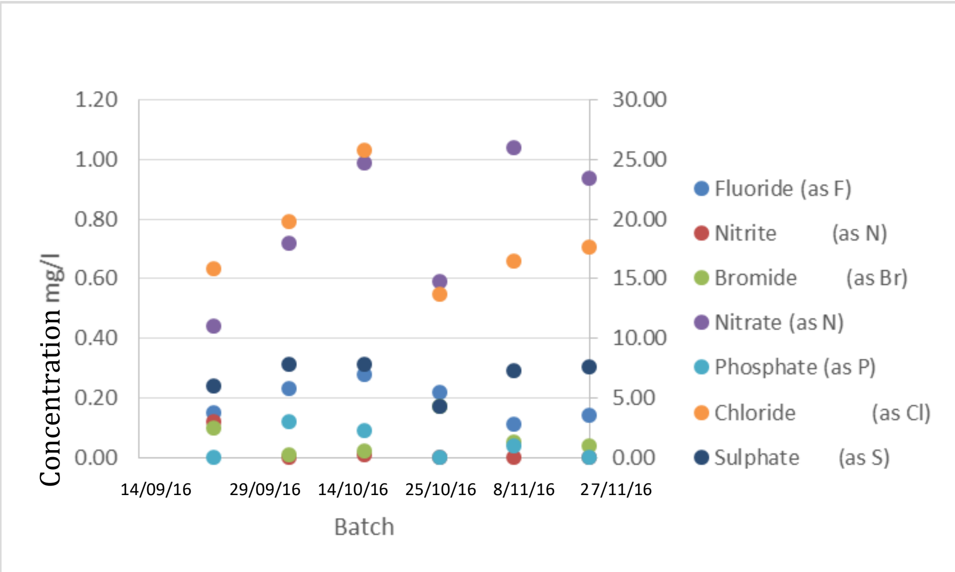

Figure 5.21 Anion concentrations at D10, Chloride and sulphate are to be read from the right y axis, all figures are in mg/l.

Sampling point D10 is downstream of the STW (Figure 5.21). Fluoride concentrations at D10 exceed the 0.1mg/l threshold as suggested by Chapman (1992) with a mean concentration of 0.2mg/l. Nitrite is undetected in four of the batches. Nitrite detection limits are 0.01mg/l. Nitrate thresholds as defined by Moorkens (2000) are 0.125mg/l; nitrate at D10 regularly exceeds this threshold with an average of 0.6mg/l. Phosphate thresholds as defined by Moorkens (2000) are 0.05mg/l; due to detection limits of 0.02mg/l, these data can only suggest whether there is a concentration of phosphate over this limit. For D10 there are 3 batches which cannot detect any phosphate in the system; the batches where it detects phosphate, concentrations reach 0.1mg/l. Chloride concentrations at D10 exceed pristine water conditions and are higher than concentrations in the headwaters, which according to Chapman (1992) in pristine water freshwaters are expected to be lower than 10mg/l. D10 has an average concentration of 18.20mg/l. Batch 3 has the highest concentration of chloride 25.76mg/l. The range for sulphate in natural waters is considerably broad with natural waters usually containing between 2 to 80mg/l of sulphate (Chapman 1992) (Figure 5.21).

Moorkens (2000) suggests ammonium concentrations above 0.01mg/l are deemed harmful for *M. margaritifera.* In batch 3 ammonium peaks to 0.4mg/l, more than an order of magnitude higher than the recommended 0.01mg/l. Sodium mean concentration at D10 is 11.0mg/l, with a peak at batch 3 of 18.0mg/l. Potassium concentration peaks during batch 3 at 3.1mg/l. Potassium levels can increase due to an influx of salts used in industry and fertilisers, thus effluent from the STW will elevate levels of potassium. Links between potassium and discharge are frequently cited, as vegetation surfaces and decomposing litter are activated during rain and runoff events (Stott and Burt, 1997).

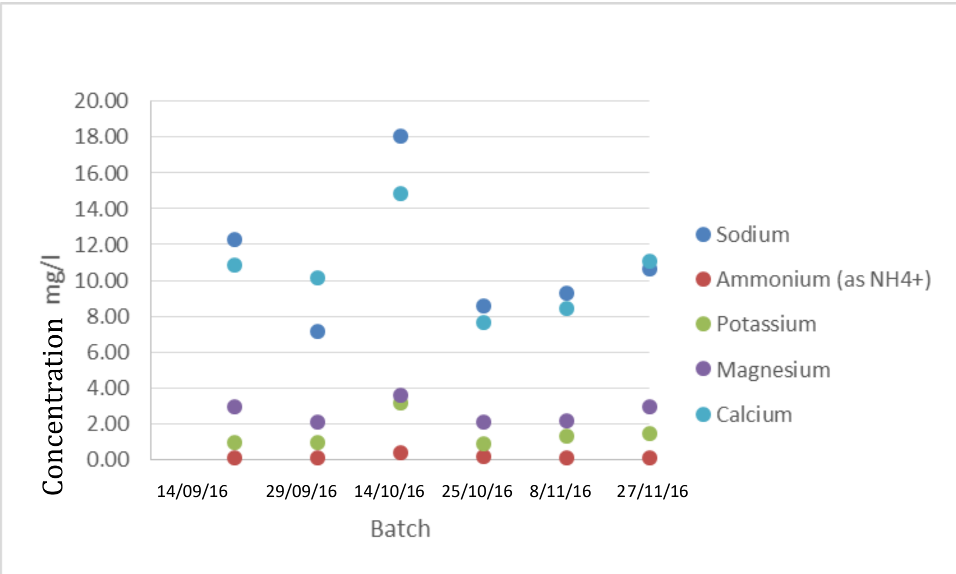

Figure 5.22 Cation concentrations at D10, Chloride and sulphate are to be read from the right y axis, all figures are in mg/l.

Figure 5.22 shows Magnesium concentration to be relatively stable at around 2mg/l. Batch 3 sees an increase in magnesium to 3.6mg/l. Calcium concentration in natural waters is typically less than 15mg/l (Chapman, 1992). D10 has an average concentration of 10.5mg/l, peaking in batch 3 at 14.9mg/l. Typical trends for D10 show an increase in cation concentration from batch 4 onwards.

D10 provides an example of how sampling at a point source location shows clear evidence of water degradation and the impact a STW has on water quality. By directly measuring a point source area water quality degradation can be quantified and if applied on diffuse pollution the impact caused by diffuse pollution could be quantified.

5.6.2 Botton Wastewater Treatment Plant

Botton wastewater treatment plant drains and processes sewage from Botton Village, using a variety of filtration methods to purify water. Downstream (D12) and upstream (D13) locations were monitored to compare the inputs from the waste water plant. Fluoride concentrations at D12 are 0.2mg/l, with a peak in batch 3 at 0.3mg/l. Nitrite concentration is untraceable in all batches, whereas Nitrate concentration has an average concentration of 0.6 mg/l (Figure 5.23). Nitrate peaks in batch 4 with a concentration 0f 1.1mg/l. Phosphate concentration is undetectable in batch 4 and 6, its highest in batch 2 with a concentration of 0.1mg/l. Chloride mean concentration is 16.6mg/l lower than D10 average concentration at 18.20mg/l. Chloride peaks in batch 3 with a concentration of 20.8mg/l. Sulphate concentration has an average concentration of 5.8mg/l. Sulphate peaks in batch 5 with a concentration of 6.85mg/l.

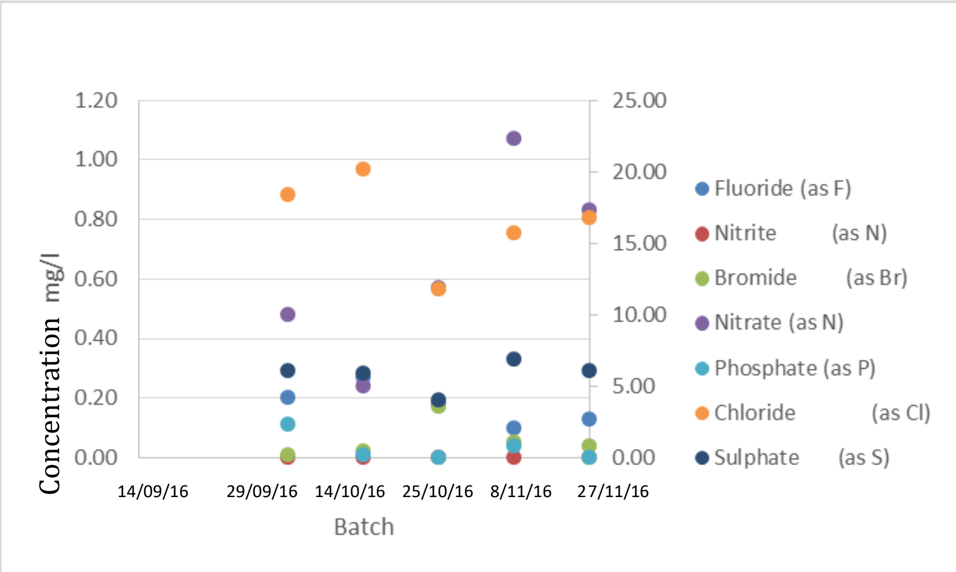

Figure 5.23 Anion concentrations at D12, Chloride and sulphate are to be read from the right y axis, all figures are in mg/l.

D12 cation concentrations are higher than D10 concentrations; however, when the average concentration is calculated, differences are reduced. Sodium concentration peaks in batch 2 with a concentration of 13.3mg/l (Figure 5.24). Mean concentration is 10.3mg/l, marginally higher than D10 average concentration. Magnesium concentration shows a decreasing trend from batch 2 to batch 4 before increasing to batch 6. Highest concentration is in batch 2 with a concentration of 3.5mg/l. Calcium concentration is highest in batch 2 with a concentration of 13.53mg/l. Average concentration is 9.8mg/l which is slightly lower than D12 at 10.5mg/l. Ammonium concentration is undetectable in batch 2, and peaks in batch 3 with a concentration of 0.2mg/l. It has an average concentration of 0.1mg/l lower than D12's 0.13mg/l concentration, however; due to the low concentration, differences between catchments are hard to identify. Potassium concentration peaks in batch 3 with a concentration of 1.78mg/l. Average concentration is 1.2mg/l, with an increasing trend, which is flushed through the system after batch 3, before it starts to increase again. This is a similar trend for all cations measured; suggesting river levels are a crucial element to nutrient enrichment.

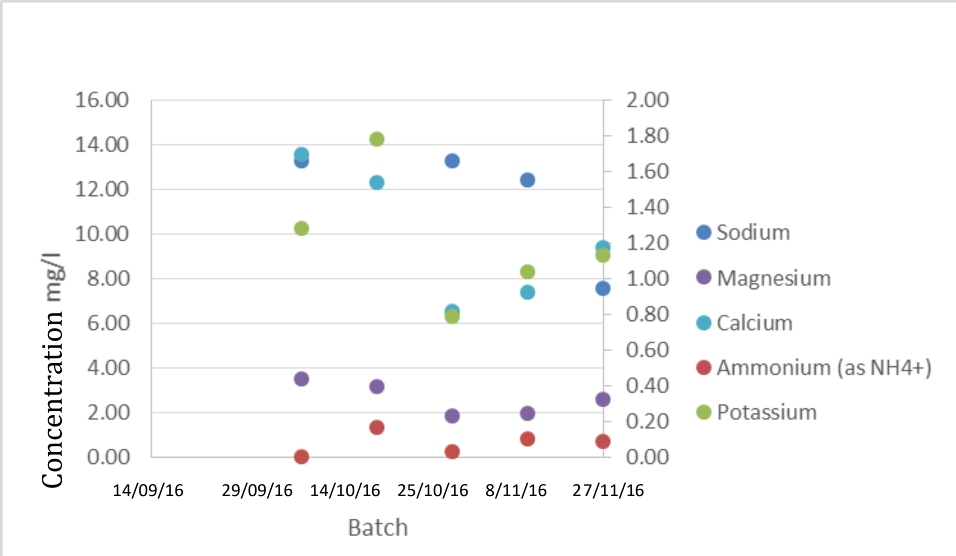

Figure 5.24 Cation concentrations at D12, Chloride and sulphate are to be read from the right y axis, all figures are in mg/l.

D13 is the upstream location of Botton sewage treatment works; in theory anion and cation concentrations should increase downstream due to the influx of nutrients released from the treatment works. D13 fluoride concentration has an average concentration of 0.2mg/l, which is marginally lower than D12's average concentration (Figure 5.25). Fluoride peaks in batch 3 with a concentration of 0.3mg/l. Nitrite concentration at D13 is undetectable in all batches except batch 1 which has a concentration of 0.1mg/l. Nitrate concentration on the other hand is considerably higher with an average concentration of 0.6mg/l. Nitrate peaks in batch 5 with a concentration of 1.0mg/l and decreases significantly in batch 3 with a concentration of 0.19mg/l,

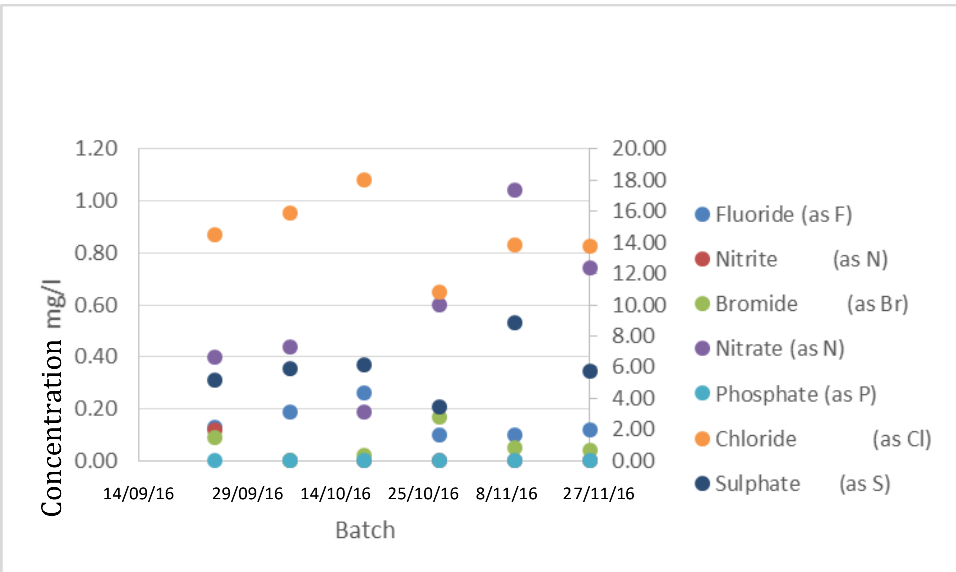

Figure 5.25 Anion concentrations at D13, Chloride and sulphate are to be read from the right y axis, all figures are in mg/l.

similar to a decrease in nitrate at D12. Phosphate concentration is undetectable at D13 throughout all the batches, when comparing it to D12 phosphate concentrations there is a clear indication of Botton treatment plant inputting phosphate into the beck. Chloride average concentration of 14.5mg/l is lower than D12's mean concentration of 16.6mg/l. Chloride peaks in batch 3 with a concentration of 18.0mg/l. Sulphate average concentration is 5.9mg/l marginally higher than D12's 5.8mg/l. Concentration peaks at batch 5 with a concentration of 8.9mg/l.

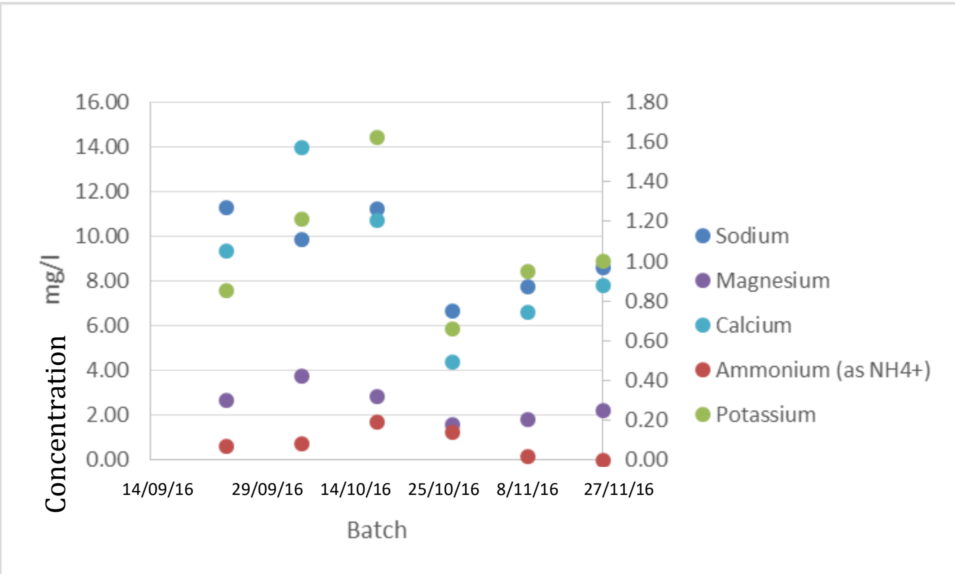

Figure 5.26 Cation concentrations at D13

Sodium average concentration at D13 is 9.2mg/l lower than D12's mean concentration of 10.3mg/l (Figure 5.26). Sodium peaks at batch 1 with a concentration of 11.3mg/l. Magnesium average concentration is 2.5mg/l, lower than D12's average concentration of 2.6mg/l. Magnesium peaks at batch 2 with a concentration of 3.7mg/l. Calcium average concentration is 8.8mg/l lower than D12's average concentration of 9.8mg/l. Calcium peaks at batch 2 with a concentration of 14.0mg/l. Ammonium average concentration is the same as D12's average concentration of 0.1mg/l. Ammonium peaks at batch 3 with a concentration of 0.2mg/l. Potassium average concentration is 1.05mg/l, lower than D12's average concentration of 1.2mg/l. Potassium peaks at batch 3 with a concentration of 1.6mg/l. To a certain extent the majority of anions and cations peak in batch 3 (October 11th 2016) before nutrients are flushed into the water course and downstream entering the River Esk. Elevated flow levels increase connectivity within a catchment, therefore increasing the amount of nutrients which can enter a river. Comparing upstream and downstream locations surrounding Botton WTP shows clear inputs from the treatment plant. According to WFD, the nutrients entering the system, from the plant are still within guidelines.

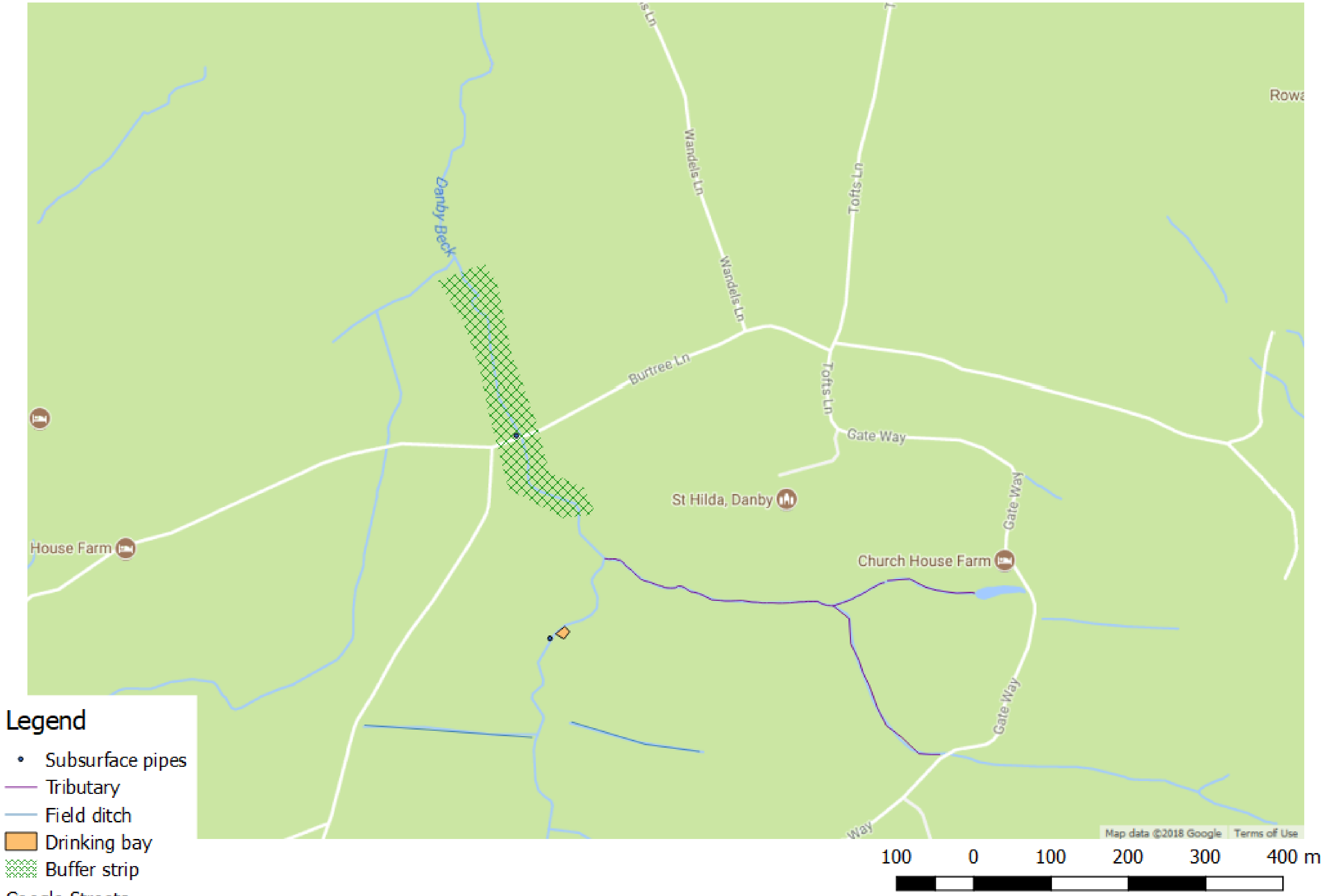

Figure 5.27 Map showing multiple pressures faced by a headwater tributary.

5.7 Summary

Yorkshire Sewage Treatment Works release nutrients into the catchment that are within EA guidelines, but above thresholds suggested by Moorkens, Oliver and Bauer (2000, 1998) in relation to Pearl Mussel survival. When comparing point source and diffuse locations, the amount of nutrient content varies. Tributaries have higher nutrient concentrations than areas where dilution can occur. Outfalls like those found at Yorkshire Sewage Treatment works are higher than those found at Botton Wastewater treatment plant, which could suggest the three-stage filtration process at Botton filters out nutrients to a slightly lower content than industry standards as followed by Yorkshire Water. The correlation between flow levels and nutrient content is shown at all sample locations, with batches after flood events showing higher nutrient levels.

Nutrient concentrations tend to increase downstream in all three catchments. Great Fryup and Toad Beck have much higher concentrations than Danby Beck, which can be associated with a lack of riparian buffer zones filtering the nutrients. As land use changes increase the intensity of agricultural practices there will be an increase in nutrient supply. Flow levels affect the amount of degradation that occurs on a river as dilution can be less prevalent. Concentrations of anions associated with sewage and septic tank run off are higher and peaks can be identified. This suggests water quality is most affected by the connectivity that land drains, ditches, tributaries and runoff have at a local catchment scale.

6. Discussion

6. 1 Introduction

Using a catchment-based approach to investigate water quality issues allows managers to critically assess conditions in their catchment area. Water quality will be discussed within a spatial and temporal context, investigating how it changes within a catchment and what this means for future catchment management. The results presented in this thesis suggest that catchments are subjected to episodic variations in water quality caused by septic tanks, tributaries and flushing of nutrients during storm events; all need to be managed differently.

6.2 Spatial variations

The spatial fluxes reported in Chapter 5 show how measured anions and cations can vary across a catchment. There are two significant trends were identified from the data collected: firstly, significant increases of measured cations downstream (see Figures 5.13 and 5.15); secondly, minor increases in measured anions downstream (see Figures 5.6 – 5.8). Locally, anion and cation changes in concentration can be attributed to point sources contributing an influx of nutrient supply and thus creating spikes in anions such as phosphate and nitrate. For example, Toad Beck shows a strong link with a built-up area and elevated levels of nutrients. Figure 5.6 shows the elevation in nutrient levels, whilst Figure 3.4 shows the types of pollutants entering Toad Beck. Surface water pipes located in urban areas of Toad Beck catchments are contributing to higher levels of nutrients. As human settlement increases downstream in the Toad Beck catchment, there is no significant increase or spikes in nutrient concentrations. Although human settlement dominates Toad Beck catchment, agriculture in the upper catchment also alters the water chemistry of the river significantly. Nutrients remain high throughout the river length on Toad Beck. Danby Beck is more susceptible to spikes in nutrient concentrations due to point sources such as anthropogenically constructed ditches, pipes and tributaries (see Figure 3.4). Phosphate spikes are very apparent – identifying areas of point-source locations. Figure 3.4 highlights the types of pollutants entering Danby Beck which using the sample locations on Figure 3.3 signify reasons for high phosphate concentrations. . Similar to phosphate, nitrate and nitrite show spikes in concentration downstream, also emphasising point-source locations. Similar trends can be seen with cations suggesting Danby Beck catchment is influenced significantly by spatial changes in point-source locations. Great Fryup Beck shows clear indications of point-source locations bringing an influx of anions such as nitrite into the catchment, shown by the types of pollution sources located in the Great Fryup Beck catchment on Figure 3.4. This is also observed in cation concentrations, particularly ammonium. Although nutrient inputs are usually described as diffuse, they are often much more focused than generally realised (Burt *et al.,* 2015). The significance of all three catchments showing spatial variations of anions and cations clearly emphasises how catchments are influenced by point-source influxes and natural variations within at the headwater. By clearly identifying areas of point source at a catchment scale (Figure 3.4), the issue of diffuse pollution can be more effectively targeted, thus improving water quality and reducing the degradation on a catchment.

Improvements in water quality could be hindered by the proportion of degradation attributed to diffuse pollution. Catchment management and catchment-scale studies have become increasingly more important in determining the impact of human development on water quality (Silva & Williams, 2001). Typically, these studies have become more common in the past 20 years (Silva *et al.,* 2001); however, they leave many questions unanswered. Catchments have a unique combination of characteristics that influence water quality; therefore, although the frequency of studies has increased, it remains difficult to draw conclusions applicable to other catchments (Silva *et al.,* 2001). A study undertaken by Silva *et al* (2001) focused on three catchments in Canada concluded that urban land use has a significant impact on water quality. Silva and Williams (2001) found urban land use to be the most important predictor of water quality variability. They conceded the relationship may have been influenced by both point and diffuse pollution (2001).

Spatially, water quality is affected by geomorphological features in a river; riffle-dominated sections aerate water, thus transforming nutrients. The dilution effect alters the proportion of suspended sediment in a water column and sediment-bound nutrients. Storm events increase nutrient concentrations; however, alterations in sampling areas will affect nutrient concentration. Fast-flowing riffle sections will have elevated levels of DO compared to slow-moving pool sections. Slow-flowing pool areas can act as source areas for nutrients and thus have higher concentrations.

Silva and Williams (2001) suggest there are three landscape factors excluding urban land use that determine water quality which are; forested land use, (the standard deviation of) slope, and soil type (the fraction of silt-clay). In the three catchments studied in the current research forested, agricultural and urban land use (effects previously discussed) are the main determinants of water quality.

6.3 Temporal variations

Changes in DOC and pH in all three catchments can be attributed to seasonal variations; the wetting of peatland post storm events flushes through nutrients into the catchment, lowering pH and increasing DOC concentrations. Figure 6.1 shows an example of the discoloration caused by storm events running over moorland dominated by peat. Likewise, conductivity changes are witnessed as increasing post storm events as autumnal weather affects the catchment controls. It is interesting to note that conductivity remains above recommended *M. margaritifera* thresholds for the entire data-collection period, which highlights the importance of flow diluting ions and thus conductivity. However, as flow increases banks become less stable and sediment is likely to be released into the catchment. An influx of sediment into a water body can increase the concentration of sediment-bound nutrients. Therefore, although dilution should reduce conductivity, storm events will flush through a higher proportion of sediment, thus maintaining a higher level than the Bauer (1988), Oliver (2000) and Moorkens (2000) suggest.

Figure 6.1 A beck discoloured from DOC entering the catchment from the upland moor and peat covered landscape.

There are conflicting views over whether water quality is more influenced by the land use of a catchment or the riparian zone (Osborne & Wiley, 1988, Delong & Brusven, 1991, Johnson *et al.,* 1997). The riparian zone of Danby Beck catchment is perhaps more integral to reducing the quantity of nutrients entering the river. Danby Beck has a higher proportion of improved grassland; however, the results show nutrient concentrations are lower than Great Fryup Beck. Aerial photography can be used to identify the proportion of fields applied with fertiliser throughout the catchments. Fields that appear darker green have nitrogen and phosphorus added to improve yield. Danby Beck has a higher proportion of fertilised fields towards the lower catchment. Great Fryup Beck, in comparison, has significantly less fertilised fields. Toad Beck has a section of improved fields in the centre of the water course. This increase in fertiliser downstream of the headwaters could suggest why there are elevated levels of nutrients. Thus the influence of the riparian zone is a dominating factor for water quality.

Dissolved oxygen is one of the most vital components of water quality (Brooks et al., 1997). As shown by the data collected between July and November 2016, dissolved oxygen gradually falls during the summer months as the uptake from respiration increases due to an abundance of plant growth, shown in Figure 4.1. There is a lag in dissolved oxygen saturation response, with the critical level reached in September, when the combination of low flow and excessive plant growth reduces dissolved oxygen to below 90%. Measurements then slowly increase over the winter months. With regards to *M. margaritifera* the critical level reached by all three catchments is lower than the thresholds proposed by Bauer, *et al* (1988, 2000). As flow increases with rainfall in autumn and plant growth reaches equilibrium, the dissolved oxygen levels increase to 100% saturation, restoring a suitable habitat for *M. margaritifera.* However, the rise in dissolved oxygen and the temporal instabilities throughout the season should be considered for *M. margaritfera* conservation as dissolved oxygen continuously falls below thresholds proposed. The spatial variability of these effects influences the overall water quality; throughout the summer months dissolved oxygen reduces to a 'critical' level as defined by Moorkens (2000) which cannot sustain *M. margaritifera*.

Similarly, variations in DO, shown in Figures 4.2-4.10, and temperature are associated with seasonal variations. Water temperature is strongly controlled by seasonal fluctuations as shown in Figure 4.21; therefore, decreases in temperature towards the end of data collection were expected. DO variations are influenced by flow and groundwater controls; as flow increases, the aeration of oxygen in a catchment increases the concentration during the autumnal months, see Figure 4.1. Additionally, excessive plant growth requires oxygen for respiration thus reducing concentrations of DO in the summer months. Temperature affects the saturation constants of dissolved gasses including oxygen (Chevalier *et al.,* 1984). Dissolved oxygen varies non-linearly with temperature; as temperature increases, solubility decreases and thus DO decreases (Sear *et al.,* 2014). Periods of low DO which occur rapidly and quasi-independently of discharge, are considered to represent conditions where the rainfall has locally elevated groundwater levels within the floodplain (Malcolm *et al.,* 2009). Locally elevated groundwater levels will flush into a water course, creating lower than expected levels of DO. Therefore, low DO levels could be associated with upwelling of low-DO groundwater (Sear *et al.,* 2014). As shallow groundwater passes through organic-rich sediments, oxygen is stripped from the water (Lerner, 2009) and used in chemical reactions.

EEA (2004) and Hargreaves (2003) estimate 500,000 ha of peatland was afforested between the 1950s and 1990s in the UK. DO levels can be controlled by forestry activities, as vast areas of forests reduce the amount of suspended sediment and nutrients entering a catchment. The upper reaches of Danby Beck are forested with coniferous woodland, thus reducing the amount of nutrients entering the catchment. This explains the absence of certain nutrients from the upper catchment on Danby Beck. A reduction in nutrient concentration reduces the availability of organic and inorganic material to sustain plant growth; in areas where nutrient supply is limited there is less plant growth, thus dissolved oxygen is not readily used up by respiration.

Lockaby (1997) suggests forest clear-felling will introduce brash material increasing organic matter supply and potentially increasing BOD. Management techniques on Danby Beck use brash and woody debris to reduce bank erosion, which would increase organic material and BOD, which could explain why BOD levels on Danby Beck are highest. However, mitigation works are carried out at a small scale and therefore may not be the sole cause. Elevated levels of organic material in a river consume oxygen more quickly, reducing DO levels, which could act as a control on water degradation.

Controls on conductivity are flow, climate, land use and bank erosion. Areas densely populated with stock can poach the ground releasing solutes. Danby Beck has much lower levels of conductivity, especially in the upper catchment. As previously stated, Danby Beck has had a significant amount of river restoration and buffer strips installed in the catchment reducing the sediment supply, unlike Great Fryup Beck. Similar to dissolved oxygen, conductivity concentration is affected by levels of flow; between July and September conductivity levels on all three catchments are consistently above 100µs. After the flood events in November (8th and 22nd) conductivity levels are reduced to below 100µs, which suggests that the amount of solutes which can create a current for monitoring purposes is reducing. Levels of conductivity in Toad Beck remain high consistently throughout the data-collection period, thus suggesting a high level of connectivity with pathways. In the upper catchment of Toad Beck, stock rotation changed from sheep to cattle, increasing the amount of poaching on the land. Higher levels of conductivity were found in grassland areas in a study undertaken by Anderson et al (2013) which is supported by the current research which found higher levels of conductivity in the three catchments studied for this thesis. However, stock rotation should not be considered the main factor of elevated levels of conductivity, the connectivity between surface drains in a built-up area and the proximity to altered landscapes could play a significant role.

6.4 The role of tributaries

Tributaries which can connect previously unconnected areas to a water body are bringing high levels of chloride, fluoride, nitrate and phosphate into all three catchments. Small tributaries are an efficient method of draining an area and reducing ponding in fields and on moorlands. A wealth of studies such as Nakona *et al* (2008), Taseli (2006) and Riou *et al* (2007) have investigated the impact that tributaries have on lakes or water bodies. Monitoring tributaries over a period of 6 months showed seasonal variation mirrored by agricultural activity such as stock rotation and crop management. Farmers install ditches which create a new network of tributaries, to reduce the effect of soil saturation and ponding on areas of fertile land. Figure 5.27 demonstrates the additions of field ditches added by landowner's increases connectivity within a landscape. Previously, slopes and channels were decoupled, with material stored on slopes instead of reaching a water course (Fryirs *et al.,* 2008). Disconnected tributary systems can trap sediments behind flood-plain pockets at confluences (Brierley and Fryirs, 1999). Lateral linkages between a slope and channel impact the sediment concentration and can reflect the ability of channels to transfer sediment (Fryirs *et al.,* 2008). Areas with more lateral and vertical connections through tributaries and ditches will have a shorter response lag time.

6.4.1 Transportation

Organic and inorganic nutrients are transported by water flow either in solution, associated with particles or incorporated by microorganisms (Schoumans, 2013). The amount of nutrient transported depends on the form of transportation; for example, in dissolved form organic nutrients can carry more nitrogen than phosphorus (Schoumans, 2013). Bank erosion releases sediment into a catchment, which carries sediment-bound nutrients into a river. After flood events, if substantial bank erosion occurs, there is the potential for spikes in nutrient concentrations. Banks became unstable, losing sediment and pathways previously episodic became wetted transferring nutrients from sinks back into the catchment. After the flood event of November 8th, all three catchments saw an increase in nutrient concentrations. This is due to the interconnected network of tributaries, ditches and overland flow becoming re-connected with rainfall. As the previously disconnected pathways were reconnected to the main beck, nutrients currently being stored were remobilised and transported downstream, back into the water course. Summer flows lead to a higher proportion of nutrients being stored in a catchment, which after the first storm can cause an influx of sediment and nutrients. Schoumans (2013) states phosphate is released via particles eroded from agricultural soils; increases in phosphate after the 8th November are witnessed in all three catchments, supporting these findings. Although influxes of nutrients bound to sediment will increase concentrations of anions and cations, the influence of groundwater and thus solutes could be more significant for nutrient concentrations.

6.4.2 Pathways

The main pathways of phosphorus are through the soil and artificial drainage (Chapman *et al*, 2005, Chardon and Schoumans, 2007). Nutrients enter water systems by surplus runoff flowing over farmland (Schoumans, 2013). Tributaries in all catchments play integral roles in the movement and recycling of nutrients. Septic tanks filter nutrients through the soil; rainfall can remobilise these pollutants and transport them via subsurface flow into ditches, which were created to naturally drain a field. Figure 6.2 shows sewage fungus growing downstream of a septic tank location, the sewage fungus is exacerbated by low flows. As the demand for food and resources increases, so too do the ditches and subsurface pipes installed to drain a field. A typical field in Danby catchment will have at least one tile drain to drain the soil, with further ditches bordering the field boundaries; in total there could be at least 3 different sources for nutrients to enter a river per field. Subsurface pipe sizes can vary in a field, but usually are less than 20cm in diameter; however, areas where fields are wetter, and almost bog like, pipe sizes can increase up to 50cm. 30% of the UK uses tile drainage for agricultural land (Brown & Van Beinum, 2009). Tile drains channel water directly to a river increasing potential phosphorus transports and loads in rivers (Chardon & Schoumans, 2007). Clay and silt soils are also important pathways for nutrient transport, as they create rapid water flow (preferential flow) through the soil pores (Jarvis, 2007). Preferential flow increases the connectivity between stored nutrients and remobilises them into a water course.

Figure 6.2 The white growth on the river bed is sewage fungus, caused from the discharge of a septic tank, this photo was taken downstream of the effluent pipe, taken of Commondale Beck upstream of becks studied.

6.4.3 Soil Compaction

Soil compaction through intense grazing and heavy machinery significantly alters the pathways for soil erosion and sediment to enter a river. Intense grazing compacts the soils, reducing the macro pores which otherwise allow water to percolate through the soil. Danby and Great Fryup Beck have both cattle and sheep as the predominant livestock; cattle compact soil through upward and downward movement, whilst sheep cause surface compactions (Betteridge, 1999). Although currently livestock density is not an issue in the North York Moors, it can affect evapotranspiration as biomass is reduced (Pattison & Lane, 2011). As soil is compacted, water has to adapt to the reduction in underground pathways and in extreme cases surface rivers or gullies can form overland. Fields recently fertilised will have nutrients present on the surface, which will mobilise and move downstream during a storm event, see Figure 6.3. However, applying fertiliser in Nitrate Vulnerable Zones is forbidden between 15th September and 15th January (GOV, 2015). Intense grazing of unfenced areas as demonstrated on Great Fryup Beck increase bank erosion, and increased frequency of direct faeces into the watercourse, and thus the availability of nutrients in a system. Great Fryup has the highest concentration of nutrients after the storm event of November 8th, which suggests that due to the unfenced nature of the catchment, sediment-bound nutrients are connecting to the system and thus influence concentrations. As well as sediment bound nutrients, upwelling from groundwater increases solutes in a catchment and thus elevates nutrient levels.

Figure 6.3 Satellite imagery obtained from Google (2018), used in Arc GIS to highlights fields where fertilised is applied, shown by the darker grass in the centre of the image.

6.5 Septic tanks

Small domestic discharges such as septic tanks pose an environmental risk to freshwater habitats (May, 2010, Withers, 2011). Local sewage network maps (held by Yorkshire Water) highlight properties using septic tanks, unfortunately data is sporadic and local knowledge from project officers is key to targeting rural areas. Septic tanks contribute to diffuse pollution through the direct introduction of contaminants such as pathogenic bacteria, nutrients, organic matter, and indirectly by freshwater inputs, which can result in enhanced contaminant transport and/or survival of microbial agents (Reay, 2004). In the UK it is estimated about 90-95% of septic tank locations are unknown (May *et al.,* 2010). Reay (2004) suggests water quality concerns regarding the expanded use of non-sewered waste disposal include the introduction of nutrients and pathogenic organisms into ground water and surface water resources. Septic tanks are regulated by the EA; however, as our understanding of water quality improves, the legislation and management of septic tanks is criticised. Previously a septic tank could use a soakaway to drain sewage effluent into a river. New legislation prohibits the use of soakaways, wells and boreholes for discharging effluent. The EA instead states a drainage field or permit must be issued before discharging can occur.

Concern arises when septic tanks installed before 1983 pre-British Standards do not have to conform to current legislation. May and Withers (2015) conclude the age of a septic tank can reduce its effectiveness in treating domestic wastewater. In their study, choosing septic tanks with ages between 2 – 50 years, that are rarely inspected, emptied or repaired, it was concluded that older tanks release high levels of phosphorus to the environment. The breakdown of nutrients in a tank requires frequent emptying and a high retention time to allow anaerobic processes to take place. Otherwise, soakaways can become blocked with organic matter and drainage reduces. May and Withers (2015) conclude current legislation of installing a septic tank at least 100m from a water course is insufficient.

May and Withers (2015) suggest there are a number of variables which require more data before a comprehensive understanding of septic tanks can be achieved. They conclude there are three key ideas which require a deeper understanding: firstly, how the lifestyle of a household and how they manage their septic tanks can affect effluent quality; secondly, the distance over which nutrients such as phosphorus travel through the soil; and thirdly, how local environmental conditions affect nutrient transport.

Many of the septic tanks in both Danby and Great Fryup catchment are greater than 100m from the main water course; however, the tributaries, ditches and pathways which connect the farms are outside the 100m boundary connecting what was once a disjunct pollution source directly to a water course. Sources of pollution can enter a catchment through ditches, ponds and tributaries, entering the river channel system from areas previously thought to be outside of pollution areas, as previously discussed. The results show spikes of phosphorus and nitrogen in all three catchments.

Septic tanks are not efficient at removing nutrients (Hardistry, 1974). Hardistry (1974) Andreoli (1979) and Valiela (1997) suggest as little as 5 to 18% of nitrogen and 20 to 30% for phosphorus. Reay (2004) concludes that, although septic tanks are inefficient at nutrient removal, their ability to convert organic forms of phosphorus and nitrogen to inorganic forms through anaerobic processes is satisfactory. Studies in New England undertaken by Valiela and Costa 1988, Giblin and Gaines (1990) and Weiskel and Howes (1991) indicate that effluent from residential septic tanks is significant and detrimental. Studies undertaken by Hagedorn (1981) reported microbial contamination of shallow ground water and transport of coliform bacteria within the saturated subsurface environment. Reay (2004) concludes elevated levels of nitrogen are found downstream of septic tank drainage, which is corroborated by this study. Danby Beck shows a clear trend of elevated nitrate and nitrite concentration downstream of the catchment. A study undertaken by Natural England (2015) examined septic tanks that were more than 100m away from a water course and 2m above the water table. They suggest septic tanks at these locations are less likely to cause detrimental effects to a water course (Natural England, 2015).

Using Yorkshire Water sewage network maps, an estimate of how many septic tanks in each catchment were obtained by the River Esk Catchment Partnership Officer. Using this estimate, the places where potential septic tanks could directly enter a river were established. It is thought that Danby Beck has 70 septic tanks and Great Fryup has 55; Toad Beck is on the sewerage network. Septic tank runoff is unlike that from a sewage treatment works. Sewage treatment works are continuous in outflow and release consistent levels of nutrients into a river. In contrast, septic tanks drain into a field and percolate through the ground, creating a sporadic flow largely dependent on rainfall. The discontinuity between nutrient load and flow has created difficulties when trying to quantify how much damage septic tanks can cause to a catchment.

In rural catchments such as Danby and Great Fryup Becks, water quality will be heavily influenced by the frequency of septic tanks, the intensity of agricultural activity and any mitigation works within the catchment. Separating septic tank runoff and agricultural runoff is almost impossible; this is due to the negligence surrounding septic tank maintenance. Septic tanks use tile drainage and ditches to connect to a water course, similar to agricultural runoff. A study by Nakano *et al* (2008) accounted for differences between agriculture and sewage by investigating tributaries of similar water quality but connectivity areas controlled heavily by agriculture or sewage. To a certain extent results presented in this thesis suggest that septic tanks are degrading the water course marginally more than agriculture, demonstrated by comparing the catchment of Danby Beck which is heavily mitigated, with fewer septic tanks, to Great Fryup Beck which is has no mitigation and far more septic tanks. The important difference between the two catchments seems to be more associated with the mitigation of the riparian zone rather than the abundance of septic tanks. Agricultural land use of improved grassland is higher on Danby Beck (see table 3.1), therefore N and P concentrations should be higher, however Great Fryup Beck has the higher concentrations see Figures 5.1-5.4. Additionally, Danby Beck has a STW and Botton WTP which are shown by spikes in concentrations (Figures 5.21 -5.26), however Great Fryup Beck has almost double the amount of septic tanks and therefore should see double the amount of nutrients. The data collected does not show this, which could suggest there are unknown processes at work. The significant difference between the catchment is the installation of buffer zones reducing nutrient concentrations.

6.6 Sewage treatment works

There are five sewage treatment works (STWs) in the upper Esk catchment, with two in the Danby Beck catchment, see Figure 3.4. Yorkshire Water and Camphill Village Trust have two very different approaches to treating sewage. Botton Wastewater and Treatment Plant (WTP) uses filtration via rocks and reed beds to remove excreta from the surface water, ensuring anaerobic processes to reduce nutrients. Yorkshire Water state that there are two basic types of system: a combined system which collects rainwater and uses waste water, or alternatively a separate system that puts rainwater through a surface water system which can lead to a river or soakaway, and uses waste water through a separate foul system connected to a waste water treatment works or other means or disposal. For the Danby Beck catchment, Yorkshire Water uses separate systems to filter rainwater and waste water, releasing treated water into Danby Beck. Unlike Botton Wastewater Treatment Plant, Yorkshire Water must conform to strict regulations to reduce the impact of sewage effluent. STWs, although constrained by legislation, release elevated levels of nutrients into a catchment; the guidelines suggested by the EU do not adhere to the strict thresholds required by *M. margaritifera.* Therefore, although within regulation, the STWs are degrading water quality to a standard uninhabitable for *M. margaritifera.*

6.7 Flood Events

The greatest change in concentration an driverine transport of nutrients often happens during storm events (Evans & Johnes, 2004, Haygarth *et al,* 2005, Heathwaite *et al,* 2006, Rozemeijer & Broers, 2007, Haygarth *et al,* 2012). Solutes have been observed to increase in concentration with storm discharge only during post-drought flushing; dilution is the typical response (Stott and Burt, 1997). There are three factors which influence solute losses during storm events: the interaction of hydrological pathways, sediment inputs and the chemical properties of the transporting water (Stott & Burt, 1997). Rapid removal or flushing of supply can occur during flood events, reducing the amount of solutes previously accumulated during a drought (Stott & Burt, 1997). Links between potassium and discharge are frequently cited, as vegetation surfaces and decomposing litter are activated during rain and runoff events (Stott and Burt, 1997). The behaviour of potassium in the upper sub-catchment highlights the importance of the hydrological pathways and their dynamic interactions with source areas of potassium during the course of a storm (Stott & Burt 1997). New solute sources for potassium were observed by Stott and Burt (1997) as soil saturation expanded. Both Danby and Great Fryup Beck have good hydrological connectivity to their landscapes as shown by the nutrient response to higher flows. The 8th November and 22nd November show a spike in nutrient concentrations as the catchment responds to an increase in hydrological connectivity joining previously disconnected areas to the beck.

6.8 Agriculture

Toad Beck has higher concentrations of nutrients in comparison to Danby and Great Fryup Beck catchments. It has been previously stated that agriculture impacts nutrient concentrations as a dominating factor (Biddulph, 2013). The continuously high nutrient concentration throughout Toad Beck catchment suggests the influence of agriculture, as it is well connected in the upper and central catchment. Additionally, there is an absence of mitigation and riparian buffer zones on Toad Beck, suggesting runoff and bank erosion connects directly to the beck without filtration. Pastoral farming is prevalent in Toad Beck; however, unlike Danby and Great Fryup Beck, the distance for dilution to reduce nutrients is substantially less which impacts on the nutrient concentration. Furthermore, Toad Beck is the most built-up of all three catchments; therefore, surface drainage from roads and houses enters the beck directly, which is evident in elevated levels of chloride and fluoride (Figures 5.7, 5.7, 5.13 and 5.14) which are not present in Danby and Great Fryup Beck. The combination of a beck dominated by agriculture and human settlement creates elevated levels of nutrients which are considered harmful to *M. margaritifera.*

6.9 Riparian buffer strips and mitigation

Comparing Danby and Great Fryup shows stark differences between nutrient concentrations. Nutrient concentrations are lower on Danby Beck, even with the installation of Danby STW and Botton WTP. Danby Beck is relatively well protected from nutrients flowing overland, but not subsurface flow and entering the beck due to the riparian buffer strips which line the length of the river, see Figure 5.27. A significant alteration in management approach is clear between both Danby and Great Fryup Beck catchments, which can be quantified from the reduction in nutrient concentration on Danby Beck. Buffer strips on Danby Beck are 5m wide, promoting the growth of rough grassland and trees. Sections of Danby Beck have natural colonisations of woodrush, which reduce bank erosion, and promote bank stability; this method has been applied to the main River Esk, in the hope of improving bank stability. Mitigation works on Danby Beck catchment have occurred continuously for the past 10 years, therefore trees and vegetation are well established in comparison to Great Fryup Beck. Thus, nutrient filtration and capture removes and reduces nutrients from entering the catchment. Both catchments have similar amounts of pastoral farming; however, fences and drinking bays installed in the Danby Beck catchment reduce the amount of poaching occurring on the fields and therefore the amount of sediment and nutrients which could be mobilised by rainfall or high flows. By installing drinking bays, vegetation, buffer strips, riparian zones, nutrient concentration decreases in a catchment allowing natural dilution to ensue.

6.10 What this means for freshwater pearl mussels

This thesis has shown there is more to be done in the catchments upstream of the current *M. margaritifera* population*.* Mitigation on one beck is almost redundant if other becks go unmanaged. Rivers are known to have 'self-regulating' abilities; however, the influx of nutrients created by human activity has reduced the ability of a river to remediate water quality issues. It is necessary to reduce the nutrient pathways at the source by altering the way the UK farms, for instance adopting a more sustainable approach to increasing crop yield. Furthermore, riparian buffer zones have been shown to reduce the impacts of potassium and nitrogen on Danby Beck; therefore these practices and restoration techniques must be adopted on Great Fryup and Toad Beck too. The issue of septic tanks in a rural catchment has shown that mismanagement and a lack of awareness of how connected septic tanks can be requires immediate management if successful recruitment of *M. margaritifera* is going to be achieved. For catchments such as the Esk, the impact of septic tank mismanagement is likely to be significant, shown in the elevated concentration of anthropogenic nutrients entering the tributaries in the downstream section of the catchments, see figures 5.5 and 5.6. The high frequency of septic tanks in a relatively small catchment that are inputting directly into a river is seriously impacting the water quality of all three becks.

The work currently being undertaken at the FBA facility in Lake Windermere is a prime example of how conservation efforts of *M. margaritifera* are recruiting juveniles and rearing them to ages where relocation to the wild is appropriate. Although the River Esk's juveniles are at such a crucial stage in their cycle, glochidia encysted on host fish, it is showcasing that it is possible, and once the Esk is under the thresholds suggested by Bauer (1988), Oliver (2000) and Moorkens (2000), the proposal of juvenile mussels being released onto the Esk can be achieved. It will be interesting to observe the success of the River Irt *M. margaritifera* release into their river and how juveniles cope with water quality that can change daily.

Current efforts to involve citizen science and engagement on the River Esk such as river-fly monitoring will help to ensure pollution effects which may be detrimental to the lifecycle of *M. margaritifera* to be observed and mitigated. Similarly 'Adopt a stream' initiatives will further help with the management of water degradation and pollution incidents that are currently being overlooked by a lack of continuous monitoring.

6.11 How can investigations undertaken at a catchment scale be applied to protect species elsewhere?

This thesis has examined water quality using a local-scale catchment approach to mitigation with regards to *M. margaritifera*; however, by using an umbrella species to promote awareness of water quality issues and how they can be resolved, this approach can be transferred to other locations. Supporting catchment managers, stakeholders and legislative bodies to consider how water quality will change and be influenced by point sources will enable a more coherent approach to catchment management to be utilised. The water quality required (see Table 2.1) for *M. margaritifera* is a strict threshold for successful reproduction and conservation; therefore, catchment managers could be dissuaded from taking any action because of the high cost required to achieve such standards. However, this thesis and the approaches it has used to measure water quality, such as the thorough investigation into both point and diffuse pollution sources should be used as a guideline for other catchments. High-frequency monitoring, identifying point/diffuse sources, their dynamics and the category of source is transferrable to other catchments. As the shift towards CaBA becomes widely adopted, there will be an increase in the amount of managers which use catchment approaches to quantify and mitigate water quality.

6.12 Summary

Nutrient levels respond to elevated flow levels, land use change, hydrological connectivity and mitigation methods. Toad Beck provides a good example of how human settlement and agriculture impact on nutrient concentrations, whilst Danby Beck provides a good example of how utilising riparian buffer zones and vegetation can reduce nutrient concentrations and allow dilution to occur downstream. Great Fryup Beck provides a good example of how not to manage a catchment; good hydrological connectivity to moorland areas can influence pH and nutrient levels, whilst poor stock management can lead to poaching and nutrient increases. It also shows how the mismanagement of septic tanks can influence water degradation. Examining how point and diffuse source pollutants change at a catchment scale and degrade a water course is beneficial for future river conservation.

7. Conclusion

7.1 Assessing aims and objectives

This study has examined the patterns of water quality in a rural catchment, both spatially and temporally, offering explanations for why water quality degrades in a catchment and how it degrades downstream. It has concluded there are multiple variations in headwater catchments which cannot be detected with end of tributary spot sampling, thus *M. margaritifera* conservation requires spatial and temporal sampling before reintroduction on the River Esk. Furthermore, the effectiveness of implementing a traffic light system which can be used by local project officers to understand and prioritise areas to target is paramount to *M. margaritifera* conservation. Assessment of the aims and objectives set out in the introduction must be undertaken to assess whether this thesis has completed its aim. The objectives were as follows:

1. To examine water quality in three catchments (Danby Beck, Great Fryup Beck and Toad Beck) through undertaking various water quality analyses such as conductivity, temperature, pH, dissolved oxygen, anions and cations, COD and BOD.
2. To compare water quality in all three catchments investigating temporal and spatial changes to water quality in a catchment.
3. To provide solutions for point source and diffuse pollution within the scale of a catchment in the hope of conserving *M. margaritifera.*

Objective 1 and 2 were achieved by investigating a variety of water quality parameters and examining spatial and temporal trends has identified key areas where catchment management could benefit the water quality. Objective 3 was achieved by reviewing the effect of riparian buffer strips and comparing Danby catchment to Great Fryup Beck; thus providing quantifiable evidence of how simple restoration methods can improve the water quality.

7.2 Key findings

This study has demonstrated the following:

1. The need to address multiple river restoration techniques across a catchment and sub-catchment scale. To improve water quality to a 'High' status for *M. margaritifera* land use, hydrological connectivity and anthropogenic activities must be considered before lasting water quality improvements can be observed.
2. Catchments with buffer strips and changes in agricultural land use have resulted in improvements in water quality.

3. This study has demonstrated the need to address diffuse pollution in headwater catchments before noticeable improvements will occur to provide a self-recruiting population of *M. margartifera*.
4. Septic tanks are a challenge to water quality in the River Esk and impacts need to be assessed and managed more actively to improve the water quality and habitats.
5. The traffic light system is a useful tool to spatially highlight areas of concern around water quality for catchment managers,

7.3 Limitations and future work

This study managed to obtain 6 months of fortnightly samples, encompassing a variety of parameters and therefore providing a wealth of data which will help with the conservation of *M. margaritifera* and management of the catchments. The limitations of this thesis were similar to previous work on the River Esk. Time constraints with monitoring, such as not investigating water quality during the winter months, could inhibit the conclusions of how water quality changes and degrades spatially and temporally. Additionally, issues with water quality analysis, see section 3.3.2, has limited the amount of analysis undertaken in this research.

Future work should investigate and attempt to categorise certain anion and cation thresholds which have been previously overlooked. The literature reviewed suggests bromide, sulphate and other ions to be of little significance to *M. margaritifera* or alternatively there could be issues with funding that are currently inhibiting investigations. Additionally, further work should investigate catchments where septic tanks are managed and maintained yearly, to establish quantifiable data on the effects a control catchment can have on water quality; for example, the project in the North York Moors National Park. Further work could include altering the current farming strategies to adopt a more sustainable and less intensive approach to farming, thus reducing the fertiliser and agriculture pollution caused from runoff.

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