The hydrochemistry of the hyporheic zone: Assessing ecotone properties for juvenile freshwater pearl mussel (Margaritifera margaritifera L.) survival in the River Esk, NE England

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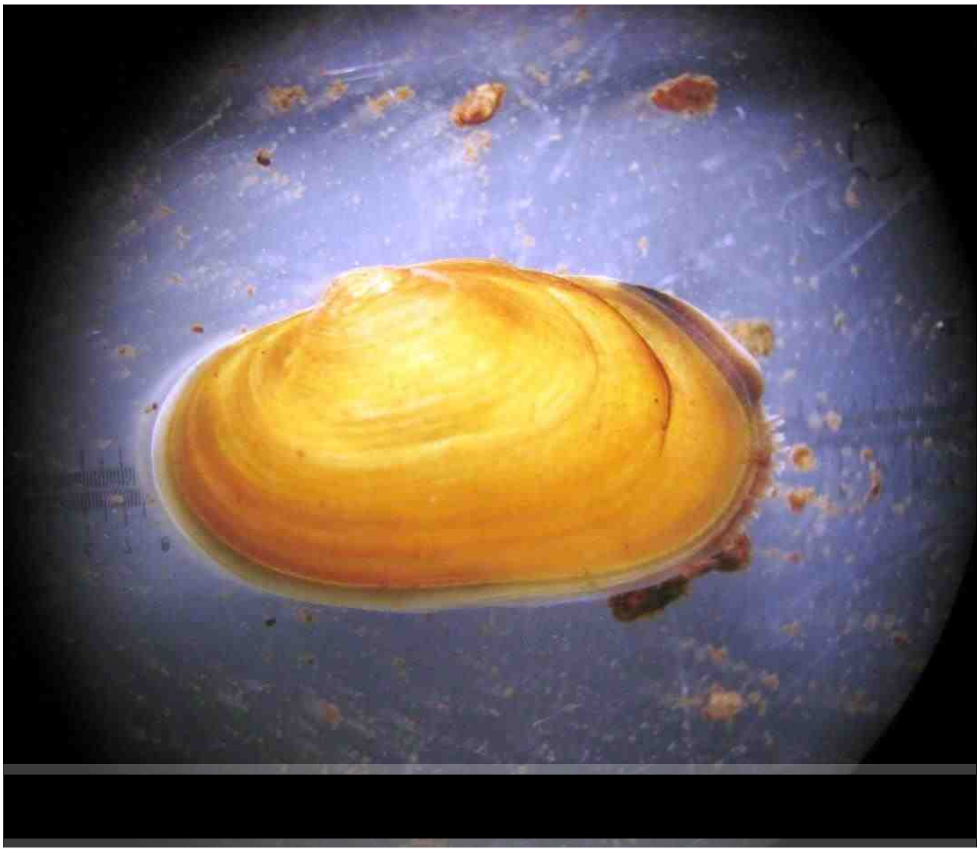

This online e-thesis edition has been edited so that detailed location information on *Margaritifera margaritifera* has been concealed. The redaction of locations was implemented to reduce the potential, albeit small, of illegal pearl poaching.

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Thesis submitted for the degree of Master of Science by Research (MSc *by Research*)

The hydrochemistry of the hyporheic zone:
Assessing ecotone properties for juvenile freshwater pearl mussel (*Margaritifera margaritifera* L.) survival in the River Esk, NE England

Abstract

The hyporheic zone is intrinsic to river ecosystems. Nutrient breakdown rates in shallow riverine sediment occur at rates faster than in marine sediments. This means that where water exchanges between stream and substrate, key alterations occur to the chemistry of sediment pore waters and lower river water column. A river unit's hydrogeomorphological setting and spatial configuration is linked to exchange flow generation between terrestrial and aquatic ecotones – a hyporheic flow pathway. Hydrological process connectivity occurs at scales from valley-scale enclosures through to meanders and riverbed forms, such as pool-riffles. Together, the hyporheic pathways coupled with the surface turbulent oxygenation processes in riffle flow, are significant in altering river water chemistry over short distances. This is considered vital, as the central focus of the European Union Water Framework Directive (2000/60/EC (EU WFD) is to achieve good ecological status, hyporheic processes significantly contribute to this. In this thesis bio-indicator species abundance, in the form of *Margaritifera margaritifera* Linnaeus (1758), an oligotrophic bivalve, is investigated as having an affinity with hyporheic processes. The impact of point-source pollution, and species absence, is also investigated.

Hyporheic zone, in-stream and groundwater hydrochemistry and hydraulic measures are assessed at three sites in this study – a braided woodland reach, an agricultural reach and a sewage treatment works, using a dense monitoring approach comprising piezometers and automatic pump water samplers augmented by manual sampling. The findings show that through a 23-metre pool-riffle sequence, where water injects at riffle-head and subsequently ejects at the riffle-tail, there is a 5 percent reduction in mean in-stream nitrate-N, and in the hyporheic zone, 73% reduction in pore water concentration. A similar pattern is presented for phosphate-P. Nitrate-N, dissolved oxygen, ammonium and phosphate-P are all subject to acute nocturnal sag, often doubling daytime concentrations. These water quality stresses and the impact of sewage outfall are assessed in respect of the last remaining Yorkshire freshwater pearl mussels, *Margaritifera margaritifera* L., an endangered species in decline throughout its geographical range and a bio-indicator under the EU WFD. The Freshwater Biology Association now has a cohort of hatchery-reared molluscs awaiting reintroduction. This study concludes that riffle-tails are the prime site for reintroduction of these juveniles, due to cool alluvial oligotrophic discharges at the riffle-tail creating metabolic hotspots and refugia. Sewage outfall is presented as a major risk imperilling long-term *Margaritifera margaritifera* viability. Statistical tests confirm river gravel compaction and pore water hypoxia at a degraded reach, compared with high pore water oxygenation at a much less impacted river reach.

Key words: Hyporheic zone, aquatic bivalve, hydrochemistry and hydrological connectivity

Table of Contents

Page

Chapter 1: Research Context

Chapter 2: Literature Review

Chapter 3: Recovery Catchment and Reach-Scale Monitoring Sites

Chapter 4: Methodology

Chapter 5: Hydrochemistry Analysis

5.2 Lealholm – Crunkly Gill

5.3 Danby – Sewage Treatment Works

5.4 Danby – Moors Centre

Chapter 6: Discussion

Chapter 7: Conclusions

List of Figures

Chapter 1: Research Context

Chapter 2: Literature Review

Chapter 3: Study Area

Chapter 4: Methodology

Chapter 5: Hydrochemistry Analysis

Chapter 5.1: Lealholm – Crunkly Gill

Chapter 5.2: Danby – Sewage Treatment Works

Chapter 5.3: Danby – Moors Centre

Chapter 6: Discussion

List of Tables

Table **Page**

Chapter 2: Literature Review

Chapter 4: Methodology

Chapter 5: Hydrochemistry Analysis

List of Maps

Map **Page**

Chapter 3: Study Area

Chapter 5: Hydrochemistry Analysis

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.

Statement of Copyright ©

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My parents and friends, for rallying me through the writing process and, on one occasion, bank-side scribing YSI probe readings whilst I yell them-out in the pouring rain, I later found the “log” function!

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Things get written despite the impracticality of reconciling competing time demands. This thesis got completed because certain people believed I could do it and invested their support to ensure that I got it done. To those people I owe a debt of gratitude.

Glossary

Allochthonous / Autochthonous

River matter from within the wetted perimeter. In aquatic ecology organic matter is inputted from macrophytes, algae, flora and fauna, including not only reproduction, but death and decay of species. Allochthonous refers to the immediate terrestrial inputs, including from riparian leaf-shed.

(Meadows, 2000:34)

Dioecious

An organism having separate reproductive organs in the male or female forms, never both; the opposite of *monoecious*, asexual organisms.

Endemic/Endemism

(1)Occurrence of organisms or taxa (termed endemic) whose distributions are restricted to a geographical region or locality, such as an island or continent.

(Abercrombie *et al.,* 2004)

Epifauna / Inafauna

Animals that live on the bottom of aquatic environments (benthic fauna) and on the substrate surface, as opposed to living within the substrate (infauna) or resident in burrows.

(Lancaster, 1998)

Epilithon

From epilithic ‘growing on the surface of a rock or stone’ (Moore, 1998), the term has a close association with biofilm, referring to the gelatinous organic coating of river and lake beds (Carlow, 1998).

Geophagy

The organism consumption of dirt, earthy matter, including clay and chalk, for mineral intake balance, but also to avert starvation (Sterner and Elser, 2012)

Hypoxic

Deficient in dissolved oxygen, typically within the interstices

Labile

(1) Open to change; readily changeable or unstable: labile chemical compounds; tissues with labile cell populations. (2) Fluctuating widely

(Labile, 2011)

Leaching Class (GWWP)

H1 - Soils of high leaching potential, which readily transmit liquid discharges because they are either shallow, or susceptible to rapid bypass flow directly to rock, gravel or groundwater

(Hollis, 1991, Palmer *et al.,* 1995)

Lysis

Sensu stricto ‘the breaking down, e.g. of a cell’, from the Greek words lysis – dissolution, lýein – *to* loosen/unbind, often by physical destruction of cell walls and membranes (Chambers, 2003:885).

Oligotrophic/ Oligotroph

A term related to the nutrient status of an aqueous or terrestrial media: ‘*eutrophic* (rich in nutrients), *oligotrophic* (poor) and *mesotrophic* (transitional)’ (Barber, 2000: 342)

Parafluvial

Similar to the littoral zone in limnology literature, the parafluvial zone is applied to river shoreline environments to describe both the extent and processes operating on bars, between flood maxima and drought. This is the waters edge alluvium that is dry in low-flow and submerged during spate, loosely associated with what Junk *et al.* (1989) terms the Aquatic-Terrestrial-Transition-Zone (ATTZ) (Fig 2.3).

Periphyton

A term sometimes applied to the community of bacteria and algae that occurs in the littoral or benthic zones of Lakes, and found attached to natural substrates such as larger plants (epiphyton), stones and rocks (epilithon), and sand grains (epipsammon).

(Battarbee, 1998)

Photoautotrophic (Cf. Photoautotrophs)

Photoautotrophs are photosynthesizing and contain chlorophyll, the catalyst that facilitates the entrapment of energy from sunlight (Meadows, 2000:35). Autotrophs are key in primary production. They synthesize, cycle and transform seston and bioseston from ‘simple inorganic materials’ into various aqueous dissolved fractions (Meadows, 2000:35).

Piedmont “Effect”

Traditionally the *piedmont zone* means mountain foot. This is a planar alluvium area flanking steep high energy mountain environments. The contrasting landforms and focusing of catchment energy, from enclosure to expanse, creates instability and energy dissipation, expressed morphologically as meandering and multi-thread braiding (Dunkerly, 2000:373). *Sensu Latto* the piedmont effect describes smaller-scale geomorphological settings, such as narrow gills (e.g. Crunkly Gill) flowing out into a wider alluvial valley (see Fig 1.1(a)., 6.7).

Polyphyletic

(1)Of or relating to a group of taxa that does not include the common ancestor of all the members. (2) Of or derived from more than one stock or source.

(Polyphyletic, 2011)

Principal Aquifer (Aquifer Grade)

Formerly termed major aquifers, 'these are layers of rock or drift deposits that have high inter-granular and/or fracture permeability - meaning they usually provide a high level of water storage. They may support water supply and/or river base flow on a strategic scale' (Environment Agency, 2013).

Zoocoenosis

The mixed community of plant and animals (a biotic community) in a particular habitat. It may be artificially partitioned into three components: a plant community (phytocoenosis), an animal community (zoocoenosis) and a community of micro-organisms (micro-biocoenosis)

(Mathews, 2000:49)

Spermatozeugmata

The aggregate dispersal of semen my male unionids around July to August. The processes results in fertilisation and glochidia brooding, where the sperm makes contact with the female hosts (Strayer, 2008; Hastie and Young, 2000).

Stygofauna

Groundwater fauna, or stygofauna, comprise the animals that live in underground water.

(Hancock *et al.,* 2005; Humphreys, 2006)

Syllogism

A deductive logic of reason based on essential factors for the occurrence of phenomena, in a particular circumstance (Greek syllogismos, *conclusion*, *inference*; Barnes, 2009).

Symbiosis (inc. Endosymbiotic)

Symbiosis/ symbiotic/ symbiont (Greek σύν – together, βίωσις – living) a term used to describe the mutual affinity of species living together, which through their individual ecology, can enhance the conditions and life of the other. In extreme cases this can include inter-dependence. Anton De Bary (1879) in his seminal paper *Die Erscheinung der Symbiose* denotes the term to mean 'the living together of unlike organisms'. Endosymbiont refers to an organism living on or within another host, for some or the entirety of its life-cycle.

Chapter 1 Research Context

1.1 Rationale

Freshwater habitats are one of the planet's most imperilled ecosystems (Renofalt *et al.,* 2010), with recent data from North America showing freshwater fauna decline at 4% per decade, a rate 4 to 5 times higher than that in terrestrial ecosystems (Ricciardi and Rasmussen, 1999; Dudgeon *et al.,* 2006). Improving water quality and restoring natural conditions in the environment is therefore critical and is underlined by the introduction of regional, national and European legislation such as the Water Framework Directive (EU WFD (CD: 2000/60/EC), Habitats Directive (EU HD (CD: 92/43/EEC) and Shellfish Waters Directive (CD: 79/923/EEC), all of which have been transposed into UK statute. Meeting the European Union's strategic objectives for Biodiversity 2020 and that of the Bern Convention (1982), including the halt in decline and the rehabilitation of freshwater fauna populations, requires that the nature of water quality stresses on protected species are appraised and reconciled (Chapman, 1992; Young *et al*., 2003; Boon *et al*, 2006; Defra, 2011). The aspiration is that freshwater ecosystems can be returned to good ecological status (GES) and associated referenced states of non-perturbed, pristine standard, thereby increasing habitat potential (European Commission, 2000; Newson and Large, 2006).

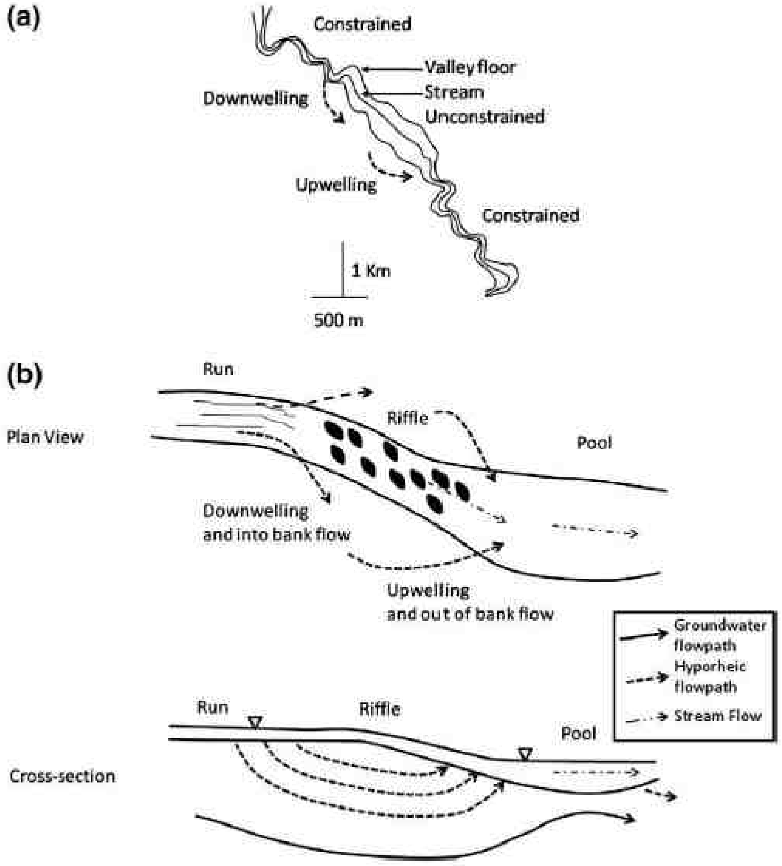
Of all groups of freshwater fauna, Freshwater Pearl Mussels (FWPM) *Margaritifera margaritifera* (denoted *M. margaritifera*), an aquatic bivalve mollusc of the family *Margariferidae,* are under particular threat of extinction (Ricciardi and Rasmussen, 1999; Strayer, 2008). They are in decline throughout their geographical range, afforded endangered status on the International Union for Conservation of Nature (IUCN) Red Data List, and are a UK Biodiversity Action Plan (BAP) priority species (IUCN, 1991; Skinner *et al*., 2003; Bolland *et al.*, 2010; Geist, 2010). Sweeting and Lavictoire (2013) found that only 9 remaining English rivers supported *M. margaritifera* populations. The River Esk is the only river in Yorkshire to have a monitored population, making it an area of regional importance for the *polyphyletic* northern group of *M. margaritifera* (Hastie and Young, 2001; JNCC, 2007; Carrithers *et al*., 2011; Bracken and Oughton, 2012). FWPMs are filter feeders and respire 50 litres of water per day in maturity (Zuiganov *et al*., 1994), whilst existing *epifaunally* in the upper interstitial gravels of the streambed (Geist and Auerswald, 2007). The oligotroph is therefore particularly susceptible to nutrient, abiotic and wider hydrochemistry changes expressed in surface and groundwaters, which are dynamically mixed at the streambed interface - the hyporheic zone (Gee, 1991; Strayer, 2008; Buss *et al.,* 2009).

The Freshwater Biology Association (FBA) together with Natural England (NE) and the competent authority for environmental preservation and regulatory enforcement (enacted 1995 Environment Act and therein), the Environment Agency (EA) have instigated an *ex situ* conservation programme for *M. margaritifera* (Gum *et al.,* 2011; Lavictoire and Sweeting, 2012, 2012A, 2012B). The FWPM Arc project was instigated in 2007. Of the estimated 500,000 individuals remaining in English waters (12,000,000 UK), a total of 357 FWPMs were taken from the 9 BAP Rivers to the FBA Arc rearing facility – of these 29 have been trans-located from the Yorkshire Esk, 6 have since died (Jackson and McLeod, 2000; Lavictoire and Sweeting, 2012, 2012A, 2012B). The facility seeks to emulate the natural environment, with a flow-through system pumping water from Lake Windermere (Gum *et al.,* 2011). Large tanks are stocked with host fish *Salmo salar* (Atlantic Salmon), *Salmo trutta* (Brown Trout) and *Salvelinus alpinus* (Arctic Char) and baskets filled with a cobble-stone-sand matrix to re-create FWPM epifaunal meso-habitats (Schmidt and Vandré, 2010; Gum *et al.,* 2011:748; Lavictoire and Sweeting, 2012, 2012A, 2012B). The artificial creation of a semi-natural aquatic ecosystem has facilitated the reproduction, rearing, culturing and propagation of *M. margaritifera* for re-introduction back into wild habitats, serving as both a safeguard to declining and imperilled polyphyletic regional populations and a 'last-minute rescue tool' for river restoration authorities (Gum *et al.,* 2011:748).

Reintroduction back to host rivers is a critical phase in the conservation Decision Making Exercise (DME). Schmidt and Vandré (2010), Geist (2010) and Gum *et al* (2011) have monitored a loss of fitness in hatchery reared juveniles. River microhabitat system 'state' is the basis to the life chance of species (Harper *et al.,* 1992; Hastie *et al.,* 2000). Responsible authorities must identify microhabitats with suitable resistance, resilience, stability, and flexibility (Pullin *et al.,* 2003 see Kilsby *et al.*, 2004:6 for definitions). This is especially vital where global warming is predicted to enhance river hydraulic seasonality (Hastie *et al.,* 2003; Kilsby *et al.,* 2004).

In their natural form *M. margaritifera* exist in aggregated dense beds forming spatially sporadic and 'patchy' communities (Ross, 1988; Beasley, 1996; Hastie *et al.,* 2000: 59; Hastie *et al.,* 2003A). The concept of hotspots – activity centres and patches that show disproportionally higher metabolic rates relative to the surrounding fluid – partially explain this by the situational physical provisioning of resources, faster breakdown of nutrients and higher quality water (Triska, 1993; McClain *et al.,* 2003; Groffman *et al.,* 2009). A paucity of protocols exist for re-introduction (e.g. Bolland *et al.,* 2010; Fowles *et al*., 2010); of the few that exist, many scantly elucidate the importance of subtle reach-scale (c1 – 10m) variability, form and processes implicated hydrochemical patches (Strayer, 2006, 2008; Schmidt and Vandré, 2010). Habitat heterogeneity and the role of hyporheic exchange biogeochemistry, including nutrient spiralling and cycling, are implicit in water quality variability at the stream-hyporheic zone interface which is vital under FWPM Threshold Values (TV) (Geist and Auerswald, 2007).

Water chemistry and its spatial variability both within a reach and within subsurface flow is crucial to *M. margaritifera* habitat. Hendrick's (1993:71) seminal paper first noted the influence of bed topography on advective flow through hyporheic sediments in pool-riffle-pool sequences. Riffle heads and flow inundation in adjacent pools generate downwelling currents (bed infiltration) which subsequently up-wells (bed exfiltration) at riffle-tails (Hendricks, 1993:71; Ibrahim *et al.,* 2010; see figure 1.1). The assemblage of photoautotrophic organisms within interstitial sediments, including diatoms, fungi, denitrifying bacteria such as *Pseudomonas* are responsible for the reduction of nutrients, under certain conditions. Pinay *et al.* (2008) reported a strong correlation ($r^2 = 0.76$) between hyporheic travel time and nitrate-N reduction. Lansdown *et al* (2012:394) similarly recorded the highest denitrification rate in riffle units at 11 N g^{-1} h^{-1}. It is hypothesised that the riffle-tail is a hotspot site, a site of upwelling hyporheic water that has been chemically reduced and cooler (Hendricks, 1993:71; Dent *et al.,* 2001; Fleckenstein *et al*., 2008). This hypothesis runs concurrent to the patchy abundance of mollusc beds, with Hastie *et al* (2003A:221) observing higher densities 'immediately below rapids'. *M. margaritifera* is both a sensitive and sessile filter feeding oligotroph, its upper TV for nitrate-N is 1.0 mg N L^{-1} (Oliver, 2000).



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This thesis investigates the theory that hydrochemistry patch mosaics are linked to in-stream habitat units with unique flow kinematics, hydraulic performance (streambed roughness) and exchange with different source waters. The physical properties of reach-scale habitats will be investigated as causal factors in survivability and reintroduction of *M. margaritifera* to specific microhabitats (Hastie *et al.,* 2003A; Emery *et al*., 2003). The hotpots of explicit stoichiometric metabolic activity and natural oligotrophy are seldom linked to habitat ‘niche’ availability (Young and Williams, 1983A; Environment Agency, 2004). Hence, this research aims to fill the knowledge gap between the hydraulic performance of microhabitats and their governance of in-stream and hyporheic hydrochemistry, biotic and abiotic parameters. Adopting a dual methods approach of the River Habitats Survey (RHS), a rapidly parameterised and routine survey carried out by the Environment Agency, coupled to in-stream, hyporheic and groundwater abiotic and biotic monitoring results, it is anticipated that a new screening protocol for the reintroduction of juvenile *M. margaritifera* can be developed (Environment Agency, 2003; Emery *et al*., 2003; Hastie *et al.,* 2003A).

1.2 Aims and Objectives

The aim of this study is to investigate the spatiotemporal variability in water quality parameters over three hydromorphologically distinct reaches, to determine the influence of hyporheic flow conditions on stream habitats.

The research is focused around the following specific objectives:

1) To determine the hydrochemistry of the hyporheic zone, and whether it is suitable for the survival of juvenile *M. margaritifera*. This will be based on hydrochemical monitoring of upper streambed interstitial waters.
2) To quantify river reach-scale heterogeneity in water quality across discrete hyporheic biotopes. This will be achieved by monitoring and analysis of the spatiotemporal variance in water quality through dynamic riparian source waters (groundwater, in-stream and hyporheic) over varying time-spans, seasons and flow conditions at three geomorphologically distinct reaches on the main River Esk:
    2.1 Lealholm Crunkly Gill (gravel bed, braided and anabranching reach) – good ‘eco hydromorphology’ ‘quality’ naturally vegetated riparian reach (Newson and Large, 2006; Vaughan *et al*., 2009).
    2.2 Danby Sewage Treatment Works (meander) – anthropogenic, degradated and nutrient enriched.
    2.3 Danby Moors Centre (straight, entrenched reach) – lowland agricultural pasture setting.

3) To identify patch dynamics and their importance in creating distinct ecotones and mesohabitats (Thorp *et al.,* 2006; 2008).
4) To determine the impact of water quality in the hyporheic zone on habitats in the River Esk.

1.3 Thesis Structure

Chapter 2 begins by providing background to the *M. margaritifera* aquatic bivalve, its lifecycle and habitat ‘niche’ preference. During the latter half of the chapter biotope preference is then put into context of ecological functioning of the reach scale, the form, process and pattern of physical biotopes. This frames the physical hydrology template in which to discuss hydrochemistry changes linked to flow mechanics within the reach. Chapter 3 details the field sites for the research. Chapter 4 then explains the methodology for this study. Chapter 5 is the results section, partitioned into 3 sub-chapters for each of the three sites – (1) Lealholm, (2) Danby - Sewage Treatment Works and (3) Danby – Moors Centre. Finally chapter 6 evaluates the results and chapter 7 presents the conclusions.

Chapter 2 Literature Review

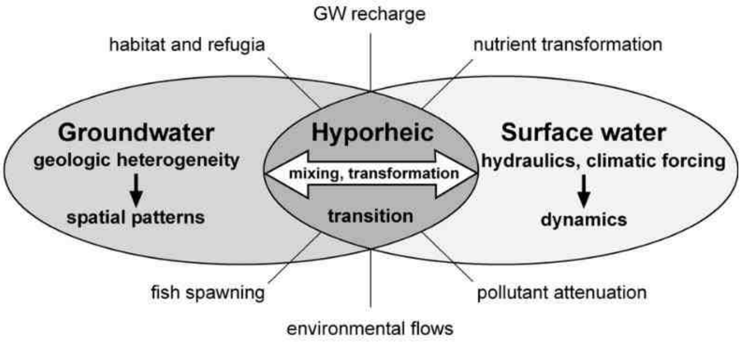
2.1 Introduction

This chapter reviews relevant literature in order to present a background understanding on the hydrochemistry of the hyporheic zone (HZ) and its importance for organism habitation and distribution. Initially, the HZ is defined by its physical properties, internal connectivity and interface interactions between aquatic and terrestrial systems – a biotope. Scale and dimension are examined as the spatial metrics used to delimit the nested HZ within the fluvial hydrosystem. This abiotic template is built upon though the appraisal of hyporheic hydrochemistry, where a metabolically active HZ is defined by source surface water (SW) runoff and groundwater (GW) contact and mixing. An assessment of anthropogenic perturbation to this hydrochemical equilibrium is briefly detailed. Having established the fundamental principles of HZ hydrology and hydrochemistry, an appraisal of hyporheic bivalve ecology takes place.

Given the water quality variability physical processes give rise to a background to *Margariferidae* ecology and life-cycle is detailed. Hyporheic flowpathways are dominant physical processes involved in metabolic hotspot formation. Hotspots contain important ecological information. The routing of pathways often creates stream patches which are vital to the respiratory needs of *M. margaritifera,* an oligotroph which establishes only in the right conditions. Flow pathways occur through multiple dimensions of the reach-scale (fig 1.1). Longitudinal dimensions of GW/SW mesoscale exchange through streambed forms will be assessed as hyporheic exchange flow (HEF). HEF is vital for aerobic and anaerobic and biotic nutrient cycling processes and is driven by topographical hydraulics of river bedforms, in addition to surrounding riparian influences. In a pre-cursor to the sites and methods chapters, unit-scale concepts for habitats are briefly described in addition to the (in)sensitivity of monitoring scale. This is finally set in context of the overarching EU WFD monitoring framework, setting the science-policy-legislation framework in which *M. margaritifera* is to be reintroduced to host rivers.

2.2 A Hyporheic Biotope?

The HZ is a fluvial ecosystem interface where source GW and SW hydro-dynamically mix effecting endemic organisms, biogeochemistry, flow and temperature (Lovejoy *et al.*, 1986; Smith, 2005; Buss *et al*., 2009; Krause *et al.,* 2011; see figure 2.1.). Orghidan's (1959, 2010) seminal paper rooted the concept in the Greek words *hypo* – below and *rheos* – flow and stated the case for the HZ biotope. This is a fertile and active transitional zone. In nature species nourishment, richness and abundance frequently occur between adjacent ecological systems where provisioning, foraging, exploitation and refugia from different ecosystem mediums can occur, creating an ‘edge effect’ (after Hyporheic Refuge Hypothesis Williams and Hynes 1974; Lovejoy *et al*., 1986:257).



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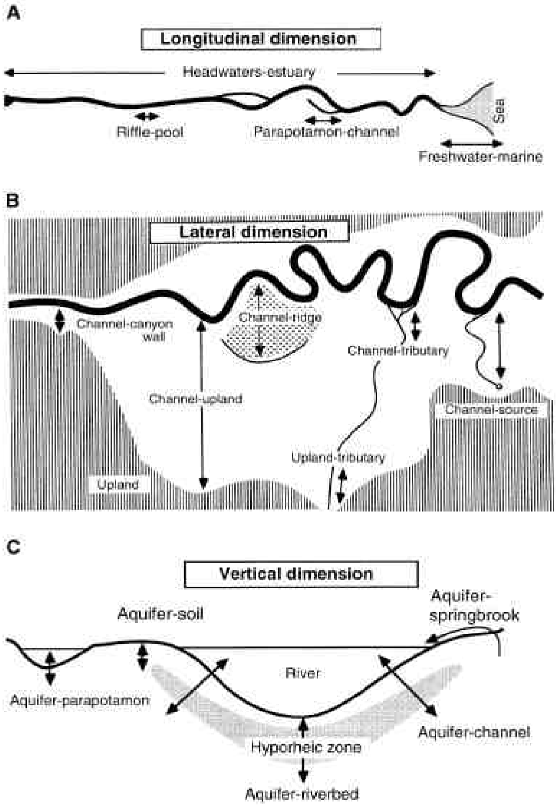
The HZ is a unique biotope where abiotic factors (auto ecology) interrelate with complex intra-species relationships (syn ecology) creating distinct environmental conditions (Sabater and Vila, 1991; Stanley and Boulton, 1993; Burt *et al.,* 2010; Orghidan, 2010). In alpine river settings ‘clean’ hyporheic clasts may exist as an intricate interstitial network, connected laterally to the riparian zone, and longitudinally through porous streambed features such as riffles, steps and dunes (Hendricks, 1993; Burt, 2005A; Zimmerman and Laponite, 2005). Bedform porosity creates an ‘extraordinary complicated system of channel and conduits connecting numerous chambers’ (Hancock *et al*., 2005; Orghidan, 2010:292). While hydrology has traditionally compartmentalised groundwater and rivers as discrete entities within riverscapes, the recent advancement of hydrological connectivity conceptualises the importance of linkage (Bracken and Croke, 2007; Wainwright *et al*., 2011; Bracken *et al*., 2013). HEFs are a mesoscale element of structural connectivity where ‘landscape units are physically linked to one another’ to create important surface and subsurface flowpaths acting as landscape ‘filters’ (Poff, 1997; Hancock *et al.,* 2005; Wainwright *et al.,* 2011:387). This makes stream-aquifer relations, including those in the parafluvial zone fundamental hydrodynamic process in this ecotone (Triska *et al.,* 1993; Fleckenstein *et al.,* 2008; see figure 1.1, 2.1.). Subsurface connectivity is a pathway process in inflow and outflow from the HZ (Smith, 2005; Buss *et al,* 2009). Streams can be gaining, from coupled hillslope water inflow, or losing through perching above the phreatric surface, or through-flow streams (Velickrovic, 2004: 173; Stubbington *et al.,* 2009; see figure 2.2.).

Disturbance maintains connectivity (Knighton, 1998; Thoms, 2006). Flood-pulse events re-work gravels and create a shifting mosaic, recycling clasts through hydrodynamic bed aggradation and degradation (Bormann and Likens 1979; Junk *et al.,* 1989). This creates a matrix of bed clasts filled with smaller particles in the pore spaces (Velickovic, 2005). Collision, saltation and traction scour the gelatinous biofilm coverings of clasts (Williams and

Hynes, 1974; Orghidan, 2010). Heterogeneous sorting and colmation, where fines are trapped in the skeleton, creates variable interstitial flow - hydraulic conductivity, *K* and spatially and temporally variable specific retentions (Velickovic, 2005:167).



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2.2.1 Source Water Biogeochemistry – Defining The Hyporheic Zone

Flow is the maestro that orchestrates pattern and process in river ecosystems

Thoms (2006:116) as citing Walker *et al.* (1995)

Ecohydrology has long recognised that flow via different surfaces (e.g. runoff) and strata (e.g. aquifer intergranular flow) bears the characteristics of the landscape unit from which it drains (Davis, 1899; Hynes, 1979; Bencala, 1993; Burt and Pinay, 2005). Where hydrochemical parameters are used as a tracer of source waters, they facilitate a spatio-temporal definition of the HZ based on chemical gradients (White, 1993). The physico-chemical attributes of source GW are fundamentally different to those of SW and the interface between them may delineate the HZ (White, 1993; Dahm *et al.,* 1998; Smith, 2005). Accounting for transmissivity and seasonal variability, in the absence of daylight and held within the specific porosity voids, GW and aquifer flow is often c.10ºC, cooler relative to SW, deoxygenated due to lack of exchange with the atmosphere and chemically reduced (Allen *et al.,* 1997; Smith, 2005; Malcolm *et al.,* 2008). Surface waters, under the influence of solar radiation, can be warmer c.15ºC, relatively oxygen saturated because of turbulence enabling dual volatilisation and diffusion of oxy-gaseous bubbles, and generally more *labile*

(Sprent, 1987; Hendricks and White, 1995). The variable contact and mixing of GW and SW at the HZ creates a gradational transition zone from saturated to unsaturated conditions (Smith, 2005; Fleckenstein *et al.,* 2008; Ibrahim *et al*., 2010; across 4 dimensions, figure 2.1,2.2.). Triska *et al.* (1989) define the hyporheic zone as saturated sediment with 10 – 98 percent advection from stream waters. When unstirred inter-granular fluid is less than 10 percent stream water it may no longer be considered hyporheic water (Boulton *et al.,* 1998, 2010; Hancock *et al.,* 2005). Krause *et al.,* (2011:482) proposed an interdisciplinary definition of the hyporheic zone as: *A temporally and spatially dynamic saturated transition zone between surface water and groundwater bodies that derives its specific physical (e.g. water temperature) and biogeochemical (e.g. steep chemical gradients) characteristics from mixing of surface—and groundwater to provide a dynamic habitat and potential refugia for obligate and facultative species.*

The inextricable linkage of GW and SW in the HZ mean it is a vulnerable receptor of biotic nutrients and pollutant pathways such as pesticides, herbicides and sheep dips (Sweeting, 1993; Smith, 2005; Hancock *et al.,* 2005; Howden *et al.,* 2011). Non-invasive sampling of the HZ is therefore an integrated catchment monitoring method (Bus *et al.,* 2009; Dearden and Palumbo-Roe, 2010). In degraded agricultural systems, such as the ones identified as field sites in this investigation, nitrate, sulphate and ammonium have been sampled at elevated concentrations in the upper HZ (Soulsby *et al.,* 2001; Crenshaw *et al*., 2010). Fertiliser (nitrogen, N phosphorus, P and potassium, K) use compounds this where inputs exceed crop requirements and land drainage (e.g. ridge/furrow, tile drainage) mobilises solutes rapidly to the adjoining watercourse – 'leaky agriculture' (White & Howe, 2004:263; Walsh *et al.,* 2005:708; Walsh *et al.,* 2005A; Jarvie *et al.*, 2008 Stenberg *et al.,* 2012; Howden *et al.,* 2013). Accordingly UK terrestrial soil nitrate-N flux at the streambed interface has increased; from 240 ktonnes N yr $^{-1}$ in 1925 to 1,463,240 ktonnes N yr $^{-1}$ in 2007 (Worrall *et al.,* 2012:98). Hyporheic ingress from GW increases SW nitrate-N concentration. The River Thames mean nitrate-N was 1.5 mg N L^{-1} in 1867 increasing to 8.1 mg N L^{-1} in 1998 (Howden *et al.,* 2013:401).

Lag leachate of biotic nutrients results in 'ghosts of the land use past', feedbacks influencing the aquatic environment long after the initial input or disturbance (Harding *et al.*, 1998; Allan, 2004:273; Howden *et al.,* 2013). Historic peak fertiliser crop application in the world wars (I and II) are a prime example of this. The majority application runs-off in a year, but subsurface flow reaches rivers by base flow later, more than thirty years where deep aquifers exist (Howden *et al*., 2011:44; Howden *et al.,* 2013). The temporal fates of environmental pollutants are critical to defining the spatial extents of the HZ based on hydrochemical gradient methods (Dearden and Palumbo-Roe, 2010). In human impacted systems where tile drains oxygenate shallow GW, saturation gradients may not be apparent (Soulsby *et al.,* 2001 Crenshaw *et al.,* 2010). Overall biotic nutrient concentrations are implicated in the anthropogenic eutrophication of waters (Deflandre and Jarvie, 2006; Jarvie *et al.,* 2013). Agriculture contributes ‘approximately two thirds of nitrogen that leads to over-enrichment and acidification of sensitive soils, habitats and fresh water’ (Defra. 2013).

2.3 Hydroecology Of The Hyporheic Zone

The HZ performs a key ecosystem function in the attenuation, transformation and fixation of biotic nutrient input by benthic primary production (Orghidan, 2010, see figure 2.3, 2.4.). The passage of fluid through alluvial interstices performs key transformations to stream water (Dahm *et al.,* 1998). Pinay *et al.,* (2008) reported a correlation coefficient of $r^2 = 0.76$ between hyporheic travel time and nitrate-N reduction in Lynx Creek, Alaska. In an agricultural stream in Michigan, Hendricks and White (1995) recorded SRP (Soluble Reactive Phosphorous) currents infiltrating stream sediments at 2 – 4 µg P L^{-1} and exfiltrating via return flow at 15 and 30 µg P L^{-1} (See also Hendricks and White, 2000), potentially due to degradated GW (e.g. Howden *et al.,* 2011). In addition to research on nitrogen and phosphorus, there is extensive literature on hyporheic carbon (Stubbington *et al.,* 2009; Trimmer *et al.,* 2012) and oxygen (Fleckenstein *et al*., 2012) stoichiometry (see Dent *et al.,* 2001; Krause *et al.,* 2011 for an overview).

Biotic nutrient cycling is undertaken by the hyporheos, the community of organisms endemic to this biotope, photosynthesising and respiring within connected interstices (Williams and Hynes 1974; Stanley *et al.,* 1993; Orghidan, 1959; 2010). Meiofauna (~ ⌀ <1mm), detrivors, molluscs, algae, bacteria, macrophytes and plankton are some of the many species that will be discussed later. Certain species such as the detritivore *Fonticola* are endemic to this biotope (Orghidan, 1959; 2010). Microhydrology, fluid movement at particle surfaces and through the cellular mucilaginous membranes of biofilms, is the spatial dimension under assessment (Hendricks, 1993:74). The HZ is critical zone. Of the 300 methods to measure ecological status under the EU WFD, c.85 percent of monitoring takes place in the upper benthos (Birk *et al.,* 2012).

2.3.1 Vegetal Fragments – Basal Energy, Food and Buffer

Beyond solar irradiation and abiotic resources, carbonaceous detritus is the trophic component driving the majority of the net primary productivity in the hyporheic biotope (Sabater and Vila, 1991; Trimmer *et al.,* 2012). Labile organic carbon (C) is an energy source which provides for photoautotrophic (light available) and chemoautrophic (light unavailable) production of biomass used by algae, bacteria and plants (Singleton and Sainsbury, 2006; Trimmer *et al.,* 2012). Vegetal material from outside the wetted perimeter, organic allochthonous, later being entrained by the river as autochthonous is the key source of much of this energy (Jansson *et al.,* 2000; Burt *et al.,* 2010A). Organic detritus in the form of leaf abscission and fragmentation are the primary resources for productivity, containing chloroplasts (chlorophyll-*a* and carotenoids) and glycoside (plant sugars). As Eybe *et al.* (2013:964) note, 'detritus functions not only as a food source but also as a biologically active compound which reduces harmful ions such as ammonium and nitrate'. Vegetation supports the food web, but also buffers harmful anionic and cationic concentrations in *M. margaritifera* juvenile pedal feeding substrate (*Vide Supra*). Urgent research is required on the nutritional requirements of FWPM in order to avoid malnutrition and biotic nutrient fatality in wild post-hatchery rivers (Gum *et al.,* 2011), especially in the hyporheic pores in which juveniles grow.

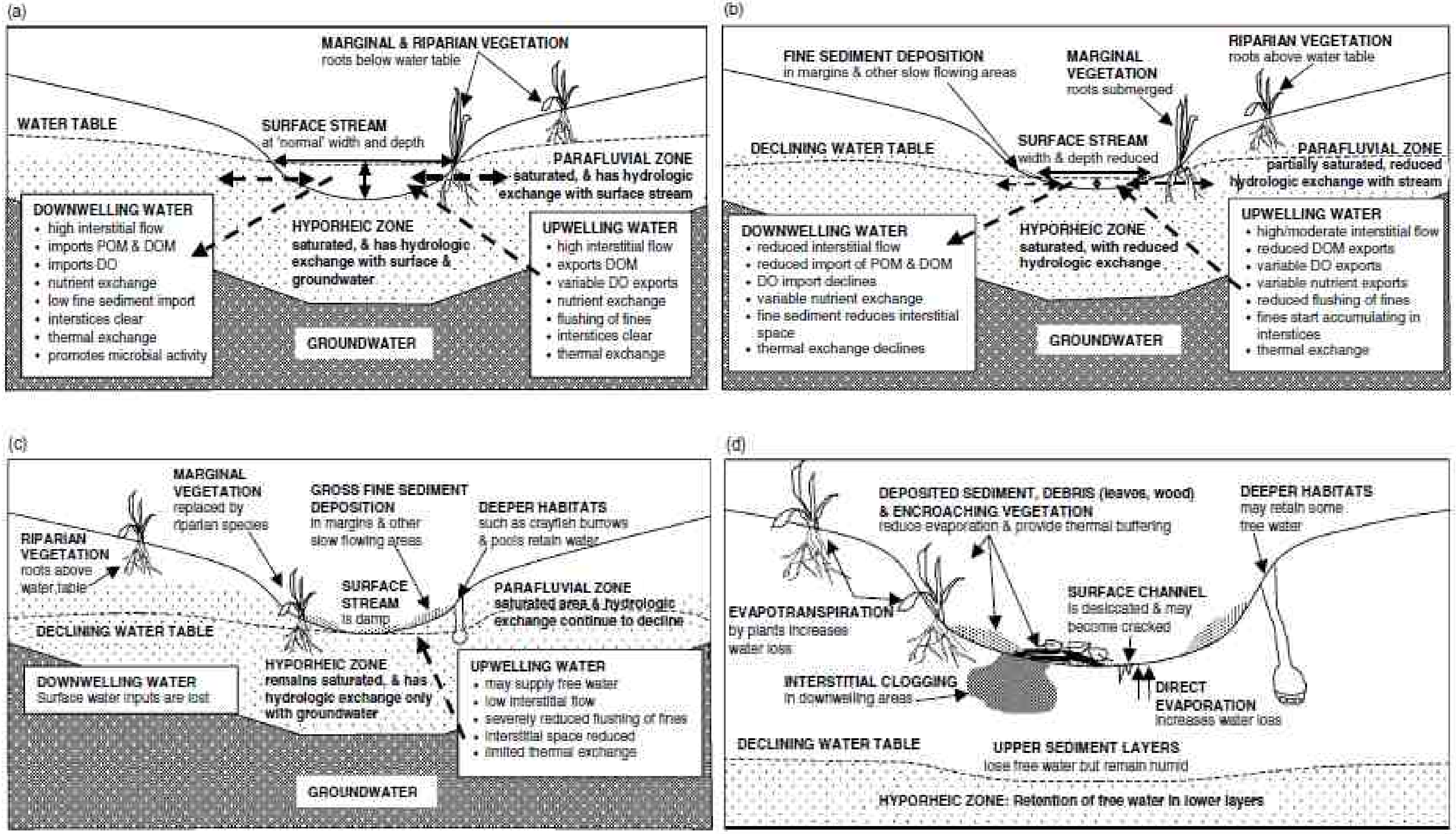
2.4 Hyporheos As Agents In Hydroecological Function

The hydromorphic form of the river and its dynamism has impact on POM (particulate organic matter) processing and the spatially heterogeneous delivery of these primary resources creating an anisotropic hyporheic zone. Hannah *et al.* (2004:3439) introduce hydroecology as the concept explaining the interface between biology (cf. ecology) and hydrology. Hydroecology is the 'focus on plant – water relations in terrestrial and aquatic ecosystems' (Baird and Wilby, 1999: 5). Inevitably there is a hydromorphological element in channel planform and shoreline sedimentary processes reworking new material into the water column (e.g. Vaughan *et al.,* 2009). The riparian foreshore transition to the *parafluvial* zone between terrestrial and aquatic zones exerts key influence, *sensu stricto* where bankside vegetation overhangs the river (Burt *et al.,* 2002:129 as citing Tansley, 1911; see figure 2.3.). Cumulatively ecological elements, including vegetation, are control mechanisms on riverine biota assemblage and distribution (Bormann and Likens, 1979; Burt *et al.,* 2010A). Patch canopy light interception silhouettes solar rays into light and dark patches penetrating the stream water column. Some species such as salmonids migrate for shade and temperature refugia, an autoecological response to changing environmental conditions that also occurs diurnally when salmon retreat bankside, similar shell closure occurs in mussels too (Sabater and Vila, 1991; McCormick *et al.,* 1998; Skinner *et al.,* 2003; Stanley and Boulton *et al.,* 2010). Light mottling creates SW patch mosaic thermal emissivity. Basal tree root nodulation from non-leguminous Green alder (*Alnus crispa*) within the capillary fringe fixates nitrate-N (N-NO_3^-), symbolically denitrifying salmon redds for spawning, *de facto M. margaritifera* habitat too (Pinay *et al.,* 2008, *et alibi*).

Trees do not solely regulate the physical properties of habitats (Newbold *et al.,* 1982; Mander and Hayakawa, 2005). In laterally extensive braided systems, parafluvial zone wetted perimeter cycling between terrestrial and aquatic phase facilitates the re-working of CPOM (Coarse Particulate Organic Matter) into finer detrital debris – FPOM (Fine Particulate Organic Matter, ⌀ < 1mm, but > 0.45 μm, *sensu* Junk 1989; Thoms, 2006; Turowski *et al.,* 2013; see figure 2.3.). Silage (leaf-shed decay) patches occur on the bed interface, in addition to decomposing and microbially active vegetal and animal fragments, creating a gelatinous biofilm over the bed and bank substratum (Orghidan, 2010). This is an important heterotrophic food source and element for hyporheos with implications for net primary productivity (Bormann and Likens, 1979 Jansson *et al.*, 2000; see figure 2.3, 2.4.). Capillary fringe variability incorporates this rich material into the HZ, once sufficiently fine or dissolved. Granular mortaring of particles during spate disturbance disintegrates biomass, particularly in bar environments where radially active eddies shed bank-ward flow (Buffin-Bélanger *et al.,* 2005). Algal lysis describes the process by which cell rupturing may release available energy into the water column (*circa* UPOM, Ultrafine Particular Organic Matter, < 50 µm but > 0.45 µm).

Anthropogenic impacts impair the ability of streams to generate energy in this way. Only 11 per cent of UK rivers now flow as ‘pre-human’ or ‘natural’ (Petts *et al*., 1988, 2002). Only 10 percent of floodplains are in their former near natural state along the key rivers of the Rhine and Mississippi (Rahaman and Varis 2005:20). The majority of riparian zones may be considered ‘genetically modified’ through measures such as development, impoundment and canalisation (Lewin, 2013), starving the river of its intrinsic connection to the floodplain.

Irrespective of anthropogenic impacts, processing by heterotrophs remains a fundamental process in the breakdown of leaf silage and humic substances on the streambed (Maltby, 1992; Poff, 1997; Walsh *et al.,* 2005A). The endemic hyporheos *Fonticola* (detritivore), including general taxa *turbellarians*, *nematodes* and *oligocheates* maintain detrital and biofilm equilibrium in combination with benthic grazer, shredder and filter feeders (Maltby, 1992; Orghidan, 2010). *Fonticola* differs from aquifer and groundwater stygofauna which are eyeless and without pigmentation (Orghidan, 2010). Digestion and turnover of translucent vegetal and decomposed patch biofilm by detritivores endosymbiotically enhances periphyton photoauthotrophic activity and granular cleansing (Newbold *et al.,* 1982; Maltby, 1992; Fisher *et al.,* 1998). Even in anthropogenically impacted food-deficient environments, geophagy (not detritivory) may occur: the ‘consumption of dirt’ for mineral intake balance. However, this is seldom documented in benthic environments (Mai *et al*., 2005).


(a)
MARGINAL & RIPARIAN VEGETATION
roots below water table
WATER TABLE
SURFACE STREAM
at 'normal' width and depth
PARAFLUVIAL ZONE
saturated, & has hydrologic exchange with surface stream
DOWNWELLING WATER
high interstitial flow
imports POM & DOM
imports DO
nutrient exchange
low fine sediment import
interstices clear
thermal exchange
promotes microbial activity
HYPORHEIC ZONE
saturated, & has hydrologic exchange with surface & groundwater
UPWELLING WATER
high interstitial flow
exports DOM
variable DO exports
nutrient exchange
flushing of fines
interstices clear
thermal exchange
GROUNDWATER
(b)
FINE SEDIMENT DEPOSITION
in margins & other slow flowing areas
MARGINAL VEGETATION
roots submerged
RIPARIAN VEGETATION
roots above water table
DECLINING WATER TABLE
SURFACE STREAM
width & depth reduced
PARAFLUVIAL ZONE
partially saturated, reduced hydrologic exchange with stream
DOWNWELLING WATER
reduced interstitial flow
reduced import of POM & DOM
DO import declines
variable nutrient exchange
fine sediment reduces interstitial space
thermal exchange declines
HYPORHEIC ZONE
saturated, with reduced hydrologic exchange
UPWELLING WATER
high/moderate interstitial flow
reduced DOM exports
variable DO exports
variable nutrient exports
reduced flushing of fines
fines start accumulating in interstices
thermal exchange
GROUNDWATER
(c)
MARGINAL VEGETATION
replaced by riparian species
GROSS FINE SEDIMENT DEPOSITION
in margins & other slow flowing areas
DEEPER HABITATS
such as crayfish burrows & pools retain water
RIPARIAN VEGETATION
roots above water table
SURFACE STREAM
is damp
PARAFLUVIAL ZONE
saturated area & hydrologic exchange continue to decline
DECLINING WATER TABLE
HYPORHEIC ZONE
remains saturated, & has hydrologic exchange only with groundwater
DOWNWELLING WATER
Surface water inputs are lost
UPWELLING WATER
may supply free water
low interstitial flow
severely reduced flushing of fines
interstitial space reduced
limited thermal exchange
GROUNDWATER
(d)
DEPOSITED SEDIMENT, DEBRIS (leaves, wood) & ENCROACHING VEGETATION
reduce evaporation & provide thermal buffering
DEEPER HABITATS
may retain some free water
SURFACE CHANNEL
is desiccated & may become cracked
EVAPOTRANSPIRATION
by plants increases water loss
INTERSTITIAL CLOGGING
in downwelling areas
DIRECT EVAPORATION
increases water loss
DECLINING WATER TABLE
UPPER SEDIMENT LAYERS
lose free water but remain humid
HYPORHEIC ZONE: Retention of free water in lower layers

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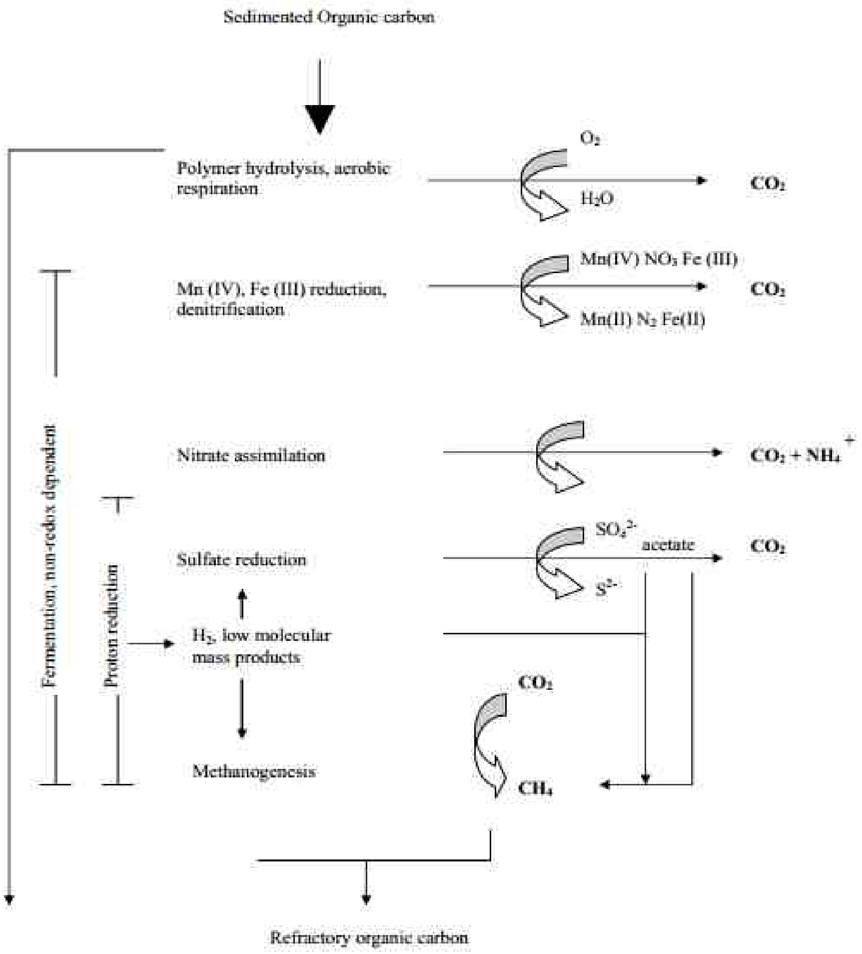
Detritivoral excretion of material into the interstices of the benthos can result in bio-accumulation, caking and the form of epilithic mats where obligate species cannot sequester detritus (Haack and McFeters, 1982; Navel *et al.,* 2013). The actions of *M. margaritifera* and other taxa of Unionoida, alongside salmonid redd (nest) is vital in the HZ (Skinner *et al.,* 2003; Hendry and Cragg-Hine, 2003; Zimmerman and Laponite, 2005). Re-suspension and bioturbination of fine trapped seston and biosestion is performed by *M. margaritifera* and spawning/nesting of female salmonids (Vaughn and Hakenkamp, 2001; McCormick et al., 1998). Mussel foot movement dislodges conglomerated clasts creating proximal aeration, whilst redd (nest) excavation proactively extricates clasts (Ziuganov *et al.,* 1994; Yeager *et al.,* 1994; McCormick *et al*., 1998; Soulsby *et al.,* 2001; Vaughn and Hakenkamp, 2001; Hendry and Cragg-Hine, 2003). *Margariferidae* dual pedal (upper streambed ~ 10 cmbd), and filter feeding (water column) in the epifauna ensures dual detrital processing and food source exploitation (Gee, 1991; Ruppert and Barnes, 1994). This is why abundance and distribution of the species is so vital to ecosystems (Wilson, 1992), particularly in the maintenance of functional connectivity – defined as the interplay of geomorphic, ecologic and hydrologic processes (Wainwright *et al.,* 2011:387). Nalepa *et al.* (1991) observed unionid beds utilizing 13.5 percent of total stream phosphorous and bio depositing 63 percent of this – undertaking a form of ‘biological oligotrophication’ (Welker and Walz, 1998). This is a process vital in maintaining effective permeability of chambers and conduits through the HZ waters which obligate (restricted) and facultative (discretionary) meiofauna (~ ⌀ <1mm) require in order to survive, predate and refuge (Orghidan, 1959, 2010; Williams and Hynes 1974; Robertson and Wood, 2010). Hypermobile water mites (*hydrachnidiae*) are one such example (Orghidan, 1959, 2010; Stanley *et al.,* 1993).

Microbiology is as inherently important in alluvial hydraulic stoichiometry as invertebrate ecology (*vide supra*). Endosymbiotic (*actinorrhiza*) nitrogen-fixing bacteria on root nodules of alder are an example of the role bacteria play in the HZ (Sprent, 1987; Actinorrhiza, 2006; Pinay *et al.,* 2008, *et alia*). The ensemble of biofilm and planktonic trophic bacteria are intrinsic in nutrient cycling along with other mutualistic hyporheos (Jones, 1985; Triska *et al*., 1989, 1993; Hendricks, 1995). Diatoms, fungi, and denitrificans such as *nitrobacter winogradskyi* with anaerobic filamentous chemoautotrophic and Anammox (ANaerobic AMMonium OXidation) archaea and bacteria, of the taxon *thiobacillus* and *candidatus* are nitrogen cycle examples (Haack and Feters, 1982; Sprent, 1987; Triska *et al*., 1993; Kelly *et al.,* 2008; Trimmer *et al*., 2010). The transient passage of water through the interstitial network where bacteria operate, often in biofilm, results in fundamental stoichiometric alterations particularly to key biotic macronutrients (C, N, P, S) (Hendricks and White, 1991; Triska *et al*., 1993; Lansdown *et al.,* 2012; Turowski *et al.,* 2013). Assimilation of chemical species generally occurs in oxic (oxidising) conditions where electron donors are available, whilst dissimilation occurs in reducing environments deficient in oxygen – hypoxic or anoxic conditions that are often electron accepting (Stubbington *et al.,* 2009; Lansdown *et al.,* 2012; see figure 2.4.).



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Thus far this section has considered the hyporheic hydroecology in a quasi-stationary perspective, defining the hyporheic zone as a SW/GW mixing exchange interface, the literature review has been focussed on the lateral (e.g. riparian, parafluvial zone) and vertical dimensions (e.g. depth chemical and light gradients, see figure 2.3. 2.4.). A third fundamental dimension is the stream-wise longitudinal dimension of the lotic ecosystems (Ward, 1989; White, 1993; Ward and Wiens, 2001, see figure 2.2.). Fluvial hydrosystems constrain coherent flow structures causing fluid to exchange between hydrogeological media, examples may include riffles, dunes, steps, glides, secondary and relict paleo channels (Thompson, 1986; Dehm *et al.* 1998; Fleckenstein *et al.,* 2008). Hydromorphology is an inherently spatio-temporal discipline (Vaughan *et al.,* 2009), and therefore Ward (1989) introduces time as the fourth dimension in hyporheic hydroecology. Given the preceeding introduction of hyporheos, the next section will address *M. margaritifera* ecology.

2.5 The Freshwater Pearl Mussel (*Margaritifera Margaritifera*) – Background and Lifecycle

Margaritifera margaritifera is an aquatic bivalve mollusc of the family *Margariferidae,* belonging to the superfamily *Unionoidea* whose larva is glochidium (Cummings and Bogan, 2006; Strayer, 2008:11). *Maragariferidae* extends throughout the geographical range of North America, Europe and Asia (Northern hemisphere only) and has 12 species (IUCN, 1991; Strayer, 2008). Whilst small, restricted and declining throughout this range, where they do occur sporadically, they frequently do so in abundance, often forming dense beds (>100 invertebrates m^2 - Skinner *et al*., 2003:11;Strayer, 2008:11). The (inter)catchment metapopulation dynamics of the FWPM breeding cycle is critical but remains a complex phenomenon that has seldom been studied (Strayer, 2008:25). Genetic diversity is an important aspect of maintaining resilience to disturbance as cryptic speciation is thought to play a key role in adaption to particular biotope properties (Tokeshi, 1993; Geist and Kuehn, 2005;). Females have an extraordinary high reproductive potential, being able to eject between 1 and 4 million glochidia in up to 48 hours and switch to a hermaphroditic state when there is a low proximal density of males (Haste and Young, 2001; see figure 2.5.). It is thought that this makes pearl mussels relatively resistant to in-breeding depression and explains the 'low measures of genetic diversity accomplished by high consensus population sizes' (Geist and Kuehn, 2005:436). Maintenance of phyletic genetic diversity is considered critical as filter feeders have no counterpart in terrestrial invertebrate zoology (Gee, 1991).

M. margaritifera is typically a dioecious species with a morphogenetic lifecycle that is complex (Stayer, 2008). Two critical life phases are apparent – a parasitic stage on a host fish and a post-parasitic phase, in which juveniles live to adulthood in shallow interstitial gravels and substratum, at depths of 4 – 10 cmbd (Skinner *et al.,* 2003; Geist and Auerswald, 2007, see figure 2.5.). Conchology studies vary in age maxima for *M. margaritifera*. Most suggest an age of over 100 years (Bauer, 1992; Skinner *et al.,* 2003). Lifespan estimation for *M. margaritifera* is problematic: surveys can underestimate by decades and even century timespans (e.g. Bauer, 1992, Anthony *et al*., 2001). *Maragariferidae* mature in the ranges of 10 – 15 years, where length starts to exceed 65mm, dependent on ecotone nourishment and diet (Bauer, 1992, Skinner *et al.,* 2003). Fertility may be prolonged into old age (Bauer, 1987). The largest mussels can be 150 – 170 mm in length (Degerman *et al*., 2009).

The fertilisation process plays a pivotal role in freshwater pearl mussel fecundity and local abundance. *Spermatozeugmata* describes the process by which males broadcast their sperm via the *Anodonta grandis* into open waters (Hastie *et al.,* 2003; Degerman *et al*., 2009). The process occurs around July – August (*ibid*). Proximity and downstream flow paths to females are critical as the sperm cannot swim. Sperm – by chance occurrence –

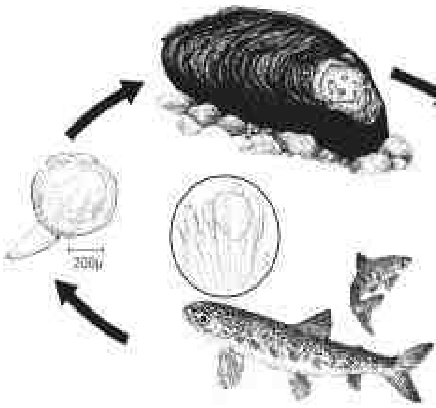
enter into the female via the incurrent/inhalant siphon and fertilize the eggs held in the female's gills (brood chambers) (Moorkens *et al.*, 2007). They develop into the larval stage, termed glochidia; with gestation occurring over a period of 380 – 420 days, growing to lengths of 0.6 – 0.7mm (Skinner *et al.*, 2003). FWPM fertilised eggs mature during the spring and summer. In the run-up to glochidia release, gravid mussels (females with glochidia in the gills) wait until around July to September when they broadcast high numbers of glochidia into the water column (Moorkens *et al.*, 2007). Bauer's (1987) German study found that the mean broadcast frequency was 4 million glochidia, with a range from 1 to 9 million. In Scotland around 30-60 per cent of females were found to be gravid (Young and William, 1984). Glochidia release period varies with polyphyletic populations. Larsen (1999) observed it occurring over a period of 2 weeks, whilst UK studies have observed it occurring over a 1 or 2 day period (Hastie and Young, 2001).


Mark Young

Unattached glochidia.


Mark Young

Encysted glochidia on host gills.



Mussel larvae, known as glochidia, are released in summer and attach themselves to the gill filaments of a juvenile salmonid. Here they encyst and grow until the following spring, when they drop off on to clean gravel and begin maturing. This association does not seem to harm the host fish, and facilitates mussel dispersal.


Mark Young

Newly settled juvenile mussel.


Adult and juvenile mussels from a stable population in Scotland.

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The critical parasitic phase of glochidia release is explained by different theories, which seek to determine what specifically induces the release – environmental or zoological factors. The normative theory is that an environmental threshold event, such as abrupt temperature change or oxygen stress induced release (Skinner *et al*., 2003; Bauer, 1987:693). While this may be a probable causal mechanism for release, the simple notion that glochidia are broadcast into the water column, with a chance probability of contact with the key host, is receiving attention by invertebrate behaviour scientists (Zuiganov *et al*., 1994; Geist, 2010). Unionids have been observed to use more sophisticated methods to get glochidia to attach to hosts, including 'elaborate moving lures', or 'glochidia packages to resemble fish food' (Kreamer, 1970; Haag *et al.,* 1995; Hartfield and Hartfield 1996; Haag and Warren, 1997; Watters, 1999, 2002; Haag and Warren, 1999, 2003; Corey *et al.,* 2006; see Strayer, 2008:14, figure 2.5., 3.3.). A majority of the literature suggests glochidia broadcast is a 'highly synchronised' event (Hastie and Young*,* 2001; Skinner *et al.,* 2003).

The broadcast glochidia resemble small mussels (Skinner *et al*., 2003; see figure 2.5.). Dispersal of the parasites is a critical point of survival and susceptibility in the life cycle with most attachments occurring within a few hours (Hastie and Young, 2001). Young and Williams (1983) found that failure to find a host in 24 hours occurred 99.9% of the time. Many glochidia are swept downstream and die, although they can remain viable for up to 6 days (Zuiganov *et al*., 1994). Successful glochidia encyst the fish host using the minute shell and adductor muscle to clamp onto host gills (Zuiganov *et al*., 1994). *M. margaritifera* glochidia may also be inhaled by fish hosts (Bauer, 1987).

Recent hatchery monitoring by the FBA reveals that young (0+ and 1+) sea trout (*Salmo trutta*) has the highest encyst frequency for River Esk *M. margaritifera* (Lavictoire and Sweeting, 2013). Parr and Smolt Atlantic salmon (*Salmo salar*) are known to host, as is common in other UK rivers, but have a lower hatchery encyst rate for R. Esk *M. margaritifera* (Skinner *et al*., 2003; Moorkens *et al*., 2007). A minority of glochidia belonging to the polyphyletic northern populations are able to use arctic char (*Salvelinus alpinus*) as a host too (Hastie and Young, 2001; Lavictoire and Sweeting, 2012).

Once successfully encysted, parasitic glochidia live in the hyper-oxygenated valves close to the filament of gills; here the glochidia absorb and digest nutrients from the fish hosts gills (Zuiganov *et al*., 1994; Skinner *et al*., 2003). The length of exposure time to the larvae also means the host fish immune system has time to react (Degerman *et al*., 2009). Whilst deriving nutrients no damage is done to the host fish at sustainable infection rates (Moorkens *et al*., 2007). During attachment, glochidia grow to around 6 times their original length then drop of into river substrate in May – June, requiring physicochemical streambed characteristics that are clean, oligotrophic, gravely, sandy with sufficient refugia (Skinner *et al*., 2003; Moorkens, *et al*., 2007; Hastie *et al*., 2000). This is the post-parasitic, second life stage of the *M. margaritifera* life cycle critical to continued recruitment and survival (Skinner *et al*., 2003). The early second stage is also acknowledged as the most sensitive phase

(Geist and Auerswald, 2007; Hastie and Young, 2001). For it is only those mussels that land in suitable interstitial habitat (*ibid*), such as boulder stabilised beds with intermitted sand patches (Skinner *et al.,* 2003), with low hyporheic residency times, sufficient mixing (HEFs) and connectivity between the water column and upper interstitial hyporheic zone, that survive (Geist and Auerswald, 2007; Malcolm *et al*., 2008; Buss *et al*., 2009).

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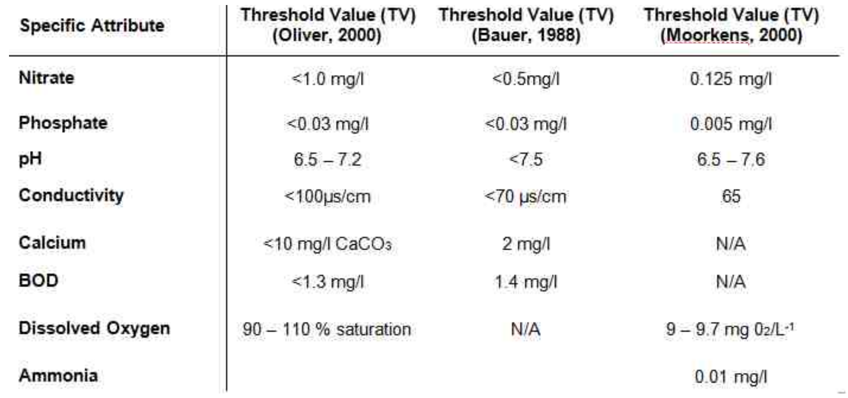


Specific Attribute	Threshold Value (TV) (Oliver, 2000)	Threshold Value (TV) (Bauer, 1988)	Threshold Value (TV) (Moorkens, 2000)
Nitrate	<1.0 mg/l	<0.5mg/l	0.125 mg/l
Phosphate	<0.03 mg/l	<0.03 mg/l	0.005 mg/l
pH	6.5 – 7.2	<7.5	6.5 – 7.6
Conductivity	<100µs/cm	<70 µs/cm	65
Calcium	<10 mg/l $CaCO_3$	2 mg/l	N/A
BOD	<1.3 mg/l	1.4 mg/l	N/A
Dissolved Oxygen	90 – 110 % saturation	N/A	9 – 9.7 mg $0_2/L^{-1}$
Ammonia			0.01 mg/l

Key oligotrophic TV (Target Values) are required to ensure survivability of *M. margaritifera*. These standards apply to the water column for active filter feeding, interstitial water for post-encystment phase development and for disturbance of ‘trapped’ interstitial water by foot movements (Skinner *et al*., 2003; Geist and Auerswald, 2007; Stayer, 2008; see table 2.1). Buddensiek’s (1995) seminal paper on culturing juvenile *M. margaritifera* in cages contributed key and previously unknown water quality needs for the species. Buddensiek’s experiment used linear regression between chemical exposure to parameters outlined in table 2.1 and mortality rates of *M. margaritifera* (Buddensiek, 1995). Buddensiek (1995) concluded that exposure to key hydrochemistry attributes directly correlated with *M. margaritifera* fatality. This was supported by the later research of Young, (2005), Bauer (1988), Oliver (2000), Moorkens (2000) who have observed concentrate metals and pesticides correlate with increased mortality rates. Recently, horticultural molluscicide (inc. metaldehyde) runoff has been a key concern, with exposure linked to increased fatality (Waller *et al.,* 1993). Detailed realistic studies are needed to quantity the effects of excessive nutrient enrichment on in-stream and hyporheic waters and the influence hydraulic habitat parameters have on natural buffering of these in respect of *M. margaritifera* survival TV (Young *et al*., 2003; Hastie *et al*., 2000; 2003A; Fowles *et al.,* 2010). Scant attention has been given to HFP stream pressure head gradients on the osmoregulation and selectivity of *M. margaritifera* filter feeding. It is anticipated that high pressure in riffle-heads may not be conducive to respiration and associated selective dormancy (Trueman, 1966; Gee, 1991; Hastie *et al*., 2003A).

2.6 *M. margaritifera* Reintroduction – The Law, Habitat Identification And Scale Sensitive Measures

> *Despite the strong conceptual basis for sustainable river management, scientists are challenged to define ecosystem needs clearly enough to guide policy formulation and management action that balance competing demands and goals*
>
> Poff (2003:298)

Internationally 10,000 unionids remain extinct or imperilled in conglomerate beds far from monitoring points, where only “snap-shot” water quality data is generated (Marston, 2000; Strayer, 2006:271; Reid *et al*., 2012). Monitoring through mixed taxa invertebrate scoring, fish surveys and chemistry sampling costs, and so scales and locations of monitoring are spatiotemporally reduced to make them commensurate to environmental authority OPEX (Operational Expenditure) budgets (Church 1996; Marston, 2000; João, 2002). EU member states (inc. UK) are compelled under the EU Habitats and Species Directive (CD: 92/43/EEC) (espoused from the Bern Convention (1979 - 82)) to implement strategies for rehabilitation (Young *et al*., 2003; JNCC, 2007). A Species Action Plan (SAP) is the integral part of the UK BAP policy implementing the Wildlife and Countryside Act (1981) schedule 5 component for the listed *M. margaritifera* ‘priority’ species recovery (Skinner *et al*., 2003; JNCC, 2007; Defra, 2011; Reid *et al*., 2012). A trajectory of literature now demonstrates that the only means to rehabilitate ‘non-functional’ populations is to rear *M. margaritifera* in an ex-situ hatchery facility and then re-stock river environments following the establishment of ‘protected areas’ with the correct conditions (Geist, 2005; Preston *et al*, 2007; Bolland *et al*, 2010; Gum *et al.,* 2011; Reid *et al*., 2012). However, the entirety of some populations now exist in hatcheries, reducing the impetus to restore the freshwater environment back to the required standards along with an impairment to ecosystem function via a loss of filter feeding capacity (Moorkens, 2000, 2007; Schmidt and Vandré, 2010; Gum *et al.,* 2011).

The EU WFD (CD: 2000/60/EC) aims to improve water quality to a naturalistic state. The legislative instrument compels ‘environmental outcomes’ (European Commission, 2000; Everard, 2012). European Court infringement proceedings are bought against member states failing to achieve GES in all waterbodies (groundwater, surface and transitional waters) by the end of the first round in 2015, or delay to the end of 6 yearly cycles – 2021, 2027, in the event an overriding reason (European Commission, 2000, 2010, 2011; Solimini *et al.,* 2006). In the face of declining water quality, a legacy of river training (including canalising, impounding), increasing freshwater abstraction and riparian disputes, a new standardised framework for water quality monitoring, reporting and restoration was developed (McNeil, 2000; Giordano and Wolf, 2003:163; Quevauviller *et al.,* 2005; Solimini *et al.,* 2006).

Under the central premise of ‘good status’, the directive requires evidence submission to the EU council for each waterbody (surface [inc. lakes, ponds, reservoirs], groundwater, coastal, and transitional) by 2015, with two subsequent public disclosures on aquatic assessment being required in 2021 and 2017 (House of Lords: European Union Committee, 2012, See Article 18 of the EU WFD - European Commission, 2000). ‘Good status’ is both ‘good ecological status’ and ‘good chemical status (European Commission, 2000, 2010, 2011). For both, the gradational status from ‘high’ to ‘bad’ is defined by the deviation from the ultimate target of non-impacted ‘natural systems’ (Diamond, 1987; Newson and Large 2006; European Commission, 2010:2).

Ecological status is defined by reference standards on the composition and abundance of aquatic flora and fauna through in-stream waters and benthic waters (inc. macro-invertebrates, diatoms), nutrient conditions and chemical pollutants and hydromorphological quality elements – e.g. the physical integrity and functioning or the river (European Commission, 2000; 2010; 2011; Deflandre and Jarvie, 2006).

Chemical status is defined with respect to ‘thirty three new and eight previously regulated chemical pollutants of high concern across the EU’, all under a priority substance list (European Commission, 2010). Substances were also later bought under the Integrated Pollution Prevention Control Directive (CD: 2008/01/EC) (European Commission, 2000, 2001, 2010, 2011; Ruiz-Jean and Aide, 2005; Deflandre and Jarvie, 2006).

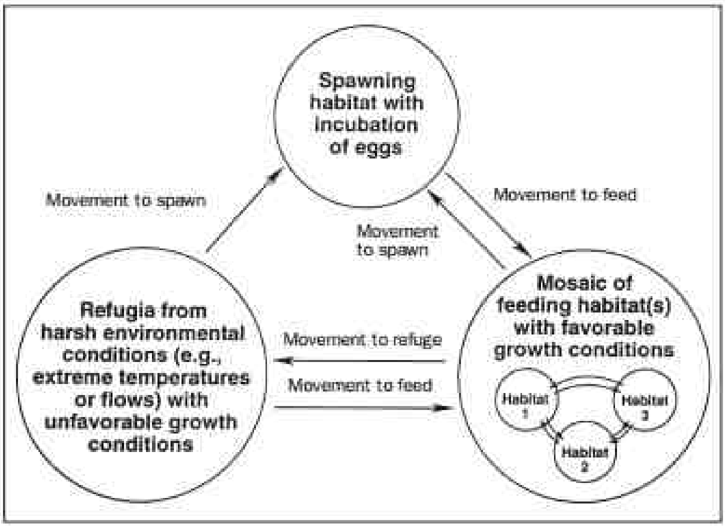
The EU WFD is a successor to monolithic chemical and fish monitoring, not only are chemical metrics now used but also riverine flora, fauna and biota bringing consilience (Sweeting, 1994:24; Kelly *et al.,* 2008, see CEN, 2004 and Newson and Large, 2006:1608). This is precisely the holistic hyporheic eco – hydromorphology quality assessment required for *M. margaritifera* (*et alibi,* section 2.4). As an umbrella directive embodying past directives including the EU Nitrates Directive (91/676/EEC), EU Waste Water Treatment Directive (91/271/EEC) and the EU Drinking Water Directive (98/83/EC) the management objective evolved from mere pollution control to holistic ecosystem integrity (European Commission, 2000, 2001, 2010, 2011; Ruiz-Jean and Aide, 2005; Deflandre and Jarvie, 2006; Solimini *et al.,* 2006, Borja *et al,* 2008).

M. margaritifera is a flagship, umbrella and bio-indicator species that can be used as a barometer of EU WFD aquatic ecosystem health (Geist, 2010; 645). Filter feeding at a rate of 50 L D^{-1}, it is a keynote process species (Zuiganov*et al*., 1994; Barbier *et al.,* 1994). Turning over FPOM and aqueous nutrients improves water quality symbiotically (Welker and Walz, 1998, Geist, 2010). Through biological oligotrophication mussels are a natural restoration species (*ibid*). Considering the detailed chemistry TV *M. margaritifera* has (e.g. Buddensiek, 1994), abundance and functional recruitment are a strong indicator of ‘high’ EU WFD ecological status (Vaughn and Hakenkamp, 2001; Birk *et al.,* 2012).

Few records exist on pre-disturbed hyporheic water chemistry, nor contemporary, with sampling methods being developed late-on by Lee and Cherry (1978). Hence the study of water quality in-stream and hyporheic is vital to the bio-indicator *M. margartifiera.* Although reach-scale water quality is not thought to be homogenous, but temporally and spatially heterogeneous due to habitat and riverbed hydraulics.

2.7 Hyporheic Exchange Flow (HEF) Through Pool-Riffles — The stoichiometry of Hot Spots and Hot Moments

Pool-riffle units remain the most frequently surveyed bedform in benthic sampling literature, and also most common in EA River Habitats Surveys (RHS) results (Padmore, 1997; Newson and Newson, 2000:201; Newson *et al.,* 2012). Their geometric form and physical exertion on flow properties drives autoecological abundance and distribution of species which is fundamental to the implementation of monitoring programmes (Pringle *et al*., 1988; Stanley and Boulton, 1993; Tokeshi, 1993; Schlosser, 1995A; Poff, 1997; João, 2002). The channel unit scale feature of a pool and riffle is vital to fluvial bedform ecology, representing the highest elevated alluvium within the wetted perimeter after bars (Richards, 2000; Ward and Wiens, 2001). Its vertical dimension is a landscape 'filter' (Schlosser, 1995A; Poff, 1997; figure 2.6., 2.8). Seeking to generate understanding of patchy ecological abundance Poff *et al*. (1997) introduce the predictive concepts of 'filters' and 'pass'. A filter is a hydroecological unit of interacting biotic and abiotic resources in which a species establishes a functional relationship, it 'passes' nested filters through landscape in order to flourish at the given locale, given the specificity of environmental attributes that only suit certain taxa (Sabater and Vila, 1991, Poff 1997, and Stanley and Boulton, 1993). Pool-riffle bedforms are a 'filter' to the species 'pass' of *M. margaritifera* (Poff, 1997; Hastie *et al.,* 2003A). An explanation of stoichiometric vectors of exchange flow or functional connectivity through the medium of a riffle is critical to the microhydrology patch provision of resource species 'pass' (Poff, 1997).



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2.7.1 Pool-Riffle Hydraulics

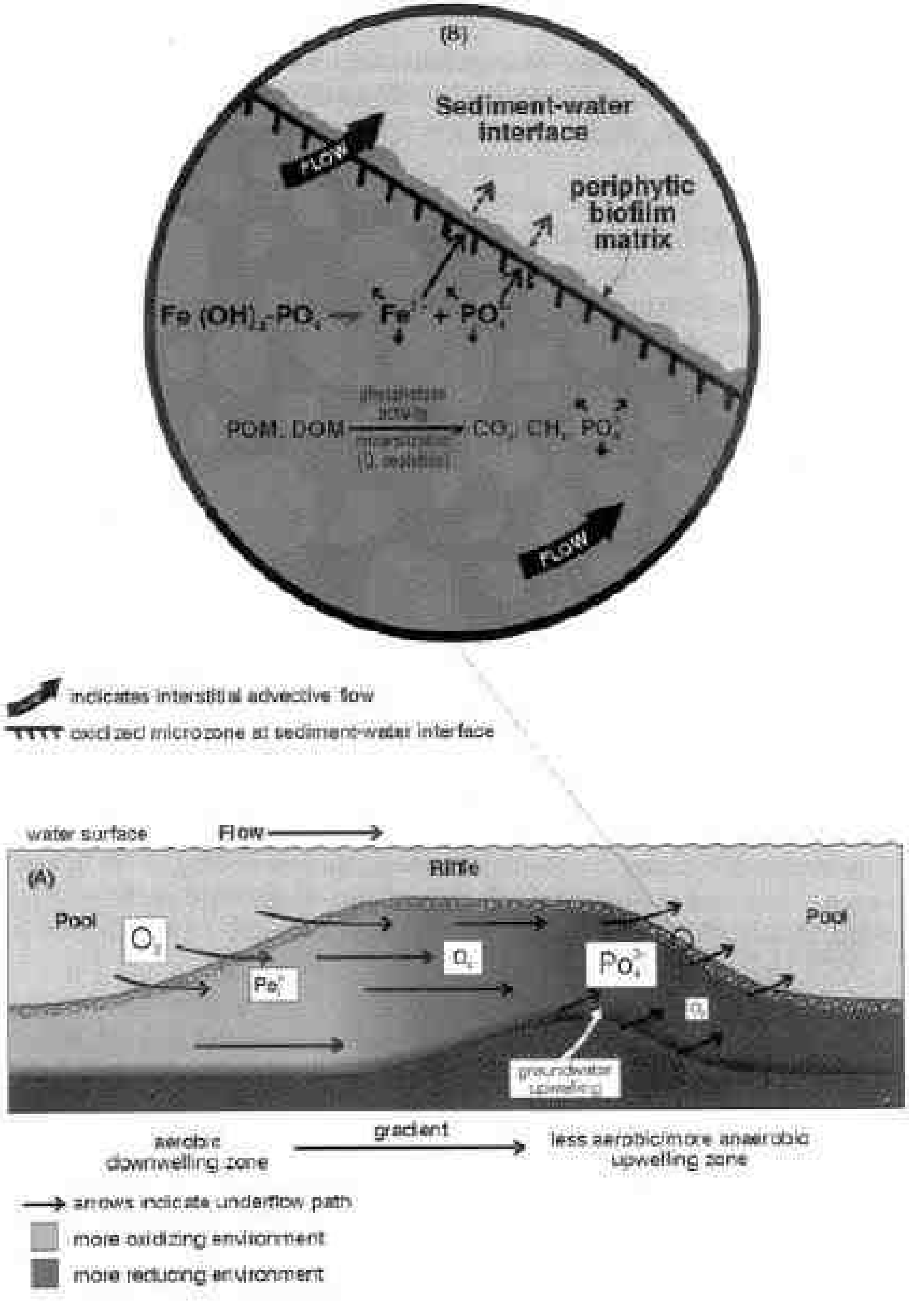
The form of hollowed, depressed bed commonly floored with fine grained alluvium – pools, or 'topographical heights representing accumulations of coarser pebbles and cobbles' – riffles, impact that way water exchanges between the stream and the bed (Thompson, 1986; Henricks 1993; Hendricks and White, 1995; Richards, 2000). The eco-hydrogeology of bed alluvium (e.g. effective permeability, transmissivity) and the flora composition, for instance biotic epilithon and algal matts influence the rate of exchange after the effects of overall discharge and channel constraint (Haack and McFeters, 1982; Malcolm, 2003; Zimmermann and Lapointe, 2005; Fleckenstein *et al.,* 2008; Wainwright *et al*., 2011, see figure 1.1., 2.1 and 2.7.). Sorption – desorption is also a key none-destructive process to nutrient processes through the hyporheic zone which is invariably influenced by sediment type (Triska *et al*., 1989, 1993; Ibrahim *et al.,* 2010). Organic rich silt and clay fractions have been associated with increased P (SRP) sorption capacity (Stones and Murdoch, 1989; Surridge *et al.,* 2005).

Pools create a zone of runoff accumulation and inundation before riffle cascading (Ibrahim *et al.,* 2010; Wainwright *et al.,* 2011). A volume of runoff may sweep this zone and immediately flow down the rapid/riffle (Thompson, 1986). However, when the hydrostatic pressure of unstirred pool water exceeds that of any groundwater piston upwelling, rate variable stream water advection, bed injection and downwelling into the hyporheic substrate occurs (Smith, 2005; Hancock *et al.,* 2005). Pools and riffles have 'pressure head gradients in the stream' which HEF accommodate (Wainwright *et al.,* 2011:391). The downwelling water is transported as downslope shallow hyporheic 'return flow' (Thompson, 1986; Henricks, 1993). Upon reaching the riffle-tail, the shallow hyporheic flow path (HFP) ejects due to the interception at the microhydrological 'basin' site of the pool unit (Hancock *et al.,* 2005; Hendricks, 1993; Zimmerman and Laponite, 2005). This creates a zone of upwelling water. Ibrahim *et al.* (2010) determined the specific discharge into a riffle-head at -1.17 cm/day (VHG 1.8%, site P1) and 0.34 cm/day (VHG 3.2%, site P3) out of a riffle-tail. Vertical Hydraulic Gradient (VHG) reflects downwelling, if negative, or upwelling, if positive (Ibrahim *et al.,* 2010: 1394, VHG after Dahm *et al.,* 2006). It is theorised that this HFP creates a form of secondary longitudinal piston flow – a CUSF (Channel Unit-Scale Hyporheic Flow Path) seldom appraised in the literature (Thompson, 1986; Fleckstein *et al*., 2008; Ibrahim *et al.,* 2010; Wainwright *et al.,* 2011).

A turbulent SW runoff pathway exits through the riffle unit, with different hydrogeology, bed roughness and clast make-up to the surrounding unit - bed alluvium (Buffin-Bélanger *et al.,* 2000; Emery *et al*., 2003; Hardy *et al*., 2009). Lansdown *et al.* (2012:392) sampled river units on the River Leith (Cumbria), finding gravels (≤ 20cm) were most common in riffles with the highest median grain size through the reach. The presence of larger clasts corresponds with eddy generation and turbulent energy through riffles, both due to shallowness and bed roughness coefficient, what Emery *et al.* (2003) terms habitat hydraulic performance (Hendricks and White, 1991; Thompson, 1986; Hendricks 1993; see figure 2.7.). Rough, larger clasts in the riffle and the depositional fines (e.g. SOM – soil/sediment organic matter) in the pool create variable sorption – desorption zones (Chiou *et al.,* 1979, 1985). Pools are prime areas for sorption of biotic nutrients because of their composition of fines. However, SOM may result in process change to ammonification which may alter the trophic status and affect mollusc habitability (Chiou et al., 1979, 1985; Lansdown *et al*., 2011; Strayer, 2008). The riffle facilitates dual volatilisation (unsteady state water surface) and diffusion of gases within the water column, including oxygen saturation through downward bubble movement and ingress into gravels (Sprent, 1987). Lansdown *et al* (2012:394-395) recorded a highest denitrification rate in riffle units at 11 N g^{-1} h^{-1}, an average rate 10 times faster than in pools (e.g. Pinay *et al.,* 2008; Lansdown *et al.,* 2012 and others). The quantification of exchange flow through the riffle, between piston flow and runoff, remains poorly constrained or quantified in HZ ecology literature (Emery *et al*., 2003; Fleckstein *et al*., 2008). River unit hydraulics are critical to *M*. *margaritifera* survival, with Hastie *et al*. (2000) suggesting a velocity TV (Target Value) of 0.25 – 0.75 m s^{-1}.

HEF through variable in-stream and hyporheic media, including through various biotic organism complexes, makes riffle-head down-welling chemistry markedly different to the water upwelling at the riffle-tail (Hendricks, 1993; Hendricks and White, 1991; Stubbington *et al*., 2009). Riffle-heads are a zone of aerobiosis. Advection currents of oxygenated in-stream waters facilitate respiration, methane oxidation, nitrification and sulphate oxidation (Hendricks, 1993; Hendricks and White, 1991; Stubbington *et al*., 2009; see figure 2.4.,2.7.,2.8.). Riffle-tails are zones of anaerobiosis, ejection of proportionally de-oxygenated hyporheic water is determined to accord with processes of denitrification, nitrate reduction, ammonification, sulphate reduction and methanogens (Hendricks, 1993; Hendricks and White 1991, Lansdown *et al.,* 2012).

Activity centres which produce a disproportionately higher reaction rate and resource balance relative to the surrounding matrix are hotspots, or hot moments, if they are ephemeral in nature (McClain *et al.,* 2003: 301, see shifting mosaic in Bormann and Likens 1979). The physical connection of different landscape units provides hydroecological systemic permanence at an ecotone scale, such as a boundary at the aquatic terrestrial interface. Where, for instance, the ‘edge effect’ between chemically and thermally different cooler groundwater and in-stream waters occurs (Lovejoy *et al*., 1986; Junk *et al*., 1989; McClain *et al.,* 2003: 301; Groffman *et al.,* 2009). Time is fundamental in this respect. Hot moments are more transient in nature, ‘bursts’ of activity occurring at variable spatial scales from catchment freeze-thaw cycles through to re-wetting of side bars and natural berms (McClain *et al.,* 2003; Groffman *et al.,* 2009; 1986; Junk *et al*., 1989). Hotspots and hot moments provide the vital flux of resources, organisms and energy within riverscape elements (Triska *et al*., 1993; Fausch *et al*., 2002). The activity centres are syllogistically understood to be representative of underlying biogeophysical mechanisms under study (Richards, 1990; Church, 1996; Groffman *et al.,* 2009).



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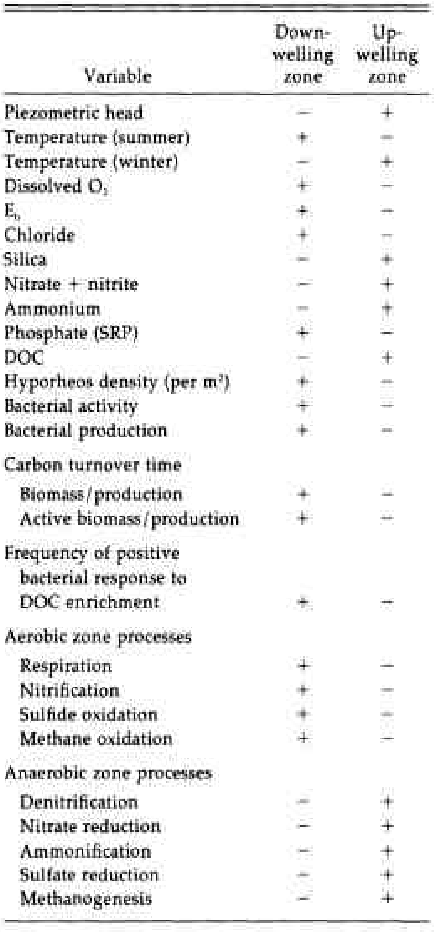
The removal of N and P from hyporheic and in-stream hydromorphic habitats has clear microhabitat significance for sensitive *M. margaritifera* oligotrophic filter and pedal feeding (see Geist and Auerswald, 2007; Hastie *et al*., 2000; 2003A). Crucially, recent population survey evidence suggests that dense mollusc beds usually occur at riffle-tails (Hastie *et al*., 2003). The physical biotope is therefore fundamental to the survivability of *M. margaritifera*, with early post-settlement re-introduction being an extremely sensitive phase (Hastie *et al.,* 2000). Detailed and reliable habitat data is therefore vital in order to maximize the chances of long-term success (Young and Williams, 1983A; Hastie *et al.,* 2003:214). Hastie *et al.* (2000:59) cites Ross (1988) Beasley (1996) in noting that ‘at the 1–10m scale, M. margaritifera typically exhibits highly aggregated distributional patterns’. Furthermore, ‘less attention has been paid to physical alterations than to changes in water quality […] although insufficient research has been undertaken, and the extent of the problem is largely unknown, there is anecdotal evidence that physical factors are important in considering the conservation status of pearl mussel populations’ (Hastie *et al*., 2003:214).



Variable	Down-welling zone	Up-welling zone
Piezometric head	−	+
Temperature (summer)	+	−
Temperature (winter)	−	+
Dissolved O_2	+	−
E_h	+	−
Chloride	+	−
Silica	−	+
Nitrate + nitrite	−	+
Ammonium	−	+
Phosphate (SRP)	+	−
DOC	−	+
Hyporheos density (per m^2)	+	−
Bacterial activity	+	−
Bacterial production	+	−
Carbon turnover time		
Biomass/production	+	−
Active biomass/production	+	−
Frequency of positive bacterial response to DOC enrichment	+	−
Aerobic zone processes		
Respiration	+	−
Nitrification	+	−
Sulfide oxidation	+	−
Methane oxidation	+	−
Anaerobic zone processes		
Denitrification	−	+
Nitrate reduction	−	+
Ammonification	−	+
Sulfate reduction	−	+
Methanogenesis	−	+

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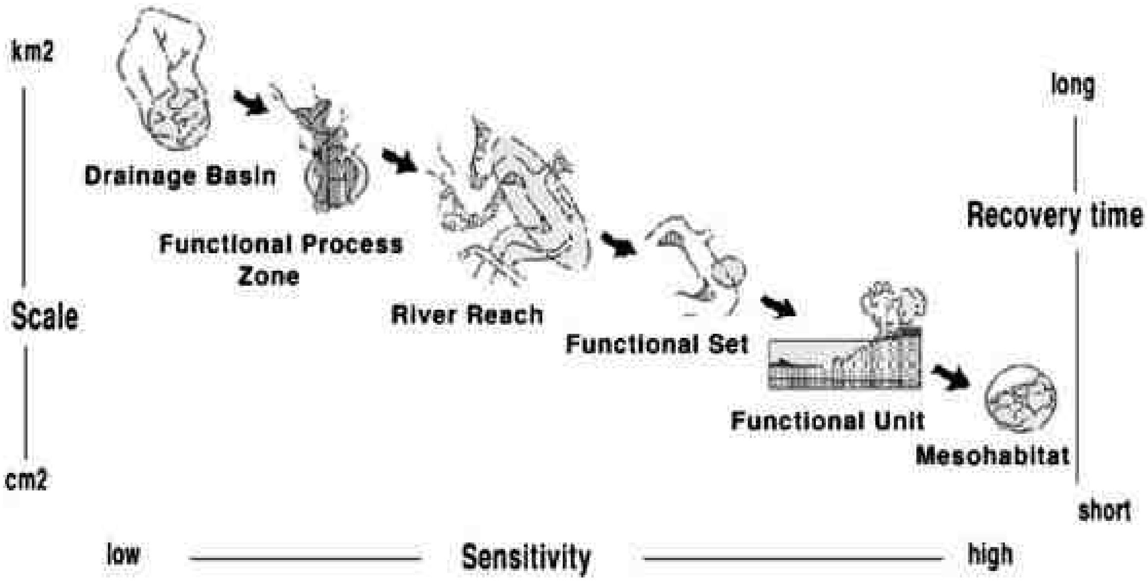
Many studies fail to epistemically link water quality to the unit of physical habitat, despite the need for holistic data on life chances for *M. margaritifera* success (Geist and Auerswald, 2007; Hastie *et al*., 2000; 2003A). Both reintroduction of juveniles and survival of pre-existing *M. margaritifera* will require detailed microhabitat water quality monitoring (Bolland *et al,* 2010). It is therefore critical to understand *M. margaritifera* ecology and lifecycle in respect of habitat. Particularly since 'the development of the "patch dynamics concept" of stream ecosystems' (Pringle et al. 1988, Townsend 1989) has meant that 'heterogeneity that previously had been perceived as noise, was recognised as important ecological information*'.* (Fausch *et al.,* 2002:485).

2.7.2 Field Literature On Hierarchical Fluvial Hydro-Systems

Rivers, rather than being landscape 'homogeneous entities' are instead intrinsically influenced by their surrounding 'topography, hydrogeology, land-use and biological communities, affecting the water cycle at multiple spatial scales' (Ward, 1998; Wiens, 2002:504; Allen, 2004; see figure 2.9.). Ward's (1998) 'riverscape' model underwrites unit influences by synthesising landscape ecology with riverine form, process and pattern. The model has six tenets, including patches differ in quality, patches affect flows and connectivity is critical (Wein, 2002:501; Fausch *et al.,* 2002). Within the fluvial hydrosystem the scale of patch mosaic influence is fundamental, riverscapes emphasises that spatially discrete and nested controlling factors of patches exerts key influence on species (Allen, 2004), these local processes and feedbacks are thought to be critical to *M. margaritifera* (Johnson and Brown, 2000). Thorp *et al*. (2006, 2008) RES (Riverine Ecosystem Synthesis) advances the riverscape model by elucidating a series of discrete hierarchical hydrodynamic units through rivers – Functional Process Zones (see figure 2.9., Tokeshi, 1993; Fausch *et al.,* 2002).



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At the reach-scale (c.1 - 10 m), which this research will be conducted, there is a multiplicity of hydro-systems (Petts and Amoros, 1997). Given the scale of enquiry, mesohabitats have the highest sensitivity, but shortest recovery time so it is logical that enhancing and repairing reaches can enhance overall river ecosystem function, particularly for sessile local species (Bernhardt and Palmer, 2011; Meitzen *et al.,* 2013; figure 2.9). Each unit performs a role in material transformation for species energy, matter and nutrients (Pringle *et al., 1988*; Hastie *et al*., 2003A). An example of lateral 'material spiralling' via the functional unit of a riparian seep may be the provisioning of inflow for mesoscale enrichment or pollution (Fisher *et al.,* 1998; Krause *et al.,* 2009; see figure 1.7.):

> ***Receptor:*** *M. margaritifera* in s*itu* of biotope **> Pathway:** Overland flow via a riparian seep **> Source**: Proximal and soluble molybdate-reactive P from organic/humic pore water exchange during saturation and scour – bioavailable for algal growth (Reynolds and Davies, 2001; Surridge *et al.,* 2005).

2.7.2.1 Reach-Scale Habitats Form, Pattern and Process Indicative Determination for *M. margaritifera*

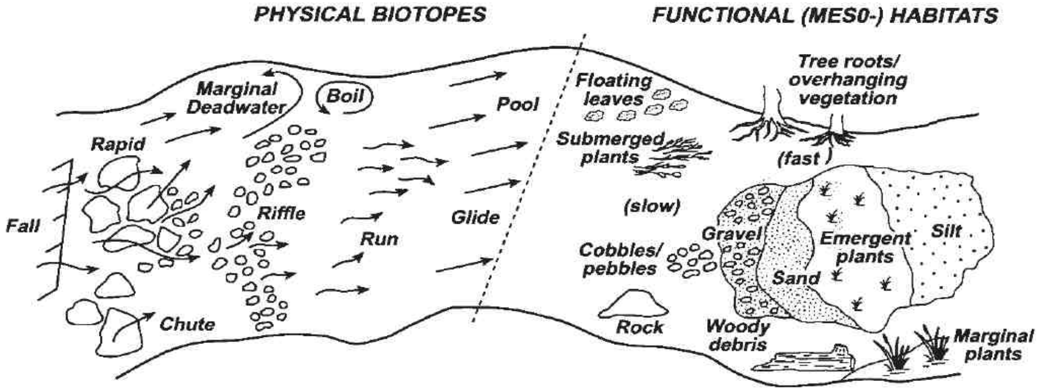
Given the evidence on physicochemical facets of biotopes, it is important to reconcile theories on the form, process and delimitation which may explain HZ anisotropy. At the reach-scale, two competing concepts are proposed to classify patch types, defined as:

Mesohabitats

> *Visually distinct units of habitat within the stream, recognizable from the bank with apparent physical uniformity [a term which] introduces a scalar dimension which the term biotope does not have … In-stream habitats are defined in terms of characteristics such as physical structure, organic content, stability and heterogeneity.*
>
> Pardo and Armitage (1997:111)

Physical/Hydraulic Biotope

> *The hydraulic biotope may be defined as a spatially distinct in-stream flow environment characterised by specific hydraulic attributes (Wadeson, 1994) […] the essential link between geomorphology and ecology. The morphological unit and associated hydraulic biotopes provide the basic building blocks of the system whilst the catchment and its sub zones control the driving forces*
>
> Wadeson (1999:3; Wadeson 1999 citing Wadeson 1994)



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Habitat is the unit of survivability for *M. margaritifera,* its sessility means that unlike its salmonid host, which can migrate from unfavourable habitat conditions, it is directly vulnerable to patch change and disturbance (Williams and Hynes 1974; Moorkens, 1999, Skinner *et al.,* 2003; see figure 2.9.1.). The rehabilitation of the water environment under Hynes' (1979) "the valley rules the stream" notion can take decades to bring improvements in receiving waters (e.g. Howden *et al.,* 2011; Worrall *et al.,* 2012), with lag-effects (e.g. Harding et al., 1998, Howden *et al*., 2013, section 2.2.1.) and post-normal science problems (e.g. Jarvie *et al*., 2013). Therefore the unit scale of habitat seems the obvious scale at which to assess hyporheic habitat 'quality' and undertake proactive restoration measures, having the greatest recovery time (see figure 2.9.) and predictability that intervention will have intended consequences – repairing the reach-scale filters to save the catchment (Bernhardt and Palmer, 2011; Meitzen *et al.,* 2013).

The IUCN re-introduction guidance for *M. margaritifera* states: 'the principal aim of any re-introduction should be to establish a viable, free ranging population in the wild […] and should require minimal long-term management' (IUCN, 1998; Bolland *et al*., 2010). Preservation of fluvial geo-diverse habitat forms buffering and filtering flows, energy and nutrients between ecosystem mediums is a key method to achieving such long-term viability during catchment-wide restoration programmes (Poff, 1997; Mander and Hayakawa, 2005; Wohl, 2011). These eco – hydromorphology forms safeguard and form a *prophylaxis* to environmental and anthropic disturbance through their biophysical attributes (Mander and Hayakawa, 2005:42; Geist, 2010; Degerman *et al.,* 2009:16; Burt *et al*., 1993, 2010). The functional connectivity afforded by the stream units is an unequivocal regulating ecosystem services that supports the delivery of resource (Daily, 1997 Hussain *et al.,* 2010; TEEB, 2010). Stream units are the building blocks of river continuums and the overall function a rivers plays in the breakdown of materials.

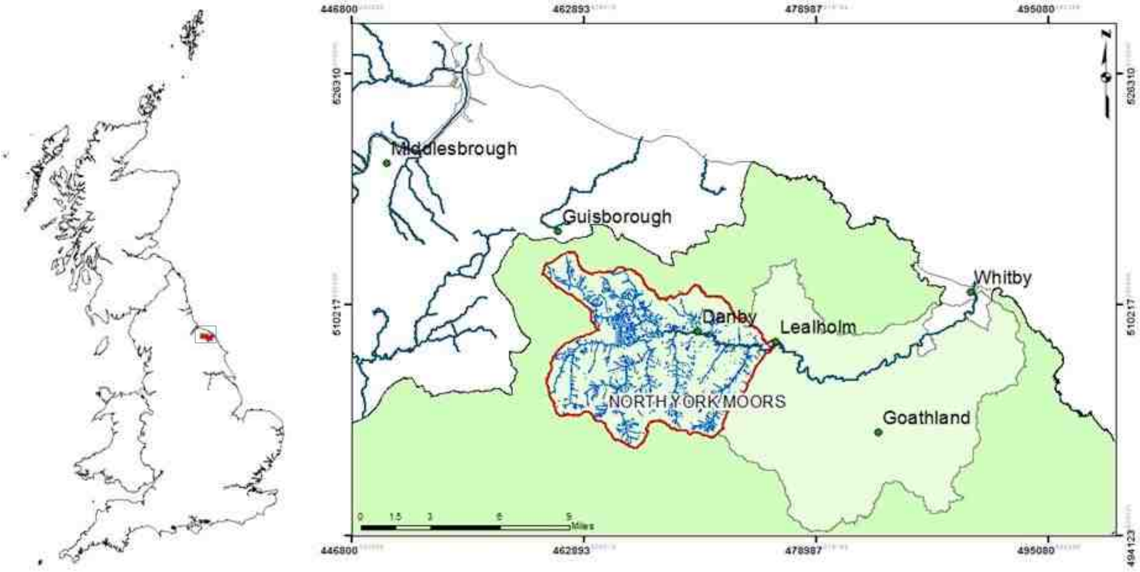
2.8 Summary

- Relevant literature has been critically appraised in this chapter to highlight the current understanding on hyporheic hydrology, chemistry, ecology and ecotone management.
- Initially literature on the abiotic hydrogeology of the HZ was assessed as the background to HZ ecology, including the colonisation of alluvium with vegetation through to meiofauna and other such keynote process hyporheos. The physical hydrology template situated an assessment of the vulnerability of the HZ, due to the zones inextricable linkage to SW and GW systems: distal hillslope actions by man can impact the physicochemical quality of HZ.
- *Margariferidae* ecology and lifecycle was detailed, after which the importance of habitat hydrochemistry was explained.
- After considering the quasi-stationary view of the HZ, the dimension of flow and bedform hydraulics was discussed to provide the hydrodynamic background to the stoichiometry of subsurface flow pathways as important landscape ‘filters’. This provided the basis to argue that hot spots and patch dynamics are the causal mechanisms driving *M. margaritifera* abundance and distribution at the reach scale – the species ‘pass’.
- The institutional policy—science—legislation nexus was discussed as the governance structure for *M. margaritifera* re-introduction to host rivers.
- A review of habitat literature on methods to identify field reach-scale habitats and their interplay with spatial ecology was detailed, in the final sections.
- Many of this chapters themes – including hyporheic chemistry, HEF and exfiltration effects on abundance – will be re-assessed through the ensuing chapters, quantified with methodological approaches for field data collection to yield results. This is in order to contextualise *M. margaritifera* survival in patch hyporheic substrate.

Chapter 3 Study Area

3.1 Introduction

This chapter provides a geographical description of the research catchment and the three intensively monitored river-reaches. When considering hyporheic ecology and chemistry it is clear that key river functions are affected by HZ processes, which once altered at catchment level, conversely affect the HZ (Bus *et al.,* 2009). This chapter first considers the catchment as the precursor to hyporheic chemistry and organisms, primarily symbiotic *M. margaritifera* and *salmonidae.* The latter section downscales to the stratified reach-scale sites



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3.2 Catchment Characteristics

The Esk is a key malacology river because it is one of nine remaining English rivers supporting an *M. margaritifera* population (Oliver and Killeen, 1996; Sweeting and Lavictoire, 2013), the second river in north east England after the Rede (Tyne), (Jackson and McLeod, 2000; JNCC, 2007). Eskdale hosts the lowest ranked population estimate for both UK BAP rivers and for the imperilled phylogenetic northern group (*ibid*). The small catchment size of 363km^2 and minimal intensive land-use of 4,700 ha owes itself to the greatest restoration potential of similar UK BAP sites (João, 2000; McDonald *et al.,* 2004; JNCC, 2007; Bolland *et al*., 2010; Fowles *et al.,* 2010; Bracken and Oughton 2013). The Esk is a prime riverscape for intense hydrochemistry investigation.

The catchment is located 25 miles south east of the industrial conurbation of Middlesbrough. Discharging into the North Sea near to Whitby, the Esk flows west to east with a length of 42km (Bracken *et al*., 2009; Bolland *et al*., 2010, see map 3.1). The source peat moorland headwaters occur at a maximum elevation of 433 mAOD (Cockayne ridge and Glaisdale moor) with the river predominantly draining the rural North York Moors National Park.

The intensive study reaches occur in a third-order stream dominated by pool-riffle, minor step-pool and run-pool sequences. Negligible salmonid redd excavations have been recorded through recent years, fisheries specialists have recorded spawning in riffles that clean and oxygenate eggs (NYMNPA, 2013; Environment Agency, *Pers. Comm.* 2013), making these channel units vital to investigate for both *salmonidae* and the *M. margaritifera* symbiont (e.g. Soulsby *et al.,* 2001; Zimmermann and Lapointe, 2005; Newson *et al.,* 2012).

3.3 Recovery Sub-Catchment Characteristics

In the face of respective declines in *M. margaritifera* and no juveniles (Oliver and Killeen 1996; Killeen, 1999; Hirst *et al*., 2012), *salmonidae* rod catch (Environment Agency, 1999; 2011; see figure 3.0) and water quality (McNish *et al.,* 1997; Evans *et al.,* 2014), the smaller recovery catchment was defined above the EU WFD sampling and stage monitoring point of Lealholm (see map 3.1, Hirst, 2012; Hirst *et al*., 2012). [redacted]. This is in addition to the high stream order (after Schumm, 1977) which is a positive factor for prime s*almonidae* spawning habitat in headwater cool, high-altitude, sandy-gravely substrate (Poff, 1997; Hendry and Cragg-Hine, 2000; Hendry *et al.,* 2004).

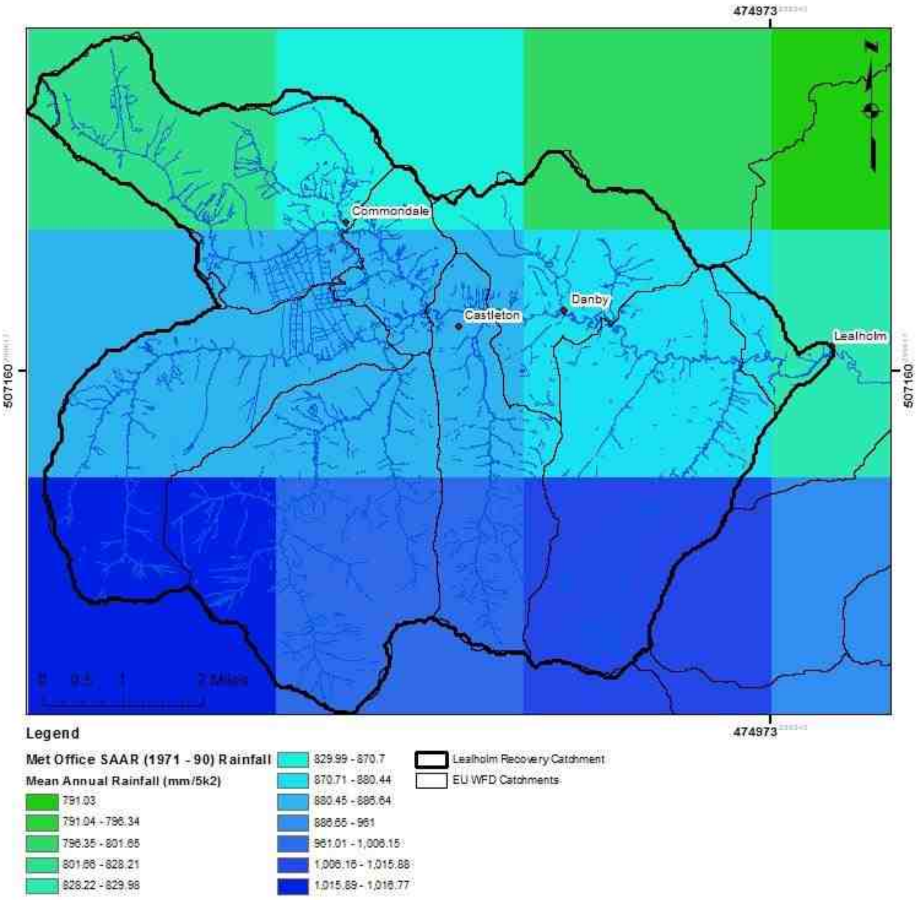
During the last two decades the catchment has been the focus of multi-agency restoration efforts with the objective of improving stream water quality. This includes the targeting of government agricultural–environment schemes (NYMNPA, 2013) such as the *Catchment Sensitive Farming Grant* (CSF)*, citizenship science (for instance Evans *et al.,* 2014), and most recently the establishment of a River Esk Pearl Mussel and Salmon Recovery Project (EPMSRP), a local vanguard of integrated scientists, stakeholders and service agencies with a full-time dedicated project officer (Rogers, 2006; Bracken and Oughton, 2013). The groundwork has established the "Yorkshire Esk Rivers Trust" (YERT) community-based initiative (Rogers, 2006; Carrithers *et al*., 2011, Bracken and Oughton, 2013).

**UK Natural Resource Management (NRM) expenditure on agri-environment schemes, principally the Catchment Sensitive Farming (CSF) capital grant is a tool in restoration (Newson, 2010). £110 million has been invested by Defra in their 'catchment based approach' (Defra, 2014).*

3.3.1 Catchment Hydrology

The mean discharge at Sleights is Q = 4.79 m^3 s^{-1} with highest Q_p being 944.83 m^3 s^{-1} on 6th November 1968 (CEH NRFA, 2014; map 4.3). ‘Flow is natural at the 95th percentile of flow’ (*bid*). The catchment has few minor abstractions most of which are ‘non-consumptive’, returning a high percentage of abstracted water to the hydrological cycle (Environment Agency, 2013; CEH NRFA, 2014).

The total consented abstraction rate is at 198,200 m^3 a^{-1} (map 3.5.1.), with discharge consent at 1,259,505.50 m^3 a^{-1} (Environment Agency, 2014A, map 3.5.4.). Abstraction is not assessed in Fowles *et al* (2010) or Bolland *et al* (2010) *M. margaritifera* reintroduction protocols, yet it reduces the wetted perimeter where it occurs in surface water and depletes base flow from riverine aquifers (Stubbington *et al.,* 2009, figure 2.3.) Discharge sources include Combined Sewer Overflow (CSO), Small Sewage Discharges (SSD), Sewage Treatment works (STW) and farm discharges (Environment Agency 2014). The catchment standard-period average annual rainfall (1961-1990) is 882 mm a^{-1} (CEH NRFA, 2014), with highest rainfall totals occurring on Baysdale and Stockdale Beck at c.1,100 mm per km^2 (see CEH NFRA for 1km^2 SAAR, map 3.2.). Based on these indicative water resource balance statistics the River Esk is a relatively discharge–rich catchment.



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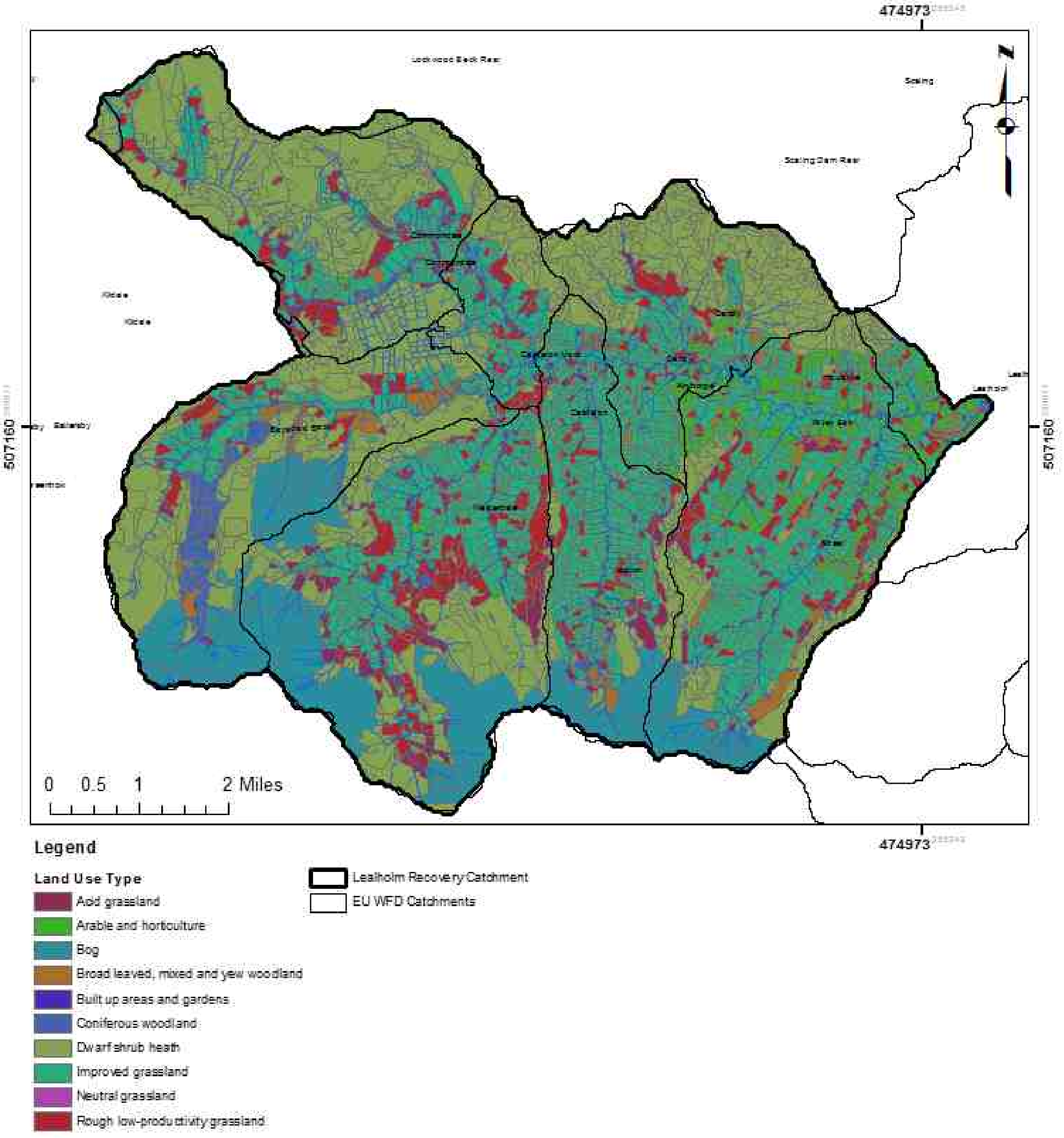
3.3.2 Catchment Geology

The River Esk geology is permeable with a Jurassic sandstone catchment (195 – 140 MYA) bedrock overlaid with middle Oolite and Middle Lias superficial drift cover (Allan *et al.,* 1997; CEH NRFA, 2014; map 3.5.5., 3.5.6.). The sedimentary bedrock is mainly undifferentiated Saltwick and Cloughton formation sandstone, siltstone and mudstone, being previously dominated by swamps and fluvio-deltaic forms (BGS, 2014). Superficial drift is confined to the valley bottoms; this mainly is Devensian (110,000 – 12,000 BP) glacio-fluvial till from Lake Eskdale (Evans, 2005; BGS, 2014; map 3.5.6.). The Egton basalt dyke intersects the headwaters, in addition to dormant minor faults that break the strata bedding sequence (*ibid*). Both superficial drift and bedrock are minor Secondary-A or lower class aquifers (Allan *et al.,* 1997; Environment Agency, 2013). The absence of principal (formerly major) grade strata which afford greater functional connectivity by flow provision is potentially at the detriment to ecological abundance of *M. margaritifera* (Danielopol, 1989; Allen and Vaughn 2010). Undisturbed groundwaters provide nutrient depleted cooler inflow vital to equilibrial maintenance of the epifaunal. This is particularly true of karstic aquifers (*ibid,* figure 2.2.).

3.3.3 A Brief History of an Anthropocene Riverscape

Anthropocene river, as used to describe the new age of ‘overwhelming effects’ by human impacts, is a neologism in river science (Wohl, 2011; Brown *et al.,* 2013; Lewin, 2013). Anthropocene influences on River Esk freshwater biodiversity rehabilitation by habitat monitoring through to reestablishment is profound (Bogan, 1993; Dudgeon *et al.,* 2006). The impetus to achieve pre-disturbed natural standards – ‘as first seen by Europeans’ – concurrent to agricultural intensification catering for population growth may be technically unfeasible (Diamond, 1987). The concept has fundamental ramifications for reintroduction habitat with low trophic status – the aim of this thesis (Wohl, 2011; Brown *et al.,* 2013, see section 2.2.1.). The proceeding history of the River Esk may present a chronological case for an Anthropocene river (Carrithers *et al.,* 2012).

From late Pleistocene (Devensian) de-glaciation (c.10,000 BC) with the draining torrents of Lake Eskdale, Kildale became the first settlement (c.8,500 BC) (Atherden & Simmons, 1989: 20; Muir, 1997: 27; Blaise Vyner & Land Use Consultants, 2000). Successive settlement around the parishes of Danby, Grosmont and Glaisdale then arose (Atherden and Simmons, 1989). Later infrastructure improvements brought by the 1865 Esk Valley railway and subsequent road networks catalysed transportation between population centres and farms (McDonnell, 1989: 133-9; Harrison & Roberts, 1989: 98). Accordingly, farming practices evolved, from predominantly cereal farming to dairy farming (*ibid*). During the twentieth century agriculture became the catchment mainstay. Moorland commons vegetation decreased from 49 to 35 per cent between 1853 and 1986, clearance accommodated hill sheep farming pasture (Hardin, 1968; Statham, 1989:201). Mechanisation altered the riverscape. Danby's 17th century watermill (NZ 70725, 08317) which was initially installed to grind corn now remains redundant. The mills weir, which has a high crest (>1m), and long acute angle downstream boulder face (>3m), without a provisioned fish pass, is a key longitudinal barrier to migratory fish. The impoundments sluice diverts high flow into the water wheel channel, meaning that during *salmonid* runs there is insufficient flow over the structure to aid jump, creating an obstacle (Hendry and Cragg-Hine, 2003). This is in addition to 16 other barriers through the drainage network (map 3.4.). The impediment to *salmonidae* upstream migration and subsequent redd nesting is at the detriment to mollusc abundance, since the salmon seeks the unreachable headwaters stranding the *M. margaritifera* symbiont (Zuiganov, 1994; Skinner *et al*, 2003).



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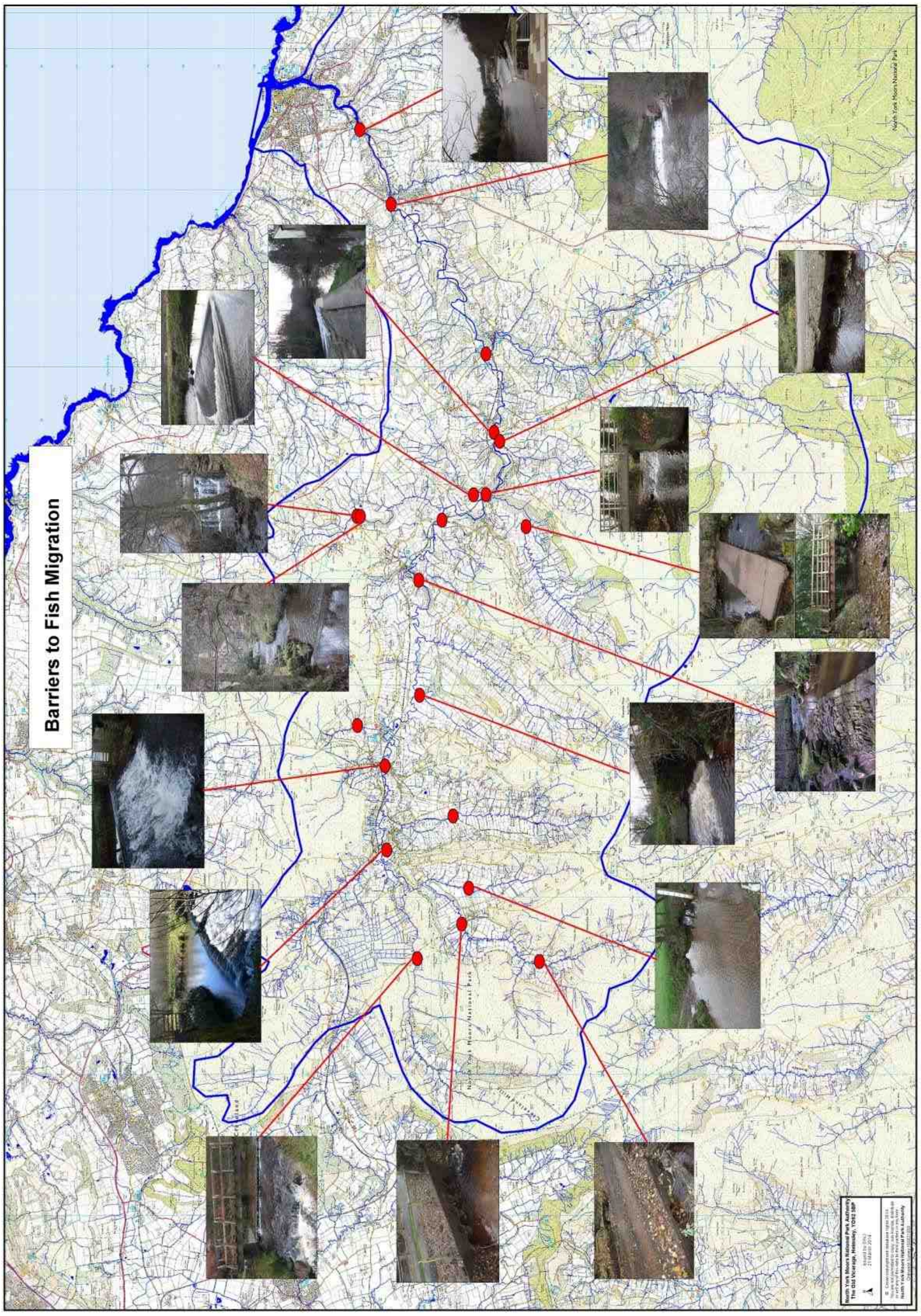
Virtually all land in Eskdale is now agricultural, respectively composed of 47 percent upland heath, bog and moorland (grazed), 32 percent improved grassland, 10 percent woodland, 8 percent arable and horticultural pasture and 0.3 percent urban (CEH NRFA, 2014, map 3.3.). The latest round of EU WFD assessment (2009) revealed that only 3 surface water bodies (17%) were classified as 'good' ecological status, 11 as moderate and 3 as poor and 2 heavily modified and artificial (Environment Agency, 2009, 2011). The same is predicted for first cycle submission to the European Commission in 2015 (*ibid*). 'High' ecological status is needed for *M. margaritifera:* the status carries physicochemical standards the same or similar to mollusc TV (Oliver, 2000; Clausen *et al.,* 2006; Solimini *et al.,* 2006; Birk *et al.*, 2012, see table 2.1.).



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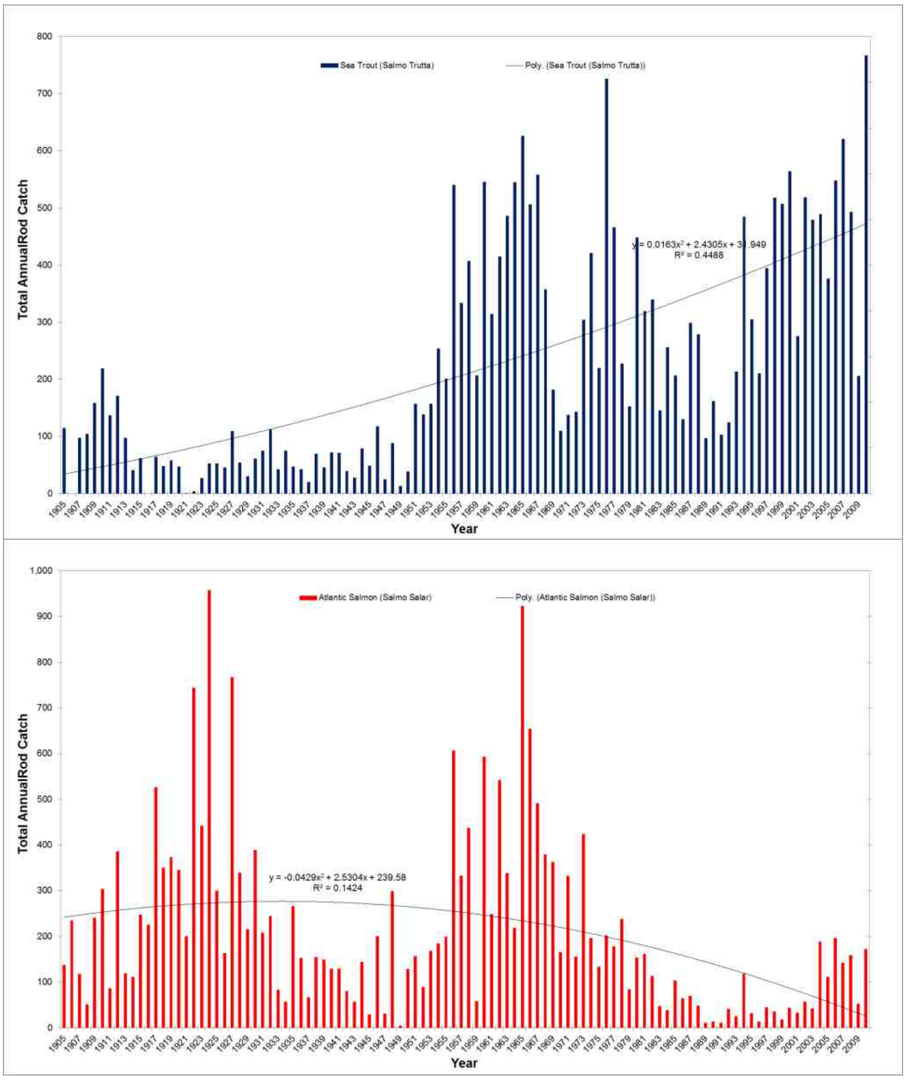
3.3.4 *M. margaritifera* and *Salmonidae* Metapopulation Dynamics

M. margaritifera consensuses on the River Esk provide variable total counts of specimens. The viability, rehabilitation and lifecycle completion of *Margaritiferidae* stocks through to adulthood requires sustainable numbers of salmonid hosts for glochidia infection (Zuiganov, 1994; Geist, 2005, figure 2.5 and 3.1.). This applies equally to hatchery-reintroduced specimens (*ibid*). Bauer (1991) suggests a minimum density of > 0.2 fish m^2 above mussel beds, Zuiganov (1994) and Fowles *et al.* (2010) suggests > $1m^2$, yet none of these studies are based on statistical regression for encystment success (Skinner *et al.,* 2003:8). Atlantic salmon and sea trout rod catch data show a recent population recovery through the River Esk, though Atlantic salmon is greatly reduced in comparison to its 1900's population (figure 3.1 – 3.2). When intensively examining the reach-scale for reintroduction, the determination of host salmonid density is critical. A reduction in total stock correlates with a density reduction above mussel beds, reducing the life-cycle chances of both symbiotic species (Strayer, 2008, figure 3.1 – 3.3.).



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Since *Salmonidae* carry *M. margaritifera* glochidia, sustainable fish numbers are a long-term factor in the population status of unioniods (Zuiganov *et al*., 1994; Strayer, 2008; figure 3.3.). The most recent *M. margaritifera* survey in August 2012 reported a frequency count of 727 adults, with a further indicative population estimate of 1,000 to 1,500 specimens (Bracken and Oughton, 2012; Hirst, 2012). This is the highest count recorded. Past surveys respectively recorded adult frequency at 114 mussels in 1999 and 323 in June 2007 (Oliver and Killeen 1996; Killeen, 1999, 2006; Bolland *et al.*, 2010:700). This may reflect an increase in *Salmo Trutta* numbers, the preferential host of Esk *M. margaritifera* (Lavictoire and Sweeting, 2012; 2012A, 2012B).

Malacologists survey using the standard methodology of ECS (Evaluated Corridor Sections) and SERCON (System for Evaluating Rivers for CONservation) for replicable mollusc frequency counts (Young *et al.*, 2003). Despite this, the physical inaccessibility of some waters and extensive drainage area to surveyor ratio prevents a full species count (Boon, 2000). The recent discovery of 40,000 molluscs in Leningrad oblast (Russia) (Ostrovsky and Popov, 2011), in addition to anecdotal evidence *M. margaritifera* beds in streams not known to monitoring authorities, reflects the absence of full spatial monitoring (Underwood, 1994; Oliver, 2000; Young, 2003).

Prima facie, census totals should not be taken as a primary indicator of population health, fecundity or viability (Young *et al*., 2003). The current population viability remains endangered, with previous surveys recording no juveniles (2007), or few smaller specimens (2012) (Bracken and Oughton, 2012; Hirst, 2012). No specimens have been recorded at less than 30 years of age (*ibid*). Accordingly, the River Esk has been denoted a "non-functional" population (see Geist, 2005), with inference of 'adequate recruitment being indicated by 20% of the population being less than 20 years old' (Hastie *et al,* 2001; Skinner *et al*, 2003:6 citing Young *et al.,* 2001). The current population is not recruiting to adulthood or self-sustaining. Thus, with the passage of time and no intervention, the population will become extinct as aged mussels successively die or are imperilled through disturbance. The role of the FBA hatchery facility in re-introducing sufficient numbers of juveniles is therefore critical – the 'last minute rescue tool' (Bolland *et al.,* 2010; Gum *et al.,* 2011).

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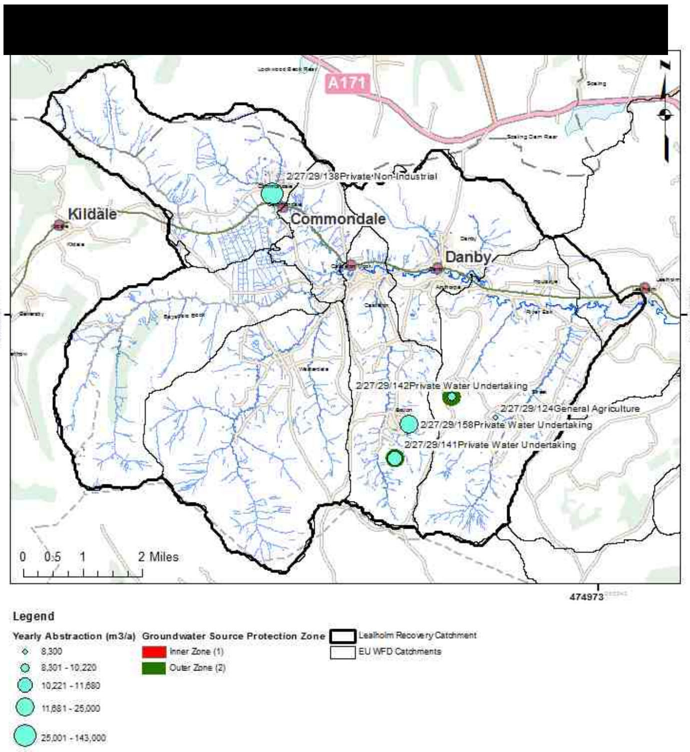

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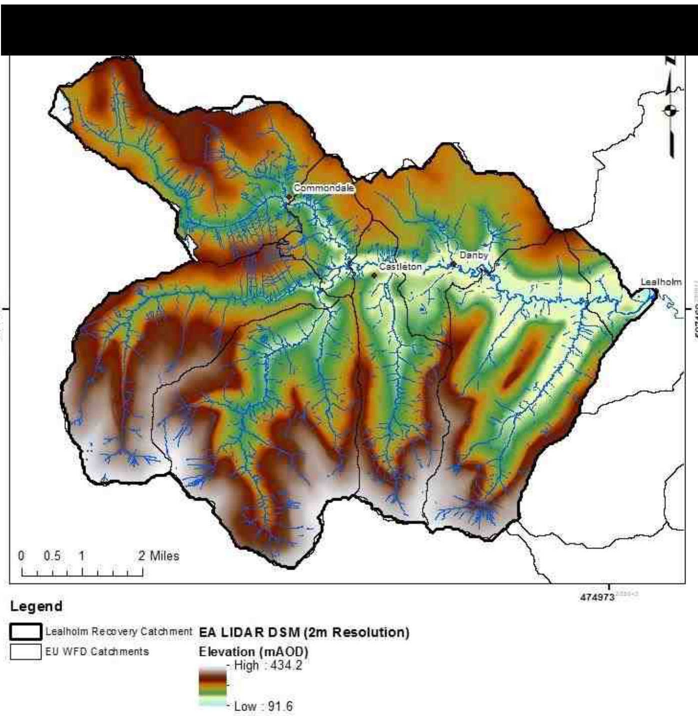

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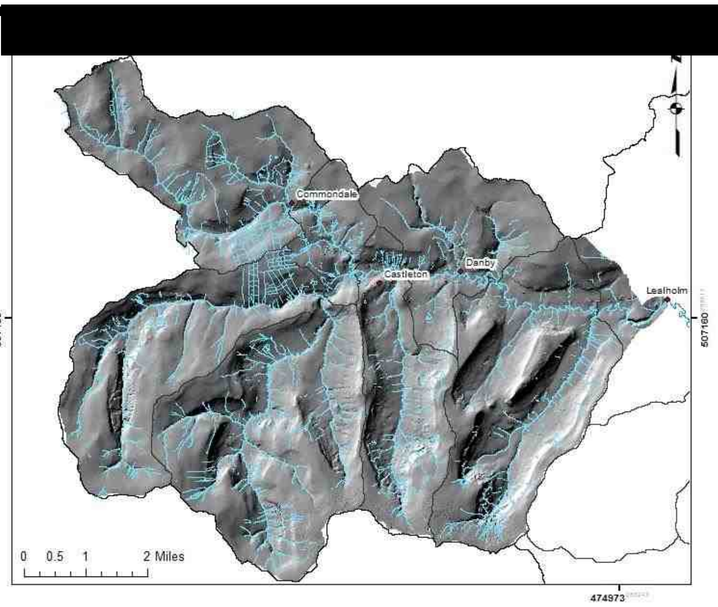

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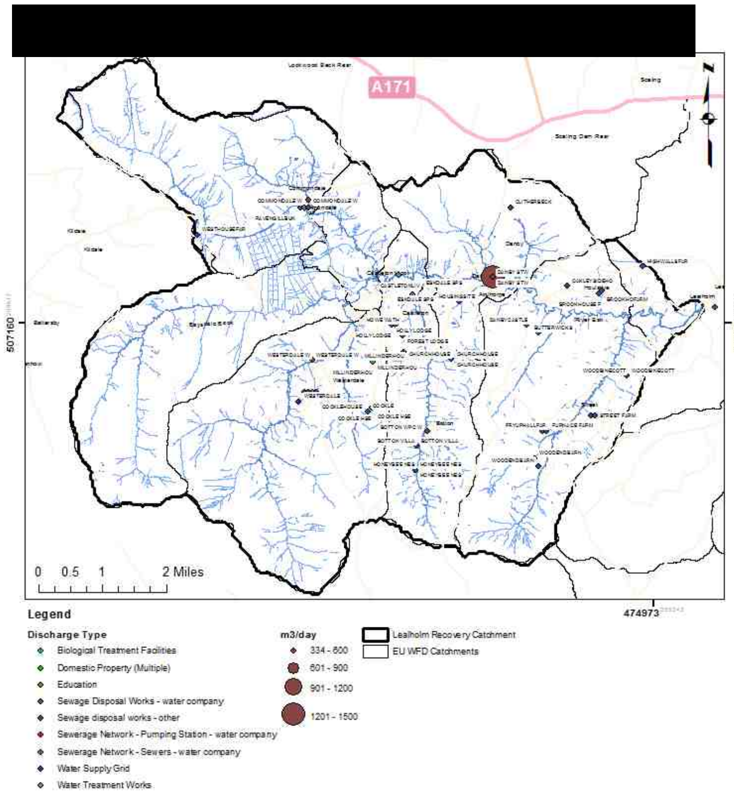

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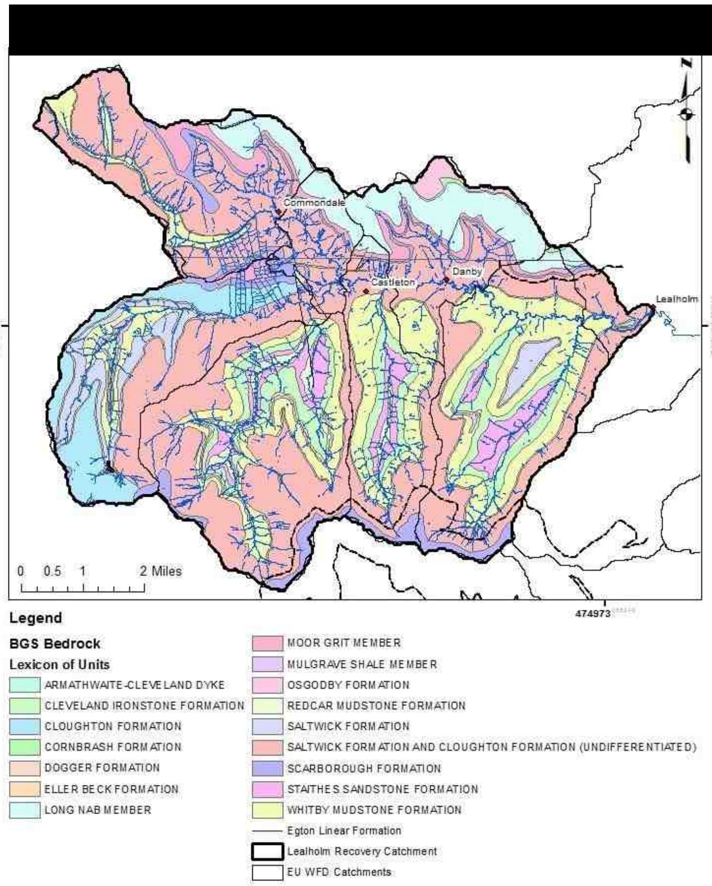

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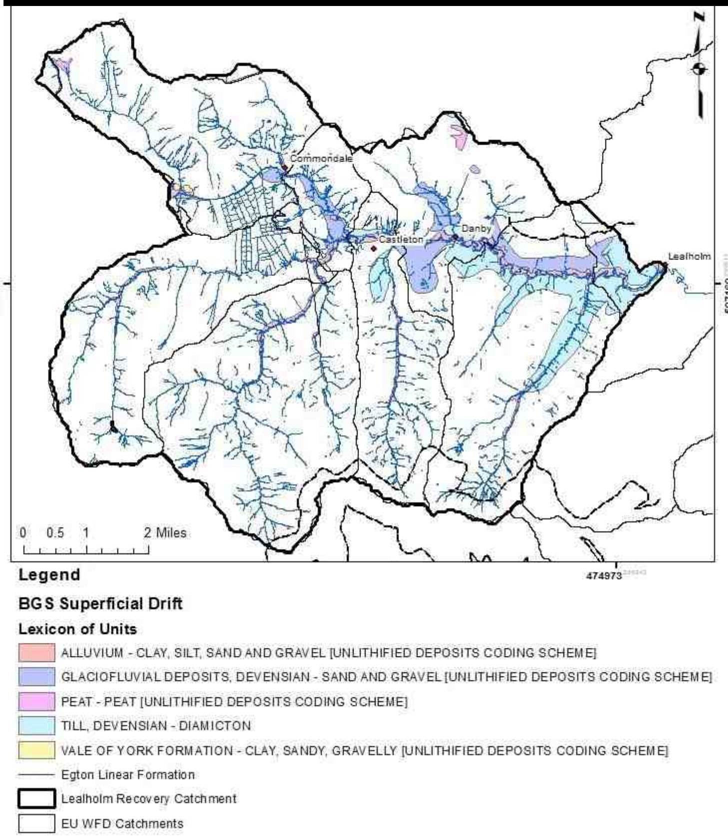

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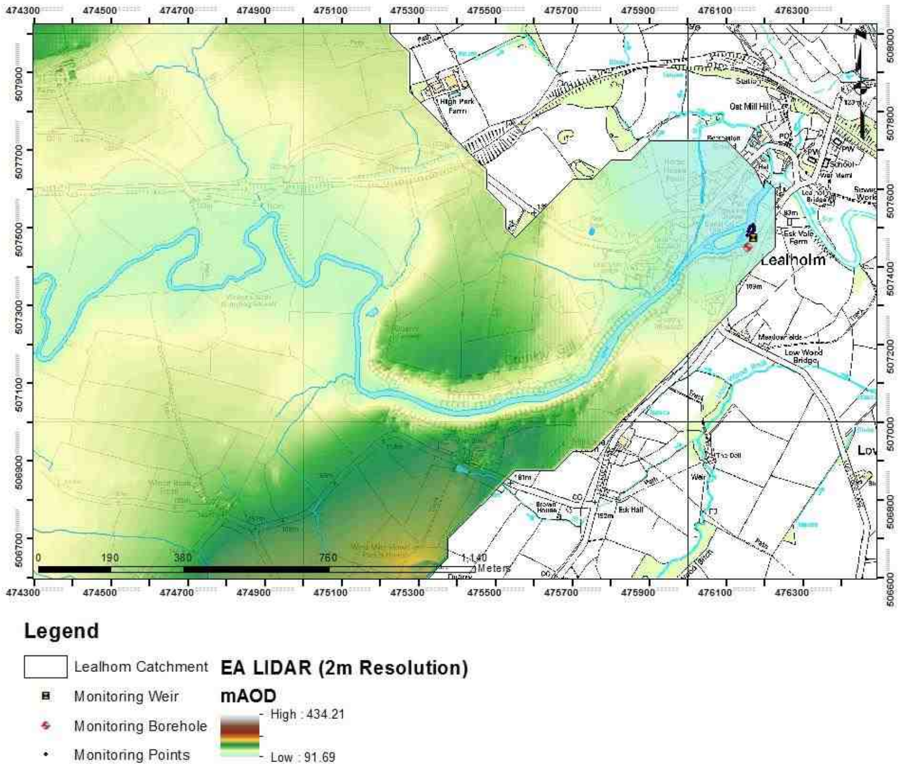
When mussels are ready for reintroduction, identification of hyporheic exchange stoichiometry and the water quality heterogeneity this creates at the reach-scale is fundamental. In relation to this heterogeneity, the rationale for the three intensive field sites will be outlined in turn:

(i) Lealholm, Crunkly Gill,
(ii) Danby, Sewage Treatment Works,
(iii) Danby, Moors Centre.

3.4 Lealholm – Crunkly Gill

Lealholm's Crunkly Gill is the most densely populated *Margaritiferidae* site through the River Esk and accordingly the preferred re-introduction location (Oliver and Killeen 1996; Killeen, 1999, 2006; Hirst *et al*., 2012, map 3.6. and 3.6.1). This reach monitoring impetus derives from environmental protection legislation for *M. margaritifera* (section 2.7, *et alibi*), which is currently an 'institutional void' in present day practice – an absence of 'clear rules' or 'norms' in the conduction of policy between institutions (Hajer, 2003:175; Bolland *et al.,* 2010: 699). Surveillance and monitoring under chapter 4 of the conservation of habitats and species regulations (2010) requires monitoring that is *ad hoc* to EU HD Annex listed *M. margaritifera* (Great Britain, 2010). In response, the Environment Agency has installed a multi-parameter SONDE continuously logging Ammonium (NH_4^+), Dissolved Oxygen (mg O^2 L^{-1}), pH and some of the *M. margaritifera* TV parameters (Hirst, 2012, NYMNPA, 2013).

The dimensions of HEF are neglected at this location, meaning that HFP nutrient buffering remains poorly constrained or quantified for juveniles (section 2.5.). Biddulph's (2012) spot monitoring derived a respective arithmetic mean nitrate-N (N-NO_3^-) at 0.52 mg N L^{-1} and 0.80 mg N L^{-1} in HZ and SW. Both values exceed Moorken's (2000) lower TV (table 2.1.). Crunkly Gill's braided channel has diversity of key pool-riffle forms (map 3.7.2., 3.7.1), large Devensian boulders – generating subsurface flow and lee-side refugia – and a valley-scale HFP where the valley alters from unconstrained to constrained (Schumm 1981, 1985, map 3.6. and figure 1.1(a)). Structural and functional connectivity theory suggests that valley-scale HFP contributes significant groundwater discharge through the bed, this is likely to be enhanced by the accumulation of high bulk-transmissivity Devensian till (Allen *et al*., 1997; Fleckenstein *et al.,* 2008; Ibrahim *et al.,* 2010; Wainwright *et al.,* 2011, map 3.5.6., 3.7.3.). Due to the presented array of geomorphological forms that generate HEF, this location was considered a prime candidate for further in-depth monitoring.



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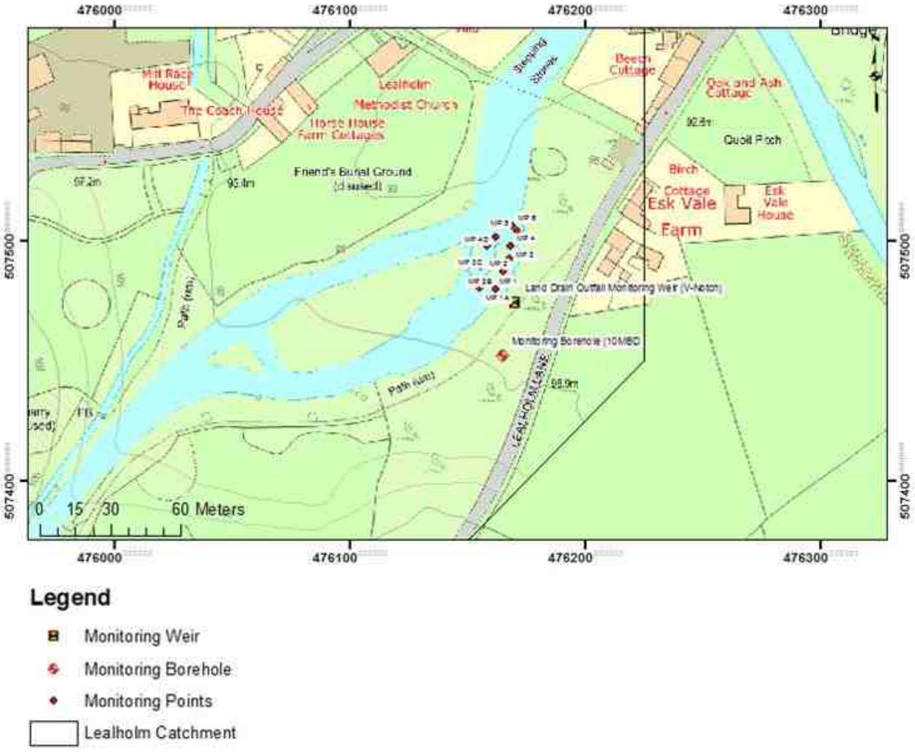

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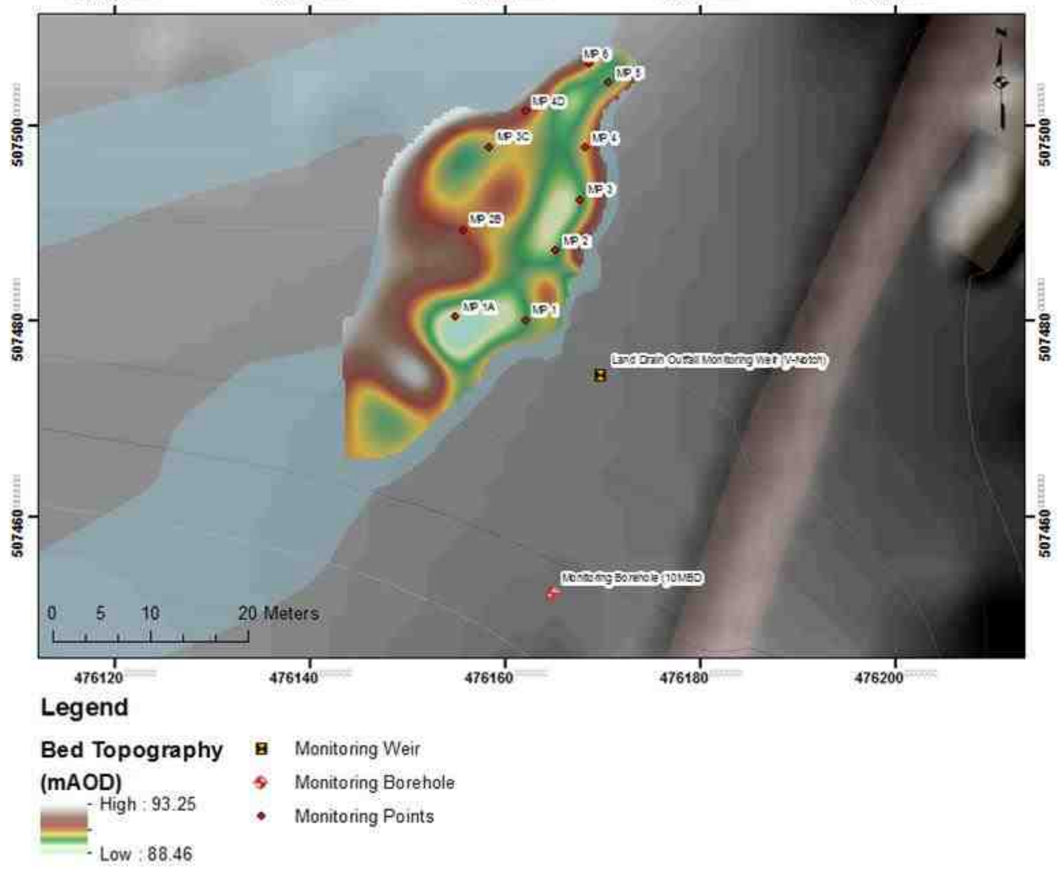

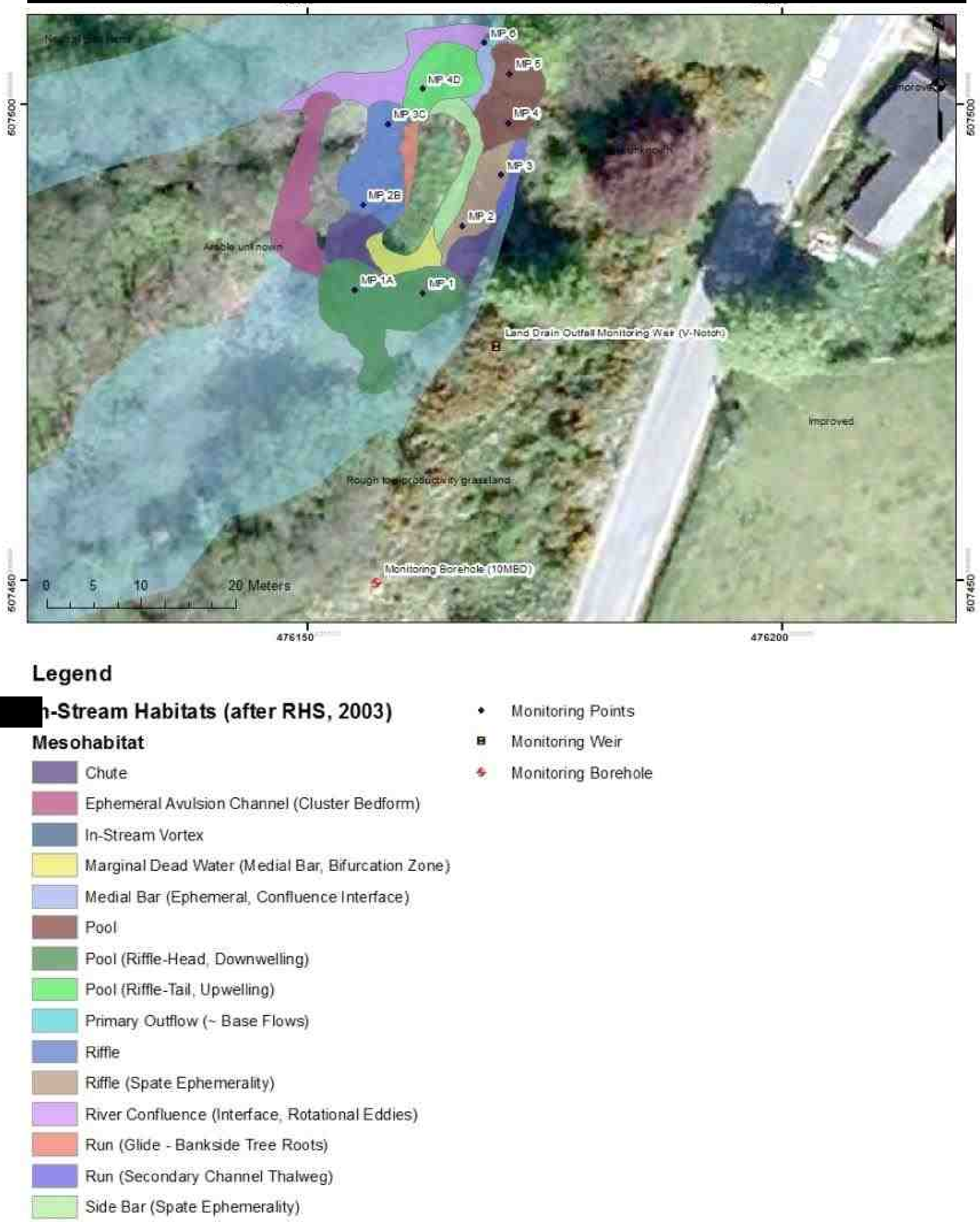

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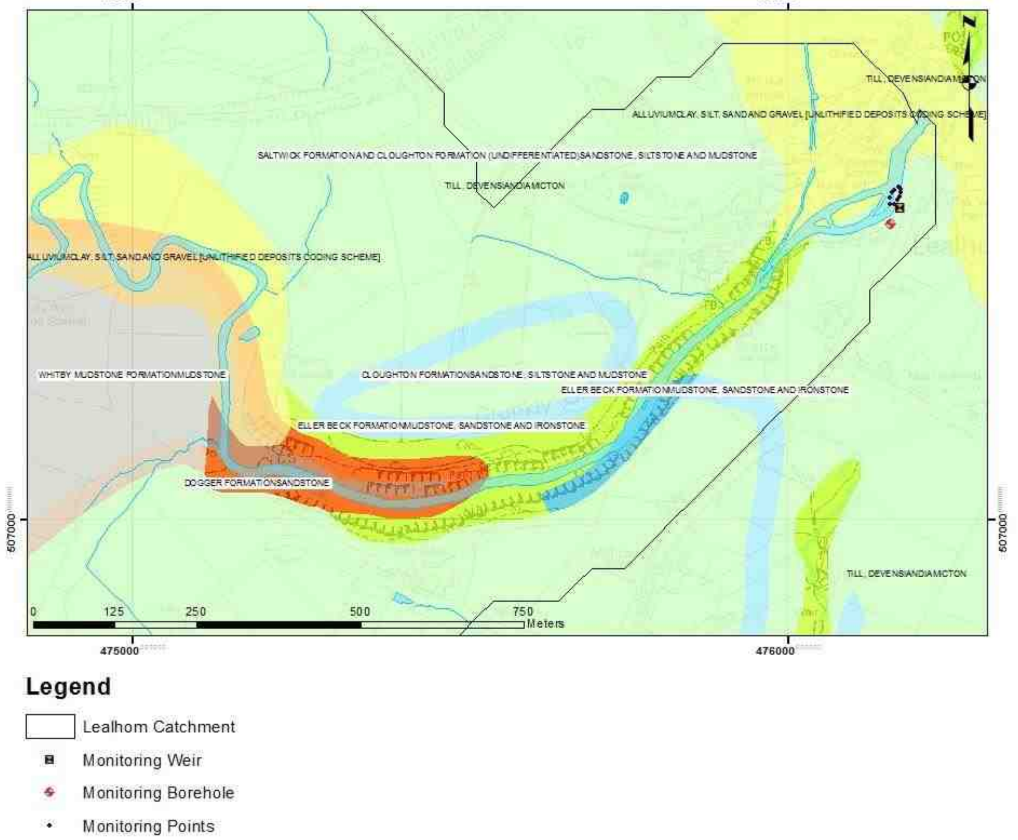

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3.5 Danby – Sewage Treatment Works

Under reintroduction guidance for *M. margaritifera* (Fowles *et al.,* 2010), it is not feasible for specimens to be trans-located from hatchery to a sewage treatment works (STW) outfall reach. Yet previous investigations from Balmford (2011), Biddulph (2012) and Perks (2013) did not quantify the strategic significance of point source wastewater pollutants or their sources (Jarvie *et al.,* 2006, 2013; Neal *et al.,* 2010), despite the fatality that ortho-P and other effluents cause to *Margaritiferidae* (Buddensiek, 1994). Point-source pollution therefore represents a knowledge void in the River Esk water quality literature.

Serving a population equivalent of 932 persons, the highest in the recovery catchment (Environment Agency, 2014A), Danby STW was considered a key site to investigate (maps 3.8.). Establishing the longitudinal fate or "sag" of pollutants from outfall is critical as a few sporadic and remnant *M. margaritifera* exist downstream of the STW (Bauer, 1988; Moorkens, 2000). The bed-substratum at the location is prime *M. margaritifera* boulder-stabilised sand habitat (Geist and Auerswald, 2007). However, the Saltwick sandstone formation has the highest leachate category (GWWPP H1 – see glossary) and low ion exchange capacity for buffering pollutants (Alloway and Ayres 1994:37).

Danby STW has consented discharge at 240 and 1,447 $m^3 d^{-1}$, for 'dry-flow' (Q_p < 1 in 6) and 'storm-flow' conditions, respectively (London Gazette, 2005:9852; Environment Agency, 2014A). Undiluted discharge of Ammonia-N ($N\text{-}NH_3$) on 23rd April 2012 was recorded at 1.6 mg N L^{-1} and BOD (5 day ATU) at 85 mg L^{-1}, the latter breaching the EA consent and both breaching *M. margaritifera* TV (see table 2.1, *ibid*). These pollution concentrations are detrimental to most forms of aquatic life and human drinking water standards (Chapman and Kimstach, 1996, EC Drinking Water Directive (80/788)).

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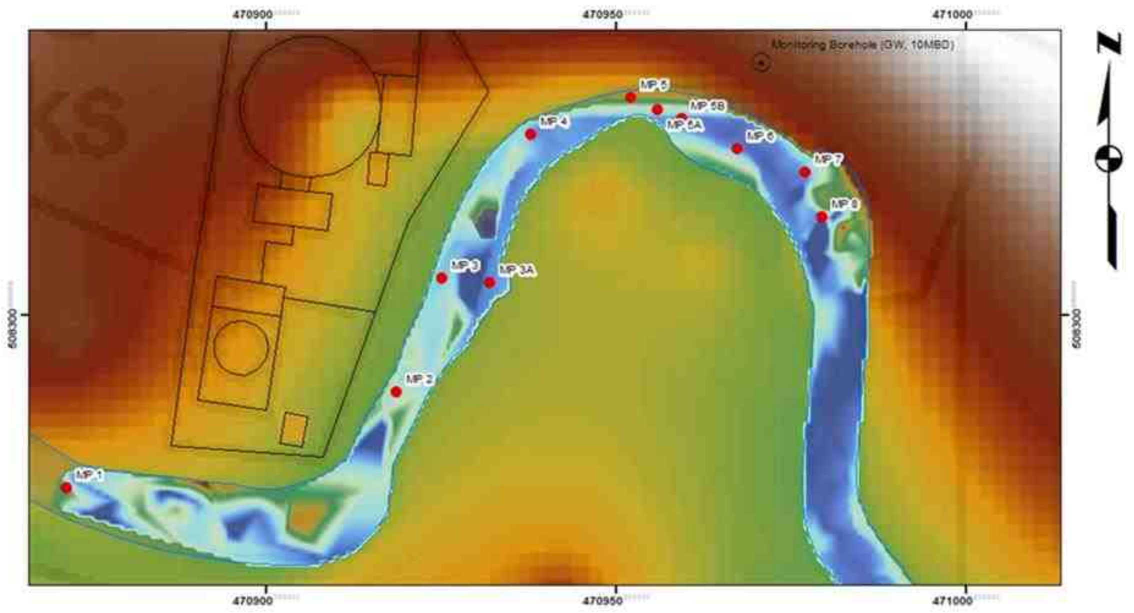

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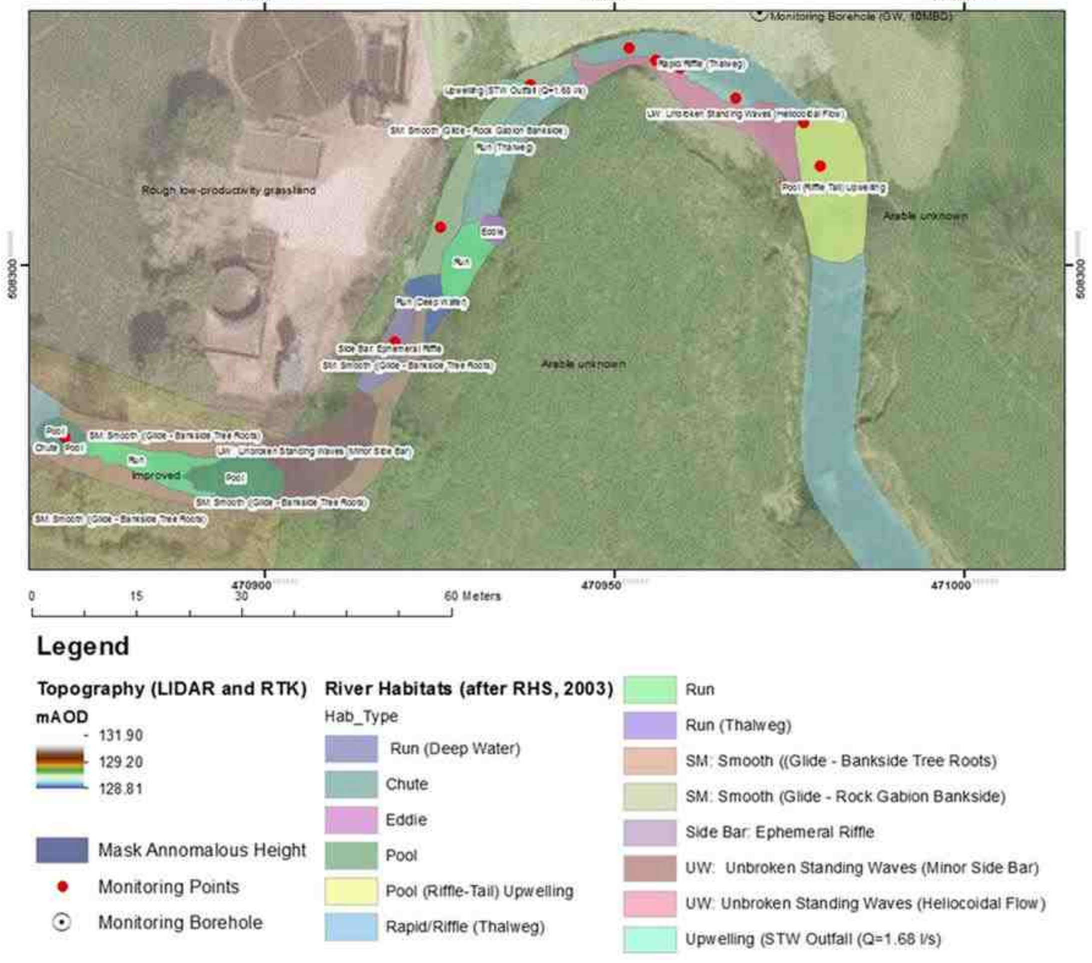

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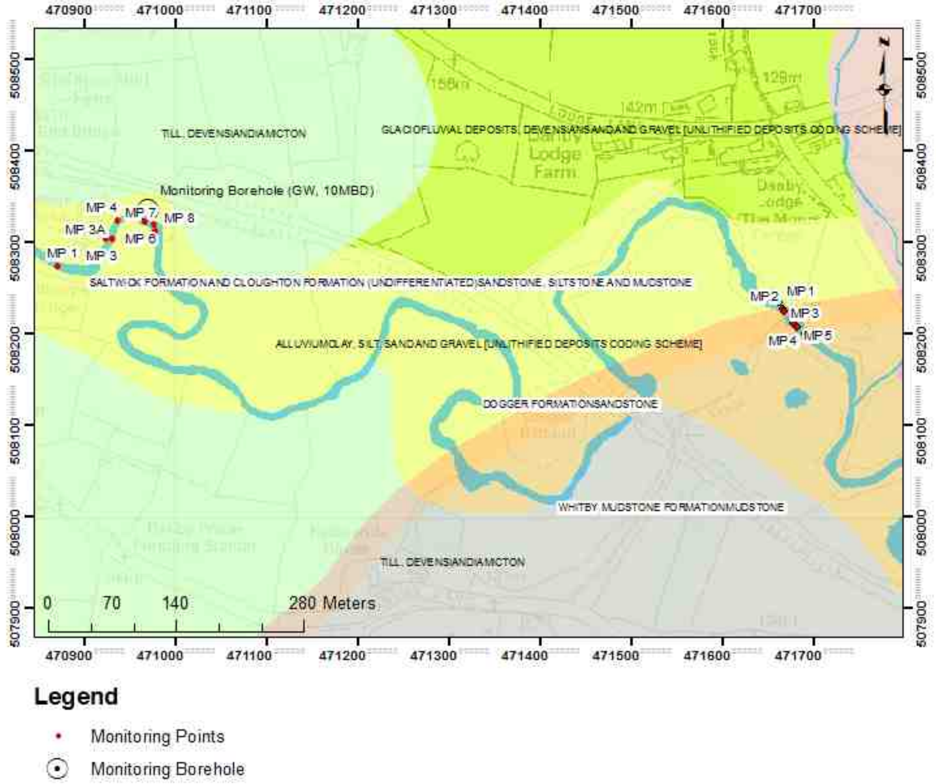

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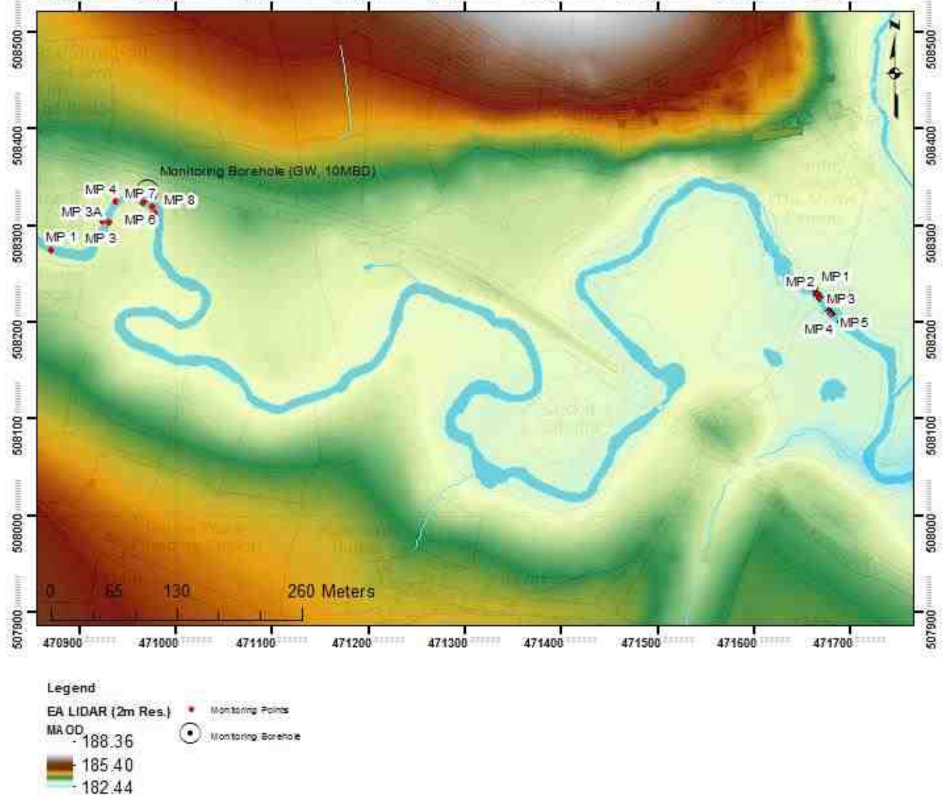

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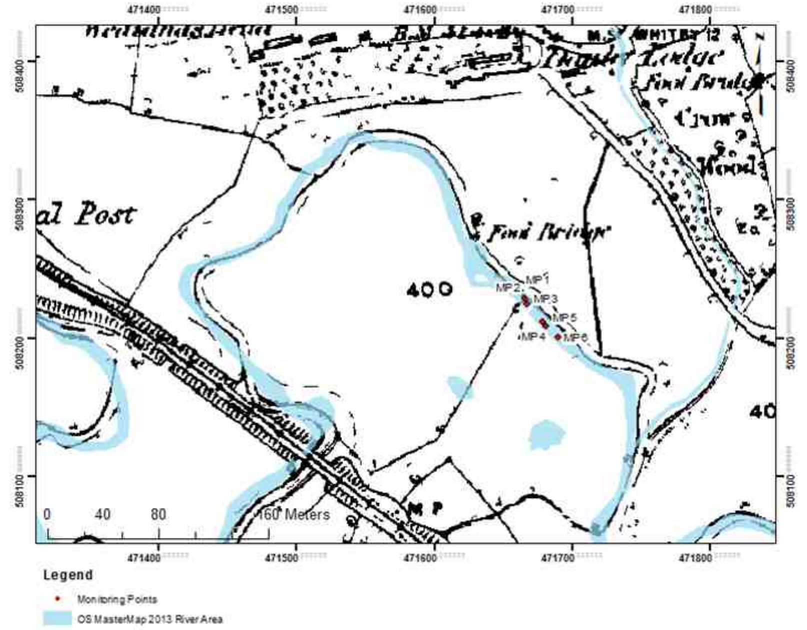
3.6 Danby – Moors Centre

This site was selected because it is located 650m downstream from the STW (maps 3.8.2., 3.8.4.), experiences longitudinal pollution affects, but also has a vertically pronounced pool-riffle sequences (map 4.1), with a c.60 year old *M. margaritifera* existing on a riffle-tail (Killeen, 2006; Hirst, 2012).

Danby Moors Centre site is the upstream extent of the remnant *M. margaritifera* population (*ibid,* maps 4.0). It is surrounded by high-input nutrient improved pasture (NERC (CEH), 2011, see section 2.2.1. for HZ effect, map 4.2). The recent fencing-off of the watercourse has prevented further extensive cattle poaching (Environment Agency, 2009, 2011; Hirst *et al., 2013*). Poaching generates fine sediment through riparian erosion, that 'entombs [salmonid] embryos preventing their natural escape from the gravel', impacting post-parasitic glochidia in the same way (Young, 1984; Zimmermann and Lapointe, 2005; Buss *et al*, 2009:128; Reid *et al*., 2012).

The reach is a now recovering (Environment Agency, 2009; 2014A), but a long history of river training is anticipated to have 'legacy effects' on HEF and therefore the survival of *M. margaritifera* (Soulsby *et al.,* 2001). The main channel has a new course after being re-trained during the construction of the 1865 River Esk railway (see map 3.9.1, McDonnell, 1989:133-9; Harrison & Roberts, 1989:98). The present day channel plan-form is now entrenched and compound (Schumm, 1985). The lateral geomorphic constraint is hypothesised to drive greater stream-wise vertical exchange flow through bedforms, making it a key location to test hydromorphic-hyporheos interaction (Smith, 2005; Bus *et al.,* 2009).Finally, a redundant hyporheic well from Biddulph's (2012) monitoring remains at monitoring point 5 (map 4.1). This enables the re-establishment of a past record, vital to the quantification of longer term *M. margaritifera* pollution stress.



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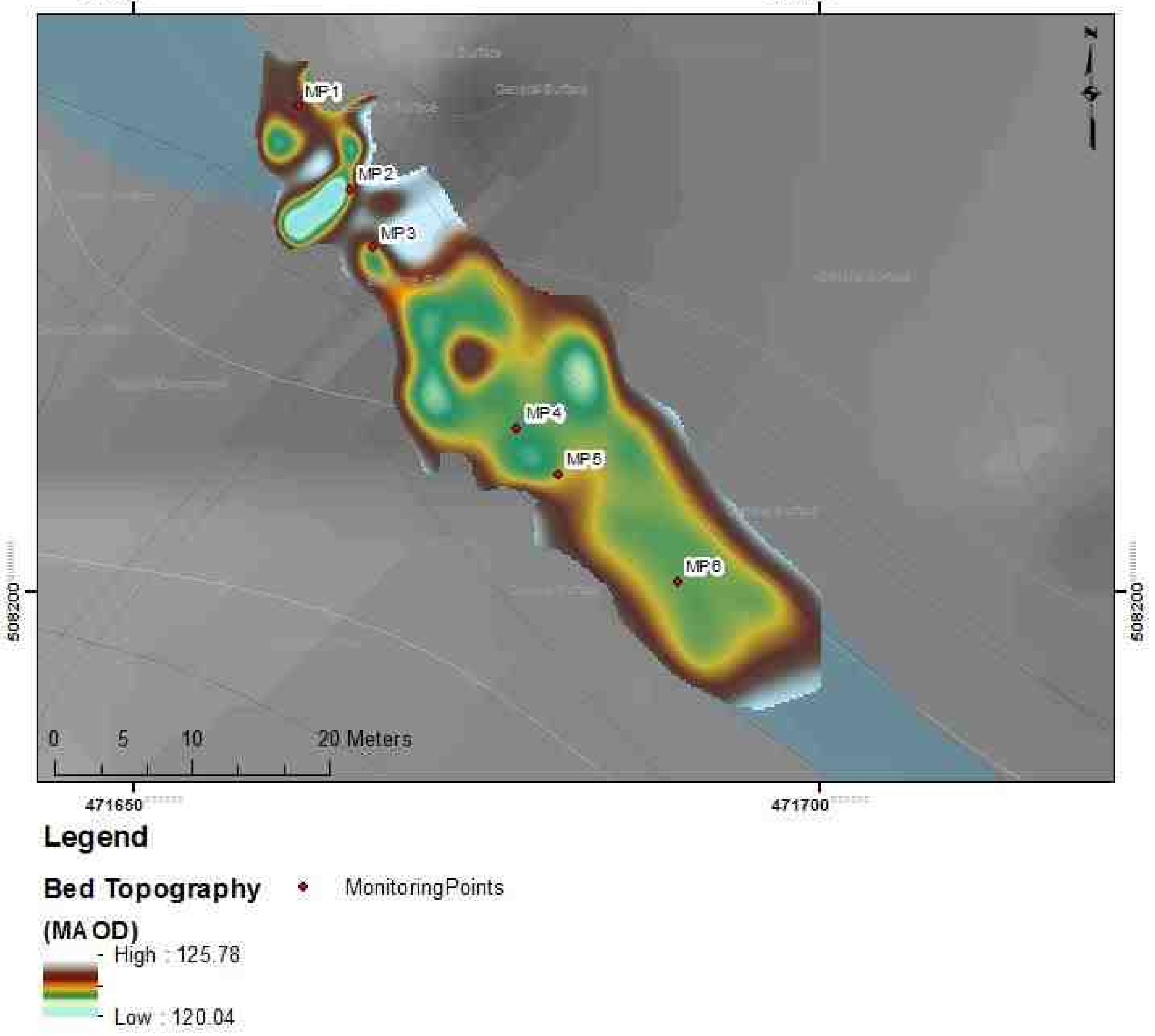

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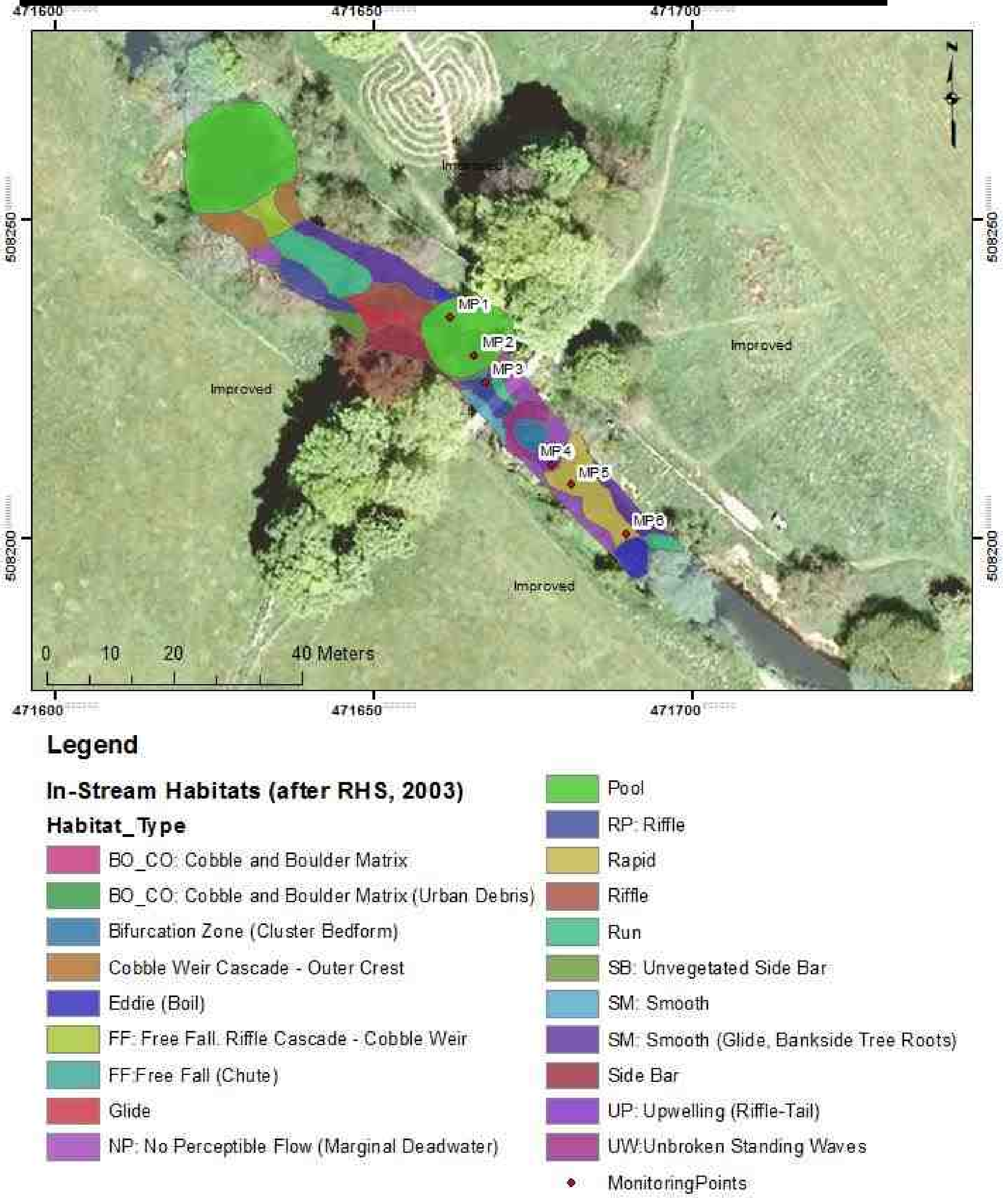

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3.7 Summary

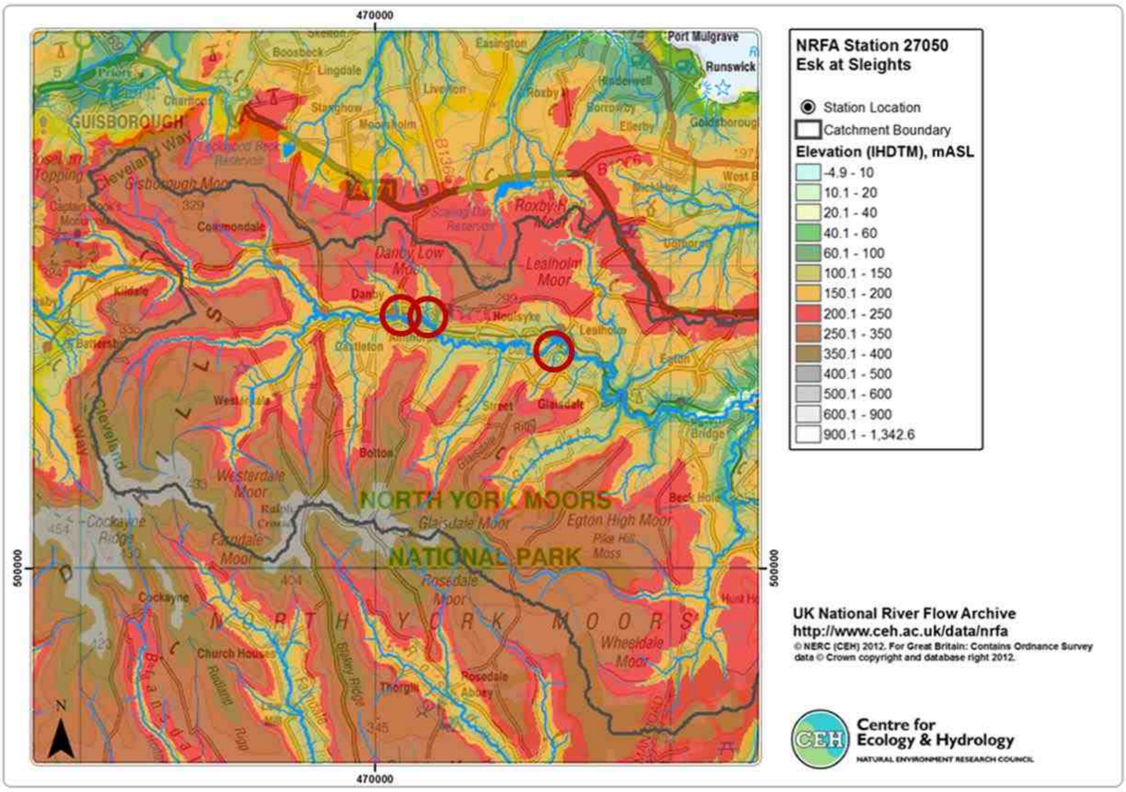
These sites along the River Esk were chosen to gain a representative sample of:

(i) The overall influence of vegetative hydroecology on hyporheic chemistry, Lealholm, Crunkly Gill.

(ii) The degradation from STW outfalls on hyporheic ecology and habitat chemistry, Danby, STW, and

(iii) The impact of intensive pastoral agriculture on biotic nutrient concentration, Danby, Moors Centre.

Through the detailed site investigations at all three locations, it was expected that land-use effects on hyporheic chemistry could be better quantified and understood, in order that environmental enforcement and rehabilitation could be targeted using an evidence-based approach (Pullin and Knight, 2003; Roni and Beechie, 2012; map 4.3.). More salient, by observing, mapping and detailing stream-unit habitats in these different eco-hydromorphology settings, the key physicochemical attributes of different biotopes were identified for reintroduction (Hastie *et al.,* 2003; Emery *et al.*, 2003). By assessing catchment activities first, then downscaling to the reach-scale, it was hoped the 3 different sites could formulate a benchmark for cross-referencing to different sites for reintroduction, whilst providing information on activities that degrade habitat.



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Chapter 4 Methodology

4.1 Introduction

> *Ecological processes are better studied in smaller and simpler units*
>
> Danielopol (1989:21)

Given the hydrochemical anisotropy of the hyporheic waters and the complexity of their interaction with stream and ground waters which are isotropic, a reach-scale approach has been adopted to allow a significant level of detail to be investigated (e.g. Allen and Vaughn, 2010). This would be technically infeasible to investigate on a single case catchment basis, an approach adopted by Balmford (2011) and Biddulph (2012) (Richards, 1990, 1996; Harvey and Wagner, 2000:6).

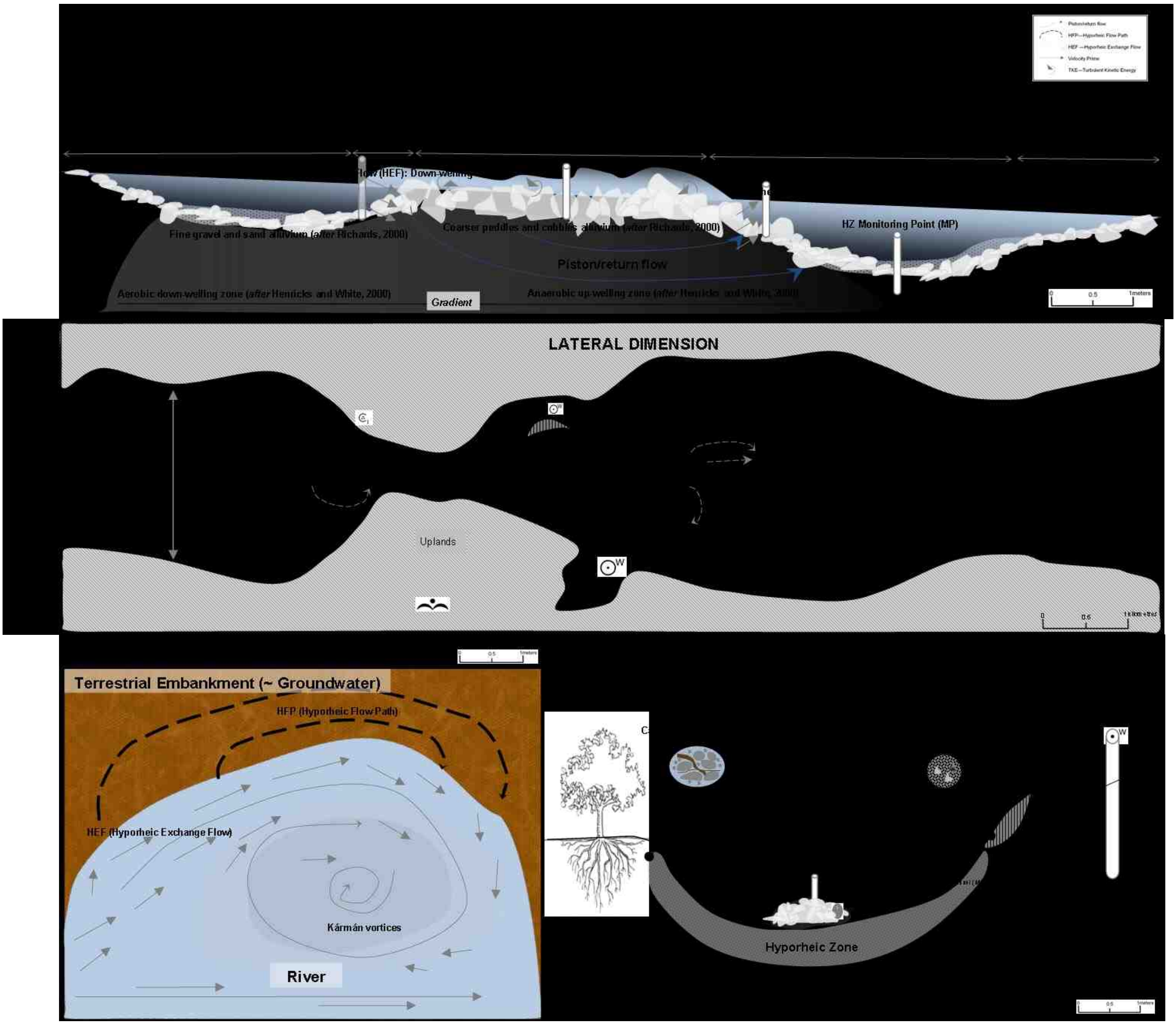
Quantitative method is central to the sampling strategy and aims to give characteristic attributes to hydrodynamic processes and chemical forms (Richards, 1996). This thesis uses water quality sampling methods supported with hydrometric data to explore the stream unit effects on hydrochemistry in hyporheic zone, groundwater and surface waters. Field methods are logically assessed first; then laboratory methods used to analyse samples are documented. The physical metrics of structure, time and space (*cf*. place) serve as the dependent variables and ‘window’ in which to assess form, pattern and process (Davis, 1899; João, 2000). The sample spatial distribution is described first, then temporal sampling after, the choice of field apparatus for collecting data will be scrutinised towards the chapter end.

4.2 Research Design – Quantifying Process in the Hyporheic Zone

4.2.1 Spatial Sampling Strategy

Given that stream units within reach-scale systems are related to geomorphological mechanisms which drive the momentum of flow, exchange with mediums and the physically properties of water that reach organisms, a robust sampling design must separate causal processes (e.g. Amoros *et al*., 1996). Schumm (1988) argues that all fluvial systems are ‘process-response’ systems in which physical form is the template for process operation.
As such, Thom’s (2006, 2008) aforementioned landscape RES, scalable to mesohabitats and hydraulic biotopes, provides the framework in which the investigator sees the reach-units through the ‘lens’ of demarcation criteria (Richards, 1996, section 2.7.1.). Through this ‘lens’, each unit has its own nested internal consistency and functional connectivity with other units (Poff, 1997; Wainwright *et al*., 2011). The criterion of demarcation support the

underlying patch dynamic concept, 'filters' and 'passes' (*after* Pringle *et al*., 1988; Poff, 1997, see section 2.5.). As Richards (1996:196) notes, the 'criteria for acceptance of a theory are not based on its predictive success, but on explanatory power'. Iterative observation through different sampling conditions leads to holistic explanation which avoids the empirical approach hypothesis testing and its pursuit of falsification (Richards, 1990). Mechanistic explanation is vital to *M. margaritifera* biotope zoology, through generating iterative understanding the avoidance of conjecture in the reintroduction of an IUCN red list species can be achieved (IUCN, 1991; 1998; Sutherland *et al.,* 2004). Under the RES and stream unit framework (*vide supra*) boreholes were installed in riparian seeps, and basal adjoining hillslopes, with in-stream and hyporheic monitoring points installed units noted for the HEF potential. Figure 4.1 shows the site specificity of monitoring points and the source waters they seek to quantify.



4.2.2 Riverbed Topographic Survey

A detailed hydrographic survey was conducted in order to help physically delineate stream units, particularly pool-riffle forms, which are readily detectable by bed elevation changes (Wadeson, 1994; Richards, 2000; see section 2.5.1). Surveying detects the geometry of the bed, its undulation, convexities and concavities which are synonymous properties of units undiscernible to the naked eye (*ibid*). It is therefore the baseline to siting of monitoring apparatus.

The RTK (Real Time Kinematic) survey was conducted with a base station and rover unit. RTK-GPS surveying yields high-resolution data, the ranging staff operates below the wetted perimeter upto a depth of approximately 1 metre. The rovers mobility is indispensable to surveying the riverine environment (Rizos and Han, 2003). Accuracy was ensured by installing the base station on a pre-defined Ordnance Survey spot height (OS Mastermap, 2003); raw data difference was offset by any residual height (ODN (Ordnance Datum Newlyn)), latitude and longitude (OSGB 36) difference from the cardinal base station records z, x and y. All spot heights were inspected against EA LIDAR DSM (LIght Detecting And Ranging, Digital Surface Model) and OS Land-Form PROFILE DTM (2013) coordinate-labelled rasters. The data showed an excellent level of agreement, even after raster subtraction. Set positional error (e_{pos}) had a variance threshold of (σ^2) of 5%, with real-time values over that disregarded. Positional coordinate corrections ($\Delta\tilde{x}$) were active during the survey. At Lealholm Crunkly Gill, a total of 181 raw dGPS were collected over an area of 702.15m^2, giving a surface density of 1 point per 3.88m^2. At Danby STW 963 points were collected over an area of 3,288.22m^2, giving a surface density of 1 point per 3.42m^2. At Danby MC 224 points were collected over an area of 557.11m^2, giving a density of 1 point per 2.28m^2.

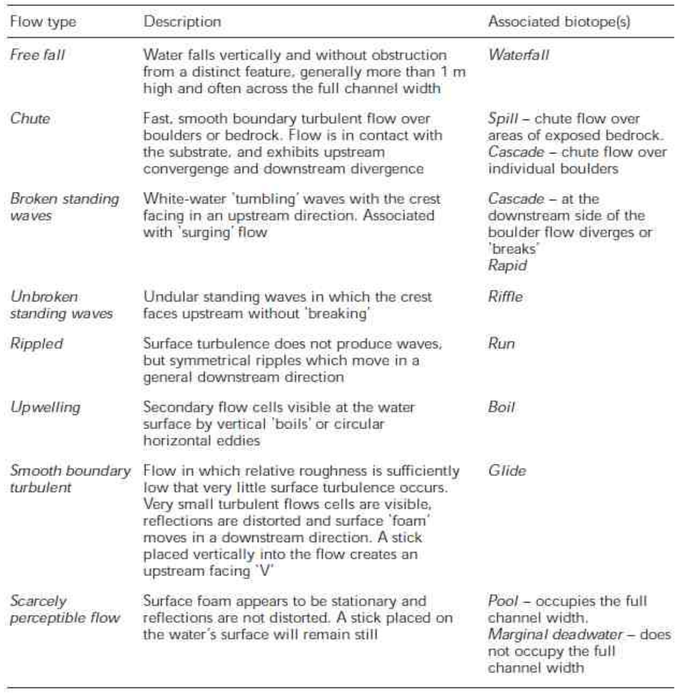
A higher level of precision could be achieved by validating the survey data against the OS RINEX network (OS RINEX, 2014). However, the 45-day restrictive covenant, whilst laboratory analysis was underway, negated validation by this method (*ibid*). Appendix 1 includes maps of the survey point data. Point topography was post-processed in Arc GIS 10.2. The integrated bed and riparian topography were piecewise splined, a polynomial function within the Arc toolbox. Splines generated a raster with weighted channel thalwegs, emphasising stream-wise (U vector) flow pattern. Surfer plots were mainly used for riverbed topography. Plots were Gaussian interpolated between the points by the kriging algorithm, again producing a continuous raster.

4.2.3 Field Identification of River Units: Environment Agency River Habitats Survey Mesohabitats and Physical Biotopes

> *Clearly in-stream habitat is a multidimensional feature, even within the realm of physical variables*
>
> Newson and Newson (2000:200)

Upon mapping riverbed topography, surveying of habitats was undertaken, in order to determine the different stream units to sample; a method that synthesises mesohabitats and physical biotopes was adopted (see section 2.7.1.1.). This follows Padmore's (1997) pioneering inter-calibration of mesohabitat and physical biotopes, a study that intensively monitored 11 sites during variable flow conditions and cross-correlated units between flow structures, streambed roughness and flow type (see Newson *et al*., 1998, and Padmore 1997; see table 4.1. and figure 2.9.1). This included one site on the North Tyne, a river that hosts a similar polyphyletic northern group of *M. margaritifera* (Lavictoire and Sweeting, 2012; 2012A, 2012B, Padmore 1997). Field sampling was conducted with the EA RHS (2003, V1) field guide, visual aids, diagrams and descriptions including figure 2.9.1 and table 4.1.

[redacted]



Flow type	Description	Associated biotope(s)
Free fall	Water falls vertically and without obstruction from a distinct feature, generally more than 1 m high and often across the full channel width	*Waterfall*
Chute	Fast, smooth boundary turbulent flow over boulders or bedrock. Flow is in contact with the substrate, and exhibits upstream convergenge and downstream divergence	*Spill* – chute flow over areas of exposed bedrock. *Cascade* – chute flow over individual boulders
Broken standing waves	White-water 'tumbling' waves with the crest facing in an upstream direction. Associated with 'surging' flow	*Cascade* – at the downstream side of the boulder flow diverges or 'breaks' *Rapid*
Unbroken standing waves	Undular standing waves in which the crest faces upstream without 'breaking'	*Riffle*
Rippled	Surface turbulence does not produce waves, but symmetrical ripples which move in a general downstream direction	*Run*
Upwelling	Secondary flow cells visible at the water surface by vertical 'boils' or circular horizontal eddies	*Boil*
Smooth boundary turbulent	Flow in which relative roughness is sufficiently low that very little surface turbulence occurs. Very small turbulent flows cells are visible, reflections are distorted and surface 'foam' moves in a downstream direction. A stick placed vertically into the flow creates an upstream facing 'V'	*Glide*
Scarcely perceptible flow	Surface foam appears to be stationary and reflections are not distorted. A stick placed on the water's surface will remain still	*Pool* – occupies the full channel width. *Marginal deadwater* – does not occupy the full channel width

The rationale for a synthesis approach was based on the differences in method: mesohabitats strength over physical biotopes is in the absence of empirical equations which consider the HZ as vertically impermeable from the stream (Buffin-Bélanger *et al.,* 2000; Newson and Newson, 2000; Hardy *et al.,* 2009). This is despite key evidence on HEF (e.g. Smith, 2005, Ibrahim *et al*., 2010, see section 2.5.1.). Also, once streambed geomorphology alters, previous hydraulic and dynamic velocity determinations lose validity for physical biotopes. Climate change ensemble models (~UKCIP09) predict increased frequency streambed slope failure and shift mosaic aggradation – degradation (e.g. Hastie *et al*., 2003; Conlan *et al*., 2005; Kilsby *et al*., 2006). However, the empirical basis of physical biotopes equates to predictive strength. Primary hydraulic attributes quantify the prevailing physical habitat conditions for benthic zoology. Since *M. margaritifera* downstream velcocity TVs are 0.25 – 0.75 m s^{-1}, and 0.3 – 0.4m for depths (Hastie *et al*., 2000). Allen and Vaughn (2010:391) determine that high flow relative sheer stress (RSS) model derived and average $w_i =$ 0.299, (Akaike Information Criterion (AIC_c)), which ranked the highest casual factor for patch species richness (unionids > 36 species) on the Red River, Oklahoma. Yet sampling sufficient hydraulic data to predict abundance and richness can become intensive and diversionary from determining key mussel respiratory survival parameters, hence the adoption of a synthesis approach, commensurable to limited resource short-duration sampling.

One of the key challenges confronting the stream ecologist is the development of a holistic predictor that explains distribution and abundance of species *in vivo* patch biotopes (Poff, 1997; Pringle *et al.,* 1988). Abundance is the natural signal of zoocoenosis – the animal community existing in an ecotone – which justifies this thesis' 'bottom-up' unit approach for *M. margaritifera* (Newson and Newson, 2000; Mathews, 2000).

4.3 Hyporheic Monitoring Points

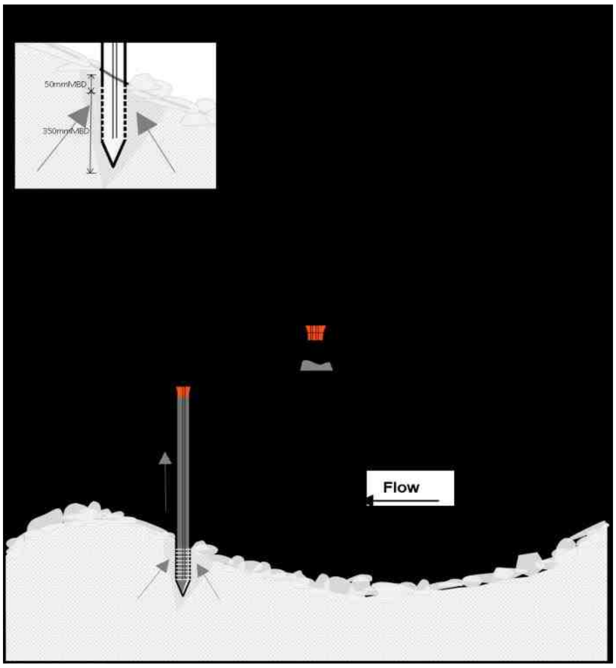
Streambed relief maps and subsequent habitat demarcation meant that knowledge on nested internal process was understood prior to hyporheic wells siting in units where hyporheic flow paths bore influence on ecotone hydrochemistry (figure 1.1., 2.7 and 4.1). There were a total of 24 hyporheic monitoring points at the 3 reach sites, with the majority stratified to Lealholm, Crunkly Gill, 10 Danby Sewage Treatment Works, 8 and Moors Centre, 6 (see table 4.2.).

4.3.1 Sampling From The Hyporheic Zone

A plethora of methods to sample from the HZ exist (see Bus *et al.,* 2009; Dearden and Palumbo-Roe, 2010). The majority recognise the role of hyporheic sampling in the assessment of stream ecosystem health (Orghidan, 1959; Pinay *et al*., 1990). The hyporheic monitoring apparatus used in this thesis is an adaptation on the early mini-piezometers developed by Lee and Cherry (1978) and very similar to a Bou-Rouch sampler (see Gibert *et al*., 2001). Mini-piezometers (denoted hyporheic wells) consist of a 1.5 metre length of UPVC tube, with a diameter ⌀ = 25mm. The bottom 350mm of the well is perforated round its circumference with numerous small holes ⌀= ≤ 2mm and crimped at the tip in order to allow ease of protrusion into the HZ, following auguring. To avoid the mixing of stream and hyporheic water in the well, 50mm of the impermeable shaft section was driven below the streambed surface (see figure 4.2., 4.3.). This sampling apparatus is very similar to that used by Soulsby *et al.,* (2001) to monitor salmon redds. A representative sample of upper interstitial water is vital because drop-off juvenile *M. margaritifera* live 5 years in buried substrate (infaunal) at depths of 40 – 100 mmMBD (Skinner *et al.,* 2003; Geist and Auerswald, 2007, Gest, 2010, see figure 2.5.). Therefore, below the 50mm of non-perforated section, the remaining 350mm of well was sunk into hyporheic substrate to ascertain representative data, particularly because of the steep chemical gradients that occur with depth (Triska *et al.,*1989; Boulton *et al.,* 1998, 2010, figure 4.2.).

These gradients are influenced by rates of down-welling and upwelling between SW and GW. Ibrahim *et al.* (2010:1398) recorded specific Q in the range of 0 – 7.76 cm d^{-1}, a rate which has influence on labile SW well ingress or depleted GW egress, particularly in high flow (Triska *et al.,* 1989), hence the protrusion at extra depth. Following installation, wells were hand-pumped for a 5-minute period, similar to groundwater borehole pump-tests; this was in order to ensure effective porosity between alluvial clasts and the prevention of clay "squeeze" (see table 4.2. for wells in clay), which can resulting in leachate and artesian conditions (Dearden and Palumbo-Roe, 2010). The wells were then sealed with a rubber bung and left to settle for 2 weeks allowing natural hyporheic flow to recharge the well. In order to avoid the build-up of aerostatic pressure with variability in hydraulic head (Δh), a small exhaust was installed at the top of the well.

To sample the well, the rubber bung is removed, the peristaltic hand-pump sampler line inserted with the bung sealing the well, the sample is then abstracted (figure 4.2.). The same method is applied to ISCO (6712) automatic sampling, with the purge function disabled and line-water rejected from sample collection.



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4.3.1.1 HEF (Hyporheic Exchange Flow) – Hydraulic Gradients and Fluxes

Due to relief of the streambed, hydrostatic pressure head gradients develop where discharge cannot be readily be alleviated by downstream flow; this is pronounced in step-pool and pool-riffle-pool sequences (see section 2.5.). Hydrostatic pressure is known to have impact on *M. margaritifera* locomotion and buoyancy. In caged experiments, regulation by haemodynamics, blood flow and external forces, is the observed physiological movement adaptations of the mollusc (Trueman, 1966). Low pressure is associated with greater mobility and use of hydrostatic mechanism (*ibid*). It is not only the hydrostatic pressure of stream-units that is vital, but the nutrient status and rate in which the waters infiltrate (riffle-heads) or exfiltrate (riffle-tails) (see section 2.3.). Therefore, the hyporheic wells were used to measure streambed vertical hydraulic gradient and determine specific discharge, related to geomorphological constraint of stream-wise flow (section 2.5.1). Adopting the principles of Darcy's law, VHG is determined by the following equation (Dahm *et al.,* 2006):

$$\text{VHG (\%)} = 100 \times \frac{(hs-hp)}{L} \qquad \textbf{Equation 4.1}$$

where VHG is Vertical Hydraulic Gradient, *hs* is the difference between the top of the hyporheic well to the stream stage (m), *hp* is the difference from the top of the well to water level inside the tube (m) and *L* is the length of well buried in the riverbed (m) (Dahm *et al.,* 2006, Bus *et al.,* 2009).

Vertical hydraulic conductivity (K_v) of hyporheic alluvium was assumed to be 10% of *horizontal hydraulic conductivity* (K_h), as under the Hvorslev method (Dahm *et al.,* 2006:137; Ibrahim *et al.,* 2010). This value was used to estimate the specific discharge of HEF. A minimum of three repeated slug tests were performed recording drawdown and volumetric of abstraction per unit time in a graduated tube. The results were interpreted using the Hvorslev equation:

$$K_h = \frac{r^2}{2L\,(t2-t1)} \times 1\text{n}\,\frac{(L)}{(\text{R})} \times 1\text{n}\,\frac{(H1)}{(H2)} \qquad \textbf{Equation 4.2}$$

r means the graduated tube radius (m), L the length of the well section (m), R is the radius of the well section (m) and $H1$ and $H2$ are respectively the drawdown ratios at time $t1$ and $t2$ (s) (Ibrahim *et al.,* 2010:1394). The specific discharge was calculated using the following equation (Dahm *et al*., 2006):

$$q = k_v \times \frac{VHG\ (\%)}{100} \qquad \textbf{Equation 4.3}$$

where q is vertical specific discharge (m/s) and K_v is the vertical hydraulic conductivity (m/s) (Ibrahim *et al.,* 2010:1394, *s*ee section 2.5.1.).

[redacted]

Reach	In-Stream and Hyporheic Monitoring Points (MP)	Grid Reference (NZ)	Groundwater Monitoring Borehole (MB)	Shallow Groundwater Monitoring Weir (GWMW)	Monitoring Point River-Unit Mesohabitat and Physical Biotope
Lealholm – Crunkly Gill (Main Channel)	MP1A	476144.93, 507467.81	1 (NZ 476157.09, 507449.72)	1 (NZ 476169.85, 507747.41)	Pool, riffle-head
	MP 2B	476149.05, 507475.48			Riffle, chute
	MP 3C	476149.32, 507480.07			Pool, riffle-tail
	MP 4D	476156.55, 507499.75			Run, pool
— Secondary Channel	MP 1	476162.85, 507478.87			Pool, riffle-head, bifurcation zone
	MP 2	476167.33, 507486.50			Chute, riffle, wet-dry ethereality
	MP 3	476168.44, 507490.20			Riffle thalweg, minor channel
	MP 4	476168.25, 507497.77			Pool, clay bed
	MP 5	476170.76, 507504.46			*ibid*
	MP 6	476169.82, 507502.34			Pool, confluence
Danby – Moors Centre	MP 1	471662.01, 508234.8	N/A	N/A	Pool
	MP 2	471665.8, 508228.8			Pool chute, riffle-head
	MP 3	471667.4, 508224.7			Pool, riffle-tail
	MP 4	471677.9, 508211.7			Pool
	MP 5	471681, 508208.5			Riffle-tail, pool-run
	MP 6	471689.7, 508200.8			Pool, run
Danby – Sewage Treatment Works	MP 1	470871.53, 508275.36	1 (NZ 470970.87, 508336.26)	N/A	Chute
	MP 2	470919.54, 508291.31			Side Bar, wet-dry ethereality
	MP 3	470924.72, 508304.26			Run, smooth flow
	MP3A	470932.14, 508304.51			Eddie, Boil
	MP 4	470938.02, 508325.74			Upwelling— sewage outfall, rate1.66 L S^{-1}
	MP 5	470952.30, 508331.00			Riffle/Raid, Thalweg
	MP 5 A	470955.84, 508329.49			Riffle - head (minor)
	MP 5B	470959.23, 508328.01			Riffle-tail (minor)
	MP 6	470967.52, 508323.77			Rapid, Thalweg
	MP 7	470977.22, 508320.17			Riffle-tail, run
	MP 8	470979.55, 508314.04			Pool

4.4 Sampling In-Stream

In-stream waters were sampled at the same location as hyporheic monitoring points. Point sampling occurred just above the streambed to obtain samples that were characteristic of conditions for juveniles. Sample abstraction was performed with a peristaltic hand-pump, inserting the suction end into the lower water column. Approximately 10mm above the bed was considered a sufficient height to not draw out pore water, yet be representative of channel water (Amoros *et al*., 1996). Established *M. margaritifera* functionally filter feed higher in the water column, with average height in adulthood at 65mm, but up to 150 – 170 mm for older mussels in warmer streams (Bauer, 1992, Skinner *et al.,* 2003; Degerman *et al*., 2009). Water column sample height is critical to sampling due the rates of streambed surface biofilm nutrient transformation and flux from upwelling—downwelling, potentially leading to chemical gradients in the water column (e.g. Triska *et al.,* 1993, see section 2.4., *et alibi*).

4.5 Sampling From Groundwater and Shallow Groundwater

Two groundwater monitoring boreholes were actively sampled at the Lealholm (Crunkly Gill) and Danby (STW) site (see figure 3.6., 3.7.). Access and borehole capping safety issues prevented borehole installation at Danby Moors Centre.

4.5.1 Lealholm – Crunkly Gill

[redacted]

This borehole was sunk to a depth of 10mBD at 92.94mAOD and was positioned in a dextral riparian seep (figure 4.4.). On 17/08/2013 at 10:30 the groundwater table was measured as 0.3mBD at an elevation of 92.64mAOD. A concurrent river stage transect measured at 88.24 mAOD. This was two days after installation, in order to allow for aquifer head stabilisation (Brassington, 2007). The source water was determined to be hillslope water, with groundwater being effluent to the river based on a hydraulic head difference of 4.4m (Δh) and positioning on an enclosed hillslope valley at 3.6° (map 3.6.1, *ibid*).

The riparian land at Crunkly is held in “common land” under Danby Court; during the twentieth century this was intensively livestock grazed (S. Hirst, *Pers. Comm.* 2013, section 3.2.3.). Rudimentary land drains cover the floodplain and where an incised seepage face exists parallel to the river, a pipe serves to discharge these (figure 4.5., table 4.2.). Considering the hillslope land use effects on hyporheic water quality (section 2.2.1), shallow GW monitoring was considered vital. Sample vials were filled directly from the pipe and abiotic measures made by inserting the YSI multi-parameter probe into the shaded monitoring weir trough.

[redacted]

4.5.2 Danby – Sewage Treatment Works

A pre-existing borehole (figure 4.6.), installed for geotechnical monitoring following river and railway embankment engineering by Network Rail, was adopted for monitoring. On 17/08/2013 at 10:10 groundwater elevation was 1.85mBD or 172.37mAOD. On a transect river stage was measured at 170.34mAOD, giving a difference of 2.03m (Δh); the groundwater is therefore effluent to the river, mainly due to the hillslope angle of 6.9°. However, because of the meander, river waters are expected to be driven into the floodplain at high flow thus GW samples may be “mixed” by HEF (Brassington, 2007; Fleckenstein *et al.,* 2008).

4.6 Sampling Temporality

Upon the installation of hydrochemistry and hydrometry monitoring apparatus in a spatial array that captures hydrodynamic source waters, a temporal sampling strategy was executed. The *M. margaritifera* post-parasitic settlement period, when juveniles establish themselves in sediment, is acknowledged by malacologists as the most critically sensitive life-phase (Hastie *et al.,* 2000; Skinner *et al.* 2003, section 2.6.). The temporal sampling was designed to in order to account for interstitial water quality during the drop-off phase, during late spring, *circa* May – June (Skinner *et al.* 2003; Scheder *et al.,* 2011). Drop-off is concurrent to the *Salmonidae* run which territorially return carrying glochidia infection from the previous season (Zuiganov *et al*., 1994; Hendry and Cragg-Hine, 2003).

Physicochemical sampling was therefore conducted during the period 19th March 2013 to the 15th October 2013, with contextual hydraulic well sampling on Friday 15th August 2014 to quantify HEF (Section 4.3.1.1.). A total number of n = 440 water quality samples were taken during this period, Lealholm (Crunkly Gill) the active *M. margaritifera* site was most intensively sampled, n = 236, with 180 samples over 24hrs, then Danby (Sewage Treatment Works), n = 169, with 82 over 24hrs, and finally Danby (Moors Centre), n = 35, with 17 in less than 24hrs. New monitoring time-frames were also sampled in, including diurnal cycles and adverse hydrometeorology conditions. Balmford (2011) and Biddulph (2012) quantified the effects of flooding on in-stream and hyporheic hydrochemistry, yet neither quantified the impact of low flow, despite the imperilment to mussels (e.g. Stubbington *et al.,* 2009) and to pollution concentrations – less dilution, more concentrate pollution (Sweeting, 1993).

4.7 Laboratory Analysis

Once collected, samples for cation and anion tests were collected in 50m vials. Vials were rinsed in the waters they sampled prior to abstraction. In accordance with Eaton *et al.* (2005) standards akin to the EA "Blue Book", sample containers were filled to the brim to avoid oxygen diffusion and enhanced microbial breakdown (Environment Agency, 2011A). They were then immediately placed in a cool-box for transportation. Upon arrival in the laboratory, all samples were refrigerated. 10 ml of the sample was filtered through a 0.2 μm pore size syringe filter; this diameter (⌀) was chosen to strain-out bacteria, c.1.0 μm. 1 μl of sample was loaded into the Dionex ICS 3000 (Ion Chromatography System) to measure concentrations of anions and cations. Table 4.3 (below) outlines the parameters the Dionex monitors, in addition to the detection limits.

Table 4.3.
Detection limits of compounds by supressed conductivity. * denotes detection by UV/vis at 210 nm for nitrate and 220nm for nitrite.

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

Samples for Dissolved Organic Carbon (DOC) were loaded into the TOC (Total Organic Carbon) analyser which uses ultraviolet visible spectrometry at 254nm to measures concentration at a detection limit of 0.20 mg C L^{-1}. Chemical Oxygen Demand (COD) analysis was performed on settled specimens. Samples were analysed using the macro colorimetric method set out by Jones *et al.* (1985) using low range test tubes (0-150 mg L^{-1}).

In-stream waters were sampled for Suspended Sediment Concentrations (SSC) with samples being extracted using a 1000ml bottle. Pre-weighed Whatman grade 934AH glass micro-fibre papers with a pore size of 1.5 µm were installed in the Buchner flask and the sample pulled through using a vacuum pump. The sediment laden filters were oven dried at 103 ± 2° °C for 24hrs, placed in a desiccator to cool, before being reweighed. The difference in filter weight proportional to sample volume was used to calculate SSC in mg L^{-1} (Equation 4.4.).

$$SSC = \Sigma M \frac{M}{V}$$ **Equation 4.4**

where SSC is suspended sediment concentration (mg L^{-1}), m = mass of sediment less the filter paper weight (mg) and, V = volume of sample water (L).

Since *M. margaritifera* are filter feeders, with juveniles requiring bioseston for nourishment, determination of the organic content of SSC was vital to adequate food sources in reintroduction biotopes (Gee, 1991; Strayer, 2008). Having determined the SSC, and therefore the known mass of sample, the sample was placed in a pre-weighed crucible. Before this, the crucible had been in an oven at 105 °C for 24 hours to eliminate any moisture. The sample and crucible were then placed in a muffle furnace at a temperature of 550°C for 4 hours. The samples were subsequently cooled in the desiccator before being reweighed (g) (MAC). The mass of the ash material (g) (Ash_{550}) was then calculated using the equation:

$$Ash_{550} = MAC - MC$$ **Equation 4.5**

From which the organic content (%) is calculated:

$$LOI\%_{550} = \frac{MS - Ash_{550}}{MS} \cdot 100$$ **Equation 4.6**

4.8 Summary

- This chapter has appraised a range of methods used to address the aims and objectives of this thesis, outlined in chapter one.
- A densely instrumented sampling procedure was adopted to research hydrochemical change at a sufficient resolution so that metabolic nutrient processes which alter concentrations above or below *M. margaritifera* TV could be analysed.

- Spot sampling of VHG in the hyporheic wells, in addition to GW elevation proportional to river stage, allowed the spatiotemporal determination of HFP and whether stream waters were down-welling into hyporheic substrate, or *vice versa*. Borehole measurements determined whether streams where gaining or losing from immediate hillslopes.
- Together, the intensively sampled (n = 440) chemical and one-off (n = 1) hydraulic results served to determine the aerobic status of water, the vectors of HEF, and the estimated rate of exchange between source waters. In context of patch dynamics concept and Henricks (1993) pool-riffle stoichiometric zones, the determination of reach-scale infiltrated and exfiltrated water quality was vital to the identification of *M. margaritifera* reintroduction stream-units, the thesis aim.
- Budgetary constraint resulted in limitations to the field apparatus, BAT (Best Available Techniques) were used in absence of more expensive equipment. Boreholes were not sealed on the surface foundation or vertical casing; this potentially results in contamination from surface waters, resulting in a non-representative groundwater sample. Due to the inaccessibility of the narrow hyporheic well shafts, ex *situ* measures of hyporheic abiotic parameters were sometimes made, potentially making temperature and dissolved oxygen recordings unreliable; a more reliable method is proposed by Riss *et al.* (2008). The RTK survey reported erroneous height values because of tree signal interference in Crunkly Gill, these values were disregarded. The reduction in bed topography points meant there were fewer survey points to interpolate a raster, partially resulting in a non-representative bed. A improved method would be to support RTK data with total station transect surveys.
- The spatial setting of in-stream units was derived from a hybrid method with key relevance to reintroduction authorities, adopting EA RHS (2003) methodology for habitat surveys.
- The data presented in the following chapters are a direct result of the series of field and laboratory techniques documented. These techniques are consistent across different catchments and suitable, given the available resource.

Chapter 5 Hydrochemistry Analysis

5.1 Introduction

This chapter examines the physicochemical properties of the water transferred to exchange monitoring points (MP) at the stream-hyporheic interface. Through the analysis of biotic nutrient data derived from source-water monitoring, metabolic hotspots and ephemeral hot moments can be discovered, demarcated and mapped (section 2.5., McClain *et al.,* 2003). Using the methods discussed in the previous chapter, hydrochemical variability along MPs of streambed profile are examined. This includes biotic nutrient (C, N, P, S) concentration, (an)aerobic (cf. redox) status, suspended sediment concentration and, the organic content of sediment – Loss-On-Ignition. The early presentation of discharge rate (Q_v) into and out-of the streambed at pool-riffle-pool MPs provides a hydraulic quantification of exchanges rates. These data are statistical analysed to develop a conceptual model of streambed exchange-flow hotspots which can be up-scaled based upon key topography and hydrogeology features.

This chapter is divided into three subchapters:
(5.2) [redacted] site and hydromorphological setting for valley unit scale hyporheic flow path (VUHFP, Fig 1.1(a)).
(5.3) Danby, Sewage Treatment Works (STW) – a site where anthropogenic impacts of sewage outfall and river training occur – river bank rock armouring.
(5.4) Danby, Moors Centre – the site of a pronounced deep pool-riffle sequence which is hypothesised to drive high rate exchange flows.

5.2 Lealholm – Crunkly Gill

The series of 10 MPs were hyporheic and in-stream monitored during the mussel drop-off and salmon run period (section 4.6). These points were in addition to the borehole (BH) (10mBD) and shallow groundwater monitoring weir (GWMW) (Figs 3.5., maps 3.7., 3.8 and 4.0).

5.2.1 Synopsis

This section starts by addressing the reach-scale streambed DEM, setting the hydraulic habitat context for monitoring points (MP). Initially, hydraulic investigation results are presented for variables including VHG (Vertical Hydraulic Gradient) and Q_v (specific discharge). These data provide rate context, for injection and ejection, between stream and substratum. After appraising hydrology results, reach-scale hydrochemistry data are presented for all hydrochemical parameters at each monitoring point, longitudinally, since U-prime (stream-wise) velocity is normally the highest (Buffin-Bélanger *et al*., 2010). Summary statistics for each water quality parameter are then presented at each MP of hydraulic habitats. Using hydrochemical parameter data arrays, the statistical difference between monitoring points is determined, in addition to the probability of one monitoring point exceeding another, for a given water quality parameter. Upon establishing reach-scale variability; diurnal, flood and drought changes are analysed. Data trends are temporally up-scaled and linked to YSI Sonde data for the monitoring period. This facilitates the long-term appraisal of ammonium (NH_4^+), turbidity and abiotic stress on *M. margaritifera*. Bulk reach-scale arithmetic means are presented for hydrochemical parameters of source waters – SW, HZ and GW. The statistical difference (*t*-test) between these groups of source waters is then analysed. Finally, principal component analysis (PCA) results are analysed to unearth compositional trends in the data and infer which physicochemical parameter is primarily responsible for the variability in other variables.

5.2.2 Hydraulic Gradient And Flux Across A Pool-Riffle-Pool

Monitoring derived n = 440 physicochemical observations that revealed metabolic hot spots and hot moments with nutrient, temperature, conservative solutes and dissolved oxygen concentration being used as a tracer (McClain *et al*., 2003; Burt and Pinay, 2003; Burt, 2003). Later hyporheic well slug tests and VHG measurements confirmed locations of HEF for riffle–head downwelling and riffle –tail upwelling (section 4.3.1.1., 4.6).

[redacted]

Figure 5.1 presents VHG through the main channel pool (MP1A), riffle (MP2B) and pool (MP3C) sequence (PRP). MP1A has a negative VHG of -4.39, where hydraulic head (Δh) was below stream stage, indicating a weak presence of downwelling. Both MP2B and MP3C have respective VHGs of 4.97 and 10.50, indicating upwelling water where h is above relative river stage. Ibrahim *et al*. (2010:1395) reports positive VHGs in riffles.

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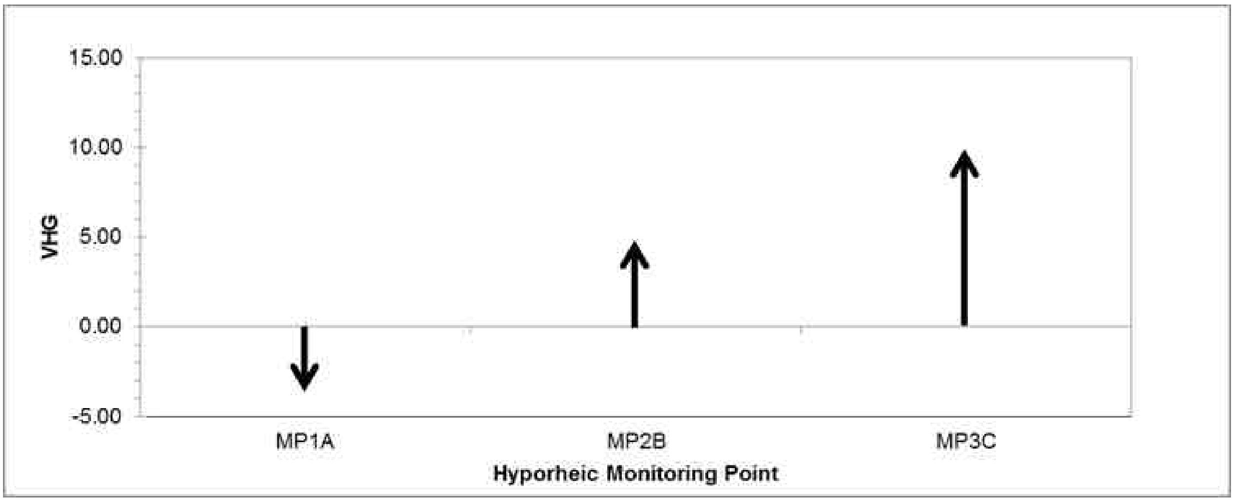

The bar chart in figure 5.2 displays vertical specific discharge (Q_v) at rates shown in table 5.2. The riffle-tail shows the highest vertical specific discharge at 0.25cm s^{-1} which equates to a daily Q_v at 217.78 m d^{-1}, -83.43 m d^{-1} for riffle-head and 16.28 m d^{-1} for riffle (MP2B).

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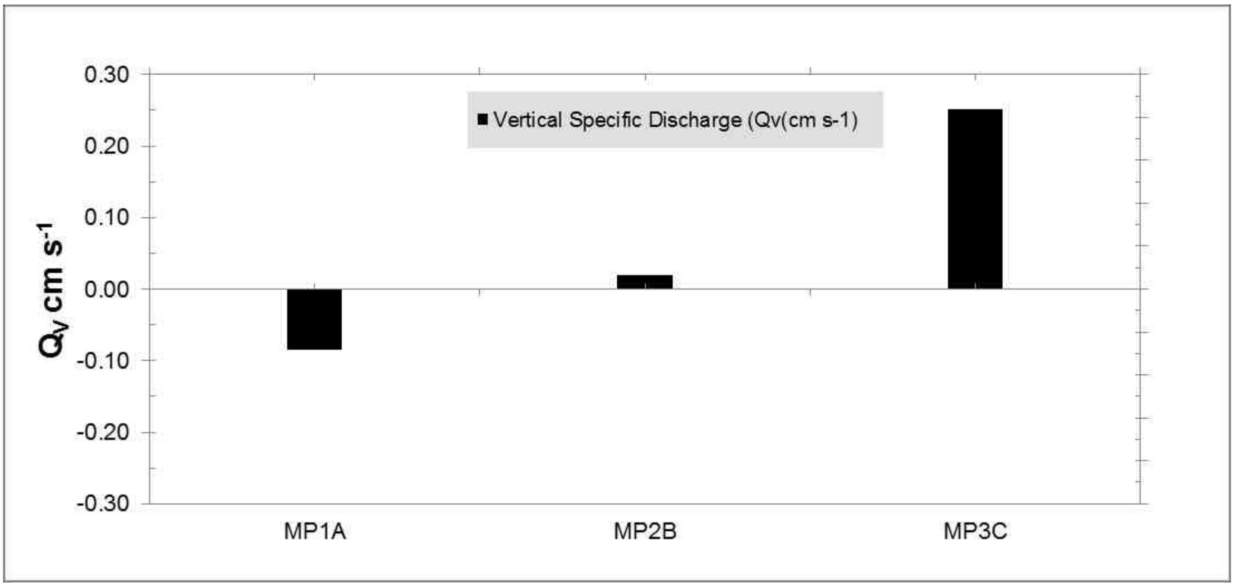


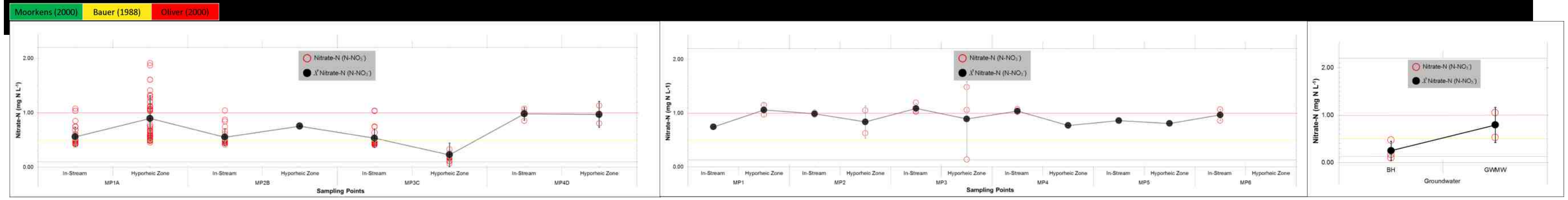
5.2.3 Reach-Scale Hydrochemistry

5.2.3.1 Dissolved Organic Carbon And Nitrogen: Fine-Scale Variability

Dotplots present nitrogen speciation change through the reach-scale, through two anabranching channels and in groundwater (Figs 5.31–5.33). All in-stream water initially appears hydrochemically isotropic, potentially due to mixing. However there is marginal concentration reduction, which is important since Moorken's (2000) TV (Target Value) is at 0.125 mg N L^{-1}. The transition through the main channel PRP sequence results in an arithmetic mean concentration reduction in in-stream nitrate-N from 0.57, 0.56 to 0.54 mg N L^{-1}. These values all exceed Bauer's (1988) TV of 0.50 mg N L^{-1} (Table 2.1). The most fundamental change is in hyporheic values, from means of 0.90, 0.76 to 0.24 mg N L^{-1}, the latter being the lowest average value through the reach. The low nitrate-N at the riffle-tail (MP3A HZ) is a probable result of the relatively oligotrophic groundwater, at a mean of 0.25 mg N L^{-1}, ejecting from riffle-tail as hyporheic return flow (Fig. 5.31., Appendix 8).

Sampling at MP1A HZ was double the size of other sample points, at n = 49 (Fig. 5.31). The cluster of 24 hour data above Oliver's 1.00 mg N L^{-1} is derived from riffle-head pore water monitoring on 28th July 2013. This was at a time of prolonged summer low flow (see Fig. 5.42. for stage-graph). Higher concentration is probably a result of numerous nitrate rich point source discharges not being adequately diluted in the base flow (Deflandre and Jarvie, 2006, map 3.6.4). Danby STW discharge consent some 7.7 km upstream has an ammonia-N threshold of 30 mg N L^{-1} at a rate of 240 m^3 d^{-1}, in dry weather flow Q_p <1 in 6 years (Appendix 6, London Gazette, 2005). 6 kg N ha^{-1} a^{-1} of nitrogen is produced per capita from humans in the UK (Royal Society, 1983).

[redacted]



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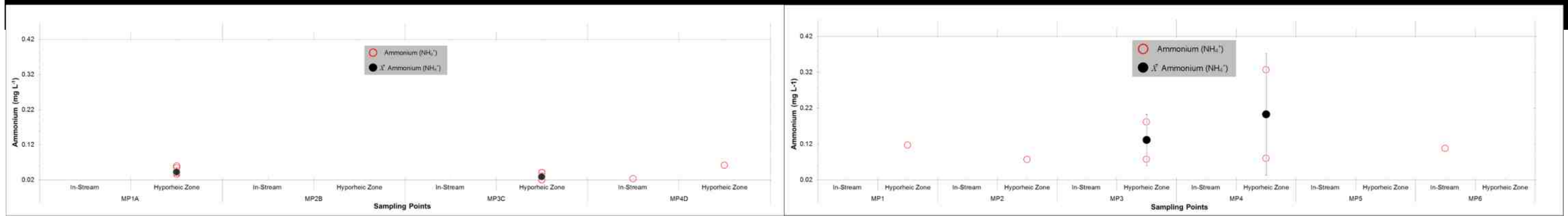

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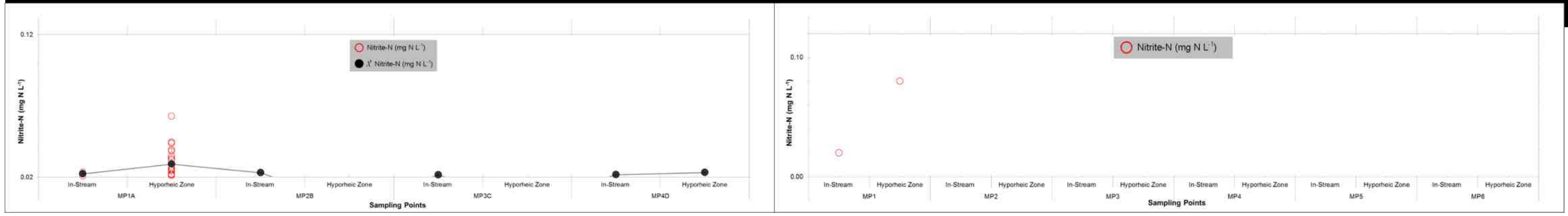

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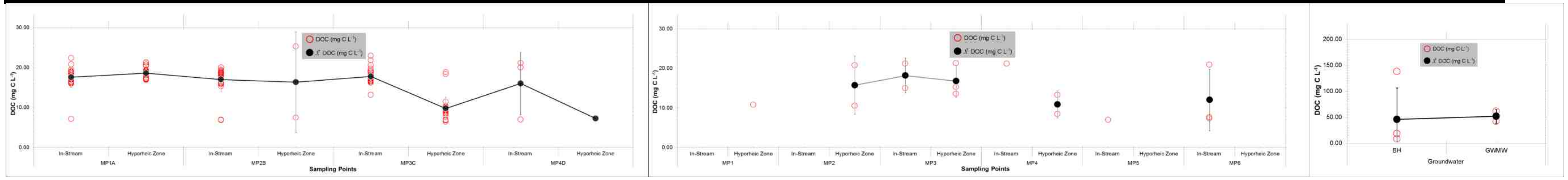

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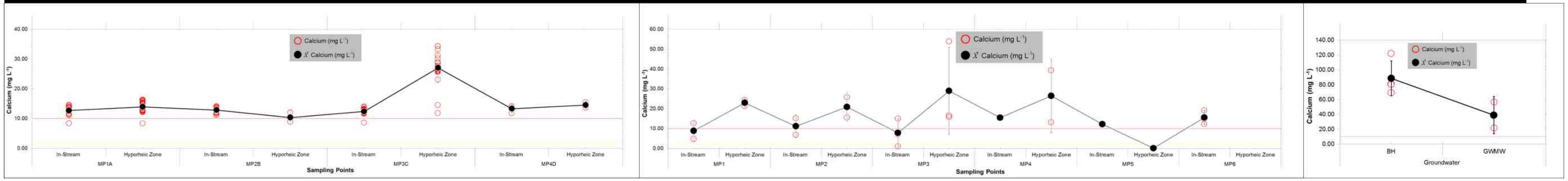

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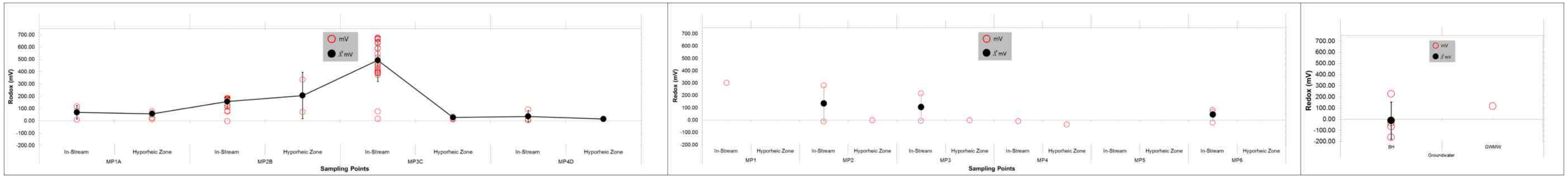

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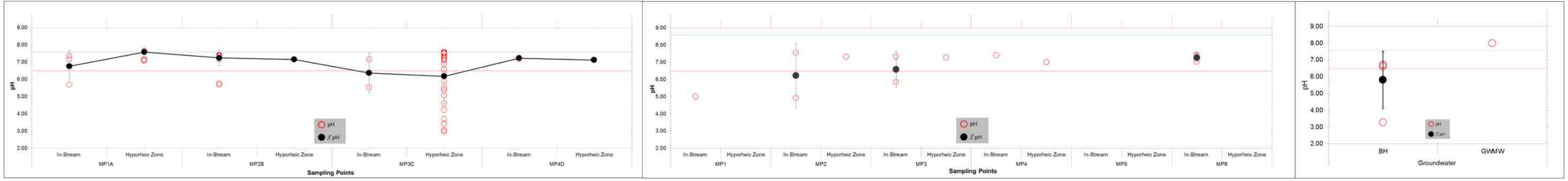

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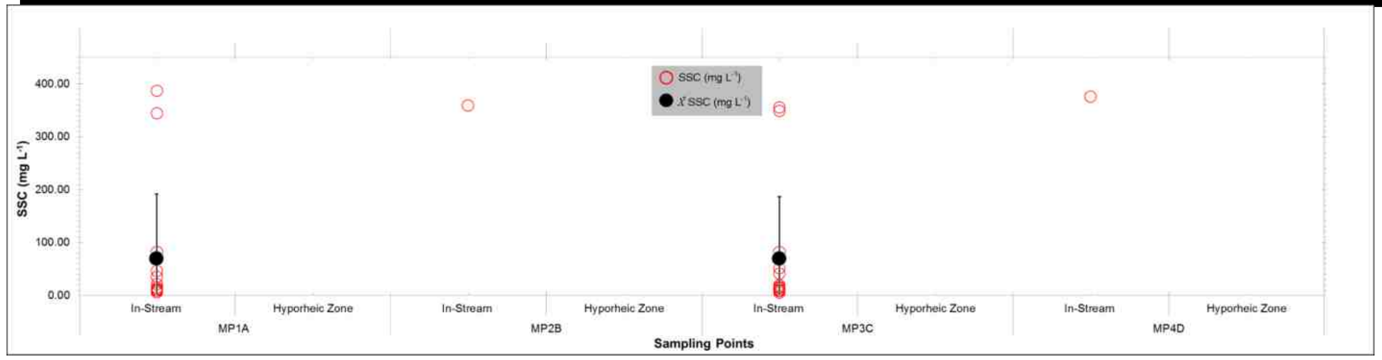

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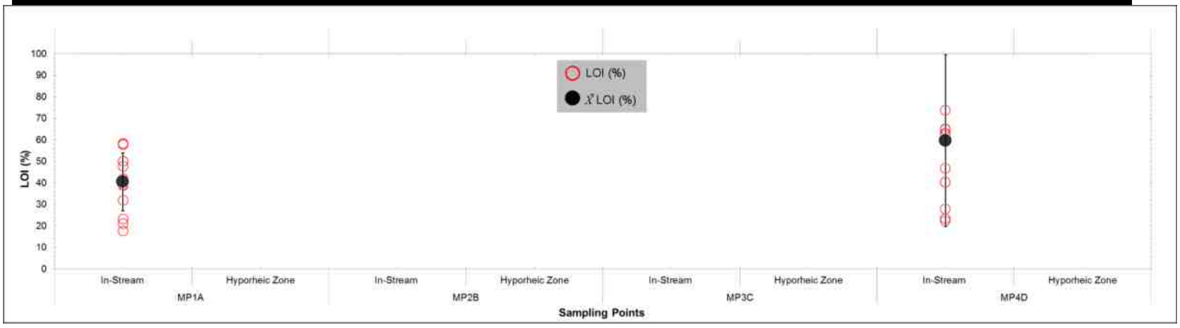
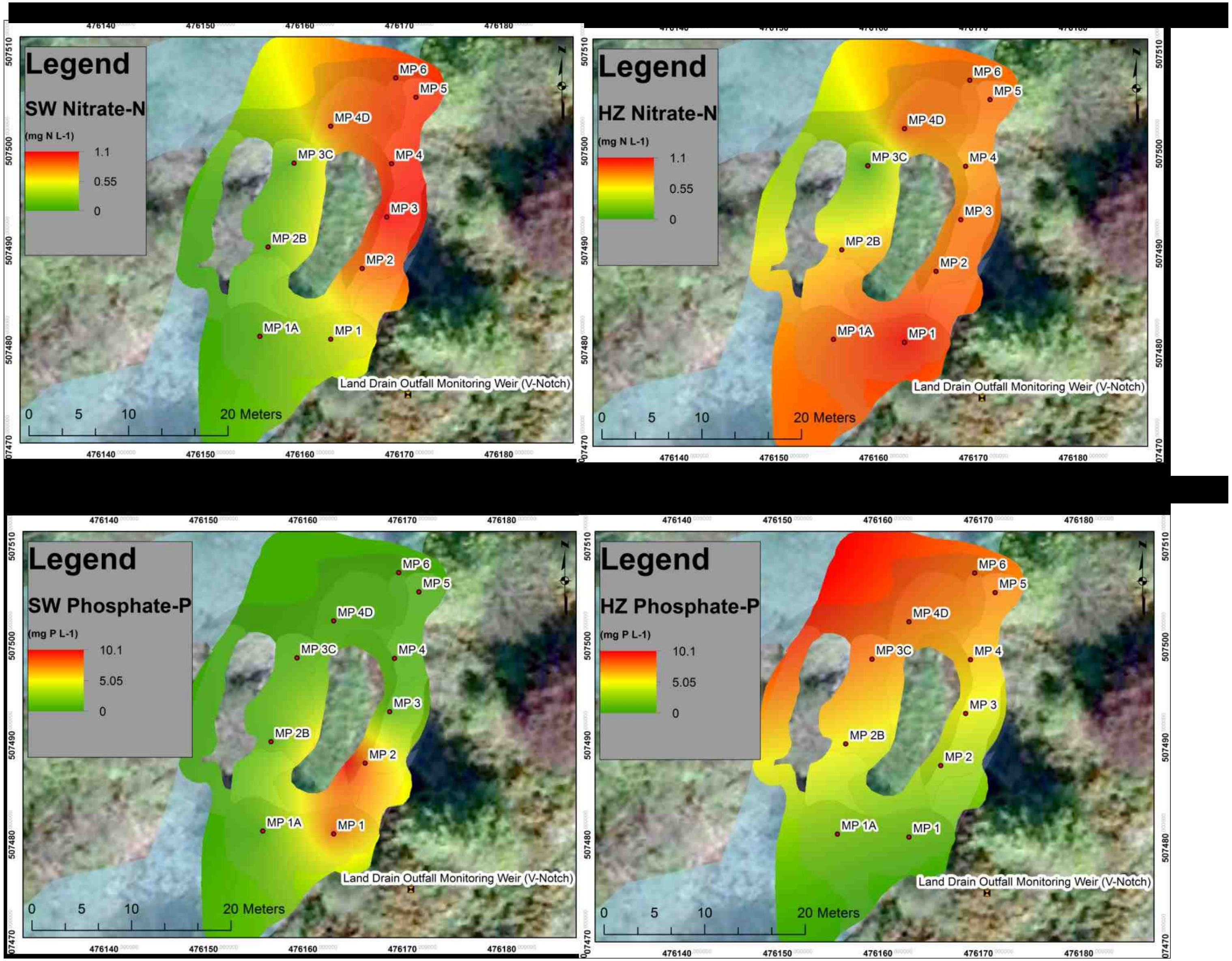


Dissolved Organic Carbon (DOC) concentration variability is correlated with nitrogen speciation trends (Fig. 5.31, 5.34), particularly for nitrate-N and TIN (Total Inorganic Nitrogen), reducing in hyporheic zone through the pool-riffle-pool, from an arithmetic mean of 17.90, 16.36 to 9.78 mg C L^{-1}. The Wilcoxon-Mann-Whitney (WMW) U test derives a p = of 0.0000 between HZ riffle— head and tail, denoting statistical difference and high probability that riffle head DOC concentration is higher than at the tail (Mann and Whitney, 1947). The same p value applies to HZ nitrate-N too (Table 5.2.2, inc. medians). No ammonium (as NH_4^+) was detected in-stream waters, with the exception of MP6 at 0.11 mg L^{-1} on 14th March 2013. This is contrary to HZ samples. NH_4^+ is measured thorough the secondary channel proximal to bank erosion of the Salop (711m) soil (Map 5.2.1., Fig. 5.32). This stagnogley clay soil is waterlogged and slowly permeable (NSRI, 2013; Appendix 7). The abandonment of livestock farming and ploughing on the adjacent floodplain has created an environment for seral formation of a humic rich Ap soil horizon, composed of native deciduous plant residues producing a peaty layer, over clay (*ibid*). Bank slump through the meander edge of the secondary channel, coupled with flow abandonment in the summer droughts, create warmer stream waters at a suitable thermal equilibrium for organic N mineralisation to ammonium (Chiou *et al*., 1979; Chiou and Shoup, 1985, Sprent, 1987; Figs 5.31 – 5.33.). This would explain high ammonium in the secondary channel, and very high DOC concentration in the groundwater monitoring weir which drains the Ap and Eg soil horizons (Fig. 5.34; Clark *et al*., 2007; Worrall *et al*., 2004, 2012). During 24 hours of monitoring, no ammonium was detected in the HZ of MP1A, MP2B, but was detected at the riffle-tail (MP3C) HZ (Fig 5.43). The majority of nitrite-N samples were <LOD (Limit of Detection, table 2.2.3, Fig 5.33), generally determined at c. 0.01 mg N L^{-1}. The remaining samples were below the detection limit.

During the summer months groundwater provides cooler water riparian leachate which mixes with stream waters. In winter this is reversed with warmer waters being leached in the parafluvial zone (Appendix 8). This seasonal switch is likely to provide thermal buffering from main-stream temperature, an important ecotonal aspect of backside *M. margaritifera* habitat (Lovejoy *et al.,* 1986; Danielopol *et al*., 1989; Geist and Auserwald, 2007).



Maps 5.1 Reach-scale spatial variability in average Phosphate-P (Ortho-P) and Nitrate-N (N-NO$_3^-$) across in-stream and hyporheic waters

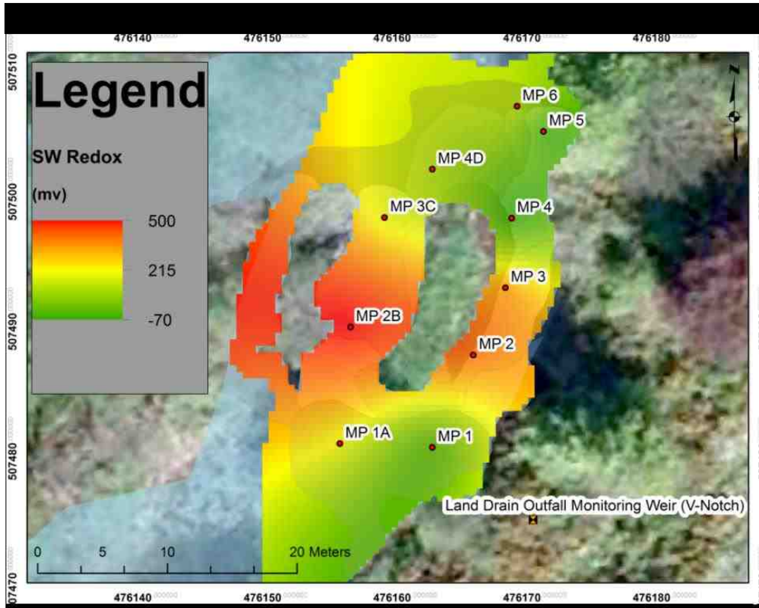
Source: OS Mastermap (2013), Google Earth (2009B), NERC (CEH) (2011)

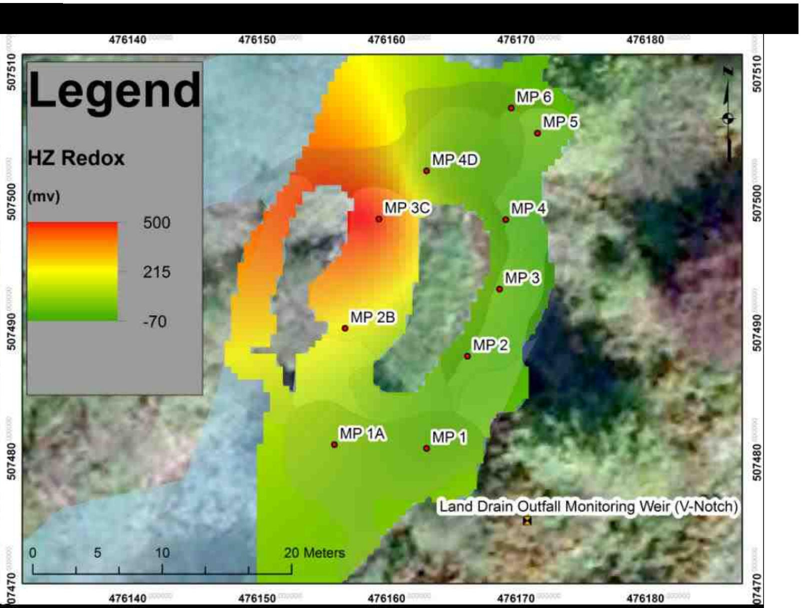
Map Properties

Coordinates: British National Grid (GCS_OSGB_1936)

Projection: Transverse Mercator

[redacted]





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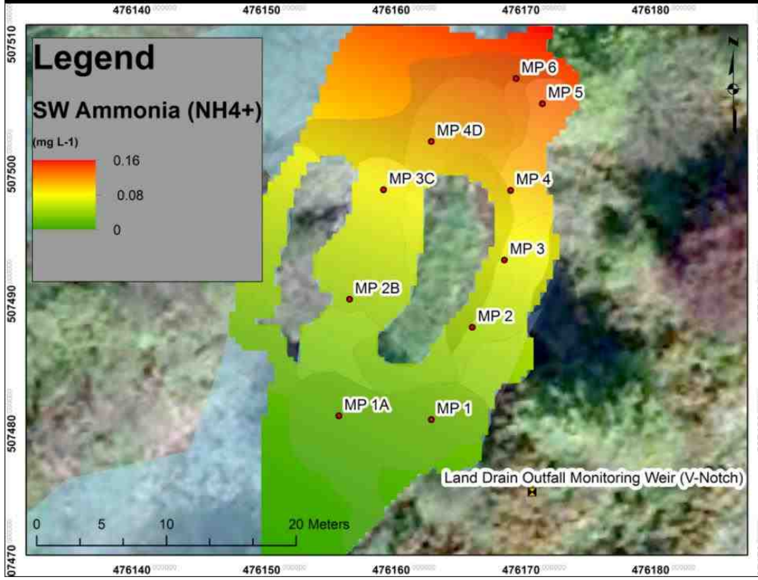

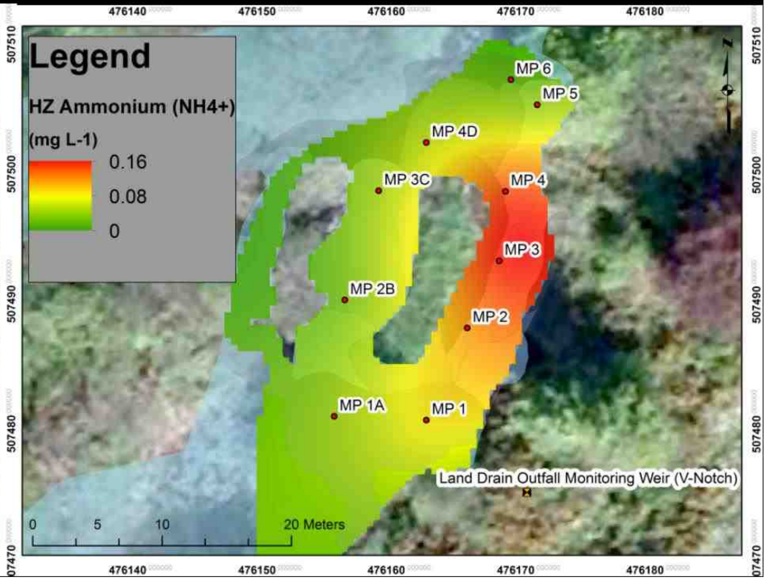

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5.2.3.2 Redox And Dissolved Oxygen: Fine-Scale Variability

Redox data trends are influenced by physical biotopes, with high mean redox in the hyporheic zone of riffles at 155 mV (Fig. 5.36., Map 5.2.1., 5.2.2). A lag-effect occurs on in-stream waters, with peak redox at 488 mV occurring at the riffle-tail, but not in the riffle (Map 5.2.1 –2, Fig 5.1). In-stream and pore water values indicate highly oxidizing conditions with abundant electron donors resulting from riffle-bed roughness and TKE-induced HEF (Triska *et al.,* 1993; Buffin-Bélanger *et al*, 2000; Soulsby *et al*., 2001). Negative redox occurs in the secondary channel denoting reducing conditions and electron acceptors, a result of depleted groundwater inputs (Fig. 5.36., Burt *et al*., 2010A). Again, HZ redox is elevated due to the riffle in the secondary channel (MP2). Dual groundwater inputs occur from bankside leachate and the discharging land drain (Fig. 4.5., Maps 5.2.1–2). The inflow from these sources is particularly prominent during channel flow abandonment during summer low flows.

Dissolved oxygen (% sat.) presents a spatial pattern corresponding to redox, again peaking with hyper-saturation in the water column of the riffle-tail (Fig. 5.38). Apart from in-stream riffle (MP2B) and hyporheic riffle-tail (MP3C, 4D) concentrations, all other DO arithmetic mean percentage saturation values are within Oliver's TV (2000) range (Fig. 5.38). Riffle-tail DO was particularly depressed as a result of alluvial groundwater discharging out of the riverbed at the riffle-tail (MP3C HZ, Fig. 5.38).

5.2.3.3 Suspended Sediment Concentration, Electrical Conductivity, Phosphate, Calcium And pH: Fine-Scale Variability

A paucity of in-stream samples renders the determination of a representative suspended sediment concentration (SSC) map problematic. On October 14 – 15th riffle-head in-stream monitoring resulted in arithmetic mean 70.08 mg L^{-1} SSC, in-riffle 358.26 mg L^{-1} (*n=1*) and in riffle-tail 69.88 mg L^{-1} (Fig 5.40., *n* = 24). ISCO auto-sampler failure meant the riffle-unit (MP2A) was sampled once; this was anticipated to be anomalous. A keynote trend, is however, presented in the Loss-On-Ignition (LOI) results, 40.38% increases to 59.54, from riffle – head to –tail (MP1A – MP3C., Fig. 5.41.), indicating that the suspended matter in the water column is (bio)seston and organic rich (Ball, 1964; Heiri *et al*., 2001). The Tinsley method correlates LOI with the organic C content of suspended sediment. Organic C precision under the LOI method is perturbed by salt crystals and clay, the latter being presented in the superficial drift onsite (Ball, 1964; map 3.7.3., Appendix 7). Autochthonous POM (Particulate Organic Matter), SOM (Soil Organic Matter), phyto— and zoo— plankton, diatoms, vegetal and macroinvertebrate excretion and detritus are some potential ingredients of LOI percent (Ball, 1964; Newbold *et al*., 1982; Heiri *et al.,* 2001; Clark *et al.,* 2007). High LOI percent represents organic matter which acts as a biologically active compound enhancing ion-exchange resins and is fundamental in reducing 'harmful ions such as ammonium and nitrate' (Chiou *et al.*, 1979; Eybe *et al.*, 2013:694). This in turn explains the statistically significant reductions in these parameters through pool-riffle-pool across in-stream and hyporheic waters (Fig. 5.31 – 5.31).

[redacted]

Moorkens (2000) Bauer (1988) Oliver (2000)

[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]
[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]
	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]
[redacted]	[redacted]	[redacted]	0.51 (0.57)	[redacted]	0.50 (0.56)	[redacted]	[redacted]	0.48 (0.54)
	[redacted]	[redacted]	0.74 (0.90)	[redacted]	0.76	[redacted]	[redacted]	0.19 (0.24)
[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]
	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]
[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]
	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]
[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]
	[redacted]	[redacted]	0.04 (8 >LOD)	[redacted]	[redacted]	[redacted]	[redacted]	0.03 (24 >LOD)
[redacted]	[redacted]	[redacted]	12.90 (12.77)	[redacted]	12.95 (12.91)	[redacted]	[redacted]	12.56 (12.44)
	[redacted]	[redacted]	13.83 (13.96)	[redacted]	10.46	[redacted]	[redacted]	27.77 (27.77)
[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	6.34
	[redacted]	[redacted]	7.60 (7.56)	[redacted]	4.07	[redacted]	[redacted]	6.99 (6.15)
[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	71.12 (75.63)	[redacted]	[redacted]	[redacted]
	[redacted]	[redacted]	[redacted]	[redacted]	86.00	[redacted]	[redacted]	73.54 (74.05)
[redacted]	[redacted]	[redacted]	145.00 (154.33)	[redacted]	169.91 (164.44)	[redacted]	[redacted]	158.00
	[redacted]	[redacted]	162.23 (163.47)	[redacted]	138.50	[redacted]	[redacted]	171.74 (170.11)
[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]
	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]

Calcium since being an alkaline earth metal is closely associated with pH (Webster and Patten, 1979). Indeed, both variables appear to correlate in alluvial up-welling into the stream at the riffle-tail, which are calcium-rich and acidic (Figs 5.35., 5.39). Both respective arithmetic means exceed *M. margaritifera* TV at 26.77 mg L^{-1} and pH 6.15. Transmitted through the interstitial pore network of the hyporheic zone these alluvial waters are likely to be an indicator of the natric and calcic groundwater chemistry, namely associated with the

Dogger, Ellerbeck and Cloughton formation sandstones, mudstones and ironstones through Crunkly Gill (McNish *et al*., 1997, map 3.7.3). The acid nature of groundwater is regionally observed in bedrock aquifers, such as the Triassic Sherwood Sandstone, where cation exchange capacity is high (Allan *et al*., 1997). The relatively acidic alluvial groundwater flux is also associated with industrial pollution acid deposition (Evans *et al*., 2014). Together the calcic effects of limestone and, the dissolution of calcite induced by CO_2 diffusion (riffle) producing carbonic acid for dissolution, are insufficiently strong to buffer the dominant acid conditions from the Triassic sandstones (Webster and Patten, 1979; McNish *et al*., 1997; Allan *et al*., 1997), hence both the acidic and calcium-rich upwelling.

Calcium (Ca) transformation to calcium Carbonate ($CaCO_3$) may occur due to labile diffusion of $CO_{2,}$ generated during turbulent riffle exchange coupled with heterotrophic carbon respiration, explaining the peak in concentration in Ca (Webster and Patten, 1979; Trimmer *et al*., 2012). Temperature data shows that stream riffle temperatures, compared to pools are approximately 1°C cooler in winter months, resultant from bed roughness induced exchange with the cooler air temperatures (Hardy *et al*., 2009; Appendix 8).

Calcium (Ca) alone cannot be used for shell building but soluble $CaCO_3$ can (Gee, 1991; Strayer, 2008). The majority of phosphate-P (Ortho-P (PO_4^{3-}) was <LOD, or not detectable on the Dionex chromatograph (Table 4.2.3). Ortho-P is anticipated to occur in trace concentration however (map 5.1.4). The granular limit of detection negates accurate determination of this, however. Under the same biphasic TKE-induced riffle hydrolysis (*vide supra*), Ca may speciate to octacalcium phosphate (OCP ($Ca_8H_2(PO_4)_6$), only where there is trace presence of reactive Ortho-P (Stone and Murdoch, 1989).

Electrical conductivity (µS/cm) (EC) shows no discernible pattern (Fig 5.37). Groundwaters appear to have elevated EC. The values may be anomalous resulting from inadaquate borehole installation with inadequate cap sealing preventing surface water ingress and contamination from friable surface soil peat disturbance.

5.2.4 Diurnal Physicochemical Change

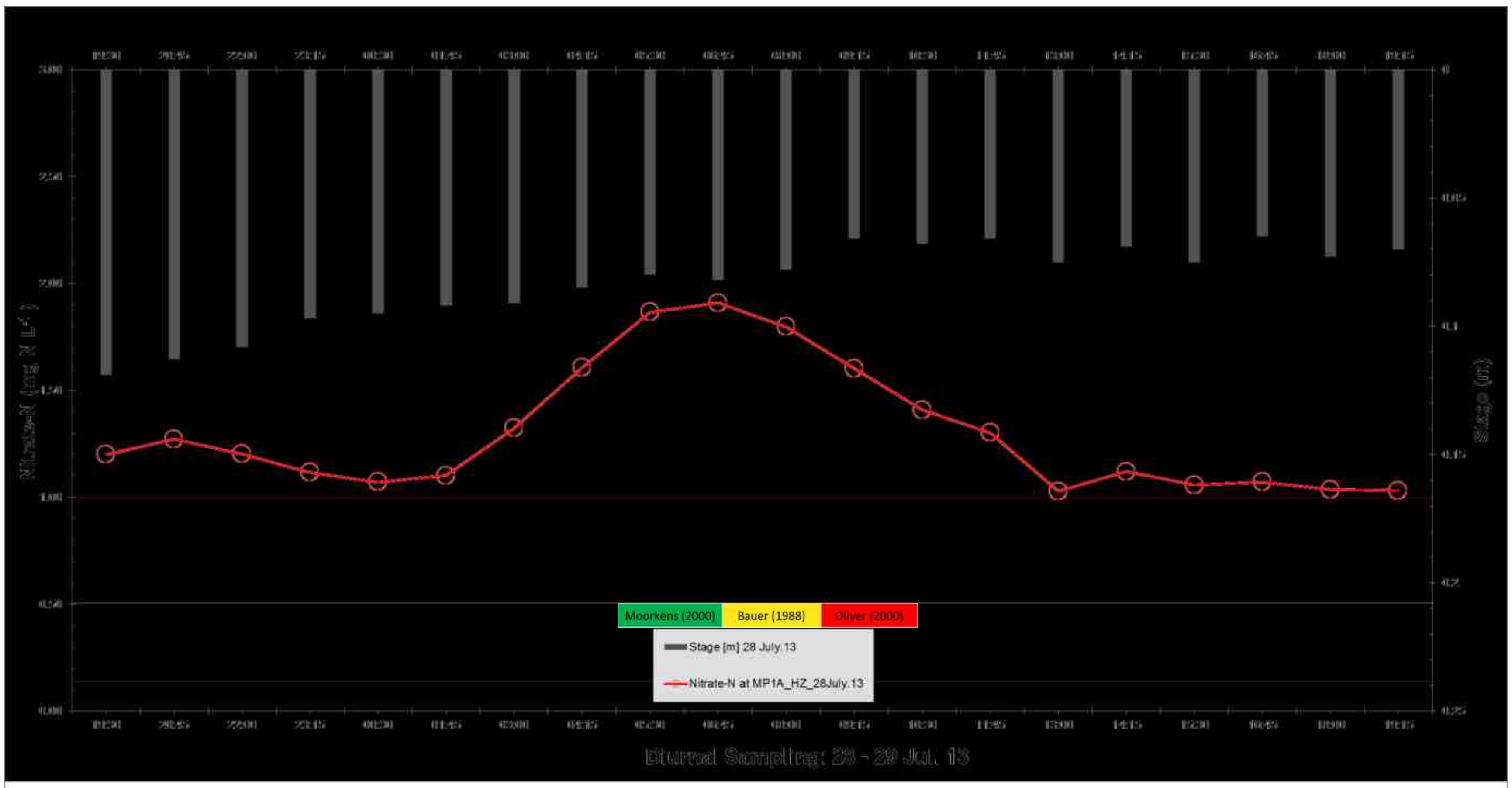
Day—night biotic nutrient concentrations, particularly for soluble nitrate-N (DIN), reveal a variability that results in critical *M. margaritifera* TV exceedance during night-time hours, c. 02:00 – 06:00, when in-stream and hyporheic temperatures drop, often 1°C, with implications for primary productivity (Fig 5.42 – 5.43) .

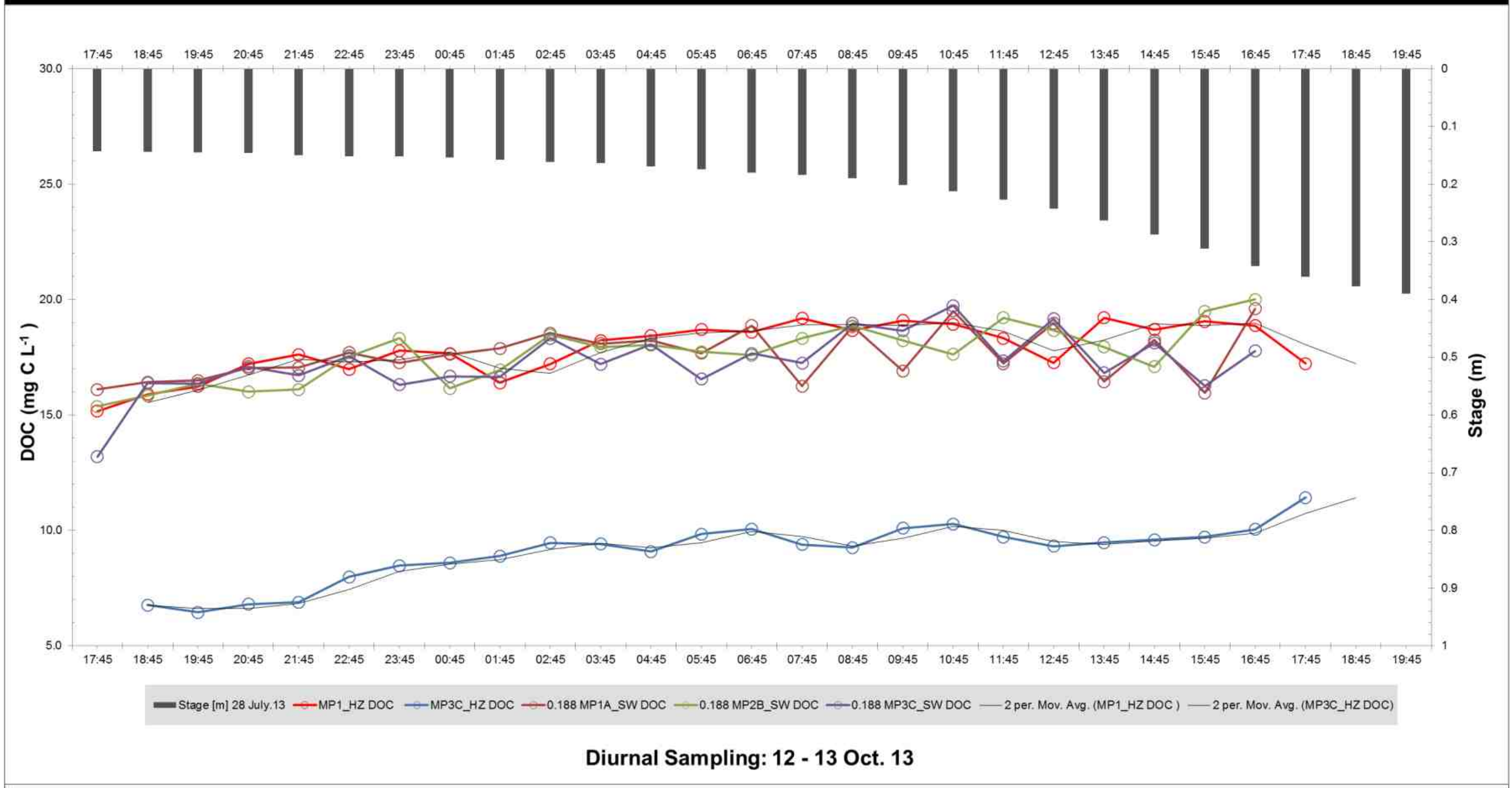
Diurnal monitoring, from 19:45 – 14:45 on 28 – 29th July 2013, during low-flow conditions and in the absence of c.1 month antecedent rainfall, reveals a night-time peak nitrate-N at 1.91 mg N L^{-1}, almost double Oliver's (2000) TV in the hyporheic water of the riffle-head (Fig. 5.42). The same pattern is observable in the 24 time-series nitrate-N data on 12 – 13th October 2013 (Fig. 5.42).

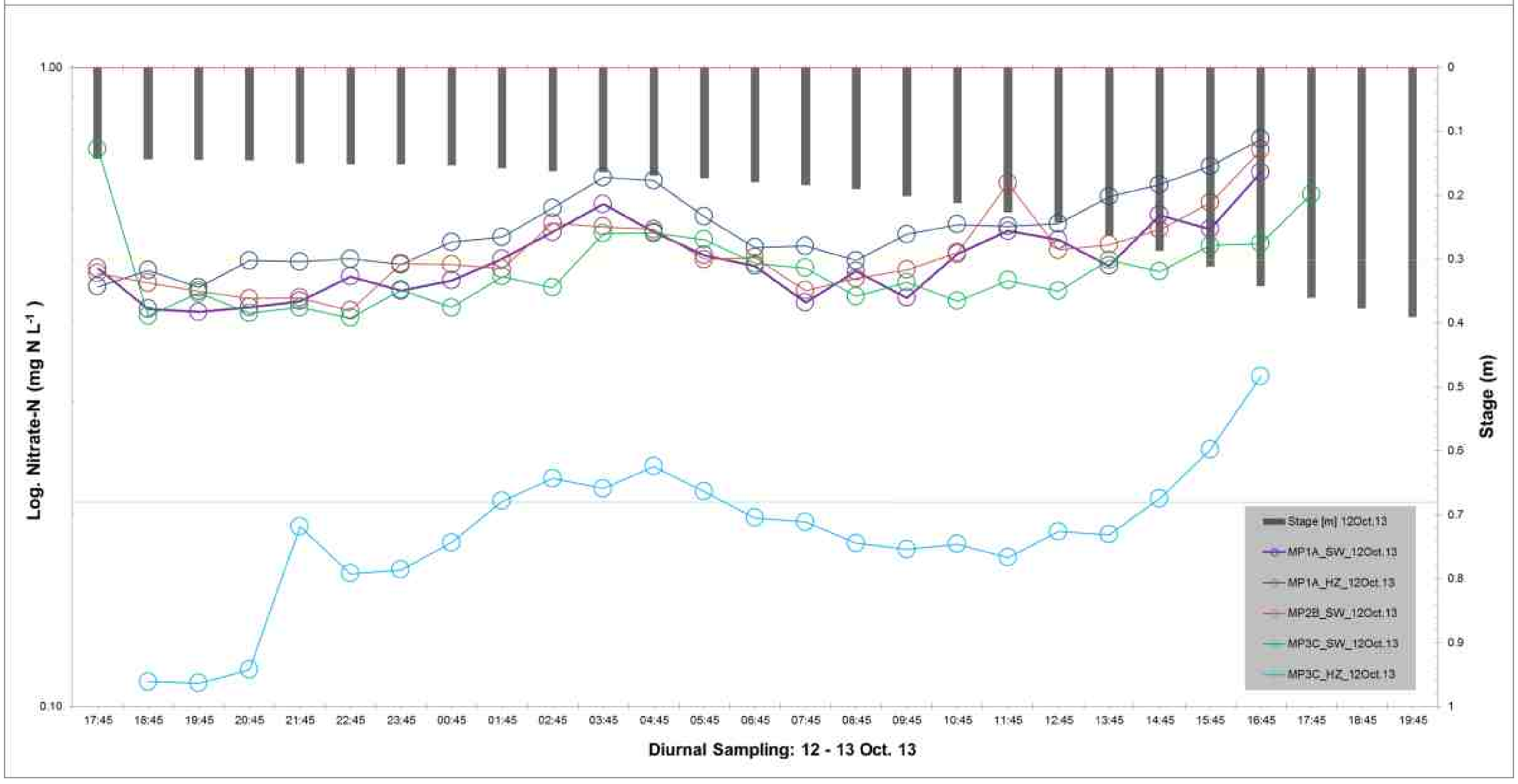
Conversely, when data presented in figure 5.42 are categorised into day and night using local sunset and sunrise times, the daytime nitrate-N arithmetic mean is 0.62 (med. 0.53) mg N L^{-1}, and nocturnal 0.53 (med. 0.48) N L^{-1}. The effects of flood-pulse onset on the 13th October (14:00 –) corresponds to increased daytime nitrate-N, resulting in highest N in the 24-hour time series data being recorded at 16:45, at each monitoring point (Fig. 5.42.) In turn this peak thwarts the validity of a cumulative rank-difference test. Nitrate-N concentrations across in-stream and hyporheic waters during the day are statistically different to concentration at night, with the WMW U test giving a $p>z$ = 0.0087, below the 99% confidence level of $\alpha < 0.01$ (Appendix 8). The $p>z$ value also infers a statistically high probability that daytime in-stream waters will exceed night-time concentrations (Mann and Whitney, 1947).

The diurnal difference is a probable impact of respective equinoctial solar irradiance and temperature, cessation and reduction (Fig 5.42 – 5.43). Daytime photoautotrophs, macrophytes and phytoplankton photosynthesizers switch to nocturnal respiration resulting in a corresponding reduction in dissolved oxygen across ecotones (Fig 5.44 – dissolved oxygen, Hendricks, 1993; Ward, 1989). Reduction in photoautotroph activity also explains the moderate increase in DOC during the night (Trimmer *et al*., 2012; Lansdown *et al*., 2012). The diurnal oscillation in DO and temperature, marked by nocturnal rapid reduction of DO both in SW and HZ, is a likely result of increased chemotrophic activity, synthesising the inorganic energy sources from oxidation of electron donations, from, for example, ferruginous iron (from ironstone, map 3.7.3) and ammonium (Fig. 5.43). This primary productivity switch from photosynthesis to respiration is marked by peak ammonium during dusk (Fig 5.43, 20:00 –23:25), then immediate reduction (23:45 – 08:45). Nitrate-N presents an inverse relationship to this, with N reduction during dusk (Fig. 5.42) followed by peak concentration during the late night (23:45 – 08:45). Theoretically, this may be the point at which oxygen starvation causes a cessation of denitrification and switch to nitrification which results in reduced Ammonium (NH_4^+) (Sprent, 1987), after the draining of sunlit catchment waters, creating a lag-effect (Ward, 1989; Amoros *et al*., 1996).

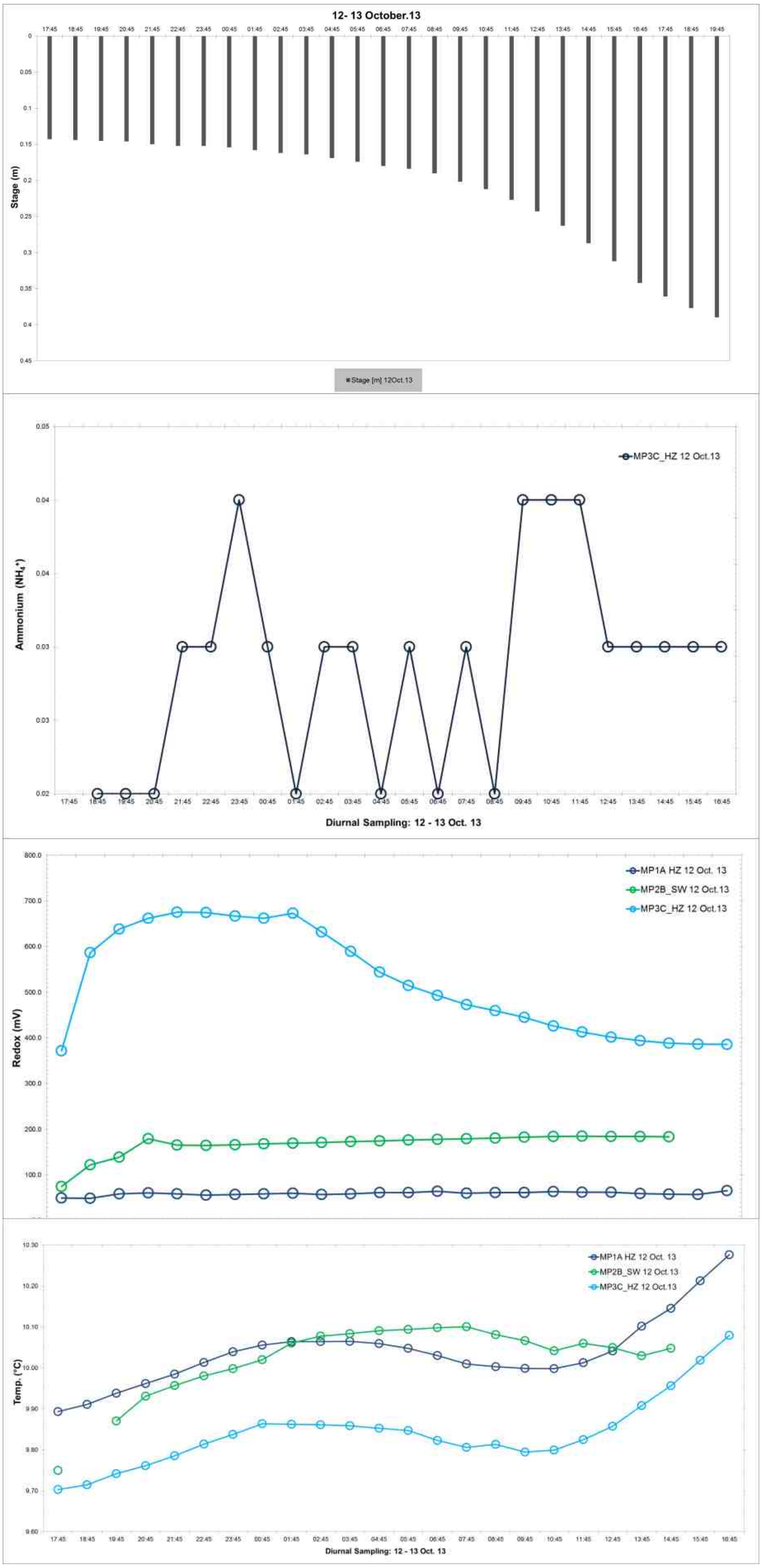
Ammonium (NH_4^+) was mostly below the limit of detection (< 0.02 mg L^{-1}) for all in-stream and hyporheic MPs with the exception of the riffle-tail, at hyporheic MP3C (Fig. 5.43) during 24-hour monitoring on 12 – 13th October. *M. margaritifera* TV for Ammonia (NH_3^+) is 0.01 mg L^{-1}, 0.01 mg L^{-1} below the Dionex ICS 300 detection limit, therefore all hyporheic concentrations at MP3C exceed Moorken’s (2000) TV, when ionized to Ammonium in acidic conditions.


Nitrate-N (mg N L-1)
Stage (m)
Moorkens (2000)
Bauer (1988)
Oliver (2000)
Stage [m] 28 July.13
Nitrate-N at MP1A_HZ_28July.13
Diurnal Sampling: 28 - 29 Jul. 13

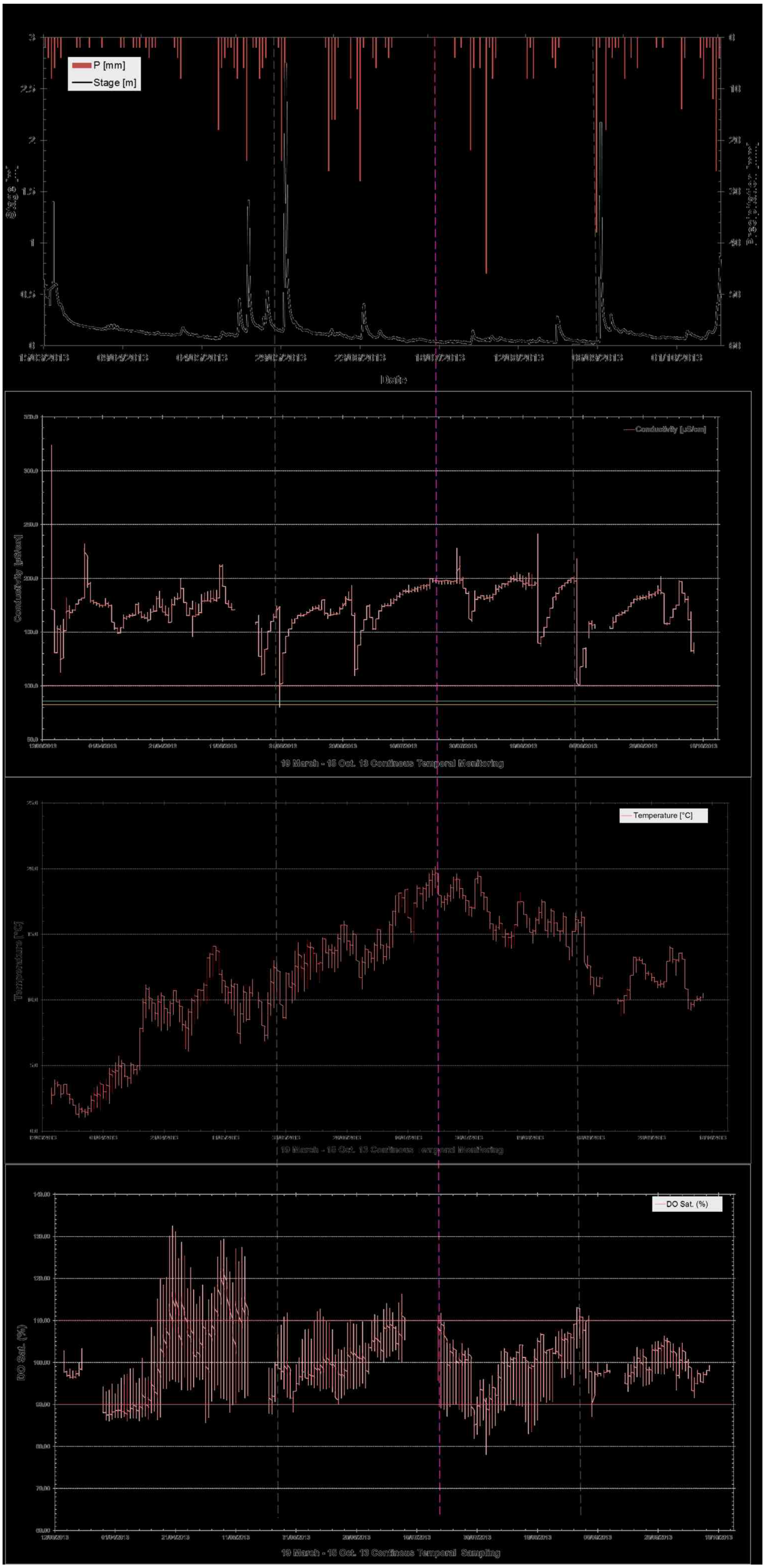

17:45 18:45 19:45 20:45 21:45 22:45 23:45 00:45 01:45 02:45 03:45 04:45 05:45 06:45 07:45 08:45 09:45 10:45 11:45 12:45 13:45 14:45 15:45 16:45 17:45 18:45 19:45
30.0
25.0
20.0
15.0
10.0
5.0
DOC (mg C L-1)
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
Stage (m)
Stage [m] 28 July.13
MP1_HZ DOC
MP3C_HZ DOC
0.188 MP1A_SW DOC
0.188 MP2B_SW DOC
0.188 MP3C_SW DOC
2 per. Mov. Avg. (MP1_HZ DOC)
2 per. Mov. Avg. (MP3C_HZ DOC)
Diurnal Sampling: 12 - 13 Oct. 13


1.00
0.10
Log. Nitrate-N (mg N L-1)
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
Stage (m)
Stage [m] 12Oct.13
MP1A_SW_12Oct.13
MP1A_HZ_12Oct.13
MP2B_SW_12Oct.13
MP3C_SW_12Oct.13
MP3C_HZ_12Oct.13
17:45 18:45 19:45 20:45 21:45 22:45 23:45 00:45 01:45 02:45 03:45 04:45 05:45 06:45 07:45 08:45 09:45 10:45 11:45 12:45 13:45 14:45 15:45 16:45 17:45 18:45 19:45
Diurnal Sampling: 12 - 13 Oct. 13

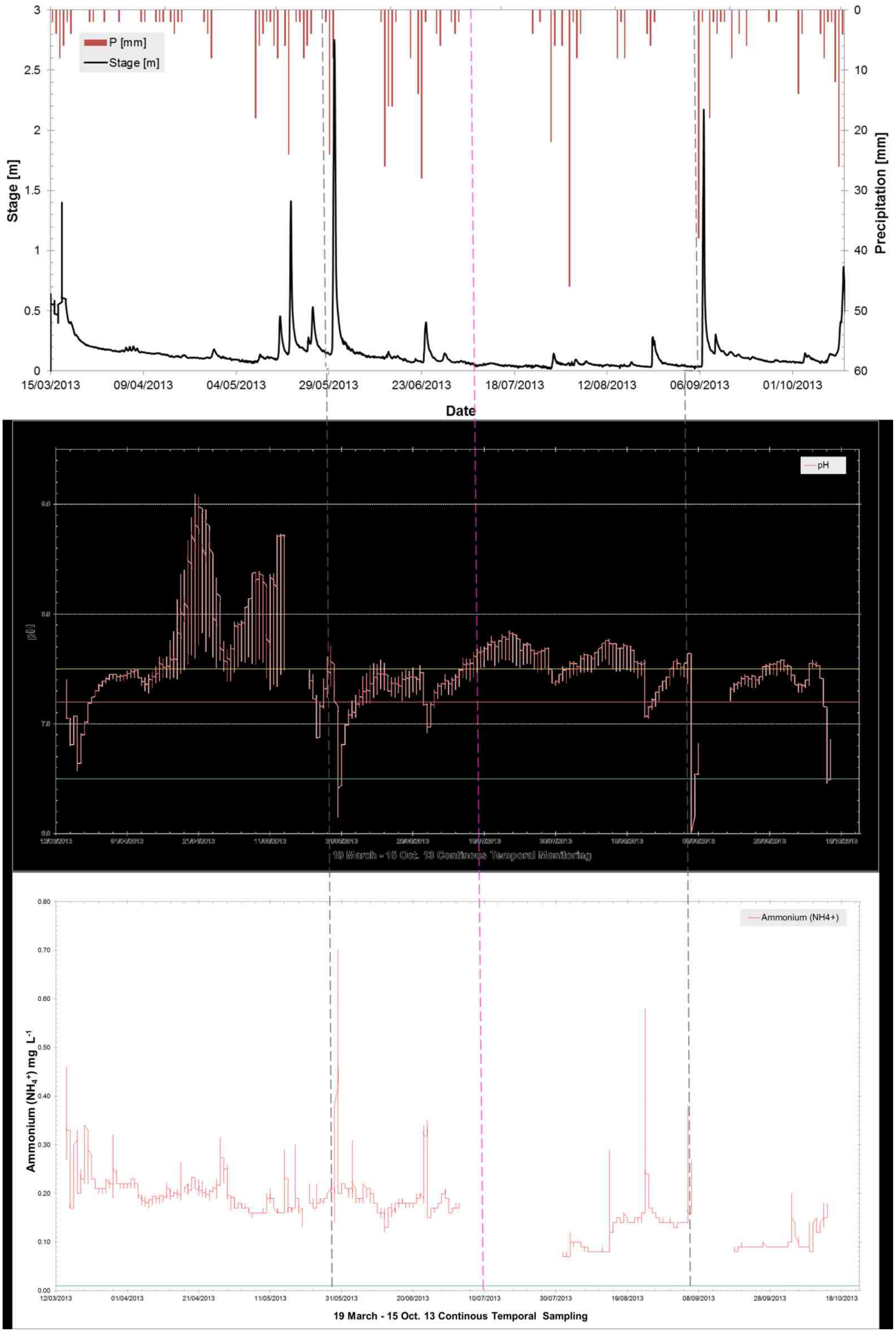
[redacted]


12- 13 October.13
Stage (m)
Stage [m] 12Oct.13
Ammonium (NH4+)
MP3C_HZ 12 Oct.13
Diurnal Sampling: 12 - 13 Oct. 13
Redox (mV)
MP1A HZ 12 Oct. 13
MP2B_SW 12 Oct.13
MP3C_HZ 12 Oct.13
Temp. (°C)
MP1A HZ 12 Oct. 13
MP2B_SW 12 Oct.13
MP3C_HZ 12 Oct.13
Diurnal Sampling: 12 - 13 Oct. 13

[redacted]


P [mm]
Stage [m]
Stage [m]
Precipitation [mm]
Date
15/03/2013
09/04/2013
04/05/2013
29/05/2013
23/06/2013
18/07/2013
12/08/2013
06/09/2013
01/10/2013
0
0.5
1
1.5
2
2.5
3
0
10
20
30
40
50
60
Conductivity [µS/cm]
Conductivity [µS/cm]
50,0
100,0
150,0
200,0
250,0
300,0
350,0
12/03/2013
01/04/2013
21/04/2013
11/05/2013
31/05/2013
20/06/2013
10/07/2013
30/07/2013
19/08/2013
08/09/2013
28/09/2013
18/10/2013
19 March - 15 Oct. 13 Continous Temporal Monitoring
Temperature [°C]
Temperature [°C]
0,0
5,0
10,0
15,0
20,0
25,0
19 March - 15 Oct. 13 Continous Temporal Monitoring
DO Sat. (%)
DO Sat. (%)
60,00
70,00
80,00
90,00
100,00
110,00
120,00
130,00
140,00
19 March - 15 Oct. 13 Continous Temporal Sampling

[redacted]


P [mm]
Stage [m]
Stage [m]
Precipitation [mm]
3
2.5
2
1.5
1
0.5
0
0
10
20
30
40
50
60
15/03/2013
09/04/2013
04/05/2013
29/05/2013
23/06/2013
18/07/2013
12/08/2013
06/09/2013
01/10/2013
Date
pH
pH
9.0
8.0
7.0
6.0
12/03/2013
01/04/2013
21/04/2013
11/05/2013
31/05/2013
20/06/2013
10/07/2013
30/07/2013
19/08/2013
08/09/2013
28/09/2013
18/10/2013
19 March - 15 Oct. 13 Continous Temporal Monitoring
Ammonium (NH4+)
Ammonium (NH4+) mg L-1
0.80
0.70
0.60
0.50
0.40
0.30
0.20
0.10
0.00
12/03/2013
01/04/2013
21/04/2013
11/05/2013
31/05/2013
20/06/2013
10/07/2013
30/07/2013
19/08/2013
08/09/2013
28/09/2013
18/10/2013
19 March - 15 Oct. 13 Continous Temporal Sampling

[redacted]

5.2.5 Upper Crunkly Gill – Hydrodynamic And Seasonal In-Stream Physicochemical Trends

During the monitoring period 19th March – 15th October 2013 the fundamental physicochemical 'quality' of discharge entering Crunkly Gill is altered by the prevailing hydro-meteorological conditions (Figs 5.44 – 5.45). Firstly, electrical conductivity (µS/cm), taken as aqueous conductance of electricity through inorganic ionic solution, is affected by anions$^{(-)}$ such as nitrate, phosphate and chloride or, cations$^{(+)}$ such as calcium, sodium and iron (Foster *et al*., 1982; Eaton *et al.,* 2005). EC is reported in microsiemens per centimetre (µS/cm), reflecting ion concentration (*ibid*). Distilled pure waters have an EC range of 0.5 – 3 µS/cm. The *M. margaritifera* upper TV is 100 µS/cm (Table 2.1., *ibid*), the YSI probe auto-references EC to 25°C since ion activity is influence by temperature. Where organic compounds such as oil, chlorophyll and Invisible Dark Organic Matter (IDOM) are presented in solution EC has a low accuracy (Foster *et al*., 1982; Eaton *et al.,* 2005; Pereira *et al*., 2014).

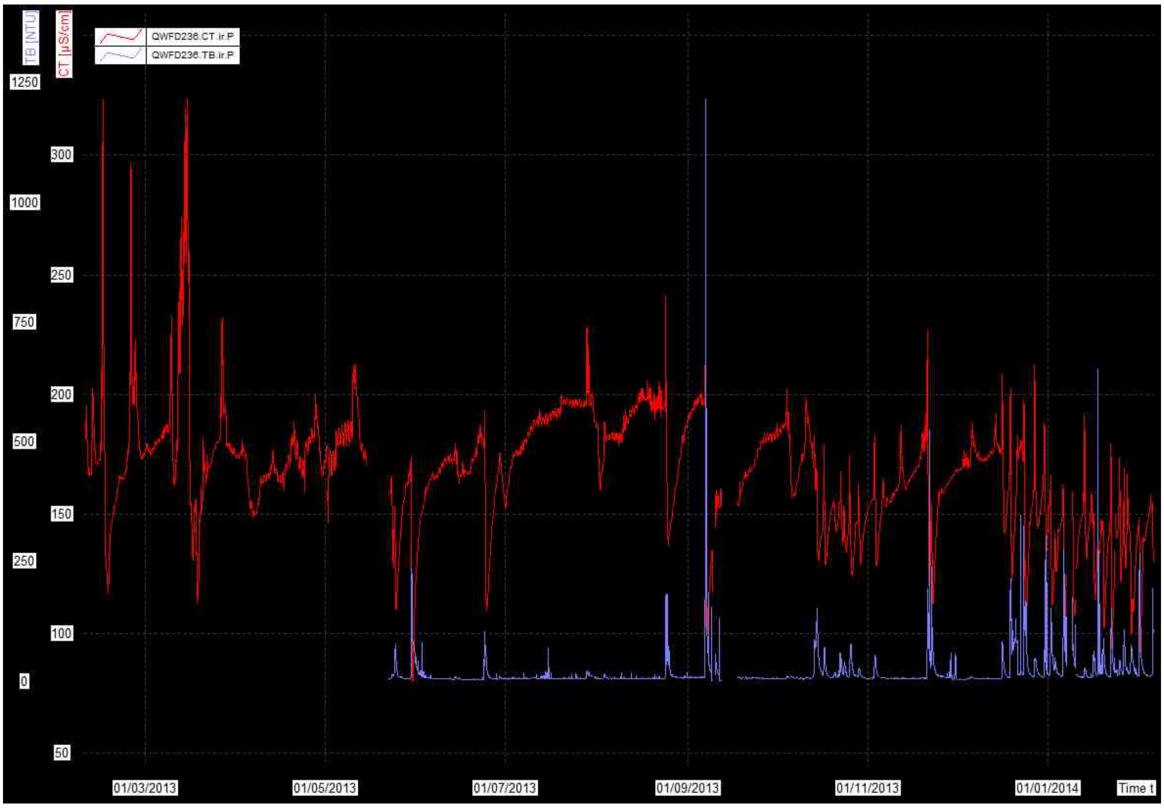
EC (Fig. 5.44) generally fluctuates above Oliver's (2000) upper *M. margaritifera* TV, with a sample on 30th May 2013 at 80.7 µS/cm being the exception, but still exceeding Bauer (1988) and Moorken's (2000) TV. The monitoring period arithmetic mean EC is 174.36 µS/cm (s = 20.09). EC data present a varied relationship with discharge (Q) and precipitation (P), for instance on 20th March 204; Q_p and P_{max} coincides with a peak EC at 322.7 µS/cm (Fig. 5.44). In the period January to March the North East region's rainfall was 76 percent of its Long-term Average (LTA, 1971 – 2000; CEH, 2013). Below average antecedent P, but heavy snow accumulation and catchment freezing resulted in a light P_{max} event at c.10mm h^{-1} producing a flood-pulse (*ibid*). The combined antecedents of soil moisture deficit, soil freeze and subsequent snow thaw where likely solute flow pathway generation mechanisms delivering labile 'new' ions to channel waters (Bishop *et al*., 2004; Burt and Pinay, 2005). Frozen soils have reduced relative k_v, enhancing hydrophobicity and repellence of P, generating overland flow pathway connectivity (Burt and Williams, 1976; Bracken and Croke, 2007, CEH, 2013). The data presented in EC graph of figure 5.44 also have an inverse relationship, where EC "troughs" concur with, or have lag effect after $Q_{p.}$

Temperature (°C) exhibits a clear seasonal trend, peaking at 20.17°C on 17:31 19th July 2013 in a period of extensive low-flow. Concurrently a reduction in DO occurs, causing prolonged salmonid and mussel stress (Skinner *et al*., 2003; Hendry *et al*., 2003). DO is at its lowest percentage saturation at 78.1% on 2nd August 2013, 11.9% below Oliver's (2000) TV band at 90%. As aforementioned there is also diurnal oscillation in DO and temperature.

pH presents a clear trend with flood hydrograph discharge (Fig. 5.45). The monitoring period mean pH is 7.48 (s = 0.34). However spate acid flush occurs, with the lowest spot pH = 6.01

on 6th September 2013 during a day of P_{max} = 38mm h^{-1} and stage reaching 2.27 m. A flood of this nature, with early onset $Q_{P,}$ low lag-time and leptokurtic-shaped hydrograph, suggests a ‘flashy’ hydrological regime with overland flow connectivity (Junk *et al*., 1989; O’Connell *et al*., 2007). These acid flushes exceed *M. margaritifera* TV (Table 2.1). The arithmetic mean alone does not exceed Bauer’s (1988) and Moorkens’ (2000) TV, but does exceed Oliver’s (2000). However the standard deviation (*s*) infers some variability, often to excessively alkaline conditions too.

Ammonium (NH_4^+) concentration rises and falls with the flood hydrograph (Fig 5.45). Arithmetic mean ammonium (NH_4^+) = 0.17 (*s* = 0.06), exceeding *M. margaritifera* TV (Table 2.1). Discharge entering upper Crunkly Gill appears to suffer from the ‘muddy floods’ phenomena rich in suspended sediment from potential surface runoff generation and erosion where hillslope and riparian surfaces remain liable to mobilisation of surface matter (O’Connell *et al.,* 2007; Bracken and Cloke, 2007; Bracken *et al*., 2013). This dissolved, colloidal and suspended matter contributes to scaled water opacity (Eaton *et al., 2*005). Clarity is measured by turbidity (NTU) using light-ray penetration and scatter through a specimen to derive an NTU (Nephelometric Turbidity Units) (*ibid*). Figure 5.46 shows extreme peaks in turbidity, followed by a lag-peak in EC. Potentially this occurs due to seston and abioseston breakdown and fining. Upon reaching a state of solution, free ions may be available to exchange, hence the lag peaks in EC (Alloway and Ayres, 1994; Bishop *et al*., 2004). The peak turbidity at 1,217.6 NTU on 6th September 20:13 (18:31) occurs with a post August temperature peak, since turbid water has a low albedo coefficient and will absorb greater solar (ir)radiation where there is no riparian shading.



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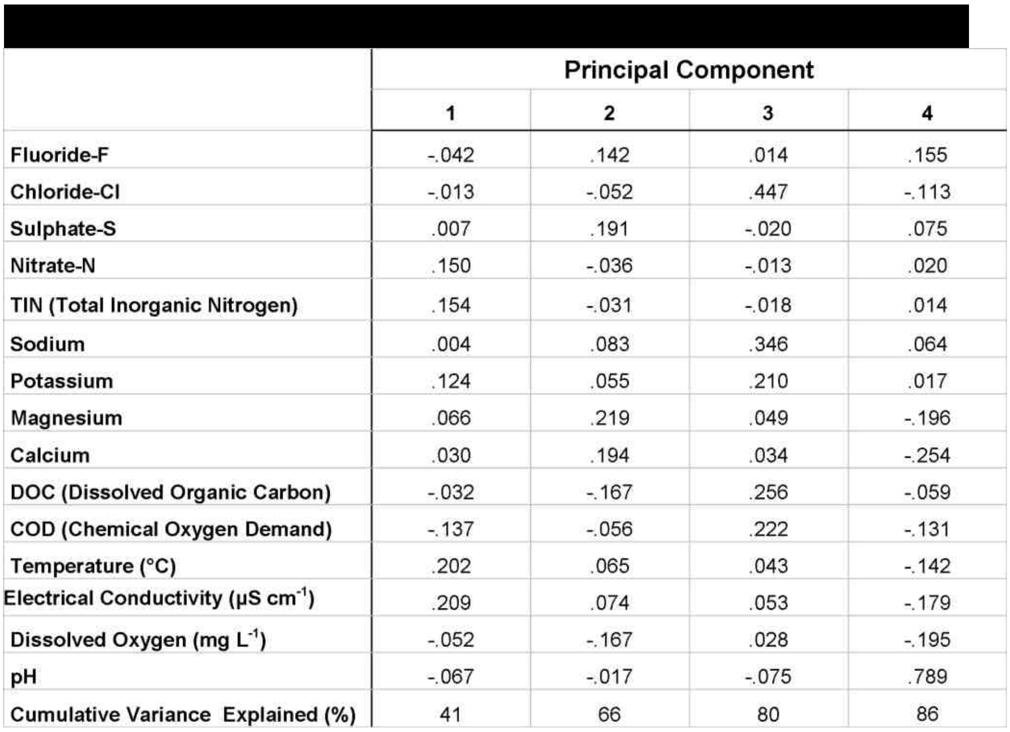
5.2.6 Data Reduction and Variance Analysis – Principal Component Analysis (PCA)

The inductive factoral approach of PCA was adopted as a means of transformational dataset reduction, considering the sample *n=440* which included numerous physicochemical variable (Jolliffe, 2002). PCA is a multivariate statistical procedure that produces components from large data arrays (Jolliffe, 2002; Hamilton, 2004). The analytical power comes from the summary pattern (reproduced) correlations which are determinants of the 'relationship between elements in a dataset' (Nelson, 2003:118). Components being, *sensu lato* 'combinations of the variables that contain most of the variance', which are derived from an observed correlation matrix (Hamilton, 2004: Stata, 2013). Orthogonal PCA was adopted for analysis in this instance, forcing the factor rotations to be oblique right angles (Jolliffe, 2002).

Since PCA is scale-dependent, dataset values were standardized under the Fisher z – transformation in order to harmonise, scale and represent the data (Jolliffe, 2002; Hamilton, 2004; Stata, 2013). Outliers and extreme values were removed from the dataset, where they rarely exceeded 3 sample (*s*) standard deviations (99.7300204%) – a removal of 0.2697796%. Data from the YSI Sonde were not included in this PCA analysis since samples were from a distant upstream location.

[redacted]

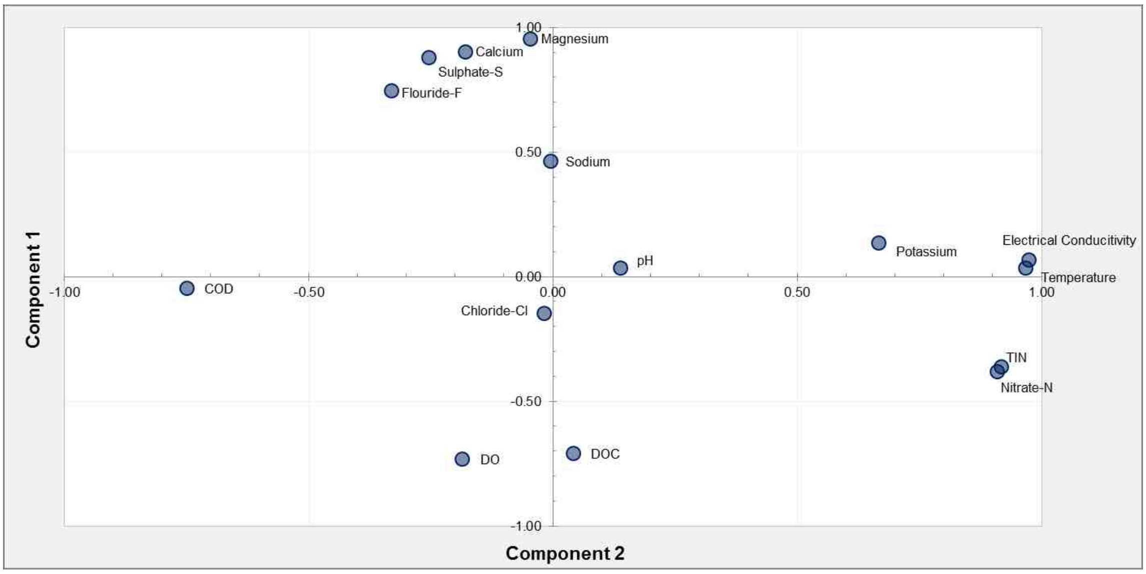


	Principal Component			
	1	2	3	4
Fluoride-F	-.042	.142	.014	.155
Chloride-Cl	-.013	-.052	.447	-.113
Sulphate-S	.007	.191	-.020	.075
Nitrate-N	.150	-.036	-.013	.020
TIN (Total Inorganic Nitrogen)	.154	-.031	-.018	.014
Sodium	.004	.083	.346	.064
Potassium	.124	.055	.210	.017
Magnesium	.066	.219	.049	-.196
Calcium	.030	.194	.034	-.254
DOC (Dissolved Organic Carbon)	-.032	-.167	.256	-.059
COD (Chemical Oxygen Demand)	-.137	-.056	.222	-.131
Temperature (°C)	.202	.065	.043	-.142
Electrical Conductivity (μS cm^{-1})	.209	.074	.053	-.179
Dissolved Oxygen (mg L^{-1})	-.052	-.167	.028	-.195
pH	-.067	-.017	-.075	.789
Cumulative Variance Explained (%)	41	66	80	86

In order to test the adequate correlation between variables a Bartlett's Test of sphericity was performed, deriving $X^2 = 0.000$ (Jolliffe, 2002; Hamilton, 2004). $X^2 = \alpha < 0.01$. Being below the 99% confidence level – the data are therefore statistically significant for PCA (*ibid*). The Kaiser-Meyer-Olkin (KMO) Measure of Sampling Adequacy scored 0.557, with 0 inferring too little in common between variables and 1 indicating, according to Kaiser (1974), 'marvellous'! In order to extract the significant eigen values for analysis data were plotted on a scree plot, any factors less than 1 were excluded for extraction and subsequent PCA, leaving 4 factors (Appendix 9).

The largest amount of variance explained by the component analysis solution is expressed as a percentage in the communalities table (Appendix 9). In this 4 component model the top 3 percentage values which account for most of the variance are TIN at 98.7 %, nitrate-N at 98.6% and EC at 96.4%. This pattern is also represented in the component scores in figure 5.47 and loading tables in Appendix 9. For principal component 1 which cumulatively explains 41% of the variance, TIN holds the highest weighting score (Appendix 9).

Inspection of the pattern matrix further reveals the underlying structure of the data (Appendix 9). When EC increases, temperature also changes, whilst TIN and nitrate concentration vary with the other parameters, in the first component (Appendix 9). Temperature effects are a keynote influence on anion activity, potentially where influences of cool, depleted groundwater exchange results in variability of other hydrochemical parameters (Hancock *et al*., 2005). Again, the weighting correlation for hydrochemical parameters in the second component exceeds 0.9 for magnesium and sulphate and, for calcium is 0.879, each of which are source water tracers inferring the influence of groundwater on the ecosystem (Worrall *et al*., 2003, Fig 5.47).



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5.2.7 Examination Of Reach-Scale Average Hydrochemistry Concentrations And Statistical Difference Between Ecotones

Grouping data into source-water categories of in-stream, hyporheic and groundwater – borehole and land-drain – facilitated the determination of average concentrations for key *M. margaritifera* physicochemical parameters in riparian ecotones. In the main-channel (Table 5.2.4), where a statistical confidence level of $\alpha < 0.05$ (95%) was adopted, in-stream waters *vs* hyporheic waters are different for nitrate-N, DOC and, for calcium, they are very different $p = 0.00$ (99%). For all observations, with the exception of DOC, average concentrations are higher in the hyporheic zone (Table 5.2.4). Nitrate-N, ammonium, calcium, DO and EC exceed respective *M. margaritifera* TVs, following Moorkens' (2000) TV there are some parameters which still do not have TVs, for example DOC (Table 5.2.4., Fig. 5.34). Carbon appears dominant over nitrogen, expressed in a DOC (Organic): TIN (inorganic) ratio. While indiscriminate for organic-C content in TIN, the ratio suggests nutrient limitation and potential DOC inputs from C – rich peaty headwater POM loss and allochthonous (Worrall *et al*., 2003; 2004; Burt *et al*., 2010A). Anthropogenic atmospheric deposition may also be implicit in N reduction, for instance 'a doubling of CO_2 concentration reduces plant N content by about 16%, on average' (Sterner and Elser, 2012). The absence of light in the HZ explains a higher C/N ratio, where reduced photosynthetic rate occurs (GPP, Gross Primary Productivity), decreasing autotroph activity – the "fixers" of DOC (Singleton and Sainsbury, 2006; Sterner and Elser, 2012).

In the secondary-channel (Table 5.2.5) the patterns exhibited in the main-channel are largely repeated. However, there are some fundamental concentration differences. Nitrate-N is more concentrated and exists immediately below Oliver's (2000) TV, nitrate-N concentrations is marginally higher in SW as opposed to HZ, an opposite affect compared to the main-channel. Low flow occurs through the secondary channel, with flow adopting the route in times of spate – forming thread overflow channel. This is represented in the oxygenation of the riverbed gravels (Table 5.2.5). The deep floodplain groundwater are acidic with an arithmetic mean of pH = 5.82 (Fig. 5.39). Conversely the mean pH = 8 in shallow groundwater suggests alkaline surface horizons. EC is particularly high and may be an impact of bank slump and immobilisation of fine run-off from clay lens on the outer meander (MP4, Fig 5.37).

Moorkens (2000)	Bauer (1988)	Oliver (2000)

			0.57 (σ = 0.18)				0.02 (1*x*, *n* 86 <LOD)	12.73 (σ = 1.02)		79.85 (σ = 16.57)	163.28 (σ = 16.86)		
			0.68 (σ = 0.46)				0.03 (σ = 0.01)	18.07 (σ = 6.74)		84.34 (σ = 15.66)	166.03 (σ = 11.06)		

Moorkens (2000) Bauer (1988) Oliver (2000)

		0.95 σ = 0.13)		8.06 (σ = 5.79)		0.03 (σ = 0.05)	12.30 (σ = 4.37)		86.51 (σ = 8.43)	192.63 (σ = 34.70)		
		0.90 (σ = 0.38)				0.14 (σ = 0.09)	25.07 (σ = 13.42)		57.30 (σ = 29.21)	256 (σ = 53.07)		
		0.79 (s = 0.37)					38.90 (s = 24.73)	8.00 (x)	85.60 (x)	1,027 (x)		
		0.25 (s = 0.20)					87.94 (s = 23.21)	5.82 (s 1.71)	10 (s = 7.56)	1,271 (s = 128.30)		

5.2.8 Conclusions

This section applied a variety of instrumentation and statistical procedures to determine hydrochemistry change over the reach-scale and through in-stream, hyporheic, deep and shallow groundwater. Each measure sought to determine the physical and chemical properties of the considered ecotone within the hydraulic biotope. Where flow discharged into— and out off— the riverbed, data showed statistically significant change (*u* and *t*) and stoichiometric transformation. Notably riffle-tail water is depleted, particularly for nitrate-N, presenting similar physicochemical attributes as the monitored alluvial groundwater. Fluvial geomorphology is determined to be fundamental with riffle streambed roughness generating more TKE (Turbulent Kinetic Energy) and subsequent in-stream oxidation peak at the riffle-tail, once it meets calmer pool-habitat waters in-stream. The inductive factoral approach of PCA determined that TIN, nitrate-N, EC and temperature are responsible for a majority of dataset variance in a four component model explaining 86% of the cumulative variance. [redacted] This provided the basis to compare the location to a site where anthropogenic impacts were prominent, Danby Sewage Treatment Works (Section 3.5).

5.3 Danby – Sewage Treatment Works

5.3.1 Synopsis

This section builds upon section 5.2 to assess hydrochemistry through a reach that is eco-hydromorphologically impacted by humans; by STW outfall, meander rock-armour bank protection and intensive livestock grazing resulting in riparian poaching (Section 3.5). The STW reach geomorphology contrasts to both the Moors Centre reach which is entrenched and straight and the Crunkly Gill reach which is anarbranching, braided and where high velocity flows emanate out from a steep-sided gill into a planar setting – *sensu latto* the piedmont effect (Map 3.6; Schumm, 1985; 1988; Dunkerly, 2000; see glossary).

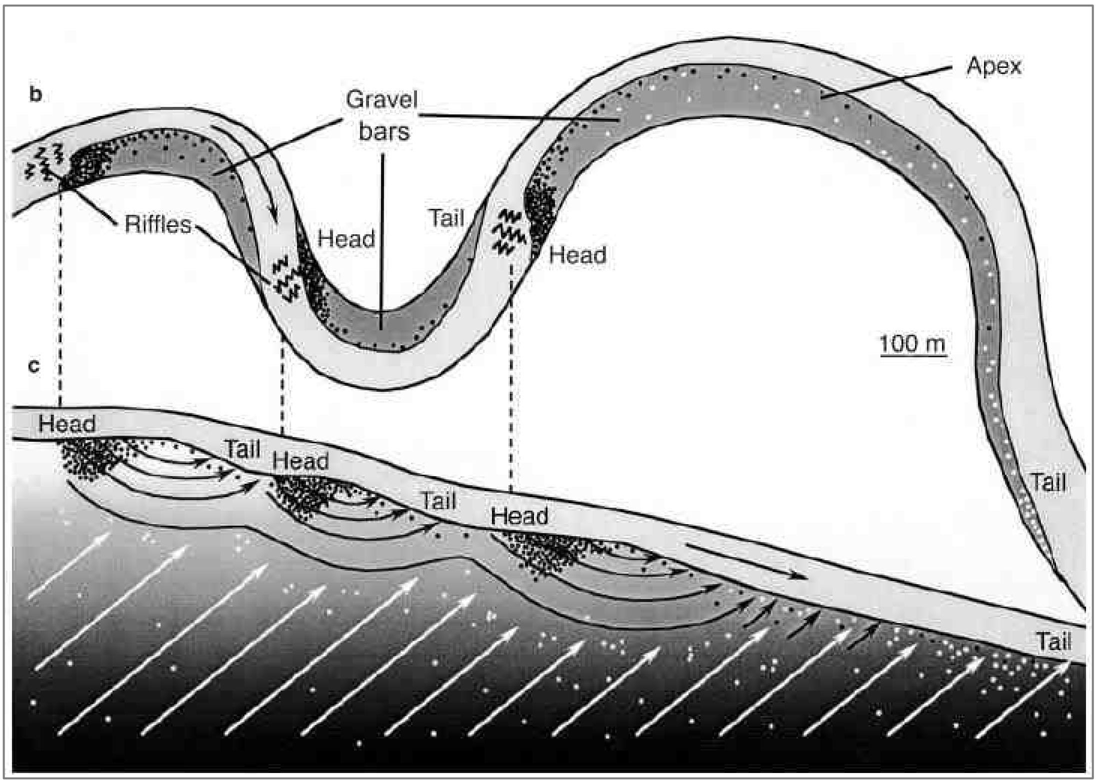
Unlike Lealholm Crunkly Gill and Danby Moors Centre, a full set of VHG and Q_v were not sampled. In the absence of sewage tertiary treatment, sampling health and safety presented a risk, particularly coliforms (Appendix 10, Sweeting, 1993). In view of this risk, slug tests were not performed. One VHG was derived at the riffle-tail MP8, coupled with solute data; there is evidence of exchange flows (Bus *et al.,* 2009; Dearden and Palumbro-Roe, 2010). The data provide HEF context, for injection and ejection, between stream and substratum. Hydrochemistry variables, particularly chloride-Cl, sulphate-S, temperature (°C) and calcium serve as conservative tracers of variable source water contributions (Worrall *et al.,* 2003), in addition to obvious biotic-nutrient rich discharges (Jarvie *et al*., 2006; 2013). Following hydrogeological exchange determinations, reach-scale hydrochemistry data are presented for all parameters at each monitoring point. *Ranunculus fluitans* (water crowfoot) and *Amblystegium riparium* (moss) assignment of Species Trophic Rank (STR) indicates longer-term artificial enrichment of this reach (Holmes and Newbold, 1984; Holmes *et al,* 1999).

This section completes by presenting reach-scale average values for *M. margaritifera* hydrochemical parameters, the statistical difference between the groups of source water (SW, HZ, and GW) and between monitoring points upstream, proximal to and, downstream of STW effluent outfall. Principal component analysis (PCA) results are finally presented.

5.3.2 Hydraulic Gradient And Flux Across A Pool-Riffle-Pool

During standpipe monitoring on 15 August 2014 at 16:16 VHG = 10.76. HEF was discharging out of the bed and up-welling at riffle-tail (Dahm *et al*., 2006; Ibrahim *et al.,* 2010; Huang *et al.,* 2014). This supports observations by Malard *et al.* (2002) (Fig. 5.48). The convex in-stream surface profile suggests up-welling in the pool (Buffin-Bélanger *et al*., 2000; Fig 5.48), potentially with a high vertical and downstream flow component (Bennett and Best, 1995).

However, this ejection may be a flow artefact, potentially where a thermocline upwardly displaces warm STW discharge and the relatively un-mixed colder adjoining stream water (Ferguson *et al*., 2003). Riffle-head water (MP4) is cold and is anticipated to discharge into the riverbed in accordance with monitoring at all other sample reaches, theory and thermocline displacement (Thomspon 1986; Ferguson *et al*., 2003; Fig. 1.1., Appendix 11). YSI probe temperature data and field observation note colder water inflow displacing warmer discharges to the inner inflexion of the meander (Appendix 11). Downwelling into the riverbed where warmer "new" discharges are high, rates up to a consented 60.29 $m^3 h^{-1}$ in storm flow suggests thermodynamic displacement (Appendix 6, Ferguson *et al*., 2003; Buffin-Bélanger *et al*., 2000).



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Analysis of temperature, conservative solutes and eutrophic hydrochemical concentration change, supports riffle-head downwelling and riffle-head upwelling patterns (Hancock *et al*., 2005). Fundamentally, the hydromorphological setting of a meander with high transmissivity riparian superficial drift affords a reach field site where in-stream to groundwater exchange during spates can be examined. This is in addition to meander truncation by a HPF discharging into the eddy and exfiltrating as leachate between MP7 and 8 (Thompson, 1986; Malard *et al.,* 2002).

5.3.3 Reach-Scale Hydrochemistry

5.3.3.1 Dissolved Organic Carbon and Nitrogen: Fine-Scale Variability

Dotplots in figures 5.49 – 5.51 present groundwater, in-stream and hyporheic reach-scale longitudinal hydrochemical concentration variability, for nitrate-N, ammonium (NH4+), nitrite-N, DOC and phosphate-P; many of these vary in tandem. MPs 1 and 2 are upstream of the sewage outfall, with MPs 3 and 4 being proximal to the storm flow (>Q_p 1 in 6 years, Σ1, 447 m^3 d^{-1}(all outfalls)) and dry flow effluent outfalls (<Q_p 1 in 6 years, 240m^3 d^{-1}) (Appendix 6, Fig. 5.62; Maps 3.8). In-stream and hyporheic nitrate-N concentration is similar prior to dry flow outfall at MP4, varying in surface water means (MP1 – 3) of 0.62, 0.68, 0.60 mg N L^{-1}, and in the hyporheic zone 0.71, 0.80, 0.60 mg N L^{-1} (Fig. 5.49). At MP4 nitrate-N peaks to the highest mean concentration through monitoring-reach, in-stream at 12.3 mg N L^{-1}. The highest spot concentration at all monitoring points was at MP4, 25.7 mg N L^{-1} on 18:42 on 27 July 2013, during a period of extensive low flow. A nitrate-N value at this concentration is harmful to the majority of aquatic life and exceeds the human EC Drinking Water Directive threshold of 11.3 mg N L^{-1} (Sweeting, 1993; Chapman and Kimstach, 1996; EC Drinking Water Directive (80/788)). No threshold for nitrate-N concentration exists in the Danby STW discharge consent (Appendix 6 and 11). MP4 hyporheic nitrate-N is reduced compared to SW, which has a mean concentration of 1.38 mg N L^{-1} (s = 0.63) (Fig. 5.49, Map 5.3.1-2). *Amblystegium riparium* (moss) covers the hyporheic well draw-down alluvium at this location, so bioavailable nitrate-N may readily be fixed (Haack and McFeters, 1982, Fig. 5.61). Following outfall in-stream nitrate-N concentrations rapidly dilute and reduce; however, concentration averages remain higher in the riffle-tail at MPs 6 – 8, particularly in the HZ, suggesting HEF from ingress of nitrate-N rich in-stream waters (Fig 5.49, Appendix 11, Crenshaw *et al*., 2010).

Detailed assessment of ecotonal nitrate-N shows a lag-effect input for pore-waters of the hyporheic zone, potentially related to in-channel velocity generating hyporheic flow pathways (Thompson, 1986; Malard *et al.,* 2002). Groundwater arithmetic mean nitrate-N is 7.51 mg N L^{-1}, with outer meander bend MPs sampling high nitrate-N in the HZ (Fig. 5.49, Map 5.3.1–2). Outer meander hyporheic and groundwater nitrate-N is from three main source-pathways: in-stream concentrate nitrate-N “driving” into the floodplain during spates with downward percolation (Triska *et al*., 1993; Crenshaw *et al*., 2010), livestock excrement and detritus vertical ingress to the groundwater table (Jarvie *et al*., 2008) and a groundwater pollution plume from base of the STW compound, transmitting effluent toward topographical depression (Smith, 2005; Howden *et al*., 2011; 2013). 0.0108 kg N d^{-1} of nitrogen is produced by humans (Heathwaite, 1993), with intensive livestock farming contributing a land loading as high as 1600 kg N ha^{-1} a^{-1} (Loehr, 1974), cattle slurry has a 6.0% N dry matter content (Gostick, 1982). All in-stream, hyporheic and groundwater nitrate-N data (n=169) exceeds the *M. margaritifera* TV with no single value falling below Moorkens (2000) TV.

Nitrite-N exhibits a similar trend of nitrate-N, with concentrations in the hyporheic zone being reduced compared to in-stream values. SW Arithmetic mean TIN is 1.66 mg N L^{-1} and 1.01 mg N L^{-1} in HZ (Table 5.3.3), unlike the in-stream and hyporheic waters at Crunkly Gill which are statistically different for TIN (p = 0.02), Danby STW waters are not statistically different (p = 0.58). Potentially this is due to the sandy bulk transmissivity of the Ellerbeck soil which rapidly facilitates HEF/HFP (Alloway and Ayres, 1994:37; Smith, 2005; NSRI, 2013B).

Phosphate-P displays a pattern with nitrate-N and nitrite-N (Fig. 5.49., 5.53., Maps 5.3). However no P was detectable prior to mixing with STW discharge waters, the same is generally true of NH_4^+ with the exception of 0.03 mg L^{-1} and 0.14 mg L^{-1} (Appendix 6). These samples were taken on the 27th and 28th July 2013 during low flows where only macropore flow existed through the riffle gravels (<1cm) (Fig 5.44 (stagegraph)). Groundwater arithmetic mean phosphate-P concentration is 0.33 mg P L^{-1} (Fig. 5.53).

Ammonium (NH_4^+) shows an overall similar trend to NO_3^-–N and NO_2^-–N. A key difference is that MP3A monitored an elevated NH_4^+concentration both in-stream and in the hyporheic zone of the eddy that circulates discharge from the storm flow outlet, when discharging (Figs 5.49–5.51., Map 5.4.1–2). This pattern is not observable in the spatial distribution of phosphate-P or nitrate-N. Moreover, bankside leachate of enriched NH_4^+ occurs between MPs6 – 8, where NH_4^+ patch concentration is higher relative to other MPs (Map 5.4.2). The patch enrichment is a likely result of a HFP, where discharge into the bank occurs and is transmitted through the floodplain (Dent *et al*., 2001; Boulton *et al*., 2010; Wainwright *et al.,* 2011). Where NH_4^+ or P is detected, it exceeds all *M. margaritifera* TV (Table 2.1).

DOC concentrations are relatively isotropic through reach-scale in-stream and hyporheic waters. There is little DOC variability in groundwater (Fig. 5.52). However DOC occurs at reduced hyporheic concentration at MP3A and MP5 where DO (Fig. 5.58) percentage saturation is low and reducing conditions prevail, generally below 0mV (Fig. 5.55). Unlike phosphate-P, nitrate-N, TIN and ammonium; DOC has statistical difference (p=0.00) between SW and HZ, at arithmetic means of 17.73 and 12.72 mg C L^{-1} (Table 5.3.3.). Outfall results in a marginal increase in DOC concentration (Fig. 5.52). Nitrate and TIN are statistically different in the main-channel at Lealholm Crunkly Gill reach, with a p = 0.04 and 0.02, respectively (Table 5.3.4.). Prior to outfall (MP1) the concentration of phosphate-P and TIN in in-stream and the HZ is statistically different to the waters at the STW outfall (MP4), and MPs downriver (Table 5.3.1). Where ortho-P was not detected on the chromatograph, zero values were used for MPs Mann-Whitney U-test difference.

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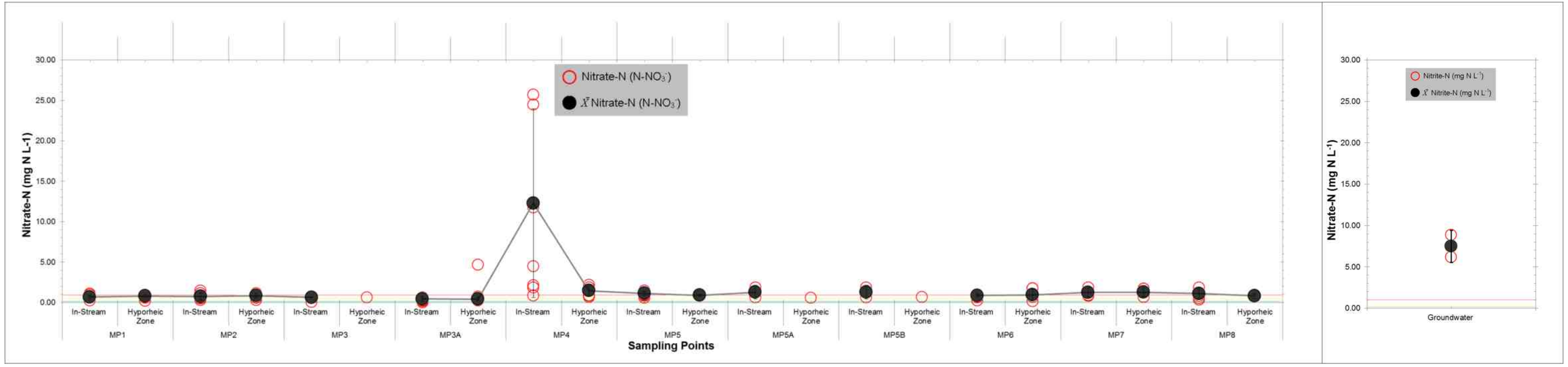
🟩 Moorkens (2000) 🟨 Bauer (1988) 🟥 Oliver (2000)



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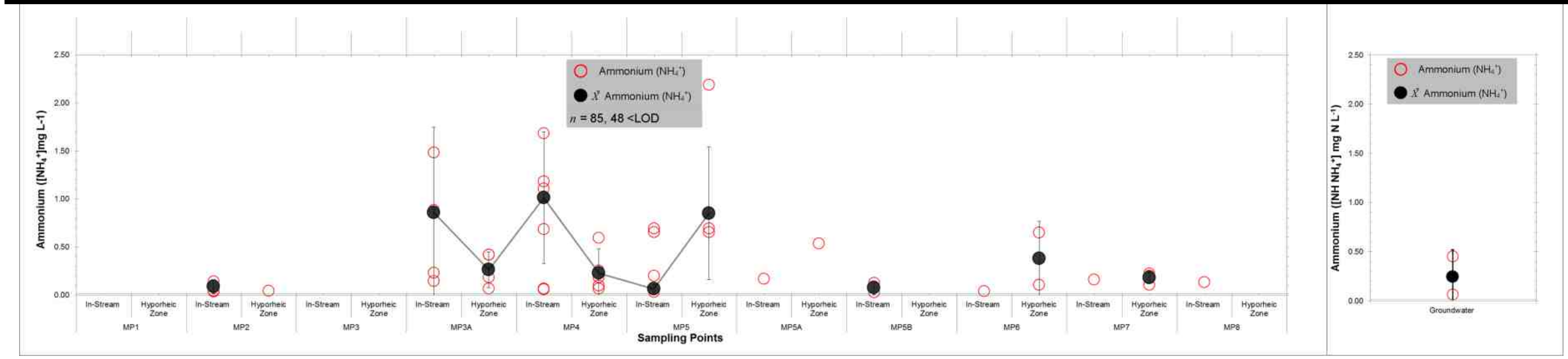

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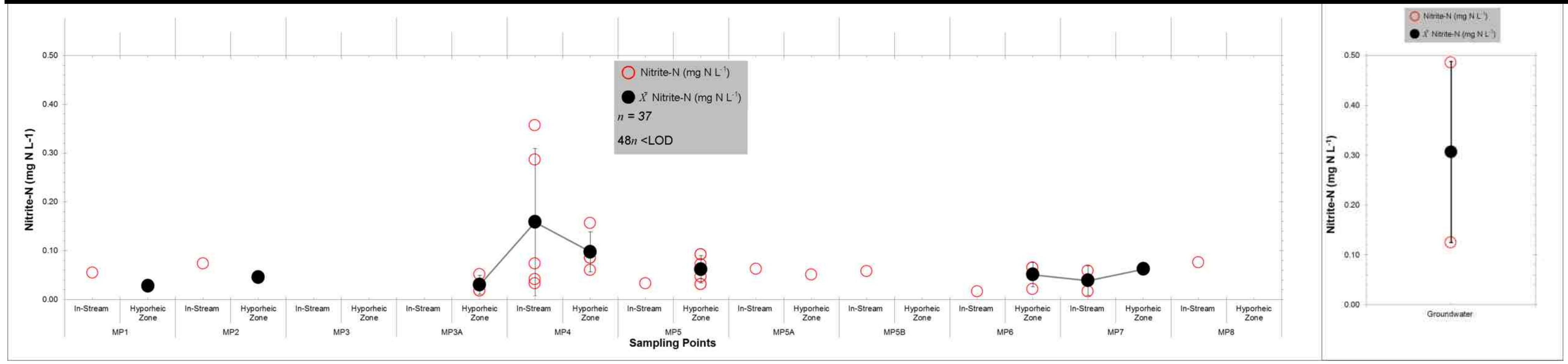

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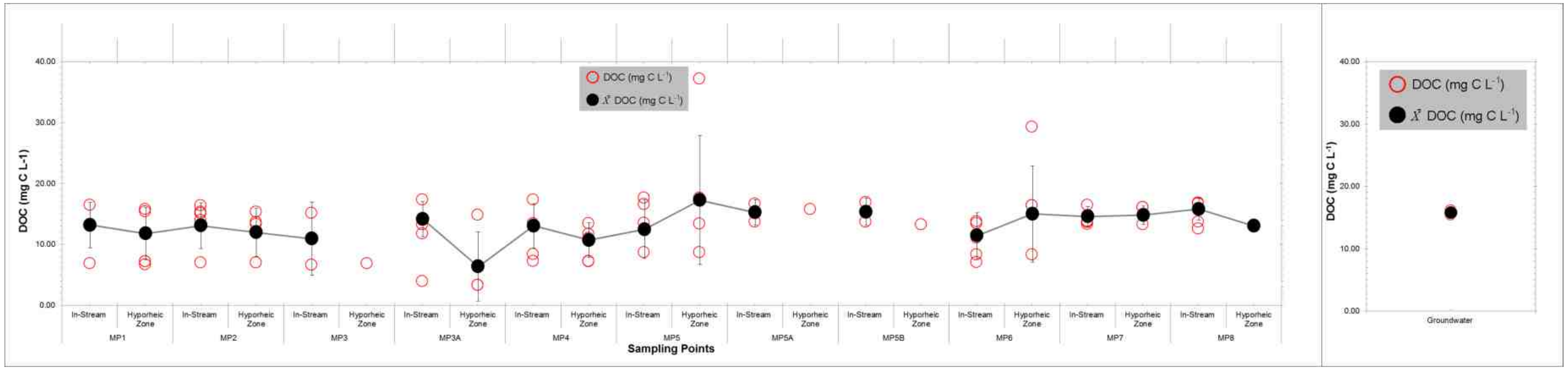

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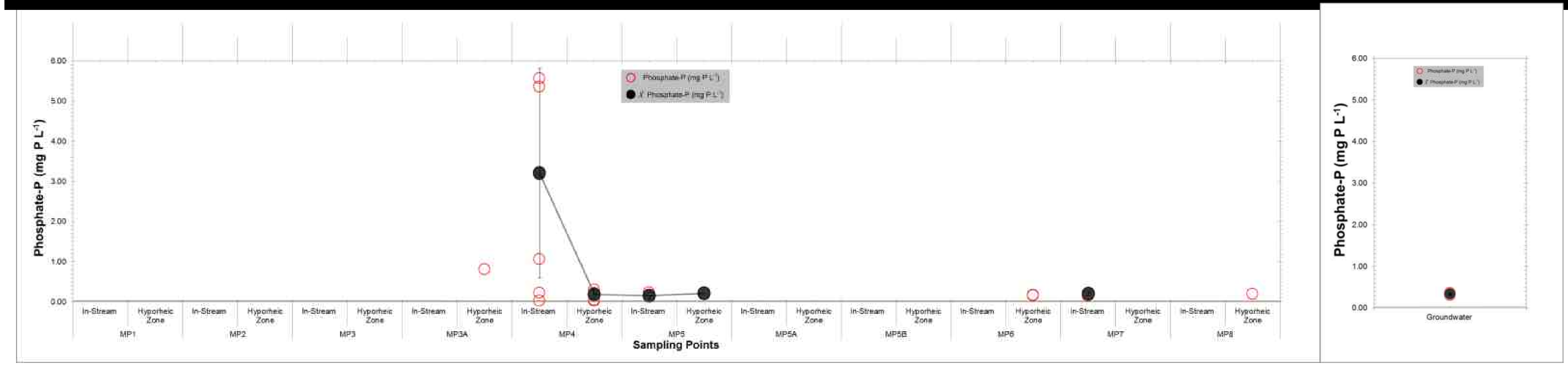

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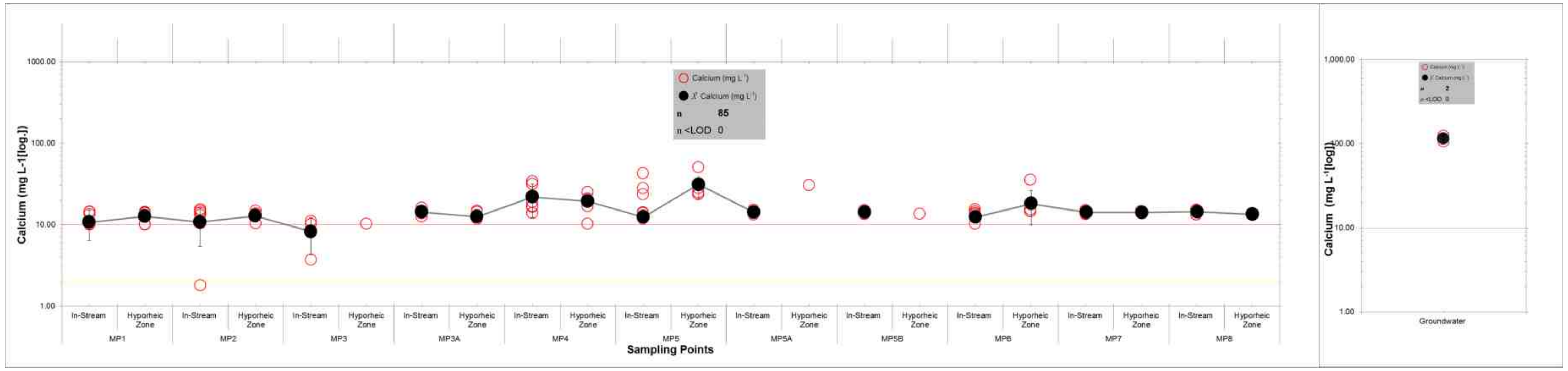

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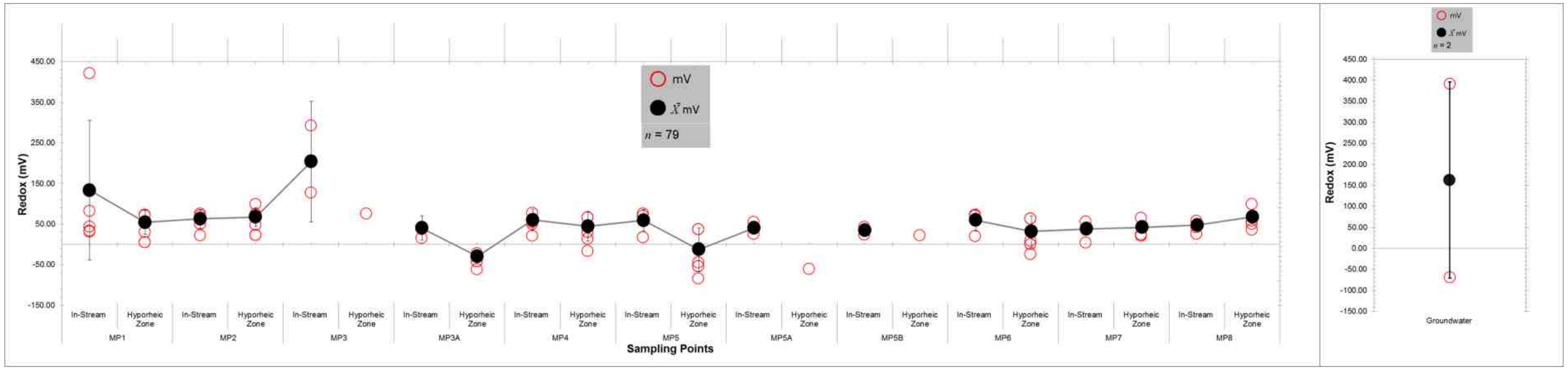

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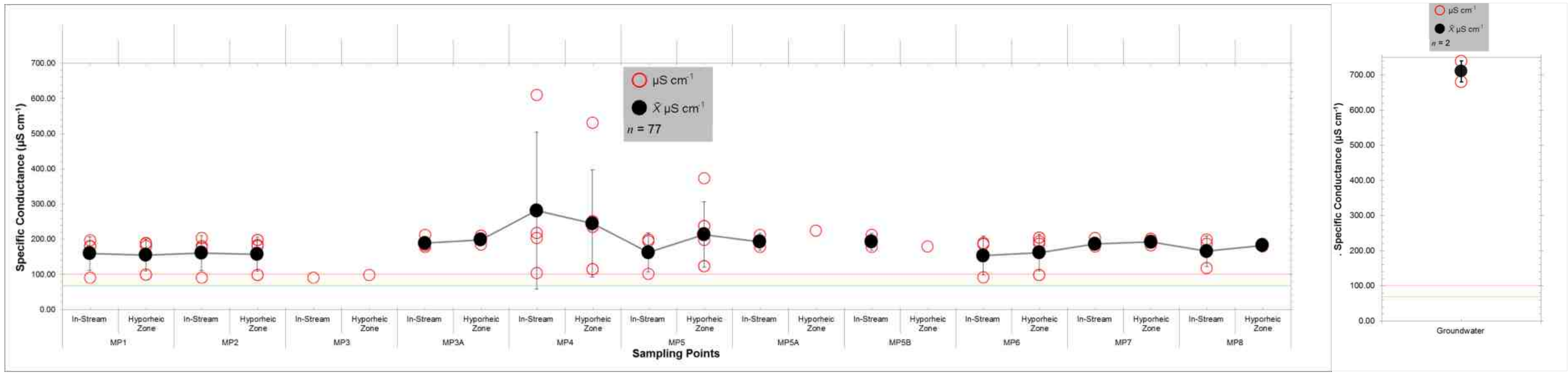

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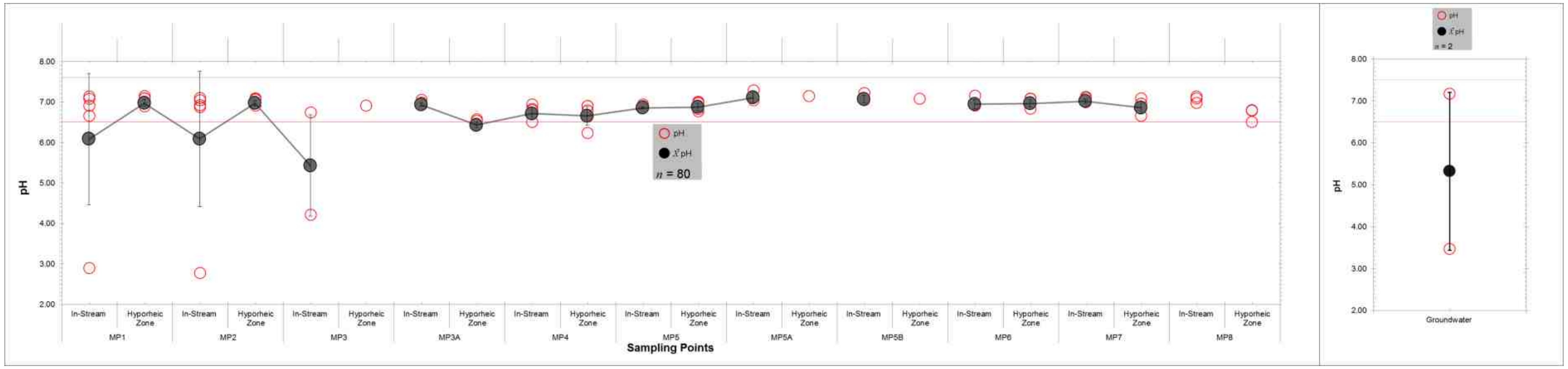

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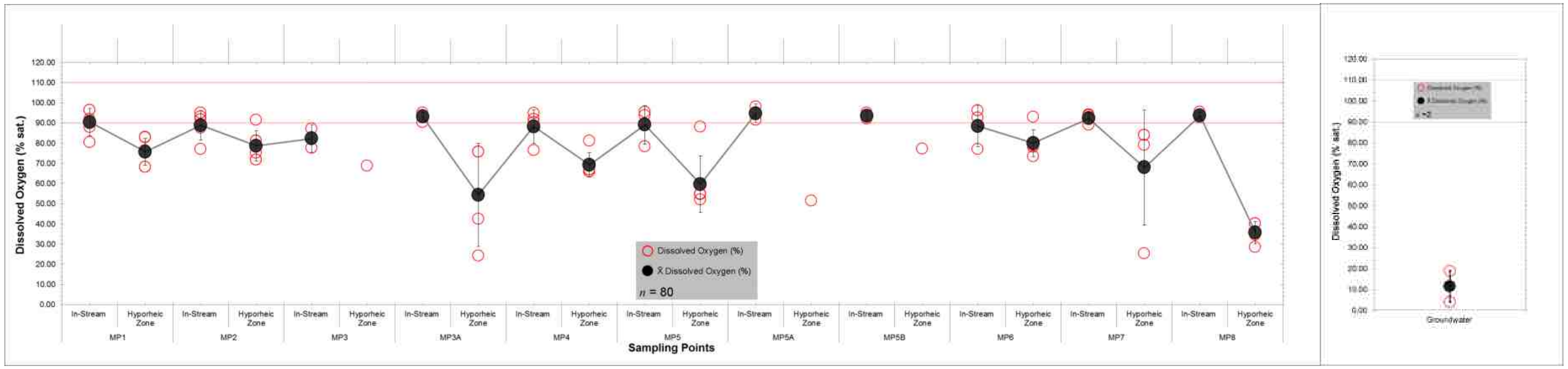

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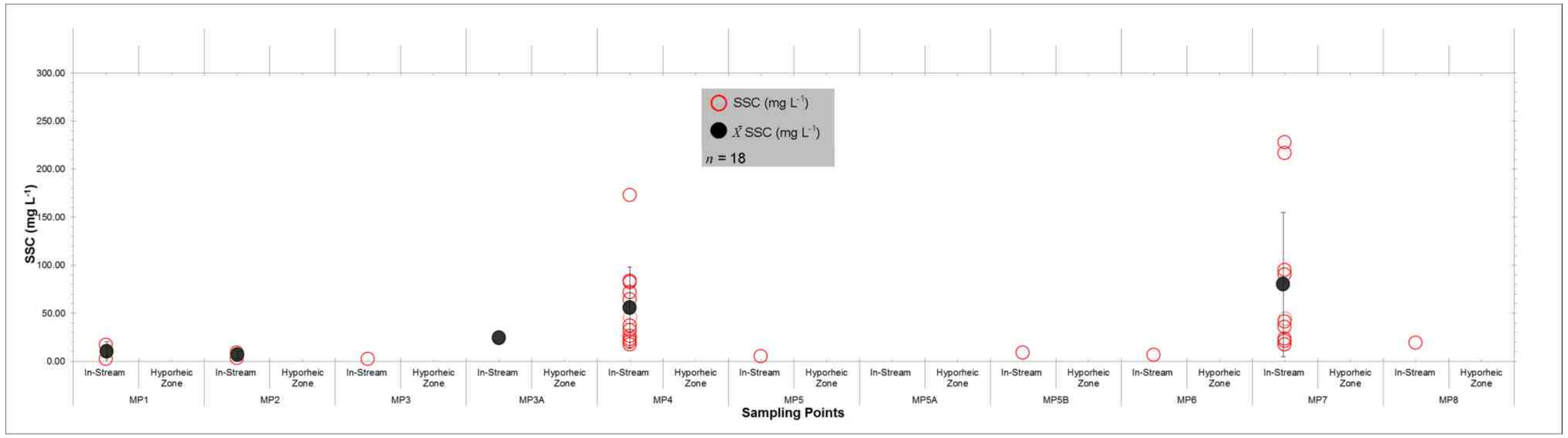

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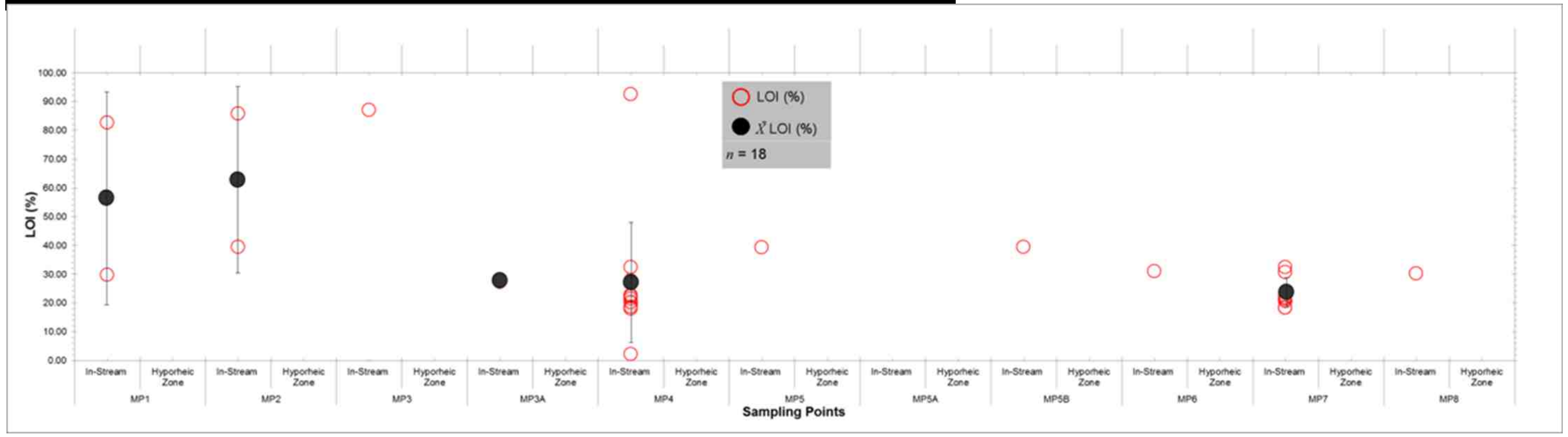
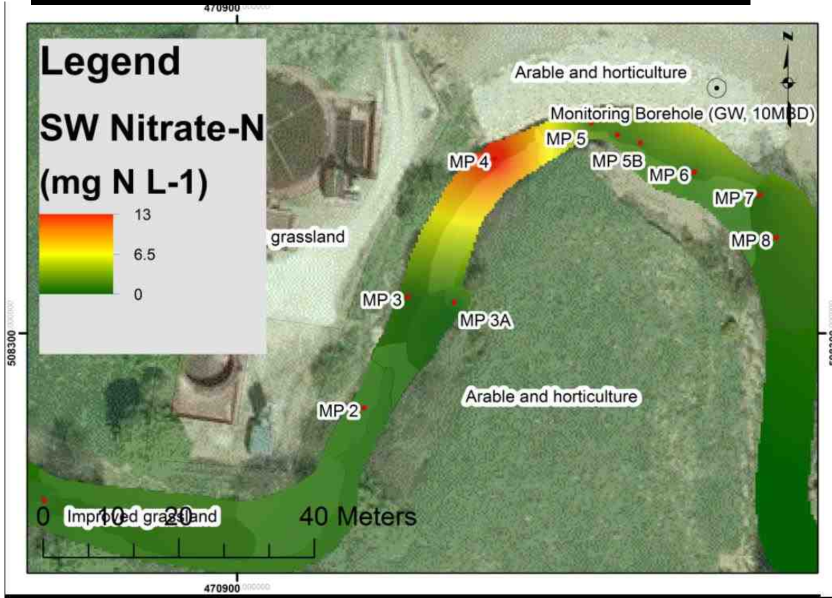
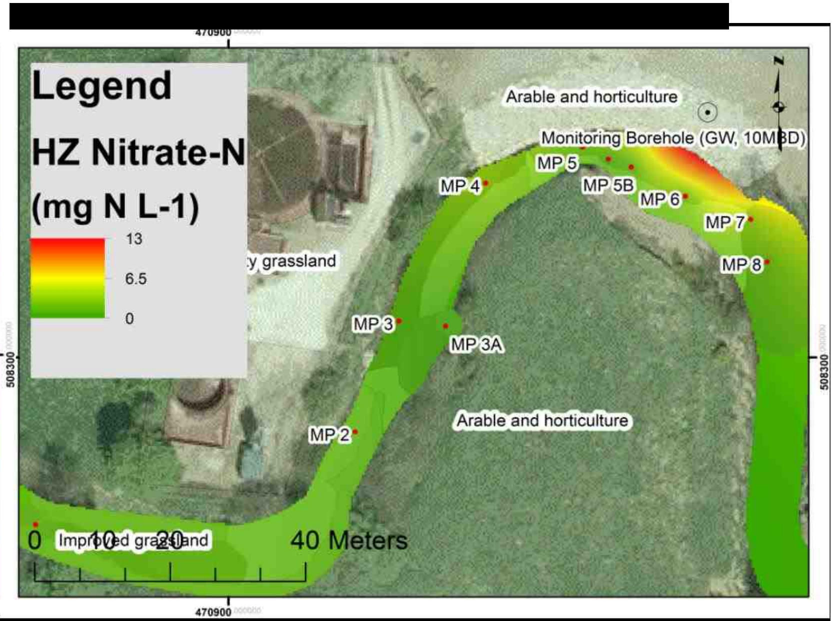


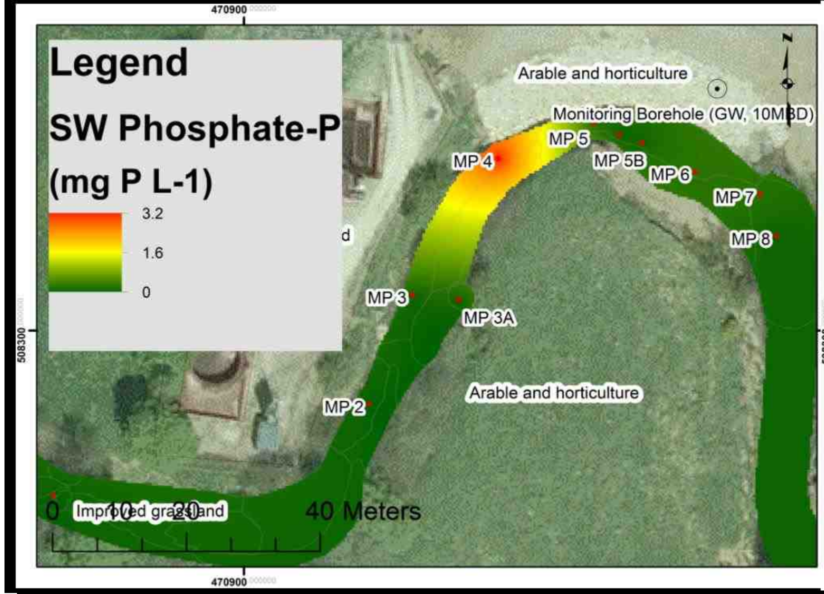
5.3.3.2 Redox And Dissolved Oxygen: Fine-Scale Variability

DO (% sat) longitudinal data present an oxygen sag below the outfall (Fig. 5.58). The difference in percentage DO saturation, between in-stream and hyporheic, prior to outfall is lower than after outfall, where the difference is greater and alluvial pore water becomes hypoxic, relative to river water. For example arithmetic mean DO at MP1 is 90.52% (*s* = 6. 74) SW, and 75.8% (*s* = 6. 64) HZ, whereas at MP3A it is 93.1% (*s* = 2.4) SW and 54.5% (*s* =22.5) HZ. Moreover, there appears to be greater variability in hyporheic DO saturation, for example the standard deviation at MP3A HZ, MP5 HZ and MP7 HZ is larger than at other monitoring points (Fig. 5.58., Appendix11). Alongside groundwater, the lowest mean DO is observed at MP8 HZ = 35.90% (*s* = 5.54), similar to the groundwater = 11.35%. The riffle-tail (MP8 HZ) drains the hyporheic and ground water of upstream monitoring points, namely MP4 – 6 and BH. Despite the hypoxia in the HZ, there is still a post-riffle rebound in water column redox at MP8 (Map 5.4.3 – 4, Fig. 5.55., Hendricks and White 2000, Ward and Wiens, 2001). HZ gravels are less oxygenated after outfall (Table 5.3.1).

Using the *t*-test to infer alluvial compaction and impeded HEF, shows a statistically significant difference between in-stream and hyporheic waters DO percentage saturation (Petts, 1983; Dahm *et al*., 2006), with *p* = 0.00 (Table 5.3.3), whereas *p* = 0.21 (Table 5.2.4) in the main channel of Lealholm Crunkly Gill and Danby Moors Centre. No statistical difference between the DO content of pore water and in-stream water occurs at the other sites, inferring gravel oxygenation and mixing where greater SW-HZ structural and functional connectivity exists (Wainwright *et al*., 2011). This does not apply on the STW, potentially as a consequence of filamentous algae and epithilic matt formation and *ranunculus fluitans* (water crowfoot) establishment post-outfall and downriver (Fig. 5.61., Haack and McFeters, 1982). The macrophyte hydraulics of *ranunculus fluitans* generates greater laminar flow and retards the boundary layer (‘law of the wall’) where U – velocity normally dissipates (log.) towards the bed (Baird and Wilby, 1999; Jones *et al*., 2012). High oxidising conditions prevail at the riffle-tail and on a riffle adjacent to a storm water outfall at MP3 (Fig. 5.55). Reducing conditions occur at MP5 and in the eddy where ammonium (NH_4^+) is highest along with peaks of SW nitrate-N and SW phosphate-P (Maps 5.3 – 4, Figs 5.49 – 5.53, see Map 3.8.3 for habitats). The contrained bank-full discharge at this location is predicted to be the area of highest sheer stress as flow is constricted through a knickpoint between MP 4 and 6 (Milan *et al.,* 2001). There is no SW redox peak in the riffle-unit at the STW, unlike at Lealholm Crunkly Gill (MP5 – 7, Fig. 5.55., 5.9; Maps 5.2 and 5.4). Potentially, clast *epithilon* and rununculus establishment reduce the roughness coefficient of riverbed gravels and inhibit TKE generation because of gelinous (biofilm) bed covering and caking (Milan *et al*., 2001; Hardy *et al.,* 2009).


Legend
SW Nitrate-N
(mg N L-1)
13
6.5
0
Arable and horticulture
Monitoring Borehole (GW, 10MBD)
MP 4
MP 5
MP 5B
MP 6
MP 7
MP 8
MP 3
MP 3A
MP 2
grassland
Arable and horticulture
Improved grassland
0 10 20 40 Meters
470900
508300


Legend
HZ Nitrate-N
(mg N L-1)
13
6.5
0
Arable and horticulture
Monitoring Borehole (GW, 10MBD)
MP 4
MP 5
MP 5B
MP 6
MP 7
MP 8
MP 3
MP 3A
MP 2
y grassland
Arable and horticulture
Improved grassland
0 10 20 40 Meters
470900
508300


Legend
SW Phosphate-P
(mg P L-1)
3.2
1.6
0
Arable and horticulture
Monitoring Borehole (GW, 10MBD)
MP 4
MP 5
MP 5B
MP 6
MP 7
MP 8
MP 3
MP 3A
MP 2
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Arable and horticulture
Improved grassland
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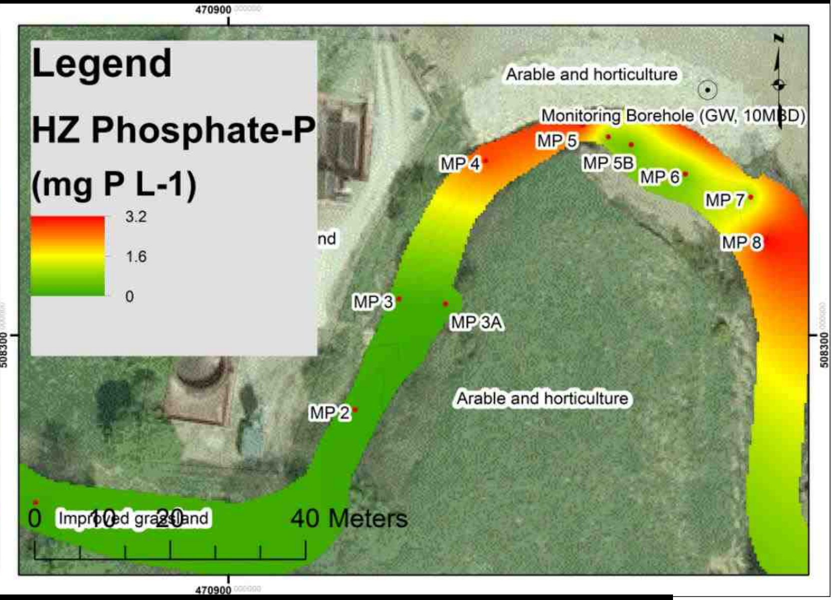
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(mg P L-1)
3.2
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Arable and horticulture
Monitoring Borehole (GW, 10MBD)
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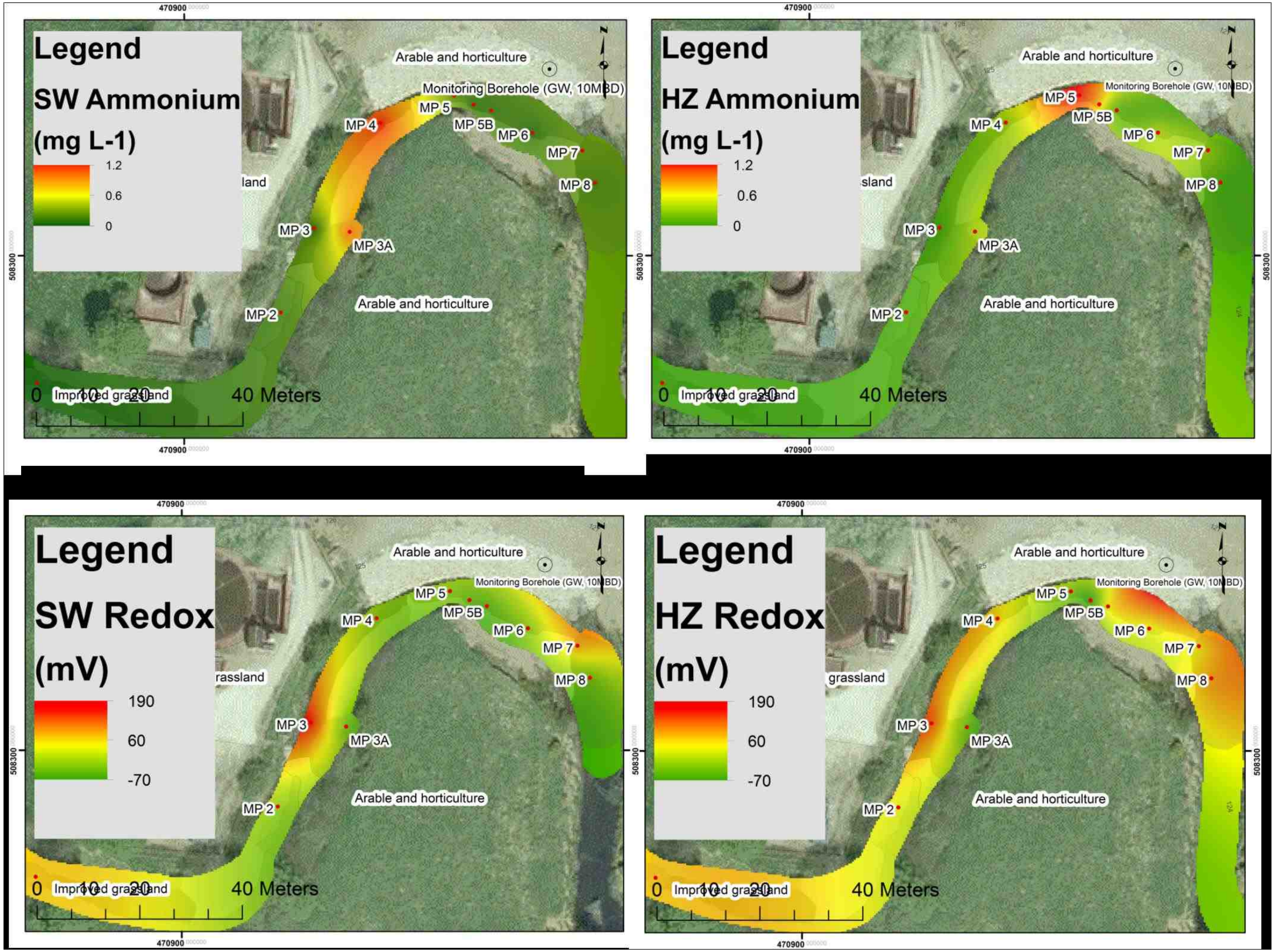

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Moorkens (2000) | Bauer (1988) | Oliver (2000)

		0.54 (0.61)		4.66 (12.27)		0.87 (0.80)			0.80 (1.04)
		0.65 (0.72)		1.33 (1.38)		0.65 (0.86)			0.88 (0.75)
				3.20 (3.19)		0.21			
				0.21 (0.16)					0.20
				1.14 (1.01)		0.04			0.13
				0.07 (0.15)		0.16 (0.27)			
		12.03 (10.75)		16.44 (22.08)		13.33 (12.44)			15.04 (14.50)
		13.89 (12.73)		18.97 (19.57)		15.71 (18.32)			13.51 (13.48)
		6.90 (6.13)							
		7.57 (7.67)							
				91.05 (88.33)		92.60 (88.57)			
		76.40 (75.80)		66.80 (69.35)		78.55 (80.08)			37.40 (35.90)
		178.50 (160.75)		209.50 (282.75)		185 (154.67)			186 (167)
		183.00 (156.17)		234 (246.17)		189.50 (163.50)			186 (184)

5.3.3.3 Suspended Sediment Concentration (SSC), Electrical Conductivity (EC), Phosphate, Calcium And pH Fine-Scale Variability

SSC varies both through the reach and with discharge (Fig. 5.59). Low flows do not appear to result in increased SSC; however, with flooding SSC increases markedly (Appendix 8). In addition to reach-scale spot sampling, 24-hour monitoring conducted on 14 – 15th October 2013 during flood hydrograph recession presents a trend of high SSC which decreases in tandem with discharge reduction (Fig. 5.44 (stagegraph)). In-stream arithmetic mean SSC at MP4 is 55.2 mg L^{-1}(s = 42.2) and at the MP7, the riffle-tail is 79.3 mg L^{-1} (s = 75.1). The EA consent for STW SSC is 60 mg L^{-1} (Appendix 6). During diurnal monitoring the highest SSC at MP4 was recorded at 172.91 mg L^{-1} (14/10/2013, 14:00) potentially constituting a breach of consent. Final effluent outfall SSC threshold was previously breached at 414 mg L^{-1}on 23/04/2012 (*ibid*). During 24-hour monitoring at MP4 and MP6 on 14-15th October no sample was collected at MP1. The data trend for other samples at MP1 shows reduced SSC prior to outfall, averaging a SSC of 9.49 mg L^{-1} (Fig. 5.59). Furthermore, the STW operator final effluent water quality return data to the EA will outline any potential breach in SSC threshold, as was the case in the last reported exceedance (*vide supra,* Appendix 6). STW effluent water is visually turbid and appears to be inadequately screened for sewage waste (Fig. 5.61-62). Dotplot LOI (%) data shows that at MP1 and 2 the organic content of SSC is high, over 50%; post outfall the organic content of sediment is reduced, c. 30% or lower (Fig. 5.60).

The ionic strength of all ecotones waters generally exceeds *M. margaritifera* TV. EC increases at STW outfall locations with a sample on 22nd July 2013 (15:10) being 609 µS cm^{-1}, a ionic concentration over 6 times greater that Olivers (2000) maximum *M. margaritifera* TV (Table 2.1, Fig. 5.56), EC remains elevated through all downstream monitoring points after outfall. The chloride-Cl and sulphate-S concentration across in-stream and hyporheic water markedly increase upon mixing with STW effluent; samples also recorded exceptionally high carbonate concentration which accords with the formation of scum and precipitate (Alloway and Ayres, 1994)

Calcium concentrations remain marginally higher in hyporheic waters relative to in-stream waters; again this is associated with the calcic groundwaters, averaging 114.6 mg L^{-1} (Fig. 5.54). However, STW effluent discharges significantly concentrated calcic water. Inflowing waters are statistically different to those being discharged and lower in concentration (Table 5.3.1). All calcium concentrations exceeded *M. margaritifera* TV (Table 2.1), except 2 out of 85 samples on 19th March 2013 at MP2 and 3 SW. STW effluent buffers pH. The pH of interstitial water in the HZ of MPs 1 – 3 is acidic, post outfall the other pH values generally fall within the *M. margaritifera* TV range (Fig. 5.57). Groundwaters through the reach are acidic.

The Dionex ICS 300 detection limit of 0.02 mg L^{-1} is insufficient at detecting ortho-P concentration for Moorkens (2000) lowest TV at 0.005 mg P L^{-1} (compare Table 2.1 and 4.3). Given the natural P deficiency of plankton, hetro— and auto— trophs and the fact that dissolved phosphate-P (Ortho-P (PO_4^{3-})) ions are the most aqueous bioavailable, soluble and labile fraction, a low-resolution detection limit of 0.02 mg L^{-1} rendered 41/169 samples undetectable on the chromatograph (Reynolds and Davies, 2001, Appendix 11). Irrespective, where ortho-P is detected it exceeds *M. margaritifera* TV (Table 2.1). The Environment Agency (2000) aquatic eutrophication strategy sets a TV of 0.02 mg P $L^{-1}$for upland headwaters which is exceeded at Danby STW. The artificially enrichment of the reach with N/P ratio at 1.06 in-stream and, 0.17 hyporheic (Table 5.3.1. and 5.5.3) is observed to result in both macrophyte and filamentous algal bloom and crowding (Mainstone and Parr, 2003, Fig. 5.61). Plant respiration is predicted to result in an acute nocturnal sag for DO and nitrate-N, similar to Lealholm, but amplified by outfalls resulting in multiple aquatic mortalities in fish and macroinvertebrates (Mainstone and Parr, 2003). Post-parasitic drop-off glochidia and salmon redd eggs/alevin are particularly vulnerable (Hendry and Cragg-Hine, 2003, Table 2.1). Phosphate-P has a lag-effect in the hyporheic zone in groundwaters and is likely to remain bioavailable further downstream, presenting further aquatic risk by retention and return-flow with spates and pool-riffle piston flow (Jarvie *et al*., 2006; Neal *et al*., 2010). Low organic-C and iron content of Ellerbeck soil impedes the hydrolysis required for PO_4^{3-}—P and NO_3^{-}—N ion exchange (NSRI, 2013; Trimmer *et al*., 2012; Lansdown *et al*., 2012; Chiou and Shoup, 1985; Map 3.8.2). No ortho-P was detected prior to effluent outfall (Fig. 5.53., Appendix 11).

5.3.4 *Ranunculus fluitans* – An Indicator Of Long-Term Eutrophication?

Perennial and annual macrophytes establish, given balanced physicochemical properties of temperature, trophic nutrient status and river geomorphology (Holmes *et al.,* 1999; Baird and Wilby, 1999). The artificial enhancement of riverine environments with biotic nutrients and thermal discharges enhances both photosynthetic and transpiration rates of plants (Appendix 11), which for the former processes allows greater sugar storage (Baird and Willby, 1999). Jarvie *et al.* (2013) correlate (r^2 = 0.24) total phosphorus-P (TP) with (bio)sestontic chlorophyll–a. Chlorophyll–a is a photoreceptor which actively absorbtions solar radiation. Together TP and Chlorophyll–a are fertiliser for green growth and compounds biomass accumulation (*ibid*). Since certain plants flourish given the right environmental conditions, their presence, assemblage, richness and abundance has been determined by Holmes *et al* (1999) to be an inference of trophic nutrient status in a surveyed reach. The British NVC (National Vegetation Classification), a national habitat reference of macrophyte and riparian bryophytes is used as a basis to Species Trophic Rank (STR) (Holmes *et al.,* 1999). Holmes *et al*. (1999:XI) STR as: *A value assigned to a species on a scale of 1 to 10, designed to reflect the tolerance of that species to eutrophication. Low scores indicate tolerance or cosmopolitan distribution (i.e. no preference). High scores indicate preference for less enriched conditions or intolerance of eutrophic conditions.*

Two eutrophic indicator species were observed downstream of STW outfalls at the reach: *Amblystegium riparium* (moss) adjacent and surrounding the outfall (Fig. 5.62) which has a STW = 1; and, *Ranunculus fluitans* Lam. (water crowfoot (Fig 5.61) which has STR = 7 (Holmes *et al*., 1999). *A. riparium* is cosmopolitan moss distributed in running, stagnant or nutrient sewage waters (Holmes *et al*., 1999; Baird and Wilby, 1999).

[redacted]

Moorkens (2000)	Bauer (1988)	Oliver (2000)

[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]
[redacted]	[redacted]	1.57 σ = 0.64)	[redacted]	0.85 (σ = 1.65)	[redacted]	0.36 (σ = 0.51)	11.11 (σ = 5.42)	[redacted]	[redacted]	166.49 (σ = 96.48)	[redacted]	[redacted]
[redacted]	[redacted]	0.84 (σ = 0.47)	[redacted]	0.17 (σ = 0.09)	[redacted]	0.25 (σ = 0.41)	17.76 (σ = 8.40)	[redacted]	56.48 (σ = 27.75)	166 (σ = 96.48)	[redacted]	[redacted]
[redacted]	[redacted]	7.51 (s = 1.89)	[redacted]	0.33 (s = 0.04)	[redacted]	0.26 (s = 0.27)	114.64 (s = 13.14)	5.32 (s = 2.62)	11.35 (s = 10.39)	709.50 (s = 41.72)	[redacted]	[redacted]
[redacted]												
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Ranunculus fluitans had an estimated established biomass of 2.4 m^3, following quadrat surveys of the 2 plant species (Fig. 5.61). Down-river of the intensive study reach, the aquatic herb is further established as a series of individual plants.

[redacted]

R. fluitans is member of the flowering buttercup family, a perennial that grows over 6m in length in favourable conditions (NIEA, 2005). On 22nd July 2013 (18:41) the larger plant had a length of 4.21 m (Fig 5.61), whilst the smaller measured 2.83 m. The species is found in mesotrophic and eutrophic rivers (Spink *et al*., 1993; Holmes *et al*., 1999; NIEA, 2005), Cook (1966) observed *R. fluitans* tolerance to pollution, though die-back and mortality occurs with excessive turbidity and SSC (NIEA, 2005). IUCN (1991) classifies *R. fluitans* as a species being of 'least concern'. The abundance in floating matts modifies flow by the stem hydraulics which are elongate and smooth, lee-side under-plant velocity dissipation results in deposition of fine sediment (Spink *et al*., 1993; Baird and Wilby, 1999; Jones *et al.,* 2012). Fines provision favourable niche refugia for *gamaridae* (scuds/shrip), *lymnaeidae* (snails) larvae and nymphs (NIEA, 2005); however, compact colmation is unfavourable to bivalves and salmonids (Soulsby *et al*., 2001; Zimmermann and Lapointe, 2005; Bracken *et al*., 2009). Epilithic matt, biofilm and macrophyte establishment is determined to be the reason for hyporheic hypoxia flow separation and statistical difference against in-stream waters (Table 5.5.3; Baird and Wilby, 1999; Zimmermann and Lapointe, 2005; Jones *et al*., 2012).

Excessively turbid waters through the reach prevented macrophyte species identification. If clear water conditions prevailed, a Mean Trophic Rank (MTR) (10 – 100) survey is predicted to have derived a high score, MRT >60, indicating eutrophy (Holmes *et al.,* 1999). However upland rivers often have cool temperatures, low DOC, coarse alluvium and energy, rendering them not always suitable for MTR surveys (Vannote *et al*., 1980; Holmes *et al.,* 1999).

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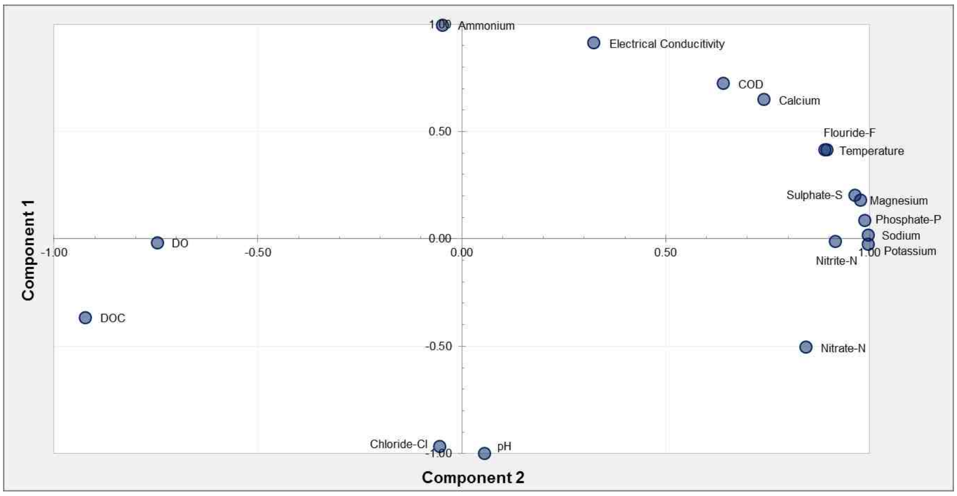
5.3.5 Data Reduction And Variance Analysis: Principal Component Analysis (PCA)



Data [redacted]ibed in section 5.2.7 and passed the same test criteria (Appendix 11). In a two component model which explains 94% of the cumulative variance (Table 5.3.4), Phosphate-P, magnesium, sodium and sulphate–S appear to correlate strongly together on the first component, explaining 61% of the variance. The statistical inference is that when phosphate-P is at high aqueous concentration so too is Sulphate-S and the base metals (Jolliffe, 2002, Fig. 5.63., Table 5.3.4). Temperature and fluoride-F also correlate with marginally lower loadings on the first component. For component two, ammonium, EC, COD and calcium correlate together. This may be an influence of the groundwater base flow component and bankside egress (Fig. 5.50., 5.56., 5.51., and 5.63), unlike the variables in component one which are all primarily related to sewage effluent (Jarvie *et al.,* 2006; Neal *et al*., 2010, Appendix 11).

[redacted]

	Principal Component	
	1	2
Fluoride-F	.075	.044
Chloride-Cl	.037	-.191
Sulphate-S	.092	-.002
Phosphate-P (Ortho-P)	.100	-.026
Nitrite-N	.097	-.042
Nitrate-N	.111	-.138
Ammonium	-.049	.201
Sodium	.104	-.040
Potassium	.106	-.048
Magnesium	.095	-.007
Calcium	.049	.097
DOC (Dissolved Organic Carbon)	-.081	-.033
COD (Chemical Oxygen Demand)	.036	.116
Temperature (°C)	.076	.043
Electrical Conductivity (μS cm^{-1})	-.006	.168
Dissolved Oxygen (mg L^{-1})	-.078	.029
pH	.050	-.201
Cumulative Variance Explained (%)	61	94

5.3.6 Conclusions

This section has demonstrated the physiochemical impacts that STW effluent has, not only on in-stream and hyporheic waters, but also on the outer edge of a meander contaminating alluvial groundwater. The analysis has found:

(1) Inflowing in-stream and hyporheic waters are statistically different for nitrate-N, TIN, phosphate-P, ammonium and calcium. Ammonium and phosphate-P are not detected in samples prior to outfall.

(2) Where artificial enrichment from STW outfall occurs in the form of phosphate-P, nitrate-N and ammonium, in-stream waters soon recover downriver. However, there is a lag effect from these biotic nutrients which appear to become concentrated in groundwater and hyporheic zone, thus highlighting the retention for future exfiltration with flow variability. While surface waters recover, the nutrient parameters remain in exceedance of *M. margaritifera* TV through the remaining monitoring points. Indeed, hyporheic zone and groundwater concentration patterns from hyporheic exchange flow and hyporheic flow pathways suggest that pollution is transmitted alluvially through intergranular flow for long distances.

(3) The EA discharge consent is not commensurate with *M. margaritifera* respiratory requirements. This is compounded by the operator’s failure to comply with the consent. Moorkens (2000) Ammonia-N TV for *M. margaritifera* is 0.01 mg N L^{-1}. The discharge consent threshold is 30 mg N L^{-1}, 3,000 times higher.

(4) Down-flow of STW outfall, macrophyte assemblage is an indicator of long-term biotic nutrient enrichment, which, through the processes of colmation and epilithic matt growth, may be implicated in hypoxic pore water and statistical difference against in-stream waters.

(5) Low flows and drought conditions amplify the effects of biotic nutrients due to an absence of adequate dilution.

(6) Orthogonal factor analysis results infer that the STW primary effluent parameters control much of the variability in other physicochemical parameters. The analytical power of PCA at the STW was high, accounting for 94% of the cumulative variance.

(7) Acid conditions through all ecotones reduce microbial breakdown rates and further the longitudinal fate of P and N, post STW outfall, particularly in intergranular flow.

Longitudinally, Danby STW is the investigations most upstream monitoring reach, where point-source discharge of eutrophic effluent occurs. This section served to contrast a degradated reach-scale with an agricultural entrenched reach – Danby Moors Centre – located 650m downstream where the residual depth of pools, relative to riffles is most pronounced, more than at any other reach-scale site (Maps 3.8).

5.4 Danby Moors Centre

5.4.1 Synopsis

This section follows the same approach as the previous chapters, initially presenting VHG and Q_v rate for up-welling and down-welling, between stream and substratum (Maps 4.0). Reach-scale physicochemical data are then presented. Using average reach-scale hydrochemistry data arrays, the statistical difference between the hyporheic zone and in-stream waters are determined. The sporadically establishment of *Potamogeto sp* (fennel pondweed) a symbiont of *R. fluitans,* has its STR presented and accorded to the longitidional fate of biotic nutrient enrichment from Danby STW – pollution macrophyte connectivity (Spink *et al*., 2003). The section finalises with PCA and then factoral analysis, appraising which hydrochemistry parameters are responsible for the variability in other variables.

5.4.2 Hydraulic Gradient And Flux Across A Pool-Riffle-Pool

Monitoring revealed the occurrence of metabolic hotspots within the reach-scale. Measurements confirmed locations of HEF riffle-head down-welling and strong riffle-tail up-welling (Table 5.4.1, Fig. 5.64 – 5.65), which was also supported by temperature data (Appendix 12).

[redacted]

[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]
[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]
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[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]
[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]

Figure 5.64 presents VHG through a pool riffle-head (MP1 and MP4), riffle (MP2 and MP5) and pool, riffle-tail (MP 3 and MP 6). MP1 has a weak negative VHG of -1.70, where hydraulic head (Δ*h*) was below stream stage, indicating a weak presence of downwelling (Appendix 12). Conversely, all other MPs are positive, particularly MP3 = 69.15 VHG, indicating upwelling, where *h* is above relative river stage (Table 5.4.1).

[redacted]

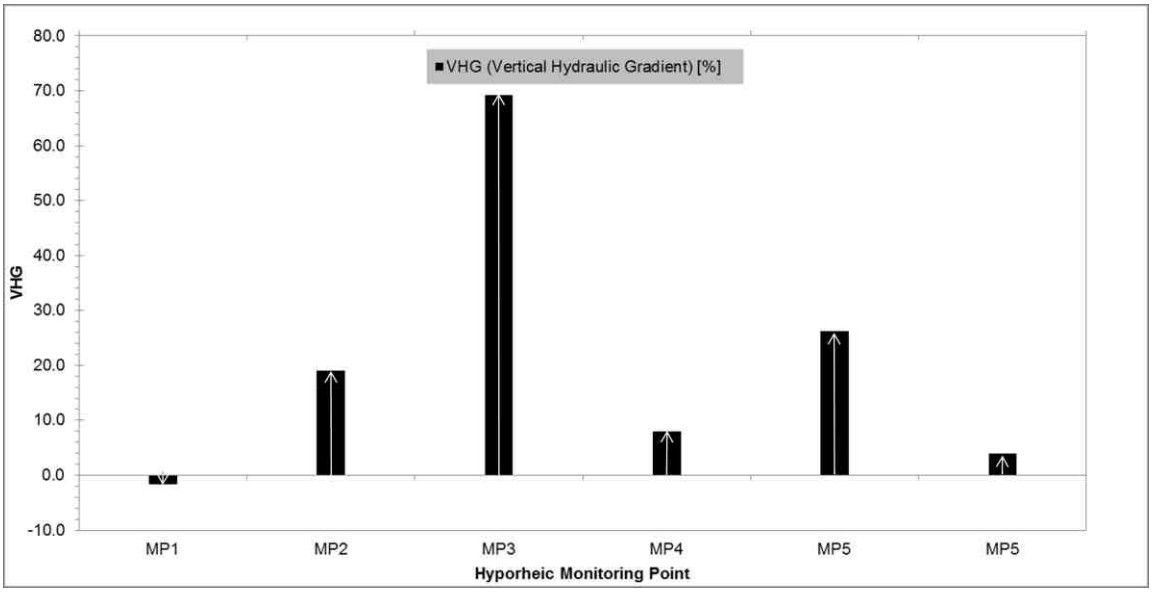

Figure 5.65 presents vertical specific discharge (Q_v) at rates shown in table 5.4.1. MP2 and 3 were located in a clay lens and measured positive VHG (Fig. 5.64). Both underwent the slug tests. However, monitored well recharge was exceptionally slow. Dahm *et al.* (1888, 2006) reports sampling taking over 24 hours in some instances. MP4 sampled the highest Q_v = 0.87 cm s^{-1} discharging from HZ into the water column, -0.43 cm s^{-1} was also discharging into the riffle-head from in-stream to HZ. All other Q_v are positive (Table 5.4.1).

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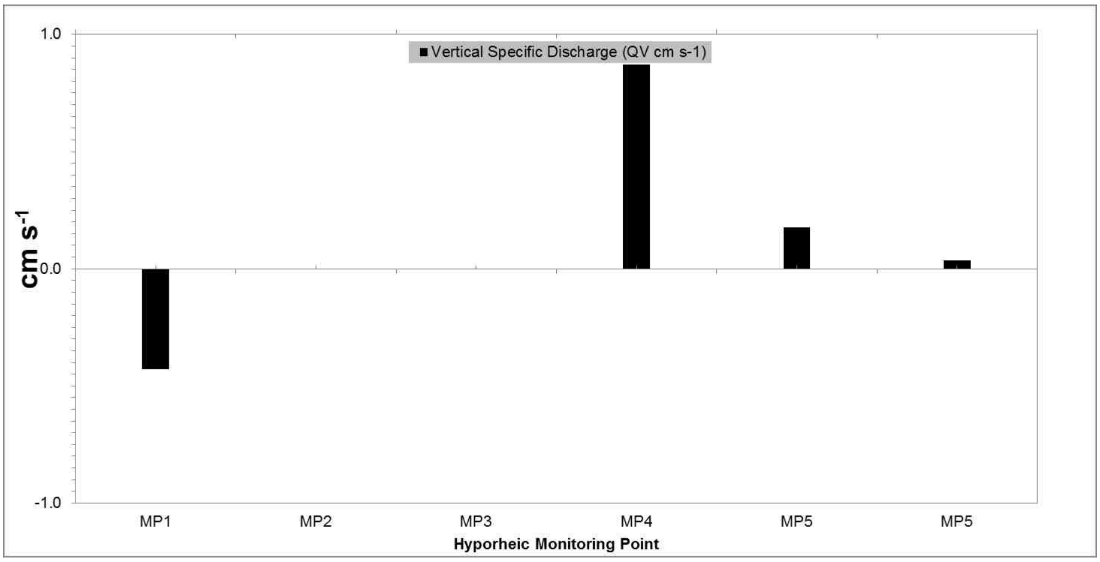

5.4.3 Reach-Scale Hydrochemistry

5.4.3.1 Hydrochemical Fine-Scale Variability

Arirthmetic mean nitrate-N in the water column was higher relative to hyporheic concentration, at 0.60 mg N L^{-1} compared to 0.46 mg N L^{-1}. Conversely, for DOC, in-stream mean concentrations are higher at 14.85 mg C L^{-1}, compaed to 13.56 mg C L^{-1} (Table 5.4.2). While DOC and nitrate-N are higher in in-stream concentration, flow ejections out-of the hyporheic zone is reduced for nitrate-N falling below Moorkens (2000) TV (Fig. 5.67; Maps 5.5) – the same as at the pool-riffle-pool at Lealholm. The concentrations of DOC and nitrate-N are not statistically different between SW and HZ.

The hyporheic zone at MP5 is marked by depleted DO and high calcium groundwater influence, as monitored in local groundwaters (Figs 5.68., 5.73). Low oxidising conditions occur which become reducing conditions at MP6 (Fig. 5.69; Maps 5.6). Where groundwater discharges through the riverbed at MP5 there is also at hot spot of total dissolved solids (TDS), suggesting suspension of some bed material (Fig. 5.72., 5.74., Thompson, 1986). Hyporheic flux (Section 5.4.2), solute data and YSI-probe samples show the existence of a cold oligotrophic groundwater plume ejecting from MP3 (Fig. 5.64 – 5.65; Appendix 12). At MP3 the hyporheic concentrations of nitrate-N is reduced and a single c.60 *M. margaritifera* associated with this upwelling groundwater existed.

Similar results to Lealholm Crunkly Gill (Maps 5.2.1 – 2) are presented, in that redox oxidising conditions peak in the riffle-unit (Fig. 5.69), both in-stream and in the hyporheic zone (Maps 5.6). All ammonium and phosphate-P fell below the LOD (Appendix 12).

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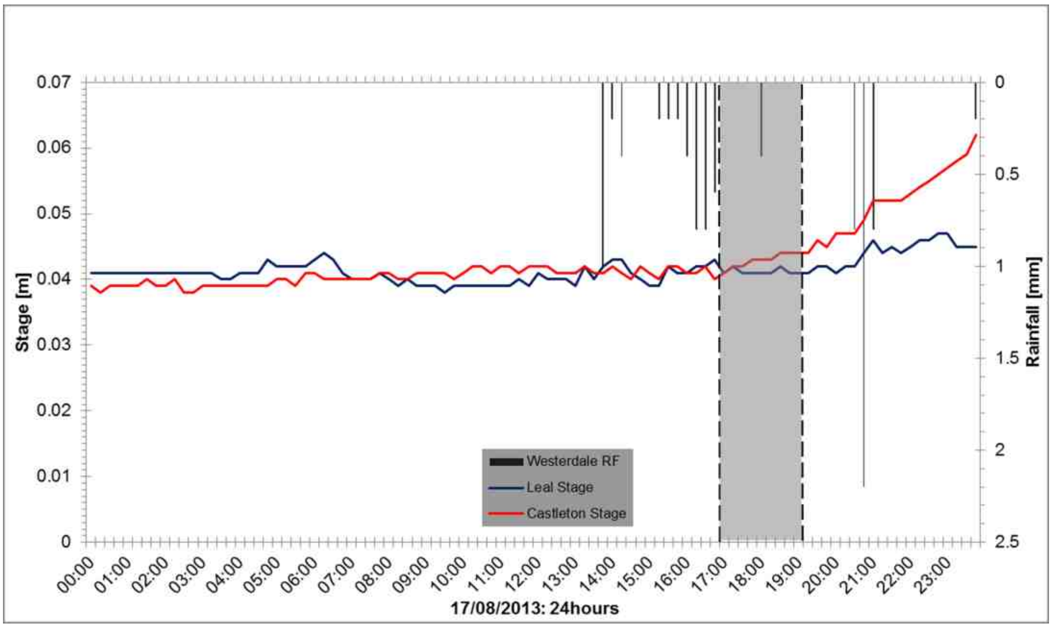

Moorkens (2000)	Bauer (1988)	Oliver (2000)

		0.60 (σ = 0.01)					13.60 (σ = 0.10)	11.30 (σ = 0.17)		168.33 (σ = 3.35)		
		0.46 (σ = 0.17)					14.70 (σ = 0.84)	7.47 (σ = 0.37)		171.67 (σ = 9.48)		

5.4.4 Sporadic *Potamogeto sp.* – An Indicator Of Persistent Enrichment?

Despite the dilution of concentrated nitrate-N and phosphate-P effluent from Danby STW (Table 5.3.3), both remain above the *M. margaritifera* TV (Table 5.4.2). Assembledge and certain riverine macrophytes 'tend to be associated with particular nutrient concentrations' since they are permanently exposed to river water chemistry they are a useful long-term bio-indicator (Holmes and Newbold, 1984; Spink *et al.,* 1993:113). *Potamogeto sp* is established sporadically through the Danby Moors Centre reach (Fig 5.75) and has an STR of 1 (Holmes *et al*., 1999). In a flume experiment where Spink *et al.* (1993) raised ortho-P from 40 µ P L^{-1} to 200 µ P L^{-1} *Potamogeto pectinatus* outcompeted *R. fluitans* weighing in with a higher established biomass and ortho-P concentration in the plant tissues.

[redacted]

Moorkens (2000)	Bauer (1988)	Oliver (2000)

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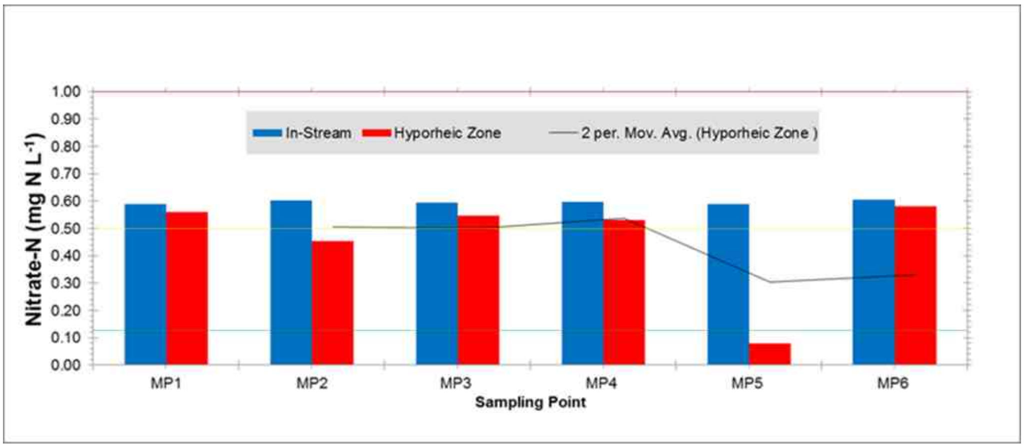

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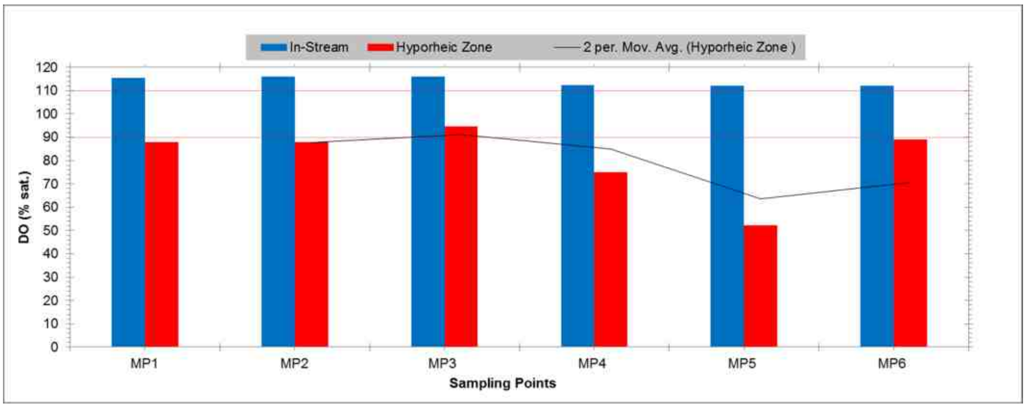

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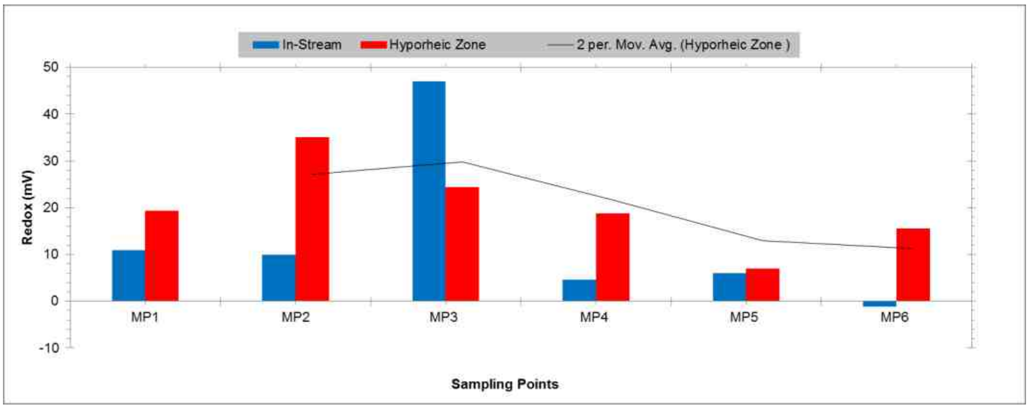

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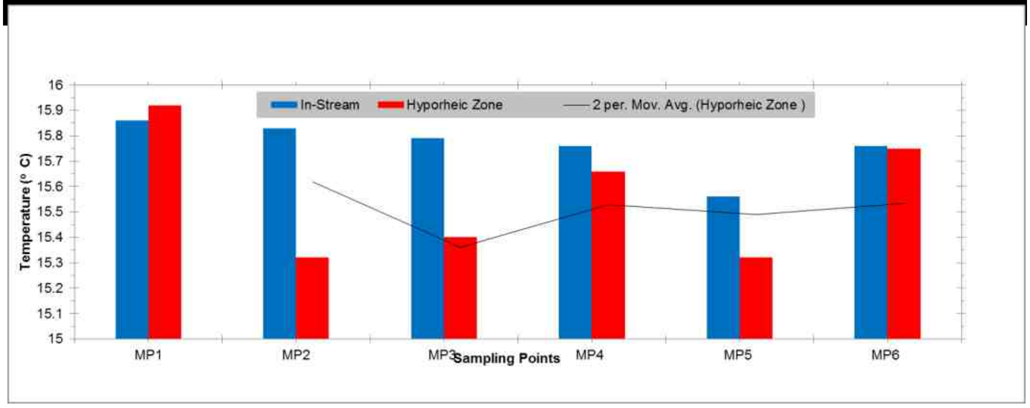

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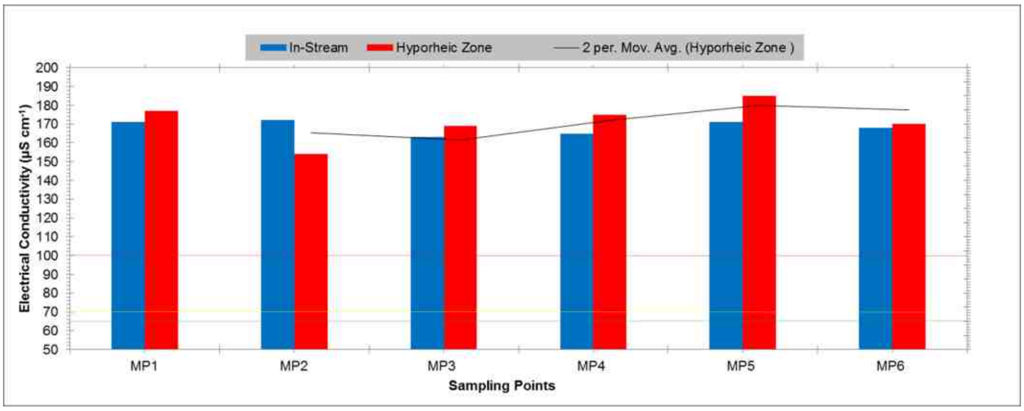

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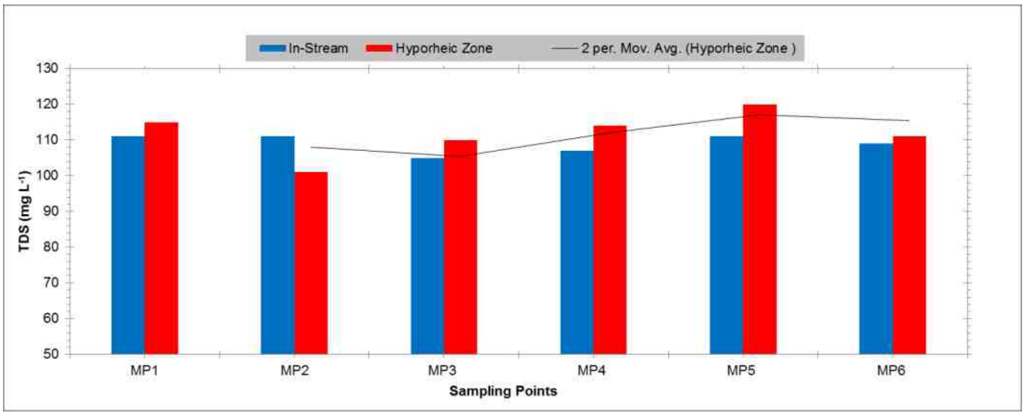

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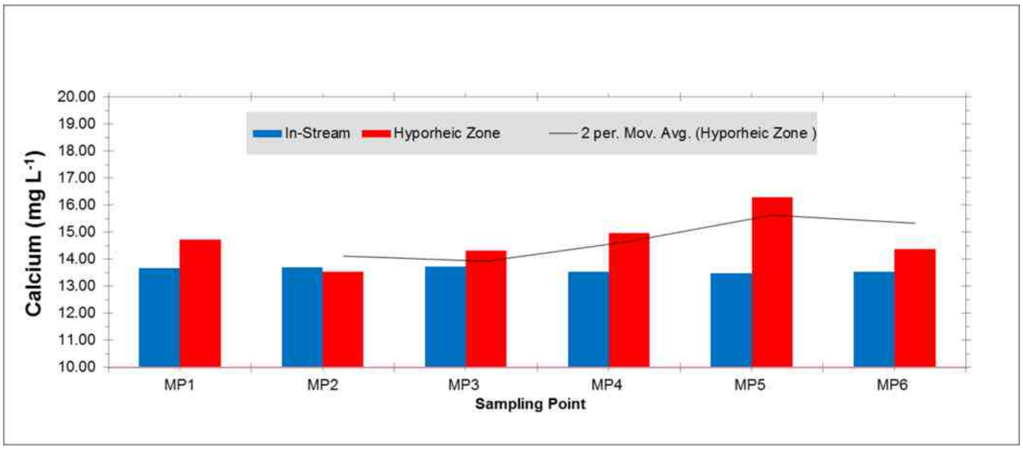

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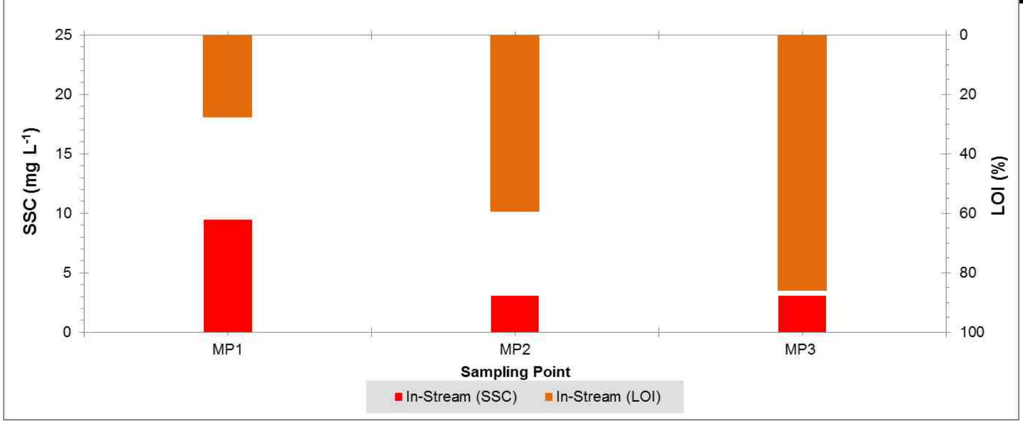

Butcher (1993) observed that where *R. fluitans* establishes due to enriched conditions, subsequent displacement by *Potamogeto sp* occurs. Microscope assessment places specimen in the *Potamogeto pectinatus* (fennel pondweed) taxonomy; however, because the plant was not bearing fruit during monitoring it may also be *Potamogeto filiformis* (slender leaved pondweed) *P. filiformis* is not assigned a STR (Holmes *et al*., 1999). *P. pectinatus* is the likely established species since its only recorded distribution is in England and Wales, whereas *P. filiformis* is in eastern Scotland and, *P*. *Vaginatus* restricted to Norway, Sweeden and Finland (Butcher, 1993; Holmes *et al*., 1999). *Potamogeto sp* reproduces vigorously, through pollination, seeds dispersion and plant propagule entrainment in flow, turions, the plant buds formed at the end of Summer – Autumn also drop-off in substrate and grow in spring (Jones, 2004).

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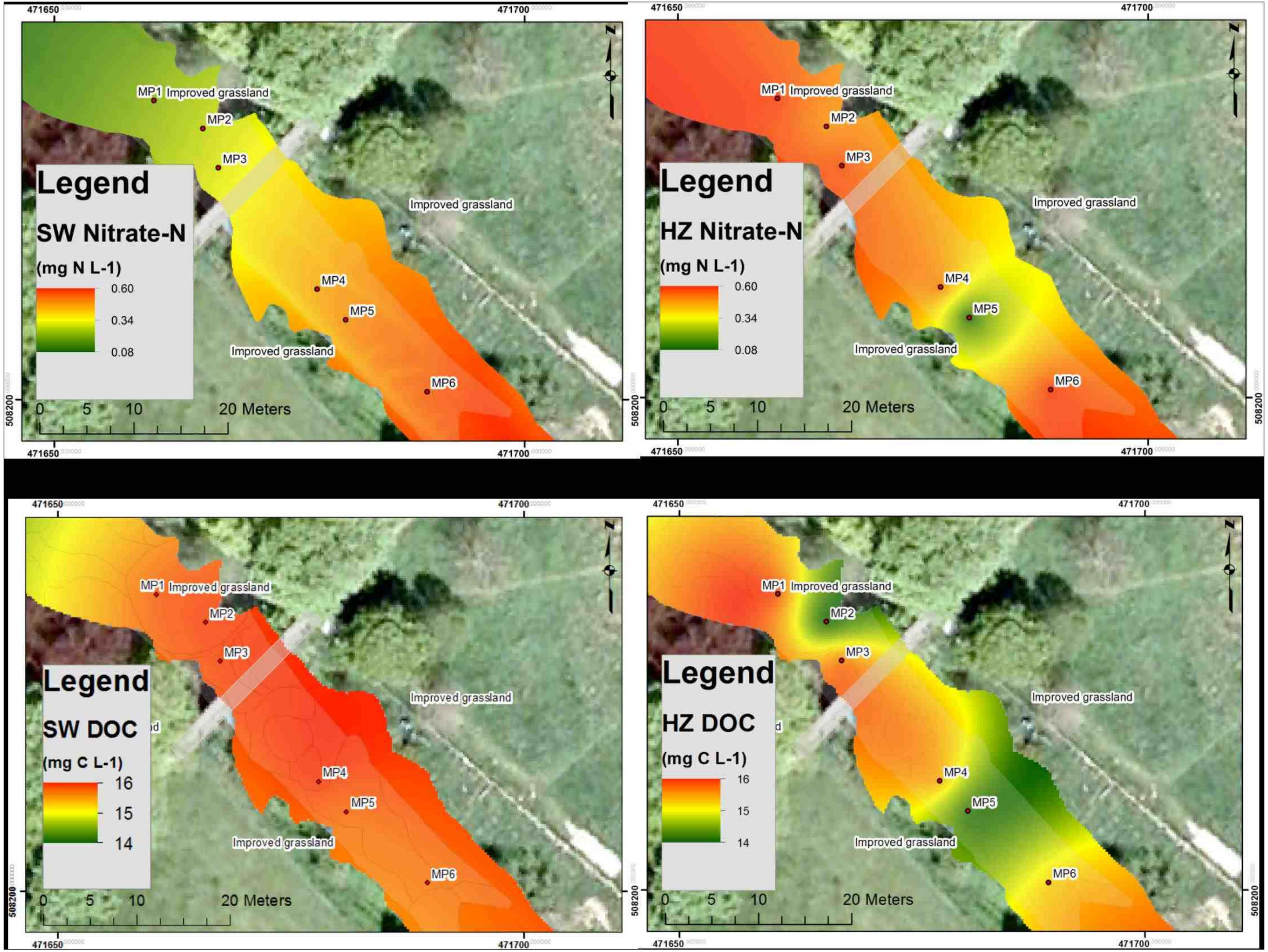

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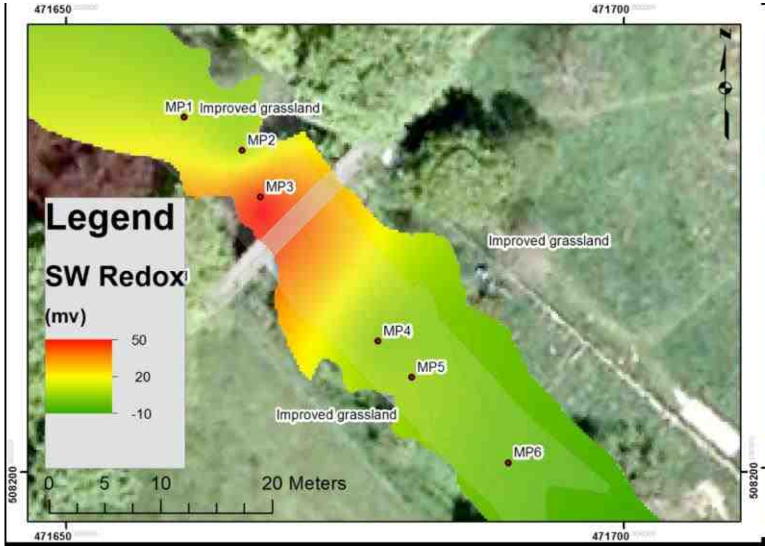

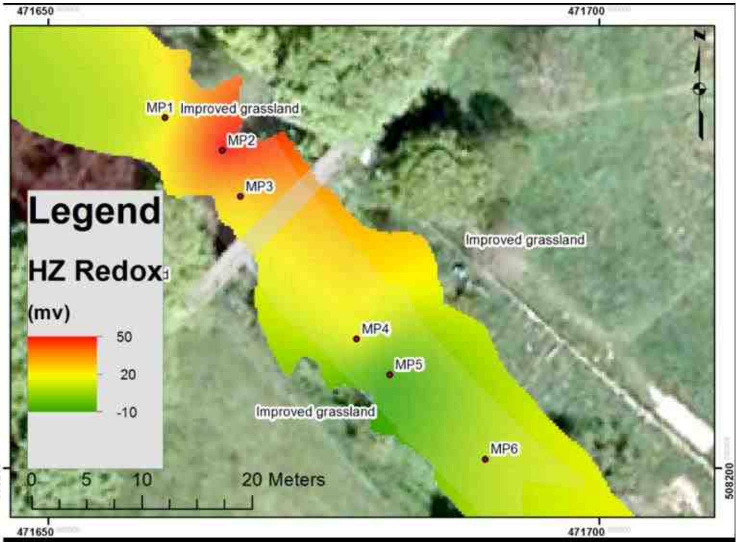

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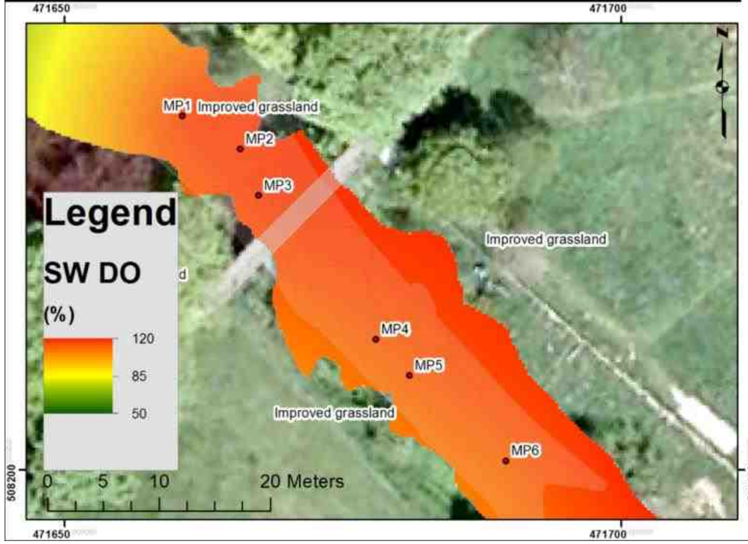

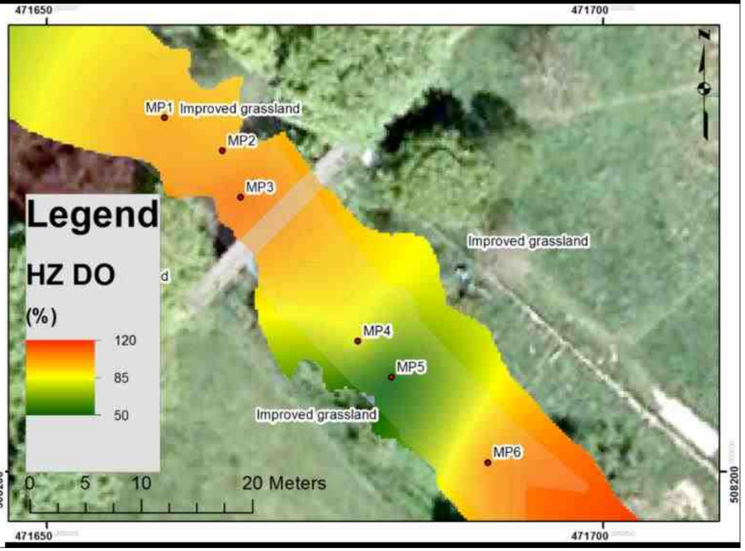

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Potamogeto sp prevelance is problematic since its vigorous growth outcompetes available substrate for *M. margaritifera* juvenile establishment. The hydraulically-induced deposition of water column suspension through straining, by numerous stipules (straw/stalk), is implicated in colmation and caking of sandy cobbly *M. margaritifera* habitat (Baird and Wilby, 1999; Geist and Auerswald, 2007; Jones *et al.*, 2012). The NVC denotes the typical habitat *P. pectinatus* as 'still/flowing, eutrophic, often polluted waters' with an Ellenberg nitrogen value of 7, 1 indicating infertile – extremely rich situations being 8 (Palmer, 2008:27). Given the observations of Spink *et al.* (1993) *Potamogeto sp* growth in P rich conditions, the Ellenberg N value and STR are bio–indicators of long-term reach enrichment. Biddulph (2012) also monitored flood-pulse nitrate-N peaks through 48-hour rainstorm monitoring at MP5. However, unlike Danby STW, the gravels appear to be oxygenated, within *M. margaritifera* range and not statistically different to in-stream waters (Table 5.4.2). This is anticipated to be a result of the reaches' hydrogeomorphological from, where a deep pool and shallow riffle drive high rates of HEF (Section 5.4.2, Hendricks, 1993). Morover *Potamogeto sp* resides epifaunally and lower lying in the water column, unlike *R. fluitans* which drives streamwise flow along its stems horizontally orientated to water surface (Fig. 5.61), which may influence rates of exchange (Hendricks, 1993; Jones *et al.*, 2012).

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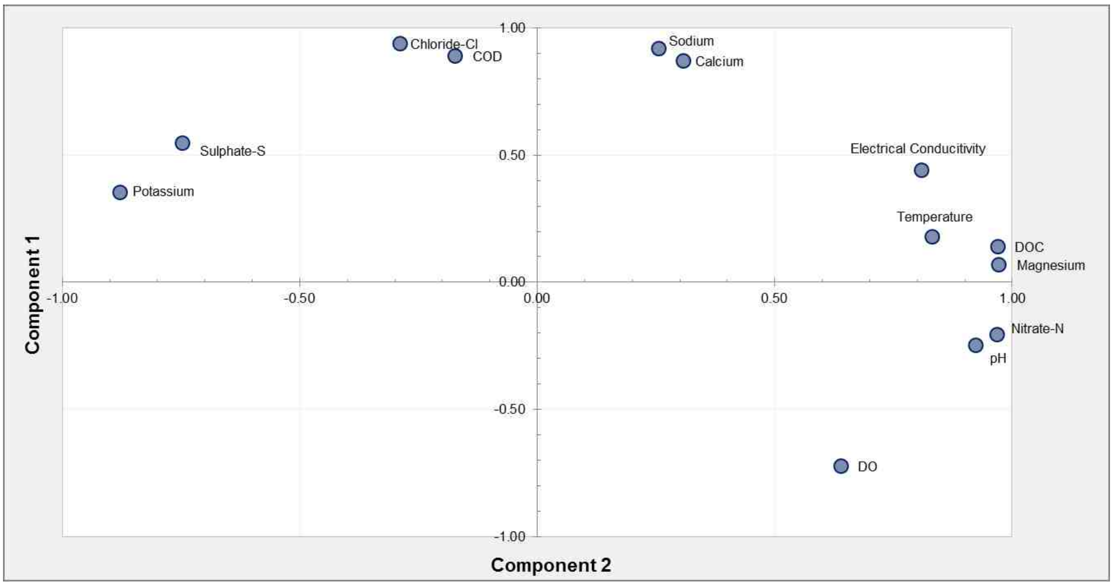
5.4.5 Data Reduction And Variance Analysis: Principal Component Analysis (PCA)



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In a two-component model which explains 89 percent of the cumulative variance, nitrate-N, DOC, magnesium, pH and temperature correlate with each other on the first component explaining 56% of the variance (Fig 5.76 and Table 5.4.3). Inspection of the communalities table reveals that nitrate-N accounts for 95% of the variance, similarly in the pattern matrix when nitrate-N is concentrated so is magnesium and DOC, pH is more acidic (Appendix 12). Magnesium, which has a high component loading at Danby STW, may be a trace of sewage effluent at the Moors centre since chemical variability of other parameters does not occur with magnesium at Lealholm Crunkly Gill. In the second component; chloride, sodium, COD and calcium correlate together. Again, this is a likely groundwater signal which was monitored at all other sites (Fig. 5.76 and Table 5.4.3).

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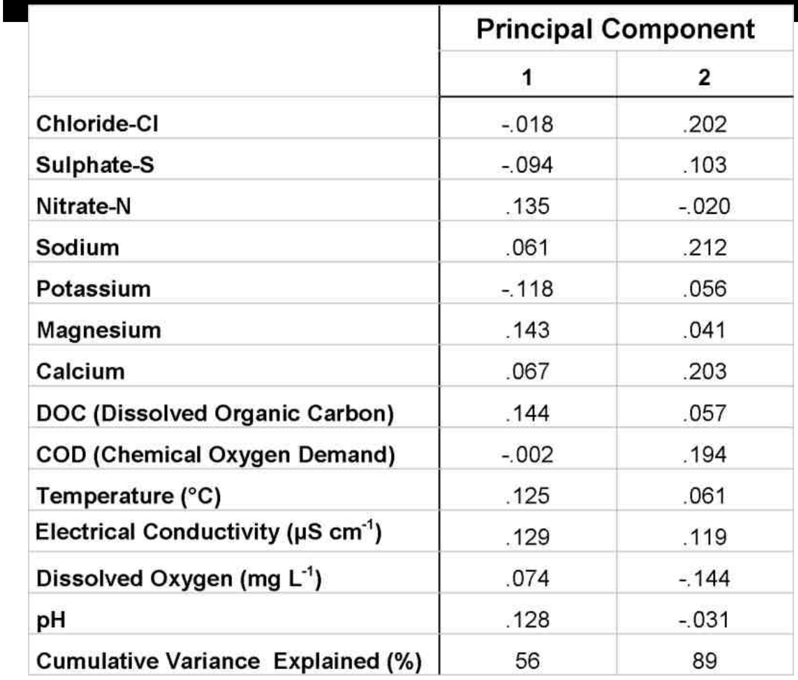


	Principal Component	
	1	2
Chloride-Cl	-.018	.202
Sulphate-S	-.094	.103
Nitrate-N	.135	-.020
Sodium	.061	.212
Potassium	-.118	.056
Magnesium	.143	.041
Calcium	.067	.203
DOC (Dissolved Organic Carbon)	.144	.057
COD (Chemical Oxygen Demand)	-.002	.194
Temperature (°C)	.125	.061
Electrical Conductivity (µS cm^{-1})	.129	.119
Dissolved Oxygen (mg L^{-1})	.074	-.144
pH	.128	-.031
Cumulative Variance Explained (%)	56	89

5.4.6 Conclusions

This section has demonstrated the hydrochemical impacts of HEF through a pool-riffle-pool sequence. [redacted] mussel is at the longitudinal terminus of its population on the Esk (Killeen 1999; 2006; Hirst *et al*., 2012). During spate, riffle-tail ejection provides cool oligotrophic alluvial groundwaters to this zone, buffering high in-stream nitrate-N concentrations and overall isotropic water column temperatures, a metabolic hotspot vital to bio indicator species survival.

Through the use of multivariate statistical procedures and macrophyte associations, a conceptual longitudinal link to upstream point-source discharge of STW effluent, c.650 m upstream, was facilitated. Despite dilution and exchange flows from STW through to the Moors Centre, reach-scale nitrate-N remains above *M. margaritifera* TV. COD is also elevated. The compound and entrenched geomorphological form of the channel concentrates flows through pool-riffle-pool sequences and is responsible for the highest Q_v monitored at any of the reach-scales. This final results section serves to frame the ensuing discussion of keynote hydrological and ecological processes which provision patch hot-spots within the otherwise ‘noisy’ reach mosaic. This is a vital step to the procedural identification of *M. margaritifera* survival and reintroduction sites.

Chapter 6 Discussion

6.1 Introduction

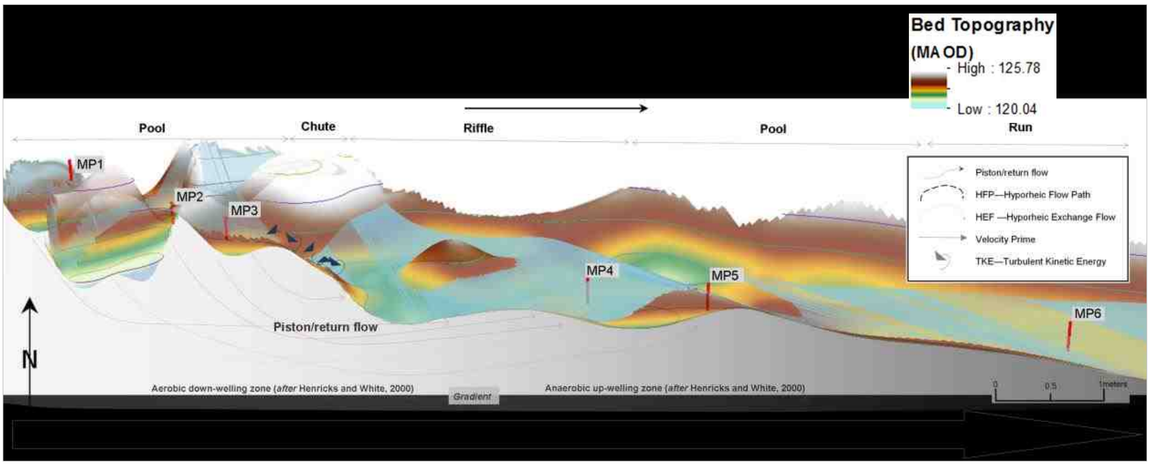
As the key aim of this thesis was to investigate hydraulic habitat influence on in-stream and hyporheic physicochemical water quality, one purpose of this discussion is to assess the results from the previous chapters in a wider academic context. The hyporheic zone can be defined from varied perspectives. Its situational context as a terrestrial aquatic ecotone lends itself to the conceptual opportunity of inter-disciplinary research (Chapter 2). Chapter 5 assessed fine-scale variability linked to pool-riffle, eddy and ephemeral overflow channel processes, which are responsible for concentration changes to key biotic nutrients, principally nitrogen-N (Fig 6.1). The chapter also assessed the impacts of macrophyte establishment at a polluted reach where mosses and ranunculus sporadically covered bed alluvium.

Initially section 6.2 starts by assessing reach-scale functional connectivity and water transfer through subsurface hyporheic flow pathways. The section also reviews the physical properties of hydraulic habitats and their effect on physicochemical patches. Vegetation management is also investigated in terms of its effects on HEF rate and therefore biological uptake and denitrification (Figs 6.2., 6.6). Section 6.3 briefly analyses the statistical difference between physicochemical elements of in-stream and hyporheic water. In addition to the detailed assessment of HFP metabolic hot spots (permanent) and hot moments (ephemeral), section 6.4 assesses diurnal changes where a nocturnal peak of nitrate-N, DOC and ammonium occurs. These conditions are associated with primary productivity rate change, including process switch from photosynthesis to chemosynthesis. Summarising this section, the key physicochemical and hydraulic monitoring parameters for *M. margaritifera* are detailed, along with the water quality differences between riparian reaches and river habitats. In conjunction with monitoring evidence, habitats serve as a basis to explain physicochemically fit reach-scale point locations for hatchery *M. margaritifera* reintroduction. The review of evidence finishes with a discussion on the influence of hyporheic and hydraulic habitats form and processes on catchment-wide monitoring programmes, including the EU WFD (2000/60/EC) monitoring which is predicated on bio-indicator species including *M. margaritifera* (Birk *et al.,* 2012). In the closing section 6.6 a summary of the research key findings are presented along with a discussion of the limitations of both the methodology and evidence. Recommendations for future research agendas are provided along with potential habitat rehabilitation strategies to prime sites for re-introduction.

6.2 Reach-Scale Connectivity Through Hydromorphology Forms: Implications For Hydrochemistry

Water bears the characteristics of the landscape medium from which it drained (Hynes, 1979; Allan, 2004; Bracken and Croke, 2007). Given this, source-waters are often characterised by chemical elements, temperatures or trophic status "signatures" (Burt and Pinay, 2005; Jarvie *et al*., 2008). Sampling has generated an extensive dataset, allowing physicochemical tracers from source-waters to be identified. Sampling has given evidence of exchange between stream water and the substrate through conservative solute tracers, hydraulic determination of strong VHG, $Q_{v,}$ temperature and redox status change between ecotones (Harvey and Wagner, 2001; Ibrahim *et al.,* 2010; Wainwright *et al.,* 2011). Dense monitoring has isolated where metabolic hotpots occur with reduced nutrients and temperature, supporting niché biota refugia in otherwise enriched stream conditions generally unfit for *M. margaritifera* filter-feeding (Dent *et al*., 2001; McClain *et al*., 2003). Hyporheic flow paths bear key hallmarks on hydrochemically isotropic in-stream waters (Chapter 5, inc. Figs 5.31., 5.67.). The evidence reiterates that the geo-diversity of geomorphic forms impacts on processes, particularly biogeochemical reductions of nutrients (Groffman *et al*., 2009).

As previously discussed (Section 4.2.2), there are many methods to identify stream hydraulic habitats. The bed topography survey undertaken in this study supports the characterisation of habitat identification tools available to practitioners, including the EA RHS and the hydraulically calibrated meso-habitats method proposed by Newson *et al.* (1998). All VHG and Q_v measurements in the riffle-heads of pools show downwelling, or injection into riverbed alluvium (Section 5.1, 5.3.2, 5.4.2). During the course of a day this occurs at a considerable rate, at the riffle-tail of Crunkly Gill (MP3C) = 217.8 m d^{-1} (Appendix 12). Riffle-units show a weak positive VHG and Q_v inferring minor discharge out of the cascade. At the down-river monitoring points, at the riffle-tail, a strong positive VHG and Q_v is monitored where discharge occurs out of the riverbed.



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It is not only hydraulic gradient that contrasts between the head and tail of a riffle, but also the hydrochemistry concentrations of particular parameters. Chloride and Calcium were particularly concentrated in both shallow floodplain and deep groundwaters at Crunkly Gill and Danby STW. At the riffle-tail of all monitoring points Cl and Ca concentration is statistically different to that at the riffle-head (Table 5.2.2 and 5.3.1, Appendices 8, 11, 12), with a significant probability that concentrations at the tail will be higher than those at the head (Chapter 5). This pattern is an alluvial groundwater signal where hyporheic flow paths discharge through the riverbed altering the physicochemical properties of hyporheic water (Fig. 2.6 and 4.1; Smith, 2005; Ibrahim *et al.,* 2010; Boulton *et al.,* 1998; 2010). There is also an increase in acidity where flow ejects, because of the dissolution of the Triassic sandstones (Allan *et al*., 1997; BGS, 1999). This acidity is rapidly buffered by mixing with in-stream waters making it generally fit for *M. margaritifera* respiration (Allen and Vaughn, 2010).

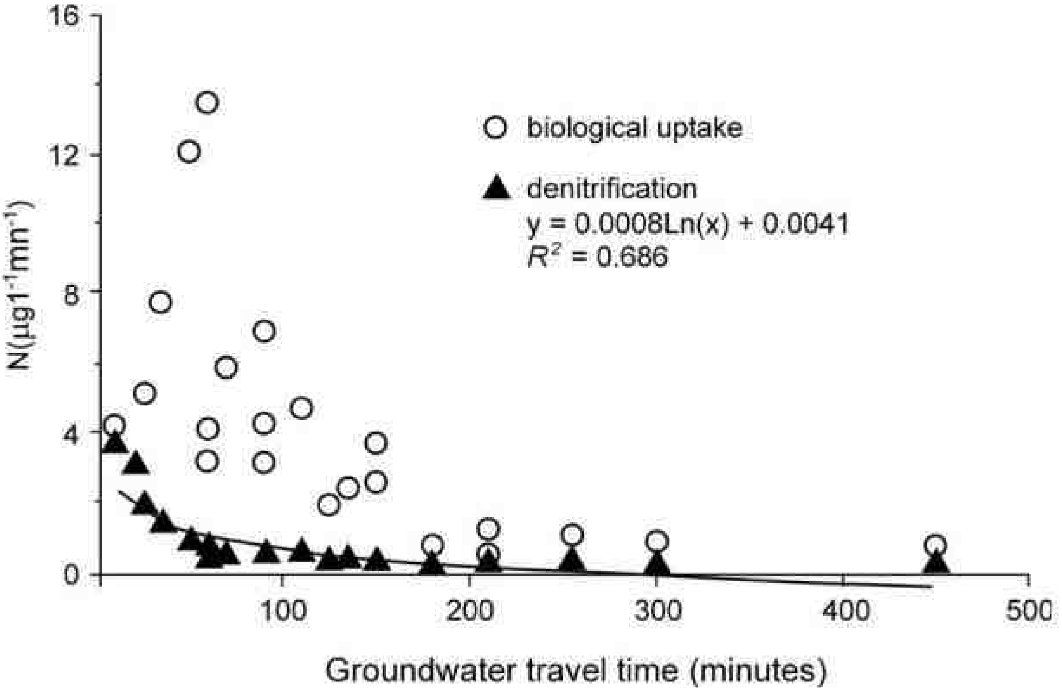
A fundamental change to the trophic status of water also occurs, both in-stream waters, but markedly in the pore water of the hyporheic zone, between the head and tail of a riffle. At a more natural site, Lealholm Crunkly Gill, the arithmetic mean nitrate-N concentration of downwelling waters is higher at riffle-head than tail, reducing by 73% and falling below the Bauer (1988) TV to 0.24 mg N L^{-1}, and only exceeding Moorkens (2000) TV of 0.125 mg N L^{-1} during nocturnal sag (Chapter 5.1). A similar trend is presented for DOC. Ammonium (NH_4^+) is not anticipated to be harmful to *M. margaritifera,* unlike Ammonia (NH_3^-). However, ammonium (NH_4^+) may present a risk if transformed through nitrification to nitrate (NO_3^-). Aqueous NH_4^+ may also volatise, which may explain why no ammonium (NH_4^+) was detected in MP2B at the Lealholm riffle where TKE exists (Sprent, 1987; Pinay *et al.,* 2008; Ranalli and Macalady, 2010). Anammox – anaerobic ammonium oxidation – may be one pathway in this respect (*ibid*). In increasingly alkaline conditions, which episodically occur, NH_4^+ may speciate to NH_3^- due to the loss of a hydrogen ion, where relative hydrogen activity changes (Sprent, 1987; Alloway and Ayres, 1994). Even in at the eutrophic and degraded reach of Danby STW, hyporheic nitrate-N is reduced at the riffle tail, compared to outfall MP4 and the intermediary 4 monitoring points. However, by the end of the reach nitrate-N does not recover to its pre-outfall concentration at MP1 (Chapter 5.3).

A series of key reduction pathways are significant, including for nitrate-N, nitrite-N and ammonium-N (TIN), as well as for phosphate-P and DOC, through the pool-riffle-pool sequence. Firstly, the fundamental process of piston/return flow is the mechanism whereby in-stream flow down-wells at the riffle-head and subsequently up-wells at the riffle-trail, creating a HFP. This only applies to a portion of total in-stream discharge. The positive VHG in the riffle unit suggests weaker HFP egress and discharge through the cascade (Dahm *et al.,* 2006). The step hydraulic gradient accords with exertion of pool hydrostatic pressure on the riffle stoss. This is where bankfull discharge is physically constrained by the chute bedform from the wider wetted perimeter of a pool, to a riffle (Wainwright *et al*., 2011). This hydraulic pressure is alleviated on the lee side, where flow cascades and riffles. Due to a reduction in water column depth, positive VHGs and HFP discharge occurs through the riverbed (Thompson, 1986; Ibrahim *et al*., 2010). Low pressure in the riffle and relatively higher pressure in the pool creates a gradient and riffle-tail ejection is most prominent and the intersection between riffle and pool where bedform laterally extends (Henricks 1993; Henricks and White, 1995; 2000; Fig. 1.1., 4.1., Maps 5.1.1). The relative importance of this underlines a new conceptualisation of return flow, as piston-flow where "new" water pushes through "old" water as it does in steep riparian seeps (Thompson, 1986; Burt and Pinay, 2005). Accordingly, hydrostatic pressure alleviates and so does pore water pressure in the interstices on the far lee-end. Assessing nitrate-N and DOC, a series of key mechanisms for concentration reduction are functionally critical:

(1) A reach-scale HFP through a pool-riffle-pool, occurring as piston flow. This is a pathway where in-stream waters are transmitted though the interstitial pore water network, through biofilm and over mucilaginous algal rich clast coatings, where heterotrophic microbes decompose and assimilate biosestonic matter (Maltby, 1992A; Hendricks, 1993; Zimmermann and Lapointe, 2005). Clast mortaring of fragmental leaf silage is also likely to be key process driving POM into the interstices, coupled with benthic shredders and grazing communities (Newbold, 1992; Newbold *et al*., 1982; Trimmer *et al*., 2012). Section 2.4 outlines specifically how hyporheos are agents in stoichiometry.

Two key eco–hydrology processes are thought to result in nitrate-N depletion. The first relates to vegetation, principally common alder (*Alnus glutinosa*) distribution throughout the River Esk riparian corridor (Peterken, 2002). *A. glutinosa* bacteria-root symbiotic relationship is well established for *actinorrhiza,* an endophytic denitrifican coating the non-leguminous roots nodulated within the saturated zone and capillary fringe of wetted bar (Sprent, 1987; Triska *et al.,* 1989, 1993; Actinorrhiza, 2006). Where 'new' flow is pistoned through interstitial water, this bacteria-root system undertakes denitrification (*ibid*). Pinay *et al.* (2008) recorded the occurrence with *Alnus crispa* in salmon redds of Lynx Creek, Alaska. Figure 6.2 shows the rapid rate of denitrification, with plant and microbial uptake reaching 14 mg NO_3^-N L^{-1} min^{-1} (Pinay *et al.,* 2008). Secondly, microbial processes coupled with an ensemble of detritus processing macroinvertebrates are fundamental to biotic nutrient fixation (Maltby, 1992A; Hendricks, 1993). Determination of microbial processes is problematic because only 0.25% of freshwater and benthic bacteria can be isolated (Jones, 1987). Heterotrophic microbial investigation remains outside the remit of this investigation; however, Maltby (1992A) in addition to Jones (1987) provides a good introduction. DOC reduction towards the riffle-tail is an indication of heterotrophic micro-organism mineralisation, probably of ^{14}C, in a form such as ^{14}C-glucose, used in respiration to generate CO_2 (Jansson *et al.,* 2000;

Trimmer *et al.*, 2012). Evans *et al* (2014) recorded the diatom *Eunotia orthohedra* through Danby Beck, a photoautotroph which favours acid conditions. Obligate *Thiobacillus denitrifican* is noted as an anaerobic DNRA (Dissimilatory Nitrate Reduction to Ammonium) bacterium in sediments which sources sulphur in pyrite (Grimaldi *et al.,* 2004). At Lealholm the groundwaters are sulphur-rich and this pathway would explain ammonium (NH_4^+) occurrence only in the pore water of the riffle-tail during 24-hour monitoring on 12 -13 Oct. 13 (Chapter 5.1, Appendix 12, BGS, 2009; NSRI, 2013).



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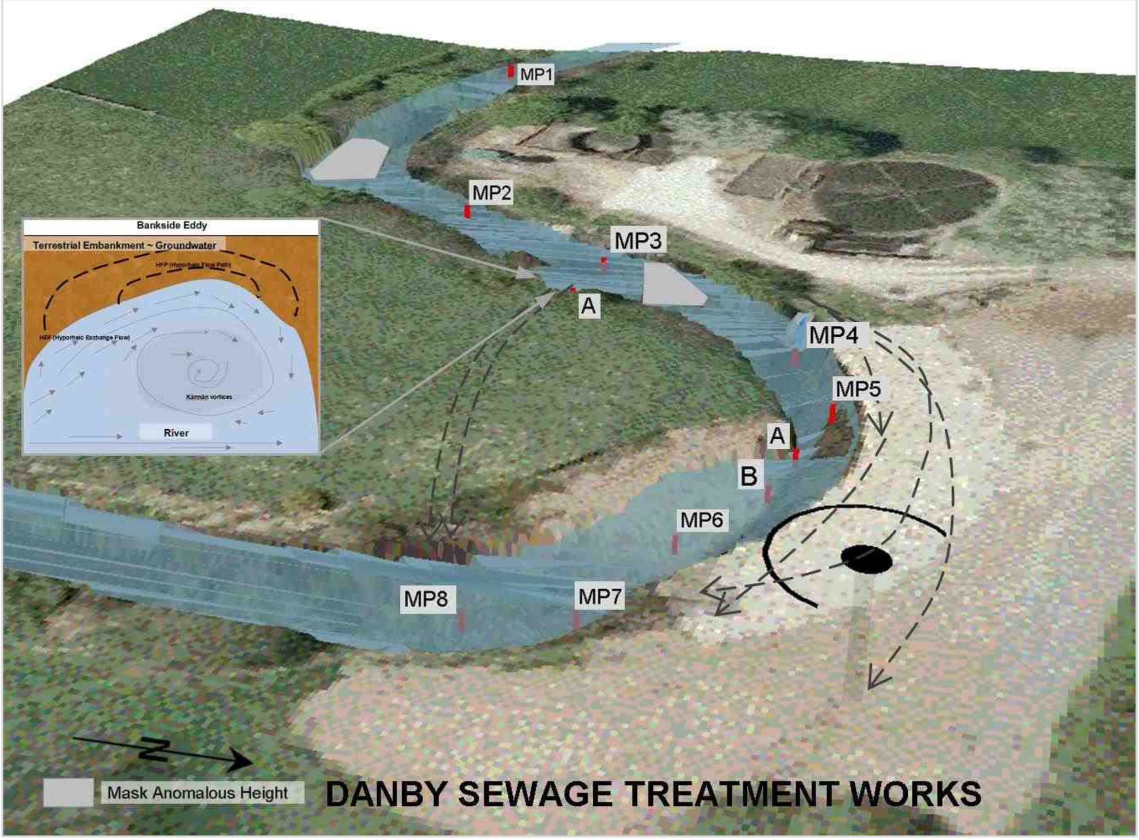
(2) Dilution of nitrate-N enriched surface waters by oligotrophic groundwaters (Smith, 2005; Buss *et al.,* 2005). Where HFPs introduce “new” in-stream waters to alluvial groundwater, they mix and are subsequently discharged at the riffle-tail, also altering groundwater hydrochemistry (Wainwright *et al.*, 2011; Hancock *et al.,* 2005; Boulton *et al.,* 1998; 2010). At Leaholm Crunkly Gill, mean groundwater nitrate-N = 0.25 mg N L^{-1}, whereas in-stream = 0.95 mg N L^{-1} and at the riffle-tail (MP3C) = 0.19 mg N L^{-1}, inferring heterotrophic processes are responsible for further reduction.

(3) In-stream processes are as functionally critical as subsurface processes (Emery *et al.,* 2003; Allen and Vaughn, 2010). At Lealholm Crunkly Gill the suface water pool-riffle-pool (PRP) reduces nitrate-N from a mean of 0.57, 0.56 to 0.54 mg N L^{-1} (Table 5.2.2., Map 5.1.1 – .2, Fig. 5.31). A critique of Ibrahim *et al.* (2010) and Wainwright *et al.* (2011) is the de-coupling of riffle processes which also have keynote influence on stream-chemistry. While only a 5.3.% decrease in nitrate-N, the concentration comes not only

closer to Bauer’s (1988) TV, but infers that over much larger PRP, in higher discharge fluvial systems, N reduction is may be higher (Emery *et al.,* 2003 McClain *et al.,* 2003; Arntzen *et al.,* 2006). Riffle units have different hydraulic properties in comparison to surrounding units. The alluvial gravels consist of larger angular clasts with few fine sediments. Accordingly, higher roughness coefficient prevails (Richards, 2000; Emery *et al.,* 2003; Emery *et al.,* 2004). Roughness functions as a flow control, creating turbulence (expressed as TKE) and secondary cells (*ibid*, Buffin-Bélanger *et al.,* 2000). Volatization and denitrification are key processes, with TKE generating higher rate exchange with river sediments, higher oxygenation of gravels and DOC deliverance (Sprent, 1987; Allen and Vaughn, 2010; Trimmer *et al*., 2010). Anammox generates N^2 and this would explain why no ammonium was detected in-stream waters or HZ, compared to riffle—head or —tail, at Lealholm Crunkly Gill (Table 5.2.2., Ranalli and Macalady, 2010). Denitrification occurs with the supply of DOC where nitrogen ions are oxidised, under constant oxygen (O_2) loss: nitrate-N (NO_3^-), nitrite-N (NO_2^-), nitric oxide (NO) and then dinitrogen gas (N_2) (Sprent, 1987; Ranalli and Macalady, 2010). Denitrification is biogeochemically significant since it sinks N into the atmosphere, whereas biota death returns N to the ecosystem (*ibid*).



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Riffle habitats are also occupied by macroinvertebrates with grazing specificity; for instance riffle beetles (*Coleoptera: elmidae*) are noted to graze on periphytic and filamentous algae, detritus and decaying vegetal materials (Elliott, 2008). Turn-over of detrital matter, including by gammarides (<2 hours consumption to excretion), concurs with reduced in-stream DOC and may well cleanse clasts for *M. margaritifera* (Maltby, 1992). The riffle-tail is marked by a ‘redoxcline’ (Buss *et al*., 2005), a boundary layer between oxygenated riffle-gravels and deoxygenated groundwater ejection, where in-stream redox jumps to highly oxidating conditions, met with groundwater reduction. The redox and trophic status gradient creates a dynamic ecotone edge-effect (Lovejoy *et al.,* 1986).

6.3 Does Hyporheic Flow Pathway Ejection Out of A Riffle-Tail Create Unique Oligotrophic Refugia For *M. margaritifera*?

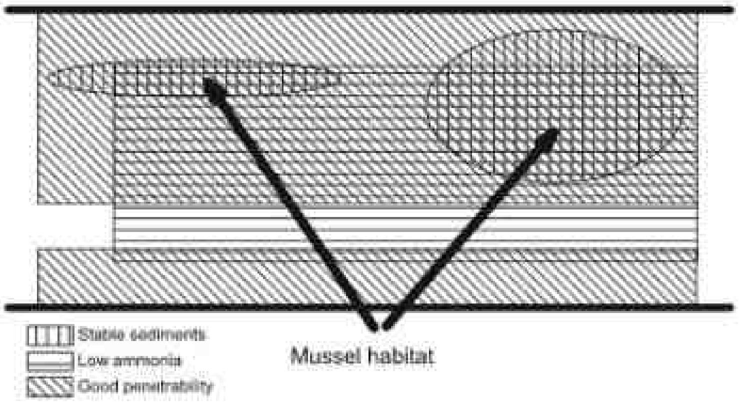
Prior to detailing the influence of geomorphic–biological interactions on hydrochemistry, it is critical to stipulate that given the *M. margaritifera* stringent filter feeding TV (Table 2.1) and the exceedance of those thresholds by numerous parameters, no points within the three reach-scales of the River Esk are suitable for reintroduction of hatchery reared *M. margaritifera* (Chapter 5, Bauer, 1988; Moorkens, 2000; Oliver, 2000). However HFP and hydromorphic features that encourage functional connectivity have stoichiometry effects, generally reducing biotic nutrient concentrations below *M.margaritifara* TV in pore-water and marginally in in-stream waters at the three sites. Oligotrophic groundwaters are important to *M. margaritifera* survival, with geomorphological agents encouraging exchange being a potential factor in metabolic hotspots (Triska *et al.,* 1989, 1993; McClain *et al*., 2003; Boulton, 1998; 2010). Ward and Tockner (2001) observe that: *Large homogeneous patches provide little habitat for edge species, whereas small patch size excludes interior species. Maximum diversity should occur where there is an optimal mix of patch and edge habitat.*

Given the anthropocentric re-plumbing of riverscape to make flow commensurate to human practices and conventional drainage practice, subsequent widespread extinction of fluvially diverse geomorphological forms has ensued (Hooke, 1994; McNeil, 2000; Mainstone and Holmes, 2010; Brown *et al*., 2013, Section 2.2.1.1). Section 6.2 demonstrated how pool-riffle forms have an hydrodynamic effect on the physical chemistry of pore water, creating a redoxcline, plumes of cooler groundwater which are depleted in DOC, TIN and phosphate-P concentration. In-stream ecohydraulic processes associated with turbulence altered stoichiometric processes resulting in 5% reductions in variables such as mean nitrate-N through a pool-riffle unit (Ranalli and Macalady, 2010; Emery *et al.,* 2013). This section only appraises hydrochemistry results at Lealholm Crunkly Gill and Danby Moors Centre, since groundwater contamination at Danby STW results reduced concentration return-flow for phosphate-P, nitrate-N, high EC and other variables which imperil *M. margaritifera.*

At the non-disturbed reaches, bulk arithmetic mean nitrate-N is 0.57 mg N L^{-1} and 0.60 mg N L^{-1}, at Crunkly Gill and the Moors Centre, both slightly exceed Bauer's (1988) middle TV at 0.50 mg N L^{-1}, but not Oliver's (2000) at 1.0 mg N L^{-1}. The most notable change is in hyporheic pore phosphate-P and nitrate-N concentrations at the riffle-tail. At Danby Moors Centre spot sampled hyporheic nitrate-N at MP5 was 0.08 mg N $^{-1}$ compared to an in-stream mean of 0.60 mg N L [redacted] he lowest mean within the reach-scale monitoring. Both average concentrations fall below the lowest nitrate-N TVs, set by Moorkens at 0.125 mg N L^{-1} which is exceeded during a nocturnal sag at Crunkly Gill between 01:00 – 06:00 on 12 – 13th October 2013, peaking to 0.24 mg N L^{-1} at 04:45 (Fig. 5.42, Appendix 8).

Physical habitat biogeochemistry is a function of fluvial form and process. Fischer *et al.* (2005) observed that C and N cycling in river sediments occurs at a rate five times faster than marine sediments. They thus coined metabolic functions in the hyporheic zone as a 'river's liver'. At Crunkly Gill COD was significantly lower in the hyporheic zone than in-stream. COD was also lowest in riffle-tail pore water (Chapter 5, Table 5.2.2). While the riparian zone is a lateral filter in riverine biogeochemistry (Mander and Hayakawa, 2005; Burt *et al*., 2010; 2010A), the residual elevation and depressions from a riverbed logarithmic line, pool-riffle units, are the vertical filter (Richards, 1990; 2000; Boulton, 1998; 2010; Triska, 1993). Using PCA and the EA RHS (2003) Hastie *et al*. (2003) determined: *At the 50 – 500m scale, a positive association with rapids was observed. This may be explained by the fact that mussel beds are often found* ***not in, but immediately below rapids*** *(Baer, 1969; Vaughn, 1997).*

The dynamic edge-effect between the rapid/riffle and pool also dissipates sheer velocity allowing stability of alluvial bed sediments, while upwelling and run to the next pool may be sufficient to prevent siltation (Richards, 2000; Ibrahim *et al*., 2010; Thompson, 1986). Hatcheries can be used to learn more about molluscs (Schmidt and Vandré, 2010; Gum *et al.,* 2011). Following recommendations from Killeen (2011) to FBA Arc hatchery, monthly cleansing of juvenile substrate trays and flow improvement over both adult and juvenile beds has resulted in observed lower stress (Sweeting and Lavictoire, 2013). HFP discharge through the riffle-tail may be sufficient to prevent colmation and the excessive deposition of bioseston (Blaschke *et al.,* 2003; Zimmerman and Lapointe, 2005; Velickovic, 2005). These compaction factors are implicated substratum oxygenation and periphyton growth (Haack and McFeters, 1982; Holmes and Newbold, 1984).



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Daytime nitrate-N and phosphate-P concentration in the hyporheic zone of riffle-tails at both the Moors Centre and Crunkly Gill fall below Moorken's (2000) TV. However, one phosphate-P spot sample (1/26 samples) at riffle-tail of Crunkly Gill (MP3C) on 14th April 2013 was 0.02 mg P L^{-1}, exceeding Moorkens (2000) TV but not Oliver's (2000) or Bauer's (1988) (Appendix 8, Table 2.1). Other physicochemical parameters fall outside *M. margaritifera* TV at the riffle-tail, namely calcium, pH, DO and EC (Tables 5.2.2., 5.4.2.). Concentrate calcium is a monitored groundwater signal. Calcium TV exceedance may not be unfit for *M. margaritifera* filter feeding, since Skinner *et al*. (2003) monitored atypical English and Irish populations tolerating the calcareous water chemistry associated with catchment geology. Moreover, through functional filter feeding, unionids sequester calcium for shell building, which is particularly important in nacre enamel production (e.g. Gee, 1991; Strayer, 2008). Due to the role of century-timescale polyphyletic speciation of *M. margaritifera in situ* of baseline riverine hydrochemistry on the River Esk, small calcium fluctuations above TVs are not considered a threat to *M. margaritifera* in this thesis.

Calcium (Ca) transformation to Calcium Carbonate ($CaCO_3$) may occur due to labile diffusion of CO_2, generated during turbulent riffle exchange coupled with heterotrophic carbon respiration, explaining the peak in concentration in Ca (Webster and Patten, 1979; Trimmer *et al*., 2012). YSI temperature data recorded riffle temperatures being cooler than pools, by approximately 1°C in winter months, resulting from bed roughness-induced exchange with the cooler air temperatures (Hardy *et al*., 2009; Appendix 8). Riffle-tail water column thermal dynamics may therefore be more susceptible to atmospheric conditions, analogous to a river "lung" function (Fig. 5.70). This may be one of the underlying mechanisms for temperature-induced larval release of *M. margaritifera* (Hastie and Young, 2001).

The exfiltration of hyporheic return flow through a pool-riffle unit provides a unique habitat depleted in biotic nutrient concentration and with cooler waters (Stanley and Boulton, 1993; Boulton *et al.,* 1998, 2010; Allen and Vaughn, 2010; Fig 5.31., 5.43.). Although hydrogeological aspects of DO, calcium and EC may be in exceedance of FWPM thresholds, the hydraulic lag-effects from riffle processes, namely turbulence, create an in-stream oxygen saturated environment, for instance mean DO = 101.30% at MP3C, Crunkly Gill (Section 5.2.3). Although DO saturation falls below *M. margaritifera* TV in hyporheic pore water, high oxidating conditions prevail, at a mean of 488mV, suggesting surface water processes affect groundwater redox status with a lag-effect (Smith, 2005; Arntzen *et al.,* 2006; Malcolm *et al.,* 2003; 2008). High redox provisions electron donors in hyporheic pore water. Through discriminating microhabitat features of *Margaritifera hembeli* Johnson and Brown (2000:271) determined: *Mussels were rare in deep, stagnant pools with silt-covered bottoms, and were more common in shallow, wide areas of streams with higher current velocities and in sediments with larger particle sizes.*

Despite no monitoring point in this investigation finding complete physicochemical water quality parameters in the range of *M. margaritifera* TV, riffle-tails due to their discharging of cool oligotrophic alluvial waters, coupled with in-stream reduction processes are deemed most suitable for the reintroduction of hatchery reared *M. margaritifera* (Thompson, 1986; Stanley and Boulton, 1993; Buss *et al.,* 2005, Fig 5.31., 5. 67.). Loss-on-ignition data also presents the highest arithmetic mean carbon concentration in suspended sediment (Fig 5.41). Given the unique ecology of riffle macroinvertebrates (Section 6.2) such as elmidae (e.g. *Elmis aenea*) and rapid gut transition by gammarids among other invertebrates, periphytic drift POM can be shredded down into excreted FPOM and UFPOM suitable for *M. margaritifera* filter feeding (Newbold, 1982; Gee, 1991; Maltby, 1992; Elliott, 2008). This is once riffle-to-pool velocity dissipation encourages bioseston deposition (Newbold *et al.*, 1982; Arntzen *et al.,* 2006; Lansdown *et al*., 2012). POM is colonised by aquatic fungi and bacteria which may also form part of juvenile and adult diet (Gee, 1991; Moss, 1998; Yeager *et al*., 1994). Section 2.3.1 demonstrated the functions of detrital matter in reducing harmful ions (e.g. Eybe *et al.,* 2013).

Currently, the oldest *M. margaritifera* of the River Esk hatchery reared cohort is 7 years of age (Sweeting and Lavictoire, 2013; Lavictoire *pers. comm.* 2014). 10 years old is the intended reintroduction age back to host rivers as this marks the onset of reproductive viability (*ibid*, Skinner *et al*., 2003; Geist, 2010; Reid *et al.,* 2012). Thus, investigation of post drop-off habitat data is urgently needed to provide reach-scale hydrochemistry information for *M. margaritifera*, which in the early life states <5 years is inaffaunal – the hyporheic zone (Hastie *et al*., 2001; 2003A; Geist and Auerswald, 2007). In transition to adulthood, the water column is more heavily used for respiration, so conditions here also need to be hydrochemically suitable (*ibid,* Table 2.1). Bolland *et al.* (2010), Fowles *et al.* (2010) and the IUCN (1998) reintroduction protocols provide a salient risk based approach to pollution. However, further downscaling to individual units is now required to quantify the role of ‘geomorphic-hydrologic features in determining physicochemical patterns’ (Stanley and Boulton, 1993; Hendricks, 1993:73). This is particularly necessary given *M. margaritifera* TV and the association of exceedance and imperilment (Buddensiek, 1994; Bauer, 1998; Oliver, 2000; Moorkens, 2000). The evidence presented in this thesis shows that riffle-tail HFP ejection contributes to the quantified oligotrophication of pore water. Not are pore water concentrations reduced by 73% for variables such as nitrate-N at the *M. margaritifera* active area – Crunkly Gill – but the hydraulic actions of riffles reduces biotic nutrient concentration, removing all ecotonal ammonium in the riffles at Crunkly Gill. The need for detailed spatiotemporal and ecotonal hydrochemistry evidence in the production and of reintroduction frameworks is critical (Sabater and Vila, 1991; Stanley and Boulton, 1993; Pullin and Knight, 2003; Sutherland et al., 2004). Stoichiometric reasoning needs to be adjoined to pre-existing habitat surveys such as the EA RHS (2003) so that conservation managers can delineate habitats of suitable water quality without intensive fluid mechanics determinations (e.g. Allen and Vaughn, 2010; Newson *et al.,* 1998; Beechie *et al.,* 2010).

The Ballinderry hatchery provides a vital case for further work to understand hydraulic microhabitats processes and their impact on water quality (Seal, 1991; Wilson *et al*., 2012; BBC, 2014). 500 hatchery-reared specimens await reintroduction (*ibid*). Conservation managers have recently extricated sporadic pre-existing *M. margaritifera* and “re-planted” them in re-aggregated beds at points within the reach-scale creating ‘sanctuary sites’ (Wilson *et al*., 2012; Reid *et al.,* 2012; BBC, 2014). The theoretical underpinning of re-aggregation is based upon the principle that *M. margaritifera* is a keynote processes species which primes juvenile habitat through filter-feeding biological oligotrophication and aeration of substratum by foot movement (Young and Williams, 1983A; Nalepa *et al.,* 1991; Vaughn and Hakenkamp, 2001; Section 2.4). The method is associated with improved breeding success, particularly during fertilisation stages (Geist, 2010; Reid *et al.,* 2012). The main guiding principle in the case of Ballinderry was to place molluscs behind large boulders to protect them from flood-pulses (Wilson *et al*., 2012; BBC, 2014). Boulders retard coherent flow structures resulting in Kelvin-Helmholtz instabilities which can generate lee-side bedload deposition (Bennett and Best, 1995). Wilson *et al*. (2012) sets out the Northern Ireland reintroduction guidance for *M. margaritifera*, adopting elements of the IUCN (1998) protocol. Wilson *et al*. (2012) discuss Species Distribution Modelling (SDM) for favourable landscapes and soft reintroduction, with an acclimatisation period; however, the hyporheic zone remains unmentioned throughout.

A paucity of reliable hydro-ecological evidence exists for reintroducing *M. margaritifera,* particularly for reach-scale habitats (Hamilton *et al.,* 1997; Hastie *et al.,* 2000; 2003A; Bolland *et al.,* 2010). Given the monitored loss of fitness in hatchery-reared *M. margaritifera* (Geist, 2010; Gum *et al.,* 2011), the pre-existing coherent body of evidence for the pool-riffle piston-flow (Thompson, 1986; Boulton *et al.,* 1998, 2010; Hendricks, 1993; Hendricks *et al.,* 1995; 2000), functional connectivity (Ibrahim *et al*., 2010; Wainwright *et al.,* 2011), nitrate retention (Triska *et al.,* 1989; 1993; Buss *et al.,* 2005), and vital metabolic hotspots together hydraulically generate oligotrophic niche refugia (Schlosser, 1995; McClain *et al.,*2003). Evidence collected during this research has demonstrated the vital importance of these processes in reducing nutrients, temperature and COD whilst delivering a higher bioseston concentration in suspended sediment. Paying heed to the importance of habitat hydraulics and HFP is critical since *M. margaritifera* is a habitat specialist rather than generalist, despite FWPM abundance and distribution being described as 'noisy' (Hamilton *et al.,* 1997:537; Hastie *et al.,* 2000; 2003A). Using the chi squared test (χ^2) Hastie *et al.* (2003A:217) previously determined *M. margaritifera* abundance was most positive association number of riffles, unbroken standing waves and broadleaf/mixed woodland ($p < 0.001$). These are precisely the monitored geomorphological facets of Lealholm Crunkly Gill. The impetus is now to link pool-riffle unit biotic nutrient processes to practicable reintroduction strategies, connecting fisheries science with ecohydrology (Hendricks, 1993; Hamilton *et al.,* 1997; Krause *et al*., 2011). Indeed, where proactive conservation managers have rehabilitated water quality, tools already exist to improve hyporheic flow and functional connectivity through hyporheic substrate. One example includes using fallen tree stem foliage to orientate flow into the hyporheic zone, flushing the interstices and introducing stream DOC (Emery *et al.,* 2003; Buss *et al.,* 2009). A clear risk of *M. margaritifera* imperilment is presented if the stream ecosystem metabolic hotspots are not identified within the reach scale (Hamilton *et al.,* 1997), particularly since cumulative filter feeding in beds may not fix/assimilate bio-available biotic nutrient concentrations below TV for all specimens (Vaughn and Hakenkamp, 2001; McClain *et al.,* 2003). HFP through a pool-riffle unit is an indispensable vertical and longitudinal landscape filter for *M. margaritifera* survival following captive breeding (Hendricks, 1993; Stanley and Boulton, 1993; Hamilton *et al.,* 1997).

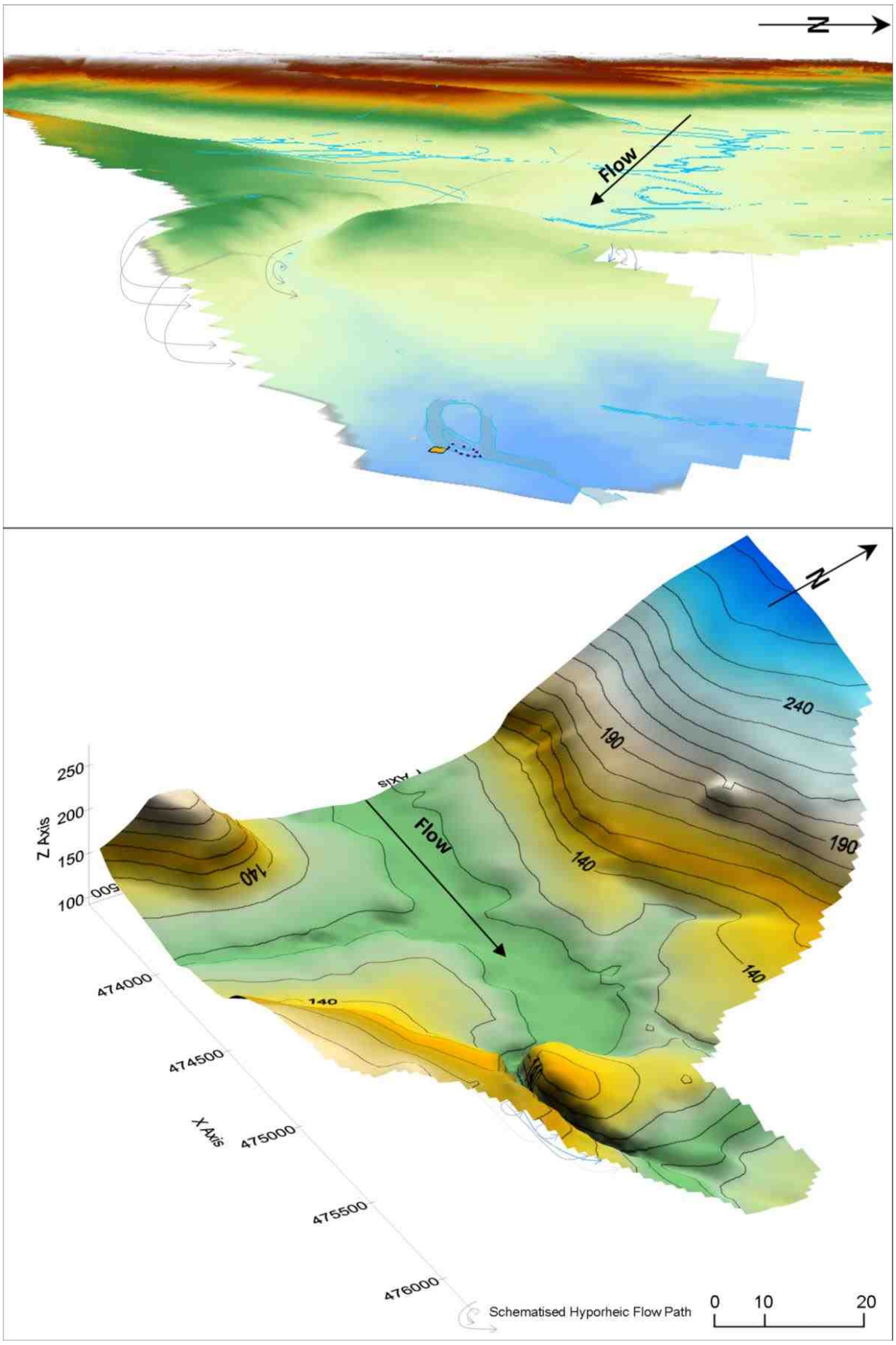
6.3.1 *M. margaritifera,* A Groundwater Dependent Species? Abundance At Lealholm Crunkly Gill

Because *M. margaritifera* is long lived and sessile, its structure and abundance may be a reflection of particular interaction of groundwater-surface water ecosystems (Soulsby *et al.,* 2005). Abundance may also be a signal of buffer zones, vegetation and catchment influences on water quality in addition to the diversity of in-stream habitats and hydromorphological diversity (Hastie *et al.,* 2000; 2003A; Strayer, 2008). In general *M. margaritifera* has been associated with headwater streams of the first and second stream order (Young and Williams, 1983A; Schlosser, 1995A; Beasley, 1996; Vaughn, 1997; JNCC, 2007; Strayer, 2008). The long-term absence of *M. margaritifera* in the headwaters of the River Esk may be an effect of persistence acidification, not only from industrial emissions (e.g. Evans *et al*., 2014) but erosion of peat since deforestation stemming back to clearance 8,500 BC, some 1,500 years after deglaciation (Atherden and Simmons, 1989: 20; Muir, 1997: 27; McNish *et al.,* 1997; Blaise Vyner & Land Use Consultants, 2000). 16 subsequent longitudinal barriers, some dating the to 17th century, inhibit the upstream range of *Salmo*

Salar and *Salmo Trutta,* which carry the *M. margaritifera* drop-off glochida to complete its life cycle (Hendry and Cragg-Hine, 2003; Skinner *et al.,* 2003; Map 3.4).

Section 6.3 detailed how pool-riffle units served as physical, chemical and biological filter within the reach. Although the spatiotemporal ecology of non-consolidated sediments is diverse and continually undergoing hydromorphological change at the reach-scale (Pringle *et al.,* 1988), larger valley-scale features remain in systemic permanence and may hold clues to long-term *M. margaritifera* establishment [redacted] Geist and Auerswald (2007:2300) recognise the importance of stream-aquifer interactions in maintaining *M. margaritifera* ecotone physicochemical balance. Other aquatic ecologists have long recognised groundwater importance too (e.g. Orghidan, 1959; 2010; Danielopol, 1989; Stanley and Boulton, 1993; Gibert *et al.,* 1994; Boulton *et al.,* 1998; 2010). Inland aquifers contribute 97 percent of the world's unfrozen fresh waters so should not be overlooked as an aquatic ecological resource equivalent to lotic and lentic surface system provisioning (Gibert *et al.,* 1994). Continuing the theme of longitudinal and vertical filters, landscape units are up-scaled from meso-scale to sub-catchment scale, depicted in Figure 6.5 and 1.1(a).

Valley closure and openings have potentially larger scale effects on streambed conditions (Wainwright *et al.,* 2011, Fig 1.1(a)). Ibrahim *et al.* (2010) determined that lateral closure of alluvial valleys contributed to strategically significant discharge of mineral oxidants through the streambed in constrained reaches. Lealholm Crunkly Gill topography displays these same features (Fig. 6.5). During the late Devensian deglaciation, a depositional plane formed before the Gill constraining outflow. Lake Eskdale was the proglacial lake formation, which during a warming phase drained with torrents (Gregory, 1965; Evans *et al.,* 2005). The partially resultant diverse superficial drift is shown in Map 3.5.6 (*ibid*). The proglacial lake zone makes-up the majority of superficial drift in the Lealholm recovery catchment and is functionally significant for structural connectivity – the physical linkage of landscape units (Wainwright *et al.,* 2011: 387). Where channel runoff is funnelled from a wide flanking valley through a narrow Gill, changes to the bulk transmissivity drift occur, becoming more extensive (Map 3.5.6., Gregory, 1965; BGS., 2014). The transition occurs to till, alluvium and Devensian glacio-fluvial deposits of sand and gravel and with this changes to K_v rate (*ibid*). In similar settings Hancock *et al*. (2005:98) observed that where dual transmissivity and containment effects occur *K* rates can changes from mm or cm per day, to metres per day with downwelling of up to '10's of meters' carrying labile in-stream DOC and DO. While meiofauna are important in pool-riffle decomposition, the actions of stygofauna in deep groundwaters are of equal functional significance, particularly for matrix flow within a greater till macropore structure. Hancock *et al.* (2005:98) note that 'subsurface fauna (stygofauna) graze biofilms, alter interstitial pore size through their movement, and physically transport material through the groundwater environment'



The [redacted] through until it discharges through the bed, exfiltrating in the hyporheic zone and affecting *M. margaritifera* streambed conditions (Hancock *et al*. 2005; Ibrahim *et al*., 2010; Wainwright *et al*., 2011). Like a pool-riffle system, nutrient spiralling in the superficial drift occurs, but on a much larger scale and potentially contributing to greater reduction of temperature, nitrate, phosphate and carbon concentration (Danielopol, 1989; Gibert, 1994; Hancock *et al*., 2005; Soulsby *et al.,* 2005). Chemoautotrophy may derive energy sources from rock mineral leachate in the subterranean environment, particularly in inter-granular flow structures (*ibid*). Carbon may be supplied by leachate (phloem) tree roots through the dense woods of Crunkly Gill, in addition to allochthonous sources (Turowski *et al.*, 2013). The impact of sub-catchment scale groundwater upwelling on *M. margaritifera* remains poorly appraised in the literature (Quinlan *et al.,* 2014). The abundance of *M. margaritifera* at [redacted] While the reduction and retention of nutrients in deep groundwaters is likely to be beneficial to *M. margaritifera,* the de-oxygenated groundwater egress is not (Buss *et al.,* 2005; Table 2.1). The cobble bed riffle system through the Gill, with interspersed Devensian boulders, may however, generate sufficient turbulence and oxygen gravel diffusion to offset depleted GW upwelling (Arntzen, 2006). The redzina soil covering the Gill hillslopes affords minimal baseflow or lateral piston-flow into the hyporheic zone. Considering the critical status of R. Esk *M. margaritifera*, valley unit-scale flow paths require urgent attention, for two reasons. Firstly, groundwater abstraction drawdown (Map 3.5.1) imperils phreatic microbes, including denitrificans, and may reduce the occupiable saturated zone space of endemic stygofauna in macropore structures (Gibert, 1994; Grimaldi *et al.*, 2004; Hancock *et al.*, 2005). Secondly, sewage effluent, flow routes enriched waters into groundwaters, hypoxia of the groundwater and hyporheic zone interstices was observed in Chapter 5.3 (Jarvie *et al.,* 2006).

6.4 Spatiotemporal And Ecotone Policy Inadequacies In Aquatic Ecological Sampling

Research results demonstrate that there are wider physicochemical monitoring ramifications for responsible environmental authorities; for example through a length of 23 meters (Crunkly Gill) there is a 5 percent reduction in in-stream nitrate-N and 73 percent in hyporheic zone, no ammonium detected in a riffle and the highest concentration of phosphate-P sampled in the riffle-head (Maps 5.1 – 2; Loftis *et al.,* 1991; Raven *et al.,* 1997). If we consider these ecotonal changes in biotic nutrients, conservative solutes and redox in a wider perspective, through a source to sea longitudinal stream continuum, where the cumulative effects of all pool-riffle units are up-scaled, the conceptual opportunity to understand nutrient spiralling pathways and implications for water quality monitoring programmes can be realised (Boulton *et al.,* 1998; Krause *et al.,* 2011; Trimmer *et al.,* 2012). Otherwise, the physicochemical measures that are often sought to be representative of catchment conditions may yield data that are misleading and potentially invalid, particularly where distortions from hydraulic habitats occur (Underwood, 1994; Emery *et al.,* 2003). Greater acknowledgement of the ecotonal stoichiometry of pool-riffle units, hyporheic flow path meander truncations (Fig. 6.3), and bankside exchange flow, may aid our understanding of uncertainty in environmental monitoring (e.g. Balint *et al.*, 2011). Where enriched in-stream waters infiltrate hyporheic or riparian alluvium, monitoring can also determine the environmental fate and direction of pollution plumes (see Maps 5.3 – 4). This in turn may explain legacy effects of re-emerging lag-effect pollution (Harding *et al.,* 1998).

Wainwright *et al.* (2011) and Ibrahim *et al.* (2010) determine that due to the unique hydraulic conditions through a pool-riffle unit, different processes emerge resulting from a marked thermal, redox and chemical gradient. Pool-riffle units are marked by zones deposition, particularly for sestonic matter including POM and PON encouraging processes such as nitrification (Maps 5.1.1., 5.1.2.). Riffles, due to their streambed hydraulics encourage processes of volatization explaining no ammonium (NH_4^+). Concurrent remineralisation and N_2 fixation by the same process may also explain higher ammonium in riffle-tail (*ibid*, Triska *et al.,* 1993; 2007; Maps 5.1 and 5.2).

Section 6.2 (2) and (3) outlined the changes to physical hydrochemistry in the hyporheic zone. These are perhaps the most significant changes, particularly to ecological water quality monitoring programmes (Boulton *et al.,* 1998; 2010; Buss *et al.,* 2005; 2009). For instance, under the secondary cycle of the EU WFD (2000/60/EC) assessments (2015, 2021, 2027) mixed taxon invertebrate sampling is executed solely in shallow riffle units (kick sample), unless riffles are not characteristic of the overall river (British Standards, 1995; 1995A; UK TAG, 2014). *Unionidea* are among the highest scoring benthic taxon under EU WFD (2000/60/EC) WHPT (Whalley Hawkes Paisley Trigg) system, yet their abundance is generally after, not in riffles (Baer, 1969; Vaughn, 1997; Johnson and Brown 2000:271; Hastie *et al*., 2003; UK TAG, 2014; Section 6.3). Moreover, the concentration of biotic nutrients in the riffle-tail porewater at all sites is not only lower than at riffle-head, but statistically different, with a weighted probability that head concentrations would be higher than tail (Tables 5.3.1 and 5.2.2; Mann and Whitney, 1947). Taxon absence, abundance and diversity under the WHPT is taken as a long-term bio-indicator of trophic status (Birk *et al.,* 2012; UK TAG, 2014). In lieu of the changes hydraulic habitats create, there may be a capacity to revise the scope of sampling to accommodate for channel hydraulics (Pullin and Knight, 2003; Sutherland *et al.,* 2004; Arntzen *et al.,* 2006; Allen and Vaughn, 2010; Birk *et al.,* 2012). Moreover the data from this investigation show that at different reaches phosphate-P, nitrate-N, Dissolved Oxygen, redox and electrical conductivity pore water values are statistically different to those in the water column (Table 5.2.4., 5.3.3., 5.4.3). Thus, benthic surveys may not serve as a full indicator of in-stream ecological status under the EU WFD (2000/60/EC), particularly where colmation, caking and epilithic mats result in hydrological and chemical disconnection from the water column (Stanley and Boulton, 1993; Boulton *et al.,* 1998; Jones *et al.,* 2012; Birk *et al.,* 2012).

New techniques now exist to map and model pool-riffle units through the longitudinal stream continuum. Spectral methods, ground penetrating radar (GPR), bathymetric LIDAR and photogrammetry, including from UAS (Unmanned Aerial System), all offer a new paradigm in rapid determination of hydraulic habitats (Harper *et al.,* 1992; Newson *et al.,* 1998; Feurer *et al.,* 2008). Together this demarcation can be linked to Delft 3D to understand dynamic velocity structures and how they interact with pool riffles. As yet such programs cannot model infiltration and exfiltration trough structures. This could be an area for future development (Beven and Freer, 2001; Beven *et al.,* 2012). Given the remotely sensed geometry of bedforms and flow structure (Feurer *et al.,* 2008), hydraulic conductivity library values for riparian superficial drift could be assimilated together with test monitoring reaches to simulate biotic nutrient reduction rates through river corridors. Modelling of this nature is needed where international legal requirements for compensation releases from dams seeks to stimulate the hyporheic zone for fish spawning in impacted rivers (Blaschke *et al.,* 2003; Newson *et al.,* 2012).

Monitoring in this investigation has not only elucidated the reach-scale processes which affect ecotonal water quality, including in groundwater, but also the implications of diurnal solar radiation changes driving primary productivity process responses, from photosynthesis to respiration and chemosynthesis (Figs 5.42 – 5.45). This is in addition to nocturnal rate change. During-night time hours temperature decreases, often by over ± 1°C, dissolved oxygen percentage saturation drops often by ± 15%. Redox, DOC, ammonium and nitrate-N also change, but recover in daylight hours (Section 5.2.4). The nocturnal sag in nitrate-N, but also phosphate-P at the sewage treatment works, results in almost doubling of daytime concentrations (Appendix 11). Even at the relatively undisturbed reach of Lealholm Crunkly Gill night-time hyporheic nitrate-N peaks at 1.91 mg N L^{-1}, exceeding *M. margaritifera* highest TV whilst also having a pattern tangent with in-stream waters (Fig. 5.42). Under the EU WFD (2000/60/EC) CIS (Common Implementation Strategy), Article 8 and annexes, member states are required to undertake water quality surveillance that generates data which are characteristic and representative of the overall water body (European Commission 2000; 2001; 2010; 2011; Birk *et al.,* 2012). Considering that environmental authorities conduct their routine EU WFD (2000/60/EC) nutrient sampling during daytime hours, samples and reporting is likely to be unrepresentative of nocturnal conditions and *de facto* physiochemical water conditions as a whole (DeAndre and Jarvie, 2006). Breaches of EU WFD (2000/60/EC) statuses under article 4, particularly for good ecological status, may be exceeded since these thresholds were based on daytime monitoring data (Pullin and Knight, 2003; Sutherland *et al.,* 2004).

Mulholland *et al* (2006) investigation of the Forks river systems in Tennessee revealed the same pattern with higher stream nitrate at midnight and predawn, compared to midday and midmorning concentrations. Photosynthetic rate and GPP (Gross Primary Productivity) decrease during night-time hours (Mulholland *et al*., 2006). The same pattern emerges for Decre Beck on the River Eden, with chlorophyll-a decreasing during the night whilst nitrate and phosphate increase (Owen *et al.,* 2012; http://www.edendtc.org.uk/). Autotrophs play a key function in stream metabolism (Mullholland *et al*., 2006). In order to report physicochemical status more holistically, environmental authorities could spot sample in non-flood conditions at night, reporting either concentration difference from daytime concentration or offset daytime statistics.

6.5 Riparian Influences On Water Quality, Point-Source Wastewater Pollutants And "Regulated" Environmental Risk

Clear links between hydrochemistry and land use are presented at the three reach-scales of Lealholm Crunkly Gill, Danby Moors Centre and Danby sewage treatment works. In-stream STW arithmetic mean phosphate-P is 0.85 mg P L^{-1}, whereas no ortho-P was detected at the Moors Centre, only 4 samples out of 338 detected ortho-P at Crunly Gill. In addition to the eutrophic physicochemical data, nutrient-tolerant fast-growing species of *Ranunculus fluitans (River water crowfoot)* and *Amblystegium riparium (moss)* were a bio-indicator of longer-term enrichment and hyporheic hypoxia at the STW (Newbold, 1984; Holmes and Spink *et al.,* 1993; Crook, 1996; Holmes *et al.,* 1999). The associated establishment of *Potamogeto pectinatus* (fennel pondweed) through the Moors Centre reach is another sign of persistent enrichment, given the Ellenberg nitrogen value of 7 and STR = 1 (Holmes *et al.,* 1999; Palmer, 2008:27). *P. pectinatus* close association with the STW *R. fluitans* suggests pollutant pathway connectivity between both the Moors Centre and STW (Spink *et al*., 1993; NIEA, 2005). This is affirmed by no ammonium or phosphate-P being detected at MP1 prior to the STW outfall (Appendix 11). No *R. fluitans* or *Potamogeto* establishment was detected in a 265m upstream river survey to NZ 70581 08261 (upstream of Danby Mill). PCA hydrochemistry factors are also similar between Danby Moors Centre and STW (Figs 5.76., 5.63), but slightly different to the factors at Crunkly Gill (Fig 5.47).

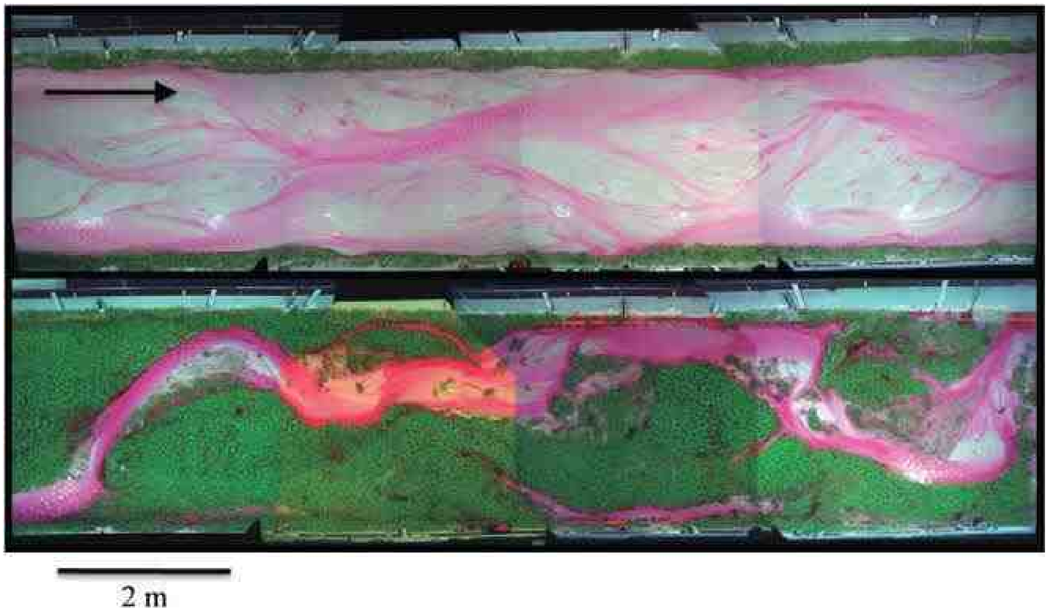
The cumulative consented waste water discharge in the Lealholm recovery catchment totals 1,259,505.50 m^3 a^{-1} (Environment Agency, 2014A, see Map 3.5.4; Appendix 6), spanning 8 STWs, numerous septic tanks and small sewage discharges (SSDs, <50m^3 d^{-1}), the latter two remaining largely exempt from consent control. Given Danby STW threshold of ammonia-N at 30 mg N L^{-1} and no threshold value for phosphate-P, nitrate-N, temperature, pH, cyanide, dissolved oxygen or electrical conductivity (Appendix 6), sewage outfall remains strategically significant both to river eutrophication and degradation of *M. margaritifera* filter feeding habitat (Bauer, 1988; Jarvie *et al.,* 2006; Dudgeon *et al.,* 2006; Neal *et al.,* 2010, Table 2.1 versus 5.3.3). Aside from diffuse agricultural pollution (non-point), which has received government-backed ecological restoration subsidy in the River Esk catchment (Defra, 2010;2013A; NYMNPA, 2013), point-source (continuous) waste water treatment outfall still contributes to the degradation of water quality, particularly as effluent enters directly into the stream without alteration from Riparian Buffer Zones (Jarvie *et al.,* 2006; Mander and Hayakawa, 2005). 22 % of EU WFD (2000/60/EC) reasons for failure in the Humber river basin district (inc. R. Esk) are due to sewage discharge (Environment Agency, 2013A).

[redacted]

Background nitrate-N remains above *M. margaritifera* water column filter feeding thresholds at all reaches, averaging 1.57 mg N L^{-1} at Danby STW, 0.60 mg N L^{-1} at the Moors Centre and 0.57 mg N L^{-1} at Crunkly Gill (Bauer, 1988; Morkens, 2000; Oliver, 2000; Table 2.1). Danby STW has key potential lag-effects, particularly in groundwaters which are likely to re-contribute enriched leachate during spate or drought. For instance, phosphate-P and nitrate-N are significantly higher in riparian groundwaters of the meander, at respective mean concentrations of 0.33 mg P L^{-1} and 7.51 mg N L^{-1} (Table 5.3.3). In comparison to Lealholm Crunkly Gill borehole, the low concentrations of conservative solutes chloride-Cl and sulphate-S in the STW groundwater confirms mixing with in-stream waters where enriched waters “drive-into” the floodplain (Burt *et al.,* 2002; 2005A; 2010A; Appendix 11, Fig 6.3.,6.92., Maps 5.3.1., 5.3.2).

The longitudinal extent of biotic nutrient enrichment, indicated by eutrophic fast-growing macrophytes (*et alibi*), the upstream terminus of *M. margaritifera* (e.g. Killeen, 1999; 2006; Hirst *et al.,* 2012) and water quality data (Chapter 5), means that sites identified for re-introduction of hatchery-reared *M. margaritifera* are unsuitable, based on water quality parameters set down by Moorkens (2000) Bauer (1988) and Oliver (2000). Figure 6.9 delineates sites identified by North Yorkshire Moors National Park as ‘suitable juvenile habitat’. However, data presented in this thesis show that the site between the STW and

Moors Centre, and the Moors Centre reach, are unfit for *M. margaritifera* of any age (Bauer, 1988; Moorkens, 2000; Oliver 2000; Geist and Auerswald, 2007; Tables 5.3.1., 5.3.3., 5.4.2).



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INFORMATION EMBARGO – ENDANGERED PEARL MUSSEL LOCATIONS

Figure 6.8. Upstream range extent of suitable juvenile *M. margaritifera* habitat

Source: NYMNPA (2013)

High nitrate-N and ammonium (*cf.* TIN) occurred through the summer monitoring period at Lealholm Crunkly Gill (Fig. 5.42., 5.43.,5.45; Appendix 8). During a time of low flow, nocturnal sags in nitrate-N occurred where in-stream temperatures were high and dissolved oxygen low (*ibid*). Within the secondary channel, previously adopted as the main channel of the Esk, bank slumping of humic rich soil horizons, with monitored ortho-P bio availability (Surridge *et al.,* 2005; Appendix 8) resulted in filamentous algal bloom (*Cladophora sp,* Fig. 6.9). The *Cladophora sp* STR of 1 not only indicates enrichment aided by disturbance, but a crowding-out of valuable juvenile interstitial and adult substratum (Holmes *et al.,* 1999:64; Johnson and Brown, 2000; Hastie *et al.,* 2003; Jones *et al*., 2012).

[redacted]

Figure 6.9 shows similar main-channel macrophyte bloom during peak in-stream summer temperatures (Fig. 5.44). The extensive vegetative coverage of moss and other species enhances night-time plant respiration rate which in turn amplifies nocturnal dissolved oxygen and nitrate-N sag (Mullholland *et al.,* 2006; Fig. 5.42.,5.44). During summer enrichment where sewage effluent is less adequately diluted, *M. margaritifera* is exposed to further filter feeding stress (Fig. 5.42., Table 2.1.). Macrophyte bloom is functionally significant, particularly in relation to hydro-system ‘legacy P’ (Phosphate) feedback (Harding *et al.,* 1998; Allan *et al.,* 2014; Jarvie *et al.,* 2012). Legacy P is the surplus derived from past land use activity, soil and sediment transfer, particularly where eco-hydromorphic features designed to cycle P become saturated and begin to release P (Jarvie *et al.,* 2012: 297). This may include riparian buffer zones, attenuation ponds (inc. SuDs (Sustainable Urban Drainage System)), infiltrations swales and natural flood management features (*ibid*). The majority of phosphate-P monitored in this investigation was observed at Danby STW, occurring in the readily bioavailable form of dissolved phosphate – ortho-P (PO_4^{3-}) (Reynolds and Davies, 2001; Fig. 5.53., Maps 5.3.3–4). However one sample of ortho-P (0.02 mg P L^{-1})

occurred at the riffle-tail at Lealholm and may be associated with both enriched conditions monitored several days prior, and a operator self-monitoring (OSM) reported consent breach at Danby STW (Appendix 6 and 8, Map 5.1.3 – 4).

Effluent dissolved P is readily sorbed in alluvial sediments, seston and fixed into plant biomass. The form of P may also change from ortho-P (PO_4^{3-}) to soluble molybdate-reactive P (SRP) (PO_4) when colloid bound (Rigler, 1973; Ryenolds and Davies, 2001:30). Reynolds and Davies (2001:45) observed 85% settlement of P into Lake Windermere from the mass export of sewage effluent P, at rate of ~0.9 g P m^{-2} $year^{-1}$. Accordingly, disturbance flood flows in lotic ecosystems can exert greater sheer stress, remobilising streambed stored P, dismember macrophytes dispersing biomass P longitudinally and cause shredding of propagules for downstream establishment (Butcher, 1933; Jones *et al.,* 2012).

Understanding legacy P is fundamental, not only to the growth of nuisance algae and macrophytes (Jarvie *et al.,* 2012; Haygarth *et al.,* 2014), including their subsequent decay which consumes oxygen, but because plant growth crowds out *M. margaritifera* habitat and prime substratum, enhances nocturnal sags and presents problematic river management implications (Butcher, 1933; Mullholland *et al.,* 2006). For instance, Jones' (2004) investigation of *Potamogeto sp* (Danby Moors Centre) observed that vigorous regrowth outstrips cutting and that dredging is the only means of effectively removal. Dredging is not consistent with *M. margaritifera* population health. The practice is likely to remove any post-drop off glochidia and strip fluvially diverse bedforms from the river (e.g. Johnson and Brown, 2000:271; Hastie *et al.,* 2003A; Geist and Auerswald, 2007). Given that Jarvie *et al.* (2012:297) document water quality response lag times from 10 – 15 years following enhanced waste water treatment and P removal, clear legacy effects from STW in the Esk recovery catchment exist. Particularly since no threshold for nitrate-N or phosphate-P exist in the current consents of Lealholm and Danby STW, which are the effluent outfalls nearest to the largest pre-established, but critically declining, *M. margaritifera* population (Killeen, 1999; 2006; Hirst *et al.,* 2012). 5.56 mg P L^{-1} was the highest recorded ortho-P sample in-stream at MP4 on 27th July 13, during low-flow (Appendix 11). The effect of dense macrophyte establishment on *M. margaritifera* habitat appears overlooked in *Unionidea* literature, including in Quinlan *et al.* (2014) recent review paper. However, Killeen's (2011) advice to the FBA hatchery to remove excessive epilithon/periphyton and bryophytes has resulted in observed lower stress in caged *M. margaritifera* (Gum *et al.,* 2011; Sweeting and Lavictoire, 2013).

Anthropogenic activities do not solely alter macrophyte biomass and stream hydrochemistry. Dense riparian tree planting can compound channels and reduce rates of stream-to-hyporheic zone and stream-to-groundwater HEF, and *vice versa* (Smith, 2005; Tal and Paola, 2010; Fig 6.7). This potentially reduces denitrification rates in the interstitial network of buffer zones and pool-riffles, as groundwater travel time is reduced (Triska *et al.,* 1993), compare, for instance, figures 6.2 with 6.7. The absence of groundwater monitoring boreholes throughout the entire River Esk catchment leaves a valuable natural resource unquantified. At the relatively undisturbed reach of Crunkly Gill, exfiltration of cool oligotrophic groundwaters provide a valuable buffer against sometimes harsh stream conditions (Appendix 8), particularly drought (Danielopol 1989; Fleckenstein *et al.,* 2008). [redacted]

[redacted]

Howev[redacted]s. For instance, Hendricks and White (2000) observed riffle-tails contributing phosphate in an intensively farmed region of the USA. Similarly at Danby STW, the high transmissivity ellerbeck drift between the eddie at MP3A and riffle-tail at MP6-7 may be a HFP vector for transportation of enriched ammonium storm-flow effluent (Figures 6.3., 6.91 and Map 5.4.4; NSRI, 2013; 2013A). The intermediary pasture is intensively grazed by highland cattle to the extent there is some loss of top soil and poaching. Even after this investigation, there is still a paucity of reliable hydrochemical groundwater data. The arithmetic mean nitrate at 0.25 mg N L^{-1} monitored at Lealholm Crunkly Gill borehole may be a realistic baseline concentration in the River Esk and is closer to Moorkens (2000) *M. margaritifera* filter feeding TV at 0.125 mg N L^{-1} (Fig 5.31). However, this pasture was intensively grazed in the past and charcoal was extracted during borehole drilling (Atherden and Simmons, 1989;

Muir, 1997; Blaise Vyner & Land Use Consultants, 2000; Map 3.7.2). The addition of manure with tilling is likely to have increased groundwater nitrate-N (Burt *et al.,* 1993), prior to current fallow and seral stage sucession. Considering the critical decline of *M. margaritifera* on the River Esk a long term record (100 years +) of nitrate and phosphate would serve to establish a pre arable subsidy 1917, dig for victory 1939 and CAP 1960 – 70 nitrate concentrations which Howden *et al*. (2013) observed resulting in increases in-stream nitrate. If such a record were able to be established, the correlation of nitrate-N with pre-existing long-term *Salmo salar and trutta* stocks could be determined (Fig. 3.1 and 3.2); this may help understand *M. margaritifera* long-term viability in the River Esk (Section 2.6; Fig. 2.8, Burt *et al.,* 2009).

This thesis's detailed analysis of hydraulic setting, unique physical and chemical properties of source waters, macrophyte growth and important distribution of the flagship species of *M. margaritifera* is fundamentally related to ecotones and interaction of stream units (Amoros *et al*., 1996). In order to meaningfully appraise and understand the variability in water quality from the catchment to the reach scale, these interaction are fundamental to monitoring programmes because of their key affects on physicochemical parameter concentrations over short distances (Triska *et al.,* 1989; Krause *et al.,* 2011).

6.6 Summary

Recent research has highlighted the critical importance of physical habitat to *M. margaritifera* survival (Hamilton *et al.,* 1997; Johnson and Brown, 2000; Hastie *et al.,* 2003A; Wilson *et al.,* 2012). This research has appraised the hydrological connectivity of physical biotope stream units together across the reach-scale, both structurally and functionally. These geomorphological connections have a fundamental effect on ecotone hydrochemistry resulting in feedbacks and observed, statistically significant reductions in biotic nutrients, particularly nitrate and phosphate through a pool-riffle-pool sequence. The alteration of interstitial water quality has been most fundamental, with the riffle-tail showing the most suitable cool oligotrophic conditions (DOC, TIN, P) for young *M. margaritifera* (Section 6.2). However, groundwater ejection is depleted in dissolved oxygen, although the immediate overlaying water column has the highest dissolved oxygen saturation and redox than any other monitoring point across a densely monitored reach, which may offset the oxygen saturation status at the *epifauna* (e.g. Figs 5.34.,5.38, Emery *et al.,* 2003; 2004). This is a lag effect of riffle turbulence and mixing with settled water of the pool, an edge-effect (Lovejoy *et al.,* 1986). Hyporheic de-compaction may be enhanced by adult foot movement aerating substratum where dense beds occur (Bauer, 1987; Strayer, 2008). Interstitial flow pathways from the reach-scale through to the sub-catchment scale have been demonstrated to be ecologically significant and may be a factor for *M. margaritifera* abundance at Crunkly Gill (Section 6.3.1). However, this thesis, like any other, has shortcomings and it has not been possible to fully achieve its aims due to time, apparatus and resource constraints. The following section will critically assess the research's limitations and scope for future investigation.

6.7 Limitations And Further Research

This study has investigated the reach-scale variability in hydrochemistry through the water column and hyporheic zone of connected hydraulic habitats over three different reaches. Groundwater was also monitored at two of the three reaches. The use of hyporheic wells or standpipes (Huang *et al.,* 2014) has demonstrated the benefits of a dense reach-scale sampling approach at low cost. However, absolute precision of hydrochemistry measures through the lateral depths of a streambed is poor compared to the methods of Ibrahim *et al.* (2010) such as the multi-level sampling, where wells are stratified into lateral chambers in order to sample pore water quality at different depths (Buss *et al*., 2005; 2009; Dearden and Palumbo-Roe, 2010). The abstracted interstitial samples in this investigation indiscriminately bulk sampled depths of 400 mmBD – 50 mmBD (BD~streambed), drawing-down a small cone of depression around the well (Fig. 4.2., 4.3.). This may have masked the variation in nitrate-N concentration at depth. Triska *et al.* (2007:68) observed higher nitrate concentrations at 0–3 cmBD, c.70–100 μ N L^{-1}, decreasing to the concentration of c. 10 μ N L^{-1} at remaining depths to 16 cmBD, during summer months. Moreover, because the YSI probe would not fit into the hyporheic well, samples were hand-pumped into a beaker then tested for physicochemical variables. This is likely to have resulted in small changes in temperature, dissolved oxygen, redox and electrical conductivity, due to the influence of different atmospheric conditions and handling (Foster *et al.,* 1982; Dearden and Palumbo-Roe, 2010). In this investigation samples were often abstracted from the upper horizons of a settled sample in the well. However, this may not be representative as *M. margaritifera* foot movement bioturbinates sediment. Decaying POM and seston disturbance may increase aqueous and labile biotic nutrient concentration (Haack and McFeters, 1982; Dearden and Palumbo-Roe, 2010). A more accurate method would be to take *in situ* measurement of the hyporheic zone using the apparatus suggested by Riss *et al.* (2008). However, the capital expense for this instrument would have precluded its deployment in this investigation. The instrument would serve a useful purpose in unobtrusively [redacted] coupled with the pre-existing in-stream YSI Sonde. Considering the preceding analysis of valley-scale hyporheic flow pathways, the area depicted in Figure 6.5 is a prime site for further hydraulic and hydrochemistry measures of the kind used in this study (Chapter 4). However, these would need to be on a larger scale in order to determine the rate of discharge through the streambed as discussed by Ibrahim's *et al.* (2010) and Wainwright *et al.* (2011).

This zone of pre-Gill superficial drift (Map 3.5.6) presents a suitable zone for a deep monitoring borehole (c. 40m +) installation, not only to determine VHG and potential downwelling rates, but also the potential impact of upstream pollutants on the hydrochemistry of groundwater which may subsequently discharge through the riverbed. Danielopol (1989) and Hancock *et al.* (2005) note the importance of extremely endemic stygofauna in deep aquifers that perform trophic cycling within a limited range. Like *M. margaritifera* there may be further symbiotic relationships with groundwater grazing fauna and flora, elements seldom appraised in fisheries science literature (Schlosser, 1995A; Quinlan *et al.,* 2014).

When implementing hyporheic monitoring programmes, hydrogeological settings are fundamental. The defined upwelling at Danby Moors Centre riffle-tail (Fig 5.64., 5.65) may not be as a result of downwelling from riffle–head but different bedrock formation geological intersection (Map 3.8.2). MP1 exists above the Saltwick formation sandstone, MP2 at the transition of Saltwick to Dogger formation sandstone and then finally MP6 exists at the intersection of Dogger to Whitby mudstone formation (BGS, 2009; 2013A; 2013B; 2014). Despite the alluvial drift remaining the same for the STW and Moors Centre monitoring points, the intersection of different bedrock from sandstone to mudstone alters bulk transmissivity and K_h (Allan *et al.,* 1997; Schwartz and Zhang, 2003). Given that superficial drift often takes the characteristics of its parent material – bedrock – this rate change may create a spring at the bed intersection, so the riffle-tail ejection depicted in Figure 5.65 may be an artesian spring rather than riffle-tail ejection site (*ibid*).

A key criticism of this research may be the lack of borehole at Danby Moors Centre, which may have quantified the impact of livestock farming and nutrient improved pasture (N,P,K) on groundwater quality (Map 4.2., Howden *et al.,* 2011). Biddulph (2012) determined that agriculturally intense farming around Toad, Little Fryup and Stonegate Beck contributed to higher in-stream and hyporheic nutrients. However, the future research agenda may focus on determining which sectors – agriculture, water companies and urban diffuse – contribute the most nutrient enrichment to the River Esk recovery catchment. Above the methods set out in this thesis, and the data from McNish *et al*. (1997), Balmford (2011), Biddulph (2012), Evans *et al.* (2014) and Environment Agency monitoring, there is requirement to understand the depth-dependent nutrient concentration of soils and superficial drift in the relevant land-use sectors. As aforementioned, a long-term establishment (100 years +) record of nitrate-P and phosphate-P may better establish a more realistic baseline for stream nutrient criteria (Burt *et al.,* 2009; Howden *et al.,*2013; Haygarth *et al.,* 2014). Presently this record does not exist but may be an influence on *Salmo salar* and symbiotic *M. margaritifera* decline (Ziuganov *et al.,* 1994; Skinner *et al.,* 2003; Hendry and Cragg-Hine, 2003). The overwhelming majority of samples did not detect phosphate-P on the Dionex chromatograph, whilst the granular limit detection may be the reason for this, Rigler (1973) observed that centrifuge particle separation or coarser Whatman filter paper yielded higher P concentrations, compared to 0.2 µm pore size filter used in this investigation (Rigler, 1973, Section 4.7).

Chapter 7 Conclusion

7.1 Conclusion

Ecotone water quality on the River Esk presents a major imperilment to endangered *M. margaritifera*. Arithmetic mean nitrate-N across all sites, in-stream and pore waters exceeds filter feeding TV (table 2.1), whilst phosphate-P generally occurred undetected. Where ortho-P (PO_4^{3-}) was detected it exceeded *M. margaritifera* TV. Sampling for colloid bound soluble molybdate-reactive P (SRP) (PO_4) may have been more apt, considering this was a hyporheic zone investigation (section 6.5, Rigler, 1973; Ryenolds and Davies, 2001:30). Nitrate-N, ammonium and dissolved oxygen all occur with nocturnal sags. So whilst daytime concentrations exceed *M. margaritifera* TV, peak night-time measures can be almost double daytime average, compounding *Unionidea* stress further (fig 5.6.1., 5.6.3., 5.6.4).

Ultimately, if direct water quality remediation measures are not taken, including further agricultural and waste water pollutant source control, it is likely that River Esk *M. margaritifera* will become extinct over the next century (Bauer, 1988; Dudgeon *et al.,* 2006; Strayer, 2006). *M. margaritifera* filter feeding requires EU WFD (2000/60/EC) 'high' ecological status because of its associated nutrient and abiotic status standards (Young *et al.,* 2003). Currently 10 percent of the River Esk catchment is at the good ecological – near "natural" conditions (Newson and Large, 2000; Environment Agency, 2009; 2013A). This is a category below 'high', which no water bodies achieve (*ibid*).

Environmental risk became a key theme of the research not solely in relation to nocturnal sags and storm conditions that lead to increasing biotic nutrient concentrations, but also pollution hotspots and risk in the form of a sewage treatment works (Jarvie *et al.,* 2006). Jarvie *et al.* (2006:252) observed that: *Monitoring data from fifty four UK river sites has indicated that point sources of phosphorus provide a greater risk for river eutrophication than diffuse sources from agricultural land, even for rural areas with high agricultural phosphorus losses.*

Phosphate-P was sampled only downstream of Danby STW. At effluent outfall this averaged 3.20 mg P L^{-1}. P was undetected in the riffle, but was re-sampled in groundwaters and riffle-tail return-flow (Hendricks and White, 2000; fig 5.4.1). Through degraded reaches like this, and the other eight sewage treatment works in the recovery catchment, legacy P becomes a key environmental management risk (Jarvie *et al.,* 2013; 2013A). As the Esk catchment population increases and livestock holding becomes 'denser, the natural chemical and biological recycling processes become overloaded' (Hardin, 1968:1245). Rather than cycling biotic nutrients, bedforms actually contribute to them, particularly during flood flows where old, enriched water is pushed out, or where siltation and traction results in colloid-bound P becoming disturbed (Harding *et al.,* 1998; Jarvie *et al.,* 2013; 2013A). The associated fast-growing macrophytes in the presence of P, but with the right ratio to N, create bloom, including nuisance filamentous algae (*Cladophora sp.*) which is likely to crowd the valuable interstitial space for *M. margaritifera* establishment (fig 7.1, Bauer, 1988; Johnson and Brown, 2000; Dudgeon *et al.,* 2006). Although macrophytes may assimilate these nutrients, their perennial abscission is likely to return N and P back into the aquatic ecosystem. Coupled with the hyporheic-stored legacy P, this presents an Anthropocene contention to the conventional preconception that ‘flowing water purifies itself every 10 miles’ (Hardin, 1968:1245).

In the pre-1900s era, where livestock farming was less intense and sewage outfall volume lower, the conventional notion of river self-purification (inc. decomposition and heterotrophic processes) and dilution over a distance may well have held true (*vide supra,* McNeill, 2001; Allen, 2004; James and Marcus, 2006; Wohl, 2011; Howden *et al.,* 2013). However, legacy P and the encouraged growth of excessive periphyton, coupled with sediment loss, for instance Perks (2013:169) monitored a catchment average loss of 56.66 (± 11.61) t km^{-2} in 2008 – 09, has resulting in a “choking” of benthic pores (Zimmermann and Lapointe, 2005; Jones *et al.,* 2012; Jarvie *et al*., 2013; Haygarth *et al.,* 2014). Through processes of colmation and caking, potential rates of exchange with the stream are impacted, and hydrologically disconnected from the hyporheic zone (*ibid*). This was observed at Danby STW where pore water was hypoxic. Stream-substratum exchange disconnection not only impacts *M. margaritifera,* but ramifications exist for the findings from this investigation, since hyporheic return flow through the interstitial network has been observed to reduce biotic nutrients significantly, particularly in pore waters. Temperature, VHG and Q_v hydraulic determinations suggests that during flood-flows ejection occurs at a higher rate, potentially resulting in greater dilution of the enriched water column (Triska *et al.,* 1993; Hancock et al., 2005). While this investigation’s evidence was derived from small reach scales (<50 m), the findings for reduction on nutrient concentrations highlights the strategic significant of stream and hyporheic zone exchange in environmental management decision making (Boulton *et al.,* 1998; Krause *et al.,* 2011). Although disturbance was not fully assessed in this investigation, the shift mosaic of bed aggradation and degradation, where the river retains the ability to extend laterally, defining its own “style”, is fundamental in mortaring clast bio-film coatings, re-sorting alluvium and creating new interstitially connected voids (Newson *et al.,* 2012). These bedload processes are vital for priming “patches” for *salmonid* smoltification and *M. margaritifera* at connected hydraulic units to allow movement (Malcolm *et al.,* 2003; 2008; Soulsby *et al.,* 2005; Newson *et al.,* 2012). In this case hydromorphology integrity is the ecological limit to aquatic ecology status, particularly under the EU WFD (2000/60/EC) and Habitats Directive (92/43/EEC) (*ibid*).

The resulting hydromorphology impacts on *M. margaritifera* and all *Salmonidae* life stages – ‘its proper understanding requires integration between the sciences of hydrology/hydraulics, geomorphology and freshwater ecology, but this integration is scarce’ (Newson *et al.,* 2012:1). This investigation sought to meet the thesis aim of discovering the spatiotemporal variability in ecotonal water quality over three hydromorphologically different reaches, to determine the influence of hyporheic flow conditions on in-stream habitats (section 1.2). Thence supporting the reintroduction of 1,283 (2012 count) juvenile River Esk *M. margaritifera*, the oldest of which is seven years old (Lavictoire and Sweeting, 2012; 2012A; 2012B; Sweeting and Lavictoire, 2013). Ten years old is the intended age of reintroduction since it marks the onset of reproductive viability (*ibid,* Lavictoire *pers. comm.* 2014). This investigation finds that at the most natural river reaches, riffle-tails, are the prime habitat for reintroduction of hatchery *M. margaritifera*, mainly due to oligotrophic pore water ejecting out the hyporheic zone which may also buffer the relative nutrient enrichment of in-stream water, which increases with flood-flows. The lowest consumption of oxygen during decomposition of organic matter occurs at riffle-tail, indicated by the lowest COD at Crunkly Gill MP3C. This environmental evidence may be incorporated into the development of detailed reach-scale reintroduction protocols for *M. margaritifera*, including hybridisation of evidence with the EA RHS (Newson and Newson, 2000; Bolland *et al*., 2010; Quinlan *et al.,* 2014).

The investigation also finds that of the nine sewage treatment works outfalls in the recovery catchment, the majority of chemistry parameters and thresholds are not commensurate with endangered *M. margaritifera* functional filter feeding. Despite *M. margaritifera* legal protection under Annexes I and II EU Habitats Directive (92/43/EEC) and Schedule 5 of Wildlife and Countryside Act (1981) (Skinner *et al.,* 2003; Great Britain, 2010). Indeed, Danby STW has no discharge concentration threshold for nitrate-N, TIN, phosphate-P, dissolved oxygen, calcium, pH and other variables noted in table 2.1, yet this location coupled with the weir impacts marks the upstream terminus of *M. margaritifera* (appendix 6; Killeen, 1999; 2006; Hirst *et al.,* 2012). Given the government £67,000 allocated to River Esk CSF investment (Defra, 2010; 2013A), inaction in re-consenting STW effluent outfalls commensurate to *M. margaritifera* filter feeding (table 2.1) may invariably be a tragedy of the commons – the context morality of consenting pollutants to harmful levels while a mollusc established since the ice age terminally declines (Hardin *et al*., 1968; Hajer, 2003; Poff *et al.,* 2003).

M. margaritifera establish at riffle-tails that adjoin silt filled pools, where nitrification is noted to occur (Vaughn 1997; Johnson and Brown, 2000:271; Hastie *et al.,* 2003A), this nitrification was mapped at Lealholm’s Crunkly Gill (see maps chapter 5.1), abundant FWPMs are therefore likely to play a key role in near streambed biological oligotrophication and re-suspension of bioseston (Vaughn and Hakenkamp, 2001; Strayer *et al.,* 2004). Concurrently, the residuals through a stream logarithmic slope (Richards, 1990; 2000), pool-riffle units through a stream source to sea continuum, are also likely to contribute significantly to biotic nutrient reduction, based on the reach-scales findings from this investigation (e.g. Triska *et al.,* 1989; 1993; 2007; Boulton *et al.,* 1998; 2010; Wainwright *et al.,* 2011). Together the mollusc and hydraulic habitats are zoological—biogeochemical agents in biotic nutrient reduction (Baer, 1969; Orghidan, 1959; 2010; Vaughn and Hakenkamp, 2001; Fig 2.6).

By isolating and situating a single fluvial form such as a pool-riffle unit within the setting of connected larger eco–hydromorphological systems, the logic of repairing reaches and enhancing flow through pool-riffle unit "filters", together with rehabilitation of *M. margaritifera* "sanctuary island" stocks, can outline the important biogeochemical cycling reduction effects zoological—hydromorphological features have together (Vaughn and Hakenkamp, 2001; Thoms and Parsons, 2002; Pinay *et al.,* 2008; Bernhardt and Palmer, 2011; Wilson *et al.,* 2012). River engineering and the compounding of channels, including through artificially dense vegetation, reduces potential rates of exchange for processes such as denitrification, fluvially diverse landscape filters may also be eradicated (Poff, 1997; Pinay *et al.,* 2008; Strayer 2008). Mollusc beds have been noted to fix bio-available phosphate and reduce downstream concentrations, both interstitially through foot pedal feeding or within the water column through filter feeding (section 2.4., Nalepa *et al.,* 1991; Welker and Walz 1998; Vaughn and Hakenkamp, 2001). This thesis has paid heed to the mutually constitutive interaction of hydromorphology and zoology systems, to provide one example of the diverse interactions the abiotic physical hydrosphere has with keynote process invertebrate species (Danielopol, 1989; Johnson and Brown, 2000; Hancock *et al*., 2005). *Margaritifera margaritifera* L. (1758) is an intrinsic symbiont of other species, part of a much larger diverse web of life in riverine ecosystem harmony, which supports, lives on (*Salmo salar/ Salmo trutta*) and enhances water quality conditions with streambed forms (Vaughn and Hakenkamp, 2001; Strayer, 2008). However, with the loss of geomorphological diversity and decline of *M. margaritifera,* there becomes a loss of ecosystem resilience and a river's ability to self-purify (Hardin, 1968; Lovejoy *et al.,* 1986; James and Marcus, 2006). Indeed, good groundwater quality in non-disturbed reaches of the River Esk is a remaining aspect of ecosystem integrity – this may not be so in groundwater polluted regions (Howden *et al.,* 2011).

A greater understanding of the contribution that hyporheic flow paths make to benthic biota conditions and water column hydrochemistry is needed both before mixed taxon assessments are made (i.e. WHPT), and before policy makers formulate effective reintroduction strategies for *M. margaritifera*. The evidence from this thesis should therefore be considered within a wider context of water quality surveys and macroinvertebrate sampling procedures that underpin wider inferences and extrapolations of river basin water quality (Richards, 1996; Newson and Newson, 2000).

7.2 Summary Conclusions

- Simultaneous subsurface hyporheic flow pathways and surface turbulent volatization in a riffle, analogous to a river's "liver" (e.g. Fischer *et al.,* 2005) and "lung" function, have been found to reduce nutrient concentrations (N,P and C) and change dissolved oxygen and redox status significantly over short distances. These alterations make the edge-effect between riffle and pool a unique microhabitat of oligotrophic interstitial water and oxygen hyper-saturation in the water column – a 'redoxcline' (Lovejoy *et al.,* 1986; Bus *et al.,* 2005). Others have quantified the rapid denitrification rates in riffles (e.g. Lansdown *et al.,* 2012; Pinay *et al.,* 2008); none have linked hyporheic oligotrophication to the abundance of endangered *M. margaritifera* at riffle-tails, as observed by Hastie *et al.* (2003A), and Johnson and Brown (2000), where hydrogeomorphological forms change SW-HZ water chemistry by return/piston flow (Hendricks and White, 2000). Riffle-tails are therefore the key microhabitats to pilot reintroduction of hatchery-reared *M. margaritifera* (Bolland *et al.,* 2010; Quinlan *et al.,* 2014).
- Unionids may have an affinity with physical bedform processes that cause exchange between atmosphere, shallow aquifer and terrestrial interstices. This research gap represents a future agenda in fisheries geomorphology and capacity for inter-disciplinary consilience, in charting the hydraulic and stoichiometry mechanics of patches and their importance to keynote riverine species – *M. margaritifera, Salmo Salar and Salmo Trutta*. Catchment water quality improvement maybe ineffectual without multiple inter-dependant habitats for keynote species to forage, reside and refuge in. Hyporheic flow pathways ensure these patch mosaics remain oligotrophic and thermally balanced.
- Policy inadequacies in monitoring are manifest in the EU WFD (2000/60/EC), since nocturnal sags in nitrate-N and phosphate-P occur, almost doubling daytime concentration – the time when samples are made by monitoring authorities. In addition to temporal problems, the spatial framing of sampling points and variability in measures because of hyporheic flow pathways undermine the validity of mixed taxon surveys (inc. WHPT) along with hydrochemistry samples, which have the intention of being representative of stream conditions. This deserves further consideration as future monitoring programmes are planned and implemented.
- Beyond the monitoring inadequacies, there are failures of environmental consent and regulation, fundamental aspects of aquatic environment protection practice. Danby STW was identified as the most strategically significant monitoring reach for nitrate, phosphate and ammonia enrichment, adding to Biddulph's (2012) and Balmford's (2011) findings. Since macrophytes (*Potamogeto sp.*, *R. fluitans*) experience river chemistry permanently, their trophic assessment supported eutrophic sample data at Danby STW and Moors Centre. Together demonstrating the extensive downstream impacts of eutrophic outfalls beyond the Moors Centre, coinciding with the upstream terminus of *M. margaritifera,* where nutrient filter feeding threshold standards are not met.

Appendices

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