Diffusive equilibrium in thin-films (DET) provides evidence of suppression of hyporheic exchange and large-scale nitrate transformation in a groundwater-fed river

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Diffusive equilibrium in thin-films (DET) provides evidence of suppression of hyporheic exchange and large-scale nitrate transformation in a groundwater-fed river

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Abstract

The hyporheic zone of riverbed sediments has the potential to attenuate nitrate from upwelling, polluted groundwater. However, the coarse-scale (5 – 10 cm) measurement of nitrogen biogeochemistry in the hyporheic zone can often mask fine-scale (<1 cm) biogeochemical patterns, especially in near-surface sediments, leading to incomplete or inaccurate representation of the capacity of the hyporheic zone to transform upwelling NO_3^-. In this study, we utilised diffusive equilibrium in thin-films (DET) samplers to capture high resolution (cm-scale) vertical concentration profiles of NO_3^-, SO_4^{2-}, Fe and Mn in the upper 15 cm of armoured and permeable riverbed sediments. The goal was to test whether nitrate attenuation was occurring in a sub-reach characterised by strong vertical (upwelling) water fluxes. The vertical concentration profiles obtained from DET samplers indicate considerable cm-scale variability in NO_3^- (4.4 ± 2.9 mg N/L), SO_4^{2-} (9.9 ± 3.1 mg/L) and dissolved Fe (1.6 ± 2.1 mg/L) and Mn (0.2 ± 0.2 mg/L). However, the overall trend suggests the absence of substantial net chemical transformations and surface-subsurface water mixing in the shallow sediments of our sub-reach under baseflow conditions. The significance of this is that upwelling NO_3^--rich groundwater does not appear to be attenuated in the riverbed sediments at <15 cm depth as might occur where hyporheic exchange flows deliver organic matter to the sediments for metabolic processes. It would appear that the chemical patterns observed in the shallow sediments of our sub-reach are not controlled exclusively by redox processes and / or hyporheic exchange flows. Deeper-seated groundwater fluxes and hydro-stratigraphy may be additional important drivers of chemical patterns in the shallow sediments of our study sub-reach.

Key words: Nitrate cycling; riverbed sediment; water quality; pollution; hyporheic zone; groundwater; pore water; DET

1. Introduction

Of the major chemical elements necessary to sustain life (nitrogen, carbon, phosphorus, oxygen and sulphur), nitrogen (N) has the greatest total mass (4×10^{21} g) in Earth's hydrosphere, atmosphere and biosphere (Galloway *et al.*, 2003). Anthropogenic acceleration of global N cycling has almost doubled 'reactive' (all N species except N_2 gas) N levels (Kulkarni *et al.*, 2008) by the spread and fertiliser-based intensification of agriculture, by atmospheric pollution, and now by climate change. In the United Kingdom, the widespread application of slurry and fertilisers in the 1960s/70s has led to extensive contamination of groundwater resources by nitrate (Butcher *et al.*, 2006; Stuart *et al.*, 2007). Recent research suggests that peak nitrate loading is now being recorded in many catchments and that it will take decades for the leached nitrate to discharge into freshwaters due to storage and slow transport times in groundwater aquifers (Wang *et al.*, 2012). This may be particularly problematic in groundwater-fed rivers as predicted warmer and drier summers as a result of climate change (Wilby *et al.*, 2006) will mean groundwater contributions to surface water will become more important, potentially leading to nitrate contamination of surface waters from groundwater. Predicted higher winter rainfall may offset groundwater-sourced nitrate contamination by dilution during short-term storm events. However, extended periods of winter rainfall in groundwater-dominated catchments may enhance groundwater flux and nitrate transport to surface water thereby counteracting any potential improvement in water quality due to dilution. Too much reactive N in surface freshwaters has environmental, economic and human health implications. High levels of nitrite (NO_2^-) and nitrate (NO_3^-) can cause algal blooms and oxygen depletion (Burt *et al.*, 2011), and stream acidification in catchments with poorly buffered soils (Curtis *et al.*, 2005), all of which reduce biodiversity (Houghton *et al.*, 2011). The removal of NO_3^- from drinking water costs the UK water industry approximately £58 million per year (DEFRA, 2006). Excess NO_3^- in drinking water can reduce the ability of the blood to carry oxygen (Bryan, 2006) and has been linked to increased risk of cancer (Yang *et al.*, 2007).

In recent years, the potential of riverbed hyporheic sediments to attenuate NO_3^- from polluted groundwater has received much attention (Krause *et al.*, 2009; Lansdown *et al.*, 2014). The hyporheic zone is typically understood to be the region of groundwater-surface water mixing in riverbed sediments (Valett *et al.*, 1993), although other definitions exist related to the ecological (Hancock *et al.*, 2005; Boulton, 2007) and hydrogeological (White, 1993) significance of this zone. As the interface and zone of mixing of biogeochemically distinct water bodies, the hyporheic zone is often characterised by steep physical and chemical gradients where transport and transformation of chemical species occurs (Hill *et al.*, 1998). Hyporheic exchange flows (HEF) generated by geomorphological features in the riverbed facilitate the dynamic flux of oxygen and organic matter in hyporheic sediments which can create biogeochemical 'hotspots' in the streambed where NO_3^- attenuation (and release) can occur (Rivett *et al.*, 2008). However, measuring pore water chemistry in the hyporheic zone at scales relevant to N cycling presents a problem for most sampling methodologies. For example, standard multi-level pore water sampling techniques (Rivett *et al.*, 2008) are only effective generally to within 10 cm of the riverbed surface providing very coarse measurements which relate to a discrete sediment stratigraphy rather than a biogeochemical zone. Pore water sippers (Huettel, 1990) have greater spatial resolution but can modify the subsurface flow field by pumping leading to mixing of pore waters and surface waters (D'Andrea *et al.*, 2002). In comparison, in-situ passive sampling technologies such as DET (Diffusive Equilibrium in Thin-Films) (Davison *et al.*, 1991; Krom *et al.*, 1994; Mortimer *et al.*, 1998) and dialysis peepers (Doig and Liber, 2000) allow for high spatial resolution (down to mm-scale) analysis of important redox-sensitive parameters without modifying subsurface flow fields. Dialysis peepers can be used to measure at a similar resolution to DET; however, DET gels are preferred over peepers as they equilibrate with solutes at a faster rate permitting shorter deployment times (Fones et al., 2011).

Wang *et al*. (2013) have estimated historical peak nitrate loading from the Penrith Sandstone has arrived in most parts of the River Eden catchment, north-west England. Several areas including parts of the River Leith sub-catchment will experience peak nitrate loading in the next 30-40 years highlighting the need to resolve spatial and temporal patterns in environmental risk associated with groundwater nitrate fluxes. In this study, we focus on a stretch of the River Leith that has been the subject of intensive research as a zone of dynamic ground-surface water exchange and N transformation. Reach-scale (200 m) observations of subsurface vertical and lateral water fluxes, together with riverbed geophysical surveys, have identified a sub-reach (50 m) preferential discharge location characterised by direct connectivity to the underlying sandstone aquifer (Binley *et al.*, 2013) (see Supplementary Material 1). The concentrations of pore water anions (from 100 to 10 cm below the riverbed) in this sub-reach (including NO_3^-) are elevated with respect to the wider river reach, and show limited evidence of attenuation under baseflow conditions either by physical mixing or chemical transformation (Krause *et al.*, 2009; Heppell *et al.*, 2013; Ullah *et al.*, 2013; Lansdown *et al.*, 2014) (see Supplementary Material 2). In the absence of hydrological or chemical data for the upper 15 cm of sediments, Munz *et al.* (2011) demonstrated in modelling experiments that surface water infiltration into the sediments is unlikely to occur under baseflow conditions, thereby suppressing the potential for HEF to attenuate NO_3^- migration to surface water from the underlying aquifer. However, this hypothesis could not be verified with direct measurements under the previous experimental setup which utilised multi-level pore water samplers. The purpose of this research was to target this 'monitoring gap' using the technique of diffusive equilibrium in thin-films to capture vertical chemical profiles of

NO_3^- and redox-sensitive solutes at high spatial resolution. Our specific objectives were the following: (1) establish detailed vertical and longitudinal patterns of NO_3^- and redox-sensitive solutes in the upper 15 cm of armoured riverbed sediments and (2) identify if chemical transformation and / or subsurface-surface water mixing acts to attenuate upwelling NO_3^--rich groundwater.

2. Methods

2.1 Study site

This investigation took place in a gaining reach of the River Leith, a tributary of the River Eden, Cumbria, England (**Figure 1a**). The River Leith catchment lies primarily on Permo-Triassic Sandstone overlain by glacio-fluvial sediments to a depth (in the riverbed) of approximately 50 cm (Kaeser *et al.*, 2009). Previous research as part of a parent project investigating hyporheic exchange and N transformations in the hyporheic zone (NERC Reference: NE/F006063/1) focussed on a 200 m reach set in a narrow floodplain comprising agricultural and pastoral landscape. Surface water nitrate concentrations are typically 2 mg N/L under baseflow conditions (Heppell *et al.*, 2013). A 50 m sub-reach (without tributaries) transitioning from a riffle to a pool environment was chosen for more intensive subsurface investigations described here (**Figure 1b**). This sub-reach has been identified as a zone of locally elevated vertical (upwelling) flux (Binley *et al.*, 2013). Furthermore, pore water chemical profiles (from 100 to 10 cm depth) have identified locally elevated pore water solutes (6.2 – 7.4 mg N/L) associated with the zone of enhanced upwelling with no evidence of attenuation by physical mixing (Binley *et al.*, 2013; Heppell *et al.*, 2013).

2.2 Experimental design

The technique of diffusive equilibrium in thin-films (DET) (Davison *et al.*, 1991) was used to obtain concentration profiles of redox-sensitive parameters (NO_3^-, SO_4^{2-}, dissolved Fe and Mn) from the upper 15 cm of the riverbed. DET samplers equilibrate with the pore water chemistry and are used here to provide concentration profiles at cm-scale. DET technology has been successfully applied in a range of 'soft' sediment environments including peatlands, lakes, estuaries and coasts (Davison *et al.*, 1991; Davison *et al.*, 1994; Zhang and Davison, 1995; Mortimer *et al.*, 1998; Bottrell *et al.*, 2007). Readers are referred to Ullah *et al.* (2012) for more detailed information on DET gel preparation. A previously described protective stainless steel cover (Ullah *et al.*, 2012) was utilised in this study to allow the deployment of DET in the armoured riverbed sediments. DET sample sites were established along the sub-reach to allow measurement of shallow sediment pore water chemistry along the length of the anomalous hydrological and chemical zone. Three probes were deployed in a riffle environment (site C) at the upstream end of the sub-reach (**Figure 1c**). Six further probes were deployed in pool environments (three at site D and three at site E).

2.3 Field deployment and retrieval of DET probes

DET probes were deployed on one occasion in September 2011 towards the end of the summer baseflow period. Deployment of DET probes in the armoured riverbed was achieved by first driving a stainless steel drive point into the sediments to a depth of 15 cm. The DET probe in the stainless steel holder was then inserted next to the drive point which was then carefully removed allowing the sediment to collapse around the probe. The probes were allowed to equilibrate with the sediment pore waters for 72 hrs before retrieval to allow equilibrium between the gel and the sediment pore water (Mortimer *et al*., 1998).

Baseflow conditions were stable in the river over the 72 hr period during which time a mean discharge of 0.69 m^3/s was measured at the Environment Agency (EA) Cliburn weir (N54:37:03; W2:38:23), approximately 200 m downstream of the study reach. Once removed, the probes were placed in zip-lock bags and stored on ice to minimise potential diffusion in the gel. Probes were then transferred to the laboratory and the gel slicing and extraction processes started within 2 hrs of retrieval.

2.4 Measurement of vertical flux and multi-level sampler (coarse-scale) pore water chemistry

The DET probes were deployed as close as possible to an existing network of nested channel piezometers installed to allow contiguous measurement of subsurface water flux and coarse-scale pore water chemistry (**Figure 1c**). Readers are referred to Binley *et al.* (2013), Heppell *et al.* (2013) and Byrne *et al.* (2013) for more detailed information on the design of the piezometer network and the measurement of subsurface water flux and pore water chemistry. In-channel piezometers were screened at 20, 50 and 100 cm below the riverbed. Vertical hydraulic gradients were measured upon retrieval of the DET probes and calculated by *dh/dl*, with *dh* being the elevation difference between local stream and piezometer water level, and *dl* being the distance between the mid-screen depth of the piezometer and the riverbed surface. Vertical flux was calculated using Darcy's Law as $q_v = K * dh/dl$, where K is the hydraulic conductivity calculated from slug tests in the same piezometers used to compute hydraulic gradients (Binley *et al.*, 2013).

Each 100 cm piezometer was fitted with multi-level pore water samplers at 10, 20, 30, 50 and 100 cm depths. Pore water samples were extracted at the time of DET probe retrieval using a syringe and flexible plastic tubing. Sampling lines and syringes were flushed with pore water before collection of samples. A sample of surface water near the piezometers was taken at the same time as pore water samples. All samples were filtered (0.45 μm surfactant-free cellulose acetate membrane) in the field. Samples for anion (NO_3^- and SO_4^{2-}) analysis were collected in polycarbonate bottles. Sample bottles were rinsed with pore water three times before filling completely with sample to avoid the presence of air pockets. Samples for metal analysis (Fe and Mn) were collected in pre-rinsed (Milli-Q water) polypropylene tubes and acidified (2%) with concentrated HCl. All samples were transferred on ice to the laboratory within 2 hrs of collection and analysed within 24 hrs of collection. One travel blank and two filter blanks were used for all analytes.

2.5 Laboratory processing of DET gels and multi-level pore water samples

DET gels were sliced into 1 cm sections using a Teflon-coated razor blade. The DET slices were then transferred to 1.5 mL vials and 1 mL Milli-Q water was added to each vial. The samples were then placed on frozen ice packs and shaken overnight on a reciprocating shaker to allow back equilibration of NO_3^- and SO_4^{2-} in the gel with the Milli-Q water. After shaking, the gels were transferred to another set of 1.5 mL vials for Fe and Mn extraction. Samples for NO_3^- and SO_4^{2-} analysis (DET and standard pore water samples) were analysed by ion chromatography (DIONEX) within 48 hrs of retrieval. The limit of detection based on 14 blank samples was 0.07 mg N/L and 0.69 mg S/L. The analytical accuracy of repeat control samples was ± 6.2% for NO_3^- and ± 5.1% for SO_4^{2-}. Gel slices for Fe and Mn extraction were eluted with 1 mL of 1M HCl and shaken overnight on a reciprocal shaker. The extracts (and standard pore water samples) were then analysed by ICP-MS (Thermo X series). The limits of detection were 0.09 μg/L Fe and 0.03 μg/L Mn. The analytical accuracy of repeat control samples was ± 3.2% for Fe and ± 3.6% for Mn. Samples from the initial Milii-Q extraction were analysed for Fe and Mn to verify there was no loss of these solutes in this extraction phase – both Fe and Mn tested below detection limits. The fidelity of DET measurements of solute gradients in pore waters has been examined in detail (Harper *et al.*, 1997). Prior to slicing the gel, solutes will diffuse from high to low concentrations and so narrow maxima (1-2 mm) in concentrations will be slightly under estimated when gels are divided. However, with the relatively coarse slicing resolution of 1 cm, where only 1-2 cm wide maxima can be identified, relaxation effects are greatly diminished, especially as probes were transported on ice.

2.6 Statistical data analysis

Analysis of Variance (ANOVA) was used to test for significant differences in vertical flux and pore water solutes (DET and standard pore water samplers) between sample locations and depths. The environmental data failed the normality assumptions for parametric analysis (Kolmogorov-Smirnov test) even after transformation; therefore, the non-parametric Kruskal-Wallis one-way analysis of variance test and the Mann Whitney U test were used to test for differences between sample locations and depths.. All statistical calculations were performed in the program PASW Statistics 18.

3. Results

3.1 Longitudinal and vertical trends in fine-scale pore water chemistry

Solute concentration profiles of shallow sediments (0 – 15 cm) within the experimental sub-reach are illustrated in **Figure 2** and summarised in **Table 1**. Probe three from site C (black circles) illustrates data from 1 to 11 cm only as the DET gel was damaged during retrieval from the sediments. The vertical DET NO_3^- concentration profiles exhibited a degree of variability both within and between sample sites. At site C, NO_3^- profiles were generally invariable with depth (**Table 1**); an exception to this linear trend being probe three (black circles) which showed high variability from the aggregated mean (5.7 mg N/L) with two maxima of 9.3 and 8.7 mg N/L at 1 and 8 cm depths, respectively (**Figure 2a**). Site D showed the most within site variability of the study sites for NO_3^-; however, this was superimposed on a generally consistent linear trend for individual probes (**Figure 2b**). Mean NO_3^- at site D was 5 mg N/L with two maxima of 7.3 and 7.4 mg N/L at 10 and 15 cm depths, respectively. Site E exhibited the least within site variability in NO_3^- concentrations with mean concentrations of 2.6 mg N/L. Concentrations of SO_4^{2-} in the sediment pore waters were higher than NO_3^- and generally exhibited more within site variability than NO_3^-. Sites C and D exhibited high variability in SO_4^{2-} concentrations over the 15 cm probe depth, ranging from 4.7 to 17.9 mg S/L and 3.1 to 20.8 mg S/L, respectively. Site E showed the least within site variability in NO_3^- and SO_4^{2-} concentrations (**Figure 2c**) with mean concentrations of 2.6 mg N/L and 9.17 mg

S/L. Mean site values indicate a trend of decreasing NO_3^- and SO_4^{2-} concentrations in the shallow sediments from site C to site E (**Table 1**). The distinctiveness of NO_3^- concentrations between sites is confirmed by Mann Whitney U tests which show concentrations are significantly different (p = < 0.01) between sample sites. Although mean SO_4^{2-} concentrations decrease from site C to site E (**Table 1**), the within site variability of the SO_4^{2-} data results in a significant difference (p = < 0.05) only between site C and site E.

Mean dissolved Fe and Mn concentrations at site C were 1.86 and 0.05 mg/L, respectively. The vertical concentration profiles of Fe and Mn at site C were generally invariable with the exception of probe three (black circles) (**Figure 2a**) which exhibited high dissolved Fe (11.3 mg/L) and Mn (0.18 mg/L) concentrations at the sediment-water interface. Two smaller Fe and Mn maxima occurred at 7 and 10 cm depths, respectively. Dissolved Fe and Mn at sites D and E showed a generally similar vertical trend (**Figure 2b and 2c**) although mean concentrations at site E (2.68 mg/L Fe and 0.53 mg/L Mn) were higher than at site D (1.09 mg/L Fe and 0.11 mg/L Mn) (**Table 1**). The vertical profile was almost parabolic in shape with elevated concentrations in the upper 1 – 5 cm, a steep decrease to relatively consistent concentrations from 6 – 10 cm and an increase in concentrations from 11 – 15 cm. For both dissolved metals and at both sites, the maximum concentration occurred at 15 cm depth. The highest dissolved Fe (12.18 mg/L) and Mn (1.99 mg/L) concentrations across all three sample sites were recorded at 15 cm depth at site E (probe 1, open circles). A spatial trend contrary to that of NO_3^- and SO_4^{2-} was observed for dissolved Fe and Mn. Generally, mean dissolved Fe and Mn concentrations increased from site C to site E (**Table 1**); the exception being Fe at site C which was influenced by the high variability in probe 3 (black circles). Mann

Whitney U tests of significance show dissolved Mn was significantly different (p = < 0.01) between samples sites. Dissolved Fe was generally significantly different (p = < 0.01) between sample sites (except between site C and site D).

3.2 Longitudinal and vertical trends in vertical flux and coarse-scale (multi-level sampler) pore water chemistry

Vertical flux calculations derived from saturated hydraulic conductivity measurements and vertical hydraulic gradient measurements taken at the same time as DET probe retrieval are illustrated in **Figure 3** alongside summary data for baseflow periods (July to September) collected as part of the parent project in 2009 and 2010. These data demonstrate a longitudinal trend in vertical flux measured at 100 cm; flux decreases in the downstream direction from site C to site E. Although no significant difference in vertical flux was observed between samples sites for aggregated depth data, flux at site C was significantly greater (p = < 0.05) than flux at site E. A significant (p = < 0.05) increase in vertical flux occurred in the sediments above 100 cm (20 and 50 cm) at site C and site E whereas the vertical flux profile was more uniform with depth at site D.

Measurements of surface water and pore water solutes obtained from the multi-level samplers and at the same time as DET probe retrieval are also presented in **Figure 3** alongside summary data for baseflow periods (July to September) in 2009 and 2010. **Table 2** presents a summary of observed coarse-scale pore water NO_3^- and SO_4^{2-} concentrations and a comparison with DET-derived values. Pore water NO_3^- concentrations were significantly greater (p = < 0.01) than surface water concentrations at all three sample sites; the reverse relationship (p = < 0.01) was observed for the SO_4^{2-} data. Pore water NO_3^- exhibited a significant (p = < 0.01) decrease in concentration from site C to site E. At site C and site E, the NO_3^- concentration profile was relatively stable between 10 and 100 cm depths; whereas, at site D, pore water NO_3^- gradually decreased in concentration towards the riverbed surface; although values were similar at 10 and 20 cm. Pore water SO_4^{2-} concentrations were not significantly different between sample depths at individual sites and also between sites.

4. Discussion

4.1 Vertical concentration profiles of NO_3^- and redox-sensitive parameters

Nitrogen transformation in the hyporheic zone has been shown to be controlled by infiltrating surface water that delivers oxygen and organic matter for metabolic processes; typically NO_3^- production occurs where oxygenated surface water enters the riverbed and NO_3^- consumption occurs farther along the flow path when oxygen has been respired (Zarnetske *et al.*, 2011). In the present study, most of the DET probes showed variability in solute concentrations with depth; however, this variability did not conform to the archetypal biogeochemical zones that represent the degradation of organic matter using successively less energy-efficient terminal electron accepting processes. Instead, the DET probes exhibited cm-scale changes in solute concentrations which suggests the absence of large-scale attenuation of NO_3^- from upwelling groundwater in our sub-reach. Extensive investigations of ‘soft’ riverine, lacustrine and marine sediments using DET technology have revealed similar, highly localised micro-scale changes in solute concentrations (Fones *et al.*, 1998; Docekalova *et al.*, 2002; Mortimer *et al.*, 2002).

The NO_3^- concentration profiles from the DET probes suggest surface water infiltration into the riverbed sediments was not significant during the study period. Were surface water infiltration significant, we would expect to see strong vertical concentration gradients due to the difference in groundwater and surface water NO_3^- concentrations. In addition, several studies utilising conservative tracers (Binley *et al.*, 2013; Byrne *et al.*, 2013; Heppell *et al.*, 2013) and numerical groundwater modelling (Munz *et al.*, 2011) have demonstrated groundwater-surface water mixing is unlikely to be occurring below 5 cm sediment depth in our sub-reach, at least under baseflow conditions. This suggests that the observed cm-scale variability in nitrate concentrations occurs at depths greater than surface water infiltration. Krause et al. (2009) observed similar variability in nitrate concentrations in deeper sediments (20 – 40 cm) of the same sub-reach. This suggests that nitrogen transformation in this sub-reach may be temporally removed from surface water infiltration under baseflow conditions. Instead, nitrogen transformation may be related to the temporary expansion of the hyporheic zone during high flow events and to the delivery of organic matter and oxygen to deeper sediments during these times (Byrne *et al.*, 2013).

Nitrate concentrations increased above 5 cm sediment depth in probe three (black circles) at site C. This could be related to down welling surface water, mineralisation of nitrogen derived from the dieback of Bur-reeds (*Sparganium spp.*) (Ullah *et al.*, 2012; Ullah *et al.*, 2013), and subsequent nitrification (Mortimer *et al.*, 2002). Of the three sample sites investigated, site C (riffle) is the most likely to experience HEF as a result of pumping exchange (Boano *et al.*, 2008) and / or changes in the hydrostatic head gradient across the riffle (Wondzell *et al.*, 2009). If the upper 5 cm is indeed an oxygenated zone, it is curious then why we see a concomitant increase, rather than decrease, in the concentration of the dissolved metals. It may be that elevated Fe and Mn at the same location may not simply represent reduced forms, but may be more reflective of oxidised colloidal complexes that are able to pass through the membrane filter and gel (Ahmed *et al.*, 2010). However, we believe that the true cause of this artefact is disturbance to the gel during deployment (the gel strip was squashed meaning division into discrete cm bands was difficult) which may have affected the volume and hence final concentration of the sliced gel strips. This artefact aside, it is clear from the low concentration gradients from the other DET probes that no large-scale changes (losses or gains) of NO_3^- are occurring in the shallow sediments, ensuring that elevated groundwater NO_3^- is transported to the surface water.

An interesting and consistent trend in vertical chemical profiles occurred for Fe and Mn at site D and site E. The vertical profile at these sites was parabolic in shape with elevated concentrations from 1 – 5 cm and 10 – 15 cm. In this pool section of the sub-reach where HEF is less likely to occur (Binley *et al.*, 2013), elevated Fe and Mn in the upper 5 cm may be related to the accumulation of leaf litter and other organic matter. At the time of the DET experiments in mid-September, the river was still in baseflow conditions; however, organic matter had begun to accumulate in the pool (site D and site E) due to the dieback of extensive channel margin Bur-reeds (*Sparganium spp.*) and leaf fall from bank-side trees. The surface peak in Fe and Mn could have resulted from the metals being major electron acceptors for the decomposition of this organic matter (Davison *et al.*, 1991; Zhang *et al.*, 1999). Leaf litter accumulation on the streambed can also modify channel hydraulic properties (Argerich *et al.*, 2011) leading to increases in water residence times which extend contact times between solutes and stream microbial communities (Haggard and Storm, 2003; Argerich *et al.*, 2008). Calculations of water residence times at 20 cm depth based on Darcy-derived vertical flux do indeed suggest higher water residence times at sites D and E. The combination of the increase in water residence times and input of organic matter could create conditions favourable for anaerobic microbial metabolism resulting in Fe and Mn reduction (Fones *et al.*, 1998). It is interesting then why we do not see evidence for denitrification in the upper sediments, given bacterial NO_3^- reduction is energetically more favourable than Fe or Mn reduction. We suggest that denitrification is probably occurring but that the resultant changes in nitrate concentration are of the order of ng/L or μg/L; these are difficult to observe when the background NO_3^- concentrations are mg/L. In contrast, the Fe and Mn background concentrations are generally ng/L or μg/L so it is possible to detect smaller concentration changes resulting from bacterial activity. Of course, reduction of all three electron acceptors (NO_3^-, Fe and Mn) could appear to occur together, especially in heterogeneous systems such as riverbed sediments where micro-niche activity is likely to be important (Stockdale *et al.*, 2009).

The largest observed increases in Fe and Mn concentrations occurred at 10 – 15 cm at site D and site E. Others have noted the occurrence of high dissolved Mn concentrations at depths of 10 – 20 cm in the River Leith (Ullah *et al.*, 2012; Byrne *et al.*, 2013). Iron and Mn peaks at similar depths have been observed also in lake and estuarine sediments (Fones *et al.*, 1998; Shuttleworth *et al.*, 1999; Docekalova *et al.*, 2002). Byrne *et al.* (2013) attributed these high Mn bands in the River Leith sediments to Mn reduction enhanced by the supply of DOC by down welling surface water at high river stage. Lateral flows from the riparian zone were also postulated to be an important source of DOC in deeper (20 – 50 cm) sediments (Byrne *et al.*, 2013; Heppell *et al.*, 2013). Lateral flux at 20 cm depth within our sub-reach is greatest around site E (see supplementary material 1). Therefore, the lateral movement of carbon-rich water originating from the riparian zone may be an important driver of biological reduction in the shallow sediments at site E.

4.2 The interaction of hydro-stratigraphy and redox-sensitive chemistry

The hyporheic zone of riverbed sediments has been proposed as a possible medium for the removal of NO_3^- from upwelling groundwater. However, the present research provides evidence that NO_3^- attenuation in the upper sediments may be limited or non-existent where strong groundwater upwelling retards the development of a hyporheic zone (defined here as a region of groundwater-surface water mixing). This raises the question of the possible role of hydrogeology and hydro-stratigraphy in controlling the chemical dynamics and concentration profiles of pore water solutes including NO_3^-. In this study, we have identified from DET samplers (1 cm resolution) and multi-level pore water samplers (10 – 50 cm resolution) a longitudinal trend of generally decreasing pore water anion (NO_3^- and SO_4^{2-}) concentrations in the downstream direction. Previous water-borne geophysical surveys identified a local high of pore water electrical conductivity persisting to 5 m depth centred on the upstream section (site C) of our sub-reach (Clifford and Binley, 2010; Binley *et al.*, 2013). This high electrical conductivity has been associated with elevated concentration of pore water solutes (including NO_3^-) to a minimum depth of 100 cm. Moreover, pore water dissolved organic carbon was lower and dissolved oxygen was higher at site C compared to a vegetated sediment stretch (~8 m upstream of site C), suggesting limitation of nitrate reduction potential by upwelling water at site C (Ullah *et al.*, 2013). Putting this evidence together, it has been suggested that this sub-reach is a zone of preferential flow of NO_3^--rich groundwater (Binley *et al.*, 2013; Heppell *et al.*, 2013). The groundwater could be sourced from a fracture in the underlying bedrock which effectively acts as a concentrated point source of NO_3^-, where groundwater flow from the Permo-Triassic Sandstone is typically diffuse in nature (Wang *et al.*, 2012).

The movement of NO_3^--rich groundwater is undoubtedly aided by the local hydro-stratigraphy and its influence on subsurface flux and water residence times. The same longitudinal trend of decreasing (downstream) anion concentrations is evident for vertical flux at 100 cm depth; although this spatial pattern is modified at shallower depths (20 and 50 cm) most likely by the influence of lateral subsurface fluxes from the riparian zone (Binley *et al.*, 2013). Elevated flux (at 100 cm) might be aided by local stratigraphy. Particle size analysis of the riverbed sediments reveals site C to have a significant fraction of pebbles, gravel and coarse sand (40-90%) persisting to at least 70 cm below the riverbed (Binley *et al.*, 2013). At site D and site E this coarse zone terminates at 30-40 cm; thereafter, the sediment is composed mainly of medium and fine sand (35-90%). Hydraulic conductivity measurements reflect the particle size data with hydraulic conductivities decreasing from site C to site E (Binley *et al.*, 2013). Together, these data perhaps explain the longitudinal trend in vertical flux at 100 cm. Calculations of water residence times based on Darcy-derived vertical flux show water residence time at all depths (100, 50 and 20 cm) to decrease in the downstream direction from site C to site E (assuming a predominantly vertical flow path). Water residence times at site E are significantly higher than at the other sites at all sample depths. Water residence time is known to significantly affect the rate of transformation of NO_3^- with higher water residence times corresponding to increased rates of denitrification (Pinay *et al.*, 2009; Zarnetske *et al.*, 2011).

4.3 A methodological note

As this paper has used both DET and multi-level pore water samplers to present and interpret biogeochemical patterns in riverbed sediments, a discussion of the merits of the two techniques is perhaps warranted. Comparing DET measurements (NO_3^- and SO_4^{2-}) over 15 cm with multi-level sampler data at 10 cm shows that the two measurements were not always consistent with each other (**Table 2**). The largest discrepancy occurred for SO_4^{2-} whereas measurements of NO_3^- were more comparable (except site D). Ullah *et al.* (2012) also observed comparable NO_3^- concentrations from DET and pore water samplers. The DET SO_4^{2-} measurements were approximately 50% greater than measurements obtained from the multi-level samplers.

The observed discrepancy in solute concentrations is most likely due to the contrasting scale and method of sample collection between the two techniques. Multi-level pore water samplers operate at a minimum resolution of 5 cm and effectively sample a volume of pore water, modifying the flow field and possibly integrating oxic and anoxic micro sites in the sediments (Kalbus *et al.*, 2006; Krause *et al.*, 2009). In the present study, multi-level samplers missed the considerable variation in solute concentrations captured by DET samplers in the upper sediments, the result being the loss of important information on the dynamics of chemical interactions occurring at cm-scale. Diffusive equilibrium in thin-films can measure solutes at sub-cm resolution providing accurate information on nutrient dynamics and biogeochemical activities in river bed sediments (Davison *et al.*, 1994; Mortimer *et al.*, 2002). Simple interpretation of DET measurements at high resolution from shallow sediments as a continuation of data from deeper multi-level pore water samplers may not be feasible because of the different scale and mechanism of sampling. Multi-level pore water samplers are an invaluable method for providing broad-scale assessment of subsurface chemistry. However, DET is especially useful when chemical data are needed from river sediments which are highly heterogeneous in nature and where dynamic subsurface fluxes can exert a significant influence on pore water chemistry.

5. Conclusions

Although DET technology has been widely applied in 'soft' lake, marine, estuarine, freshwater and coastal sediments, the utilisation of a novel delivery mechanism in this study for armoured riverbed environments permitted investigation of nitrogen dynamics in a coarse sediment lotic environment. By analysing vertical concentration profiles captured by the DET samplers, our study has revealed cm-scale changes in the concentration of redox-sensitive solutes at depths below surface water infiltration and demonstrated the important control of subsurface water flux on nitrogen biogeochemistry. Our deployment of the DET samplers in the upper 15 cm of river sediments filled a pre-existing 'monitoring gap' and provided strong evidence for the absence of surface-subsurface water mixing in our study reach under baseflow conditions. The significance of this is that strongly upwelling NO_3^--rich groundwater is not attenuated in the river sediments as might occur where hyporheic exchange flows deliver organic matter to the sediments for metabolic processes. It would appear that the general biogeochemical patterns observed in the shallow sediments of our sub-reach are not controlled exclusively by redox processes and / or hyporheic exchange flows. Deeper-seated groundwater fluxes and hydro-stratigraphy may be additional important drivers of biogeochemical patterns in our study reach. Whilst we have only investigated three sites in a 50 m stretch of river, our results suggest chemical attenuation of groundwater-sourced NO_3^- in gaining river systems may be affected by the relative magnitude of subsurface water flux. This is important in the context of predicted increases in the concentration of NO_3^- in the Permo Triassic Sandstones of north-west England and predicted warmer, drier summers as a result of climate change.

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Tables

Table 1. Mean (with standard deviation) concentrations (mg/L) of redox-sensitive parameters from DET probes in the study reach and at sites C, D and E.

	Nitrate-N	Sulfate-S	Fe	Mn
Reach	4.39 ± 2.99	9.94 ± 3.10	1.57 ± 2.11	0.15 ± 0.19
Site C	5.70 ± 1.31	10.64 ± 3.14	1.86 ± 2.81	0.05 ± 0.04
Site D	4.96 ± 1.42	9.98 ± 3.65	1.09 ± 1.32	0.11 ± 0.11
Site E	2.56 ± 0.71	9.17 ± 2.43	2.68 ± 2.57	0.53 ± 0.50

Table 2. Mean (with standard deviation) solute concentrations (mg/L) from DET (shaded) and multi-level samplers (MLS). DET values are mean concentrations from 1 – 15 cm. n = number of samples from Site C, Site D and Site E, respectively.

Depth (cm)	Site C		Site D		Site E	
	NO_3^-	SO_4^{2-}	NO_3^-	SO_4^{2-}	NO_3^-	SO_4^{2-}
Surface water (n = 15, 9, 16)	1.94 ± 0.31	11.8 ± 4.32	1.77 ± 0.26	12.46 ± 4.71	1.93 ± 0.32	11.8 ± 4.44
DET 1 – 15	5.70 ± 1.31	10.64 ± 3.14	4.96 ± 1.42	9.98 ± 3.65	2.56 ± 0.71	9.17 ± 2.43
MLS 10 (n = 14, 9, 15)	6.29 ± 0.90	7.53 ± 0.92	2.62 ± 0.30	4.86 ± 1.03	2.88 ± 0.63	6.00 ± 1.10
MLS 20 (n = 16, 9, 17)	6.97 ± 0.31	7.58 ± 0.75	2.54 ± 0.30	4.67 ± 0.82	3.27 ± 0.34	5.98 ± 0.90
MLS 30 (n = 9, 9, 9)	6.71 ± 0.15	7.32 ± 0.47	2.96 ± 0.27	4.91 ± 0.96	3.44 ± 0.37	5.56 ± 1.02
MLS 50 (n = 16, 9, 17)	6.72 ± 0.34	7.63 ± 0.73	4.12 ± 0.82	5.83 ± 1.09	2.97 ± 0.18	5.68 ± 0.93
MLS 100 (n = 16, 9, 17)	6.63 ± 0.33	7.64 ± 0.80	4.73 ± 0.23	6.97 ± 1.12	2.93 ± 0.19	5.80 ± 1.00

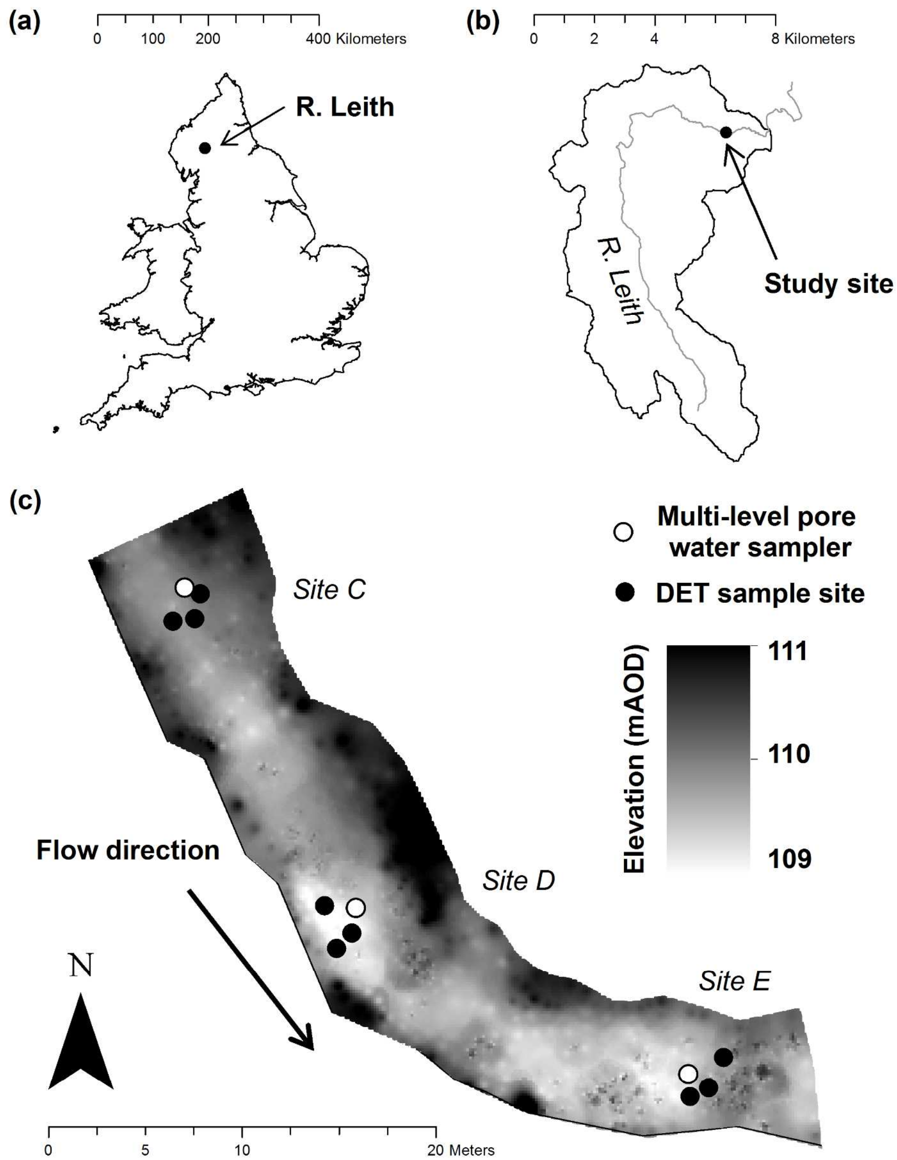

Figure 1. Maps showing (a) location of R. Leith in Cumbria, northern England, (b) location of study site within the R. Leith catchment and (c) riverbed elevation and pore water (DET AND multi-level sampler) sample sites within the study reach. Sample sites and labels are the same as those presented in Binley et al. (2013), Heppell et al. (2013) and Byrne et al. (2013).
215x279mm (300 x 300 DPI)

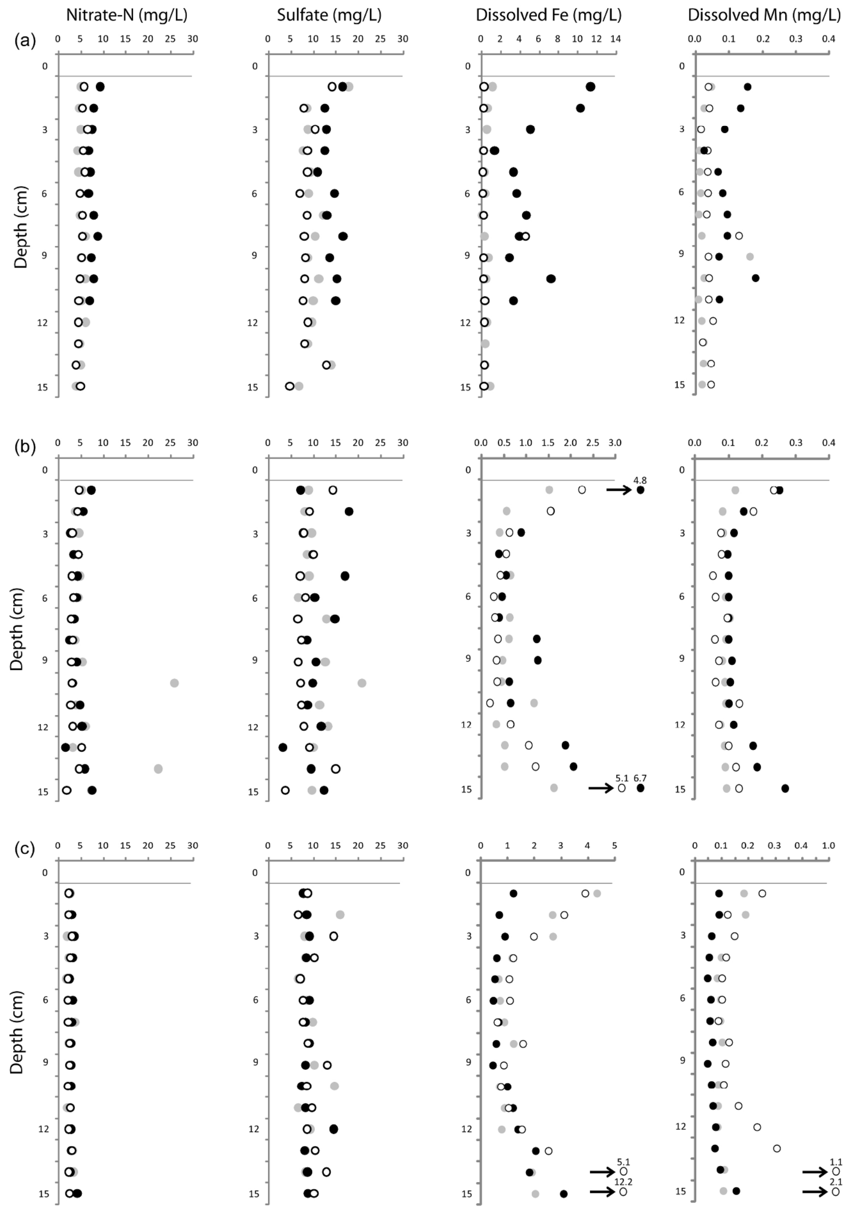

Figure 2. DET solute concentration profiles for (a) site C, (b) site D and (c) site E. Three probes were deployed at each sample site. For Fe and Mn, the abscissa scale differs at each site in order to demonstrate the variability in solute concentrations observed.
197x283mm (300 x 300 DPI)

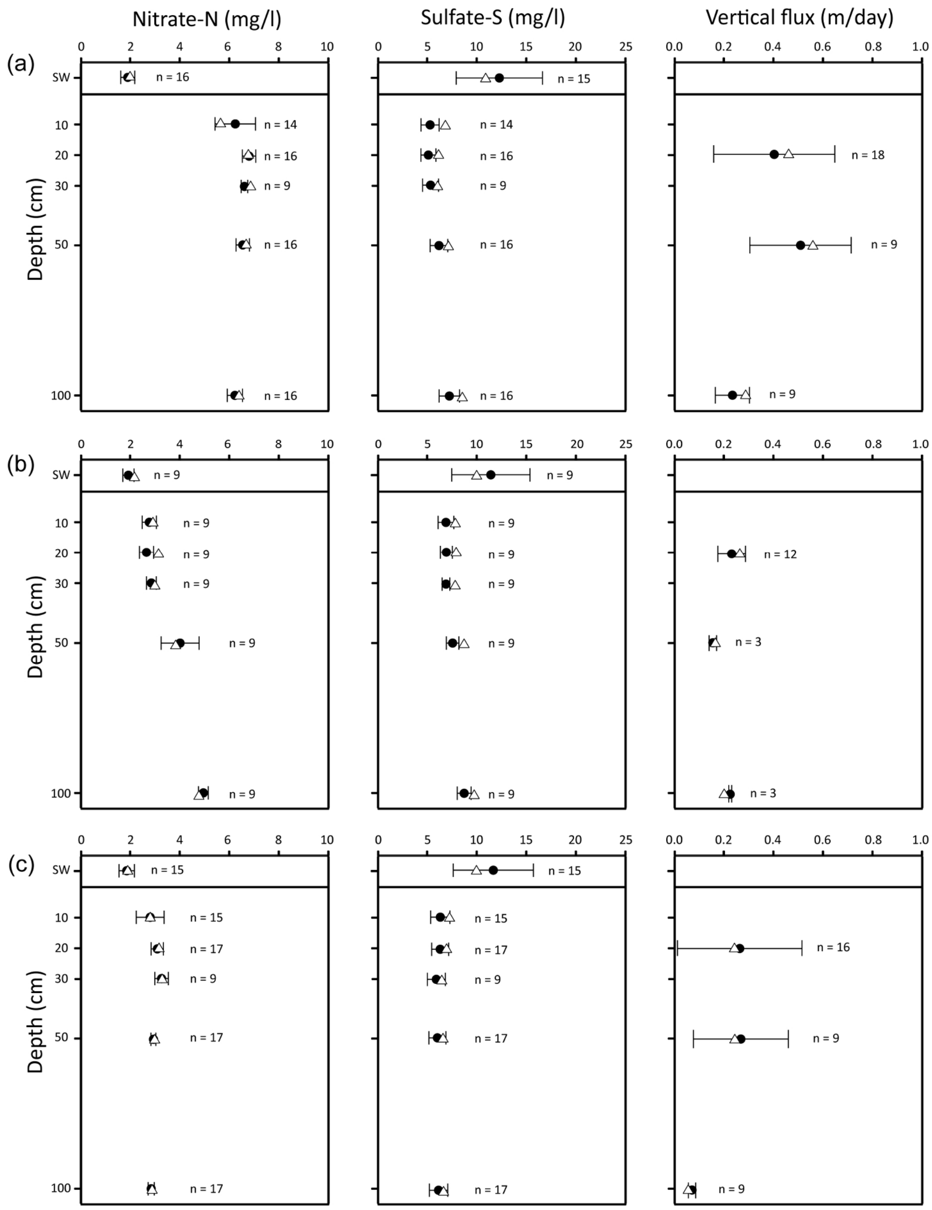

Figure 3. Vertical flux and pore water solute (NO3-, SO42-) concentrations for (a) site C, (b) site D and (c) site E. Triangles represent values recorded at the same time as retreival of DET probes in September 2011. Mean values with standard deviations are presented for samples collected during summer baseflow periods (July to September) in 2009 and 2010. SW = surface water.
170x221mm (300 x 300 DPI)