

Influence of emergent vegetation on nitrate cycling in sediments of a groundwater-fed river

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Abstract Emergent vegetation in river beds can play a significant role in nutrient cycling in riverine sediments. We analysed and compared pore water NO_3^- concentration gradients in the sediments of the River Leith, Cumbria, UK, in the presence and absence of emergent vegetation (dominated by *Spartanium* spp.). High resolution (1 cm interval), in situ, vertical profiles of NO_3^- to 30 cm depth were measured using deployment of diffusive equilibrium in thin films probes on four occasions from July to September 2010. We found significantly ($p < 0.05$) lower NO_3^- concentration under vegetated sediments (VS) compared to those under adjacent un-vegetated sediments (UVS). Concentrations of dissolved

oxygen, measured in pore water collected from multi-level piezometers at 10, 20, 25, 30 and 35 cm depths at the VS and UVS sites, were generally lower under VS (median concentration = 28 μM) than under UVS (median = 132 μM) and correlated significantly with NO_3^- concentration (Spearman's $r = 0.74$, $p < 0.05$). Similarly, pore water dissolved organic carbon (DOC) concentration was 2.8 times higher under VS compared to UVS, and correlated negatively with NO_3^- concentration (Spearman's $r = -0.39$, $p < 0.05$). Specific ultra-violet absorption at 254 nm (SUVA) and per cent aromaticity values of DOC were significantly higher under VS ($p < 0.05$), suggesting that the DOC contained more complex (aromatic) compounds than DOC recorded under UVS. We suggest that, the higher quantity of DOC and its distinct SUVA and percentage aromaticity under VS may have supported faster dissolved oxygen consumption, with the creation of anoxic zones conducive for NO_3^- reduction mainly through denitrification. Metabolic uptake and immobilization of NO_3^- by plants and microbes may have further contributed to lower NO_3^- concentrations under VS. As *Spartanium* spp. is a common plant growing in river beds in the UK, its role in NO_3^- cycling should be considered in attempts to accurately budget N cycling in river beds.

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Introduction

Plants influence nutrient cycling in soils and sediments directly through uptake of nutrients to meet metabolic demand and indirectly through priming microbial activities involved in nutrient transformations (Jackson et al. 2008). The indirect influence of plants on nutrient cycling involves the production of organic carbon through root exudates, sloughed-off cells and litter formation, which fuels diverse microbial processes, including N transformations (e.g. nitrification and denitrification) (Wigand et al. 2001; Jackson et al. 2008; Ullah and Moore 2009; Forshay and Dodson 2011). Consideration of plant impacts on nutrient cycling in the context of plant–microbe interaction in soils and sediments is critical for assessing the nutrient and pollution attenuation potential of ecosystems (Clarke 2002; Schneider and Melzer 2004; Jackson et al. 2008; Ullah and Moore 2009). Such processes are potentially important in riverine ecosystems, but as the vegetation growing in river beds tends to be patchy, its role in nutrient cycling is poorly studied (Sand-Jensen 1998; Groffman et al. 2005; Trimmer et al. 2009; Jackson et al. 2008; Forshay and Dodson 2011). Thus understanding the role of vegetation in influencing nutrient cycling is critical for accurate budgeting of nutrient cycling in the hyporheic zone (Groffman et al. 2005; Forshay and Dodson 2011).

According to Van Drecht et al. (2003), 10 % of the global riverine reactive N flux is derived from upwelling groundwater through riverine sediments into surface water. Nitrogen cascading into riverine sediments from upwelling groundwater, may be attenuated in the hyporheic zone through immobilization (sorption, and plant and microbial uptake) (Howard-Williams et al. 1982; Clarke 2002; Strauss and Lamberti 2002), and through reduction to N₂ gas by denitrification before the reactive N joins river flows (Pretty et al. 2006; Krause et al. 2009; Trimmer et al. 2009; Stelzer et al. 2011; Forshay and Dodson 2011; Harrison et al. 2012). In addition to research looking at the influence of classic geomorphic features of rivers on nutrient cycling in riverine sediments, a number of researchers have also noted the importance of evaluating the influence of different vegetation types on nutrient cycling including those growing in riverbeds (Templer et al. 1996; Wigand et al. 2001; Clarke and Wharton 2001; Groffman et al. 2005; Trimmer et al. 2009; Lefebvre et al. 2006; Forshay and Dodson 2011).

Although the role of river bed vegetation on NO₃[−] attenuation in sediments is acknowledged, studies of NO₃[−] attenuation rates are restricted to surface sediments (ca. 3–10 cm below river bed) in the rooting zones of vegetation (Templer et al. 1996; Wigand et al. 2001; Groffman et al. 2005; Forshay and Dodson 2011). However, the stimulation of the activity of microbes, including those responsible for NO₃[−] attenuation, by vegetation may extend beyond typical rooting depths (from 5 to 12 cm) in the sediments: this possibility needs investigation to be able to account for sediment NO₃[−] attenuation more accurately in and beyond the rooting depth. Even though the aerial extent of vegetation growing in river beds could be small relative to the overall area of rivers, their role in mediating NO₃[−] attenuation in river bed sediment may be significant and hence worthy of investigation. This consideration is critical, particularly during base flow conditions in summer months (plant growth season), when the relative contribution of upwelling NO₃[−] rich groundwater to surface flows are high (Krause et al. 2009; Heppell et al. 2013).

Among vegetation types growing in riverbeds, emergent macrophytes dominated by Bur Reed (*Spartanium erectum*) is the most common species in UK rivers (O'Hare et al. 2010, 2012). O'Hare et al. (2010) reported the presence of this species in 47 rivers in a region spanning from southern Scotland to southern England. While the impact of this species on river flow modulation, Manning's roughness co-efficient and trapping of fluvial sediments has been evaluated (Clarke 2002; Gurnell et al. 2006; O'Hare et al. 2012), to our knowledge, its influence on sediment nutrient attenuation, particularly NO₃[−], has not been assessed.

The measurement and characterization of concentration gradients of solutes including NO₃[−] in river bed sediments has relied either on sediment core extraction from the riverbed with subsequent slicing at coarse depth intervals or pore water sampling from piezometers or multilevel samplers attached to piezometers (e.g. Krause et al. 2009). The suitability of these techniques is limited when the interest is in characterizing chemical gradients at a fine resolution (cm or less) to enable identification of 'hot spots' of biogeochemical activity taking place in micro-sites of sediments at cm or sub-centimetre scale (Köster et al. 2008). The capability of the diffusive equilibrium in

thin films (DET) technique for measuring in situ NO_3^- concentration gradient at high spatial resolution (cm at least) in riverbed sediments (Palmer-Felgate et al. 2010; Ullah et al. 2012) provides a means of resolving zones of NO_3^- loss and gains due to biotic and/or abiotic processes (Dočekalová et al. 2002; Mortimer et al. 2002; Palmer-Felgate et al. 2010). Thus this technique allows capture of in situ fine scale dynamics of solutes including NO_3^- (Dočekalová et al. 2002; Mortimer et al. 2002; Ullah et al. 2012). Recent research has deployed DET probes in riverine sediments for characterization of fine resolution profiles of NO_3^- , NH_4^+ and soluble reactive phosphorus (Jarvie et al. 2008; Palmer-Felgate et al. 2010). The depth of DET deployment in these studies ranged from four to fifteen cm below the river bed. To our knowledge, there has been no published research on DET deployment to depths greater than 15 cm in river beds (Ullah et al. 2012), even though transformation of reactive N in river bed sediments is reported to be significant in deeper sediments (>15 cm depth) (Krause et al. 2009; Stelzer et al. 2011; Krause et al. 2013).

Here we use DET to evaluate the influence of emergent vegetation dominated by *Sparganium* spp. on NO_3^- concentration gradients at high spatial resolution in riverbed sediments extending to 30 cm depth. We test the hypothesis that the NO_3^- concentration gradient is lower in sediments under emergent vegetation than in bare sediments and explore possible mechanisms responsible for such phenomena. This study was part of a larger Natural Environment Research Council (NERC) project investigating the implications of river bed connectivity for nitrogen transformations in the hyporheic zone of a groundwater fed river in UK.

Materials and methods

Site description, DET deployment and pore water sampling

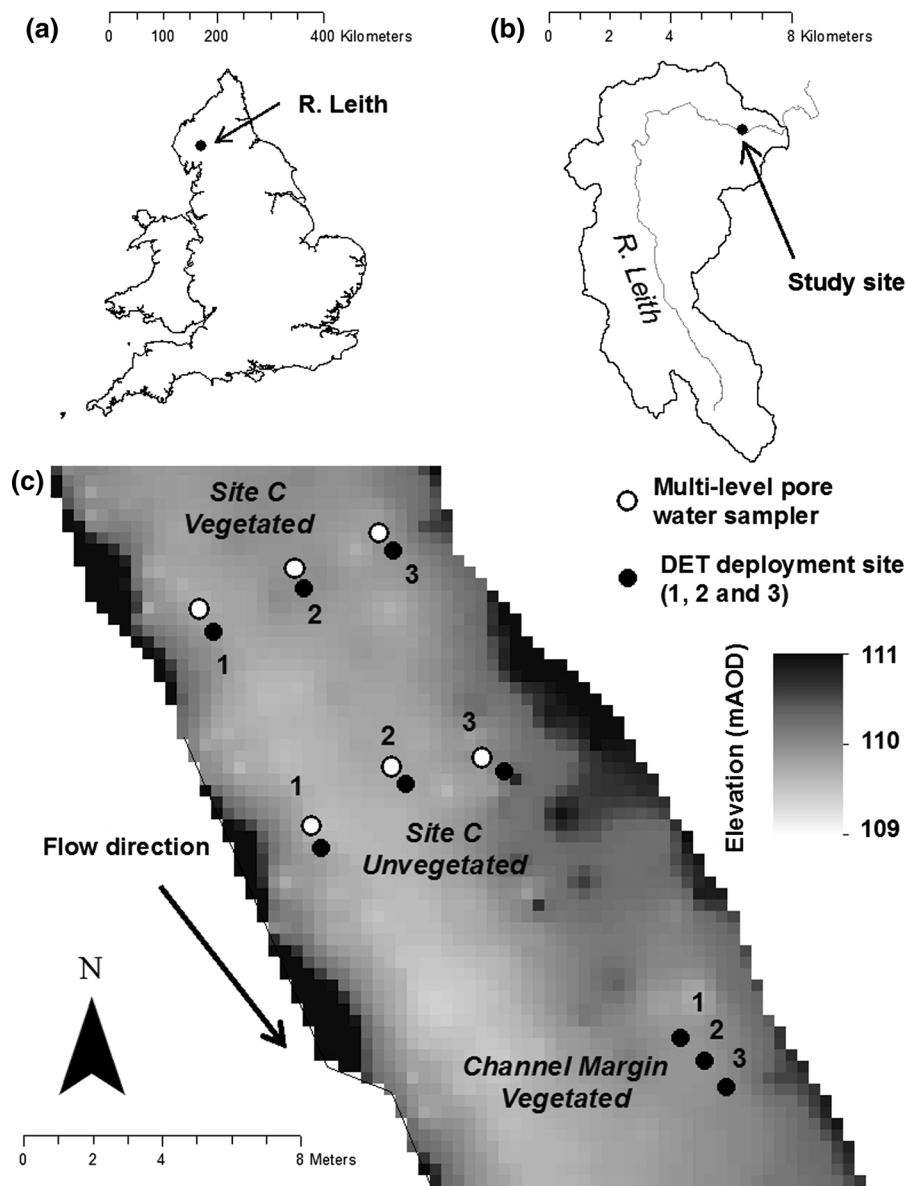
The study was undertaken in the River Leith (latitude $54^{\circ}36'45''\text{N}$; longitude $2^{\circ}38'23''\text{W}$), a groundwater-fed river in Cumbria, UK. The sediments in the experimental reach of the river were gravelly alluvium consisting of pebbles, gravels and sands (20–50 cm deep) overlying unconsolidated Penrith sandstone (Binley et al. 2013). Emergent vegetation in the

riverbed grows in both the main channel and along the channel margins (at the interface of riparian and fluvial riverine eco-tones) and is dominated by Bur reed (*S. erectum* L.) (O'Hare et al. 2012). The river meanders through a narrow floodplain and the catchment is predominantly agricultural with temporary grassland and some arable land use.

An emergent vegetated sediment patch (hereafter called 'VS') in the river channel dominated by Bur reed (*S. erectum*) and an adjacent un-vegetated riverbed sediment patch (hereafter called 'UVS') were selected for this study (Fig. 1). The study site for the research described in this paper lies within a 200 m reach of the River Leith used for the larger project: the detailed lithology and hydrology are given in Binley et al. (2013). For reference, Site C in Binley et al. (2013) corresponds to the UVS.

Particle size sieving of a sediment core collected from the thalweg of the river in the UVS revealed that about 50 % of the overlying sediments mainly consisted of gravels (>2 and <63 mm) in the upper 40 cm (Ullah et al. 2012; Binley et al. 2013), which is consistent with Krause et al. (2009). DET probes fabricated into 30 cm long plastic plates and protected in stainless steel holders were deployed into the river bed for four occasions between July and September 2010 coinciding with the main plant growth season. A single DET probe was deployed at each of three sites (C1, C2 and C3) to a depth of 30 cm into the river bed sediments in both the VS and UVS (Fig. 1). In the case of VS, the deployment of the DET probes on July 9, August 6 and September 10 was undertaken in the VS in the main river channel while the deployment on July 16 was undertaken in channel margin VS with relatively slow and/or sluggish flow conditions compared to the other three sites. Channel margin deployment of DET for NO_3^- profiles relative to NO_3^- profiles at the UVS was undertaken at the same time to establish if emergent vegetation, irrespective of their location in the river, would have similar impacts on nitrate losses, as hypothesised in the introduction above. Details of the DET probe deployment techniques in River Leith are provided in Ullah et al. (2012). All deployments were undertaken under base flow conditions with discharges of 0.11, 0.27, 0.08 and $0.11 \text{ m}^3 \text{ s}^{-1}$ on the day of DET probes retrieval in July to September. Typical base flow discharge in this river is around $0.1 \text{ m}^3 \text{ s}^{-1}$ (Kaesler et al. 2009; Binley et al. 2013).

Fig. 1 Map showing River Leith location in England (a), location of the study sites in the watershed of River Leith (b) and bed elevation (topography) with DET deployment and pore water sample collection sites within the experimental stretch of the river (c)



On each deployment date, the DET probe assemblies, secured within the stainless steel holders, was transferred on ice to the field and deployed to 30 cm depth next to piezometers in sites C1, C2 and C3 in the main channel VS and UVS. Once deployed, the DET probes were left in place for 70 h to ensure equilibration of NO_3^- in the sediment pore water with the gel through diffusion (Mortimer et al. 1998). For anions and cations, a deployment time of 24–48 h for diffusion equilibration is recommended (Harper et al. 1997; Morford et al. 2003). We used at least 70 h to allow time for the disturbed sediments to

collapse fully around the probe and re-establish conditions comparable to those prior to insertion of the DET assembly (Ullah et al. 2012). The rapid re-establishment of chemical gradients in sediments associated with redox conditions has already been recognised (Davison et al. 1994; Dočekalová et al. 2002). After 70 h, the deployed DET probes were retrieved, placed on ice and transferred to the laboratory within 1 h of retrieval. Prior to DET retrieval, pore water samples (25 mL) were collected from the multilevel samplers attached to the three piezometers at 10, 20 and 30 cm depth in the UVS (mid-channel)

and at 10, 20, 25 and 35 cm depth in the VS in the August and September sampling. The samples were filtered on site through 0.45 µm cellulose acetate filters into borosilicate glass vials and transferred to the laboratory on ice with the DET probes. Piezometers, as part of the wider project, were not required to be installed in the channel margins, consequently head measurement and pore water sampling at this location was not possible at the time of DET retrieval.

Vertical hydraulic gradient and dissolved oxygen

Ground water head in six piezometers relative to the river stage was measured using a dip meter in the UVS and VS sites during the August and September DET deployment campaigns. The piezometer screen in the VS was at 30 cm depth while in the UVS it was at 20 cm depth in the gravelly alluvium. The difference in the groundwater level relative to the river stage (in cm) was used to calculate vertical hydraulic gradient (VHG) as:

$$\text{VHG}\% = \frac{d_h}{d_l} \times 100$$

where d_h is difference in elevation of water level in the piezometer relative to the stream stage and d_l is the distance from the river bed to the mid-screen of the piezometer (Kalbus et al. 2006). Based on our calculations, a positive VHG is representative of groundwater upwelling and negative VHG indicates surface water downwelling potentials (Binley et al. 2013).

For the measurement of dissolved oxygen content during the August and September campaigns, pore water samples were collected from the multilevel samplers (5 mL, as above). Pore water was transferred slowly from the collection syringe via a three-way stopcock into an open syringe barrel containing a calibrated, fast response dissolved oxygen electrode. The 50 µm electrode had a stainless steel protective guard, and was connected via an inline amplifier to a data-logging meter (Under Water-Meter, Unisense, Denmark). The instrumental detection limit for dissolved oxygen was 3 µM with a precision of ~2 %.

Laboratory processing of DET

The DET probes were processed in the laboratory immediately on arrival from the field site. The whole assembly of the stainless steel holder was placed on a

bench top and the gel with the filter membrane was cut out from the window using a Teflon coated razor blade. The filter membrane over the DET gel was carefully removed and the gel was transferred to a glass board. The gel was then cut at 1 cm intervals with the razor blade within 2 h of its retrieval. Slicing within this time avoids significant peak relaxation of anions and cations beyond 1 cm intervals through lateral diffusion in the gel (Harper et al. 1997). Gel sections damaged during deployment and/or retrieval from the river bed, were discarded from further analysis. The sectioned gel strips were transferred into pre-labelled 1.5 mL vials. High purity water (Milli Q, Millipore), referred to here as MQ water was added to each vial containing the gel. Addition of 1,000 µL of MQ water was equal to 6 times dilution of the NO_3^- concentration in the gel. Previous mock deployment of DET in June 2012, showed that 6–12 times dilution of NO_3^- in 1 cm gel slice through back equilibration allowed measurement above the limit of detection (LOD) of the ion chromatograph (DIONEX) used for NO_3^- determination. The vials containing DET gel were capped, placed on frozen ice packs and shaken overnight on a reciprocating shaker to allow back equilibration of NO_3^- in the gel with the MQ water. Next day, the NO_3^- extract from the gel was analysed using DIONEX. At least ten blanks were run with the suite of analysis from each deployment for the determination of LOD. The LOD for NO_3^- was 0.02 mg N L⁻¹ with an analytical precision of ±6.6 %.

Processing and analysis of pore water samples

The pore water samples were analysed for dissolved organic carbon (DOC) content using a TOC analyser (Thermalox TOC-TN analyser). The TOC analyser purged the acidified samples before analysis for the determination of non-purgeable DOC contents. The LOD of DOC was 0.32 and 0.40 mg C L⁻¹ with analytical precision (repeat quality control standards) of 4.8 and 1.3 % for the August and September campaign samples, respectively.

Pore water samples were also scanned on a UV–Vis spectrophotometer in a 1 cm quartz window cuvette. MQ water was used for blank correction of the scan. The absorbance at 250 and 280 nm was recorded for the determination of $\text{SUVA}_{@254\text{nm}}$ (specific UV absorption (L mg⁻¹ C m⁻¹) = $(A_{254\text{nm}} \times 100)/\text{DOC}$) and percent aromaticity (% aromaticity = $[0.05$

$(A_{280\text{nm}} \times 1,000) + 6.74]$ (Chin et al. 1994; Roehm et al. 2009; Kothawala et al. 2012).

Sediment sampling and analysis

An intact sediment core (30 cm long) was collected from each DET deployment site for both UVS and VS (main channel and channel margin) in September 2010 (Fig. 1). A petrol driven Cobra TT drill was used to drill the river bed using a 50 mm corer equipped with a plastic liner as in Binley et al. (2013). The collected cores were sectioned into 5 cm interval at the field site, placed in zip-lock bags, transferred to the laboratory on ice and frozen until further analysis.

The sediment sections were homogenized and sieved (2 mm sieve). The sediment fraction <2 mm in size was then used for the extraction of DOC and NH_4^+ content and gravimetric water contents. A subsample of 10 g dry equivalent was weighed into a 250 mL plastic bottle. Ammonia was extracted by adding 50 mL of 2 M KCl solution shaking gently for 1 h and filtering through 0.45 μm filter. The filtrate was analysed within 24 h of extraction for the determination of NH_4^+ using a discrete colorimetric (SEAL AQ2) analyser. The LOD for NH_4^+ was 0.003 mg N L⁻¹ with an analytical precision of 3.2 %. The extraction procedure for DOC was similar to that for NH_4^+ , except 50 mL MQ water was used for extraction instead of the KCl salt. Extracted DOC was filtered and analysed on a TOC-TN analyser (Thermalox analyser) as above.

Statistical analysis

Dissolved oxygen and DOC measurements from all depths (10, 20, 25, and 30 cm depths) below the river bed and all sites were pooled together for correlation analysis with NO_3^- measured using DET at corresponding depths to that of the multilevel samplers. As the data were not normally distributed, non-parametric Spearman's correlations were determined. The mean NO_3^- concentration of each deployment campaign (mean of three profiles) was tested for significant difference between UVS and VS using the non-parametric Mann–Whitney *U* test at 5 % significance level. SUVA and aromaticity of DOC was normally distributed (Shapiro–Wilk test, $p > 0.5$) under UVS and VS were tested for differences using *t* test at 5 % significance level.

Results

When all data from the four deployments were pooled together, the concentration of NO_3^- ranged from 0.41 to 9.83 mg NO_3^- -N L⁻¹ under UVS (median value = 4.28 mg N L⁻¹), while in the VS it ranged from 0.05 to 7.31 mg NO_3^- -N L⁻¹ (median value = 0.50 mg N L⁻¹). Average concentration of NO_3^- in the surface water of the river measured at the time of DET retrievals was 1.71 mg N L⁻¹. NO_3^- profiles showed a significant difference ($p < 0.05$) between UVS and VS over the four deployment campaigns (Fig. 2) except at Site C1 in September. Generally, VS both in the main river and along the channel margins had a similar relationship with NO_3^- concentration gradients compared to profiles of NO_3^- under UVS (Fig. 2). Fine resolution NO_3^- profiles under the VS showed a decreasing trend in concentration in surface sediments from 1 to ~10 cm depth except in Site C2 and C2 of the channel margin VS. The median concentration of NO_3^- under VS at 1 cm depth was 1.85, declining to 1.44 at 5 cm, and to 0.37 mg N L⁻¹ at 10 cm depth. This trend represented a fivefold decrease in median NO_3^- concentration at 10 cm compared to concentration at 1 cm depth below the river bed under VS than under UVS.

Dissolved oxygen concentrations in the pore water showed variability with depth in the UVS and VS; however, the concentrations in the VS were generally lower than in the UVS sediments (Fig. 3). Dissolved oxygen concentrations ranged from 39 to 200 μM (median = 136 μM) in the UVS and from <LOD to 199 μM (median = 42 μM) in the VS. Dissolved oxygen exhibited significant positive correlation with NO_3^- concentration (Spearman's $r = 0.74$, $p < 0.05$, $n = 29$). Dissolved oxygen in the surface water of the river measured at the time of DET retrievals was 572 and 369 μM in August and September, respectively.

Pore water DOC values varied with depth and ranged from 0.95 to 12.90 mg C L⁻¹ in the UVS (median = 2.05 mg C L⁻¹) and from 1.86 to 16.60 mg L⁻¹ in the VS (median = 5.73 mg C L⁻¹) (Fig. 4). Pore water DOC values showed a significant negative correlation with NO_3^- concentration (Spearman's $r = -0.39$, $p < 0.05$, $n = 30$). DOC extracted from the sediments were also relatively higher in VS in the top 0–10 cm depths than in the UVS (Fig. 5a); however, the differences between VS and UVS were not statistically significant (at 5 % significant level)

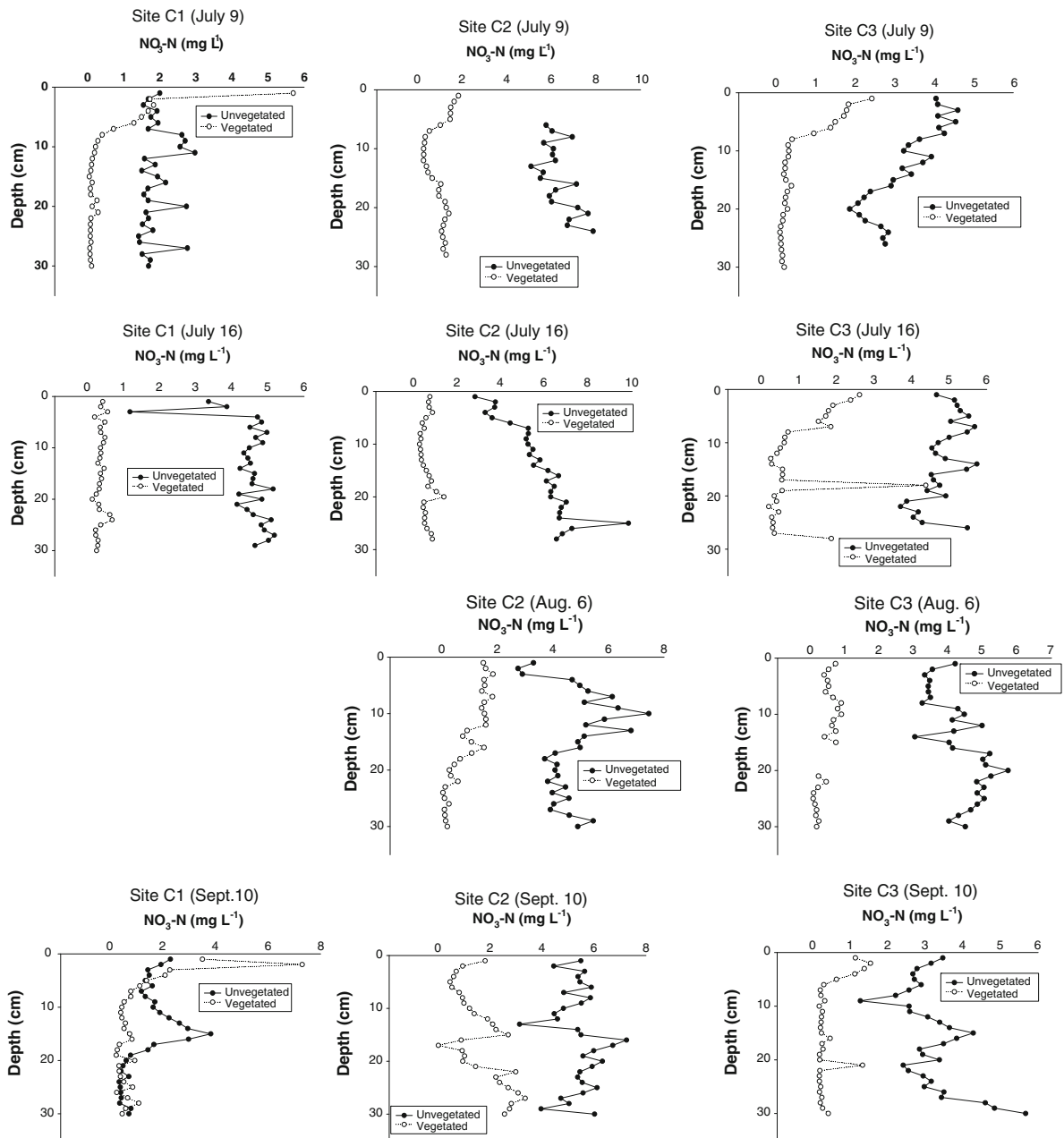


Fig. 2 NO_3^- profiles of vegetated and un-vegetated river bed sediments measured through DET. Missing NO_3^- data at a specific depth (s) in these profiles represent a damaged DET gel section (during deployment and/or retrieval from the river bed)

due to the high variability of DOC concentrations. Similar to the extracted DOC, mean NH_4^+ content in the sediment was also relatively higher under VS in the top 0–10 cm depths relative to the UVS (Fig. 5b) although the difference was not significant statistically.

that was discarded from analysis. Note that NO_3^- profiles of July 16 represent a comparison of the channel margin vegetated sediments to the un-vegetated sediments, while the rest represent vegetated sediments located in the main channel

Specific UV absorption of the pore water DOC samples in all depths ranged from 0.18 to 1.76 $\text{L mg}^{-1} \text{C m}^{-1}$ in the UVS (mean = 0.72) and from 0.31 to 2.29 $\text{L mg}^{-1} \text{C m}^{-1}$ in the VS (mean = 1.33) (Table 1). Similarly, the aromaticity

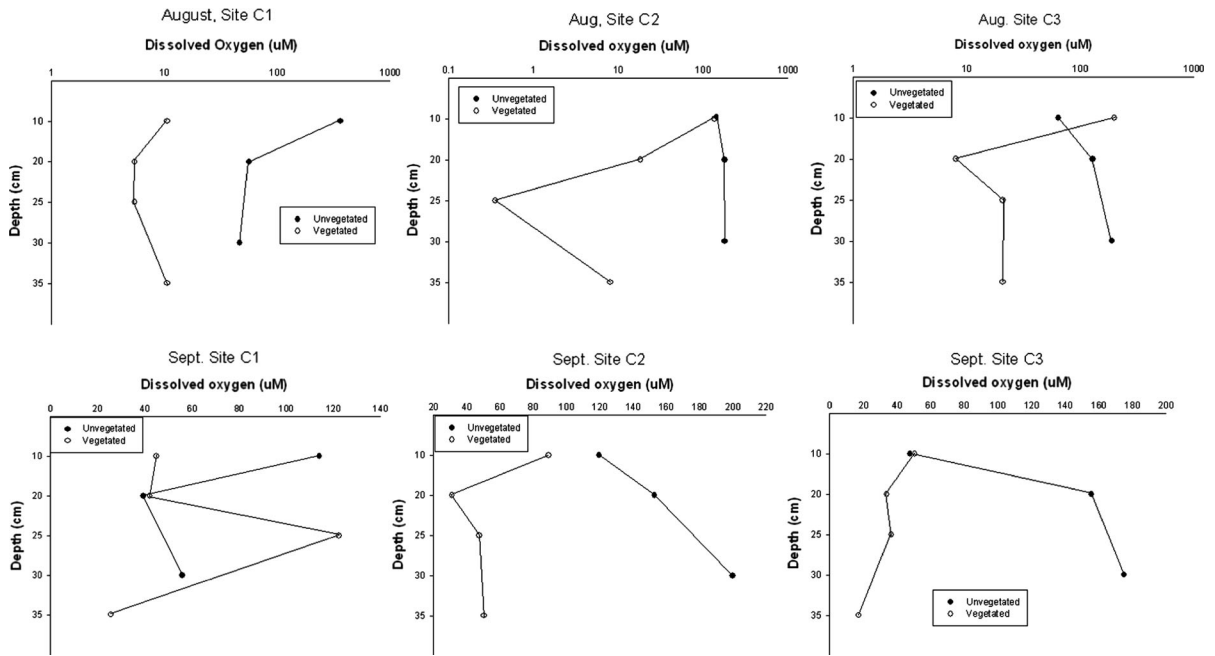


Fig. 3 Dissolved oxygen concentration (in μM) measured in the sediment pore water at 10, 20, and 30 cm depth in the un-vegetated and at 10, 20, 25, and 35 cm depths in the vegetated river sediments. Note that the dissolved oxygen at 25 cm depth

under the vegetated sediments in site C2 measured in August 2010 was lower than the instrumental detection limit for dissolved oxygen ($3 \mu\text{M}$)

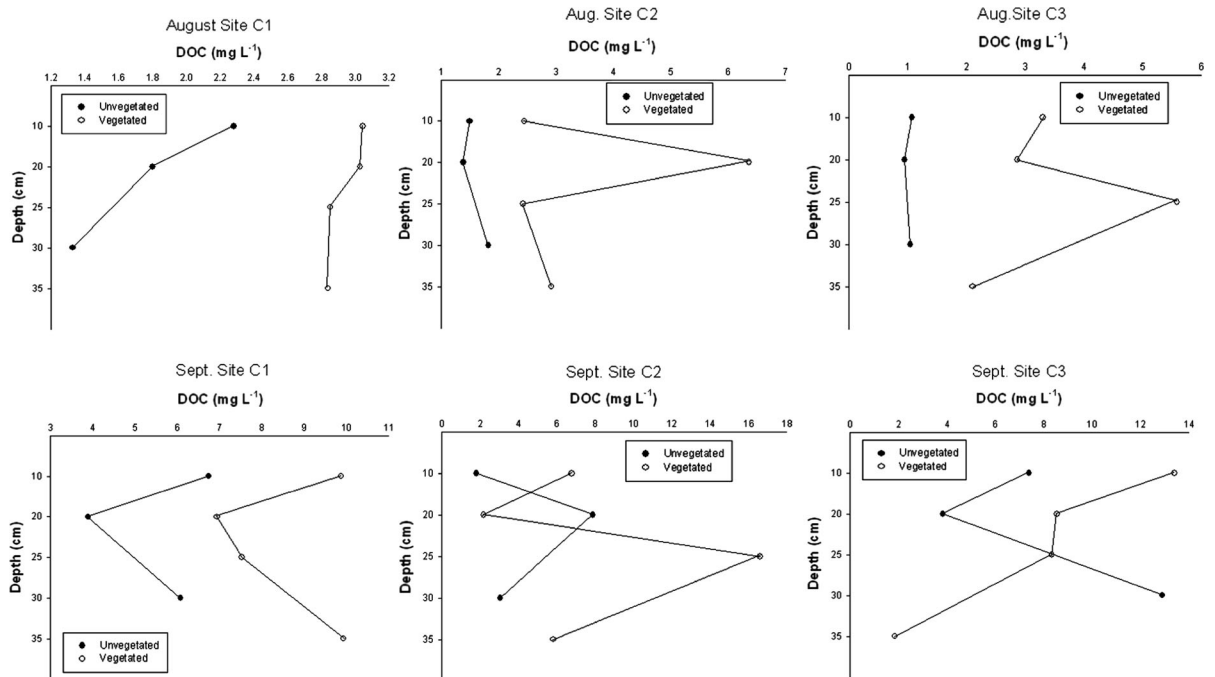


Fig. 4 Dissolved organic carbon measured in the sediment pore water at 10, 20, and 30 cm depth in the un-vegetated sediments and at 10, 20, 25, and 35 cm depths in the vegetated sediments

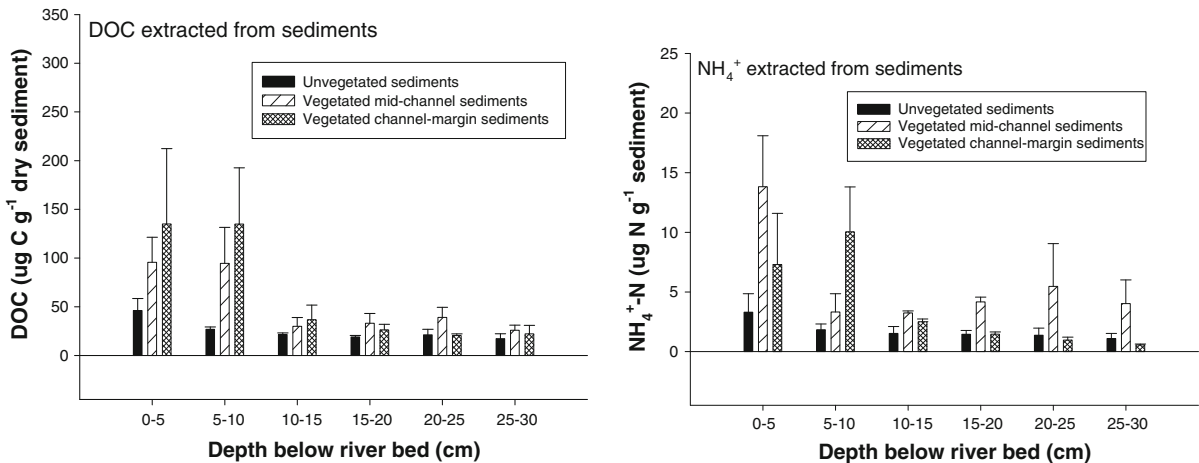


Fig. 5 Mean DOC and NH_4^+ contents (mean \pm SE, $n = 3$) of un-vegetated and vegetated river bed sediments

of these samples ranged from 6.76 to 8.22 % in the UVS (mean = 7.13 %) and from 7.28 to 9.36 % (mean = 8.23 %) in the VS. SUVA measurement based on absorption at 254 nm correlated significantly ($R^2 = 0.77$, $p < 0.05$) with aromaticity measurement based on absorption at 280 nm. Based on two sample t test, mean SUVA and aromaticity of pore water samples collected from VS were significantly higher than those collected from UVS ($p = 0.02$, and $p = < 0.001$, respectively). Vertical hydraulic gradient at 20 cm depth in the UVS averaged 16.2 and 16.7 %, while in the VS (at 30 cm depth) it averaged 2.8 and 4.4 % in August and September, respectively, indicating upwelling potentials at both sites.

Discussion

There were marked differences in the NO_3^- concentration gradients between VS and UVS under this groundwater fed stretch of River Leith (Binley et al. 2013). We did not directly measure NO_3^- reduction processes (e.g. denitrification) or NO_3^- uptake by plants and immobilization by microbes under the VS; however, the observed trends in NO_3^- concentration and its significant correlation with dissolved oxygen and DOC indicate that riverine sediments under emergent vegetation may reflect a micro-environment conducive to faster NO_3^- loss, resulting in lower pore water NO_3^- concentrations compared to UVS. The significant difference in NO_3^- concentration between UVS and VS was observed consistently over the

measurement period (July to September). Wigand et al. (2001) reported significantly lower pore water nutrient concentrations in river bed sediments planted with macrophytes compared to bare sediments. Similarly, Forshay and Dodson (2011) observed significantly faster NO_3^- reduction through denitrification under vegetated riverine sediments compared to bare sediments, which signifies the benefit of riverine vegetation in stimulating NO_3^- reduction and improving water quality. Other than reduction through denitrification, biotic uptake of NO_3^- by plants during the growing season could have been substantial. Harrison et al. (2012) observed NO_3^- uptake by plants from 42 to 63 % during the plant growth season in relic oxbow-wetlands dominated by emergent vegetation. Dissimilatory nitrate reduction to ammonium (DNRA) could be an additional sink for pore water nitrate loss beneath VS (Kelso et al. 1997); however, the potential for NO_3^- loss through DNRA was of minimal importance compared to denitrification in the un-vegetated sediments of River Leith (Lansdown et al. 2012). That said, dilution of pore water NO_3^- by down-welling surface water (with lower NO_3^- levels than the upwelling groundwater) may have been another possibility for the observed low NO_3^- under VS; however, the likelihood of significant dilution effect particularly in sediments deeper than 10 cm appear minor given the fact that the river is predominantly groundwater-fed under base flow conditions (Kaeser et al. 2009; Binley et al. 2013). Fine sediments in the surface water trapped by vegetation may have led to lower VHG % (2.8–4.4 %)

Table 1 Spectroscopic (SUVA and aromaticity) properties of pore water DOC samples collected in August 2010

Variable and unit	Depth below riverbed (cm)	Un-vegetated sediments			Vegetated sediments		
		Site C1	Site C2	Site C3	Site C1	Site C2	Site C3
SUVA ($L\ mg^{-1}\ C\ m^{-1}$)	10	1.76	0.69	0.97	2.17	1.50	1.69
	20	0.46	0.80	0.78	1.37	0.31	2.29
	25				1.30	0.80	1.21
	30	0.29	0.57	0.18			
	35				1.09	0.54	1.66
Aromaticity (%)	10	8.22	7.11	7.10	9.36	8.08	8.74
	20	6.96	7.11	6.99	8.28	7.47	9.12
	25				8.03	7.45	9.16
	30	6.84	7.11	6.76			
	35				7.81	7.28	7.93

beneath the VS with potential for relatively longer pore water residence time than under the UVS (VHG of 16.2–16.7 %). Longer pore water residence times under VS may have been an additional factor causing enhanced losses of NO_3^- under VS (Krause et al. 2013). However, such an influence appears minimal relative to direct plant mediated losses (nitrate reduction and plant uptake), given the fact that another un-vegetated pool site (~ 7 m upstream of the VS) also had a similar range of VHG (2.5–7.5 %) to that of the VS, yet its median NO_3^- in the upper 30 cm depth was $6.33\ mg\ N\ L^{-1}$ (data not shown) compared to $0.50\ mg\ NO_3^- - N\ L^{-1}$ beneath the VS.

The difference in NO_3^- profiles between UVS and VS was evident up to 30 cm depth, which is beyond the rooting zone of emergent vegetation (*Sparganium* spp.) in the River Leith (~ 5 – 10 cm). Our data suggest that the presence of vegetation may have promoted NO_3^- reduction in bed sediments that are deeper than the rooting zone. Significant down welling of surface water into the river bed sediments during high flow events have been reported by Byrne et al. (2013) in this river, which in case of the vegetated sediments, may be responsible for the delivery of DOC into sediment pore water deeper than the typical rooting depth. This observation implies that it is important to consider the impact of vegetation in deeper sediments beyond the rooting zone for accurate quantification of NO_3^- attenuation mediated by vegetation.

Lithologically, the experimental reach of the River Leith at ~ 100 cm depth consists of unconsolidated sandstone bedrock overlain by gravelly alluvium (Binley et al. 2013). Pore water NO_3^- concentration

measured at three occasions at 100 cm depth in the sandstone bedrock in July, August and September of 2009 and 2010, downstream (in the UVS) and upstream of the VS averaged at $5.36 \pm 1.45\ mg\ N\ L^{-1}$ (mean \pm standard deviation) (data not shown) and the concentrations ranged from 1.03 to $7.21\ mg\ N\ L^{-1}$. Other than the UVS at the downstream site, the upstream site was also un-vegetated and was located about 7 m upstream of the VS. Krause et al. (2009) reported similar NO_3^- concentrations in the sandstone bedrock in this river (ranging from 3.5 to $6.6\ mg\ N\ L^{-1}$). We did not measure NO_3^- concentration in the VS at 100 cm depth, but, given the consistent distribution of sandstone bedrock underlying the gravelly alluvium in this river (Binley et al. 2013), we assume a similar likely range in NO_3^- concentration at 100 cm depth under the VS. As the mean NO_3^- concentration in the upper 30 cm in the VS was much lower (mean = $0.53\ mg\ N\ L^{-1}$), it is very likely that the key driver of NO_3^- loss in the upwelling water in the upper 30 cm depth in the VS are NO_3^- reduction and loss processes enhanced by the presence of vegetation. Moreover, the influence of vegetation on sediment pore water NO_3^- concentration was similar, irrespective of whether the vegetation was growing in the main channel or along the channel margins. The channel margin site was downstream of the UVS and next to another instrumented un-vegetated site, where the mean NO_3^- concentration was $2.7\ mg\ N\ L^{-1}$ (data not shown) in the upper 30 cm compared to the $0.62\ mg\ N\ L^{-1}$ beneath the channel margin VS. This observation supports our contention that emergent vegetation mainly mediated NO_3^- losses. Mean sediment extracted DOC in the upper 10 cm in the

channel margin sediments was also relatively higher than the DOC in the UVS (135 and 46 $\mu\text{g C g}^{-1}$ sediment, respectively), which may have promoted faster NO_3^- losses, similar to those observed in the mid-channel VS.

The median concentration of dissolved oxygen in the upper 30 cm of the VS was 202 % lower than in the UVS. Lower dissolved oxygen concentration in the VS may have promoted greater loss of NO_3^- through denitrification in the upwelling groundwater compared to UVS. In general, NO_3^- concentrations were lower in locations within the sediments where dissolved oxygen contents were low, and consequently there was a positive correlation between NO_3^- and dissolved oxygen. NO_3^- reduction and loss in marine and riverine sediments have been reported at dissolved oxygen concentration of $\sim <90 \mu\text{M}$ (Dalsgaard and Revsbech 1992; Olde Venternik et al. 2003; Pretty et al. 2006). Similarly, Tessoriero and Puckett (2011) also observed faster NO_3^- reduction through denitrification when dissolved oxygen concentrations were $<60 \mu\text{M}$ in shallow aquifers. When the dissolved oxygen data was pooled to calculate the percentile distribution of the data range (box plot not shown), the concentration of dissolved oxygen in pore water in the VS at the 87th percentile was less than $90 \mu\text{M}$ compared to UVS where concentration $<90 \mu\text{M}$ were at the 33rd percentile. This pattern of dissolved oxygen in our study suggests that VS may induce extensive reduced conditions in sediments favourable for NO_3^- reduction due to respiration of DOC exudates relative to the UVS. Although aquatic vegetation transport oxygen through the aerenchyma tissues into bed sediments (Caraco et al. 2006), the observed low concentration of dissolved oxygen under the VS may be indicative of relatively faster consumption than possible replenishment through plant root transport into the sediments (Calhoun and King 1997).

Even though weak, a significant negative correlation was observed between DOC and NO_3^- suggesting that sediments with high DOC contents may support elevated NO_3^- reduction. This is consistent with the observations of Lansdown et al. (2012), who reported that NO_3^- reduction was limited by the availability of dissolved organic carbon in this river. Median pore water DOC concentrations over the 30 cm depth in VS were 186 % greater than DOC under UVS. This difference in DOC may have been due to root exudates

and decomposition of dead plant material contributed by the emergent vegetation. Moreover, emergent and submerged macrophytes in river beds have also been found more effective than bare sediment patches in trapping fine sediments from fluvial sources (Heppell et al. 2009) and exogenous particulate organic matter (Sand-Jensen 1998; Trimmer et al. 2009; O'Hare et al. 2012). The trapped fine sediments with particulate organic matter could have been an additional source of the relatively higher DOC delivery into the underlying pore water through surface water down welling during high flow events (Gu et al. 2008; Byrne et al. 2013). *S. erectum* patches across 47 river reaches in the UK contained 1.8 times higher organic matter than bare river bed sediments (O'Hare et al. 2012), which indicates higher potential for dissolved oxygen consumption through microbial respiration (Sobczak and Findlay 2002; Trimmer et al. 2009) and release of DOC to serve as an electron donor during NO_3^- reduction (Forshay and Dodson 2011).

The probable mix of autochthonous and allochthonous sources of DOC in sediment pore water in the VS appear to have led to distinct SUVA and aromaticity values compared to DOC in the UVS. Markedly higher SUVA and aromaticity of pore water DOC in the VS probably reflect a mix of DOC molecules containing more aromatic compounds than the DOC in the UVS (Chin et al. 1994; Weishaar et al. 2003; Kothawala et al. 2012). Given the difference in spectrophotometric properties between DOC in the VS and UVS, the reactivity and bioavailability of the DOC could have differed between the two sediment types. Some authors have speculated that DOC in vegetated riverine sediments is more complex (Strauss and Lamberti 2002; Findlay 2003) than the DOC in UVS, which is in agreement with our findings. Lansdown et al. (2012) found enhanced potential denitrification rates in response to addition of a complex organic C substrate (bacteriological peptone) to sediment slurries compared to un-amended slurries collected from un-vegetated sediments of this river. Therefore, it appears that DOC of higher quantity and of a complex nature beneath the VS may have supported faster NO_3^- reduction (Strauss and Lamberti 2002; Findlay 2003; Forshay and Dodson 2011). The observation of high pore water DOC and low NO_3^- beneath VS suggests that NO_3^- reduction may be NO_3^- rather than DOC limited under anoxic conditions in VS, while DOC limited in UVS

(Lansdown et al. 2012). This observation is in agreement with those of Forshay and Dodson (2011) who concluded that denitrification in riverine vegetated sediments was NO_3^- limited. Furthermore, both SUVA and aromaticity also correlated significantly with NO_3^- (Spearman's $r = -0.52$ and -0.72 , respectively, with $p < 0.05$, $n = 20$). Since the lability of the DOC in supporting oxygen consuming heterotrophs and denitrification in the VS was not evaluated directly, we recommend further studies to elucidate if DOC of a complex aromatic nature is supportive of denitrifier and general heterotrophic microbial activity.

DOC and NH_4^+ extracted from the sediments were generally higher at 0–10 cm and for the VS there was a sharp decline in concentration from 10 to 30 cm depth (Fig. 5). A fivefold decrease in NO_3^- concentration measured using DET between 1 and 10 cm depth (Fig. 2) supports the contention that high sediment and pore water DOC in the VS may have supported NO_3^- reduction (Groffman et al. 2005; Forshay and Dodson 2011; Borin and Salvato 2012). Median dissolved oxygen concentration over the measurement period also decreased from 70 μM at 10 cm depth to 25 μM at 20 cm depth in the VS, with no such consistent trend evident in the UVS (Fig. 3). Thus sediments beneath vegetation are expected to be highly reactive biogeochemically (Forshay and Dodson 2011), and can exert strong control on NO_3^- losses beyond the rooting depth within permeable sediments. This was evident from the consistently lower NO_3^- concentration gradient (from about 10 to 30 cm depth) in the VS, except in September in Site C2 where concentration peaks at 14 and 26 cm depths were followed by decreasing NO_3^- . A detailed geochemical interpretation of these concentration peaks measured through DET is desirable with respect to coupled nitrification–denitrification in sediments (Caffrey and Kemp 1992; Risgaard-Petersen and Jensen 1997), but is beyond the scope of the available data. Nevertheless, high resolution NO_3^- profiles measured using DET, which could not be obtained using coarse-scale multilevel samplers (Ullah et al. 2012) offer the potential for resolving zones of losses and gains in armoured riverine sediments due to physical and biogeochemical processes in future studies. The profiles of NO_3^- in the UVS also exhibited distinct peaks, particularly in site C2 in August and in sites C1, C2 and C3 in September. These localized zones of gain in the

concentration of NO_3^- in the UVS appear to be driven by production processes of NO_3^- (nitrification), in agreement with similar observation of gains in NO_3^- concentration along the upwelling flow paths in the same experimental stretch of the River Leith as reported in Krause et al. (2009).

Conclusions

This study provides evidence for enhanced NO_3^- attenuation in riverine sediments under emergent vegetation compared to adjacent UVS in a predominantly upwelling reach of the River Leith. The pore water NO_3^- concentration gradient in the sediment under emergent vegetation growing in the main channel and along channel margins was lower than that observed in UVS. This difference was not limited to the plant rooting zone but was recorded beyond this zone up to 30 cm depth using a specially adapted DET sampling system (Ullah et al. 2012). We suggest that the emergent vegetation may act as a source of higher and structurally more complex DOC concentrations in the sediment pore water relative to UVS and the vegetation may have mediated the consumption of dissolved oxygen (through root and microbial respiration) with consequent provision of conducive conditions for NO_3^- reduction. Metabolic uptake by plants and microbes may have been additional temporary biotic sinks for NO_3^- in the VS compared to the UVS. The overall role of emergent vegetation, particularly *Sparganium* spp., in NO_3^- attenuation need consideration while evaluating options for nutrient management and restoration of biogeochemical functions rendered by riverine ecosystems. Further studies on quantifying plant mediated NO_3^- reduction processes in riverine sediments, particularly denitrification relative to plants uptake, both during growing and non-growing seasons, are recommended (Borin and Salvato 2012; Harrison et al. 2012).

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