Heppell, C, Heathwaite, AL, Binley, A, Byrne, PA, Ullah, S, Lansdown, K, Keenan, P, Trimmer, M and Zhang, H

Interpreting spatial patterns in redox and coupled water-nitrogen fluxes in the streambed of a gaining river reach

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Journal Name	Biogeochemistry	
Corresponding Author	Family Name	**Heppell**
	Particle	
	Given Name	**Catherine**
	Suffix	
	Division	School of Geography
	Organization	Queen Mary University of London
	Address	Mile End Road, London, E1 4NS, UK
	Email	c.m.heppell@qmul.ac.uk
Author	Family Name	**Louise Heathwaite**
	Particle	
	Given Name	**A.**
	Suffix	
	Division	Lancaster Environment Centre
	Organization	Lancaster University
	Address	Lancaster, LA1 4YQ, UK
	Email	
Author	Family Name	**Binley**
	Particle	
	Given Name	**Andrew**
	Suffix	
	Division	Lancaster Environment Centre
	Organization	Lancaster University
	Address	Lancaster, LA1 4YQ, UK
	Email	
Author	Family Name	**Byrne**
	Particle	
	Given Name	**Patrick**
	Suffix	
	Division	Lancaster Environment Centre
	Organization	Lancaster University
	Address	Lancaster, LA1 4YQ, UK
	Division	School of Psychology and Natural Sciences
	Organization	Liverpool John Moores University
	Address	Liverpool, L3 3AF, UK
	Email	
Author	Family Name	**Ullah**

	Particle	
	Given Name	**Sami**
	Suffix	
	Division	Lancaster Environment Centre
	Organization	Lancaster University
	Address	Lancaster, LA1 4YQ, UK
	Division	School of Physical and Geographical Sciences
	Organization	Keele University
	Address	Staffordshire, ST5 5BG, UK
	Email	
Author	Family Name	**Lansdown**
	Particle	
	Given Name	**Katrina**
	Suffix	
	Division	School of Geography
	Organization	Queen Mary University of London
	Address	Mile End Road, London, E1 4NS, UK
	Division	School of Biological and Chemical Sciences
	Organization	Queen Mary University of London
	Address	London, E1 4NS, UK
	Email	
Author	Family Name	**Keenan**
	Particle	
	Given Name	**Patrick**
	Suffix	
	Division	Lancaster Environment Centre
	Organization	Lancaster University
	Address	Lancaster, LA1 4YQ, UK
	Email	
Author	Family Name	**Trimmer**
	Particle	
	Given Name	**Mark**
	Suffix	
	Division	School of Biological and Chemical Sciences
	Organization	Queen Mary University of London
	Address	London, E1 4NS, UK
	Email	
Author	Family Name	**Zhang**
	Particle	
	Given Name	**Hao**
	Suffix	
	Division	Lancaster Environment Centre
	Organization	Lancaster University
	Address	Lancaster, LA1 4YQ, UK
	Email	

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Abstract	Water pathways through permeable riverbeds are multi-dimensional, including lateral hyporheic exchange flows as well as vertical (upwelling and downwelling) fluxes. The influence of different pathways of water on solute patterns and the supply of nitrate and other redox-sensitive chemical species in the riverbed is poorly understood but could be environmentally significant. For example, nitrate-rich upwelling water in the gaining reaches of groundwater-fed rivers has the potential to supply significant quantities of nitrate through the riverbed to surface waters, constraining opportunities to deliver the goals of the EU Water Framework Directive to achieve 'good ecological status'. We show that patterns in porewater chemistry in the armoured river bed of a gaining reach (River Leith, Cumbria) reflect the spatial variability in different sources of water; oxic conditions being associated with preferential discharge from groundwater and reducing conditions with longitudinal and lateral fluxes of water due to water movement from riparian zones and/or hyporheic exchange flows. Our findings demonstrate the important control of both vertical and lateral water fluxes on patterns of redox-sensitive chemical species in the river bed. Furthermore, under stable, baseflow conditions ($<Q_{90}$) a zone of preferential discharge, comprising 20 % of the reach by area) contributes 4–9 % of the total nitrate being transported through the reach in surface water, highlighting the need to understand the spatial distribution of such preferential discharge locations at the catchment scale to establish their importance for nitrate delivery to the stream channel.

Keywords (separated by '-')	Hyporheic - Nitrate - Hydrological pathways - Groundwater-fed - Rivers - Water quality - Pollution
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Electronic supplementary material	Below is the link to the electronic supplementary material. **:** Spatial variations in nitrate concentration (Nitrate-N mg L^{-1}) along the study reach (a) July 2009; (b) August 2009; (c) September 2009; (d) July 2010; (e) August 2010; (f) September 2010. Supplementary material 1 (TIFF 21262 kb)**.** **:** Spatial variations in chloride concentration (mg L^{-1}) along the study reach (a) July 2009; (b) August 2009; (c) September 2009; (d) July 2010; (e) August 2010; (f) September 2010. Supplementary material 2 (TIFF 21069 kb)**.** **:** Spatial variations in sulphate concentration (Sulphate-S mg L^{-1}) along the study reach (a) July 2009; (b) August 2009; (c) September 2009; (d) July 2010; (e) August 2010; (f) September 2010. Supplementary material 3 (TIFF 21244 kb)**.** **:** Spatial variations in Fe and Fe(II) concentration (mg L^{-1}) along the study reach (a) July 2009; (b) August 2009; (c) September 2009; (d) July 2010; (e) August 2010; (f) September 2010. Supplementary material 4 (TIFF 21097 kb)**.** **:** Spatial variations in ammonium concentration (Ammonium-N mg L^{-1}) along the study reach (a) July 2009; (b) August 2009; (c) September 2009; (d) July 2010; (e) August 2010; (f) September 2010. Supplementary material 5 (TIFF 22190 kb)**.**

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Interpreting spatial patterns in redox and coupled water–nitrogen fluxes in the streambed of a gaining river reach

Catherine Heppell · A. Louise Heathwaite · Andrew Binley · Patrick Byrne · Sami Ullah · Katrina Lansdown · Patrick Keenan · Mark Trimmer · Hao Zhang

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C. Heppell (✉) · K. Lansdown
School of Geography, Queen Mary University of London,
Mile End Road, London E1 4NS, UK
e-mail: c.m.heppell@qmul.ac.uk

A. Louise Heathwaite · A. Binley · P. Byrne ·
S. Ullah · P. Keenan · H. Zhang
Lancaster Environment Centre, Lancaster University,
Lancaster LA1 4YQ, UK

Present Address:
P. Byrne
School of Psychology and Natural Sciences, Liverpool
John Moores University, Liverpool L3 3AF, UK

Present Address:
S. Ullah
School of Physical and Geographical Sciences, Keele
University, Staffordshire ST5 5BG, UK

K. Lansdown · M. Trimmer
School of Biological and Chemical Sciences, Queen Mary
University of London, London E1 4NS, UK

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Introduction

The ecosystem services delivered by groundwater-fed rivers have both *direct* valued uses, which include water supply, transportation, recreation, and fishing and *indirect* valued uses, which include flood protection, nutrient recycling, genetic material, and sustaining wetlands (Watson and Albon 2011). Attributing economic value to the latter is particularly problematic and can lead to the degradation of these services (Heathwaite 2010). Notable is the underestimation of the value of managing groundwater-fed river systems for water quality improvement, surface flow regulation, erosion control, and stream bank stabilisation. The economic importance of these services will only increase, as water quality becomes a critical issue around the globe (Rockstrom et al. 2009).

In the UK, groundwater provides 5 % of public water supply in Scotland, 8 % in Northern Ireland, and 33 % overall in England and Wales, rising to over 70 % in the south-east of England (www.groundwateruk.org). Rivers draining areas of permeable rocks, such as in the Chalk downlands of southern England, are fed almost entirely from groundwater. Groundwater-fed river flows can be vital for the dilution of discharged wastewater and for the regulation of diffuse nutrient pollution in rural catchments. However, nitrate concentrations have been increasing in groundwater since the 1970s (see for example Scanlon et al. 2007; Zhang et al. 1996; Croll and Hayes 1988) leading to increases in nitrate concentrations in groundwater-fed rivers (Howden et al. 2011). In Europe, time-series analysis of nitrate concentrations in rivers of permeable catchments has revealed continuous and sustained linear increases in nitrate concentration (Howden and Burt 2009; Burt et al. 2011). In the UK, policy interventions have been introduced to restrict the timing and amount of nitrogen applied to agricultural land in designated Nitrate Vulnerable Zones. Such measures may take many years to deliver evidence of improvement in water quality owing both to the time lags involved (e.g. Worrall et al. 2012), and to the complexity of response in surface and subsurface freshwater systems. Given the long modal residence time of water in permeable catchments, Burt et al. (2011) have suggested that it may be decades before the benefits of source control schemes are observed in groundwater-fed rivers. In Europe, elevated concentrations of the critical macronutrients, nitrogen (particularly nitrate) and phosphorus in surface waters and in groundwaters constrain opportunities to deliver the goals of the EU Water Framework Directive to achieve 'good ecological status' for fresh and marine waters by 2015. Added to this, changes in weather patterns that may be climate-related (e.g. low winter recharge in 2010 and 2011 in the UK) have recently demonstrated gaps in our knowledge about the nature of 'groundwater drought' and the physical, chemical and biological responsiveness of aquifers to subsequent recharge (Whitehead et al. 2006; Wilby et al. 2010). These observations point to the need to know more about the interactions of groundwater and surface water and the implications of these interactions for water quality improvement under baseflow conditions and a changing climate (Prudhomme et al. 2012).

For groundwater-fed rivers, the riverbed is a reactive permeable zone, termed the hyporheic zone, in which contributing waters from different sources can mix and where reactive chemicals such as nitrogen can undergo transformations (see definitions of hyporheic zone in Tonina and Buffington 2009; Krause et al. 2011). Water flow pathways through riverbeds are complex and multi-dimensional, including lateral (horizontal) inputs from the riparian zone (Ranalli and Macalady 2010) and vertical, upwelling groundwater (Stelzer and Bartsch 2012). In a gaining setting, these pathways have the potential to supply nitrate through the riverbed to surface waters. The magnitude of groundwater discharge into and through the river bed has been shown to exhibit considerable spatial variability (Conant 2004; Kennedy et al. 2009b) and the influence of different pathways of groundwater discharge on nitrate and redox conditions in the river bed is poorly understood (Poole et al. 2008). In shallow sediments, patterns in pore water chemistry will also be influenced by hyporheic exchange flows as defined by Harvey et al. (1996) to be the process by which water infiltrates the surface and returns to the surface over small distances, including intra-meander flows (Tonina and Buffington 2009; Boano et al. 2010) which enable longitudinal exchange between surface waters and pore waters in the river bed. Thus patterns in pore water chemistry in the riverbed will arise from a combination of mixing of these different vertical and horizontal pathways of water, and in the case of reactive solutes such as nitrate, patterns will also change along flow pathways in response to biogeochemical transformation. Quantifying reach-scale spatial patterns of redox-sensitive species (electron donors and acceptors) in pore waters is important owing to its influence on the spatial distribution of biogeochemical processes within the streambed (Dahm et al. 1998; Marzadri et al. 2011, 2012). Additionally, concomitant observations of conservative chemical species together with redox species offers further insights into sources of water, for example, by aiding identification of preferential discharge locations in the river bed (Stelzer and Bartsch 2012).

A number of field studies in gaining settings have focused on the importance of upwelling groundwater for nitrate flux and transformations in a streambed (e.g. Kennedy et al. 2009a; Stelzer and Bartsch 2012; Flewelling et al. 2012). Other research has focused on other groundwater-surface water exchange mechanisms such as the role of hyporheic exchange flows (Kasahara and Hill 2006) or meander bends (Zarnetske et al. 2011) for nitrogen transformations. Few studies, however, have taken an integrated approach to a river reach to consider the interaction of different flow and biogeochemical processes in three-dimensions (Lautz and Fanelli 2008; Zarnetske et al. 2011).

Lautz and Fanelli (2008) used a statistical approach, Principal Component Analysis (PCA), to reduce data dimensionality and thereby characterise the redox status of streambed pore water samples around log jams in a restored river reach. We adopt a similar approach in this study, using PCA to identify key patterns in streambed solute chemistry in a 200 m gaining river reach. For this research we have used a piezometer network that is not only spatially distributed across the reach, and also installed to 1 m depth in order to capture patterns in pore water chemistry and hydrological flux that are due to the combined effects of different groundwater-surface water exchange mechanisms (for example, hyporheic exchange flow, upwelling groundwater and lateral subsurface flows from riparian areas). We have previously examined the spatial variability in water fluxes at the reach over the same time period as this study to provide a hydrological conceptualisation for our site (Binley et al. 2013). Our experiments revealed a localised connectivity to regional groundwater (i.e. a preferential discharge location) in the upstream section of the reach, and evidence of longitudinal shallow groundwater flow in the downstream section. The work described in this paper uses interpretation of patterns in nitrate and other solutes in pore water in the river bed from samples collected during three sampling campaigns in summer 2009 and 2010, respectively. The timing of our sampling campaigns reflects our emphasis on investigating chemical patterns in the streambed under summer, baseflow conditions; as well as our desire to balance repeated with spatially intensive (both depth and areal coverage) measurements of pore water chemistry. Our samples for chemical analysis were collected in conjunction with measurements of water flux, to reveal the key spatial controls on redox and nitrate supply to the reach.

Our specific objectives were to:

(a) Describe spatial variability (both longitudinally along the 200 m reach, and to 1 m depth in the riverbed) in pore water chemistry under baseflow conditions.
(b) Use our understanding of the physical hydrology of the river reach to explain the critical factors that lead to the observed spatial signature of the pore water chemistry.
(c) Determine the importance of vertical preferential discharge for nitrate supply to the reach.

Methods

Our overall approach combined both well-tested (e.g. vertical variations in porewater solute concentrations and cutting edge (e.g. geophysical surveys; isotopic and chemical tracing of groundwater-surface water mixing) methodologies to quantify the variation in the physical hydrology and biogeochemistry of groundwater flux with depth and under baseflow conditions. We developed a nested experimental approach that is summarised below together with full descriptions of the methodologies relevant to the data reported in this paper. Detailed evaluation of the methodologies used to produce aligned data sets is reported elsewhere (i.e. Binley et al. 2013; Lansdown et al. 2012).

Study site description

The field site is a 200 m gaining reach of the River Leith, a Site of Special Scientific Interest (SSSI) and Special

Area of Conservation (SAC), which is a tributary of the River Eden in northwest England, nested within a 5 km stretch of the wider Leith catchment (total 54 km^2). The river is groundwater-fed (Seymour et al. 2008) from the Aeolian Penrith Sandstone that is a major aquifer forming part of the Permo-Triassic Sandstone (Allen et al. 1997). The sandstone bedrock extends at least 50 m beneath the channel and is overlain by unconsolidated glacio-fluvial sands and silts generally 1–2 m deep. The reach meanders within a narrow floodplain of permanent grassland (sheep and cattle) delineated by steep slopes. The river bed is characterised by sand, gravel and cobbles with riffle-pool sequences. Baseflow during summer months is typically around 0.1 $m^3 s^{-1}$, and shows a significant but delayed response to rainfall events (Kaeser et al. 2009).

Field methods

A network of riparian and in-stream piezometers (represented by all open and closed circles in Fig. 1) was installed in clusters (labelled A–I in Fig. 1) along the reach in June 2009 with a percussion drill. Each in-stream piezometer was screened at 100 cm depth below the riverbed, and fitted with multi-level pore water samplers (adapted from the design of Rivett et al. 2008) at target depths of 10, 20, 30, 50 and 100 cm. The ends of the sampling tubes were wrapped in polyester mesh to avoid clogging by particulates. The depth increments were chosen with the aim of sampling pore water from varying depths below the river bed comprising upwelling groundwater discharging to the river, and from mixtures of groundwater with surface water arising from hyporheic exchange flows. In June 2010 in-stream piezometers screened at 20 and 50 cm depth below the river bed were added to the existing network to enable better resolution of saturated hydraulic conductivity and head gradient with depth (see Binley et al. 2013 for a full description of installations). Riparian piezometers were installed to a target depth of 50 cm below the bed of the centre of the adjacent channel to compare left and right bank hydraulic responses, and one multi-level pore water sampler was fitted to each riparian piezometer to collect water from the target depth.

Pore water sampling

Pore water samples (40 mL) were collected from selected multi-level samplers (all depths) during three sampling campaigns (29th June–2nd July, 3rd–6th August and 7th–11th September) in 2009, and a further three sampling campaigns in 2010 (5th–8th July, 3rd–7th August and 6th–9th September). Piezometers used for multi-level pore water sampling in 2009 are denoted by closed circles in Fig. 1. High river flows over winter 2009/10 damaged some piezometers at clusters A and H, and so alternative piezometers, denoted by grey circles on Fig. 1, were sampled for pore water in 2010. A sample of surface water was also collected at each piezometer on each sampling occasion to establish whether there was any marked variability in surface water chemistry through the reach (for example due to inputs from preferential lateral or vertical discharge).

Pore water samples were extracted from the multi-sampler using a syringe and plastic tubing, which were flushed with pore water prior to collection. Samples for anion and cation analysis (NO_3^-, NH_4^+, SO_4^{2-}, Cl^-) were filtered (0.45 μm surfactant-free cellulose acetate membrane) in the field and stored in pre-washed polycarbonate bottles prior to analysis. Samples for Fe and Mn analysis were filtered (as above) into pre-washed polyethylene tubes and acidified with HNO_3 (final concentration of 5 % acid) in the field. All samples were stored on ice at 5 °C until transfer to the laboratory and subsequent analysis within 48 h of collection. Field and travel blanks were collected for all analytes during each campaign.

In 2010 some additional water chemistry parameters (dissolved organic carbon and reduced Fe) were added to the sampling campaign to help improve our understanding of the potential controls on nitrogen transformations in the river reach. Samples for analysis of dissolved organic carbon were filtered (as above) into acid-washed amber glass bottles and acidified to pH <2 with HCl in the field. Measurement of Fe(II) was performed using the buffered 1,10-phenathroline method, adapted from (APHA-AWWA-WPCF 1976; Grace et al. 2010) where 1 mL of pore water was filtered through an oxygen free nitrogen-flushed 0.45 μm filter into 4 mL of preservative solution and stored in the dark until analysis by UV-spectrophotometry (Evolution 100 Thermo Scientific spectrophotometer). Oxygen concentration of pore water was measured for each multi-level sampler using a calibrated, fast response oxygen electrode (50 μm electrode with stainless steel protective guard) connected to an in-line amplifier that was, in turn, connected to a data-logging meter (Unisense). We

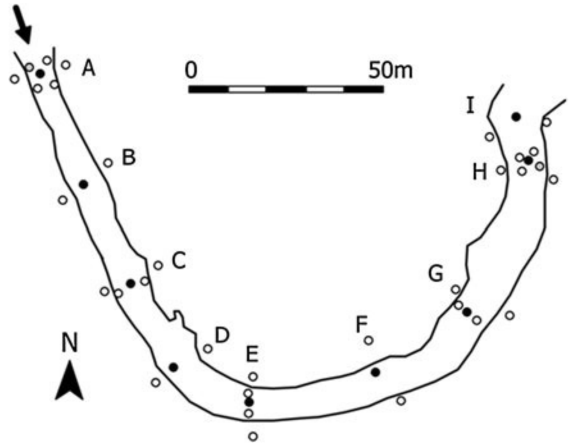


Fig. 1 Plan view of the field site and bed topography surveyed July 2010. River flow is from *left to right*. The *circles* show the locations of piezometers clusters (A–I) used to measure hydraulic head and saturated hydraulic conductivity in 2009 and 2010. The *black circles* show locations of piezometers with multi-level samplers used to collect pore water in 2009. The *grey circles* at clusters A and H show locations of 2 replacement piezometers sampled for pore water in 2010

determined that the amount of oxygen contamination that occurred during sample collection and measurement was approximately 0.4 mg L^{-1}, and corrected all measured oxygen concentrations accordingly. The limit of detection (LOD) of the oxygen electrode was 0.1 mg L^{-1}; precision of repeat measurements of samples was better than 5 %.

Hydraulic head and flux measurements

Head levels in the piezometer network (all circles in Fig. 1) were manually dipped during each field campaign using an electronic dip meter, and the local stream water level adjacent to each piezometer was also measured to enable calculation of vertical head gradient and to help assess the patterns in subsurface flow direction through the reach. Saturated hydraulic conductivity (K_{sat}) was measured using falling and rising slug tests in piezometers at 100 cm depth in 2009, and 20, 50 and 100 cm depth in 2010. Vertical water fluxes were calculated using Darcy's Law with the K_{sat} measured at 100 cm depth in 2009, and the harmonic mean of K_{sat} calculated from the measurements taken at 20, 50 and 100 cm depth in 2010 (see Binley et al. 2013 for full description). For the purposes of the work reported in this paper we use flux data from cluster C only (Fig. 1) because this was identified by Binley et al. (2013) as an area of preferential discharge in the river bed. River discharge is recorded by the Environment Agency (EA) at Cliburn weir (N54:37:03; W2:38:23), approximately 50 m downstream of the study reach.

Laboratory analysis

Chloride, sulphate and nitrate were analysed using ion exchange chromatography (Dionex-ICS2500) whilst ammonium was analysed colorimetrically (Seal AQ2) using an adapted indophenol blue methodology. The limits of detection (LOD) and precision were 0.04 mg N L^{-1} ± 3 % for nitrate, 0.03 mg N L^{-1} ± 8 % for ammonium, 0.3 mg S L^{-1} ± 3 % for sulphate and 0.7 mg L^{-1} ± 2 % for chloride. In 2009 Fe samples were analysed using ICP-OES (Varian Vista-Pro) with LOD and precision of 0.01 mg L^{-1} ± 1 %. The LOD of the measurement of Fe(II) was 0.04 mg L^{-1} due to the dilution associated with sample preservation; precision was ±1 %. Dissolved organic carbon analysis was by thermal oxidation (Thermalox TOC/TN Analyzer) using the non-purgeable organic carbon (NPOC) method. LOD and precision were 1.0 mg L^{-1} ± 8 %.

Data analysis

Our goal was to describe the variability in geochemistry in the reach with a reduced number of parameters (compared to original variables) in order to explore the key spatial patterns in pore water chemistry. Accordingly, we used the multivariate PCA technique to reduce dimensionality in our datasets whilst taking into account inter-correlation between variables (Field 2000). Each principal component describes an environmental gradient that can be interpreted by reference to the original variables that load onto it. We wanted to compare the patterns in pore water chemistry associated with each field campaign, therefore a separate principal components analysis was undertaken for each sampling campaign in each year (July, August and September).

We used SPSS (Version 19) to analyse our data using NO_3^-, NH_4^+, SO_4^{2-}, Cl^- and total dissolved Fe as input variables for 2009, and the extended set of variables which included NO_3^-, NH_4^+, SO_4^{2-}, Cl^-, Fe(II), dissolved organic carbon and oxygen concentration for analysis of the pore water samples collected in 2010. All variables were log transformed, then inter-correlation between variables was examined to check for extreme multi-collinearity and singularity. The Kaiser–Meyer–Olkin measure of sampling adequacy (KMO > 0.5) and Bartlett's test of sphericity were also performed for each analysis. Eigenvalues of principal components represent the data variance summarized by each principal component. The number of principal components to be retained for each analysis was determined by examination of the scree plot in conjunction with use of Kaiser's criterion of retaining eigenvalues >1.

A varimax rotation was used to clarify which variables related to which factors in the PCA. The rotated component matrix was used to examine the loading of each variable onto each factor, and loadings less than 0.4 were suppressed to aid interpretation following recommendations in Field (2000). Loadings represent the relative importance of each individual variable for computing the principal component score, and are thus used to interpret the meaning of the principal components. The individual factor score of each pore water sample (its score on the principal component) were also examined and plotted spatially on maps of the reach. Similarities in scores have been used previously to indicate groupings of different sources of water or patterns in chemical behaviour such as redox (Lautz and Fanelli 2008).

Results

Our study was aimed at capturing spatial variations in porewater chemistry under baseflow conditions. However, the summer of 2009 proved to be challenging in this regard due to high-intensity rainfall events in mid and late July and the start of September which resulted in significant changes in river discharge (Fig. 2a). On each occasion the increase in stage height in the River Leith caused localised inundation of the floodplain, and exceeded the upper limit of the EA gauging station at Cliburn to accurately record discharge (5 m^3 s^{-1}). The peak discharge values of c. 14 m^3 s^{-1} recorded on 18th July and 3rd September must therefore be viewed as an indication of high flow conditions (>Q_5). As a result of these storm events, pore water sampling during July 2009 was undertaken during baseflow conditions (0.1 m^3 s^{-1}; c. 90 percentile of flow), but samples during August and September campaigns were collected on the recession limb of the preceding storm hydrographs when river discharge was 0.7 and 0.9 m^3 s^{-1} (corresponding to c. Q_{20}).

In contrast, river discharge was far less variable during summer 2010 in comparison to summer 2009, and baseflow conditions (defined here as <Q_{90}) were experienced for much of the summer (Fig. 2b), with the highest discharge of 1.4 m^3 s^{-1} recorded in response to a storm event in late July 2010. Consequently, the three sampling campaigns were undertaken during baseflow conditions, at 0.06, 0.1 and 0.08 m^3 s^{-1} respectively (all <Q_{90}).

Surface and pore water chemistry

During our sampling campaign in July 2009 and all campaigns in 2010, chloride and sulphate concentrations were significantly higher in the surface water compared to the streambed (Mann–Whitney *U*, Table 1). During the sampling campaigns in August and September 2009, however, concentrations of chloride and sulphate had decreased in the river water such that there was little or no significant difference in chloride and sulphate concentrations between surface and pore waters. In contrast, nitrate concentrations in streambed pore waters were generally higher than river water, although these differences were only statistically significant in July 2009, July 2010 and August 2009 (Table 1).

Surface and streambed pore water concentrations of dissolved organic carbon and oxygen were analysed in 2010 (Table 1). Unsurprisingly, oxygen concentrations in surface waters were significantly higher than streambed pore water on all sampling occasions (Table 1); nevertheless streambed pore water was generally oxic to 1 m depth, with mean pore water concentrations of 3.5, 3.6 and 2.7 mg L^{-1} for July, August and September 2010 sampling campaigns respectively. Dissolved organic carbon concentrations were similar in pore water and surface water, however, the mean concentration (average of all depths) of dissolved organic carbon concentration in streambed pore water appeared to decline over the summer with highest mean concentrations recorded in July 2010 (5.6 mg L^{-1}), intermediate concentrations in August 2010 (3.3 mg L^{-1}) and lowest concentrations recorded in September 2010 (1.6 mg L^{-1}). Ammonium and reduced Fe concentrations in surface waters were low (generally <0.02 and <0.05 mg L^{-1} as Fe(II), respectively), and the majority of streambed pore water samples also contained ammonium at <0.1 mg L^{-1} and Fe(II) at <0.2 mg L^{-1} concentrations.

Spatial patterns in nitrate concentrations in the streambed pore water are illustrated in Fig. 3, and patterns in concentrations of other solutes in the streambed are provided as Online Resource 1–5. Nitrate concentrations in pore water were consistently highest at Clusters B and C in the river bed, and lowest at Clusters A and G (Fig. 3; Online Resource 1). During our sampling campaigns there were also a number of locations within the river reach that repeatedly exhibited comparatively elevated concentrations of Fe(II) and ammonium indicating reducing chemical conditions (Online Resource 4, 5). The significance of these sites will be discussed in the following sections.

PCA and patterns of water chemistry in 2009

We performed PCA on the surface and pore water chemistry datasets for July, August and September 2009 separately. Each dataset comprised five variables (iron, ammonium, chloride, sulphate and nitrate) selected in order to represent both redox-sensitive and conservative chemical species with the aim of distinguishing between different sources of water and chemical redox processes in the stream bed.

Two principal components together accounted for 75, 79 and 82 % of the variance within the dataset in July, August and September 2009 respectively. The first linear combination (Factor 1) accounted for 44, 53 and 62 % of the variance within the dataset in July, August and September respectively, and sulphate and chloride concentrations load highly onto this factor indicating that they are important explanatory variables (Table 2). The second linear combination (Factor 2) accounted for 31, 26 and 20 % of the remaining variance within the dataset and iron and ammonium load highly on this factor for all months (Table 2). The association of nitrate concentrations with the factor axes shifts from July to September 2009. In July 2009 nitrate loads highly (negatively) onto Factor 2; in August 2009 nitrate loads positively on Factor 1, but also loads highly (negatively) onto Factor 2; and in September nitrate is strongly positively loaded onto Factor 1 (Table 2).

Figure 4a–c displays the spatial pattern of scores on AQ4 Factor 1 for each site along the reach for July, August and September 2009, respectively. These plots enable us to identify those sites that are strongly positively associated with chloride and sulphate. The highest scores on Factor 1 are associated with pore water clusters B to D in July 2009 and B to E in August and September 2009. In clusters H and I (July 2009 only) there is a pattern of decreased scores on Factor 1 with increased depth. Figure 5a–c illustrates the spatial pattern of scores on Factor 2 along the study reach. Pore water samples from clusters A, G and I all score highly on Factor 2 indicating that these clusters that are associated with elevated concentrations of reduced iron and ammonium in comparison with the remainder of the reach.

PCA and patterns of water chemistry in 2010

We performed PCA on the surface and pore water chemistry datasets for July, August and September 2010 separately. Each dataset comprised seven variables; iron (II), ammonium, chloride, sulphate, oxygen, dissolved organic carbon and nitrate concentrations. Two principal components together account for 79, 77 and 81 % of the variance within the dataset for July, August and September 2010 campaigns respectively. Factor 1 accounts for 48, 4 and 46 % of the variance in the dataset (Table 3).

In contrast to 2009, iron (II), ammonium and dissolved organic carbon concentrations contribute strongly to Factor 1 rather than Factor 2. Pore water samples from clusters A, G and H score highly on Factor 1 (Fig. 5d), and this was consistent for each sampling campaign. Nitrate is strongly negatively loaded on Factor 1 for all three sampling visits (Table 3). Chloride and sulphate concentrations load highly on Factor 2 in July, August and September 2010 and the highest scores on Factor 2 are associated with pore water samples from clusters B to D (Table 3) whereas, oxygen concentrations in 2010 (all months) are negatively associated with Factor 1 and positively loaded onto Factor 2 (Table 3).

Discussion

Chloride and sulphate both load highly onto Factor 1 in 2009, and Factor 2 in 2010. Chloride is assumed to

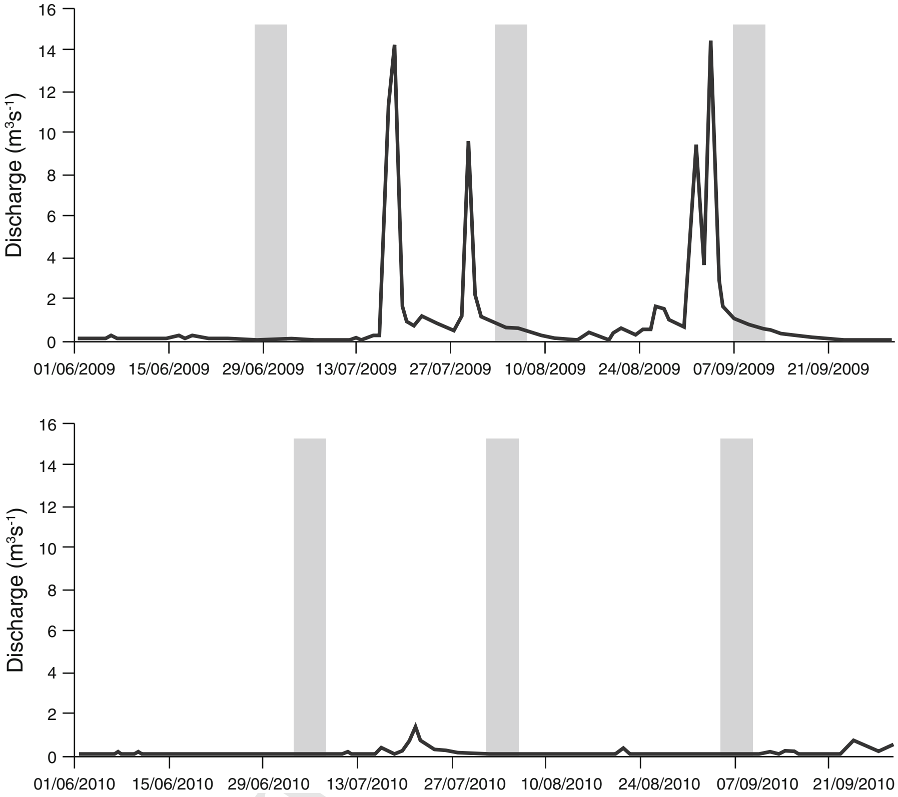


Fig. 2 Discharge of River Leith **a** June–September 2009; **b** June–September 2010

be a conservative solute, and patterns in chloride concentration in a riverbed and/or riparian setting are generally due to the mixing of water from various sources; for example due to mixing of surface and ground water (Stelzer and Bartsch 2012; Pinay et al. 1998) or the mixing of subsurface water of different origins such as deep and shallow groundwater (Flewelling et al. 2012) In contrast to chloride, sulphate is a redox-sensitive species, with oxidation of organic matter by sulphate reduction reported in various streambed settings (Lautz and Fanelli 2008; Hlavacova et al. 2005; Morrice et al. 2000), although Krause et al. (2011) suggest that reduced sulphur requires a low redox potential that may not commonly be found in the hyporheic zone. In the pore water of the River Leith strong positive correlations between sulphate and chloride concentration (log transformed data from 2009 to 2010, $r = 0.7377$, $p < 0.001$) indicate that reach-scale patterns in sulphate concentration are mainly related to mixing of different water sources rather than to chemical transformations driven by redox processes. The river bed appears to be generally characterised by oxic groundwater and surface water, at least to a depth of 1 m, combined with high nitrate concentrations and low organic matter content. Under such hydrochemical conditions, sulphate reduction is less energetically favourable than denitrification or reduction of Fe(II) and Mn(IV). Therefore the principal component related to chloride and sulphate in each year is termed the ‘source function’ to indicate that this factor represents the mixing of different sources of water in the river bed.

Figure 4 illustrates the patterns in pore water chemistry that could arise from two different exchange mechanisms in the riverbed. A decrease in ‘source function’ score with depth in the river bed at piezometer clusters H and I may be indicative of mixing between surface and pore waters of distinctly different chloride and sulphate concentrations. One possible explanation for this concerns hyporheic exchange flows around the pool-riffle bedforms (see e.g. Kasahara and Hill 2006) We attempt a more detailed explanation of the broad patterns described here in a companion paper (Lansdown et al. in review) using a mixing model approach. A marked longitudinal reach-scale change in pore water chemistry is also

Table 1 Mean (SE) values for surface water and in-stream pore water chemistry for six sampling campaigns in 2009 and 2010

	Chloride (mg L^{-1})			Sulphate-S (mg L^{-1})			Nitrate-N (mg L^{-1})			Dissolved organic carbon (mg L^{-1})		
	PW[a]	SW[b]	Sig.[c]	PW[a]	SW[b]	Sig.[c]	PW[a]	SW[b]	Sig.[c]	PW[a]	SW[b]	Sig.[c]
July 2009	15.0(0.5)	20.3(0.2)	0.000*	7.1(0.5)	14.6(0.4)	0.000*	3.5(0.3)	2.0(0.09)	0.032*	nd	nd	nd
Aug 2009	16.3(0.4)	17.5(0.5)	0.043*	6.8(0.3)	8.6(0.4)	0.092	3.4(0.3)	1.9(0.05)	0.006*	nd	nd	nd
Sep 2009	16.0(0.4)	14.6(0.2)	0.235	6.5(0.3)	7.4(0.1)	0.260	3.4(0.3)	2.0(0.03)	0.105	nd	nd	nd
July 2010	18.6(0.9)	37.9(0.4)	0.000*	6.5(0.4)	16.3(0.3)	0.000*	3.1(0.4)	1.4(0.03)	0.027*	5.6(0.6)	5.3(0.6)	0.381
Aug 2010	16.6(0.7)	29.9(0.2)	0.000*	6.0(0.4)	13.3(0.2)	0.000*	3.1(0.4)	1.8(0.02)	0.090	3.3(0.6)	3.5(0.1)	0.019*
Sep 2010	16.0(0.6)	28.4(0.3)	0.000*	6.7(0.4)	14.7(0.2)	0.000*	3.1(0.4)	1.7(0.04)	0.083	1.6(0.2)	3.3(0.1)	0.000*

	Oxygen (mg L^{-1})			Fe(II) (mg L^{-1})[d]			Ammonium-N (mg L^{-1})		
	PW[a]	SW[b]	Sig.[c]	PW[a]	SW[b]	Sig.[c]	PW[a]	SW[b]	Sig.[c]
July 2009	nd	nd	nd	0.3 (0.8)	0.2 (0.0)	0.696	0.09(0.02)	0.04(0.00)	0.709
Aug 2009	nd	nd	nd	0.1 (0.1)	0.01(0.0)	0.494	0.09(0.02)	0.03(0.01)	0.189
Sep 2009	nd	nd	nd	0.6 (0.3)	0.01(0.01)	0.121	0.04(0.01)	0.02(0.00)	0.388
July 2010	3.5(0.4)	16.0 (1.4)	0.000*	0.7 (0.2)	0.10(0.01)	0.887	0.06(0.17)	0.02(0.00)	0.936
Aug 2010	3.6(0.5)	15.6 (0.8)	0.000*	0.8 (0.2)	0.04(0.01)	0.213	0.11(0.25)	0.50(0.01)	0.318
Sep 2010	2.7(0.3)	11.0 (0.7)	0.000*	0.8 (0.3)	0.05(0.02)	0.722	0.05(0.02)	0.01(0.00)	0.082

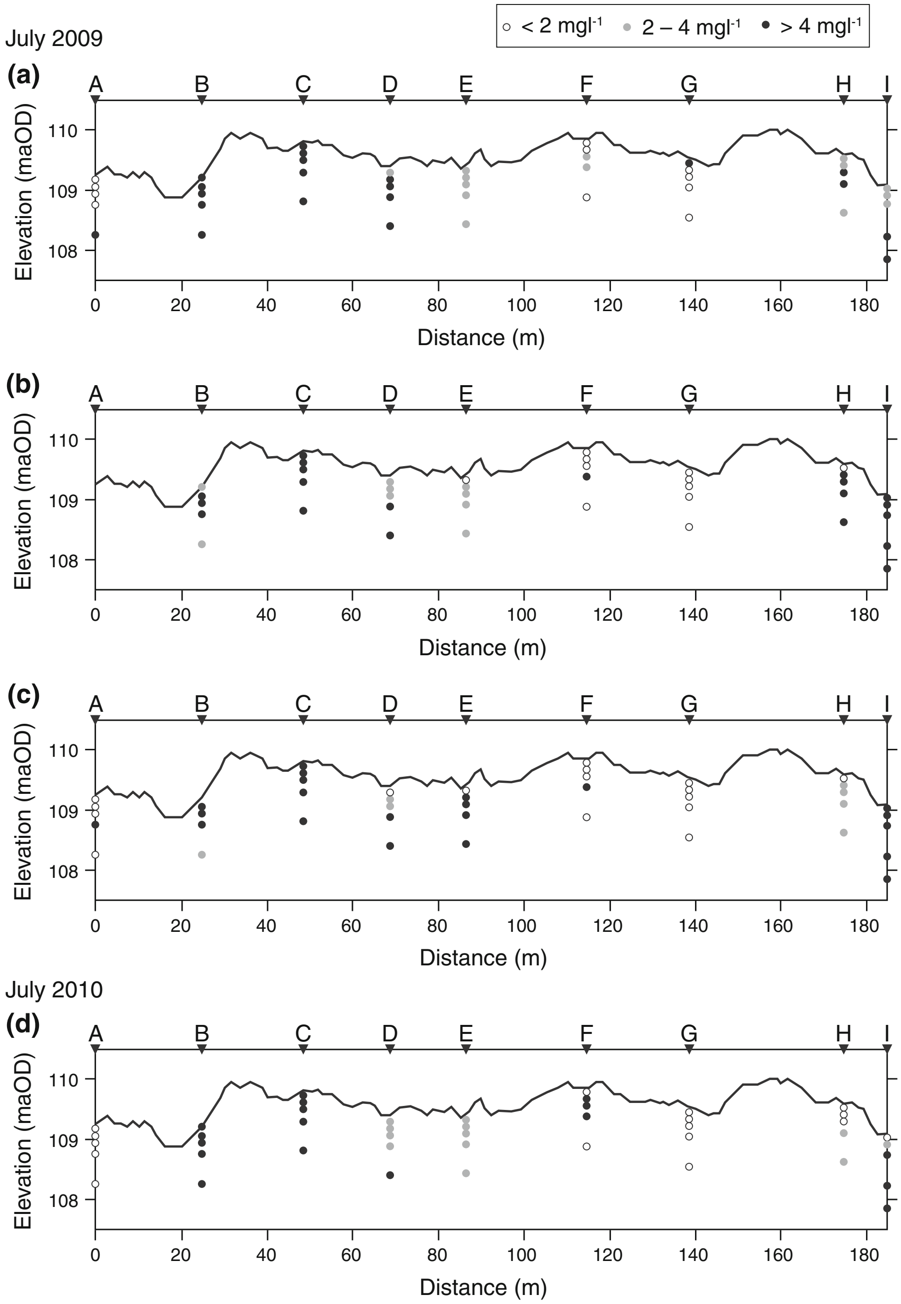
[a] PW is mean of in-stream pore water samples (all sites and depths combined) with standard error in parentheses (n = 40 in 2009 and n = 44 in 2010)

[b] SW is mean of all surface water samples collected along the reach at each piezometer cluster with standard error in parentheses (n = 8 in 2009 and n = 9 in 2010)

[c] Sig. is *p* value for Mann–Whitney *U* test * indicates that the result is highly significant and the null hypothesis is rejected

[d] Fe measured as total Fe by ICP-OES in 2009 and Fe(II) by colorimetric method in 2010

Fig. 3 Spatial variations in nitrate concentration (Nitrate-N mg L^{-1}) along the study reach **a** July 2009; **b** August 2009; **c** September 2009; **d** July 2010



highlighted in Fig. 4 by an increased ‘source function’ score in the upstream section which is focused around piezometer cluster C. This high score is due to elevated chloride and sulphate concentrations in pore water in comparison to other areas of the reach, suggestive of a different subsurface source of water. Binley et al. (2013) used a survey of riverbed electrical conductivity, combined with measurements of vertical and lateral flux, in this same region of the riverbed (around cluster C) to demonstrate that this zone is likely to be a ‘preferential discharge location’ (Conant 2004) and appears to be characterised by direct connectivity to the sandstone aquifer where elevated vertical upwelling fluxes suppress hyporheic exchange flows. Our analysis of reach-scale patterns in pore water chemistry suggests that such preferential discharge was active during each of our sampling campaigns in 2009 and 2010. Further analysis, below,

Table 2 Rotated component matrix for July, August and September 2009 showing the loading of each chemical variable onto each principal component and explained variance for the PCA

	July 2009 (baseflow)		August 2009		September 2009	
	Factor 1 'source'	Factor 2 'redox'	Factor 1 'source'	Factor 2 'redox'	Factor 1 'source'	Factor 2 'redox'
Sulphate-S	0.946		0.929		0.851	
Chloride	0.942		0.924		0.881	
Iron		0.776		0.897		0.804
Ammonium-N		0.794		0.785		0.896
Nitrate-N		−0.783	0.640	−0.585	0.885	
% Variance explained	44	31	53	26	62	20
% Cumulative variance	44	75	53	79	62	82

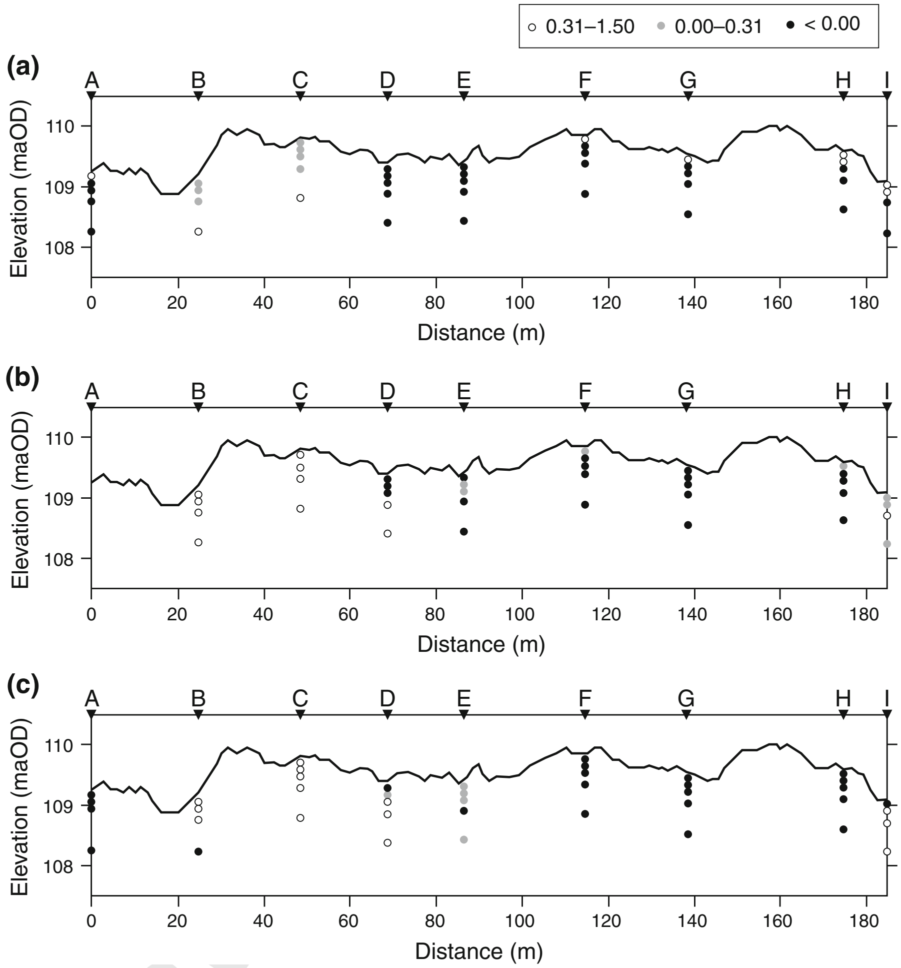
will consider the importance of this region of preferential discharge for nitrate supply to the reach, and examine the implications of our findings for nitrate supply in groundwater-fed river settings.

The variables that consistently load highly onto Factor 2 in 2009 and Factor 1 in 2010 are the redox-sensitive solutes, and products of organic matter decomposition processes; reduced iron and ammonium (Fig. 5). This principal component is therefore termed the 'redox function'. Pore water samples from two sites in the riverbed (A and G) have consistently high scores on the redox function during both years of our study, reflecting not only the reduced nature of the pore water collected at these locations, but also the inter-annual longevity of these redox conditions. In contrast two further sites (H and I) displayed high scores on the redox function during sampling campaigns undertaken in one season (2010 for H and 2009 for I), but the reduced conditions were not replicated during both years of sampling. Lautz and Fanelli (2008) have also used principal components analysis to identify spatial patterns of redox sensitive solutes in the riverbed, and to distinguish between the redox status of streambed pore water types around a log dam. Here we use a similar approach to consider the implications of chemically reduced regions of the river bed for nitrate supply and transformation in a gaining reach of a groundwater-fed river.

Distribution of chemically reduced sites in the river bed

Three sites—A, G and H—consistently scored highly on our redox function in 2010. The data from Summer 2010 is the focus here, as we have the most complete chemical dataset for these sampling campaigns. Table 4 compares the chemical composition of pore water from sites A, G and H (identified by the PCA analysis as chemically reduced) with the composition of pore water from our riparian piezometers, and from the other in-stream piezometers. The patterns in pore water chemistry suggest that at sites A, G and H some of the electron acceptors in the pore water were reduced as a result of organic matter oxidation (Morrice et al. 2000) as exemplified by significantly lower concentrations of nitrate and significantly higher concentrations of Fe(II) in the pore water at clusters A, G and H in comparison with other piezometer clusters and the riparian zone (Table 4). Mineralisation of organic matter could be occurring in the river bed itself at or near the point of sampling due, for example, to oxidation of buried (Stelzer and Bartsch 2012) or ingressed particulate organic material (Arango et al. 2007), however, analysis of sediment cores by loss on ignition provided no evidence of elevated particulate organic matter in these regions of the stream bed (data not shown). Alternatively, the chemical signature may arise from the decomposition of organic matter that is spatially (and potentially temporally) segregated from the point of sampling (Dahm et al. 1998). In the latter case the reactions may have occurred along a contributing hydrological pathway; for example a parcel of water, along with its chemical signature, has been transported to the river bed from a riparian zone or aquifer in which the organic carbon oxidation occurred. Understanding the chemistry and hydrology together is important because, on the basis of the chemical

Fig. 4 Spatial pattern of scores on Factor 1 along the study reach **a** July 2009; **b** August 2009; **c** September 2009; **d** July 2010



signature alone, a specific location in the river bed could be mis-interpreted as a 'hot spot' of biogeochemical reactivity, when in fact the organic matter processing may have taken place elsewhere, and at a different time.

Interpolation of hydraulic head data from the in-stream piezometer network in July 2010 showed that sites A, G and H (and I in 2009) are all locations where horizontal flow potential dominates over vertical gradients under baseflow conditions [see Fig. 6a; Binley et al. (2013) for data from September 2010]. Horizontal flows at these sites could comprise subsurface lateral flows from the riparian zone including intra-meander flows (Boano et al. 2010; Zarnetske et al. 2011) and/or the longitudinal movement of water from hyporheic exchange flows. When we categorise sites by dominant potential flow direction (horizontal or vertical in Fig. 6c) it becomes apparent that sites which score highly on the PCA redox function, indicating reduced conditions, are locations where the potential for horizontal fluxes of subsurface water occurs.

Depth profiles of DOC concentrations from sites G and H support our hypothesis that redox-sensitive solutes may have been supplied horizontally through the streambed during our sampling campaigns (Fig. 7). Site A has elevated DOC concentrations through the entire profile to 100 cm depth, suggesting a deeper source of DOC supply in this upstream area of the reach in comparison to G and H. The pore water from in-stream piezometers in A, G and H comprises significantly lower concentrations of nitrate, and significantly higher concentrations of Fe(II) and ammonium in comparison to the riparian zone (Table 4) and surface waters (Table 1) suggesting that A, G and H are sites of active biogeochemical

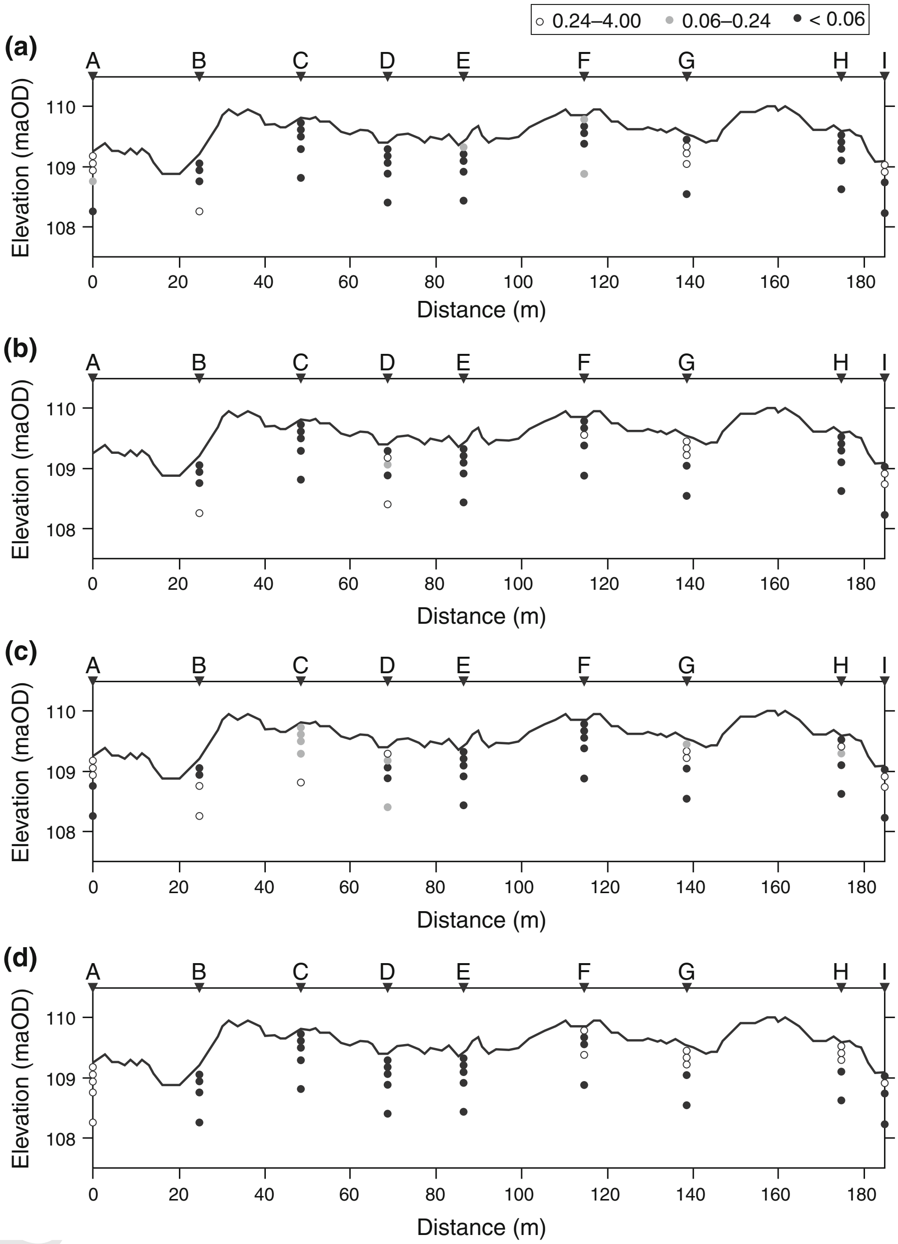


Fig. 5 Spatial pattern of scores on Factor 2 (2009) and Factor 1 (2010) along the study reach **a** July 2009; **b** August 2009; **c** September 2009; **d** July 2010

processing, and therefore biogeochemical 'hot spots' with the ability to remove nitrate from subsurface flow through heterotrophic and/or chemoautotrophic nitrate reduction processes. Based on the data from the field site, we cannot definitively distinguish between hyporheic exchange flows and lateral riparian flows as the dominant hydrological pathway here, and given the pool-riffle structures around sites A and G to I it is probable that both are occurring. These sites highlight the important role that horizontal subsurface flows can play in supplying reactants that drive biogeochemical transformations and remove nitrate from the stream bed.

Reach-scale patterns of mixing/origins of water

The upstream section of the reach, centred on site C, is an area of elevated chloride, sulphate and nitrate concentrations in pore water, which load highly onto the factor in the PCA related to water sources. The

Table 3 Rotated component matrix for July, August and September 2010 showing the loading of each chemical variable onto each principal component and explained variance for the PCA

	July 2010 (baseflow)		August 2010 (baseflow)		September 2010 (baseflow)	
	Factor 1 'redox'	Factor 2 'source'	Factor 1 'redox'	Factor 2 'source'	Factor 1 'redox'	Factor 2 'source'
Sulphate-S		0.957		0.936		0.949
Chloride		0.943		0.946		0.943
Iron (II)	0.892		0.866		0.868	
Ammonium-N	0.905		0.748		0.807	
Nitrate-N	−0.901		−0.842		−0.903	
DOC	0.766		0.788		0.650	0.578
Oxygen	−0.552	0.617	−0.627	0.658	−0.488	0.717
% Variance explained	48	31	45	32	46	35
% Cumulative variance	48	79	45	77	46	81

Table 4 Mean (SE) pore water chemical composition of sites A, G and H and comparison with other in-stream and riparian piezometers (July, August and September 2010 data only)

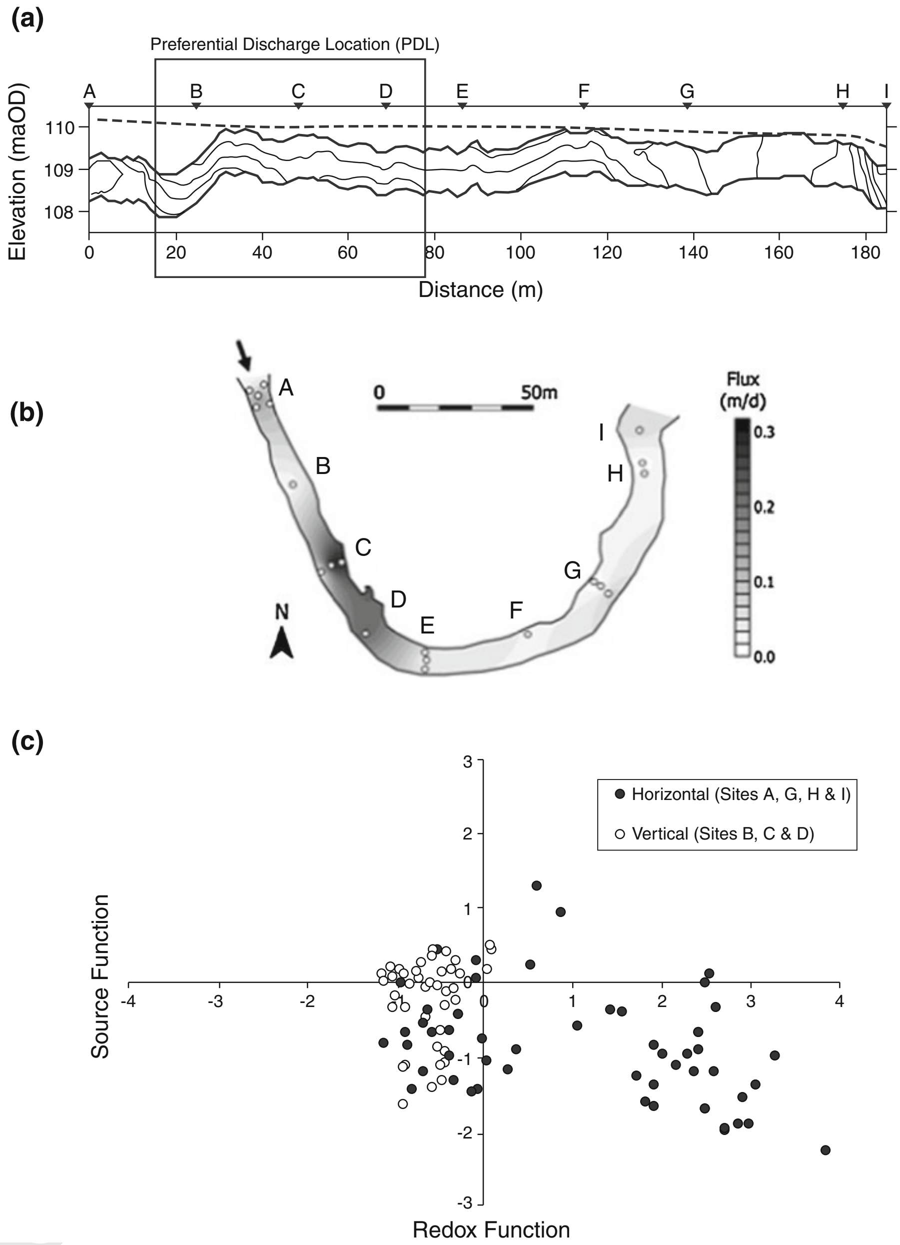
	Concentration (mg L^{-1})					Mann–Whitney *U*	
	Site A	Site G	Site H	Other in-stream	Riparian	Reduced versus riparian	Reduced versus other
DOC	5.0(0.7)	7.5(1.7)	4.7(1.1)	2.3(0.2)	7.8(2.3)	0.866	0.000*
Oxygen	1.4(0.2)	0.7(0.2)	2.0(0.5)	4.2(0.3)	2.2(0.3)	0.044*	0.000*
Fe(II)	2.8(0.37)	2.7(0.6)	1.0 (0.5)	0.05(0.00)	0.3(0.1)	0.000*	0.000*
NitrateN	0.02(0.01)	0.8(0.2)	1.4(0.2)	4.3(0.2)	2.9(0.3)	0.000*	0.000*
AmmoniumN	0.08(0.01)	0.3(0.07)	0.1(0.05)	0.02(0.00)	0.05(0.01)	0.006*	0.000*

* Significant at <0.05 level; Numbers in parentheses are Standard Error of n = 15 samples (all depths and all months combined)

horizontal banding of hydraulic head in Fig. 6a indicate the dominance of vertical head gradients in this area, whilst Fig. 6b highlights the high vertical flux recorded in this region of the streambed in comparison with the remainder of the reach. Binley et al. (2013) have identified this site to be a location of preferential discharge with strong connectivity to a local or regional groundwater body. We analysed cross-sectional profiles of sulphate, nitrate and chloride chemical species at site C but found that these revealed little variation in pore water chemistry with depth in either 2009 or 2010 (data not shown). Therefore, we postulate that the streambed between sites B and D is a region of upwelling groundwater, with a distinct hydrochemical signature, within which the strong upward flux provides little opportunity for mixing with water of a surface or riparian origin.

There is a statistically significant positive correlation (n = 6, r = 0.936, p = 0.006) between surface water discharge at the time of sampling, and the variance associated with the 'source' factor of the PCA analysis suggesting that reach-scale patterns in sulphate, chloride and nitrate in pore water may be explained by differences in discharge between our sampling campaigns. The response of nitrate to changes in river discharge is of particular interest in this study because nitrate changes from being highly, negatively loaded onto the redox function under baseflow conditions, to strongly positively loaded onto the source function under high discharge conditions (Table 2 and 3). These data suggest that under baseflow conditions, distinct patterns in nitrate concentration are characterised by areas that are well supplied with electron sources to facilitate reduction. We demonstrated earlier (and in Binley et al. 2013) that these areas of the streambed are associated with horizontal hydrological flows. Following high discharge events, however, reach-scale gradients in

Fig. 6 **a** Interpolated vertical profile of heads in river bed computed from 20, 50 and 100 cm piezometer dips and stage levels during July 2010; **b** Interpolated plan view of vertical fluxes based on mean gradient between June and September 2010 under baseflow conditions; **c** PCA scores on redox and source functions (all 2010 data) categorised by dominant potential flow direction



nitrate concentration in the streambed are controlled chiefly by the supply of nitrate-rich groundwater in areas of preferential discharge. To support this analysis further we can consider the pore water concentrations of chloride, sulphate and nitrate at cluster C during our sampling campaigns (Table 5). High concentrations of chloride, sulphate and nitrate were recorded in September 2009, intermediate concentrations were recorded in August 2009 and the lowest concentrations were found in July 2009 (Table 5), however there were no significant differences in pore water chemistry between monthly sampling campaigns in 2010 (data not shown). The significantly elevated concentration of chloride, sulphate and nitrate at site C following the high discharge associated with the storm events of 29th July and 3rd September 2009 suggests that groundwater has a major influence on streambed pore water concentrations of solutes during and following significant changes in discharge associated with storm events.

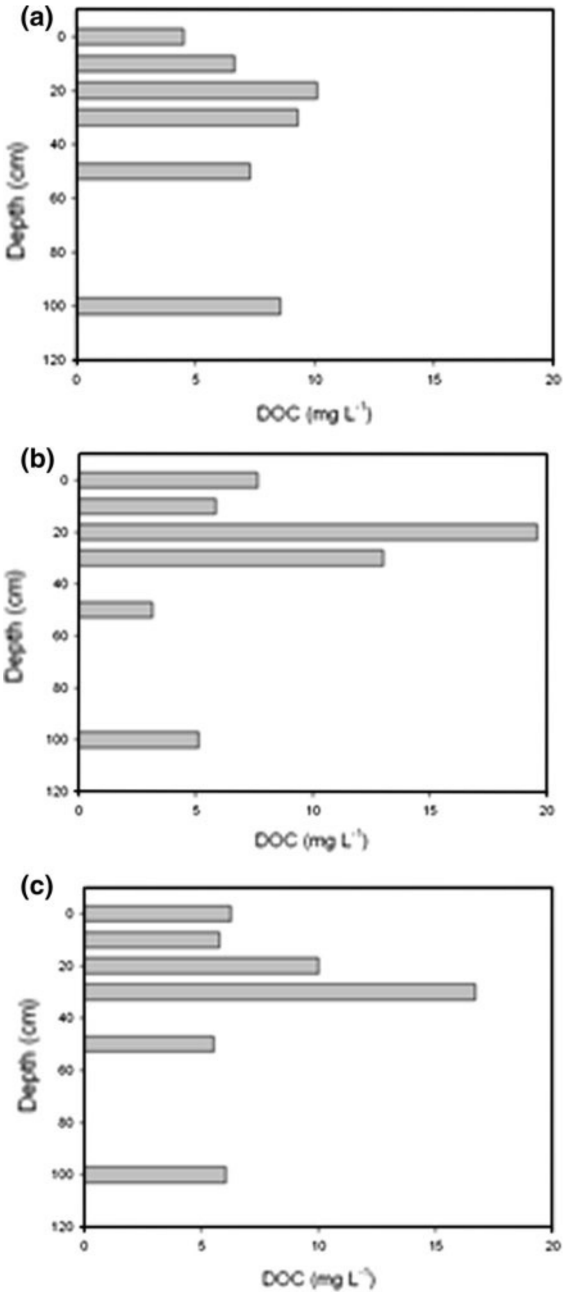


Fig. 7 Depth profiles of dissolved organic carbon concentration at sites A, G and H in July 2010

Importance of preferential discharge area for nitrate and ammonium supply to reach

Table 5 Mean (SE) porewater chemistry and comparison (ANOVA) of chemical composition for Cluster C (all depths) in July, August and September 2009

	Concentration (mg L^{-1})			F-ratio	Sig. value
	July 2009	Aug 2009	Sept 2009		
Nitrate-N	6.3 (0.03)	6.7 (0.15)	7.2 (0.06)	21.37	< 0.001
Chloride	16.7 (0.30)	20.7 (0.29)	22.0 (0.10)	120.23	< 0.001
Sulphate-S	7.2 (0.57)	7.9 (0.09)	8.3 (0.04)	64.78	< 0.001

[a] Numbers in parentheses are Standard Error of n = 5 samples (all depths)

We evaluated above the importance of hydrological controls for patterns of pore water chemistry in the streambed. We sought to understand the role that hydrology plays in controlling the supply of nitrate to surface water at the reach scale. Previous approaches to quantifying the importance of nitrate and ammonium transport from groundwater to streams have; (i) correlated surface water concentration of nitrogen species with the proportion of streamflow due to baseflow (Tesoriero et al. 2009), (ii) used a mass balance approach at the reach scale (Chestnut and McDowell 2000; Bohlke et al. 2004; Duff et al. 2008) and (iii) combined measurements of hydraulic head, hydraulic conductivity and nitrate concentration in piezometers to compute point values of water and nitrate flux (Staver and Brinsfield 1996; Kennedy et al. 2009a). Here we focus on a region of the river bed for which both hydrological and chemical data indicated stronger upwelling fluxes in comparison with the rest of the reach, i.e. a site of preferential discharge through the river bed. Therefore, we have taken a point value approach to exploring the importance of preferential discharge for overall supply of nitrate and ammonium to our river reach during our 'snapshot' sampling campaigns whereby Darcy flux is multiplied by the concentration of nitrogen species (NO_3^- or NH_4^+) in pore water at 100 cm depth to estimate nitrate and ammonium flux through the streambed during each sampling campaign (Table 6).

Binley et al. (2013) estimate that about 20 % (390 m^2) of our 200 m study reach comprises the area of enhanced groundwater seepage, marked as a preferential discharge location (PDL) on Fig. 6a. In this zone nitrate is being most rapidly transported through the streambed, at a rate of 1.61 ± 0.1 g m^{-2} day^{-1} (average of n = 6 measurements over two years). Although the preferential discharge location is an area of comparatively elevated water flux within our study site, the groundwater based nitrate flux in this area approximates the mean value of 2.0 ± 0.48 g m^{-2}

Table 6 Analysis of nitrate supply to reach due to preferential discharge at site C

	NitrateN_{SW} (mg L^{-1})	Q_{SW} (m^3s^{-1})	fN_{SW} (kg day^{-1})	NitrateN_{100} (mg L^{-1})	Q_{RB} (m day^{-1})	fN_{RB} (kg day^{-1})	fN_{RB}/fN_{SW} (%)
July 2009	1.7	0.099	15	6.2	0.23	0.56	3.8
Aug 2009	1.8	0.695	108	6.4	0.20	0.50	0.5
Sep 2009	1.9	0.815	147	7.2	0.20	0.56	0.4
July 2010	1.5	0.063	8	6.5	0.29	0.72	8.9
Aug 2010	1.7	0.099	15	6.4	0.3	0.76	5.2
Sept 2010	1.8	0.083	13	6.3	0.27	0.67	5.2

NitrateN_{SW} is the concentration of nitrate in surface water at site C; Q_{SW} is the discharge at the time of sampling; fN_{SW} is the nitrate flux through the reach in surface water; NitrateN_{100} is the concentration of nitrate in the pore water at 100 cm depth; Q_{RB} is the upwelling Darcy flux of water through the river bed; fN_{RB} is the nitrate flux through the river bed; fN_{RB}/fN_{SW} is the relative magnitude of nitrate flux through the river bed to flux through the reach in surface water expressed as a percentage

day^{-1} reported for nine different gaining reaches in agricultural watershed of the US (Kennedy et al. 2009b). Whilst nitrate concentration in groundwater is in the upper range reported in the literature for agricultural watersheds, the upwelling water flux associated with our preferential discharge falls in the mid-range reported for similar studies of permeable, gaining reaches (c.f. 0.25 m day^{-1} for our study with 0.41–0.5 m day^{-1} for Kennedy et al. (2009b) and Cey et al. (1998)).

In order to determine the relative importance of the area of preferential discharge for nitrate and supply to the reach, the upwelling flux in the preferential discharge area is expressed as a proportion of the nitrogen species moving through the reach in surface water (Table 6). Our analysis shows that under baseflow conditions, the preferential discharge pathway is an important source of nitrate to the river, contributing 4–9 % of the total nitrate flux in surface water (henceforth termed nitrate flux contribution). When samples were collected on the recession limb of a high discharge event (as for August and September 2009), however, the nitrate flux contribution is only 0.4–0.5 %. These analyses assume no net removal of nitrate as groundwater travels up through the oxic streambed in the area of preferential discharge, despite a travel time of c. 3 days, and this is supported by nitrate porewater profiles that reveal no increase in nitrate concentration with depth. Such profiles may arise due to unfavourable redox conditions for nitrate removal; a balance of nitrate removal and production along the upwelling pathway; or because the streambed is characterised by a low Damkohler number (the ratio of the timescale for transport to the timescale for reaction). A companion paper, which reports in situ reaction rates in the river bed using stable isotope techniques, will explore the relative importance of transport and reaction for nitrate export in this oxic, nitrate-rich sandy streambed.

Conclusions

In this article we present new insights for our understanding of hyporheic zone processes using a nested piezometric grid sampling to a depth of 1 m across nine sampling stations in the armoured river bed of a 200 m gaining reach (River Leith, Cumbria, UK). Our first objective was to describe spatial variability in pore water chemistry across the reach under baseflow conditions. We find that patterns in redox sensitive chemistries reflect the spatial variability of different sources of water flux in the streambed. Oxic conditions are associated with upwelling flux from preferential groundwater, whereas reducing conditions occur in areas of the stream bed where hydraulic gradients indicate that longitudinal and lateral fluxes of subsurface water are preponderant. Thus, we find that understanding the hydrology of the reach is critical to explaining the observed spatial signatures in pore water chemistry.

Antecedent conditions appear to control the pattern of nitrate concentration in porewater according to river discharge. During period of stable baseflow ($< Q_{90}$), spatial variation in nitrate along the reach reflects redox conditions at the site. Low nitrate concentrations are associated with elevated Fe(II) and dissolved organic carbon (DOC), and low oxygen conditions;

and correspond to areas of the reach where lateral hydrological fluxes are important. When rainfall events occur, elevated nitrate, sulphate and chloride concentrations are apparent in a region of the river bed (approximately 20 % of the reach) characterised by upward, vertical fluxes and high connectivity with regional groundwater, termed a preferential discharge location.

Paradoxically it is under baseflow conditions that this preferential discharge location is demonstrably important for nitrate transport to the shallow streambed, comprising 4–9 % of total nitrate transported through the reach in surface water. Following summer storm events river discharge increases by an order of magnitude and therefore fluxes of nitrate through surface water are greatly increased, consequently the preferential discharge location contributes much less nitrate to the reach on a proportional basis under these conditions.

We do not yet understand the spatial distribution of these preferential discharge locations at the catchment scale, or their geochemical properties, and so cannot determine their overall importance for nitrate supply to a gaining river. Further work is needed to establish the importance of such locations for delivering nitrate to the stream channel in sandstone and other permeable geological settings.

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