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

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Abstract	<p>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 (<math>&lt;Q_{90}</math>) 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.</p>	
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<sup>-1</sup>) 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<sup>-1</sup>) 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<sup>-1</sup>) 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<sup>-1</sup>) 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<sup>-1</sup>) 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

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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.

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**Electronic supplementary material** The online version of this article (doi:10.1007/s10533-013-9895-4) contains supplementary material, which is available to authorized users.

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43 **Keywords** Hyporheic · Nitrate · Hydrological  
 44 pathways · Groundwater-fed · Rivers · Water  
 45 quality · Pollution

## 47 Introduction

48 The ecosystem services delivered by groundwater-  
 49 fed rivers have both *direct* valued uses, which  
 50 include water supply, transportation, recreation, and  
 51 fishing and *indirect* valued uses, which include flood  
 52 protection, nutrient recycling, genetic material, and  
 53 sustaining wetlands (Watson and Albon 2011).  
 54 Attributing economic value to the latter is particu-  
 55 larly problematic and can lead to the degradation of  
 56 these services (Heathwaite 2010). Notable is the  
 57 underestimation of the value of managing ground-  
 58 water-fed river systems for water quality improve-  
 59 ment, surface flow regulation, erosion control, and  
 60 stream bank stabilisation. The economic importance  
 61 of these services will only increase, as water quality  
 62 becomes a critical issue around the globe (Rockstrom  
 63 et al. 2009).

64 In the UK, groundwater provides 5 % of public  
 65 water supply in Scotland, 8 % in Northern Ireland, and  
 66 33 % overall in England and Wales, rising to over 70 %  
 67 in the south-east of England ([www.groundwateruk.org](http://www.groundwateruk.org)). Rivers draining areas of permeable rocks, such as  
 68 in the Chalk downlands of southern England, are fed  
 69 almost entirely from groundwater. Groundwater-fed  
 70 river flows can be vital for the dilution of discharged  
 71 wastewater and for the regulation of diffuse nutrient  
 72 pollution in rural catchments. However, nitrate con-  
 73 centrations have been increasing in groundwater since  
 74 the 1970s (see for example Scanlon et al. 2007; Zhang  
 75 et al. 1996; Croll and Hayes 1988) leading to increases  
 76 in nitrate concentrations in groundwater-fed rivers  
 77 (Howden et al. 2011). In Europe, time-series analysis of  
 78 nitrate concentrations in rivers of permeable catch-  
 79 ments has revealed continuous and sustained linear  
 80 increases in nitrate concentration (Howden and Burt  
 81 2009; Burt et al. 2011). In the UK, policy interventions  
 82 have been introduced to restrict the timing and amount  
 83 of nitrogen applied to agricultural land in designated  
 84 Nitrate Vulnerable Zones. Such measures may take  
 85 many years to deliver evidence of improvement in  
 86 water quality owing both to the time lags involved (e.g.  
 87 Worrall et al. 2012), and to the complexity of response

89 in surface and subsurface freshwater systems. Given the  
 90 long modal residence time of water in permeable  
 91 catchments, Burt et al. (2011) have suggested that it  
 92 may be decades before the benefits of source control  
 93 schemes are observed in groundwater-fed rivers. In  
 94 Europe, elevated concentrations of the critical ma-  
 95 cronutrients, nitrogen (particularly nitrate) and phos-  
 96 phorus in surface waters and in groundwaters constrain  
 97 opportunities to deliver the goals of the EU Water  
 98 Framework Directive to achieve ‘good ecological sta-  
 99 tus’ for fresh and marine waters by 2015. Added to this,  
 100 changes in weather patterns that may be climate-related  
 101 (e.g. low winter recharge in 2010 and 2011 in the UK)  
 102 have recently demonstrated gaps in our knowledge  
 103 about the nature of ‘groundwater drought’ and the  
 104 physical, chemical and biological responsiveness of  
 105 aquifers to subsequent recharge (Whitehead et al. 2006;  
 106 Wilby et al. 2010). These observations point to the need  
 107 to know more about the interactions of groundwater and  
 108 surface water and the implications of these interactions  
 109 for water quality improvement under baseflow condi-  
 110 tions and a changing climate (Prudhomme et al. 2012).

111 For groundwater-fed rivers, the riverbed is a  
 112 reactive permeable zone, termed the hyporheic zone,  
 113 in which contributing waters from different sources  
 114 can mix and where reactive chemicals such as nitrogen  
 115 can undergo transformations (see definitions of hyp-  
 116 orheic zone in Tonina and Buffington 2009; Krause  
 117 et al. 2011). Water flow pathways through riverbeds  
 118 are complex and multi-dimensional, including lateral  
 119 (horizontal) inputs from the riparian zone (Ranalli and  
 120 Macalady 2010) and vertical, upwelling groundwater  
 121 (Stelzer and Bartsch 2012). In a gaining setting, these  
 122 pathways have the potential to supply nitrate through  
 123 the riverbed to surface waters. The magnitude of  
 124 groundwater discharge into and through the river bed  
 125 has been shown to exhibit considerable spatial vari-  
 126 ability (Conant 2004; Kennedy et al. 2009b) and the  
 127 influence of different pathways of groundwater dis-  
 128 charge on nitrate and redox conditions in the river bed  
 129 is poorly understood (Poole et al. 2008). In shallow  
 130 sediments, patterns in pore water chemistry will also  
 131 be influenced by hyporheic exchange flows as defined  
 132 by Harvey et al. (1996) to be the process by which  
 133 water infiltrates the surface and returns to the surface  
 134 over small distances, including intra-meander flows  
 135 (Tonina and Buffington 2009; Boano et al. 2010)  
 136 which enable longitudinal exchange between surface  
 137 waters and pore waters in the river bed. Thus patterns



138 in pore water chemistry in the riverbed will arise from a  
 139 combination of mixing of these different vertical and  
 140 horizontal pathways of water, and in the case of reactive  
 141 solutes such as nitrate, patterns will also change along  
 142 flow pathways in response to biogeochemical transfor-  
 143 mation. Quantifying reach-scale spatial patterns of  
 144 redox-sensitive species (electron donors and acceptors)  
 145 in pore waters is important owing to its influence on the  
 146 spatial distribution of biogeochemical processes within  
 147 the streambed (Dahm et al. 1998; Marzadri et al. 2011,  
 148 2012). Additionally, concomitant observations of con-  
 149 servative chemical species together with redox species  
 150 offers further insights into sources of water, for example,  
 151 by aiding identification of preferential discharge loca-  
 152 tions in the river bed (Stelzer and Bartsch 2012).

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

166 Lautz and Fanelli (2008) used a statistical approach,  
 167 Principal Component Analysis (PCA), to reduce data  
 168 dimensionality and thereby characterise the redox status  
 169 of streambed pore water samples around log jams in a  
 170 restored river reach. We adopt a similar approach in this  
 171 study, using PCA to identify key patterns in streambed  
 172 solute chemistry in a 200 m gaining river reach. For this  
 173 research we have used a piezometer network that is not  
 174 only spatially distributed across the reach, and also  
 175 installed to 1 m depth in order to capture patterns in pore  
 176 water chemistry and hydrological flux that are due to the  
 177 combined effects of different groundwater-surface  
 178 water exchange mechanisms (for example, hyporheic  
 179 exchange flow, upwelling groundwater and lateral  
 180 subsurface flows from riparian areas). We have previ-  
 181 ously examined the spatial variability in water fluxes at  
 182 the reach over the same time period as this study to  
 183 provide a hydrological conceptualisation for our site  
 184 (Binley et al. 2013). Our experiments revealed a  
 185 localised connectivity to regional groundwater (i.e. a  
 186 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 cam-  
 paigns 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 ground-  
 water 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

230 Area of Conservation (SAC), which is a tributary of the  
 231 River Eden in northwest England, nested within a 5 km  
 232 stretch of the wider Leith catchment (total 54 km<sup>2</sup>). The  
 233 river is groundwater-fed (Seymour et al. 2008) from the  
 234 Aeolian Penrith Sandstone that is a major aquifer  
 235 forming part of the Permo-Triassic Sandstone (Allen  
 236 et al. 1997). The sandstone bedrock extends at least  
 237 50 m beneath the channel and is overlain by unconsol-  
 238 idated glacio-fluvial sands and silts generally 1–2 m  
 239 deep. The reach meanders within a narrow floodplain of  
 240 permanent grassland (sheep and cattle) delineated by  
 241 steep slopes. The river bed is characterised by sand,  
 242 gravel and cobbles with riffle-pool sequences. Baseflow  
 243 during summer months is typically around 0.1 m<sup>3</sup> s<sup>-1</sup>,  
 244 and shows a significant but delayed response to rainfall  
 245 events (Kaeser et al. 2009).

## 246 Field methods

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

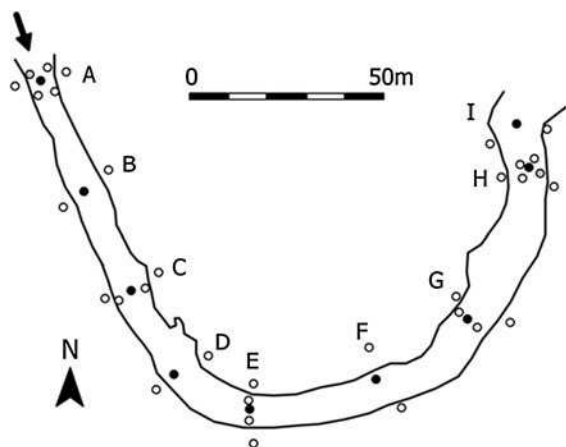
## 272 Pore water sampling

273 Pore water samples (40 mL) were collected from  
 274 selected multi-level samplers (all depths) during three

275 sampling campaigns (29th June–2nd July, 3rd–6th  
 276 August and 7th–11th September) in 2009, and a  
 277 further three sampling campaigns in 2010 (5th–8th  
 278 July, 3rd–7th August and 6th–9th September). Piez-  
 279 ometers used for multi-level pore water sampling in  
 280 2009 are denoted by closed circles in Fig. 1. High river  
 281 flows over winter 2009/10 damaged some piezometers  
 282 at clusters A and H, and so alternative piezometers,  
 283 denoted by grey circles on Fig. 1, were sampled for  
 284 pore water in 2010. A sample of surface water was also  
 285 collected at each piezometer on each sampling  
 286 occasion to establish whether there was any marked  
 287 variability in surface water chemistry through the  
 288 reach (for example due to inputs from preferential  
 289 lateral or vertical discharge).

290 Pore water samples were extracted from the multi-  
 291 sampler using a syringe and plastic tubing, which were  
 292 flushed with pore water prior to collection. Samples  
 293 for anion and cation analysis (NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup>, SO<sub>4</sub><sup>2-</sup>,  
 294 Cl<sup>-</sup>) were filtered (0.45 µm surfactant-free cellulose  
 295 acetate membrane) in the field and stored in pre-  
 296 washed polycarbonate bottles prior to analysis. Sam-  
 297 ples for Fe and Mn analysis were filtered (as above)  
 298 into pre-washed polyethylene tubes and acidified with  
 299 HNO<sub>3</sub> (final concentration of 5 % acid) in the field. All  
 300 samples were stored on ice at 5 °C until transfer to the  
 301 laboratory and subsequent analysis within 48 h of  
 302 collection. Field and travel blanks were collected for  
 303 all analytes during each campaign.

304 In 2010 some additional water chemistry parameters  
 305 (dissolved organic carbon and reduced Fe) were added  
 306 to the sampling campaign to help improve our under-  
 307 standing of the potential controls on nitrogen transfor-  
 308 mations in the river reach. Samples for analysis of  
 309 dissolved organic carbon were filtered (as above) into  
 310 acid-washed amber glass bottles and acidified to pH <2  
 311 with HCl in the field. Measurement of Fe(II) was  
 312 performed using the buffered 1,10-phenanthroline  
 313 method, adapted from (APHA-AWWA-WPCF 1976;  
 314 Grace et al. 2010) where 1 mL of pore water was filtered  
 315 through an oxygen free nitrogen-flushed 0.45 µm filter  
 316 into 4 mL of preservative solution and stored in the dark  
 317 until analysis by UV-spectrophotometry (Evolution 100  
 318 Thermo Scientific spectrophotometer). Oxygen con-  
 319 centration of pore water was measured for each multi-  
 320 level sampler using a calibrated, fast response oxygen  
 321 electrode (50 µm electrode with stainless steel protec-  
 322 tive guard) connected to an in-line amplifier that was, in  
 323 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

324 determined that the amount of oxygen contamination  
 325 that occurred during sample collection and measure-  
 326 ment was approximately  $0.4 \text{ mg L}^{-1}$ , and corrected all  
 327 measured oxygen concentrations accordingly. The limit  
 328 of detection (LOD) of the oxygen electrode was  $0.1 \text{ mg}$   
 329  $\text{L}^{-1}$ ; precision of repeat measurements of samples was  
 330 better than 5 %.

### 331 Hydraulic head and flux measurements

332 Head levels in the piezometer network (all circles in  
 333 Fig. 1) were manually dipped during each field  
 334 campaign using an electronic dip meter, and the local  
 335 stream water level adjacent to each piezometer was  
 336 also measured to enable calculation of vertical head  
 337 gradient and to help assess the patterns in subsurface  
 338 flow direction through the reach. Saturated hydraulic  
 339 conductivity ( $K_{\text{sat}}$ ) was measured using falling and  
 340 rising slug tests in piezometers at 100 cm depth in  
 341 2009, and 20, 50 and 100 cm depth in 2010. Vertical  
 342 water fluxes were calculated using Darcy's Law with  
 343 the  $K_{\text{sat}}$  measured at 100 cm depth in 2009, and the  
 344 harmonic mean of  $K_{\text{sat}}$  calculated from the measure-  
 345 ments taken at 20, 50 and 100 cm depth in 2010 (see  
 346 Binley et al. 2013 for full description). For the  
 347 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  $0.04 \text{ mg N}$   
 $\text{L}^{-1} \pm 3 \%$  for nitrate,  $0.03 \text{ mg N L}^{-1} \pm 8 \%$  for  
 ammonium,  $0.3 \text{ mg S L}^{-1} \pm 3 \%$  for sulphate and  
 $0.7 \text{ mg L}^{-1} \pm 2 \%$  for chloride. In 2009 Fe samples  
 were analysed using ICP-OES (Varian Vista-Pro) with  
 LOD and precision of  $0.01 \text{ mg L}^{-1} \pm 1 \%$ . The LOD of  
 the measurement of Fe(II) was  $0.04 \text{ mg L}^{-1}$  due to the  
 dilution associated with sample preservation; precision  
 was  $\pm 1 \%$ . Dissolved organic carbon analysis was by  
 thermal oxidation (Thermalox TOC/TN Analyzer) using  
 the non-purgeable organic carbon (NPOC) method.  
 LOD and precision were  $1.0 \text{ mg L}^{-1} \pm 8 \%$ .

### Data analysis

Our goal was to describe the variability in geochem-  
 istry 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. Accord-  
 ingly, 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 envi-  
 ronmental 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 associ-  
 ated 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  
 $\text{NO}_3^-$ ,  $\text{NH}_4^+$ ,  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$  and total dissolved Fe as input  
 variables for 2009, and the extended set of variables  
 which included  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ ,  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ , Fe(II),  
 dissolved organic carbon and oxygen concentration

392 for analysis of the pore water samples collected in 2010.  
 393 All variables were log transformed, then inter-correlation  
 394 between variables was examined to check for  
 395 extreme multi-collinearity and singularity. The Kaiser–  
 396 Meyer–Olkin measure of sampling adequacy ( $KMO >$   
 397  $0.5$ ) and Bartlett’s test of sphericity were also performed  
 398 for each analysis. Eigenvalues of principal components  
 399 represent the data variance summarized by each prin-  
 400 cipal component. The number of principal components  
 401 to be retained for each analysis was determined by  
 402 examination of the scree plot in conjunction with use of  
 403 Kaiser’s criterion of retaining eigenvalues  $>1$ .

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

## 420 Results

421 Our study was aimed at capturing spatial variations in  
 422 porewater chemistry under baseflow conditions. How-  
 423 ever, the summer of 2009 proved to be challenging in  
 424 this regard due to high-intensity rainfall events in mid  
 425 and late July and the start of September which resulted  
 426 in significant changes in river discharge (Fig. 2a). On  
 427 each occasion the increase in stage height in the River  
 428 Leith caused localised inundation of the floodplain,  
 429 and exceeded the upper limit of the EA gauging station  
 430 at Cliburn to accurately record discharge ( $5 \text{ m}^3 \text{ s}^{-1}$ ).  
 431 The peak discharge values of c.  $14 \text{ m}^3 \text{ s}^{-1}$  recorded on  
 432 18th July and 3rd September must therefore be viewed  
 433 as an indication of high flow conditions ( $>Q_5$ ). As a  
 434 result of these storm events, pore water sampling  
 435 during July 2009 was undertaken during baseflow  
 436 conditions ( $0.1 \text{ m}^3 \text{ s}^{-1}$ ; c. 90 percentile of flow), but  
 437 samples during August and September campaigns

were collected on the recession limb of the preceding 438  
 storm hydrographs when river discharge was  $0.7$  and 439  
 $0.9 \text{ m}^3 \text{ s}^{-1}$  (corresponding to c.  $Q_{20}$ ). 440

In contrast, river discharge was far less variable 441  
 during summer 2010 in comparison to summer 2009, 442  
 and baseflow conditions (defined here as  $<Q_{90}$ ) were 443  
 experienced for much of the summer (Fig. 2b), with 444  
 the highest discharge of  $1.4 \text{ m}^3 \text{ s}^{-1}$  recorded in 445  
 response to a storm event in late July 2010. Conse- 446  
 quently, the three sampling campaigns were under- 447  
 taken during baseflow conditions, at  $0.06$ ,  $0.1$  and  $0.08$  448  
 $\text{m}^3 \text{ s}^{-1}$  respectively (all  $<Q_{90}$ ). 449

## Surface and pore water chemistry 450

451 During our sampling campaign in July 2009 and all 452  
 campaigns in 2010, chloride and sulphate concentra- 453  
 tions were significantly higher in the surface water 454  
 compared to the streambed (Mann–Whitney  $U$ , 455  
 Table 1). During the sampling campaigns in August 456  
 and September 2009, however, concentrations of 457  
 chloride and sulphate had decreased in the river water 458  
 such that there was little or no significant difference in 459  
 chloride and sulphate concentrations between surface 460  
 and pore waters. In contrast, nitrate concentrations in 461  
 streambed pore waters were generally higher than 462  
 river water, although these differences were only 463  
 statistically significant in July 2009, July 2010 and 464  
 August 2009 (Table 1).

465 Surface and streambed pore water concentrations of 466  
 dissolved organic carbon and oxygen were analysed in 467  
 2010 (Table 1). Unsurprisingly, oxygen concentra- 468  
 tions in surface waters were significantly higher than 469  
 streambed pore water on all sampling occasions 470  
 (Table 1); nevertheless streambed pore water was 471  
 generally oxic to  $1 \text{ m}$  depth, with mean pore water 472  
 concentrations of  $3.5$ ,  $3.6$  and  $2.7 \text{ mg L}^{-1}$  for July, 473  
 August and September 2010 sampling campaigns 474  
 respectively. Dissolved organic carbon concentrations 475  
 were similar in pore water and surface water, however, 476  
 the mean concentration (average of all depths) of 477  
 dissolved organic carbon concentration in streambed 478  
 pore water appeared to decline over the summer with 479  
 highest mean concentrations recorded in July 2010 480  
 ( $5.6 \text{ mg L}^{-1}$ ), intermediate concentrations in August 481  
 2010 ( $3.3 \text{ mg L}^{-1}$ ) and lowest concentrations 482  
 recorded in September 2010 ( $1.6 \text{ mg L}^{-1}$ ). Ammon- 483  
 ium and reduced Fe concentrations in surface waters 484



were low (generally  $<0.02$  and  $<0.05$   $\text{mg L}^{-1}$  as Fe(II), respectively), and the majority of streambed pore water samples also contained ammonium at  $<0.1$   $\text{mg L}^{-1}$  and Fe(II) at  $<0.2$   $\text{mg L}^{-1}$  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.

## 502 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 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

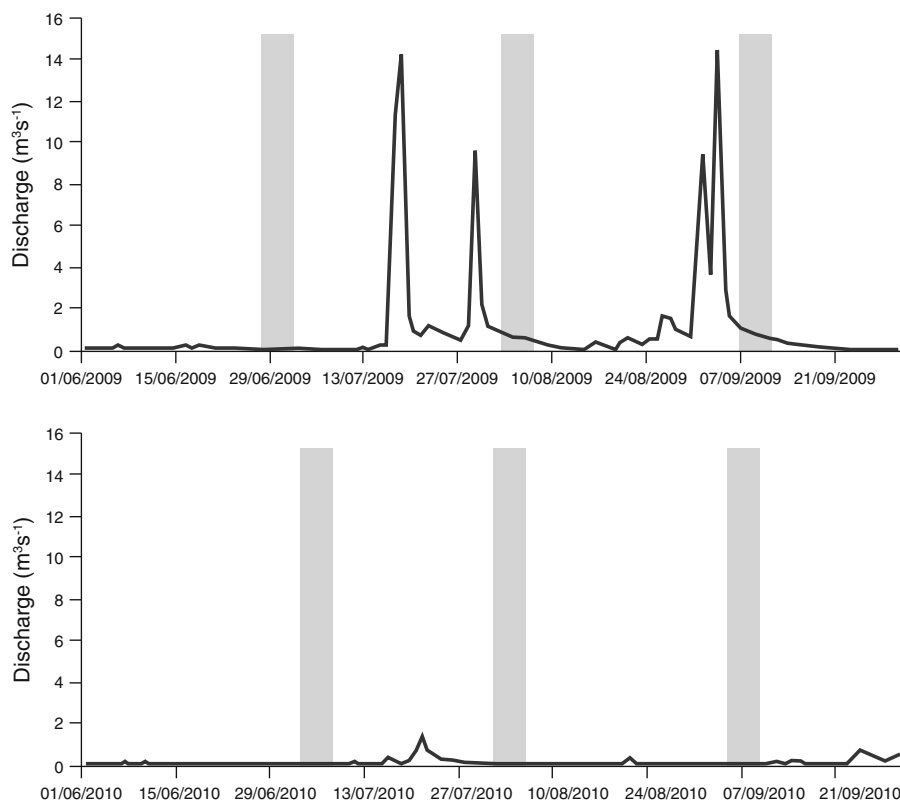
We performed PCA on the surface and pore water chemistry datasets for July, August and September 2010 separately. Each dataset comprised seven variables; iron (II), ammonium, chloride, sulphate, oxygen, dissolved organic carbon and nitrate concentrations. Two principal components together account for 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



574 be a conservative solute, and patterns in chloride  
 575 concentration in a riverbed and/or riparian setting are  
 576 generally due to the mixing of water from various  
 577 sources; for example due to mixing of surface and  
 578 ground water (Stelzer and Bartsch 2012; Pinay et al.  
 579 1998) or the mixing of subsurface of different  
 580 origins such as deep and shallow groundwater (Fle-  
 581 welling et al. 2012) In contrast to chloride, sulphate is  
 582 a redox-sensitive species, with oxidation of organic  
 583 matter by sulphate reduction reported in various  
 584 streambed settings (Lautz and Fanelli 2008; Hlavacova  
 585 et al. 2005; Morrice et al. 2000), although Krause  
 586 et al. (2011) suggest that reduced sulphur requires a  
 587 low redox potential that may not commonly be found  
 588 in the hyporheic zone. In the pore water of the River  
 589 Leith strong positive correlations between sulphate  
 590 and chloride concentration (log transformed data from  
 591 2009 to 2010,  $r = 0.7377$ ,  $p < 0.001$ ) indicate that  
 592 reach-scale patterns in sulphate concentration are  
 593 mainly related to mixing of different water sources  
 594 rather than to chemical transformations driven by  
 595 redox processes. The river bed appears to be generally  
 596 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 princi-  
 pal 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 longitudi-  
 nal reach-scale change in pore water chemistry is also

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**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 <sup>-1</sup> )			Sulphate-S (mg L <sup>-1</sup> )			Nitrate-N (mg L <sup>-1</sup> )			Dissolved organic carbon (mg L <sup>-1</sup> )		
	PW <sup>a</sup>	SW <sup>b</sup>	Sig. <sup>c</sup>	PW <sup>a</sup>	SW <sup>b</sup>	Sig. <sup>c</sup>	PW <sup>a</sup>	SW <sup>b</sup>	Sig. <sup>c</sup>	PW <sup>a</sup>	SW <sup>b</sup>	Sig. <sup>c</sup>
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 <sup>-1</sup> )			Fe(II) (mg L <sup>-1</sup> ) <sup>d</sup>			Ammonium-N (mg L <sup>-1</sup> )		
	PW <sup>a</sup>	SW <sup>b</sup>	Sig. <sup>c</sup>	PW <sup>a</sup>	SW <sup>b</sup>	Sig. <sup>c</sup>	PW <sup>a</sup>	SW <sup>b</sup>	Sig. <sup>c</sup>
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

<sup>a</sup> 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)

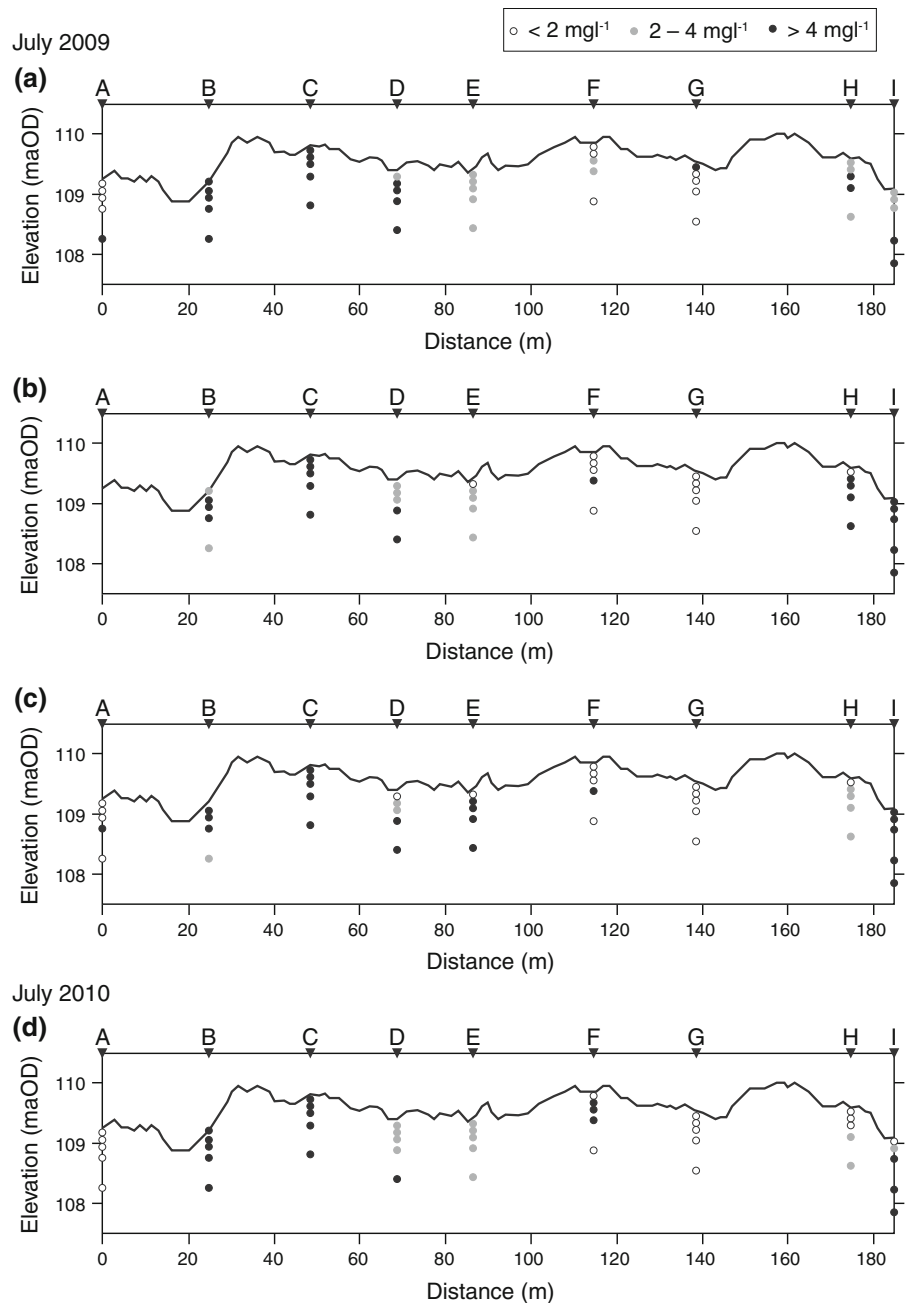
<sup>b</sup> SW is mean of all surface water samples collected along the reach at each piezometer cluster with standard error in parentheses (n = 8 in 2009 and n = 9 in 2010)

<sup>c</sup> Sig. is *p* value for Mann–Whitney *U* test \* indicates that the result is highly significant and the null hypothesis is rejected

<sup>d</sup> 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  $\text{mg L}^{-1}$ ) along the study reach **a** July 2009; **b** August 2009; **c** September 2009; **d** July 2010



620 highlighted in Fig. 4 by an increased ‘source function’  
 621 score in the upstream section which is focused around  
 622 piezometer cluster C. This high score is due to  
 623 elevated chloride and sulphate concentrations in pore  
 624 water in comparison to other areas of the reach,  
 625 suggestive of a different subsurface source of water.  
 626 Binley et al. (2013) used a survey of riverbed electrical  
 627 conductivity, combined with measurements of vertical  
 628 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,

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**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

638 will consider the importance of this region of prefer-  
639 ential discharge for nitrate supply to the reach, and  
640 examine the implications of our findings for nitrate  
641 supply in groundwater-fed river settings.

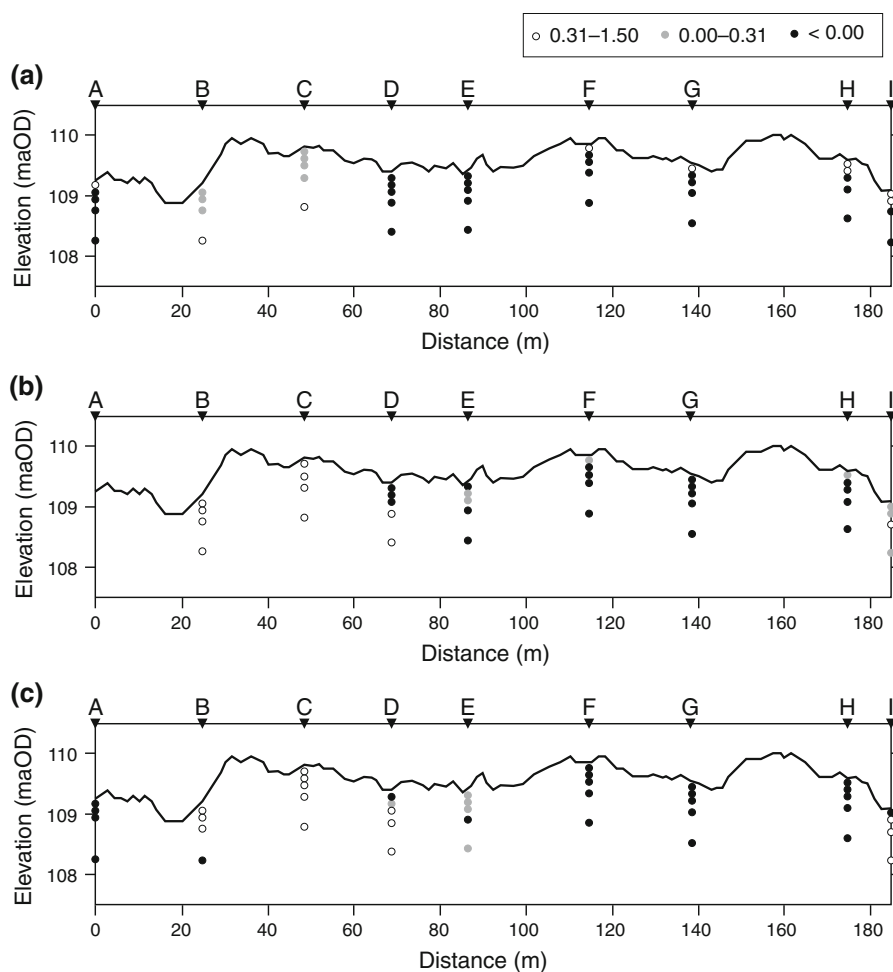
642 The variables that consistently load highly onto  
643 Factor 2 in 2009 and Factor 1 in 2010 are the redox-  
644 sensitive solutes, and products of organic matter  
645 decomposition processes; reduced iron and ammo-  
646 nium (Fig. 5). This principal component is therefore  
647 termed the 'redox function'. Pore water samples from  
648 two sites in the riverbed (A and G) have consistently  
649 high scores on the redox function during both years of  
650 our study, reflecting not only the reduced nature of the  
651 pore water collected at these locations, but also the  
652 inter-annual longevity of these redox conditions. In  
653 contrast two further sites (H and I) displayed high  
654 scores on the redox function during sampling cam-  
655 paigns undertaken in one season (2010 for H and 2009  
656 for I), but the reduced conditions were not replicated  
657 during both years of sampling. Lautz and Fanelli  
658 (2008) have also used principal components analysis  
659 to identify spatial patterns of redox sensitive solutes in  
660 the riverbed, and to distinguish between the redox  
661 status of streambed pore water types around a log dam.  
662 Here we use a similar approach to consider the  
663 implications of chemically reduced regions of the river  
664 bed for nitrate supply and transformation in a gaining  
665 reach of a groundwater-fed river.

666 Distribution of chemically reduced sites  
667 in the river bed

668 Three sites—A, G and H—consistently scored highly  
669 on our redox function in 2010. The data from Summer

2010 is the focus here, as we have the most complete  
670 chemical dataset for these sampling campaigns. 671  
672 Table 4 compares the chemical composition of pore  
673 water from sites A, G and H (identified by the PCA  
674 analysis as chemically reduced) with the composition  
675 of pore water from our riparian piezometers, and from  
676 the other in-stream piezometers. The patterns in pore  
677 water chemistry suggest that at sites A, G and H some  
678 of the electron acceptors in the pore water were  
679 reduced as a result of organic matter oxidation  
680 (Morris et al. 2000) as exemplified by significantly  
681 lower concentrations of nitrate and significantly  
682 higher concentrations of Fe(II) in the pore water at  
683 clusters A, G and H in comparison with other  
684 piezometer clusters and the riparian zone (Table 4).  
685 Mineralisation of organic matter could be occurring in  
686 the river bed itself at or near the point of sampling due,  
687 for example, to oxidation of buried (Stelzer and  
688 Bartsch 2012) or ingressed particulate organic mate-  
689 rial (Arango et al. 2007), however, analysis of  
690 sediment cores by loss on ignition provided no  
691 evidence of elevated particulate organic matter in  
692 these regions of the stream bed (data not shown).  
693 Alternatively, the chemical signature may arise from  
694 the decomposition of organic matter that is spatially  
695 (and potentially temporally) segregated from the point  
696 of sampling (Dahm et al. 1998). In the latter case the  
697 reactions may have occurred along a contributing  
698 hydrological pathway; for example a parcel of water,  
699 along with its chemical signature, has been transported  
700 to the river bed from a riparian zone or aquifer in  
701 which the organic carbon oxidation occurred. Under-  
702 standing the chemistry and hydrology together is  
703 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



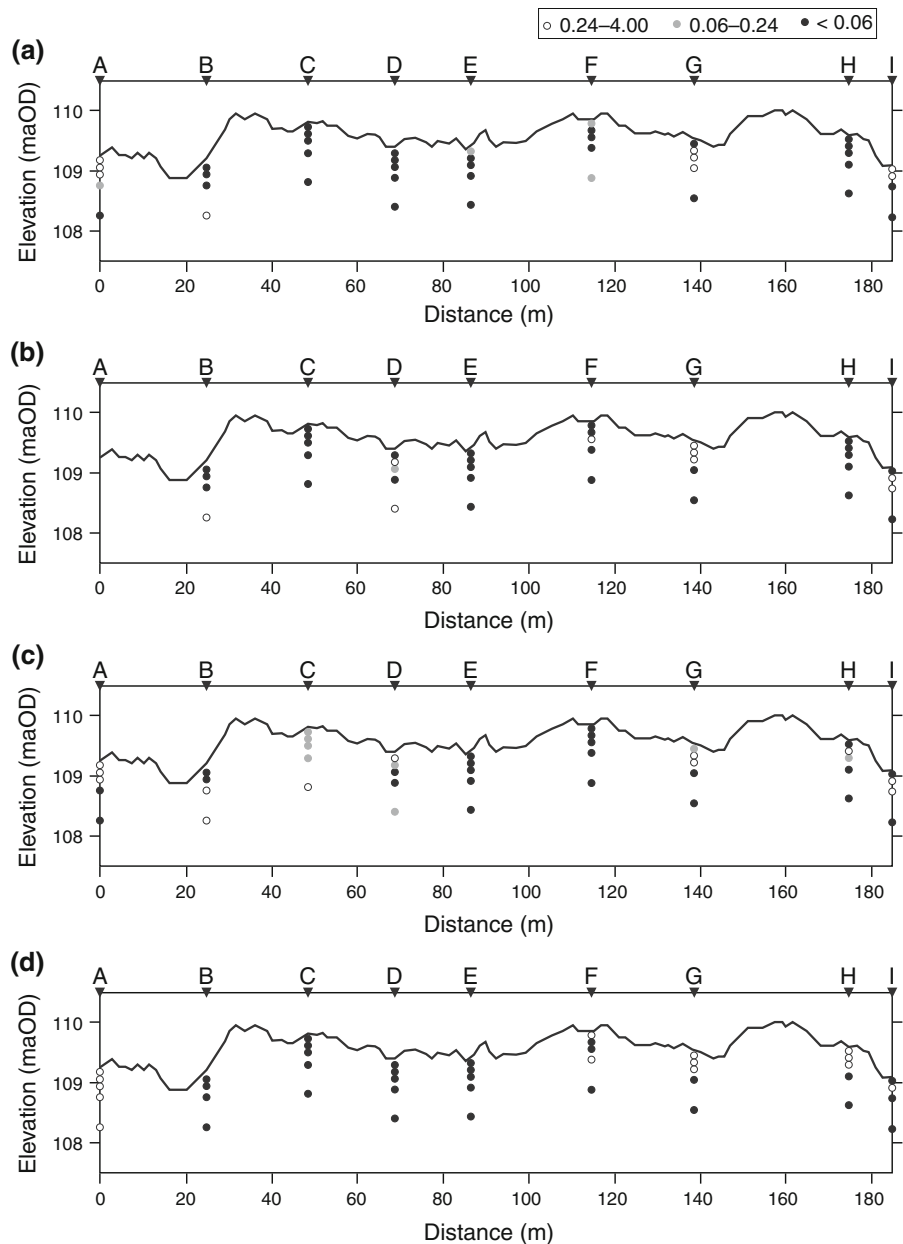
signature alone, a specific location in the river bed could be mis-interpreted as a ‘hot spot’ of biogeochemical reactivity, when in fact the organic matter processing may have taken place elsewhere, and at a different time.

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



740 processing, and therefore biogeochemical ‘hot spots’  
 741 with the ability to remove nitrate from subsurface flow  
 742 through heterotrophic and/or chemoautotrophic nitrate  
 743 reduction processes. Based on the data from the field  
 744 site, we cannot definitively distinguish between hyp-  
 745 orheic exchange flows and lateral riparian flows as the  
 746 dominant hydrological pathway here, and given the  
 747 pool-riffle structures around sites A and G to I it is  
 748 probable that both are occurring. These sites highlight  
 749 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 <sup>-1</sup> )					Mann-Whitney <i>U</i>	
	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*

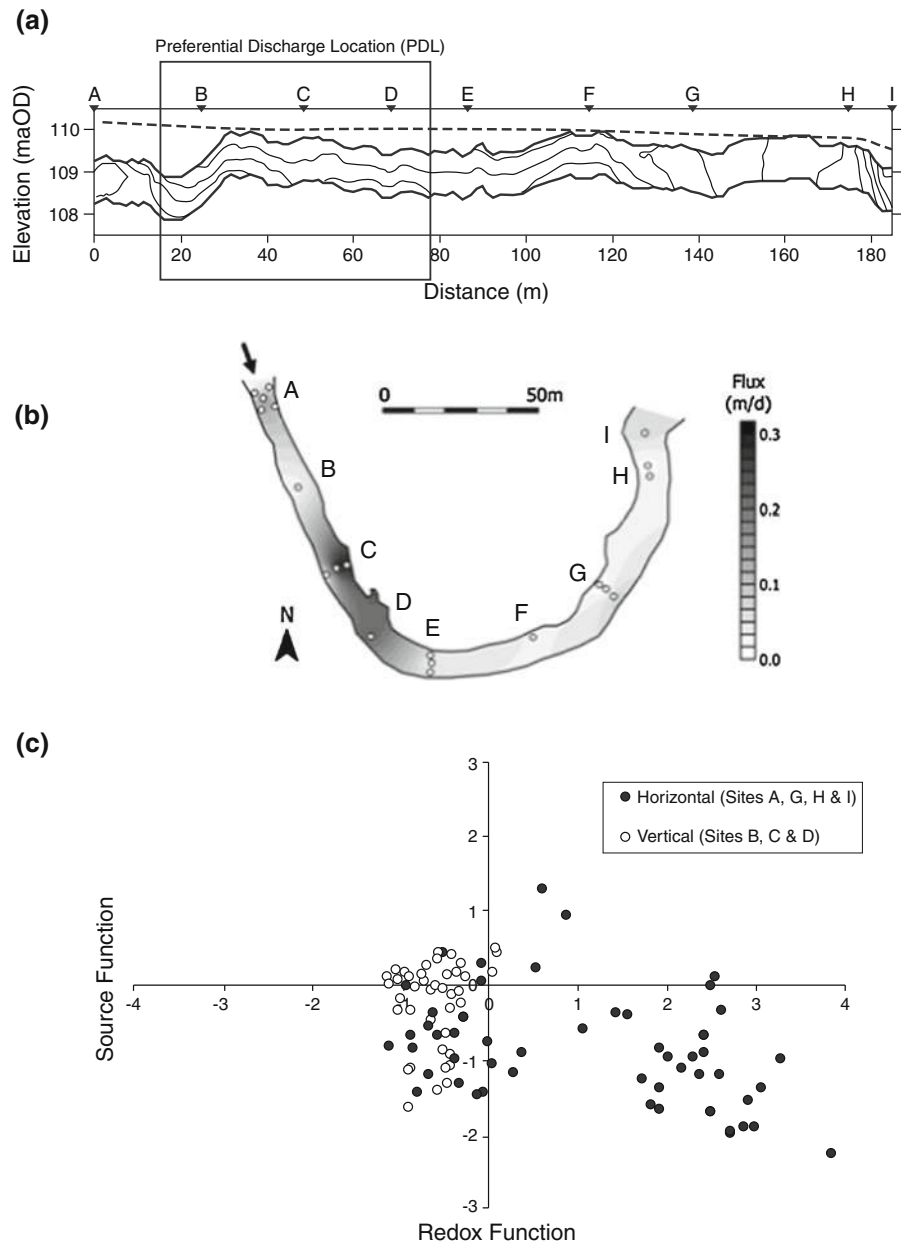
\* Significant at <0.05 level; Numbers in parentheses are Standard Error of n = 15 samples (all depths and all months combined)

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

775 There is a statistically significant positive correla-  
 776 tion (n = 6, r = 0.936, p = 0.006) between surface

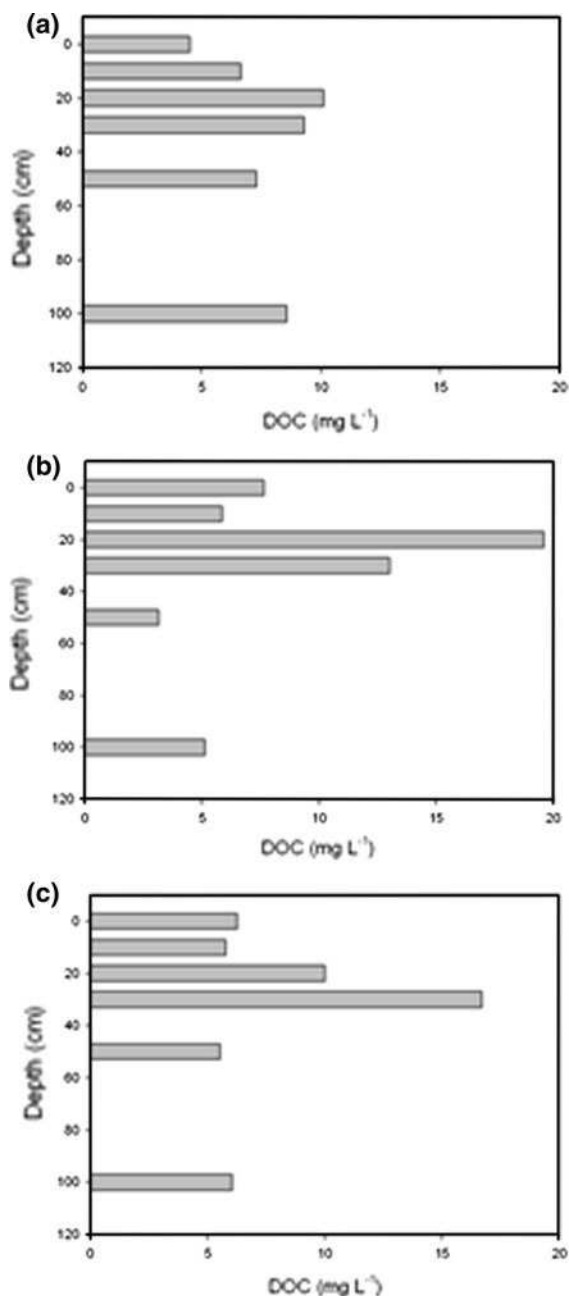
777 water discharge at the time of sampling, and the  
 778 variance associated with the 'source' factor of the  
 779 PCA analysis suggesting that reach-scale patterns in  
 780 sulphate, chloride and nitrate in pore water may be  
 781 explained by differences in discharge between our  
 782 sampling campaigns. The response of nitrate to  
 783 changes in river discharge is of particular interest in  
 784 this study because nitrate changes from being highly,  
 785 negatively loaded onto the redox function under  
 786 baseflow conditions, to strongly positively loaded  
 787 onto the source function under high discharge condi-  
 788 tions (Table 2 and 3). These data suggest that under  
 789 baseflow conditions, distinct patterns in nitrate con-  
 790 centration are characterised by areas that are well  
 791 supplied with electron sources to facilitate reduction.  
 792 We demonstrated earlier (and in Binley et al. 2013)  
 793 that these areas of the streambed are associated with  
 794 horizontal hydrological flows. Following high dis-  
 795 charge 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



796 nitrate concentration in the streambed are controlled  
 797 chiefly by the supply of nitrate-rich groundwater in  
 798 areas of preferential discharge. To support this anal-  
 799 ysis further we can consider the pore water concen-  
 800 trations of chloride, sulphate and nitrate at cluster C  
 801 during our sampling campaigns (Table 5). High  
 802 concentrations of chloride, sulphate and nitrate were  
 803 recorded in September 2009, intermediate concen-  
 804 trations were recorded in August 2009 and the lowest  
 805 concentrations were found in July 2009 (Table 5),

806 however there were no significant differences in pore  
 807 water chemistry between monthly sampling cam-  
 808 paigns in 2010 (data not shown). The significantly  
 809 elevated concentration of chloride, sulphate and  
 810 nitrate at site C following the high discharge associ-  
 811 ated with the storm events of 29th July and 3rd  
 812 September 2009 suggests that groundwater has a  
 813 major influence on streambed pore water concen-  
 814 trations of solutes during and following significant  
 815 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

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

818 We evaluated above the importance of hydrological  
819 controls for patterns of pore water chemistry in the  
820 streambed. We sought to understand the role that

**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 <sup>-1</sup> )			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

<sup>a</sup> Numbers in parentheses are Standard Error of n = 5 samples (all depths)

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<sub>3</sub><sup>-</sup> or NH<sub>4</sub><sup>+</sup>) 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<sup>2</sup>) 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  $1.61 \pm 0.1 \text{ g m}^{-2} \text{ day}^{-1}$  (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  $2.0 \pm 0.48 \text{ g m}^{-2}$



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

	Nitrate <sub>N<sub>SW</sub></sub> (mg L <sup>-1</sup> )	Q <sub>SW</sub> (m <sup>3</sup> s <sup>-1</sup> )	f <sub>N<sub>SW</sub></sub> (kg day <sup>-1</sup> )	Nitrate <sub>N<sub>100</sub></sub> (mg L <sup>-1</sup> )	Q <sub>RB</sub> (m day <sup>-1</sup> )	f <sub>N<sub>RB</sub></sub> (kg day <sup>-1</sup> )	f <sub>N<sub>RB</sub></sub> /f <sub>N<sub>SW</sub></sub> (%)
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

Nitrate<sub>N<sub>SW</sub></sub> is the concentration of nitrate in surface water at site C; Q<sub>SW</sub> is the discharge at the time of sampling; f<sub>N<sub>SW</sub></sub> is the nitrate flux through the reach in surface water; Nitrate<sub>N<sub>100</sub></sub> is the concentration of nitrate in the pore water at 100 cm depth; Q<sub>RB</sub> is the upwelling Darcy flux of water through the river bed; f<sub>N<sub>RB</sub></sub> is the nitrate flux through the river bed; f<sub>N<sub>RB</sub></sub>/f<sub>N<sub>SW</sub></sub> is the relative magnitude of nitrate flux through the river bed to flux through the reach in surface water expressed as a percentage

858 day<sup>-1</sup> reported for nine different gaining reaches in  
859 agricultural watershed of the US (Kennedy et al.  
860 2009b). Whilst nitrate concentration in groundwater is  
861 in the upper range reported in the literature for  
862 agricultural watersheds, the upwelling water flux  
863 associated with our preferential discharge falls in the  
864 mid-range reported for similar studies of permeable,  
865 gaining reaches (c.f. 0.25 m day<sup>-1</sup> for our study with  
866 0.41–0.5 m day<sup>-1</sup> for Kennedy et al. (2009b) and Cey  
867 et al. (1998)).

868 In order to determine the relative importance of the  
869 area of preferential discharge for nitrate and supply to  
870 the reach, the upwelling flux in the preferential  
871 discharge area is expressed as a proportion of the  
872 nitrogen species moving through the reach in surface  
873 water (Table 6). Our analysis shows that under  
874 baseflow conditions, the preferential discharge path-  
875 way is an important source of nitrate to the river,  
876 contributing 4–9 % of the total nitrate flux in surface  
877 water (henceforth termed nitrate flux contribution).  
878 When samples were collected on the recession limb of  
879 a high discharge event (as for August and September  
880 2009), however, the nitrate flux contribution is only  
881 0.4–0.5 %. These analyses assume no net removal of  
882 nitrate as groundwater travels up through the oxic  
883 streambed in the area of preferential discharge, despite  
884 a travel time of c. 3 days, and this is supported by  
885 nitrate porewater profiles that reveal no increase in  
886 nitrate concentration with depth. Such profiles may  
887 arise due to unfavourable redox conditions for nitrate  
888 removal; a balance of nitrate removal and production  
889 along the upwelling pathway; or because the stream-  
890 bed is characterised by a low Damkohler number (the  
891 ratio of the timescale for transport to the timescale for

reaction). A companion paper, which reports in situ  
892 reaction rates in the river bed using stable isotope  
893 techniques, will explore the relative importance of  
894 transport and reaction for nitrate export in this oxic,  
895 nitrate-rich sandy streambed.  
896

## 897 Conclusions

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

916 Antecedent conditions appear to control the pattern  
917 of nitrate concentration in porewater according to river  
918 discharge. During period of stable baseflow (< Q<sub>90</sub>),  
919 spatial variation in nitrate along the reach reflects  
920 redox conditions at the site. Low nitrate concentrations  
921 are associated with elevated Fe(II) and dissolved  
922 organic carbon (DOC), and low oxygen conditions;

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

931 Paradoxically it is under baseflow conditions that  
932 this preferential discharge location is demonstrably  
933 important for nitrate transport to the shallow stream-  
934 bed, comprising 4–9 % of total nitrate transported  
935 through the reach in surface water. Following summer  
936 storm events river discharge increases by an order of  
937 magnitude and therefore fluxes of nitrate through  
938 surface water are greatly increased, consequently the  
939 preferential discharge location contributes much less  
940 nitrate to the reach on a proportional basis under these  
941 conditions.

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

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959 Environment Agency information © Environment Agency and  
960 database right.

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Query	Details Required	Author's Response
AQ1	Please confirm the inserted city name is correct and amend if necessary.	
AQ2	Reference citation 'Rokström et al. 2009' has been changed to 'Rockstrom et al. 2009' so that it matches with the list, Kindly check and confirm.	
AQ3	References 'Seymour et al. 2008 and Field 2000' are cited in text but not provided in the reference list. Please provide references in the list or delete these citations.	
AQ4	Please provide the part figure d in Fig. 4 or delete rom the caption	