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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 ($<Q_{90}$) 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.</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^{-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).

3 Interpreting spatial patterns in redox and coupled 4 water–nitrogen fluxes in the streambed of a gaining 5 river reach

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2 beds are multi-dimensional, including lateral hypor-
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10 ter-fed rivers has the potential to supply significant
11 quantities of nitrate through the riverbed to surface
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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). 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 statu-
 99 s’ 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 km²). 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 m³ s⁻¹,
 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 (NO₃⁻, NH₄⁺, SO₄²⁻,
 294 Cl⁻) 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 HNO₃ (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

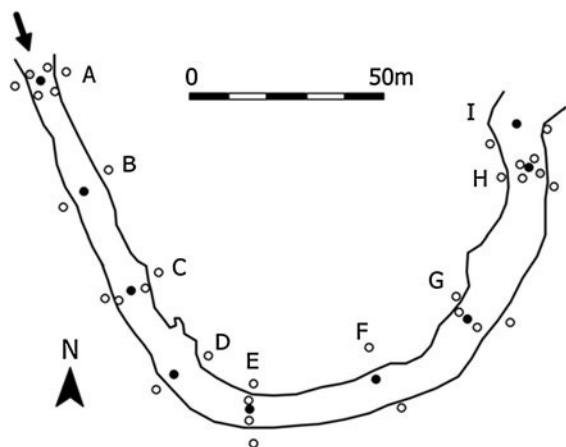


Fig. 1 Plan view of the field site and bed topography surveyed July 2010. River flow is from left to right. The circles show the locations of piezometers clusters (A–I) used to measure hydraulic head and saturated hydraulic conductivity in 2009 and 2010. The black circles show locations of piezometers 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 mg L^{-1} , and corrected all
 327 measured oxygen concentrations accordingly. The limit
 328 of detection (LOD) of the oxygen electrode was 0.1 mg
 329 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_{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_{sat} measured at 100 cm depth in 2009, and the
 344 harmonic mean of K_{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 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 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
 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

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
 storm hydrographs when river discharge was 0.7 and
 $0.9 \text{ m}^3 \text{ s}^{-1}$ (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 $1.4 \text{ m}^3 \text{ s}^{-1}$ recorded in
 response to a storm event in late July 2010. Conse-
 quently, the three sampling campaigns were under-
 taken during baseflow conditions, at 0.06 , 0.1 and 0.08
 $\text{m}^3 \text{ s}^{-1}$ respectively (all $<Q_{90}$).

Surface and pore water chemistry

During our sampling campaign in July 2009 and all
 campaigns in 2010, chloride and sulphate concentra-
 tions 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 concentra-
 tions 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}). Ammo-
 nium 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.

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

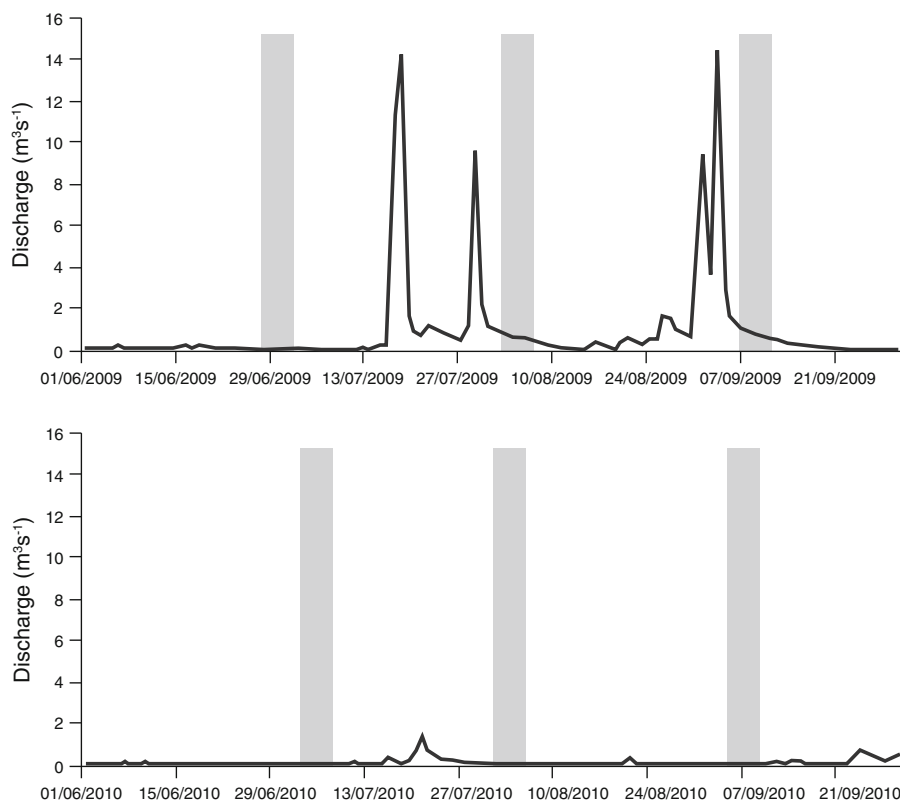
We performed PCA on the surface and pore water chemistry datasets for July, August and September 2010 separately. Each dataset comprised seven variables; iron (II), ammonium, chloride, sulphate, oxygen, dissolved organic carbon and nitrate concentrations. Two principal components together account for 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 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 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 ⁻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)											
	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	nd	nd	nd	0.3 (0.8)	0.2 (0.0)	0.696	0.2 (0.0)	0.696	0.09(0.02)	0.04(0.00)	0.709	0.709
Aug 2009	nd	nd	nd	0.1 (0.1)	0.01(0.0)	0.494	0.01(0.0)	0.494	0.09(0.02)	0.03(0.01)	0.189	0.189
Sep 2009	nd	nd	nd	0.6 (0.3)	0.01(0.01)	0.121	0.01(0.01)	0.121	0.04(0.01)	0.02(0.00)	0.388	0.388
July 2010	3.5(0.4)	16.0 (1.4)	0.000*	0.7 (0.2)	0.10(0.01)	0.887	0.10(0.01)	0.887	0.06(0.17)	0.02(0.00)	0.936	0.936
Aug 2010	3.6(0.5)	15.6 (0.8)	0.000*	0.8 (0.2)	0.04(0.01)	0.213	0.04(0.01)	0.213	0.11(0.25)	0.50(0.01)	0.318	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)	0.722	0.05(0.02)	0.01(0.00)	0.082	0.082
	Ammonium-N (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

^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)

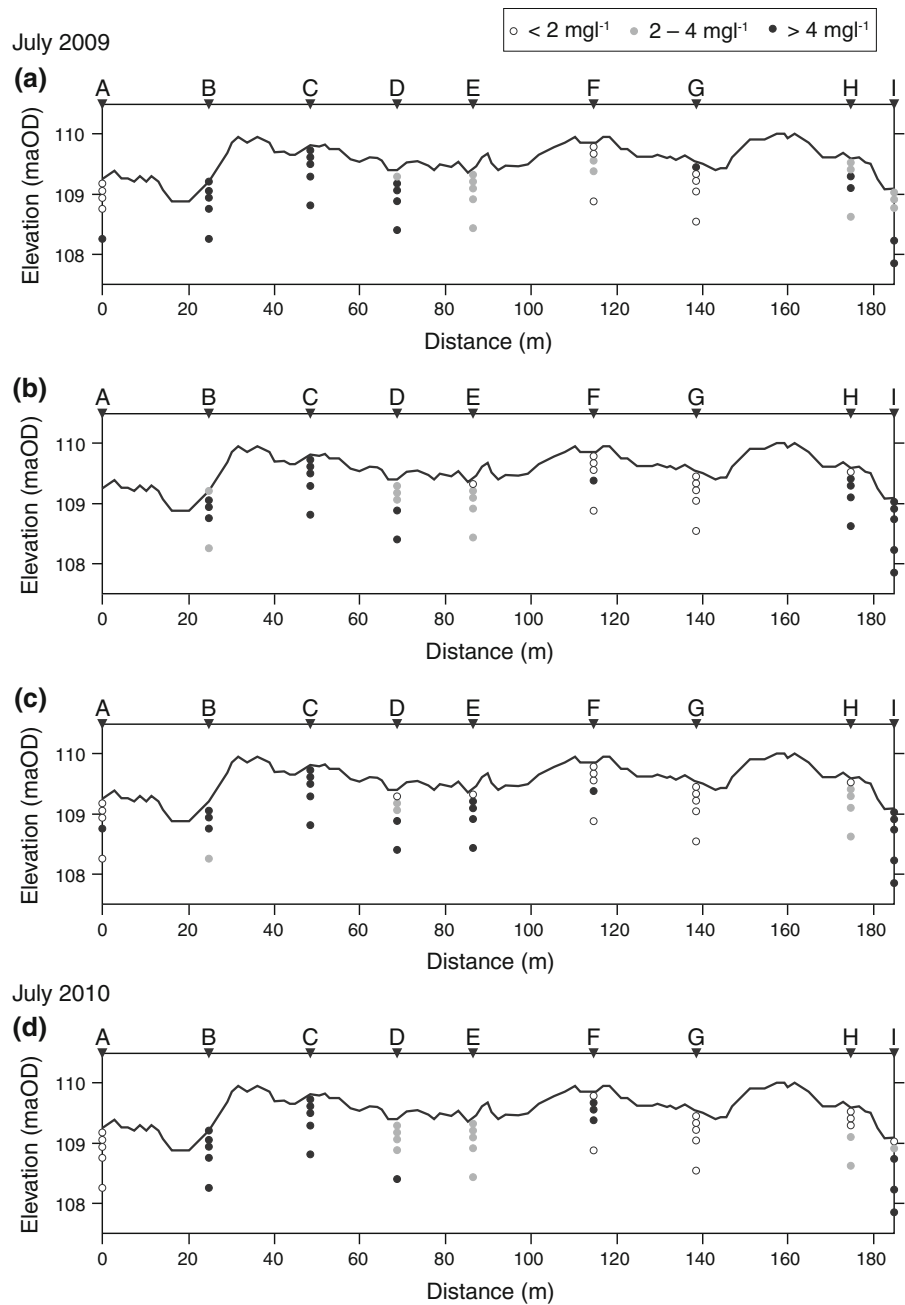
^b SW is mean of all surface water samples collected along the reach at each piezometer cluster with standard error in parentheses (n = 8 in 2009 and n = 9 in 2010)

^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



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- 670
 639 ential discharge for nitrate supply to the reach, and 671
 640 examine the implications of our findings for nitrate 672
 641 supply in groundwater-fed river settings. 673

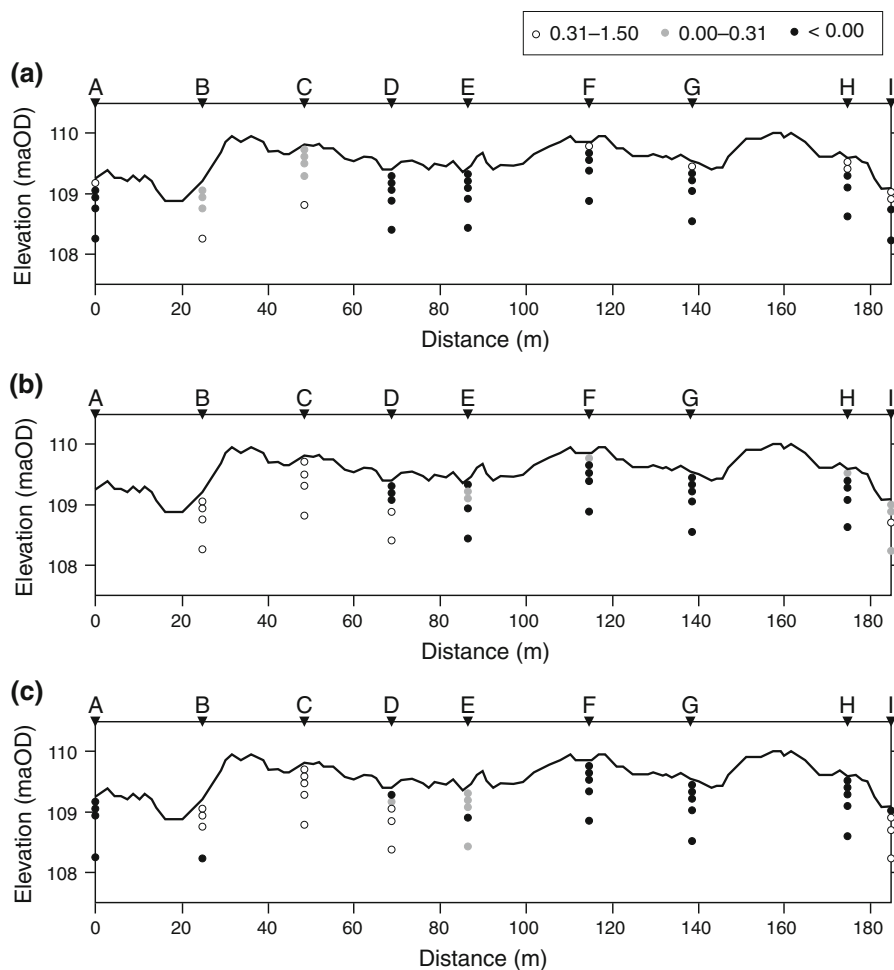
642 The variables that consistently load highly onto 674
 643 Factor 2 in 2009 and Factor 1 in 2010 are the redox- 675
 644 sensitive solutes, and products of organic matter 676
 645 decomposition processes; reduced iron and ammo- 677
 646 nium (Fig. 5). This principal component is therefore 678
 647 termed the 'redox function'. Pore water samples from 679
 648 two sites in the riverbed (A and G) have consistently 680
 649 high scores on the redox function during both years of 681
 650 our study, reflecting not only the reduced nature of the 682
 651 pore water collected at these locations, but also the 683
 652 inter-annual longevity of these redox conditions. In 684
 653 contrast two further sites (H and I) displayed high 685
 654 scores on the redox function during sampling cam- 686
 655 paigns undertaken in one season (2010 for H and 2009 687
 656 for I), but the reduced conditions were not replicated 688
 657 during both years of sampling. Lautz and Fanelli 689
 658 (2008) have also used principal components analysis 690
 659 to identify spatial patterns of redox sensitive solutes in 691
 660 the riverbed, and to distinguish between the redox 692
 661 status of streambed pore water types around a log dam. 693
 662 Here we use a similar approach to consider the 694
 663 implications of chemically reduced regions of the river 695
 664 bed for nitrate supply and transformation in a gaining 696
 665 reach of a groundwater-fed river. 697

666 Distribution of chemically reduced sites 698
 667 in the river bed 699

668 Three sites—A, G and H—consistently scored highly 700
 669 on our redox function in 2010. The data from Summer 701

2010 is the focus here, as we have the most complete 702
 chemical dataset for these sampling campaigns. 703
 Table 4 compares the chemical composition of pore 704
 water from sites A, G and H (identified by the PCA 705
 analysis as chemically reduced) with the composition 706
 of pore water from our riparian piezometers, and from 707
 the other in-stream piezometers. The patterns in pore 708
 water chemistry suggest that at sites A, G and H some 709
 of the electron acceptors in the pore water were 710
 reduced as a result of organic matter oxidation 711
 (Morrice et al. 2000) as exemplified by significantly 712
 lower concentrations of nitrate and significantly 713
 higher concentrations of Fe(II) in the pore water at 714
 clusters A, G and H in comparison with other 715
 piezometer clusters and the riparian zone (Table 4). 716
 Mineralisation of organic matter could be occurring in 717
 the river bed itself at or near the point of sampling due, 718
 for example, to oxidation of buried (Stelzer and 719
 Bartsch 2012) or ingressed particulate organic mate- 720
 rial (Arango et al. 2007), however, analysis of 721
 sediment cores by loss on ignition provided no 722
 evidence of elevated particulate organic matter in 723
 these regions of the stream bed (data not shown). 724
 Alternatively, the chemical signature may arise from 725
 the decomposition of organic matter that is spatially 726
 (and potentially temporally) segregated from the point 727
 of sampling (Dahm et al. 1998). In the latter case the 728
 reactions may have occurred along a contributing 729
 hydrological pathway; for example a parcel of water, 730
 along with its chemical signature, has been transported 731
 to the river bed from a riparian zone or aquifer in 732
 which the organic carbon oxidation occurred. Under- 733
 standing the chemistry and hydrology together is 734
 important because, on the basis of the chemical 735

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



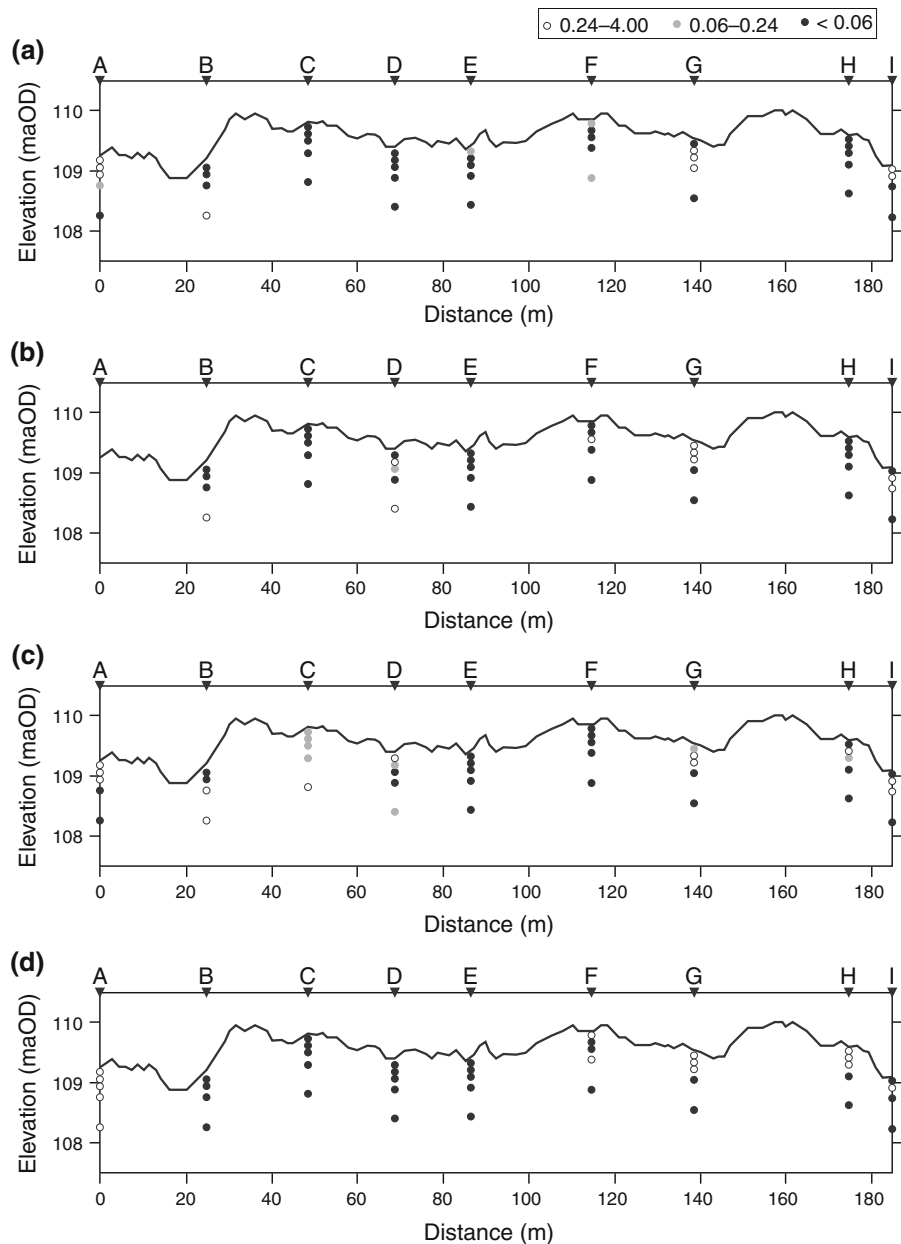
704 signature alone, a specific location in the river bed
705 could be mis-interpreted as a ‘hot spot’ of biogeo-
706 chemical reactivity, when in fact the organic matter
707 processing may have taken place elsewhere, and at a
708 different time.

709 Interpolation of hydraulic head data from the in-
710 stream piezometer network in July 2010 showed that
711 sites A, G and H (and I in 2009) are all locations where
712 horizontal flow potential dominates over vertical
713 gradients under baseflow conditions [see Fig. 6a;
714 Binley et al. (2013) for data from September 2010].
715 Horizontal flows at these sites could comprise subsur-
716 face lateral flows from the riparian zone including
717 intra-meander flows (Boano et al. 2010; Zarnetske
718 et al. 2011) and/or the longitudinal movement of water
719 from hyporheic exchange flows. When we categorise
720 sites by dominant potential flow direction (horizontal
721 or vertical in Fig. 6c) it becomes apparent that sites

722 which score highly on the PCA redox function,
723 indicating reduced conditions, are locations where
724 the potential for horizontal fluxes of subsurface water
725 occurs.

726 Depth profiles of DOC concentrations from sites G
727 and H support our hypothesis that redox-sensitive
728 solutes may have been supplied horizontally through
729 the streambed during our sampling campaigns
730 (Fig. 7). Site A has elevated DOC concentrations
731 through the entire profile to 100 cm depth, suggesting
732 a deeper source of DOC supply in this upstream area of
733 the reach in comparison to G and H. The pore water
734 from in-stream piezometers in A, G and H comprises
735 significantly lower concentrations of nitrate, and
736 significantly higher concentrations of Fe(II) and
737 ammonium in comparison to the riparian zone
738 (Table 4) and surface waters (Table 1) suggesting
739 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

750 play in supplying reactants that drive biogeochemical
 751 transformations and remove nitrate from the stream
 752 bed.

753 Reach-scale patterns of mixing/origins of water 753

754 The upstream section of the reach, centred on site C, is 754
 755 an area of elevated chloride, sulphate and nitrate 755
 756 concentrations in pore water, which load highly onto 756
 757 the factor in the PCA related to water sources. The 757

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 <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*

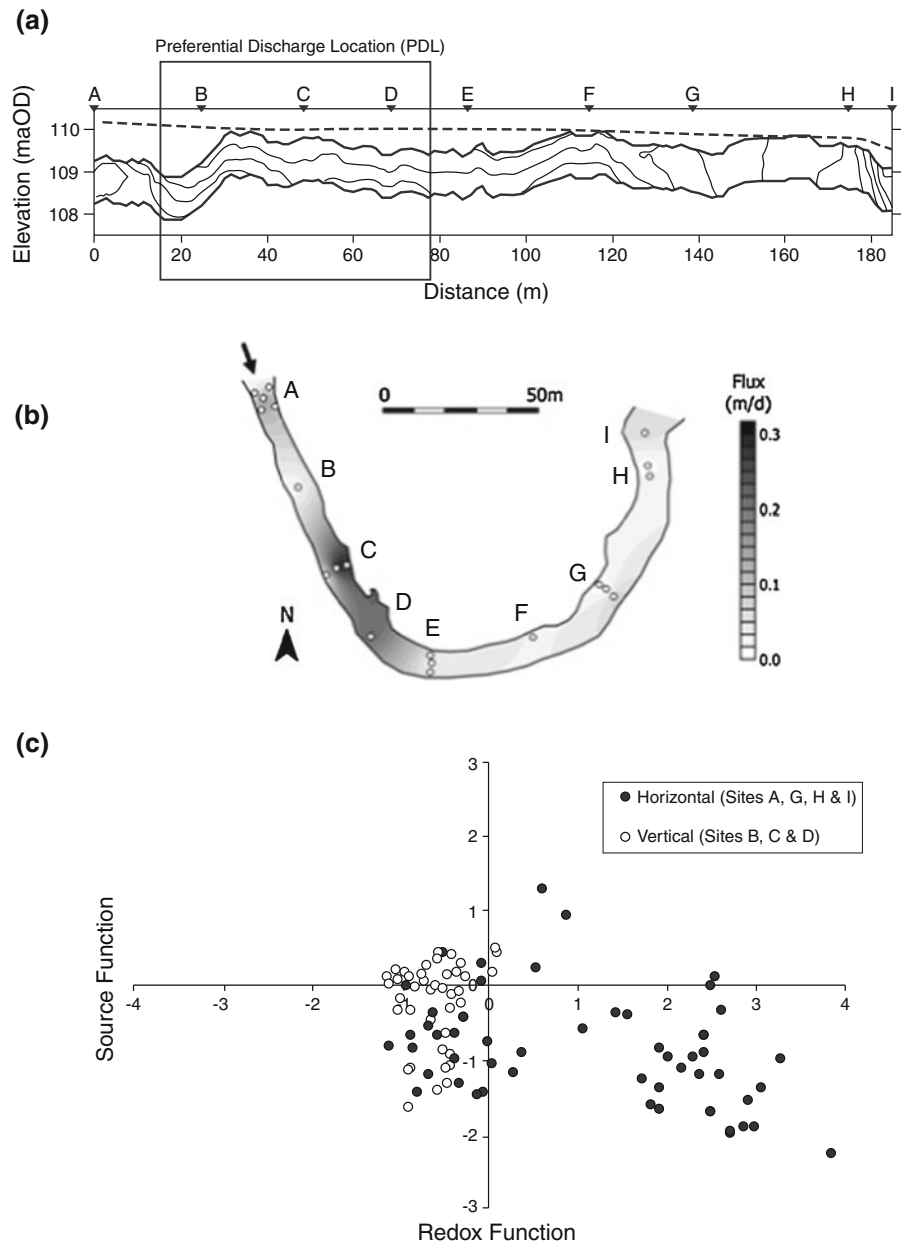
* Significant at <0.05 level; Numbers in parentheses are Standard Error of n = 15 samples (all depths and all months combined)

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.

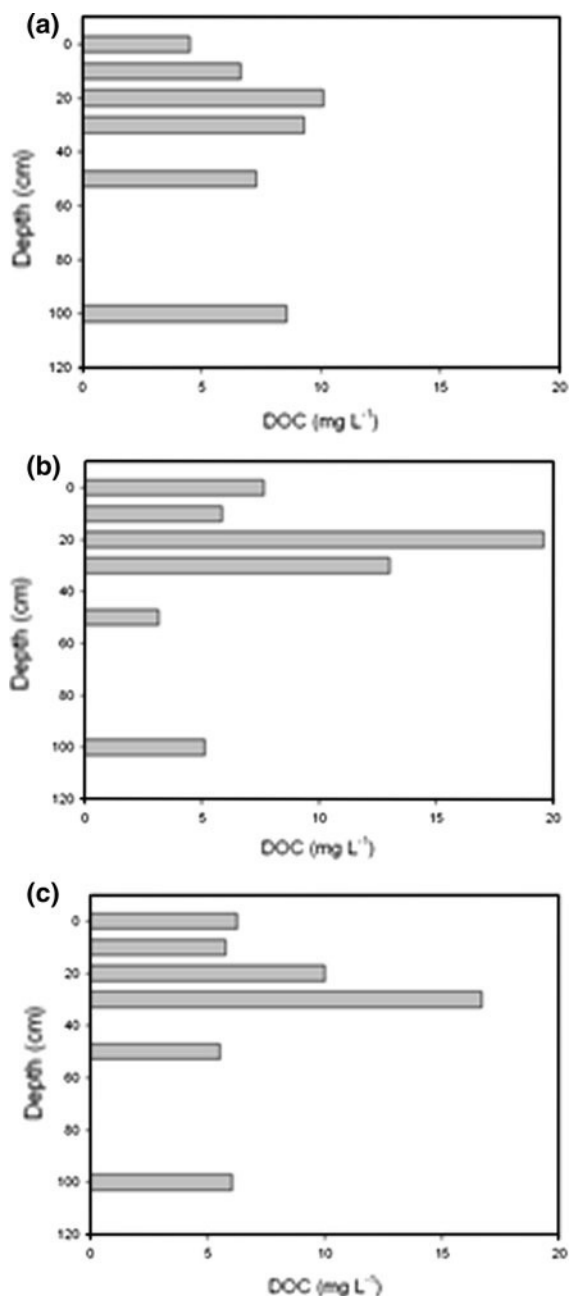


Fig. 7 Depth profiles of dissolved organic carbon concentration at sites A, G and H in July 2010

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 ⁻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)

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 (NO₃⁻ or NH₄⁺) 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 m²) 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 _{N_{SW}} (mg L ⁻¹)	Q _{SW} (m ³ s ⁻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

Nitrate_{N_{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; NitrateN₁₀₀ 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

858 day⁻¹ 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⁻¹ for our study with
866 0.41–0.5 m day⁻¹ 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 (< Q₉₀),
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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