

Spatial and temporal dynamics of nitrogen exchange in an upwelling reach of a groundwater-fed river and potential response to perturbations changing rainfall patterns under UK climate change scenarios

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Abstract

We report the complex spatial and temporal dynamics of hyporheic exchange flows (HEFs) and nitrogen exchange in an upwelling reach of a 200 m groundwater-fed river. We show how research combining hydrological measurement, geophysics and isotopes, together with nutrient speciation techniques provides insight on nitrogen pathways and transformations that could not have been captured otherwise, including a zone of vertical preferential discharge of nitrate from deeper groundwater, and a zone of rapid denitrification linking the floodplain with the riverbed. Nitrate attenuation in the reach is dominated by denitrification but is spatially highly variable. This variability is driven by groundwater flow pathways and landscape setting, which influences hyporheic flow, residence time and nitrate removal. We observed the spatial connectivity of the river to the riparian zone is important because zones of horizontal preferential discharge supply organic matter from the floodplain and create anoxic riverbed conditions with overlapping zones of nitrification potential and denitrification activity that peaked 10–20 cm below the riverbed. Our data also show that temporal variability in water pathways in the reach is driven by changes in stage of the order of tens of centimetres and by strength of water flux, which may influence the depth of delivery of dissolved organic carbon. The temporal variability is sensitive to changes to river flows under UK climate projections that anticipate a 14%–15% increase in regional median winter rainfall and a 14%–19% reduction in summer rainfall. Superimposed on seasonal projections is more intensive storm activity that will likely lead to a more dynamic and inherently complex (hydrologically and biogeochemically) hyporheic zone. We recorded direct evidence of suppression of upwelling groundwater (flow reversal) during rainfall

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events. Such flow reversal may fuel riverbed sediments whereby delivery of organic carbon to depth, and higher denitrification rates in HEFs might act in concert to make nitrate removal in the riverbed more efficient.

KEYWORDS

biogeochemistry, climate change, Damköhler, groundwater, hyporheic, nitrogen, rivers

1 | INTRODUCTION

Rivers are an important global sink for bioavailable nitrogen (N): They convert approximately 40% of terrestrial N runoff per year (~47Tg Galloway et al., 2004) to biologically unavailable N₂ gas and return it to the atmosphere (Bernhardt et al., 2005; Mulholland et al., 2008; Zhao et al., 2015). This N sink capacity includes processes occurring in the hyporheic zone of groundwater catchments (e.g., Burns et al., 2019; Krause et al., 2015; Schlesinger, 2009; Stelzer et al., 2020; Trimmer et al., 2012) where a mosaic of redox conditions is supported (Krause et al., 2011). The permeability of groundwater-fed riverbeds enables the advection and supply of reactants (such as organic matter and nitrate) to the microbial communities which drive nitrogen processing (Lansdown et al., 2015, 2016). Evidence suggests the N sink capacity of rivers is compromised by the net accumulation of N in agricultural subsoils (e.g., Van Meter et al., 2016; Worrall et al., 2015) that moves slowly through the vadose zone of groundwater systems (Ascott et al., 2017; Cuthbert et al., 2019; Stuart et al., 2011). Land management policies have sought to improve freshwater quality by reducing nitrate loading in rivers (e.g., Kanter et al., 2020; Sinha et al., 2019) but the timeframes involved may be too slow to offset other stressors on freshwater ecology (Birk et al., 2020) such as climate-driven water temperature increases (e.g., F. L. Jackson et al., 2020; Leach & Moore, 2019; Ouellet et al., 2020), as proposed by Vaughan and Gotelli (2019) in the context of offsetting climate debt.

Nitrate loading must also be understood in the context of projected changes in river flows under a changing climate, which, for the UK is similar or increased average winter river flows and reduced average summer river flows with increased storm activity (UKCP18, www.metoffice.gov.uk). While the effects of climate change impacts on river flows across the range of geologies found in UK aquifers are yet to be observed (Garner et al., 2017; Hannaford, 2015; C. R. Jackson et al., 2015; C. Murphy et al., 2019; Prudhomme et al., 2013), the chalk aquifer of the south east UK already shows evidence of an increased frequency of groundwater drought due to elevated evapotranspiration (Bloomfield et al., 2019); and intense summer storm activity, predicted to increase under UK climate change scenarios, has been shown to impact stream ecology (e.g., Hutchins et al., 2020; Woodward et al., 2015). Oscillatory climate system drivers such as the North Atlantic Oscillation (NAO) (e.g., Kuss & Gurdak, 2014) are also important. Recent work by Rust et al. (2020) shows the NAO can be statistically detected with a 7-year periodicity in UK river flow. These climate drivers have the potential to impact on regional rainfall

distributions, water resource and nutrient yields and will influence groundwater-surface water interactions including hyporheic exchange flows (HEFs) (e.g., Azizian et al., 2017; Singh et al., 2019). All these physico-chemical processes have consequence for river nitrogen sink capacity (e.g., Stelzer et al., 2020) with which this paper is concerned. Early hydrological research on the hyporheic zone (e.g., Bencala et al., 1990; Fuller & Harvey, 2000; Haggerty et al., 2002; Hill et al., 1998; Malcolm et al., 2003) focused mainly on the relationship between river water and the upper few centimetres of the sediments of the riverbed. Work by Stelzer (e.g., Stelzer et al., 2011; Stelzer & Scott, 2018) among others, revealed the importance of nitrate processing in deeper sediments. As well as downward flux from the river into the sediments of the riverbed, upward flows from groundwater through the hyporheic zone and into the river are important in understanding the evolving chemistry of groundwater as it moves through the hyporheic zone (e.g., Brunke & Gonser, 1997; Conant, 2004), and in particular the capacity for N attenuation under baseflow conditions.

This paper synthesizes the physical hydrology and biogeochemistry process-based understanding for a lowland groundwater-fed river, representative of systems where the river is continuously recharged by groundwater throughout the year. The synthesis includes new data to extend understanding of the relationship between the river channel and its riparian zone under different flow conditions. Through synthesis and new data, the broader goal is to explore potential changes to the N dynamics of groundwater-fed river systems due to external perturbations arising from changing rainfall patterns and temperatures predicted under UK climate change scenarios. To support this goal, additional research is drawn from Kay et al. (2020) who applied probabilistic climate projections based on U.K. Climate Projections 2009 and 2018 on UK river flows that were tested on a number of catchments, including the Eden, where the research reported here lies. Alterations to groundwater flows and groundwater quality arising from the climate change are likely to impact on river ecology. For example in rivers associated with chalk aquifers there is evidence that low flows may result in decline of vegetation, such as *Ranunculus pseudofluitans*, associated with priority habitats (Westwood et al., 2020). We also know that warming may impact biogeochemistry by changing the way rivers couple and transform carbon and nutrients (Hood et al., 2017; Preiner et al., 2020), and work by Kurylyk et al. (2014) and Kurylyk et al. (2015) suggests that although groundwater-fed rivers are likely to remain buffered to temperature changes in the regional groundwater, this buffering capacity may decline over time (Leach & Moore, 2019). Similar “buffering” or

chemostatic behaviour such as that observed in the Eden catchment may mask aquifer response to climate drivers where large mass stores (i.e., parent material and legacy nutrient stores) result in fairly constant intra-annual nitrate concentrations despite large variations in river flow (Butcher et al., 2008).

2 | DRAWING ON DETAILED INSIGHTS FROM A STUDY REACH TO ILLUSTRATE THE SPATIAL COMPLEXITY OF PROCESSES INVOLVED IN SURFACE-SUBSURFACE WATER INTERACTION AND NITRATE EXCHANGE

The study area (Figure 1), a 200 m groundwater-fed river reach, is part of the River Eden catchment, Cumbria UK, and comprises a loose gravel alluvium overlying unconsolidated (Permo-Triassic) sandstone with a sequence of pools and riffles. The reach has limited drift cover thus providing direct contact with the sandstone and regional aquifer flow. Our conceptual framework was akin to that proposed by Stelzer and Bartsch (2012), in that it was assumed that nitrate would be removed by denitrification from nitrate-rich, oxic groundwater as it upwelled into near-surface sediments containing buried particulate organic matter. Further, discrete patches of net nitrification and denitrification were anticipated, driven by dissolved organic carbon (DOC) supplied to the riverbed via HEFs (Zarnetske et al., 2011). To capture the effect of small and larger spatial scale processes, detailed in-channel process-based understanding was gained by combining

non-standard measurement techniques including a patch-scale isotope tracer “push-pull” (centimetre scale) technique (Lansdown et al., 2014; Lansdown et al., 2016), centimetre scale riverbed nutrient profiles (Byrne et al., 2014; Ullah et al., 2014), and decimetre to metre resolution advanced geophysical applications (Binley et al., 2015; Clifford & Binley, 2010; McLachlan et al., 2017). New data building on work by Dudley-Southern and Binley (2015) and Käser, Binley et al. (2014) extends the analysis beyond the channel and over time to refine our conceptual understanding of ecosystem control points (Bernhardt et al., 2017) or “hotspots” and “hot moments” within a broader framing of hyporheic zone processes for N dynamics under climate-driven changing river flows.

Steady state modelling of conservative solute transport undertaken by Käser et al. (2013) proposed that HEFs can be created by both macroforms (>1 m length e.g., due to riffles and emergent vegetation) and microforms (0.01–1 m length). Figure 2 illustrates the contrasting flow patterns caused by macroforms (Figure 2a) and microforms (Figure 2b) for the river reach. Hu et al. (2014) developed further the work of Käser et al. (2013) by considering reactive transport in a study of the effect of microforms embedded within macroforms in the shallow hyporheic zone. Their study illustrates how such bed forms can influence the transition between nitrification and denitrification along a flow path, and the consequences of this for nitrate loading of a stream. Using in-stream piezometric data from the study site, Käser, Binley et al. (2014) show, through the use of 3D subsurface flow modelling, the potential for relatively complex three dimensional flow patterns within the hyporheic zone. Empirical research reported by Binley et al. (2013) using in-river

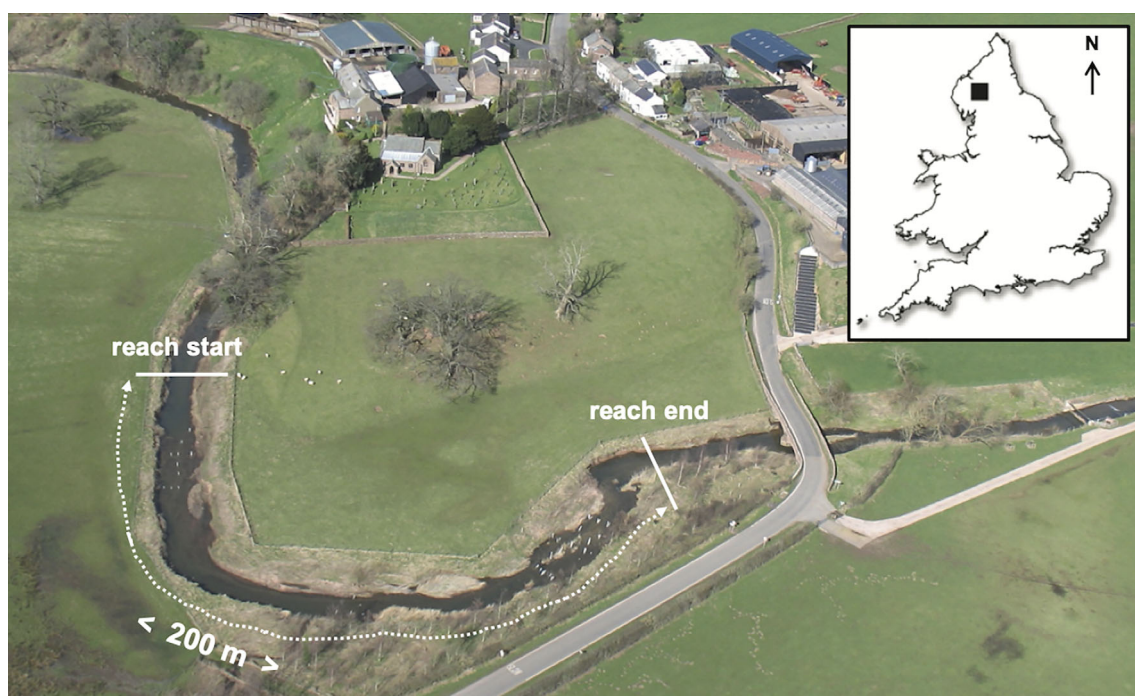


FIGURE 1 Location of the river Leith study site, a sub-catchment of the Eden, and aerial photograph (courtesy of Simon Ledingham). River flow is from left to right. The total length of river reach (200 m) represented in Figure 3a,b is shown

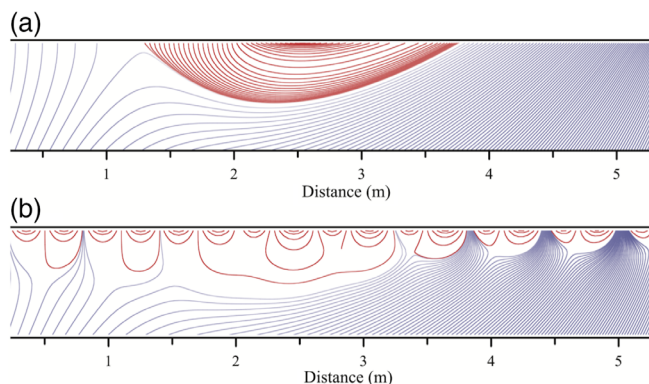


FIGURE 2 Modelled illustration of representative flow patterns arising from (a) macroforms and (b) microforms for the R. Leith riverbed geomorphology, modified after Hu et al. (2014). The red lines show hyporheic exchange flows (HEFs) and the blue lines show upwelling groundwater flow paths. River flow is left to right

piezometer tracer lateral and longitudinal dilution tests, revealed greater spatial and temporal complexity of flow paths over the reach at the groundwater-surface water interface than initially assumed. The spatial complexity could not be accounted for by variations in hydraulic conductivity alone. Under baseflow conditions HEFs are limited in both depth (c. 10 cm beneath armoured layer in upstream section of the reach; c. 40 cm beneath armoured layer in the downstream area), and path length as a result of the hydrogeological and geomorphological conditions observed in this gaining reach. Drawing from this work, the experimental reach can be visualized as two distinct geomorphological zones with contrasting flow pathways (Figure 3a). A zone of *vertical* water flux with local connection to the regional groundwater characterized by oxic riverbed conditions and dominating the upstream 20% section of the river reach. Data reported by Binley et al. (2013) and Byrne et al. (2015) found that in the upstream river section strong vertical upwelling suppressed the depth of HEFs. In the lower river reach, *lateral* water fluxes derived from the riparian zone plus *longitudinal* (following the direction of river flow) flows from soils and shallow groundwater are more important. Vertical upwelling was weaker in this zone so HEFs penetrated to a greater depth. Work by Gariglio et al. (2013) similarly report the dynamic variability in space and time of HEFs for a pool-riffle-pool sequence in central Idaho using a thermal time series approach. Fox et al. (2014) also found the competitive interaction between the overlying velocity in the stream and losing/ gaining fluxes influences the dominant mechanisms of water exchange.

These previously reported observations were largely conducted under (steady state) baseflow conditions. During high flows, modelling by Munz et al. (2011) suggested that at the beginning of peak flow conditions in particular, head gradients may substantially increase surface water infiltration into the riverbed, that is, the HEFs get deeper as a result of the stronger gradient, and downwelling conditions in general allow deeper hyporheic flows. Field observations reported by Byrne et al. (2015) found that increases in river stage arising from

intensive summer rainfall events superimposed on baseflow conditions not only led to deeper HEFs but a concomitant supply of DOC to greater depths in the riverbed in comparison to no-rainfall baseflow. Monitored depth profiles of fluid electrical conductivity in the riverbed by Dudley-Southern and Binley (2015) revealed evidence of deeper HEFs (approximately three to four times the baseflow extent in the upstream reach) and short-term reversals of flow during rainfall events. Hester et al. (2017) comment on the limited scope for physical mixing of upwelling groundwater and HEFs and refer to the limited number of field studies that have examined controls on hyporheic mixing such as spatial heterogeneity and river stage fluctuations. Our experimental studies have shown the dynamic behaviour of subsurface flow patterns at the River Leith study site. This dynamic behaviour is likely to result in movement of the HEF cells denoted in Figure 2a,b both laterally in the riverbed in response to movement in microforms, and vertically in response to storm events. That hyporheic functioning can extend to some depth (i.e., >10 cm) below the riverbed has been observed by a number of authors (e.g., Briggs et al., 2015; Stelzer et al., 2011; Stelzer & Scott, 2018). Dudley-Southern and Binley (2015) also showed how a rapid rise in river stage due to major rainfall events can result in the reversal of the direction of lateral flows at the site, adding further insight of the dynamic variability of HEFs.

Under high rainfall volumes and intensities associated with major storm events, it is possible that the HEFs prime deeper riverbed sediments with bioavailable DOC, fuelling denitrification along upwelling groundwater flowpaths. Data reported by Lansdown et al. (2012) for the River Leith study reach shows that denitrification was the dominant nitrate attenuation process in the riverbed, with dissimilatory nitrate reduction to ammonium (DNRA) of secondary importance, and no evidence of anammox. Denitrification was observed to occur throughout the riverbed, even under predominantly oxic conditions. According to Lansdown et al. (2014) nitrification occurred across a far narrower chemical gradient in the lower river reach and was inhibited by the low oxygen conditions associated with horizontal flows. The spatial pattern of nitrate removal can be described according to the dominant flow pathway, with three zones identified in Figure 3b. The majority (>80%) of nitrate removal (via denitrification) occurs in the gaining reach (Z1) within sediments not exposed to HEFs under baseflow conditions. A second zone (Z2), comprising c. 20% of the reach area, is characterized by preferential groundwater discharge (PGD) and dominated by vertical upwelling that enabled nitrate from regional groundwater to be rapidly transported to surface water with little opportunity for denitrification. Data reported by Heppell et al. (2014) suggest this zone of PGD contributes 4%–9% of the total surface water nitrate load on an instantaneous basis and c. 2% of total denitrification within the riverbed. A third, constrained zone (Z3) occupies around 2.5% of the reach by area, where anoxic lateral subsurface flow derived from the riparian zone generates a hotspot, contributing 8% of total denitrification within the riverbed (Lansdown et al., 2015).

Damköhler numbers have been proposed as a useful means of examining the capacity of different landscape units to remove nitrate

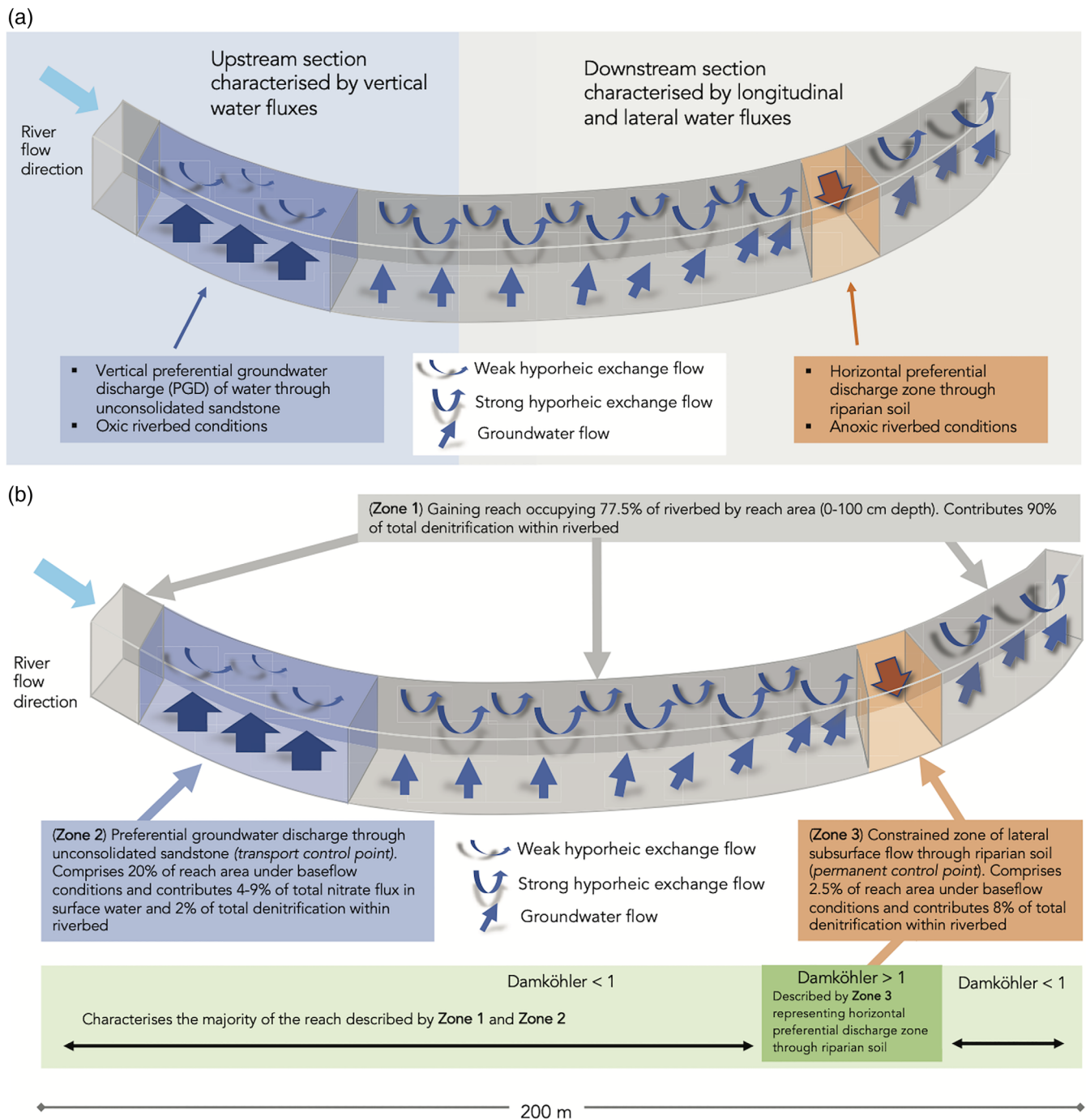


FIGURE 3 (a) Direction of water fluxes within the riverbed of a 200 m reach (River Leith) shown in Figure 1 during baseflow conditions (2009–2011), illustrating weak and strong hyporheic exchange flows (HEFs) and groundwater flow. The blue-shaded panel illustrates the upstream section and grey-shaded panel illustrates the downstream section of the reach. The size of the blue arrows indicates the strength of the flows and weak versus strong HEFs are shown. (b) The 200 m riverbed reach shown in Figure 1 divided into three sections based on dominant flow pathways and their role in nitrate removal via denitrification: *Zone 1* - the gaining reach; *Zone 2* - preferential groundwater discharge zone, and *Zone 3* - lateral subsurface flow from floodplain. Also shown is the dominant Damköhler number in different sections of the riverbed. River flow is left to right

(Gu et al., 2007; Pinay et al., 2015). Work reported by Lansdown et al. (2015) applied Damköhler analysis to the riverbed sediment as groundwater moved from 100 cm depth to the surface. Here the same method is used to report dimensionless Damköhler numbers for denitrification as

$$D_{a,den} = \frac{\tau_T}{\tau_R}, \quad (1)$$

where $D_{a,den}$ is the dimensionless Damköhler number, τ_T is the transport timescale (d) and τ_R is the reaction timescale (d). Figure 3b applies

Damköhler numbers to the three water flux zones described above. The majority of the experimental reach (Z1 + Z2) was characterized by a Damköhler number for denitrification, $D_{a,den} < 1$, indicating that nitrate removal in upwelling groundwater was limited by slow reaction rates compared to advection. The data suggest that water flux was too fast relative to the denitrification rate for complete nitrate removal from groundwater to occur. Hotspots of denitrification that had a $D_{a,den} > 1$ were associated with horizontal (lateral and longitudinal) water fluxes such as those found in the lower reach (Z3). The importance of near-surface lateral flow pathways in transferring nutrients from land to water in agricultural systems has been reported earlier by Heathwaite and Dils (2000), Heathwaite et al. (2005) and Lane et al. (2009). Not every area of horizontal water flux was a hotspot, and data reported by Lansdown et al. (2015) suggests this may be a result of differences in the bioavailability of DOC transported by different types and/or residence times of horizontal flow, for example, lateral flows from riparian soil water versus longitudinal HEFs outside upwelling zones.

Fine scale (cm resolution) in situ measurements were used to gain understanding of the patterns of nitrification and denitrification in the riverbed; the methodology is described in Ullah et al. (2012) and Lansdown et al. (2014). Adapting the model of Triska et al., 1993, Figure 4a,c illustrates the pattern of nitrification and denitrification observed for the majority of the riverbed, including the zone of preferential discharge (Z2) described above. Here, organic matter supplied

by surface water in the top 10 cm of the sediment is being mineralised to NH_4^+ (see Figure 4a), with highest denitrification and nitrification rates recorded in the uppermost part of the riverbed within the hyporheic zone (see Figure 4c). The second conceptualisation shows a hotspot where bioavailable organic carbon is being delivered to the riverbed from riparian areas (see Figure 4b). Here the zones of maximum denitrification activity and nitrification potential occur deeper in the riverbed due to the lateral flows that supply dissolved organic matter and ammonium due to mineralisation (see Figure 4d). Thus, ammonium concentrations are elevated at depth, and not just within the top 10 cm of the sediment. Maximum denitrification and nitrification rates are generally thought to occur under contrasting oxygen settings, with denitrification optimal in reduced conditions, and nitrification in oxidized conditions (Seitzinger et al., 2006). Our measurements indicated that zones of high nitrification potential and denitrification activity overlap in net oxic sediments without the discrete patches that we had originally anticipated (Lansdown et al., 2014). Although denitrification rates increased towards the sediment surface, driven by organic matter from HEFs (see Figure 5a, after Lansdown et al., 2015), they were still not high enough (over the 10 cm spatial resolution of measurements reported by Byrne et al., 2015) to consider the upper sediment as reaction-controlled except in the zone of lateral subsurface flow (Figure 5b). There may be two reasons for this. First, at depth the riverbed matrix of unconsolidated sandstone is low in organic carbon, so denitrification rates

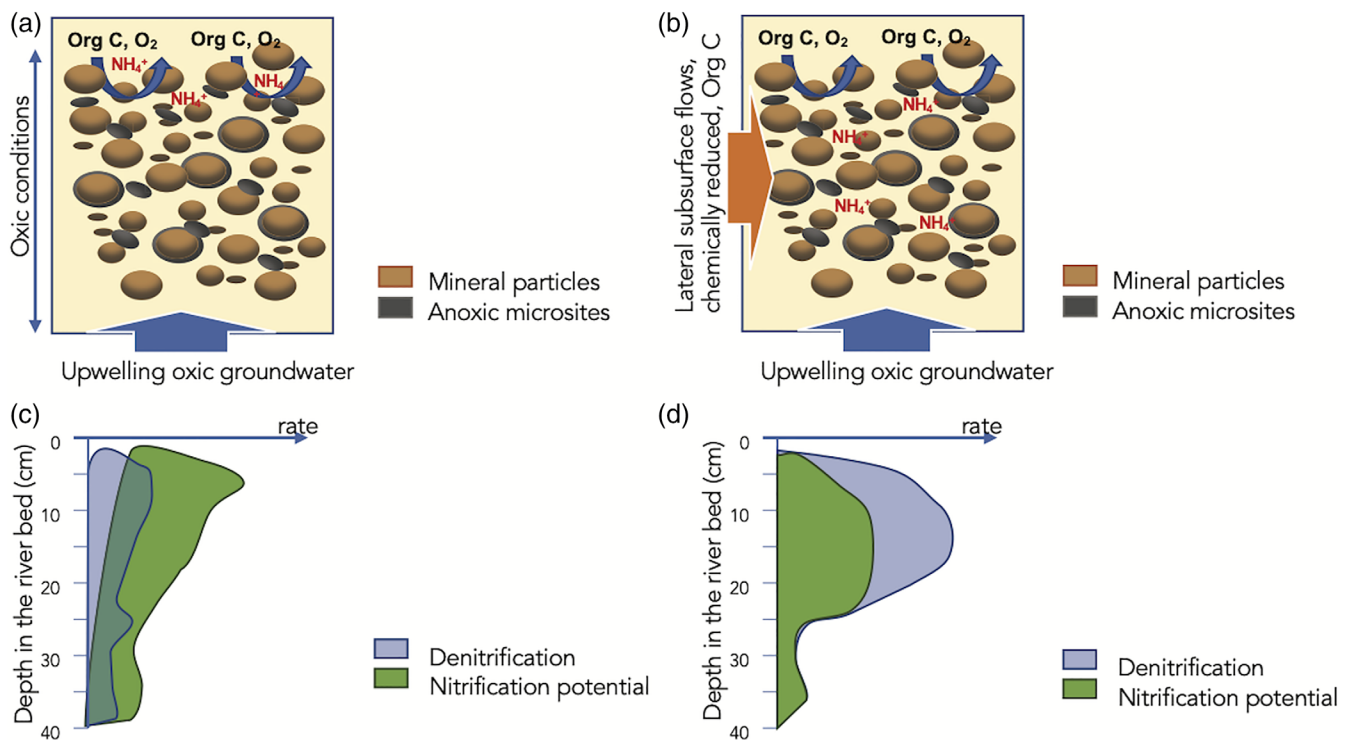


FIGURE 4 Water fluxes, redox conditions and patterns of denitrification and nitrification in the majority of the reach including the zone of preferential groundwater discharge (a,c) depicted in Figure 3b (Zone 2) and in the riverbed connected to lateral subsurface flow from the riparian zone (b,d) depicted in Figure 3b (Zone 3). Note that absolute rates of denitrification and nitrification are not comparable and are drawn at different scales (adapted from fig. 2 in Lansdown et al., 2014)

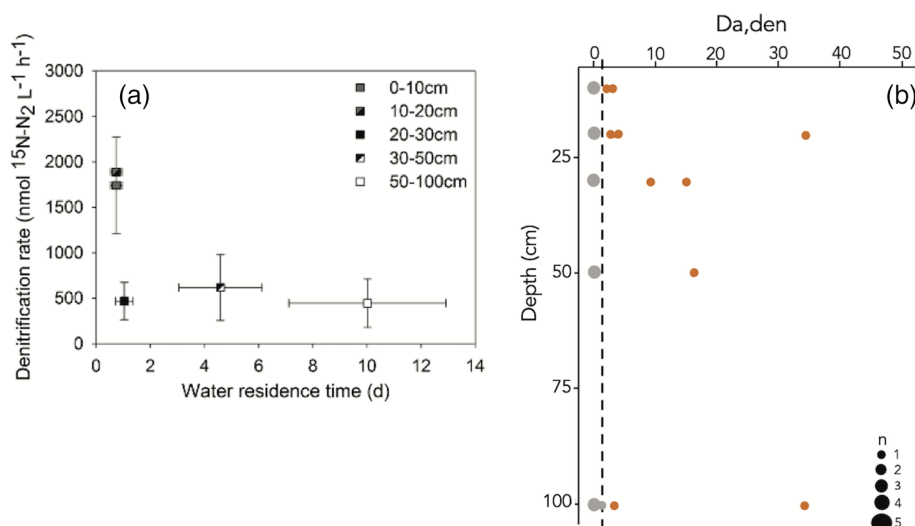


FIGURE 5 (a) Shallow sediments (10 cm and 20 cm) were characterized by fast denitrification but short residence time, while in deep sediment denitrification was slow and residence time was long, with a switch between the two scenarios at ~ 30 cm. These results illustrate that both physical and biogeochemical controls on nitrate attenuation, and the interaction thereof, can vary along upwelling flow pathways in a gaining reach (taken from Lansdown et al., 2015). (b) Damköhler number for denitrification (Da_{den}) with depth. Size of circle indicates number of measurements with same Damköhler number. $\text{Da}_{\text{den}} < 1$ for all measurements outside permanent control point irrespective of depth (grey circles), and $\text{Da}_{\text{den}} > 1$ for all measurements taken within the permanent control point (orange circles). Dashed vertical line indicates $\text{Da}_{\text{den}} = 1$

are low relative to upwelling groundwater flux. Second, the strength of the upwelling groundwater is also influencing nitrate removal through interactions with HEFs.

Previously unpublished soil mapping and geophysical surveys within the adjacent floodplain is reported here to illustrate the influence of the flooded channel on hydrological properties of land adjacent to the stream channel. Figure 6a summarizes results from an EM38 (Geonics, Canada) electromagnetic induction (EMI) terrain conductivity survey carried out in July 2013. The map, showing soil electrical conductivity over a depth of 1.5 m, reveals a localized patch of high electrical conductivity within the floodplain that was subsequently verified to be attributed to fine textured sediments. Analysis of high resolution topographic data by Käser, Graf et al. (2014) revealed that the same area is associated with a local topographic low that is likely to remain saturated for some period after a flood event (Figure 6b). The same feature is also evident from the aerial photograph in Figure 1. This local topographic low appears to supply anoxic water and DOC via lateral subsurface flow to the channel during and following significant rainfall events, acting to drive the high denitrification rates that we recorded in the sub-section of the downstream reach (Z3, Figure 3b; Heppell et al., 2017).

3 | ECOSYSTEM CONTROL POINTS IN GROUNDWATER-FED RIVERS

The synthesis of results for the river reach described above show that the nitrate sink capacity depends on the relative balance between transport versus reaction controls (in this case for denitrification). Where water moves faster than nitrate can be reduced, nitrate is

controlled primarily by hydrological processes such as mixing and dilution. Where nitrate is reduced faster than water transport, denitrification is the key control for nitrate yield. Within this single gaining reach there were clearly identifiable zones of different nitrogen exchange mechanisms and transformation rates within the broad pattern of denitrification (Heppell et al., 2014). These distinctive zones are important in the context of wider landscape controls such as changing land use practice and changing climate. Bernhardt et al. (2017) highlight the importance of whole system time and space accounting of nutrient fluxes in a river reach to contextualize the relative importance of “hot spots and hot moments” in contributing to, for example, nitrogen exchange. This spatial complexity is described above for the different zones of nitrogen removal (e.g., Figure 3b). Using the nomenclature of Bernhardt et al. (2017), two co-existing ecosystem control points can be identified for the river reach; and both are sensitive to the potential changes imposed on river flows under a changing climate:

1. Transport Control Points characterized by a zone of vertical groundwater preferential discharge supporting oxic riverbed conditions with evidence for higher denitrification and nitrification rates in the uppermost part of the hyporheic.
2. Permanent Control Points (hotspots) that connect the riverbed with lateral subsurface flow through riparian soils, which supply bioavailable organic matter and support anoxic riverbed conditions.

Understanding the future trajectory and influence of *Transport Control Points* characterized by preferential discharge areas on nitrate fluxes in groundwater-fed rivers under a warming climate is important

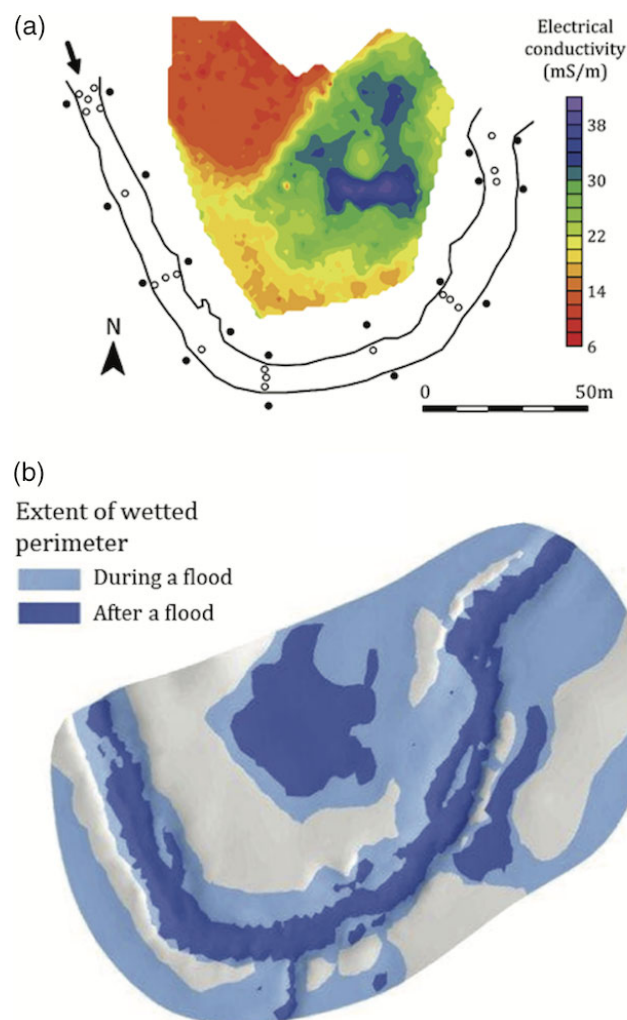


FIGURE 6 Evidence of out-of-channel behaviour. (a) Soil electrical conductivity survey results in the adjacent floodplain showing areas of relatively high electrical conductivity associated with fine textured moisture retentive soils, and low electrical conductivity associated with elevated (drier) ground. The circular symbols show the piezometric network. (b) Floodplain topography analysis carried out by Käser, Graf et al. (2014)

(see e.g., Kaandorp et al., 2019; Orr et al., 2015) and will depend on a combination of landscape structure, groundwater flow path length, type (e.g., fracture or inter-granular), and depth and residence time (Briggs & Hare, 2018; Tetzlaff et al., 2009). Over a timeframe of decades, future summer low flow conditions derived from preferential discharges from deep aquifers may manifest as areas of markedly lower temperature relative to the surrounding riverbed offering thermal refugia for fish (Geist et al., 2002; Kurylyk et al., 2014). Over the same timeframe, the past legacy of high N-fertilizer usage (see e.g., Ascott et al., 2017) is likely to continue to contribute significant flux of nitrate to the riverbed with little opportunity for nitrate removal by microbial processes. However, it is also possible that preferential discharge from shallow aquifer environments may warm faster in response to air temperature changes (Eggleston & McCoy, 2014) and nitrate concentrations may decline more rapidly in

response to diffuse nitrate management strategies (e.g., introduction of Nitrate Vulnerable Zones, which currently cover 55% land in England) than their deeper aquifer counterparts characterized by longer lag times.

For *Permanent Control Points*, data for the study reach previously reported by Heppell et al. (2014) found that lateral connectivity continued to provide sufficient DOC for high denitrification rates even under low summer flow conditions. Johnes et al. (2020) also examined riparian wetlands as permanent control points using a combination of geochemical, geophysical and isotope ratio methods. The authors distinguished wetter areas supporting denitrification from zones where plant demand for nitrate was greater than demand by denitrifiers, leading to the assimilation, breakdown and re-release of inorganic nutrient fractions in the form of dissolved organic matter (DOM), which was subsequently flushed into adjacent waters during high flow events: the flushing of macropores and micropores during storm events was observed to be the primary mechanism for the export of nutrients.

Under a changing climate, an increased incidence of high intensity summer storms superimposed on a general trend towards low flows may disproportionately impact river biogeochemistry (see e.g., Bierzo & Heathwaite, 2017; Heathwaite & Bierzo, 2020). Raymond et al. (2016) suggest that low-frequency large events, which are predicted to increase with climate change, are responsible for a significant percentage of annual terrestrial DOM input to drainage networks by “pulse-shunt” of biochemically reactive DOM via surface and subsurface pathways such as Permanent Control Points. Under such scenarios, permanent control points may exert considerable control on nitrogen attenuation. Heathwaite et al. (2000, 2005) described how parts of the landscape acting as critical source areas such as permanent control points, have potentially pivotal control on the delivery of nutrients from land to water. Lloyd et al. (2019) extended this concept to a range of catchment geologies from the perspective of developing mitigation strategies. Such strategies involve out-of-channel interventions. By integrating in-river/below riverbed measurements with “out of channel” observations in riparian piezometric networks, it is possible to extend understanding beyond the river channel to evaluate the role of “permanent control points” and to examine integrated spatial controls on system biogeochemistry. Such integration enables exploratory analysis of changing external drivers such as climate change on groundwater-fed systems to be explored.

4 | THE IMPORTANCE OF HYPORHEIC EXCHANGE FLOWS FOR NITROGEN CYCLING UNDER A CHANGING CLIMATE

The UK weather and climate is highly variable. Observed annual mean rainfall over England and Wales has not changed significantly since records began in 1766 (Jenkins et al., 2008), although the most recent decade (2010–2019) is wetter (>3% 1981–2010; >7% 1961–1990) for the UK overall (Kendon et al., 2020). The seasonal pattern of observed rainfall has changed. The proportion of winter rainfall falling

in heavy rainfall events has increased over all regions of the UK over the past 45 years (Jones et al., 2013; Sanderson, 2010). Observations suggest a long-term trend towards decreasing mean summer rainfall in all regions of the UK but the relative contribution of heavy events to total summer rainfall has increased (Jones et al., 2013). A pattern corroborated by Burt and Ferranti (2012) for northwest England, where the study catchment is located. Changes in rainfall patterns, including higher rainfall volumes and intensities have been projected by climate models for some time (Fischer & Knutti, 2016). There is a growing consensus that extreme daily rainfall rates and rainfall events are becoming more intense (Slingo et al., 2014) and the effect of climate change makes events like those recorded in northwest England in December 2015 – “storm Desmond” that caused an estimated £500 M of damage, about 40% more likely (Otto et al., 2018). For the river Eden catchment, climate projections indicate further pronounced seasonal changes in future rainfall, with a 14%–15% increase in median winter rainfall predicted by UKCP09-WG for the 2050s high emissions scenario, and a 14%–19% reduction in summer rainfall (Ockenden et al., 2017). Prolonged low summer flows are projected to be interspersed with convective high-intensity rainfall events (see Ockenden et al., 2016). A trend corroborated by Kay et al. (2020) for a wider study of 10 catchments across England that included the river Eden catchment, with predicted decreases in summer rainfall of c. 5% to 22% (50th percentile values dependent on location and region) based on probabilistic projections from UKCP2009 (J. M. Murphy et al., 2009) and UKCP2018 (Lowe et al., 2018). For the Eden catchment, this was translated into future decreases in central estimates of Q95 (low flow) river flows of c. 15% (Kay et al., 2020).

Groundwater flux is driven by many factors including surface water discharge and groundwater recharge. Given the climate projections described above, we anticipate a change in the magnitude of these variables that will likely vary between summer and winter, potentially changing the pattern of groundwater flux and consequently nitrogen dynamics within the riverbed. Simulation modelling of the implications of a changing climate for annual surface water nitrogen flux has been undertaken for the river Eden catchment (Ockenden et al., 2017) using a high-resolution (1.5 km grid) regional climate model (RCM-1.5 km) for the UK and from the UK Climate Projections 2009 Weather Generator (UKCP09-WG) combined with high-frequency surface water quality data from the River Eden Demonstration Test Catchment (www.edendtc.org.uk). Modelled predictions estimated a 71% probability of future surface water nitrate flux increasing by 2050 owing to elevated rainfall-driven nitrogen transfers from agricultural land (Ockenden et al., 2016) unless mitigation measures are put in place. The impact on surface water nitrogen may be compounded by legacy nitrogen stores in groundwater (Briggs & Hare, 2018; Butcher et al., 2008) as wetter winters lead to increased groundwater recharge rates and – outside major storm events (see below) – lead to greater groundwater upwelling. The research synthesized here along with that of others, has found that upwelling groundwater reduces hyporheic exchange (Binley et al., 2013; Gomez-Velez et al., 2014), and a recent modelling study has shown that strongly upwelling groundwater also reduces nitrate processing within HEFs

(Azizian et al., 2017). The stronger the vertical flux of groundwater the less nitrate is removed along the upwelling groundwater pathway in deeper riverbed sediments and within the overlying HEFs near the sediment surface (Azizian et al., 2017). Conversely, dryer summers may weaken upwelling groundwater fluxes. Bloomfield et al. (2019) show evidence of an increased frequency and magnitude and duration of groundwater droughts (defined as mean periods of below-normal annual groundwater levels driven by changes in evapotranspiration in conjunction with changing annual rainfall patterns), with consequences for weakened upwelling groundwater fluxes. Weaker upwelling groundwater flux would allow deeper HEFs to develop around cobbles and riffle-pool sequences; facilitating deeper transport of organic carbon and nitrate, which in turn could drive higher rates of coupled denitrification to a greater depth in the riverbed.

The superimposition of more intense rainfall (storm) events on climate change projections for seasonal rainfall and groundwater flux will likely lead to a more dynamic and inherently complex (hydrologically and biogeochemically) hyporheic zone. Increased storm activity may drive more dynamic N cycling in the hyporheic zone owing to temporary shifts in the direction of groundwater flux. For the study reach, Dudley-Southern and Binley (2015) recorded reversal of flow direction for 5% of a 21-month monitored period based on piezometric head data. The coupling of these data to the deployment of bespoke electrical conductivity sensors in the riverbed, provided direct evidence of event-duration downwelling to 30 cm, pointing to the critical influence of river stage on hyporheic mixing (e.g., Byrne et al., 2014). The events over which the suppression of upwelling groundwater (flow reversal) was observed by Dudley-Southern and Binley (2015) were typical winter storms. Such flow reversal may fuel the riverbed sediments with a temporary delivery of particulate organic carbon and DOC along deeper HEF pathways, also observed by Harvey et al. (2012). As such storm events become more frequent under projected climate change, their fuelling affect may be promoted whereby delivery of organic carbon to depth, and higher denitrification rates in HEFs might act in concert to make nitrate removal in the riverbed more efficient. The impact of storm events on N cycling is likely to retain a seasonal signal. Under summer baseflow, such “priming” of the riverbed sediments during major rainfall events may adjust the magnitude of denitrification of upwelling nitrate rich groundwater. Under winter flow conditions, where extreme rainfall may drive major flood events such as that shown in Figure 7, the impact on the transport of nitrate rich groundwater to the river may differ. Scouring of the riverbed under high river discharge may expose more permeable sediments, reduce solute travel times and enhance fluxes; alternatively, increased sediment input from surrounding agricultural land might lead to colmation and clogging of the armoured riverbed, thus modifying the occurrence and depth of HEFs and leading to less efficient nitrate removal in the uppermost sediments.

The dynamic nature of the hyporheic zone has been documented in a growing number of studies, addressing a range of drivers including major storms as discussed here (e.g., Sawyer et al., 2014) but also snowmelt (e.g., Bryant et al., 2020) and dam releases (Gerecht et al., 2011). Zhou et al. (2014), for example, suggested that under a



FIGURE 7 Photographs of the study site during a major flood and under normal flow conditions. The 2005 photograph is taken during the recession limb of a rainfall event due to 200 mm (3 months equivalent) rainfall over a 36-hour period beginning 6 January

changing climate, alternations of precipitation and evaporation will impact on the scale and shape of the hyporheic zone, and consequently biogeochemical interactions and the balance between the retention/release of nitrogen. These dynamic responses play into a future scenario of accelerated river metabolic response due to changes in the key drivers of a river's climate: light, temperature and hydrologic disturbance (Bernhardt et al., 2018). We know that low river flows, in conjunction with warming of water, in groundwater catchments are likely to reduce the amount of oxygen in freshwaters as well as concentrating the levels of pollutants. Hood et al. (2017) undertook whole-stream warming manipulations and their results illustrate that climate warming could lead to large and difficult-to-predict changes in river metabolism and its coupling to nutrient cycles. The authors suggest that responses to warming will emerge from interactions between population-, community-, and ecosystem-scale properties that presently cannot be predicted from theory. For all scenarios, the patterns and mode of delivery of nutrients and fine sediments from the catchment to the riverbed, as well as physical disturbance effects from transient high flows, will alter the biofilm microbiome in the hyporheic, which is critical to biogeochemical functioning (Battin et al., 2016). Although effort is now being made to improve models that couple the effects of groundwater and HEFs on nitrogen cycling under steady and dynamic discharge conditions, we have yet to develop predictive models that incorporate these types of hydroecological responses to climate change. Such modelling advances are also dependent on approaches to enable the extrapolation from detailed process-based understanding.

The experimental work synthesized here has focussed on detailed understanding of processes at centimetre to metre scales within in a 200 m river reach. The research shows the importance of capturing both the spatial and temporal variability in river flow on groundwater flux and nitrate processing to gain an early look at the implications of climate change projections on rainfall for groundwater flux and hyporheic zone processes. Under climate change projections, the anticipated decrease of summer flow should fuel nitrate removal while high flows may lead to organic carbon replenishment, albeit with major uncertainties in HEF dynamics in response to extreme daily rainfall

rates and rainfall events becoming more intense. Despite the improvement in process knowledge gained, two key challenges exist. First, it is impractical to extend such a spatially detailed experimental program to characterize an entire river reach and, therefore, we need to consider ways of scaling such investigations. Such a challenge is not new to hydrological science. We believe that an appropriate way forward is to use a combination of large-scale modelling tools alongside reconnaissance type field methods to identify what we term "critical points" within an entire reach. These critical points should exhibit processes that have a major influence on nitrogen exchange and may, for example, be areas of substantial groundwater recharge to the river, or zones with extensive connectivity to the riparian zone. Reconnaissance methods may include in-stream and ground-based geophysical methods, as proposed by Binley et al. (2013), alongside more traditional spatial sampling of water chemistry (including isotopes) and flow accretion. The second challenge relates to developing experimental infrastructure that can permit the monitoring of processes over longer time scales (e.g., decades) in order to reveal informed insight into long term changes to the hydrological and biogeochemical function. We are often constrained to research funding and instrumentation lasting only a few years. Although some attempts have been made to establish longer term studies (in the UK, the longest running example is the Plynllyon observatory), these remain uncommon. For such investigations we also need to consider alternative approaches to measurement. We cannot measure everything, everywhere, all of the time, and so need to develop suitable survey designs that target key dynamic signals, perhaps coupling ground-based approaches with the rapidly advancing capacity of airborne sensor technologies, while remaining sustainable and also adaptable to future change as our conceptual models develop.

5 | CONCLUSIONS

The research and new analysis synthesized here illustrates the critical importance of incorporating hydrogeological process understanding both beneath the riverbed, and from the wider landscape setting, in

predictive tools if we are to capture appropriately the role of the hyporheic zone for nitrate processing and its consequences for groundwater-fed river metabolics under a changing climate. The review and synthesis of previous reports coupled with new insights shows how a unique combination of physical hydrology and biogeochemical tools applied in detail to a river reach, can capture systematically the process understanding and complexity of the hyporheic zone. Few studies are able to spend the many person-years looking at a 200 m section so the challenge - and opportunity - lies in translating the insight and the understanding gained to frame research questions that target larger scale predictive physically-based and statistical models, which need to account for this process understanding in groundwater-fed rivers. To gain understanding of the potential impacts of a changing climate on future nitrate loads for groundwater-fed rivers, we need to improve the coupling of hydro(geo)logical, geomorphological and ecological process-based understanding through integrated field experimentation, advanced remote sensing technologies, and dynamic modelling.

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DATA AVAILABILITY STATEMENT

This article is an analysis and synthesis of research undertaken throughout the NERC-funded project. The data that support the findings of this study are available on request from the authors.

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