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1 Revealing chlorinated ethene transformation hotspots in a

2 nitrate-impacted hyporheic zone

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15 Abstract

16 Hyporheic zones are increasingly thought of as natural bioreactors, capable of 17 transforming and attenuating groundwater pollutants present in diffuse baseflow. An 18 underappreciated scenario in the understanding of contaminant fate hyporheic zones is 19 the interaction between point-source trichloroethene (TCE) plumes and ubiquitous, 20 non-point source pollutants such as nitrate. This study aims to conceptualise critical 21 biogeochemical gradients in the hyporheic zone which govern the export potential of 22 these redox-sensitive pollutants from carbon-poor, oxic aquifers. Within the TCE plume 23 discharge zone, discrete vertical profiling of the upper 100 cm of sediment pore water 24 chemistry revealed an 80% increase in dissolved organic carbon (DOC) concentrations 25 and 20–60 cm thick hypoxic zones (<2 mg O_2 L⁻¹) within which most reactive transport was observed. A 33% reduction of nitrate concentrations coincided with elevated pore 26 27 water nitrous oxide concentrations as well as the appearance of manganese and the TCE 28 metabolite *cis*-1,2-dichloroethene (cDCE). Elevated groundwater nitrate concentrations 29 (>50 mg L⁻¹) create a large stoichiometric demand for bioavailable DOC in discharging groundwater. With the benefit of a high-resolution grid of pore water samplers 30 31 investigating the shallowest 30 cm of hypoxic groundwater flow paths, we identified 32 DOC-rich hotspots associated with submerged vegetation (Ranunculus spp.), where low-33 energy metabolic processes such as mineral dissolution/reduction, methanogenesis and 34 ammonification dominate. Using a chlorine index metric, we show that enhanced TCE to cDCE transformation takes place within these biogeochemical hotspots, highlighting 35 their relevance for natural plume attenuation. 36

37 Keywords: hyporheic zone; terminal electron-accepting processes; chlorinated ethenes;
38 nitrate; dissolved organic carbon; natural attenuation.

39 **1** Introduction

40 Chlorinated ethenes (CEs) such as trichloroethene (TCE) and its metabolites cis-1,2-41 dichloroethene (cDCE) and vinyl chloride (VC) are among the most common volatile 42 organic contaminants (VOCs) detected in groundwater (Shapiro et al., 2004; Rivett et al., 43 2012, Palau et al., 2014). These organohalides are prominent chemical stressors in 44 surface water ecosystems impacted by legacy industrial sources (Roy et al., 2018; Sonne 45 et al., 2018). Dissolved-phase CE plumes often continue to migrate in aquifers with limited sorption capacity, and frequently discharge with groundwater baseflow to 46 47 streams and rivers (Weatherill et al., 2018). Back-diffusion from low permeability media to groundwater means that many plumes will continue to persist well into or even 48 49 beyond this current century (Seyedabbasi et al., 2012). Hence, given their environmental 50 health significance and widespread abundance, it is little surprise that CEs are among the most prevalent VOC class reported in surface water to date (e.g. Yamamoto, 2014; 51 52 Wittlingerová et al., 2016).

53 In complex landscapes with long histories of diverse land use practices, the 54 concurrence of multiple groundwater pollution incidences is increasingly common. For instance, the natural attenuation and fate of point-source CE plumes which co-mingle 55 with nitrate (NO_3^-) from non-point agricultural sources has not been widely considered 56 at field scale to date (e.g. Bennet et al., 2007; Lu et al., 2017). In recent decades, global 57 groundwater NO_3^- concentrations have been steadily rising as a result of increasing 58 agricultural intensification (Gu et al., 2013; Wang et al., 2016). NO_3^- is a mobile anion 59 which only weakly adsorbs to clay minerals (Meghdadi, 2018), often resulting in high 60 loadings to vulnerable aquifers in agricultural regions (Ascott et al., 2017). This 61 groundwater excess of NO₃⁻ is a well-known global environmental concern linked to 62

eutrophication of receiving waters (Boyer et al., 2006) and blue-bay syndrome
(methaemoglobinaemia) in drinking water (Addiscott and Benjamin, 2006).

Before reaching surface water, these groundwater pollutants must transit the 65 66 aquifer-river interface or hyporheic zone (HZ) where groundwater and surface water interact (Boano et al., 2014; Cardenas, 2015). The HZ offers considerable promise as a 67 68 passive biobarrier for in-situ 'treatment' of a broad range of organic groundwater 69 pollutants (Schaper et al., 2018; Gilevska et al., 2019) including CEs (Weatherill et al., 70 2018). HZ sediments are often naturally rich in organic matter, resulting in hypoxic or anoxic pore water conditions (Atashgahi et al., 2015) where CEs (such as TCE) and NO_3^- 71 are important terminal electron acceptors (TEAs) in dissimilatory microbial metabolism. 72 73 Here, fermentation of dissolved organic carbon (DOC) supplies electrons via dissolved 74 hydrogen (H₂) which drives a thermodynamic series of terminal electron-accepting processes (TEAPs) (Heimann et al., 2009). Under DOC-limiting conditions, this TEAP 75 76 succession tends to follow an ecological succession which can be predicted by the Gibb's free energy yield (ΔG°) [kJ mol⁻¹] of key redox couples: $O_2 \rightarrow H_2O$ [-238]; $NO_3^- \rightarrow N_2$ [-77 240]; $Mn^{IV} \rightarrow Mn^{II}$; [-185]; $Fe^{III} \rightarrow Fe^{II}$ [-126]; $TCE \rightarrow cDCE$ [-121]; $cDCE \rightarrow VC$ [-101]; 78 SO_4^{2-} → HS⁻[-48]; HCO₃⁻ → CH₄ [-32.8] (Wiedemeier et al., 1998; under conditions 79 80 reported therein).

81 From a thermodynamic perspective, NO₃⁻ reduction (denitrification) offers 82 considerably higher free energy yields than reductive dechlorination of TCE and cDCE in 83 heterotrophic metabolism (Weatherill et al., 2018). Hence, we hypothesise that elevated 84 groundwater NO₃⁻ will detrimentally impact the biogeochemical transformation capacity 85 of HZs where plumes discharge through agriculturally intensive landscapes. To test this 86 hypothesis, the present study aims to conceptualise critical biogeochemical gradients which govern the HZ transformation potential of a TCE plume co-mingled with nonpoint source NO_3^- . We apply a 'bottom-up' (Lansdown et al., 2016) multi-scale hydrochemical monitoring approach to: (a) resolve in-situ biogeochemical gradients controlling chemical fluxes from groundwater (b) identify potential hotspots of multipollutant transformation and (c) evaluate the impact of regionally elevated $NO_3^$ concentrations on chlorinated ethene transformation in the HZ.

93 2 Materials and methods

94 2.1 Study area characteristics

95 The study area is located in the lowland River Tern catchment (2° 53 W, 52° 86 N) in Shropshire (UK) where regional land use is dominated by intensive agriculture 96 (Krause et al., 2013). The catchment is underlain by highly permeable Permo-Triassic 97 98 sandstones with groundwater flow through a high porosity matrix (Shepley and Streetly, 2007) (Fig. 1). In this tributary of the River Severn, 76% of long-term river flow is 99 100 derived from groundwater storage (Marsh and Hannaford, 2008). The present study 101 focuses on a 40 m river reach that has been previously identified as the discharge zone 102 of a deep-seated groundwater TCE plume (Fig. 1) (Weatherill et al., 2014). The 103 unconfined regional sandstone aquifer is unlikely to significantly retard migration of the 104 plume (Smith and Lerner, 2008).

105 2.2 Multi-scale hydrochemical monitoring approach

Depth-discrete groundwater samples were collected from four sandstone bedrock
 boreholes (Fig. 1) in March 2012 with passive grab sampling (HydraSleeve[™]) under
 ambient borehole flow conditions (Weatherill et al., 2014). A 40 m reach-scale network
 of multi-level mini-piezometers (MP1-MP25) (see Supporting Information Appendix A;

110 Figure S1) deployed in the riverbed were sampled in early August 2012 during a summer baseflow recession period (S2). Reach-scale pore water chemistry samples 111 112 were extracted using dedicated air-tight syringes from PTFE sample tubes with point 113 screens in contact with sediment at 20, 40, 60, 80 and 100 cm below bed level (S1) 114 (Weatherill et al., 2014). Surface water was collected as grab samples from 20 cm above 115 the bed level from the upstream, mid-point and downstream sections of MP network 116 (S1). To provide a high-resolution horizontal window on shallow pore water chemistry, 117 a rectangular grid (0.6 x 2.8 m) of pore water samplers (PW1-PW13) with point-screens 118 at 5, 10, 20 and 30 cm depth was also included (S1, S2). In-situ luminescent dissolved 119 oxygen (DO) was measured in syringe and grab samples using an optical probe (Hach-120 Lange, UK) with a detection limit of 0.01 mg $O_2 L^{-1}$.

121 **2.3 Laboratory analysis**

122 VOC samples were analysed using a headspace GC-MS-SIM method described in 123 Weatherill et al. (2014). Dissolved metabolic gas samples were collected in gas-tight 124 Exetainer (Labco, UK) vials fixed by a 50 mol ZnCl solution to inhibit microbial activity. 125 Methane (CH₄) and nitrous oxide (N₂O) were determined using N₂ headspace GC-126 FID/µECD (Agilent GC7890A series) equipped with a 1 mL sample loop. Equivalent 127 dissolved phase concentrations were estimated from headspace gas volumetric 128 concentrations using Henry's law (Comer-Warner et al., 2018). Equivalent mass 129 concentration detection limits were <0.01 μ g L⁻¹ for both gases. This GC method was not 130 suitable to detect ethene, the non-chlorinated end-product of TCE reductive dechlorination. 131

132 Nitrate (NO_3^-) , nitrite (NO_2^-) , sulfate (SO_4^{2-}) and chloride (Cl-), were determined by 133 anion chromatography on a Dionex ICS1000 (Dionex Corporation, UK). Ammonium (as

N-NH₄⁺) was analysed using an automated indophenol blue LCK304 method with a 134 detection limit of 0.015 mg N L⁻¹ (Hach-Lange, Germany). Total dissolved iron (Fe), 135 136 manganese (Mn) and silicon (Si) were determined from inline filtered (0.45 µm) and 137 acidified samples using inductively coupled argon plasma optical emission spectroscopy 138 (ICP–OES) (Varian Vista Pro MPX) with detection limits of <0.1 mg L⁻¹ for all elements. 139 DOC samples were filtered inline by 0.7 µm pre-combusted (550 °C) glass-fibre filters to 140 pre-combusted glass sample vials acidified with HCl and analysed on a Shimadzu TOC-141 Vcpn analyser (Shimadzu Corporation, Japan) with a detection limit of 0.2 mg C L⁻¹.

142 **2.4 Data analysis**

143 Statistical analyses were performed with SPSS v19 (IBM, USA). Variable 144 distributions were tested using the Shapiro-Wilk test of normality to determine whether 145 parametric or non-parametric statistics were appropriate. Differences in means 146 between groups were analysed using paired T-tests or one-way analysis of variance (ANOVA) for normally or log-normally distributed variables. All means reported were 147 148 back-transformed from their logarithms. Non-parametric Mann-Whitney U-tests were 149 used to test differences in medians for datasets which were neither normally nor log-150 normally distributed. Principal component analysis (PCA) was performed on a subset of 151 pore water samples (n = 27) from the high-resolution pore water grid (S1, S2). PCA is 152 advocated as a key line of evidence for biogeochemical interpretation of aquifer CE natural attenuation potential in recent guidance literature (Tarnawski et al., 2015). 153

- 154 **3 Results and discussion**
- 155 **3.1 Aquifer hydrochemistry**

156 Groundwater chemistry results are presented in Table 1. cDCE, VC, Fe, Mn NH₄⁺ and

 NO_2^- were all below their detection limits and are not shown. TCE was the only CE 157 detected in the sandstone aquifer with the highest concentrations observed at the 80 m 158 159 deep HGA abstraction borehole, approximately 500 m distance from the river (Fig. 1). 160 The persistently elevated TCE concentrations (>150 μ g L⁻¹) at depth in this open 161 borehole are believed to be representative of a deep-seated bedrock plume (Weatherill 162 et al., 2014). The plume is inferred to have a migration pathway along a curved axis 163 between the HGA/HGO boreholes in the up-gradient aquifer and HBE/HBW boreholes 164 on the riverbank (Fig. 1) (Weatherill et al., 2014). The groundwater environment of the 165 up-gradient plume was rich in high-energy TEAs including DO (median: 5.6 mg L⁻¹) and NO_3^- (median: 55.3 mg L⁻¹) with moderate concentrations of SO_4^{2-} (median: 34.2 mg L⁻¹). 166 Groundwater NO_3^- was notably elevated in the riverbank boreholes (73–81 mg L⁻¹). 167 168 Dissolved N₂O was oversaturated by up to 35 times for all groundwater samples with a 169 median concentration of 18 μ g L⁻¹. The highest N₂O levels (up to 47 μ g L⁻¹) were 170 associated with the shallower depths of the up-gradient sandstone aquifer. DOC 171 concentrations were very low in the aquifer (<2 mg L⁻¹), with highly undersaturated 172 dissolved CH₄ concentrations with respect to air equilibrium ($<0.1 \mu g L^{-1}$).

173 **3.2** Vertical chemical gradients in the hyporheic zone

An overview of maximum pore water TCE and cDCE concentrations in the uppermost metre of riverbed sediment are presented in Fig. 2 with all CE results reported in Supporting Information Appendix B (supplementary tables). cDCE was detected in 10 samples with a maximum of 6.9 μ g L⁻¹ at MP7 at 40 cm. VC was only confirmed twice at 20 cm in MP18 (0.5 μ g L⁻¹) and at MP23 (0.7 μ g L⁻¹). This plume spatial variability in the riverbed sediments is consistent with previous monitoring results in the discharge zone (Weatherill et al., 2014).

181 Vertical depth-chemistry profiles are presented in Fig. 3 with comparison of pore water median concentrations at the base (100 cm) and top (20 cm) of the riverbed 182 183 sediment sequence reported in Table 2. We assume that groundwater discharge through 184 the HZ is predominantly vertical and that observed chemical gradients represent bulk 185 attenuation along groundwater flow paths through riverbed pore water pathways 186 (Krause et al., 2013). TCE concentrations exhibited an overall decline during transport through the HZ. High-energy TEAs (DO and NO_3^-) and SO_4^{2-} concentrations in deep (100 187 cm) riverbed pore water samples were similar to the underlying aquifer (Table 2). A 188 189 step change in DO concentrations from 60-40 cm to shallower sample depths with 190 hypoxic conditions (e.g. $< 2 \text{ mg } O_2 \text{ L}^{-1}$) was observed for many MP locations including the 191 cross-channel TA transect and MP18-23 (Fig. 2).

192 NO_3^- concentrations declined by one third from the aquifer median during discharge through the HZ. Samples from a group of mini-piezometers (MP12, MP15 and MP16) 193 194 exhibited exceptionally high NO_3^- concentrations (>130 mg L⁻¹) which were not associated with the up-gradient plume (Table 1). Overall, groundwater flow paths 195 196 through the HZ were not a net source of dissolved N₂O in the plume discharge zone. 197 However, six hypoxic samples from 20 to 40 cm depth had elevated N₂O concentrations (>200 μ g L⁻¹) including MP6, MP7, MP18 and MP23. SO₄²⁻ concentrations did not vary 198 199 significantly during transport through the HZ.

Pathways through the HZ were observed to be a significant source of DOC and CH_4 with marked increases from 40–20 cm for DOC and 60–40 cm for CH_4 . These samples coincide with the hypoxic locations at Transect TA and MP18-MP23 and detections of dissolved Mn (up to 9.6 mg L⁻¹) and occasionally Fe. Under the near-neutral groundwater pH conditions (Table 1), soluble Fe and Mn are assumed to be mostly a product of microbially-mediated dissolution/reduction of Fe^{III}/Mn^{IV} mineral phases
present in the sediment solids (Tarnawski et al., 2015).

207 The multi-level chemical profiles obtained at MP7, MP18 and MP223 (Fig. 2) were 208 co-located with 100 cm sediment core samples from Weatherill et al. (2014). These 209 cores provide a physical context for observed biogeochemical gradients below the 210 sediment-water interface (Fig. 4). At each location, discrete changes in biogeochemical 211 conditions takes place in the upper 20 to 60 cm layer of sediment, which is composed of 212 medium sands (MP18 and MP23) and silty peat (MP7). Here, large declines in DO and 213 NO_3^- are associated with elevated DOC, CH_4 and N_2O and the appearance of Mn and cDCE (Figs. 2 and 3). Our observations suggest that these hypoxic zones in the HZ can deplete 214 215 high-energy TEAs from groundwater sufficiently to enable lower energy TEAPs to 216 proceed allowing limited reductive dechlorination of TCE to cDCE.

217 **3.3** High-resolution pore water sampler grid

218 A consistently reactive hypoxic zone was selected for a follow up high-resolution 219 investigation using a rectangular grid pore water samplers (S2). The spatial variability 220 of selected parameters are presented in S3 with all results reported in Appendix B 221 (Table T1). The grid was designed to target horizontal chemical gradients in the area of 222 MP7 (Fig. 4) where the highest cDCE concentrations have been observed in previous 223 work (Weatherill et al., 2014). The riverbed within the grid area was composed of 224 medium quartz sands influenced by submerged macrophyte cover (*Ranunculus* spp.). 225 Comparison of solute concentration means between 5, 10 and 20 cm sample depths 226 using single factor ANOVA did not reveal any statistically significant 'depth effect' (p =227 >0.05) between depth-grouped samples. These results confirm that the sampler 228 network had intercepted pore water above the critical vertical redox gradient in the HZ

(Figs. 3 and 4).

230 TCE was present in all but four samples within the network with a maximum of 29 231 µg L⁻¹ at PW7 10 cm. cDCE was detectable in 75% of samples with six locations 232 exceeding the MP network maximum of 7 μ g L⁻¹ (Fig. 4) reaching up 16 μ g L⁻¹ at PW9 5 cm. VC was above detection limit in 27% of samples with a maximum of 2.3 μg L⁻¹ also at 233 PW9 5 cm. All PW samples had DO concentrations $\leq 2 \text{ mg } O_2 \text{ L}^{-1}$ with little variation 234 across the network. NO_3^- was more spatially variable than DO reaching a maximum of 33 235 236 mg L⁻¹ at PW5 10 cm. This high energy TEA was below detection limit in 13% samples 237 with a further 34% showing NO_3^- less than 5 mg L⁻¹. N₂O was spatially variable with 238 concentrations exceeding 100 µg L⁻¹ in six samples mostly located in the upstream 239 samplers. Very low concentrations of N_2O (<1 μ g L⁻¹) were associated with locations 240 which were also characterised by low NO₃⁻ concentrations in the downstream group of 241 samples. These samplers also exhibited elevated NH_4^+ (>1 mg N L⁻¹). SO_4^{2-} exhibited a greater range of concentrations than NO_3^- with a maximum of 66.4 mg L⁻¹ at PW1 10 cm. 242 This SO_4^{2-} concentration is comparable to the overlying river water (Table 1) and may 243 244 indicate surface water infiltration to the HZ at the upstream samplers.

245 Many samples from the downstream group of samplers exhibited DOC concentrations considerably exceeding 10 mg L⁻¹ that of river water (Table 2) and those 246 247 from the MP network (Table 2, Figs. 3 and 4). As a product of low energy mineral-248 reducing TEAPs, dissolved Mn was widespread with a large number of downstream 249 samples exhibiting Mn concentrations (>10 mg L⁻¹). Fe was also present with a range of 1-4 mg L⁻¹ and a maximum of 12.7 mg L⁻¹ at PW11 30 cm. Many samples from the 250 251 downstream part of the network exhibited CH₄ concentrations in excess of 1000 µg L⁻¹ 252 or more than twice that of the MP network maximum (Fig. 3).

Paired two sample T-tests were used to compare spatial means from paired upstream (PW1–PW5) and downstream (PW9–PW13) sample locations (Table 3). Significant declines (p = <0.05) are observed from upstream to downstream samples for TCE, NO₃⁻ and N₂O coupled with significant increases in DOC, Mn and CH₄. These results suggest that high and low energy TEAPs may be spatially organised at sub-metre horizontal scales within shallow HZ sediments.

259 **3.4 Evaluating in-situ plume transformation extent**

The chlorine index (CI) is a useful metric integrating the stoichiometric mass balance of parent compound to daughter products into a single number (Harkness et al., 2012; Freitas et al., 2015). The CI negates the confounding effects of dilution and dispersion to evaluate parent compound transformation extent:

264
$$CI_{TCE} = \frac{\sum W_i C_i}{\sum C_i}$$

Where W_i is the number of chlorine atoms in the CE molecule and C_i is the molar 265 concentration of the CE species present. The CI approach is a cost-effective alternative to 266 compound-specific stable isotope analysis (CSIA) (e.g. Gilevska et al., 2019) for single-267 parent compound plumes (Freitas et al., 2015) such as the one is this study. The 268 269 relationship between total plume mass (in nmol) and CI_{TCE} are presented in Fig. 5 270 (samples where CI_{TCE} = 3 are omitted for clarity). Because it was not possible to include 271 ethene, the minimum CI_{TCE} possible is 1 in this study. From this figure, it can be seen that 272 all mini-piezometer (blue squares) and many samples from the upstream plot-scale grid (open circles) show similar weak dechlorination extents with CI_{TCE} values >2.5 (partial 273 274 TCE to cDCE transformation). A greater degree of TCE dechlorination is indicated for 275 most samples from the downstream (black circles) and some mid-point samples (green 276 circles) with a CI_{TCE} 1.6 – 2.5 (Fig. 5) where much of the plume mass is transformed to

277 cDCE with limited cDCE reduction to VC.

278 **3.5** Principal component analysis of pore water chemistry

279 Here, we use PCA to interpret the hypoxic biogeochemical environment in which 280 reductive dechlorination occurs with concomitant TEAPs that cycle nitrogen, carbon, 281 sulfur and minerals in the HZ (Tarnawski et al., 2015). PC1 and PC2 (Fig. 6) represent 282 linear combinations of the original variables from 27 PW network samples which 283 explain 73% of the observed variance. PC1 explains 44.3% and strongly associated with 284 Mn (r = 0.92), Si (r = 0.91), CH₄ (r = 0.84), NH₄⁺ (r = 0.8) and to a lesser extent DOC (r = 285 0.63). PC1 is interpreted as a biogeochemical metabolite factor associated which is colinear with the end-products of low energy TEAPs. This factor is spatially associated 286 287 with most downstream and some mid-point sample locations, where pore water chemistry is dominated by mineral dissolution, Mn^{IV} reduction and methanogenesis. 288 Although NH_4^+ is strongly correlated, PC1 is unrelated to NO_3^- which suggests that 289 290 ammonification of organic matter is the dominant nitrogen cycling process rather than 291 dissimilatory nitrate reduction to ammonium (DNRA) (Rivett et al., 2008). PC1 negatively correlates with CI_{TCE} (r = -0.73) and to a lesser degree SO_4^{2-} (r = -0.6). Hence, 292 293 in this low-energy biogeochemical environment, TCE is a favourable TEA where 294 sediment/pore water hydrochemical interactions are enhanced.

PC2 accounts for 28.8% of the variance observed and is strongly associated with oxidised nitrogen species including NO_2^- and N_2O (r = 0.88) and NO_3^- (r = 0.76). Given the depleted NO_3^- concentrations and hypoxic pore water conditions present, NO_2^- and N_2O are likely to be intermediates of in-situ denitrification (Rivett et al., 2008; McAleer et al., 2017). NH⁺ only very weakly correlates with this factor (r = 0.34) which suggests that DNRA may play a limited role in this environment. Hence, PC2 is interpreted as a

301 *denitrification factor* which is spatially associated with most of the upstream and some 302 mid-point samples. This factor is positively correlated with CI_{TCE} (r = 0.47) and 303 negatively correlated with DOC (r = -0.5). PC2 represents active NO_3^- reduction as a high 304 energy TEAP which is spatially independent of low energy carbon, nitrogen and mineral 305 cycling in the HZ.

306 4 Discussion

307 4.1 Large scale hydrochemical gradients in the hyporheic zone

308 Reach-scale observations from multi-level profiles within the top metre of bed 309 sediments suggest that the HZ is an important sink for high-energy groundwater TEAs 310 (Table 1) with bulk attenuation of 71% for DO and 33% for NO_3^- (Table 2). Pore water 311 TCE concentrations were observed to decline by 44% in the plume discharge zone 312 (Table 2). The deeper riverbed is characterised by discontinuous lenses of peat, clay and 313 silt overlying the bedrock aquifer which may be up to several metres thick (Weatherill et 314 al., 2014). From Fig. 5, clear differences can be seen in the vertical profiles of TCE where 315 peat is absent (MP18) and present (MP7). Given that metabolites (cDCE and VC) were 316 detected in just 9.5% of MP network samples, much of the observed pore water 317 attenuation may be attributed to non-reactive sorptive-diffusive transport processes 318 (e.g. Rivett et al., 2019).

Before reaching surface water, chemical fluxes from groundwater must transit variable thickness bedforms composed of well-sorted quartz sands with porosities of 20% (Weatherill et al., 2014; Weatherill, 2015). Heat flow experiments have shown that this pore water domain is in close hydraulic continuity with the overlying surface water column (Angermann et al., 2012) due to the presence of the flow-confining structures

324 beneath (Gomez-Velez et al., 2014). Aquifer and river water Cl- concentrations did not 325 contrast significantly (Fig. 3) and hence Cl⁻ could not be used as a conservative tracer to 326 delineate hyporheic exchange zone extent (e.g. Freitas et al., 2015). On the other hand, SO_4^{2-} concentrations differed considerably (Fig. 3). Nonetheless, no evidence of surface 327 water mixing to a depth of 20 cm can be seen in the SO_4^{2-} profiles (Fig. 3) under baseflow 328 conditions. This precludes dilution from surface water infiltration as a factor in the 329 330 observed TCE attenuation under baseflow conditions in the MP network (e.g. Hamonts 331 et al., 2012).

332 Our findings suggest that in-situ reactive transport takes place within discrete 333 hypoxic envelopes associated with the TA transect MP locations (40-60 cm thick) and 334 MP18–MP23 where it is thinner (20 cm). This biogeochemically active zone is mostly 335 associated with the quartz sands layer and some peat-rich lenses in the underlying 336 cohesive deposits (Fig. 4). At MP6, MP7, MP18 and MP23, step-change declines in NO₃ are associated with greater than 10-fold increases in pore water N₂O concentrations 337 338 $(>200 \ \mu g \ L^{-1})$ (Figs. 3 and 4). N₂O production in the HZ is thought to be indicative of partial NO_3^- reduction where pore water residence times are insufficient to allow 339 340 complete transformation to N₂ (Quick et al., 2016). These hypoxic zones are also 341 associated with an 80% increase in pore water DOC concentrations and a greater than 342 20-fold increase in CH₄ from the aquifer background (Table 2). The presence of CH₄ and 343 Mn indicate that low-energy TEAPs take place where high energy TEAs are locally depleted (e.g. DO <2 mg O_2 L⁻¹; NO₃⁻ <4 mg L⁻¹) (Fig. 4). These conditions appear to be 344 capable of supporting partial reductive dechlorination of TCE to cDCE (e.g. CI_{TCE} >2.5) 345 346 (Fig. 5)..

347 **4.2** Evidence of multi-pollutant transformation hotspots

348 Evidence of discrete horizontal organisation of dissimilatory TEAPs at sub-metre 349 scales was observed within the rectangular grid (Table 3). At the time of sampling, much 350 of the riverbed at the TA transect of the MP network as well as parts of the wider river corridor was occluded by submerged Ranunculus spp. stands. In most upstream PW 351 network samples, active denitrification is suggested by depleted NO_3^- concentrations 352 (<4–30 mg $L^{-1})$ with elevated N_2O (>100 μg $L^{-1})$ and NO_2^- (0.4–2 mg $L^{-1}).$ In some 353 354 downstream and some mid-point samples, oxidised nitrogen species are mostly absent 355 and the pore water chemistry is dominated by the metabolites of low-energy TEAPs 356 including mineral dissolution/reduction, methanogenesis and ammonification (Fig. 6). 357 From a thermodynamic perspective, this low-energy metabolic regime presents a 358 favourable environment for plume transformation which is demonstrated by the low 359 chlorine indices observed in the sub-group of PW samples where $CI_{TCE} = 1.6-2.5$ (Fig. 5). 360 Overall, the reductive dechlorination potential of the hyporheic zone appears to be 361 limited to cDCE production with only minor concentrations of VC detected which is 362 consistent with previous results (Weatherill et al., 2014). This incomplete natural 363 attenuation may be ascribed to the presence of residual DO concentrations, a lack of 364 suitable cDCE dechlorinator populations or competition for reducing equivalents by 365 metal-reducing bacteria (Chambon et al., 2013; Paul et al., 2016). The presence of both NH⁺₄ and CH₄ in hypoxic samples may favour alternative cometabolic pathways for cDCE 366 and VC mineralisation at the interface between hypoxic and oxic flow paths (Mattes et 367 368 al., 2010). CSIA and molecular microbial techniques may offer additional lines of evidence to elucidate metabolic pathways and the activities of specific degraders (Badin 369 370 et al., 2016; Ottosen et al., 2019) and are advocated for future work.

371 DOC concentrations exceeding that of surface water and the underlying pore water 372 (e.g. >10 mg L⁻¹) were observed in many PW samples from the PW network. This is 373 consistent with other reports of vegetated riverbeds as important sources of pore water 374 DOC with intensified hotspots of carbon cycling in the HZ as a result (e.g. Trimmer et al., 375 2009; Ullah et al., 2014). Submerged macrophytes are thought to modify their local 376 aquatic environment by reducing river flow velocities resulting in increased fine 377 sediment deposition in spring and summer months (Sand-Jensen, 1998; Heppel et al., 378 2009) with a consequent reduction in bed permeability and an increase in contaminant 379 exposure times in reactive zones (Oldham et al., 2013). Our results suggest that the 380 hypoxic sediments at the mid and down-stream parts of the network were influenced by 381 organic-rich fine sediment derived from allochthonous surface water catchment sources 382 (Ballantine et al., 2008), resulting in elevated in pore water DOC, Mn, Si and NH⁺₄ 383 concentrations. In addition, delivery of root exudate DOC in the rooting zone which cuts 384 across the HZ may play a role in enhanced biogeochemical cycling in vegetated 385 sediments (Ullah et al., 2014). Our observations show that both N₂O and CH₄ are useful 386 indicators for hotspots of high and low-energy TEAP activity respectively in the HZ.

387

4.3 Implications of elevated nitrate on TCE transformation potential

The large metabolic energy gain from reduction of NO_3^- implies that when DOC is in excess, denitrification will take place in preference to lower energy reductive dechlorination reactions in the HZ. Liu et al. (2015) demonstrated that NO_3^- additions had an inhibitory effect on low energy TEAPs (SO_4^{2-} reduction and methanogenesis) in sewer sediments. Denitrifying bacteria can maintain pore water H₂ thresholds (<0.1 nmol) far lower than necessary for reductive dechlorination (Weatherill et al., 2018). However, considerable overlap in H₂ thresholds are observed experimental studies 395 under metal-reducing conditions with mineral bioavailability playing an important role 396 (Paul et al., 2016). Our findings suggest that reduction of NO_3^- and TCE to cDCE 397 dechlorination occur independently of one another which is supported by the PCA 398 results in Fig. 6.

Egli et al. (2010) suggest a minimum DOC concentration of 2 mg L⁻¹ is required to initiate catabolic genes involved in microbial contaminant transformation. Throughout the up-gradient aquifer, DOC concentrations were at or below this threshold (Table 1). The DOC resources required to reduce high-energy groundwater TEAs (DO and NO_3^-) are estimated using the following stoichiometry (Tesoriero and Puckett, 2011):

404
$$CH_2O + O_2 \rightarrow CO_2 + H_2O$$
 [$\Delta G^{\circ} - 238 \text{ kJ mol}^{-1}$]

405
$$5CH_2O + 4NO_3^- \rightarrow 2N_2 + 4HCO_3^- + CO_2 + 3H_2O$$
 [$\Delta G^\circ - 240 \text{ kJ mol}^{-1}$]

406 With this stoichiometry, it is possible to estimate the regional DOC demand (mg C L⁻¹) imposed by high-energy TEAPs at overlapping spatial scales within the monitoring 407 408 networks. Fig. 7 plots observed DO concentration against high-energy DOC demand from 409 DO/NO_3^- concentrations recorded in samples. Given the limited solubility of O_2 in 410 groundwater, the high-energy DOC demand is dominated by the elevated NO_3^- 411 background (Table 1, Fig. 3). By plotting observed DOC concentration for each sample 412 (denoted by the black diamonds) with the calculated DOC demand, it is possible to 413 identify locations in the HZ where DOC is in excess (Fig. 7). NO₃⁻-DOC stoichiometric 414 relationships exert important controls on groundwater redox conditions that govern 415 nitrogen export patterns at landscape scale (Taylor and Townsend, 2012; Helton et al., 416 2015). It is clear that the DOC required to reduce elevated groundwater NO_3^- produces 417 an electron donor-limited environment except for a subset of hypoxic PW samples. In 418 these locations, lower-energy metabolism is favoured including reductive dechlorination of TCE to cDCE. Therefore, elevated NO₃⁻ levels are likely to impose a critical redox
'buffer' (e.g. Diem et al., 2013) which must first be overcome when CE plumes traverse
intensive agricultural regions underlain by vulnerable oxic groundwater systems.

422 **5 Conclusions**

423 With the application of a multi-scale 'bottom-up' monitoring approach, we have 424 shown that biogeochemical processes in the HZ can locally modify chemical fluxes and 425 redox conditions in discharging groundwater. Biogeochemically active hypoxic 426 pathways through the uppermost 20-60 cm of sediment pore water are capable of 427 reducing bulk groundwater discharge of NO_3^- by one third. In these zones, active 428 denitrification is indicated by depleted NO_3^- and elevated dissolved N₂O concentrations. 429 Using the chlorine index of TCE as a metric to evaluate in-situ plume transformation, we 430 have shown that enhanced dechlorination of TCE to cDCE occurs locally within DOC-rich 431 hotspots where pore water chemistry is dominated by the end-products of low-energy 432 microbial metabolism (Mn, CH₄ and NH₄).

433 Our results highlight the importance of DOC-rich pore water associated with 434 vegetated riverbeds for seasonal ecosystem service provision in the passive 'treatment' of groundwater pollutants discharging from carbon-poor oxic aquifers. This local 435 436 electron donor excess is capable of overcoming the large stoichiometric demands for 437 carbon resources posed by high background concentrations of NO_3^- . Here, an ecological 438 succession of TEAPs is enabled where reductive dechlorination of CE species becomes 439 thermodynamically favoured. Below a critical DOC threshold, reduction of elevated 440 groundwater NO₃ inhibits the transformation of CEs in dissimilatory microbial 441 metabolism. The inclusion pore water N₂O and CH₄ in combination with DO and

442 traditional redox indicators to identify respective high and low energy microbial443 metabolic regimes is advocated further.

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Tables and figure captions

Table 1: Permo-Triassic sandstone groundwater hydrochemistry. Refer to Figure 1 for

Borehole ID	рН	EC	DO	TCE	NO ₃	SO ₄	Cl	DOC	CH ₄	N_2O
	pH units	µS cm⁻¹	mg O ₂ L ⁻¹	μg L-1	mg L-1	mg L-1	mg L-1	mg C L-1	μg L-1	μg L-1
HGA 35 m	7.6	623	5.1	89	66.2	24.8	32.6	2.19	0.08	44.3
HGA 50 m	7.6	556	6.6	137	53.1	23.1	33.0	1.64	0.09	16.1
HGA 80 m	7.5	545	6.2	162	66.7	20	34.2	1.35	0.08	18.1
HGO 20m	7.8	498	5.6	48.8	55.3	21.2	37.9	2.01	0.09	28.3
HGO 40m	7.7	502	5	74.4	52.8	20.5	36.0	1.58	0.08	20
HBE	7.1	753	6.4	26.9	81.1	28.4	29.6	2.14	0.07	5.9
HBW	7.3	661	6.8	9.38	73	22	37.5	1.94	0.09	17.2

623 location of monitoring boreholes.

Table 2: Comparison of median solute concentrations using Mann-Witney U-tests from
selected mini-piezometer samples at the bottom (100 cm) and top (20 cm) of the

527 selected mini plezonieter samples at the bottom (100 cm) and top (20 cm) of the

628 hyporheic zone (n = 16) including the aquifer (n = 7) and river (n = 3) for comparison.

Parameter	units	Aquifer	MP _{100cm}	MP _{20cm}	River	Sig. change	р
ТСЕ	μg L-1	74.4	21.1	12.0	<0.01	-43%	0.01
DO	mg O ₂ L ⁻¹	6.3	6.4	1.9	9.6	-71%	< 0.01
NO ₃	mg L ⁻¹	60.8	60.3	40.1	37.4	-33%	< 0.01
SO ₄	mg L ⁻¹	22.6	25.4	28.1	61.0	-	>0.05
Cl	mg L ⁻¹	34.2	32.3	31.6	34.3	-	>0.05
DOC	mg C L-1	1.98	2.6	4.7	7.96	+80%	< 0.01
N ₂ O	μg L-1	17.7	18.3	17.6	3.2	-	>0.05
CH ₄	μg L-1	0.08	0.17	2.86	8.22	+1582%	< 0.01

629 Significant changes are expressed as percentages.

630

Table 3: Comparison of selected mean solute concentrations at paired
upstream/downstream samples of the pore water grid using paired T-tests (n = 14)
(standard deviations in parentheses). Significant changes are expressed as percentages.

Davamatar	unita	DM	DIAZ	Sig change	n
Parameter	units	P VV upstream	P VV downstream	Sig. change	р
NO ₃	mg L-1	14.1 (2.03)	5.1 (1.47)	-64%	< 0.05
	_				
SO ₄	mg L-1	38.8 (1.38)	26.5 (1.53)	-32%	0.032
	0				
Cl	mg L ⁻¹	29.9 (1.11)	32.6 (1.06)	-	>0.05
	0				
Mn	mg L-1	2.07 (1.89)	6.11 (3.07)	+195%	< 0.05
	8 -				
DOC	mg C L-1	4.53 (1.38)	6.89 (1.58)	+32%	< 0.05
200	ing o n				
N ₂ O	μσ I1	31.5 (5.43)	6.93 (4.45)	-78%	< 0.05
	r5 1				
CH₄	ця L-1	11.6 (2.90)	266.1 (2.15)	+2196%	< 0.05
	r8 -				



Figure 1: Study area location and conceptual site model of regional aquifer and TCE
plume and its inferred discharge zone at the River Tern (adapted from Weatherill et al.,
2014). Black dots denote sampling depths in open boreholes using passive methods.



Figure 2: Spatial variability of maximum TCE and cDCE at mini-piezometer locations in the plume discharge zone in August 2012. Cross-channel plume concentration gradients are observed at the TA and TB mini-piezometer transects with the highest TCE concentrations occurring downstream of the TB transect. In-situ reductive dechlorination is indicated by cDCE detections with the highest concentrations at MP7 and MP18.



Figure 3: Vertical depth-concentration profiles for mini-piezometer locations used to compare medians (n = 16) in comparison with the up-gradient aquifer (GW) (n = 7) and surface water (SW) (n = 3).



Figure 4: Representative pore water biogeochemical profiles and riverbed sediment properties. TCE (black diamonds); cDCE (open black diamonds); VC (open black triangles); nitrate (open green diamonds); sulfate (open blue squares); DO (open triangles); DOC (open circles), Mn (open orange squares); blue stars (methane) and black crosses (nitrous oxide).



Figure 5: Relationship between total pore water CEs (in nmol) and the chlorine index of TCE (CI_{TCE}) in all riverbed samples where $CI_{TCE} = <3$. Blue squares (reach-scale minipiezometer samples); open circles (upstream PW samples); green circles (mid-point PW samples); black circles (downstream PW samples).



Figure 6: Principle component analysis of high resolution pore water chemistry including factor loadings on original variables, ordination biplot and factor scores. The values in parenthesis is the percentage variance explained by PC1 and PC2. Factor scores are grouped as upstream (open circles), mid-point (green circles) and downstream (black circles) sample locations.



Figure 7: Calculated DOC demand for reduction of dissolved oxygen and nitrate in
samples for the sandstone aquifer (orange squares); MP samples (open circles); MP
samples showing TCE degradation (blue circles) and PW samples (green circles). Black
diamonds denote observed DOC concentrations for each sample.