

Fine-scale measurement of reactive solutes in armoured riverbed sediments

Patrick Byrne¹, Hao Zhang¹, Louise Heathwaite¹, Andrew Binley¹, Sami Ullah², Dan Kaeser³, Kate Heppell⁴, Katrina Lansdown⁴ and Mark Trimmer⁴

¹ Lancaster University, UK

² Keele University, UK

³ University of Neuchâtel, Switzerland

⁴ Queen Mary, University of London, UK

1. INTRODUCTION

Groundwater-surface water mixing in shallow (0 – 15cm) riverbed sediments has the capacity to attenuate nutrients from upwelling groundwater and maintain ecological health in river systems (Krause et al., 2009). However, measurement of hydrological flux and pore water biogeochemistry in this zone is difficult and generally leads to very coarse measurements that limit process interpretation. We used the technique of diffusive equilibrium in thin-films (DET) (Davison et al., 2004) to capture chemical profiles of reactive solutes in armoured riverbed sediments at cm scale. The goal was to identify if chemical transformation and / or groundwater-surface water mixing act to attenuate nitrate from upwelling groundwater.

2. STUDY SITE

We worked on a 50m stretch of the R. Leith, Cumbria, UK, which is dominated by upwelling groundwater (Figure 1). Previous investigations, as part of an ongoing project exploring mechanisms of nitrate attenuation, have identified elevated vertical and lateral fluxes associated with this sub-reach (Figure 2a). A zone of elevated pore water solutes (including nitrate) appears to be related to the area of elevated water flux (Figure 2b). Modelling experiments have demonstrated that, under high groundwater recharge at this site, surface water infiltration into the shallow sediments (0 – 15cm) is unlikely to occur (Munz et al., 2011). However, the experimental setup and methods used hitherto have prohibited direct measurements of the hydrological and chemical characteristics of the shallow sediments.

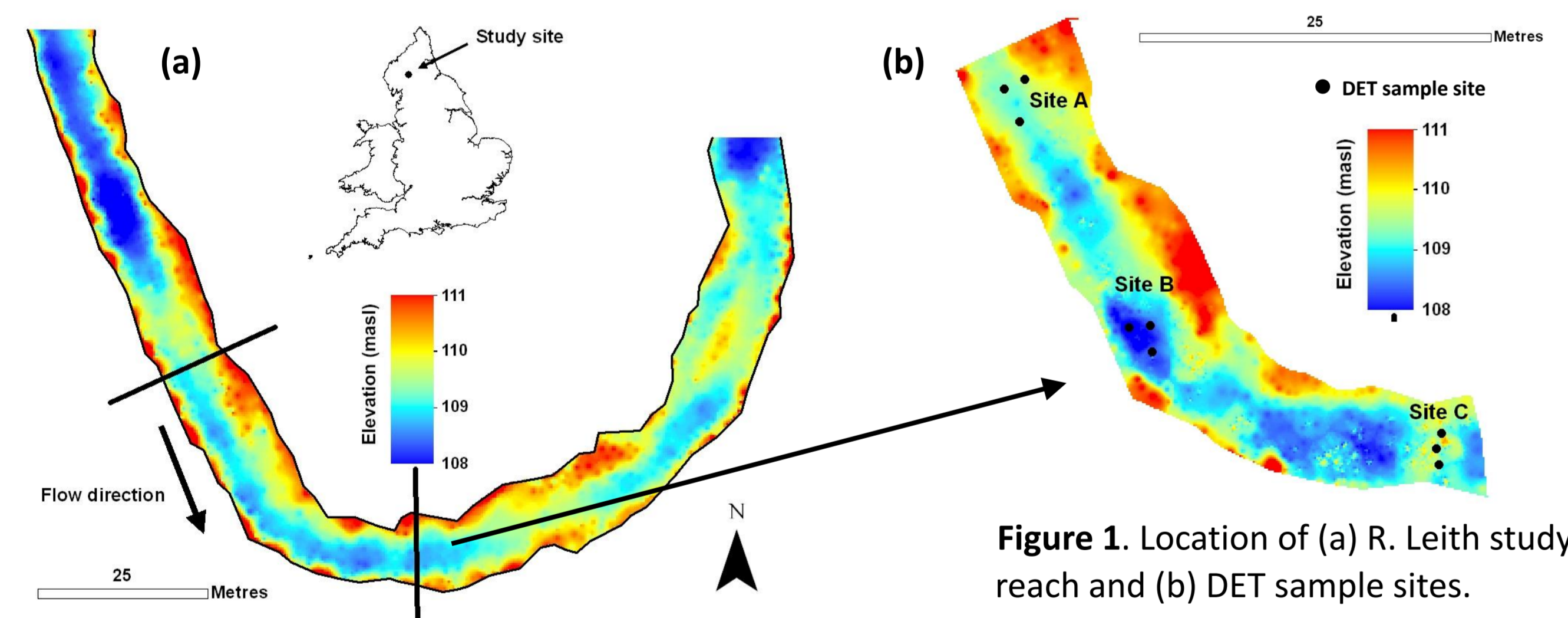


Figure 1. Location of (a) R. Leith study reach and (b) DET sample sites.

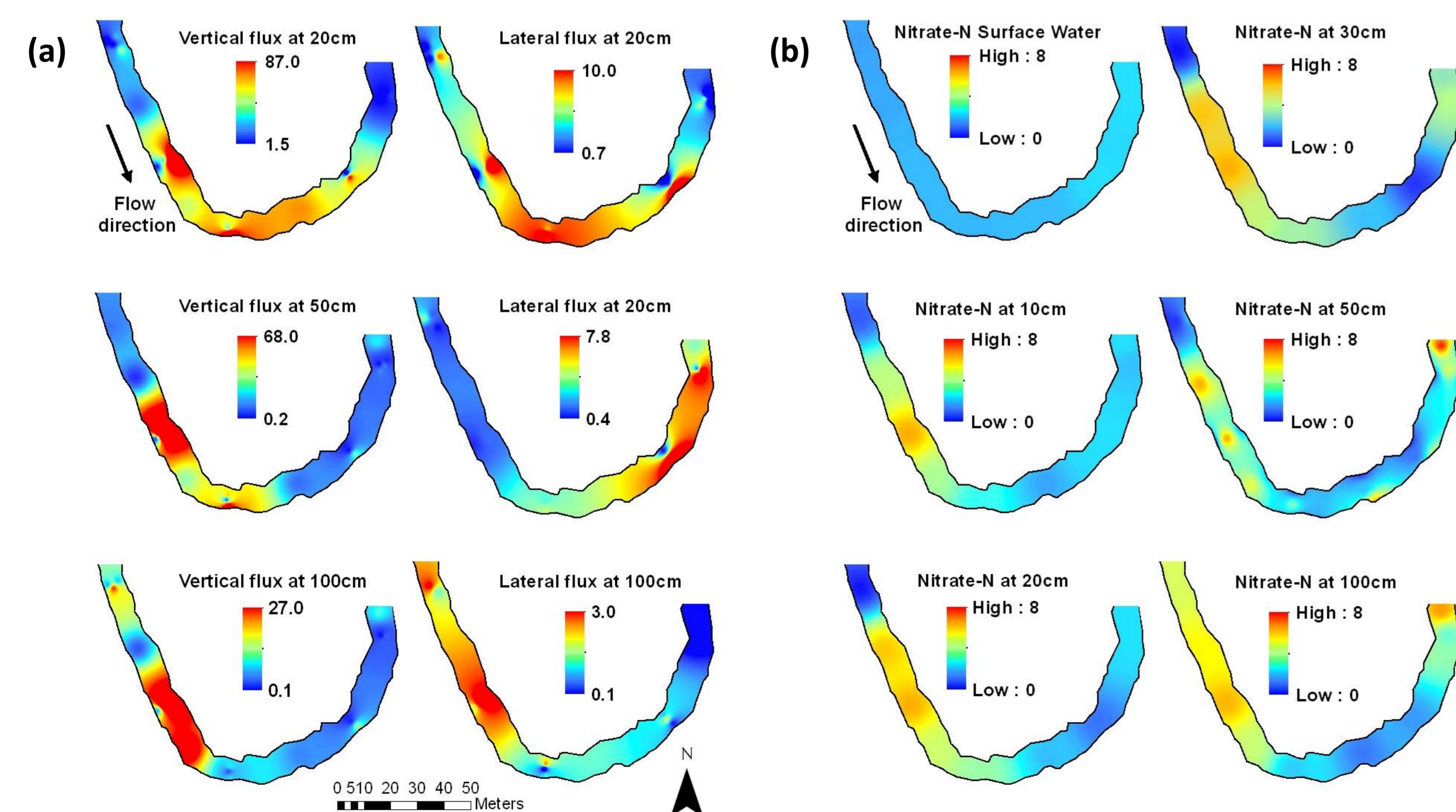


Figure 2. Measurements of (a) vertical and lateral flux (cm/day) (Feb-Sept 2010) and (b) nitrate surface and pore water concentrations (mg/L) (July 2009).

3. METHODS

We used DET to give 1cm resolution reactive solute (NO_3^- , SO_4^{2-} , Fe and Mn) concentration profiles for the upper 15cm of the riverbed. Sample sites were established along the length of the zone of elevated hydrological flux and pore water solutes (Figure 1 and 2). Field deployment of DET probes in the armoured riverbed, and extraction and analysis of solutes, followed the methodology of Ullah et al. (2012).

4. RESULTS

(A) DET solute concentration profiles (Table 1 and Figure 3)

- Nitrate concentration profiles are relatively invariable within and between the three sample sites.
- There is a general trend of decreasing nitrate pore water concentrations from site A to site C.
- Dissolved Fe and Mn exhibit a gradual change (from site A to C) from an invariable to a parabolic-shaped vertical concentration profile with elevated concentrations in the upper (1 – 5cm) and lower (11 – 15cm) sediments.
- There is a general trend of increasing Fe and Mn pore water concentrations from site A to site C.

Table 1. Summary (mean and standard deviation) of DET solute concentrations (mg/L) at the three sample sites.

Sample site	Nitrate-N	Sulphate-S	Fe	Mn
Site A	5.7 ±1.3	10.64 ±3.1	1.86 ±2.8	0.05 ±0.04
Site B	4.96 ±1.4	9.98 ±3.6	1.09 ±1.3	0.11 ±0.1
Site C	2.56 ±0.7	9.17 ±2.4	2.68 ±2.5	0.53 ±0.5

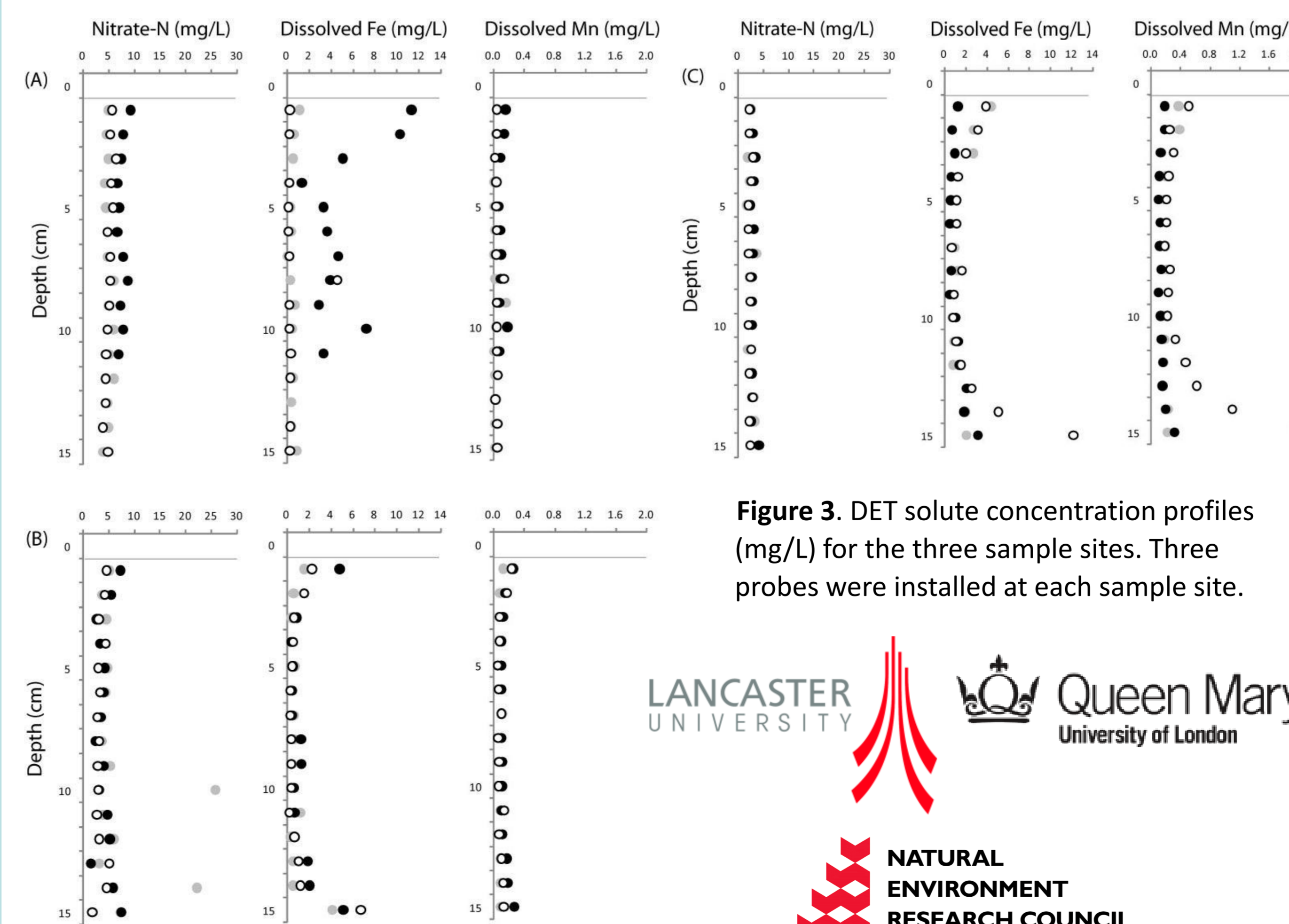


Figure 3. DET solute concentration profiles (mg/L) for the three sample sites. Three probes were installed at each sample site.

(B) DET solute relationships (Table 2)

- There appears to be a positive trend between redox-sensitive solutes at site A; however, this trend is disproportionately influenced by a single DET probe (Figure 3a – black circles).
- Excluding this probe from the dataset, the redox-sensitive solutes are uncorrelated at all three sample sites.

Table 2. Correlation matrix for the measured DET solutes at the three sample sites. Values given are coefficients of determination (r^2). ** $p < 0.01$.

Sample site		Fe	Mn	Nitrate-N	Sulphate-S
Site A	Fe	-			
	Mn	0.643**	-		
	Nitrate-N	0.663**	0.531**	-	
Site B	Sulphate-S	0.315**	0.345**	0.442**	-
	Fe	-			
	Mn	0.815**	-		
Site C	Nitrate-N	0.057	0.201	-	
	Sulphate-S	0.026	0.005	0.164	-
	Fe	-			
	Mn	0.633**	-		
Site C	Nitrate-N	0.011	0.034	-	
	Sulphate-S	0.018	0.003	0.031	-
	Sulphate-S				

5. CONCLUSIONS

- DET passive sampling technology has been used to measure reactive solutes in shallow armoured riverbed sediments at fine-scale resolution to supplement previous hydrological and chemical investigations which could not target this zone directly.
- DET solute concentrations support deeper pore water data and the existence of a longitudinal hydrological and chemical gradient in the investigated sub-reach.
- DET solute profiles and relationships suggest the general absence of chemical transformations and groundwater-surface water mixing in the shallow sediments.
- We suggest that elevated subsurface flux in our sub-reach limits contact times between solutes and sediments and constrains the development of HEF, restricting the extent of physical mixing and chemical transformation.

REFERENCES

- Davison, W., Zhang, H., and Grime, G. W. (1994) Performance characteristics of gel probes used for measuring the chemistry of pore water. *Environmental Science and Technology* 28: 1623-1632.
- Krause, S., Heathwaite, A. L., Binley, A., and Keenan, P. (2009) Nitrate concentration changes at the groundwater-surface water interface of a small Cumbrian river. *Hydrological Processes* 23: 2195-2211.
- Munz, M., Krause, S., Tecklenburg, C., and Binley, A. (2011) Reducing monitoring gaps at the aquifer-river interface by modelling groundwater-surface water exchange flow patterns. *Hydrological Processes* 25: 3547-3562.
- Ullah, S., Zhang Z., Heathwaite, A.L., Binley, A., Lansdown, K., Heppell, K., Trimmer, M. (2012) In situ measurement of redox sensitive solutes at high spatial resolution in a riverbed using Diffusive Equilibrium in Thin Films (DET). *Ecological Engineering*. Submitted for Review.



Grant No: NE/F006063/1