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Delineating the discharge zone and potential natural attenuation of a chlorinated solvent plume to a gaining lowland river: A multi-scale approach

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Chlorinated aliphatic hydrocarbons (CAHs), such as trichloroethene (TCE), are often recalcitrant groundwater pollutants which can form extensive dissolved plumes with the potential to impact on the quality of baseflow to rivers. There is a growing need to evaluate the risk to surface water posed by migrating plumes and the intrinsic potential for natural attenuation along contaminant flow paths through the groundwater/surface water interface (GSI).

This study investigates the potential discharge of a poorly defined CAH plume to an accreting section of the River Tern (Shropshire, UK). Groundwater sampling in the area has revealed the presence of TCE (with minor chloroform and carbon tetrachloride) with maximum concentrations discovered at depths of up to 80 m in a number of deep boreholes in an unconfined sandstone aquifer hydraulically connected to the river. We aim to develop a conceptual understanding of spatial patterns of plume discharge at sub-catchment to sediment-scale and assess the potential significance of biogeochemical transformation in the river bed and riparian sediments of a baseflow-dominated lowland river.

Concentrations of dissolved CAHs (including the anaerobic metabolites of TCE) were monitored in a reach-scale longitudinal channel network of liquid-liquid passive diffusion samplers, placed in direct contact with the top 10 cm of river bed sediment. Samplers comprised distilled water-filled glass vials capped by a thin (50 μm) film of commercially available LDPE tubing. A long integration time (33 days) was selected for sampler equilibration with in-situ pore water concentrations. Results provided a plan-view reconnaissance survey of TCE distribution in the river bed and indicated tentative core and fringe zones. Spatial connectivity between ground and surface water was mapped by means of an in-situ fibre-optic distributed temperature sensor system deployed in the uppermost 10 cm of sediment spanning the investigated reach. To determine changes in concentration and composition of the plume across the GSI at sediment scale, CAHs, chloride and major ions were monitored by a network of 25 multilevel mini-piezometers installed in the bed sediments with five discrete pore water sampling levels. Additionally, 15 shallow groundwater boreholes were cored to 3 m depth in the floodplain and riparian zone of the plume-affected reach and instrumented with bag-type LDPE diffusion samplers deployed for a similar integration period.

The findings of the project highlight the spatial complexity of CAH transport in a hydrostratigraphically heterogeneous GSI typical of lowland rivers. Piezometric levels and in-situ temperature observations indicate spatially variable river-aquifer connectivity with a substantial vertical component of groundwater flow through the river bed. Transformation of TCE (mainly to cis-1,2-DCE and 1,1-DCE) was found to be restricted to peat horizons and the top 20 cm of river bed sediment hosting abundant detrital organic matter. This study demonstrates the first UK application of novel in-situ technologies as part of a multi-scale investigation to characterise the behaviour and fate of an upwelling chlorinated solvent plume. Future research will focus on investigating the redox controls on biogeochemical 'hotspots' that favour transformation of TCE and the potential coupling with denitrification and production of greenhouse gases.