Durham University
Department of Earth Sciences

Dr Catherine Hirst catherine.hirst@durham.ac.uk
Professor Fred Worrall fred.worrall@durham.ac.uk
Dr Darren Gröcke d.r.grocke@durham.ac.uk

TRACING SULPHUR-DRIVEN ORGANIC CARBON DEGRADATION IN A UK RIVER CATCHMENT

1. Background

Globally, soil organic carbon (SOC) stocks are under threat due to land-use change and permafrost thaw. Of the disturbed OC, a portion is degraded in soils and a portion is transported into river waters and degraded along the hydrological continuum.

Upon land disturbance and OC degradation the form of greenhouse gas released (CO_2 or CH_4) is dependent on soil, riverbed and hyporheic zone redox conditions. Under oxygenated conditions (high O_2), aerobic respiration occurs driving the release of OC as CO_2. Under poorly oxygenated conditions (low O_2), anaerobic respiration can occur driving the release of OC as CH_4, a more potent greenhouse gas than CO_2. Across an O_2 gradient lies a cascade of alternative electron acceptors (e.g., sulphur) that when in operation, prevent the release of CH_4 to the atmosphere.

Sulphur isotopes ($\delta^{34}S$) provide a novel approach to trace OC degradation in soils and river systems, where the $\delta^{34}S$ ratios of dissolved SO_4^{2-} ($\delta^{34}S_{SO4}$, expressed in delta notation relative to a standard) mainly reflect i) the sulphur mineral source because there is minimal S isotope fractionation between this source and SO_4^{2-} during weathering or ii) bacterially mediated sulphate reduction within poorly oxic soils, riverbed sediments and the hyporheic zone.

2. Aims and methods

This project aims to use sulfur (S) stable isotopes ($\delta^{34}S$) to trace sulphur-mediated degradation of organic carbon in soils and river sediments.

Samples, including 1) soil pore waters 2) river sediment soil pore waters, 3) hyporheic zone soil pore waters and 4) river waters will be collected at Moor House, North Pennines, UK (Figure 1). Samples will be collected every 200 meters along a 1 km headwater stream reach. Soil pore waters, river and hyporheic zone sediment pore waters will be collected using multi-level piezometers. River waters will be collected using 5 L containers, filtered through 0.22 µm filters. The pH, conductivity, temperature and redox will be measured in the river, soil, and sediment waters.

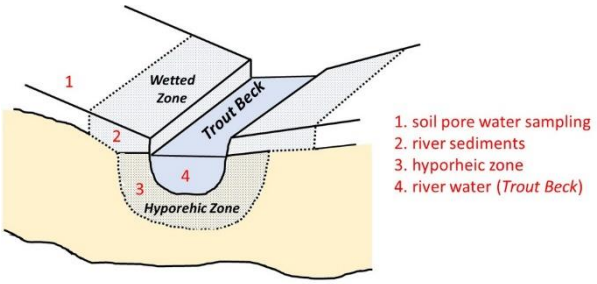

Figure 1. Locations of water collection at each sampling site along a 1km transect of Trout Beck stream at Moor House, N Pennines

To obtain SO_4 for isotope analysis, filtered soil, sediment and river waters will be loaded on columns filled with anion exchange resin. The SO_4 will be eluted off the resin and the $\delta^{34}S$ isotope composition will be determined by mass spectrometry. Isotope data interpretation will be supported with dissolved organic carbon (DOC), and cation (Ca, Mg, Na, K, Si, Fe, Mn) concentration measurements. In addition, the Fe(II)/Fe(III) redox couple will be determined using ferrozine.

3. Scientific approach

This project will use an innovative isotope approach to trace the degradation of organic carbon along the aquatic continuum in a UK river. This approach is appropriate for the following reasons: firstly, we have the range of equipment capable of sampling soil, sediment and river waters and supporting parameters in the field; secondly, we are supported by excellent laboratory facilities in Durham. These include the Stable Isotope Biogeochemistry Laboratory (SIBL) and Arthur Holmes Trace Element and Isotope Laboratories; finally, we have expertise in sulphur isotope mass spectrometry, organic carbon processing and river geochemistry which makes us uniquely placed to supervise this project.

4. Training

As an MSc by research student in the Earth Sciences Department, Durham University, you will become part of a vibrant research culture. You will closely collaborate with the academic staff, postdoctoral researchers and fellows, and postgraduate students in your research group. This project will provide a fantastic platform to gain multidisciplinary training, including in experiment development, isotope geochemistry and hydrology. The candidate will work closely with the supervisors to gain directly from their expertise. The candidate will have the opportunity to present their results at a conference in the UK.

5. Further reading & information

Worrall, F., Harriman, R., Evans, C.D., Watts, C.D., Adamson, J., Neal, C., Tipping, E., Burt, T., Grieve, I., Monteith, D. and Naden, P.S., 2004. Trends in dissolved organic carbon in UK rivers and lakes. *Biogeochemistry*, *70*(3), pp.369-402.

Frey, K.E. and McClelland, J.W., 2009. Impacts of permafrost degradation on arctic river biogeochemistry. *Hydrological Processes: An International Journal*, *23*(1), pp.169-182.

Fox, P.M., Carrero, S., Anderson, C., Dewey, C., Keiluweit, M., Conrad, M., Naughton, H.R., Fendorf, S., Carroll, R., Dafflon, B. and Malenda-Lawrence, H., 2022. Sulfur Biogeochemical Cycling and Redox Dynamics in a Shale-Dominated Mountainous Watershed. *Journal of Geophysical Research: Biogeosciences*, *127*(6), p.e2021JG006769.

Fischer, S., Jarsjö, J., Rosqvist, G. and Mörth, C.M., 2022. Catchment-scale microbial sulfate reduction (MSR) of acid mine drainage (AMD) revealed by sulfur isotopes. *Environmental Pollution*, *292*, p.118478.

Ingri, J., Torssander, P., Andersson, P.S., Mörth, C.M. and Kusakabe, M., 1997. Hydrogeochemistry of sulfur isotopes in the Kalix River catchment, northern Sweden. *Applied Geochemistry*, *12*(4), pp.483-496.

For further information contact: Dr. Cat Hirst, Dept of Earth Sciences, University of Durham
catherine.hirst@durham.ac.uk