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Using radioactive and stable carbon isotopes, LC-OCD and FT-ICR MS to understand groundwater organic carbon sources and processing

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Dissolved organic matter (DOM) concentrations typically decrease from surface to groundwater, which suggests that most groundwater DOM is sourced from the surface. DOM undergoes many removal processes in the subsurface, including sorption to mineral surfaces, biodegradation, and filtration as it moves through soils, sediment and bedrock. In addition, there is potential for subsurface sediments to act as a source of organic carbon in groundwater. However, relatively little is understood about the character of sedimentary organic carbon sources and how DOM character changes as it undergoes processing along a flow path.

We obtained 21 groundwater samples and 3 surface water samples from two alluvial aquifers and one coastal sand aquifer in New South Wales, Australia. Samples were analysed for 14C and 3H to identify groundwater recharge sources, flow paths and water residence times. Radioactive (14C) and stable (13C/12C) carbon isotopes, liquid chromatography organic carbon detection (LC-OCD) and Fourier-transform ion cyclotron resonance mass spectrometry (FT-ICR MS) were used to characterise DOM and determine DOM source and processing mechanisms. For our coastal aquifer we identify a decrease in low molecular weight neutrals (LMW-N), peptide-like, aliphatic, highly unsaturated and phenolic groups, and an increase in condensed aromatics and polyphenolic groups, with increasing DOM age. We attribute this to the contribution of old, unprocessed sedimentary organic carbon in the form of peat associated with the dune-slack morphology of the site. However, the opposite trend was observed for LMW-N, polyphenolic, highly unsaturated and phenolic groups at both inland alluvial aquifers which is likely to be associated with processing of DOM from high to low molecular weight carbon over time at sites dominated by a surface DOM source, with comparatively less sedimentary organic carbon.

This research forms part of an ongoing project which will assist in identifying the factors affecting the mobilisation, transport and sources and removal of DOM in groundwater. Importantly, quantification of the change in DOM concentration and character over time, and the relative importance of sedimentary organic carbon as a source of DOM in groundwater will help guide policy and identify the need to include groundwater resources as part of the carbon economy.