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Fluorescence and dissolved organic matter properties in a connected aquifer river system

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There have been limited investigations on the sources, distribution, and transformation of dissolved organic carbon in groundwater systems that are connected to streams and rivers. The role of such landscape settings in the terrestrial carbon cycle is therefore not well understood. We used optical methods to study dissolved organic matter (DOM) in groundwater in a connected river/aquifer reach adjacent to a limestone karst landscape near Wellington, NSW, Australia. Optical properties of water samples and their relation to DOM structure and source enables prompt evaluation of the relative abundance of organic matter components, and fingerprints the sources of DOM. We collected surface water samples along the river, and groundwater samples from alluvial and karst monitoring bores and from caves where they intercepted the groundwater table. Absorbance values were measured at wavelengths of 254, 340 and 350 nm and fluorescence properties were characterised by obtaining excitation (400 nm to 240 nm) – emission matrices (210 to 620 nm). The absorbance data were processed to provide the specific ultraviolet absorbance (SUVA) and spectral slopes. Parallel factor analysis (PARAFAC) was applied to discriminate fluorescent DOM components and to assess their dynamics in river and groundwater. Our groundwater DOM data show lower spectral slope, high SUVA values, and lower fluorescence/absorbance ratio, compared to the river. This is indicating a greater amount of relatively high molecular weight, chromophoric, and hydrophobic groundwater DOM is present in the groundwater compared to the river, which had relatively low molecular weight and hydrophilic DOM. PARAFAC modelling revealed different models were necessary for river and groundwater samples, with component one of the groundwater PARAFAC model in the ‘peak T’ region, and component one of the river model in the ‘peak C’ region. These results suggest that sedimentary organic matter in the alluvial and karstic aquifer is a major source of groundwater DOM, which is subsequently utilized by microbial activity. The results also show that there is a transition zone in the aquifer adjacent to the river (< 50 m) where DOM concentration, absorbance, and fluorescence intensity rapidly decrease from the river to the aquifer, suggesting the groundwater near the river acts as a sink for the riverine organic matter during periods where the river is infiltrating the aquifer. This research could be relevant to other alluvial and karst aquifers connected to surface waters, as well as other geological environments where there is a high concentration of organic matter present.