



Changing scales of hydrological control on dissolved organic matter composition in pools of intermittent streams

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Changes in both the frequency and intensity of flood-drought cycles of intermittent streams, either through changing climate or anthropogenic management, may have significant impacts on stream functioning. However, little is known about how and to what extent droughts already modify the concentration and composition of dissolved organic matter (DOM) and how this relates to local variation in stream hydrology. We hypothesize that with increasing time since flooding, controls on biogeochemical processes in surface water during droughts (isolated pools along main drainage channels) switch from predominantly hydrological at the catchment level to more localized environmental factors. We used $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values of surface water and groundwater together with DOM fluorescence excitation-emission spectroscopy to identify: (i) the origin and extent of evaporation of pool water and (ii) the concentration and chemical composition of DOM across four intermittent streams of semi-arid northwest Australia between May 2011 and November 2012. Pool water $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values showed wide variation both within and among streams, with greater enrichment reflecting pool evaporation as groundwater or shallow alluvial water inputs decreased with time since flooding. Parallel factor analysis (PARAFAC) revealed that DOM fluorescence in pools was generally dominated by humic-like components, most likely derived from terrestrial organic matter. Humic-like fluorescence was linearly related to $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values, but this relationship weakened as pools dried. However, where pools were isolated from groundwater inputs, protein-like components were often the major contributor to total DOM fluorescence, suggesting greater authochthonous contributions. Complementary principal component analysis of DOM fluorescence identified that with increasing time since flooding, local factors such as channel position, UV exposure, and aquatic vegetation persistence were more important in explaining the amount and composition of pool DOM. Our findings show that progressive drought after flooding strongly influences the biogeochemistry of intermittent streams, and amplifies the spatial heterogeneity of organic matter and nutrients among pools. This should be characterised by a shift in controls from catchment scale factors during and after floods to progressively more localized environmental factors as pools dry down, reflecting the changing spatial scale of the hydrological forces themselves. Recognition of the hydrologic complexity of intermittent streams is clearly necessary for more effective management strategies that seek to preserve the long-term integrity of riverine ecosystems.