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Amino acids as molecular tracers of dissolved organic matter processing history and molecular environment

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Dissolved organic matter (DOM) is present in all freshwaters globally, formed through the biogeochemical processing of organic material during transit from headwaters to receiving ecosystems. DOM concentration and composition can vary both spatially and seasonally, as controlled by catchment sources, hydrologic flow paths, land uses, biogeochemical processes and climate patterns. Included in DOM are organically bound elements (e.g., N, P & S) that equally reflect the origin and biogeochemical processing of precursor organic material. Dissolved organic nitrogen (DON), in particular, can be a significant component of DOM and present as a wide array of compounds, including: amino acids (AAs), amino-sugars, nucleic acids & heteroaromatic compounds, the bioavailability of which will vary across these molecular groups. Dissolved combined amino acids (DCAAs; i.e., bound AAs) can represent a high proportion of DON, with the relative abundance of AAs potentially providing information about the processing history and molecular environment of the DOM, as revealed through AA attributes such as nominal oxidation state of carbon (NOSC) and hydrophobicity.

In a series of studies, we have shown that DCAAs partition differentially across molecular groups (i.e., biopolymers and humic substances), revealed in the analysis of DOM characteristics in peatland storm events [1], with the relative AA abundances changing through the storm cycle. Similarly, we have demonstrated discontinuities in relative AA abundance for tributary flows into regulated rivers potentially driving increased productivity downstream of the confluence [2]. Our more recent work shows that AA distributions can also be controlled by the molecular environment in DOM (i.e., hydrophobicity-hydrophilicity), as revealed in samples collected from acidic and neutral waters using a multiple characterisation approach. While the molecular properties of DOM are commonly determined by optical and fluorescence techniques [3], we have found that FTIR spectroscopy can provide additional unique information about the DOM molecular environment. Our work suggests that the DCAA composition in DOM may represent a new tool in understanding DOM-mediated processes in aquatic ecosystems.

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