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Refining the Structural Boundaries of Dissolved Organic Matter Using Carboxyl Rich Molecule Synthetic Analogues

ALEXANDER J CRAIG, AGNES FLYGARE, LINDON MOODIE AND JEFF HAWKES

Uppsala University

The chemical composition of aquatic dissolved organic matter (DOM) determines its roles within the earth system where it transports nutrients across ecosystems, and sequesters vast amounts of carbon within the ocean. However, the sheer diversity of structural isomers with any given DOM sample restricts accurate definition of its chemical composition, obscuring insight into DOM's fluxes and the mechanisms for its transformation. Notably, aquatic DOM across all environments is rich in carboxylic functionalities (i.e. carboxylic acids), and consists of extensively branched carbon subunits. Few molecules have been isolated with these features in either natural products or synthetic chemistry, and as a result, our understanding of how they behave is restricted to approximations based on ultracomplex mixtures. Without an accurate understanding of DOM's chemical space, we cannot understand its origins or fate, and many widespread ideas within the field remain only speculative.

To improve the structural understanding of DOM, our group has iteratively synthesized carboxylic rich molecules to refine the boundaries of chemical space for the most prevalent small molecules in DOM. This has focused on investigations into hypothetical? natural compound classes such as carboxylate rich alicyclic molecules (CRAM) and poly-carboxylic polyaromatic hydrocarbons (PCAs/black carbon), and commonly invoked biomolecular inputs such as lignin and tannin. Additionally, we have iteratively investigated functional group combinations and molecular backbones to refine understanding of the mass spectrometry (MS), tandem mass spectrometry (MS2), and liquid chromatography (LC) behavior of DOM's ionizable small-molecule pool.

Here, I will discuss how our approach has advanced the understanding of DOM's structural space, and how we have worked to validate (or invalidate) common assumptions within the field. Specifically, we have highlighted the incompatibility of carbocyclic CRAM with the LC and MS2 data of both terrestrial and marine DOM, and found that aromatic carboxylic acids are unlikely to be significant contributors to the 'lignin-like' or 'tannin-like' regions in DOM MS data. Additionally, I will discuss how our recent work synthesizing carboxylic rich molecules containing quaternary oxygenated carbon atoms has investigated recent high-profile structural hypotheses in the field, and our perspective on how to further refine DOM's structural boundaries.