

Deciphering DOM-Metal speciation with 21 Tesla FT-ICRMS

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Dissolved organic matter (DOM) in terrestrial and aquatic environments is composed of a diverse suite of molecules with functional groups that can form stable complexes with metals such as Fe. Depending on the chemical composition of the organic matter and metal, these interactions can result in dissolution, colloid formation, and particle flocculation. However, a molecular level understanding of these metal-organic interactions has remained elusive due to the complexity of natural organic matter. High resolution fourier transform ion cyclotron resonance mass spectrometry (FT-ICRMS) is routinely used to profile the composition of DOM from waters and soils. Many metals have unique isotopic mass and intensity patterns that can facilitate the identification of metal species in high resolution mass spectra. In practice, however, identifying metal species within DOM based on isotope patterns is not straightforward due to the presence of tens of thousands of peaks in a single spectrum, such that unrelated features often match metal isotope patterns by chance.

Here we present a novel approach for confidently identifying metal-organic complexes from complicated DOM mixtures that takes advantage of recent developments in ultrahigh mass resolution achieved by 21 Tesla FTICRMS (>800,000 at m/z 700). With this capability, the fine isotopic structure of organic-metal complexes (e.g. ⁵⁷Fe isotopologues) can be resolved, enabling us to track the incorporation of rare metal isotopes into organic-metal complexes. Computational comparison of mass spectra of DOM derived from a soil enrichment culture spiked with ⁵⁶Fe and ⁵⁷Fe enabled the robust, rapid identification of iron-bound species. From this analysis, 30 out of 59 features that matched the iron isotope pattern were validated. Further MS/MS analysis was used to structurally characterize these iron-binding molecules, providing fundamental insight into the functional components of DOM that interact with metals.