New insights on dissolved organic sulfur chemistry by complementary atomic-level and molecular-level approaches

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Organic sulfur functional groups in dissolved organic matter (DOM), which originate from biological materials and abiotic transformations [1], influence trace metal behavior (e.g. mercury) and are an important component of the sulfur cycle. Enduring questions remain, however, on the sources, speciations, and stabilities of organic sulfur functional groups in DOM. Here, we use complementary atomic-level (sulfur XANES) and molecular-level (ultrahigh-resolution mass spectrometry) approaches to elucidate key environmental processes governing the chemistry of sulfur in DOM.

First, we present results from field and laboratory efforts investigating abiotic transformations of sulfur in DOM from the Florida Everglades by sulfurization and photo-chemical oxidation reactions. Inorganic sulfide is incorporated into unsaturated DOM molecules as primarily reduced sulfur species (86% of new sulfur) [1]. These reduced sulfur species are recalcitrant under dark oxic conditions but rapidly oxidize to inorganic sulfate (desulfurization) in the presence of sunlight. Next, we use our experimental results on sulfurization and desulfurization pathways to interpret the speciation (n = 60) and molecular signatures (n = 14) of sulfur in DOM from lakes, estuaries, rivers, and the Pacific Ocean. Across all aquatic environments, the concentration of reduced organic sulfur increases uniformly with total organic sulfur content, which we interpret to reflect sulfur addition to (sulfurization) and removal from (desulfurization) DOM at similar proportions in the environment. The results aid efforts to predict sulfur and trace metal behavior in aquatic systems.

[1] Poulin et al. (2017) *Environ. Sci. Technol*. **51**, 3630-3639.