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The Formation, Loss, and Speciation of Reduced Organic Sulfur

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Organic sulfur (S) originates from biomolecules and abiotic transformations and influences major (e.g., sulfur, carbon) and trace (e.g., mercury) element cycles. Reduced organic sulfur as thiols (R-SH) and thioethers (R-S-R') have disparate reactivity, but enduring questions remain on the sources, speciation, and stability of reduced organic sulfur in aquatic environments. This presentation covers four studies that use atomic- and molecular-level techniques that elucidate key environmental transformations and chemistries of reduced organic sulfur in aquatic environments.

First, abiotic sulfurization and photochemical desulfurization of dissolved organic matter were investigated in the field and laboratory.[1, 2] Inorganic sulfide incorporated into unsaturated dissolved organic molecules as primarily reduced sulfur species (86% of new sulfur formed thiols (R-SH) and/or thioethers (R-S-R')); the combined use of sulfur x-ray absorption near-edge structure (XANES) spectroscopy and ultrahigh-resolution mass spectrometry ruled out the prominence of disulfide moieties. Reduced organic sulfur species were recalcitrant under dark oxic conditions, but the majority (~65%) rapidly oxidized to inorganic sulfate in the presence of sunlight (Figure 1a).[2] Next, we show that thiol and thioether moieties can be resolved by exploiting changes in sulfur $K\alpha_1$ high-energy-resolution fluorescence detected (HERFD)-XANES spectra caused by thiol deprotonation ($R\text{-}SH \leftrightarrow R\text{-}S^- + H^+$).[3] Dissolved organic matter from five freshwater environments were evaluated: the proportions of reduced sulfur as thiols range from 3% to 41% with pK_a values from 7-10. Next, we use our experimental results on sulfurization and desulfurization pathways to interpret the speciation (n = 60) and molecular signatures (n = 14) of dissolved organic sulfur from diverse aquatic environments, including lakes, estuaries, rivers, and the Pacific Ocean. Across all aquatic environments evaluated, the concentration of reduced organic sulfur increases uniformly with total organic sulfur content (Figure 1b), which we interpret to reflect sulfur addition to (sulfurization) and removal from (desulfurization) organic matter at similar proportions in the environment. The results aid efforts to predict sulfur and trace metal behavior in aquatic systems.

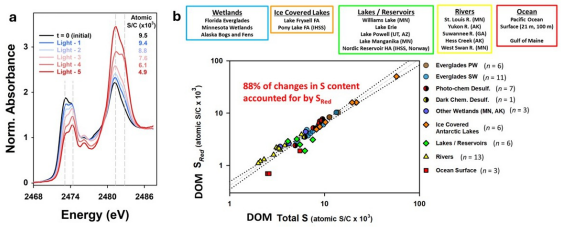

Figure 1. (a) Sulfur K-edge XANES spectra showing rapid photochemical oxidation of reduced organic sulfur [2]; (b) linear correlation between the concentration of reduced organic S in dissolved organic matter (DOM) and total organic sulfur across diverse aquatic environments.

[1] Poulin et al. *Environ. Sci. Tech.*, **51**, 3630-3639 (2017) DOI:10.1021/acs.est.6b04142 [2] Poulin. *Environ. Sci. Tech. Lett.*, **10**, 499-505 (2023) DOI: 10.1021/acs.estlett.3c00210. [3]