

The phantom of anoxia: zero-valent sulfur.

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When combined with sulfide in polysulfides, zero-valent sulfur can be an important participant in many biogeochemical processes, such as dehalogenation of hazardous halocarbons, complexing and solubilization of bioactive trace elements, formation of pyrite and cross-linking in organic macromolecules. S(0) acts in some cases as an electron donor and in others as an acceptor in microbial metabolisms. Yet because reliable methods for quantifying it at common levels are lacking, zero-valent sulfur remains a cryptic component of natural waters. Several approaches have been taken to quantifying it. Not surprisingly, methods that capture S(0) from samples by a strongly exergonic process find more analyte than methods that employ weakly exergonic processes (e.g. extraction with liquid Hg vs. with organic solvents). When multiple analytical methods have been applied to the same samples, up to ten-fold discrepancies are reported. At chemoclines and sediment-water interfaces, S(0) concentrations often reach levels sufficient to yield elemental S precipitates, but most often S(0) is invisible owing to combining with sulfide to make polysulfides or combining with organic macromolecules. It is important to distinguish between the concentration and activity of dissolved S(0). The latter is a measure of S(0)'s thermodynamic potential to drive mineral transformations, such as $\text{Cu}_2\text{S} \rightarrow \text{CuS}$, $\text{AsS} \rightarrow \text{As}_2\text{S}_3$ and $\text{FeS} \rightarrow \text{Fe}_3\text{S}_4$. It is also a measure of the potential to drive changes in trace element speciation, such as $\text{HgS}_2^{2-} \rightarrow \text{Hg}(\text{S}_n)_2^{2-}$ or $\text{H}_2\text{AsOS}_2^- \rightarrow \text{H}_2\text{AsOS}_3^-$. The activity of S(0) can be quantified in natural waters if the pH and concentrations of total S(-II) and total S(0) are known. The relationship between the activity and concentration of S(0) is non-intuitive. As an example, bottom waters of Lake Croche in eastern Canada contain $\Sigma\text{S}(0) = 0.81 \mu\text{M}$ and $a_{\text{S}(0)} = 1.42$ whereas bottom waters of Mahoney Lake in western Canada contain $\Sigma\text{S}(0) = 290 \mu\text{M}$ but $a_{\text{S}(0)} = 0.58$. Because of Mahoney's low $a_{\text{S}(0)}$ as well as its high concentration of $\Sigma\text{S}(-\text{II})$, the metabolic energy that would be available to S-disproportionating microbes is nil despite the lake's high S(0) concentration. In contrast, significant energy would be available at Croche's high $a_{\text{S}(0)}$ despite its low S(0).