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## Photochemical production of sulfate from dissolved organic matter and atmospheric aqueous phases: Is there something in common?

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In a recent study, we showed that photodegradation of dissolved organic sulfur (DOS) from a wide range of natural terrestrial environments releases sulfate ( $\text{SO}_4^{2-}$ ) and other small and highly oxidized S-containing compounds as degradation products, similar to what had already been reported for dissolved organic carbon, nitrogen and phosphorous. However, the underlying chemical mechanism of photoproduction of sulfate is still unknown.

To fill this knowledge gap, we selected cysteine as a DOS model compound and we investigated its photodegradation to sulfate using model sensitizers as the source of singlet oxygen ( $^1\text{O}_2$ ) and triplet excited states ( $^3\text{Sens}^*$ ), two photochemically produced reactive species ubiquitous in sunlit surface waters. Using a combination of steady-state photochemistry experiments, kinetic modeling and mechanistic knowledge from the biochemistry literature, we reconstructed the molecular events that likely lead to the release of sulfate. We found that the release of  $\text{SO}_2$  via triplet-sensitized fragmentation of cysteine sulfinic acid, a  $^1\text{O}_2$  degradation product of cysteine, is a key step in the reaction mechanism. In the presence of oxygen and a photosensitizer,  $\text{SO}_2$  is then rapidly oxidized to  $\text{SO}_4^{2-}$ .

Interestingly, nowadays there is great interest in the atmospheric chemistry community on the same transformation (i.e., aqueous phase oxidation of  $\text{SO}_2$  to  $\text{SO}_4^{2-}$ ) in the context of extreme haze events. Triplet-induced  $\text{SO}_2$  oxidation has already been proposed as a potential aqueous phase reaction that might explain the mismatch between measured and modelled sulfate concentrations, but the mechanism of this process is still not established. Our work provides an example of how mechanistic knowledge gained on the (photo)chemical behaviour of dissolved organic matter in aquatic systems can offer insights on processes occurring in atmospheric aqueous phases.