Organic matter photochemistry: Singlet oxygen precursor lifetimes

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Background

Dissolved organic matter (DOM) photochemistry plays a key role in pollutant fate and carbon cycling [1, 2]. Central to this are various reactive intermediates whose production and reactions can alter the DOM. These include O₂, O₂⁻ and H₂O₂, e (aq), -OH, and triplet DOM states (3DOM*) [3]. Various evidence suggests that 3DOM* is the O₂ precursor.

\[
\text{DOM} + h\nu \rightarrow \text{3DOM*} \rightarrow \text{1O}_2 \quad (1)
\]

Intersystem crossing from the excited singlet forms 3DOM* which then transfers energy to O₂. Despite many studies on O₂ production, the photophysical properties of 3DOM* are not well known. This work uses the O₂ dependence of 1O₂ quantum yields (\(\Phi_{1O2}\)) to estimate the yields and lifetimes of 3DOM* as a function of wavelength. Experiments employed a Xe lamp, bandpass filters, and furfuryl alcohol as a 1O₂ probe. Buffered D₂O was used as a solvent to increase the 1O₂ lifetime, allowing for extensive experimentation.

Results and Discussion

Figure 1 displays data for Suwannee River OM at 370 nm. The asymptote above 0.5 mM O₂ shows that all 3DOM* precursors to 1O₂ are being trapped and that their quantum yield is 0.025. The ratio of the intercept to slope of the inverse linear plot equals the lifetime of 3DOM* multiplied by the total rate constant for its quenching by and energy transfer to O₂. Assuming a total value of 10¹⁰ M⁻¹ s⁻¹ for these processes yields a 3DOM* lifetime of 6.5 µs, which is also found at 313 and 415 nm. Other samples have similar lifetimes that are also invariant with wavelength. However, the quantum yields vary by more than two-fold. This suggests that \(\Phi_{1O2}\) is controlled by absolute yields of 3DOM* rather than its decay kinetics.