The role of "long-lived" photooxidants in the transformation of aquatic organic contaminants photosensitized by dissolved organic matter

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The ubiquitous chromophoric dissolved organic matter (CDOM) is the main absorber of sunlight in surface waters and may induce the indirect phototransformation of a variety of organic contaminants [1]. CDOM-derived photochemically produced reactive intermediates (PPRIs) that are particularly effective in the transformation of electron-rich phenols at sub-micromolar concentrations were detected previously [2,3,4]. Based on kinetic arguments, these PPRIs were termed as long-lived photooxidants (LLPOs) and estimated to have lifetimes in the order of $> \approx 100$ μs, in contrast to short-lived photooxidants (such as ^{3}CDOM*) exhibiting lifetimes of only a few microseconds [3]. Upon lowering the initial organic contaminant concentration from 5.0 μM to 0.1 μM, a 6 – 16 fold increase in pseudo-first order rate constants was observed for electron-rich phenols, and a 2-fold increase in rate constant for electron-rich anilines. This ratio of pseudo-first-order rate constants for the low (0.1 μM) versus the high (5.0 μM) initial concentration of organic contaminant was taken as an indicator for the relative increase in rate constant to be attributed to LLPOs.
In summary, the observed trends in pseudo-first order rate constants support the hypothesis of target compound transformation induced by photooxidants of different lifetimes produced by irradiation of CDOM.

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