Photochemical formation of reactive oxidants by size-fractionated dissolved organic matter

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Dissolved organic matter (DOM) plays an important role in the transformation of organic pollutants. For example, the absorption of light by DOM produces a suite of reactive oxidants that are capable of reacting with a wide variety of aquatic constituents. These reactive species include excited triplet states (^{3}DOM), singlet oxygen ($^1O_2$) and hydroxyl radical ($^\bullet$OH). The photochemical reactivity of DOM is typically assessed by quantifying the steady-state concentration of reactive species produced by bulk DOM. This approach does not provide information about the fundamental properties of DOM and is of limited use in predicting DOM chemical reactivity. Fractionating DOM by apparent molecular weight (MW) is a useful technique for assessing which fractions of DOM contribute to its photochemical reactivity. Therefore, the aim of our study is to investigate the formation and quenching of reactive species in bulk and size-fractionated DOM.

In the present study, we fractionate a variety of DOM samples using sequential ultrafiltration into four apparent molecular weight classes (<3, 3,5, 5-10 and >10 kDa). We apply standard optical techniques to verify that the fractionation technique produces chemically distinct fractions of DOM. Next, we use four probe compounds to assess the quantum yield, steady state concentrations, and formation and quenching rates of reactive species. *Trans,trans*-sorbic acid and 2,4,6-trimethylphenol are used to investigate the ability of ^{3}DOM to react via energy transfer and electron transfer, respectively. Furfuryl alcohol and terephthalate are used to quantify the production of $^1O_2$ and $^\bullet$OH from photochemically excited DOM. Collectively, these measurements of probe-labile reactive species production allow for both the characterization of size-fractionated DOM populations and insight into likely reactions that occur when photosensitized DOM reacts in a natural environment. For example, we show that higher MW is a more efficient ^{3}DOM quencher and that ^{3}DOM quenching by O_2 varies with apparent MW. In addition, divergence in measured ^{3}DOM loss rates suggests varying propensities to react by electron and energy transfer mechanisms.