MSc Departmental Seminar

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Thursday, April 4, 2024 at 1:00 p.m. (Rm: CSF-1302)

Title:

Spectral Apparent Quantum Yields of Triplet Dissolved Organic Matter Provides Insight into Photochemical Processes in Surface Waters

Abstract

Phototransformation of dissolved organic matter (DOM) has been of interest to researchers for decades due to its role in degrading contaminants, mineralizing carbon, and transforming natural products. A fraction of DOM (chromophoric DOM or CDOM) absorbs photons from sunlight and undergoes an intersystem crossing from the ground state to the excited triplet state. This is the first step in many photochemical processes in natural waters. Triplet excited CDOM (^{3}CDOM*) exists for between 2-100 μs before its energy and/or electrons are transferred to surrounding dissolved species causing chemical change before returning to the ground state. The fate of ^{3}CDOM* includes decay via physical quenching by solvent (i.e. water) or dissolved molecular oxygen, while fates involving chemical change include the excitation of triplet O_2 to the singlet state and oxidation of or energy transfer to surrounding ground state (singlet) DOM. Given its transient and short-lived nature, ^{3}DOM cannot be quantified directly, but its production can be assessed indirectly through the use of probe compounds.

2,4,6-trimethylphenol (TMP) is an effective probe to assess the formation of ^{3}DOM* species that can react via electron transfer and also represents functional groups present in natural DOM. TMP offers an alternative and competitive fate for ^{3}CDOM* energy when present in high enough concentrations relative to dissolved oxygen due to its high reactivity compared to the triplet energies in the DOM pool. Probe chemistry operates under the assumption that ^{3}CDOM* exists in a steady state where the rate of its formation and decay are equal. ^{3}CDOM* decay is represented by the loss of the probe compound as it scavenges triplet energy allowing for the indirect determination of ^{3}CDOM* formation rates. Previous studies have attempted to determine apparent quantum yields (AQYs) for integrated broad spectrum irradiations (e.g. using UV-A centered lamps etc), but the true spectral nature of the AQYs for ^{3}DOM photoproduction remains unresolved. Spectrally resolved AQYs are crucial for determining the impact of photochemical processes on natural waters. Using a specially designed solar simulator system equipped with a xenon arc lamp and a series of long-pass cutoff filters, we assessed TMP loss rates to determine spectral apparent quantum yields of ^{3}DOM for contrasting water types. Additionally, many studies do not validate the steady state assumption and omit vital information

including total photon dose, specific absorption rates, and length and spectral quality of irradiation. We irradiated our samples under full solar spectrum conditions and calculated apparent steady state concentrations over time (i.e varying photon doses) to test the assumption. Our results show that the fundamental primary steps in photochemical processes in natural waters vary based on DOM source.