Recent studies of NOM excited states in the photochemical (sunlight) fate of organic compounds and application in the design and optimization of constructed wetlands

William J. Cooper
Professor
Department of Civil and Environmental Engineering
Urban Water Research Center
University of California, Irvine
Irvine, CA 92697
wcooper@uci.edu

The studies that we are conducting are aimed at better understanding the sunlight mediated photochemistry of pharmaceuticals and other emerging compounds of concern in surface waters. The ultimate goal of this research is to provide the scientific basis for designing and optimizing constructed wetlands for their removal.

Our studies have shown that the photochemical processes of NOM are relatively complex. Evaluating the variables one by one results in a quantitative understanding of the sunlight mediated photochemistry of NOM summarized in Equation 1.

$$\frac{d[P]}{d[t]} = k_{H_2O}[P] + k_{photo}[P] + k_{{}^1O_2}[{}^1O_2][P] + k_{\cdot OH}[\bullet OH][P] + k_{{}^3NOM^*}[{}^3NOM^*][P] + k_{NOM^*}[NOM^*][P] + k_{e_{aq}^-}[e_{aq}^-][P] + k_{O_2^-\cdot}[O_2^-\cdot][P] + k_{H_2O_2}[H_2O_2][P] + k_{CO_3^-\cdot}[CO_3^-\cdot][P] \quad (1)$$

Where, the first two terms are the first order rates of hydrolysis and direct sunlight photolysis of a compound, P, and, then a series of second order processes which include the reaction of P with singlet oxygen, ${}^1O_2$, hydroxyl radical, •OH, the triplet excited state of natural organic matter, ${}^3NOM^*$, and, an as yet unidentified excited state of NOM, NOM*, the hydrated electron, e_{aq}^- , superoxide radical anion, $O_2^- \bullet$, hydrogen peroxide, H_2O_2, and carbonate radical, $CO_3^-\bullet$.

We evaluate the individual variables by using a variety of techniques. These techniques involve both steady state and time resolved techniques of radiation chemistry and photochemistry. These techniques will be briefly reviewed. Once reaction rate constants are known and the steady state concentrations of the reactive species calculated, a simpler equation results that is first order in all of the variables. That equation, when coupled with fluid flow equations, can achieve our goal of designing and optimizing wetlands as a treatment process.

Recently, we have also conducted a series of studies using waters collected in the Everglades National Park where we are interested in the effect of increasing salinity on the reactivity of NOM and ultimately on the fate of organic chemicals in coastal environments. This study will be discussed briefly as it relates to an overall understanding of NOM reactivity.