Deoxygenation processes of model humic substances under simulated solar irradiation

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Deoxygenation is the major process behind generation of hypoxia and so-called blackwater in coastal waterways. However the fundamental geochemistry of deoxygenation induced by solar irradiation in such systems is largely unknown. This study investigates the magnitude and rate of dissolved oxygen (DO) consumption during simulated solar irradiation of model, humic-rich freshwaters. Specifically, we aimed to elucidate the relationships between dissolved organic matter (DOM) types and environmental conditions including pH and temperature in order to improve the understanding of the coastal hypoxia blackwater generation mechanism.

Experiments were conducted with three standard dissolved humic substances (HS): one aquatic fulvic acid (Suwannee River Fulvic Acid standard, SRFA) and two soil humic acids (Pahokee Peat Humic Acid Standard, PPHA; and Leonardite Humic Acid standard, LHA). DO concentrations were measured as a function of irradiation time in order to determine the magnitude and apparent first-order rate constant for DO consumption. In addition, spectrophotometric measurements were used to calculate the optical properties E2/E3 and SUVA280, while the redox state of the DOM was analysed by a spectrophotometric assay using the redox active dye dichloroindolphenol (DCPIP).

Results showed that all DOM solutions consumed DO during irradiation, and the majority DO consumption occurred in the initial 3 hours of irradiation. The magnitude of DO consumption was found to vary with DOM type, pH and temperature, while the apparent first-order rate constant was relatively stable. SUVA280 increased slightly after 3 hours of irradiation for all DOM solutions; E2/E3 decreased with DOM concentration, but increased with irradiation time; and redox states generally decreased slightly with DOM concentration.

The results suggest that in hypoxic blackwater systems, there is not a simple relationship between chromorphoric properties of DOM and DO consumption potential. Further studies involving other components of real blackwater systems such as trace metals and biota are required to fully understand the role of photochemistry in these environments.