Photochemistry of Dissolved Organic Matter in the Florida Everglades

Investigation of Pollutant Fate in the Environment

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Background

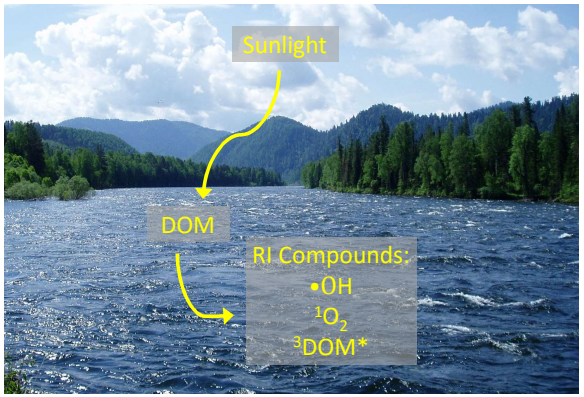
We care about dissolved organic matter (DOM) because…

- Precursor to disinfection by-products (DBPs)
- Essential to nutrient cycling because it acts as a carbon source
- Forms reactive intermediates (RI) which degrade aqueous contaminants

Role of RI compounds:

- Act as strong oxidizers
- Form via DOM photolysis reactions
- Primary mechanism by which some contaminants degrade in the environment

$$Rate\ of\ RI\ formation \propto Quantum\ Yield \propto Rate\ of\ pollutant\ degradation$$



Research Statement

- **There is an incomplete understanding of RI formation and behavior**
- **Find what properties of DOM influence RI formation**
- **Use photochemical and optical properties to create correlations**
- **Use these correlations to create models to predict RI behavior**
- **These models will allow us to predict pollutant fate in the environment**

Methods

- Experiments are performed using **surface water samples collected from the Everglades** in collaboration with FIU

RI	Probe Compound	Tracking Method
•OH	Benzene	Formation of Phenol
$^1O_2$	FFA	Decay of FFA
^{3}DOM*	TMP	Decay of TMP

- **Oriel 94041 A solar simulator** and 1000 W lamp with AM 1.5 filter (Figure 1)
  - Covers natural wavelength spectrum to mimic light in the environment

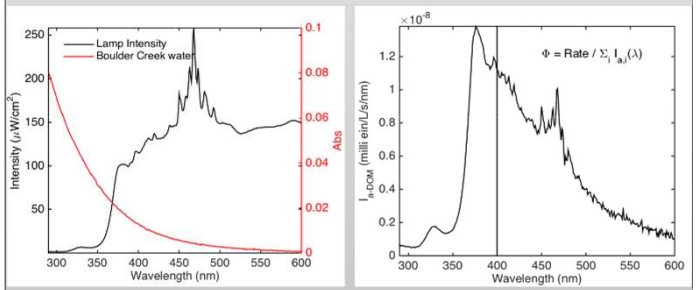


Figure 1. A visual example of the solar simulator lamp intensity overlaid with OM absorbance spectrum (left) and calculation of the quantum yield from rate of light absorption by OM, $I_{a,DOM}$ (right).

- Analysis of probe compounds by **High Performance Liquid Chromatography (HPLC)**
- Other optical properties measured with **UV Vis Spectrophotometer**

Terminology

- **DOM:** Dissolved Organic Matter
- **DBPs:** Disinfection By-Products
- **RI:** Reactive Intermediates
- **•OH:** Hydroxyl Radical
- **$^1O_2$:** Singlet Oxygen
- **^{3}DOM*:** Triplet DOM
- **FFA:** Furfuryl Alcohol
- **TMP:** Trimethyl Phenol
- **HPLC:** High Performance Liquid Chromatography
- **OM:** Organic Matter

Properties Used in Correlations

a. Optical Property: E2:E3

- Easy-to-calculate parameter obtained from absorbance scans
- Higher E2:E3 correlates with higher molecular weight DOM
  → Indicates quicker decay in DOM absorbance

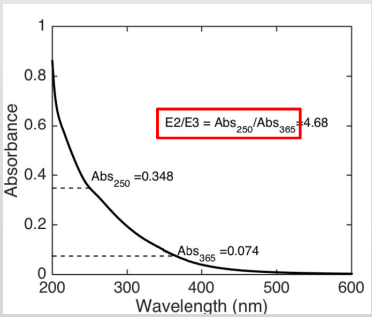
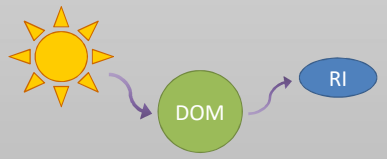


Figure 2. Example plot of wavelength versus absorbance for a water sample. Also shows calculation for the E2:E3 ratio

b. Photochemical Property: Quantum Yield, Φ

- An efficiency of the number of RI molecules formed per photons absorbed by the DOM source molecule
- Input data collected from experiments analysed by HPLC
- Output from Matlab code designed by Garrett McKay



$$\Phi = \frac{RI\ molecules\ formed}{photons\ absorbed}$$

Results / Discussion

- Results from our experiments were **compared with two other studies performed on different types of DOM** (Figure 3)
  - FL Everglades: pristine water samples
  - Dalrymple: DOM isolates (pure strains of DOM, not naturally occurring)
  - Mostafa: wastewater effluent OM
- **All three studies have similar results** -- This is good news!
- We can use these correlations as methods for modeling RI formation
- Results for •OH are not significant (Figure 4); need another correlation

Figure 3. (right) Experimental results from our experiments, Dalrymple (2010), and Mostafa (2013)

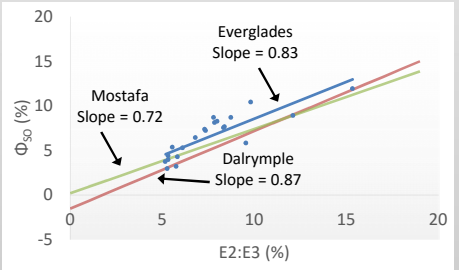
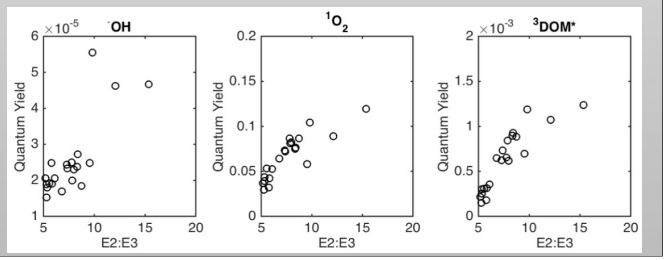


Figure 4. (below) Experimental results from our experiments for hydroxyl radical, singlet oxygen, and triplet DOM



References

- Dalrymple, R.M.; Carfagno, A.K.; Sharpless, C.M. Correlations between dissolved organic matter optical properties and quantum yields of singlet oxygen and hydrogen peroxide. *Env. Sci. and Tech.* 2010.
- Mostafa, S.; Rosario-Ortiz, F.L. Singlet Oxygen Formation from Wastewater Organic Matter. *Env. Sci. and Tech.* 2013.

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