Photochemistry of wildfire derived pyrogenic-dissolved organic matter (py-DOM) for photodegradation of aquatic contaminants

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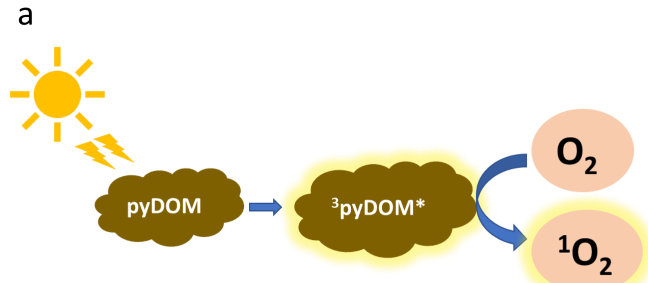
Introduction

Pyrogenic dissolved organic matter (py-DOM) is a type of chromophoric (or light absorbing) dissolved organic matter (CDOM) that can generate, in presence of sunlight or similar light sources, photochemically produced reactive intermediates (PPRI) such as singlet oxygen ($^1O_2$), the excited form of ground-state oxygen (Fig.1.a). $^1O_2$ is an important oxidant during the photo-transformation of pollutants in water and impacts their lifetimes. Currently changing wildfire frequency and intensity necessitate understanding the role of py-DOM in the production of $^1O_2$ and therefore in pollutant transformation. $^1O_2$ quantum yield (Φ_Δ, number of $^1O_2$ molecules generated upon absorption of one photon of light) for pyDOM extracted from laboratory prepared chars has been reported in previous studies, but these may inaccurately represent actual wildfire chars present in the environment.

a



b

Fig 1. (a) Photochemistry of pyDOM, (b) Colorado Grizzly Creek wildfire site

In this study, py-DOM was extracted from wildfire-derived chars and their Φ_Δ at 365 nm was determined by measuring the time-resolved $^1O_2$ phosphorescence at 1275 nm. This Φ_Δ determination method was validated by measuring Φ_Δ of SRNOM (Suwanee River Natural Organic Matter), which has been established in previous studies (1.8±0.2%) that use the same Φ_Δ determination method as here.

Methods

Biochar solids were obtained by physically scraping burnt log samples collected from the Colorado Grizzly Creek (CGC) wildfire site (Fig.1.b). Additionally, store-bought Oak wood pieces were burnt in a muffle furnace at 250 °C for 3 hours. These solids were ground and sieved to ensure maximum homogenization and then agitated in 10 mM phosphate buffer (pH=7.0) for 48 hours followed by centrifugation and filtration to extract py-DOM (Fig.2). $^1O_2$ phosphorescence signals from py-DOM and reference samples were obtained by using a tunable excitation wavelength source (365 nm) and an automated spectrophotometer coupled with a NIR-PMT detector (Fig. 3). Φ_Δ for pyDOM and SRNOM was calculated relative to a known Φ_Δ value of the reference, Perinaphthenone (95%) (Eqn. 1).

Figure 2. *(a) Collected sample portion. (b) Chipped off pieces from the sample. (c) Obtained pyDOM solution after grinding, sieving, agitation, centrifugation and filtration.*

Results and Discussion

- Extracted pyDOM solutions from CGC wildfire and Oak wood biochar produced $^1O_2$ phosphorescence signals (Fig. 3).
- Φ_Δ at 365 nm for CGC py-DOM and store-bought Oak wood pyDOM was found to be 1.25% and 1.43% respectively (Fig. 4). The difference between these quantum yields can be attributed to the different chromophoric moieties present in the pyDOM which determine their absorption of light and their rate of reaction with ground state O_2 to generate $^1O_2$.
- The determined Φ_Δ for both wildfire derived and lab-prepared pyDOM is lower than other studies that have reported Φ_Δ for lab prepared chars. This could be due to different char chemistry and/or the different $^1O_2$ measurement technique.
- Φ_Δ for SRNOM at 365nm was found to be 1.9% which is consistent with previous findings and offered as a validation of this method.

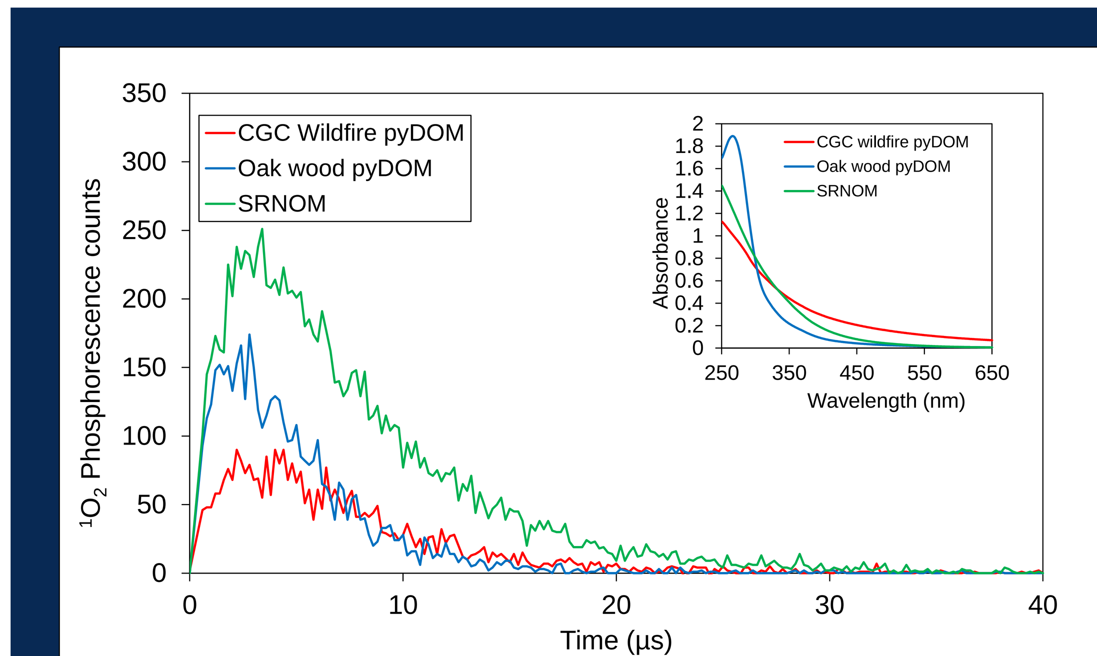


Figure 3. *Time-resolved $^1O_2$ phosphorescence kinetic trace measured at 1275 nm. Insert: UV-Vis absorption spectra for prepared pyDOM and SRNOM*

Equation 1.

$$\Phi_\Delta(Sens.) = \Phi_\Delta(Ref.) \cdot \frac{s_\Delta(Sens.)}{s_\Delta(Ref.)} \cdot \frac{R_{abs}(Ref.)}{R_{abs}(Sens.)} \cdot \frac{Coll.t\,(Ref.)}{Coll.t\,(Ref.)}$$

Sens. = Sensitizer (Here, CGC wildfire pyDOM/ Oak wood pyDOM/ SRNOM)
Ref. = Reference (Here, Perinaphthenone)
Φ_Δ = $^1O_2$ quantum yield (%)
s_Δ = Observed area of the $^1O_2$ signal
R_{abs} = Rate of light absorbance (mmol photons cm^{-3} s^{-1}) given as,

$$R_{abs} = \frac{\Sigma_\lambda I_\lambda,rel\left(1-10^{-\alpha_\lambda l}\right)}{l} \quad \text{(Equation 1.1)}$$

I_λ, rel = Relative emission intensity of the laser measured over 1 nm wavelength (λ) intervals (counts)
α_λ = Measured decadic absorbance coefficient of the solution at λ
l = Pathlength (1 cm)
Coll. t = Amount of time the signal was collected (s) (90 seconds for Perinaphthenone, 600 seconds for pyDOM and SRNOM)

a

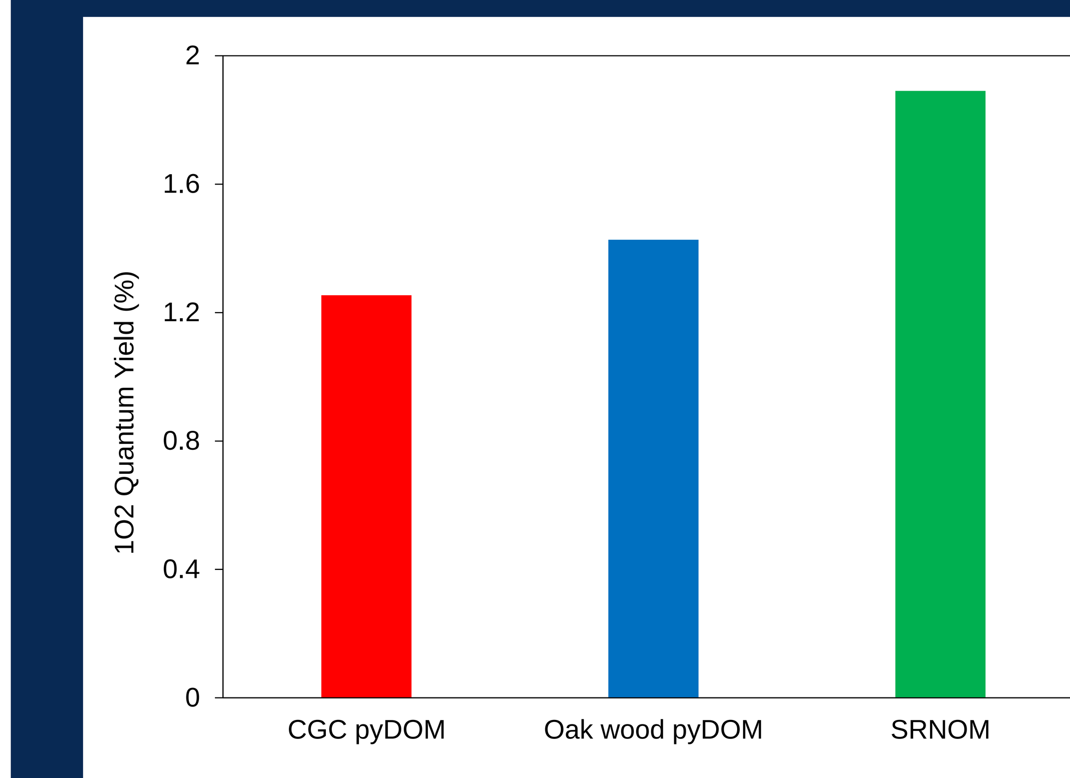


Figure 4. *Determined Φ_Δ for CGC Wildfire pyDOM, Oak wood pyDOM, and SRNOM at 365 nm.*

Conclusions and Future Work

- $^1O_2$ was produced by wildfire-derived pyDOM ($\Phi_{\Delta_{365nm}}$=1.25%) and store-bought Oak wood pyDOM ($\Phi_{\Delta_{365nm}}$ =1.43%), which indicates that pyDOM from wildfire biochar can possibly play an important role in the photo-transformation and lifetime of pollutants present water.
- Future work involves addressing the discrepancy between the determined Φ_Δ in this study and those reported in previous studies by comparing char chemistry and $^1O_2$ measurement techniques.
- Wavelength-dependent Φ_Δ for pyDOM and characterization of pyDOM is necessary to understand their $^1O_2$ production under natural sunlit environment and light-involving water treatment systems and their different $^1O_2$ production rates

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