## Seeing Molecules from Space: Tools for optically estimating CDOM composition



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#### Introduction

### Study Concept

Colored dissolved organic matter (CDOM) absorption (a<sub>CDOM</sub>) varies significantly due to differences in source material, degradation pathways and in situ production. Satellite remote sensing provides a platform to observe this variability over broad spatial scales and time.

#### Problem

Current and near future sensors are/will be limited to measurements within the UV and visible wavelengths (> 350 nm) while most optical proxies estimating CDOM composition use wavelengths < 350 nm.

#### Science Questions

**SQ1**) Can we identify different types of CDOM using optical metrics?

SQ2) Can we discern any of these differences from a hyperspectral satellite sensor?

In Situ Data: Absorption spectra were fitted using a Gaussian decomposition approach (Fig. 2a,b). Fitted Gaussian components were aggregated and clustered using a k-means cluster analysis as guidance, with location, width and normalized peak height (peak height/baseline absorption at peak location) as the basis for clustering (Fig. 3). Fluorescence peaks C and A were delineated as described in Coble (1996). *Hydrolight*: Initial remotely-sensed reflectance ( $R_{rs}(\lambda)$ ) was simulated using *in situ* absorption and scattering data. For each sampling site,  $S_{350:550}$  was calculated and  $a_{CDOM}$  spectra were simulated using observed S<sub>350:550</sub> ± 0.005 in 0.001 increments. We utilized initial  $\lambda$  values of 350, 400, 450 and 500 nm and utilized the average CDOM absorption as input to simulate differences in R<sub>rs</sub>( $\lambda$ ) due to changes in S<sub>CDOM</sub>.

Methods



Figure 1. (a) Map of study region with Hydrolight simulations using data within the teal regions and (b) Keweenaw peninsula land cover delineated by Bourgeau-Chavez et al. 2017. The green and gold boxes correspond to highlighted Hydrolight stations. Green dots indicate sampled river systems, blue dots lake stations, and brown dots study sites for soil samples.

**CDOM Optical Variability Across Different Environments** 



Figure 3. Component clusters identified using k-means cluster analysis. Cluster analysis was performed on component location, width and normalized peak height (Grunert et al. 2018). Location and width were not normalized, resulting in a hierarchy of importance for clustering of location, width then normalized peak height. Clusters defined here are used to identify components in Fig. 4-6.





Figure 4. Mean identified components in each environment. Noteworthy features include C2 acting as a common degradation product of C4 and C6, suggesting C6 is lignin of a different type and/or degradation condition (Spencer et al. 2008; Schellekens et al. 2015). As found in Grunert et al. (2018), lignin components and their derivatives largely influence spectra at short wavelengths, while components identified in coastal and open lake systems were of a similar magnitude regardless of spectral location, suggesting optical variability in these samples is driven by longer wavelength components. We note that this is consistent with a charge-transfer model for a<sub>CDOM</sub>, with the exception that individual chromophores at  $\lambda$  > 375 nm are present, and contribute significantly to autochthonously produced CDOM. This is consistent with the findings of Catalá et al. (2016).

# Coast Open

Figure 5. Samples were delineated based on the environment sampled: soil pore water from peatlands (peat) or forested watersheds (soil), streams (reach < 25 km), plume (of sampled streams), coastal Lake Superior (depth < 20 m) and open Lake Superior (depth > 20 m). Each chart represents the ecotype membership for that component. Key findings: C1, C9, C12, C16 appears to be a microbial product of soils or soil/stream systems, C5/C13 appear to be a product of coastal priming or production, C6 is almost exclusively limited to peatlands (1 pre-thaw soil sample) potentially derived from a different type of lignin or degradation pathway, and C8 is exclusive to soil pore water, likely a non-photodegraded microbial byproduct. We suggest that components identified in all ecotypes are microbial byproducts ubiquitous to most ecosystems or terrestrial compounds resistant to degradation. These compounds may be photorefractory in nature or are structurally complex in the case of lignin (e.g. C2).



both by a blue-shift in component location as well as a decrease in component width and height. C1, C7 and C9 blue-shifted and decreased in magnitude, while C14 red-shifted and decreased in magnitude from river to plume. Within the coastal environment, wholly different components were identified.



Figure 7. Mean and distribution for each ecotype following the same color scheme as Fig. 5 for (a)  $a_{CDOM}(350)$ , (b)  $S_{275:295}$ , (c)  $S_{350:400}$ , (d)  $S_{350:550}$ , (e) slope ratio ( $S_r$ ), (f)  $E_2:E_3$  ( $a_{CDOM}(250)/a_{CDOM}(365)$ ) and (g) fluorescence peak C:A ratio. Fluorescence index (FI), humification index (HIX) and biological index (BIX) were also considered but were not significantly different across environments. Spectral slope followed typical trends observed across terrestrial to aquatic gradients, with open lake S<sub>350:400</sub> and S<sub>350:550</sub> displaying a relatively large range and a mean that differs at a magnitude visible to NASA's proposed PACE sensor (see Fig. 8). E<sub>2</sub>:E<sub>3</sub> values were within the range of Suwannee River fulvic acid suggesting a relatively low electron accepting capacity (Sharpless et al. 2014), while C:A values suggest a consistent degradation of relatively fresh terrestrial material from soils to the open lake. (h) Displays the relationships between C:A and normalized peak area for components identified as lignin within this dataset, suggesting consistency between these metrics.

detecting changes in S<sub>350:550</sub> with adequate atmospheric correction at most wavelengths. As shown in Fig. 7, S<sub>350:550</sub> varies across environments and within the open lake at levels al. 2015 Geoderma, 237-238; Sharpless et al. 2014 Env. Sci. Tech., 48; greater than 0.001 nm<sup>-1</sup>. From this, we would expect to directly estimate changes in CDOM composition affiliated with S<sub>350-550</sub> variability in Lake Superior using PACE. Spencer et al. 2008 Global Biogeochemical Cycles, 22

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