Optical Characterization of the South River Estuary, MD Through EEMS/PARAFAC Analysis

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Abstract:

Chromophoric, or colored, dissolved organic matter (CDOM) is a fraction of the DOM pool that absorbs and/or emits light at discrete wavelengths when excited. The CDOM spectrum in natural waters can be used in applications including: identifying water masses, tracking physical circulation, and quantifying physiochemical cycling of OM. In October, 2014, water column data and samples were collected from the South River, Maryland (USA), a small tributary of Chesapeake Bay, and characterized using Excitation-Emission Matrix fluorescence spectroscopy (EEMS) coupled with a parallel factor analysis (PARAFAC) model. The EEMS analysis was used to associate previously identified EEMS regions of certain CDOM components to those found in the South River, suggesting an optical difference in water column CDOM properties at different stations in the South River and also with depth at each station. The three-component PARAFAC model identified a terrestrial humic-like and two phenol-like OM components as the main constituents explaining the multi-way variance of the EEMS results. These OM components are likely indicative of biochemical degradation of terrestrial plant matter within the tributary creeks that feed into the South River. An assessment of CDOM component loading values showed that salinity played a significant role in influencing the EEMS spectra between stations. Results show that EEMS/PARAFAC model analysis of CDOM can potentially be applied in sub-estuaries like the South River to qualify factors influencing optical properties of the water column. Future studies could employ similar optical approached in order to enhance remote sensing in sub-estuarine environments with limited access.

Study Area and Methods:

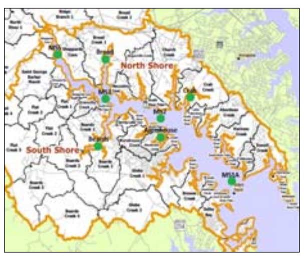
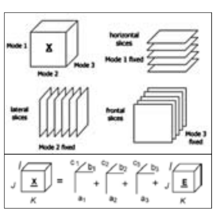


Figure 1. **Top left**. View of South River, Maryland. The stations sampled on 24 OCT 2015 are denoted by green dots. Three relative water depths were sampled at each station; surface, middle, deep. Main-stem locations are denoted by "MS-" and the end-members by their respective creek names. **Top right**. Water sample collection on the South River. Water quality data was collected at each station using a Hach DS-5X multi-parameter water quality monitoring sonde and samples were collected to measure CDOM, dissolved organic carbon (DOC), turbidity (Turb), and total suspended matter (TSM).

Data and samples were collected from the South River, Maryland (**Fig. 1**) and CDOM was characterized using Excitation-Emission Matrix fluorescence spectroscopy (EEMS) stacked in a 3-way, 3-component parallel factor analysis (PARAFAC) model that qualifies variability in water column CDOM properties (**Fig. 2**).

Figure 2. A graphical representation of the deconvolution method of three-way stacked data. This shows the incremental analysis of two modes (axes) while holding one constant. The resulting three factor PARAFAC model is a best fit explanation of the dataset based on three identified component. This produces a loading vector for each component of a, b_r, and c_r in each dimension of the matrix, with residuals in E.



EEMS Results:

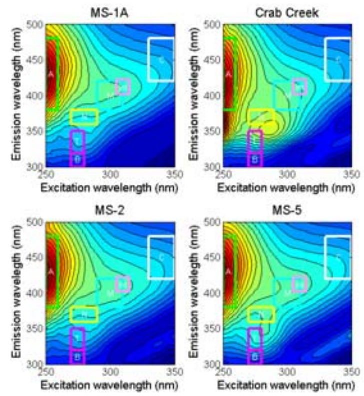


Figure 3. EEMS spectra for 4 stations in study area. Each plot represents the average of excitations-emission intensities for the three sample depths. Changes in color denote changes in intensity of the signal response from chromophoric species. Boxes within figure denote regions previously identified as being indicative of certain CDOM components identified by others in representative EEMs (**Table 1**).

Excitation (nm)	Emission (nm)	Peak[a]	Type
330–350	420–480	C, α	humic
250–260	380–480	A, α'	humic
310–320	380–420	M, β	marine humic
310	412	C-M[b]	intermediate C-M
280	370	N	unknown
270–280	300–320	B, γ	Tyrosine-protein like
270–280	320–350	T, δ	tryptophan-protein, phenol like

Table 1. CDOM Components in Representative EEMs (from Table 1, Boyd et al., 2010 [Coble, 1996, Parlanti et al., 2000]).

Figure 3 shows representative optical responses of CDOM constituents for the South River stations. Small variations can be discerned in the "A" region and between the "N" and "T" regions associated with terrestrial humic-like and phenol-like OM components.

PARAFAC Model Results:

Figure 4. Three-component PARAFAC model core consistency values. The blue line represents the theoretical target for an exact model fit to the data. The red dots each represent identified components which are gauged against the theoretical target.

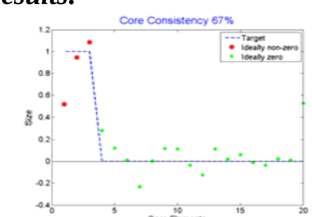
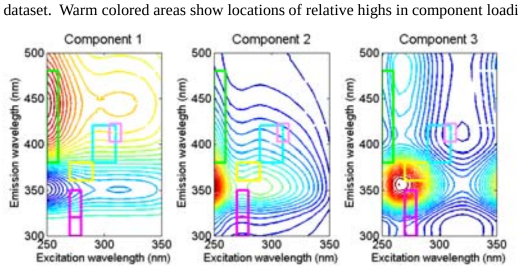


Figure 4 shows the core consistency of the three-component model. **Figure 5** shows distributions of the component loadings through the stacked EEM matrix. Component 1 shows a broadband signal through a large region, while Component 2 and 3 remain localized to a very specific region. Components 2 and 3 share a near-equal core consistency, indicating their similarity (**Fig. 4**). Component 1 can be identified as terrestrial humics, and Component 2/3 as a mix of tryptophan and/or tyrosine proteins (**Table 1**).

Figure 5. EEMS/PARAFAC results showing regions of identified components signals in dataset. Warm colored areas show locations of relative highs in component loadings.



Discussion of PARAFAC vs. WC Parameters :

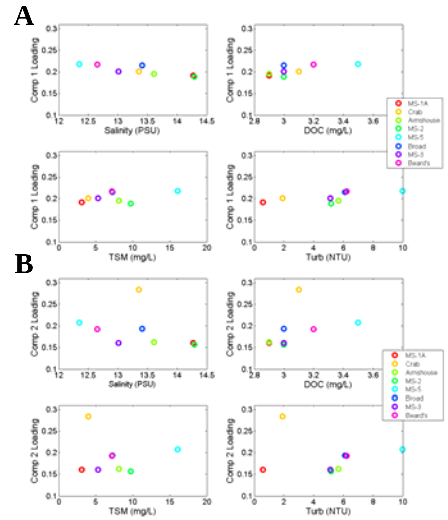


Figure 6. (A) PARAFAC results for component 1 loading vs. salinity, DOC, TSM and Turbidity. **(B)** shows the same for component 2. Loadings represent average values for the three depths at each stations.

Figure 6 shows the distribution of (**A**) Component 1 and (**B**) Component 2 with changes in salinity, DOC, TSM, and Turb. The loadings values for Component 1 and 2 generally decrease with increasing salinity but vary significantly with the other parameters likely indicative of individual creek contributions. For example, Crab Creek contributes significantly to the overall loading of Component 2. Additionally, creeks such as Beard's and Broad show similar Component 2 loading and water quality values.

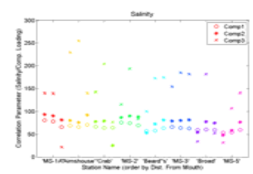


Figure 7. Correlation parameter vs. stations locations (scaled by distance from the mouth). The ratio of salinities values over component loading is explained by the parameter.

Figure 7 shows the strong connection between salinity/component loading and distance from the mouth of the South River. Together, **Fig. 3 and 6A** show that weak flow conditions (both from the creeks and from the river mouth) with a uniform salinity gradient (**Fig.** 7) contribute to a relative homogenous water column and a uniform optical signature. Distinct CDOM end-members however, such as Crab Creek, Beard's Creek and MS-5 significantly contribute to the overall optical signature of the South River.

Conclusions:

- ***The South River is likely dominated by autochthonous humic and phenol type OM potentially subject to high levels of photo- or chemical degradation.***
- ***The South River has a small salinity gradient that still significantly influences CDOM spectra but sub-tributary (creek) systems represent distinct CDOM end-members with unique optical properties.***
- ***PARAFAC analysis of EEMS fluorescence can be used to identify the contribution of CDOM by sub-tributaries to the larger estuarine receiving waters.***

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