Behavior of reoccurring PARAFAC components in fluorescent dissolved organic matter in natural and engineered systems: A critical review

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Motivation

Why is it important to characterize dissolved organic matter (DOM)?

- DOM affects ecosystem health
  - -e.g., light attenuation, nutrient availability
- DOM affects all water treatment processes
- Tracking DOM helps elucidate factors, such as land use and climate change, that affect ecosystem health

What tools or methods should be used to characterize DOM?

- Dissolved organic carbon concentration and ultraviolet absorbance are common
- Fluorescence spectroscopy shows promise
- Method involves exciting water with a range of wavelengths and measuring the wavelengths and intensities at which the sample fluoresces

Why combine fluorescence with parallel factor analysis (PARAFAC)?

- Fluorescence data are presented in excitation-emission matrices (EEMs)
- PARAFAC separates EEMs into independent fluorescent "components"
- A "component" is a group of DOM compounds with similar fluorescent qualities

Are there any weaknesses of using fluorescence with PARAFAC?

- Researchers relate the location and shape of components to previously identified components in other studies to validate results
- However, discussion on the characteristics of similar components across studies is lacking

Purpose of Critical Review

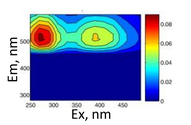
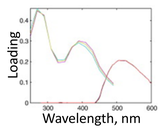
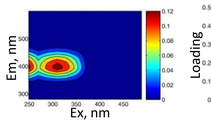
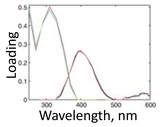
- To evaluate PARAFAC results across studies in order to understand the chemistry of reoccurring components
- To characterize reoccurring components based on:
  - -EEM location, associated ecosystems, behavior in natural and engineered systems

Methodology

Step 1-Compile & Identify:

- Compile PARAFAC studies
- Identify reoccurring PARAFAC components
  - -Table 1 shows the 3 reoccurring components in 53 studies published since 2000

Table 1. Spectral properties of reoccurring PARAFAC components

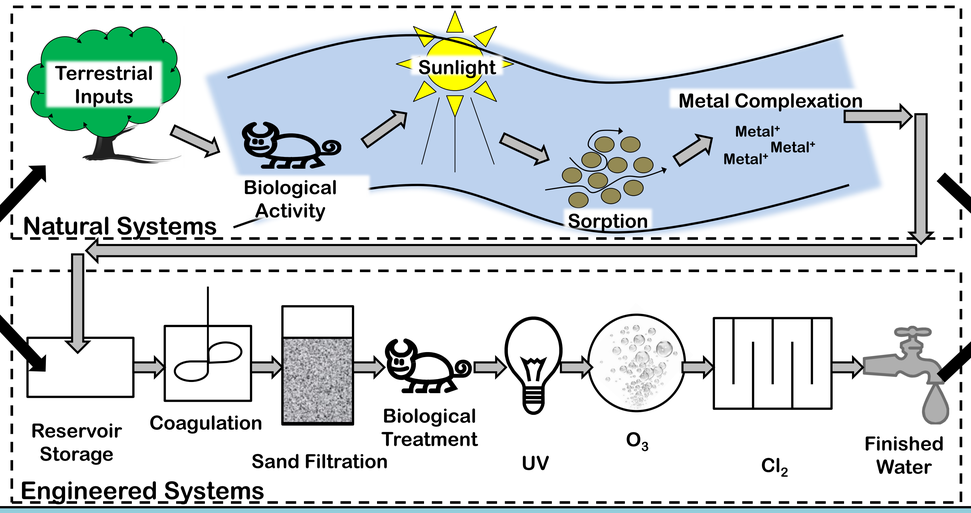
Component Label	EEM Wavelength Location	EEM	Spectral Loadings
1 (Peak A)	Ex: <230-260 nm Em: 400-500 nm		
2 (Peak A + C)	Ex: <240-275 (339-420) nm Em: 434-520 nm		
3 (Peak A + M)	Ex: <240-260 (295-380) nm Em: 374-450 nm		

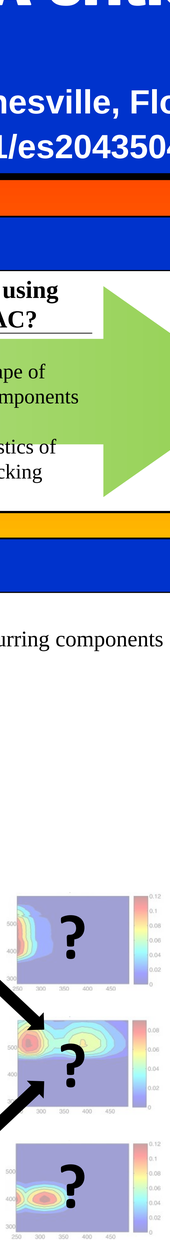
Step 2-Compare:

- Compare how processes in natural and engineered systems affect the fluorescence intensity of the 3 reoccurring components
- Determine if PARAFAC component behavior is consistent across studies

Step 3-Characterize & Evaluate:

- Characterize PARAFAC components based on consistent behavior
- Evaluate the strengths and weaknesses of fluorescence with PARAFAC





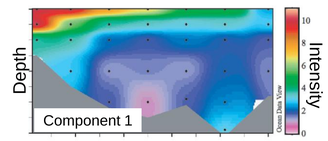
For example:

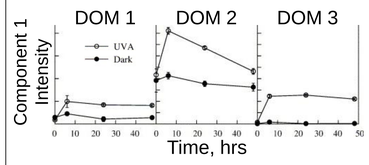
What is the photoreactivity of Component 1?

Peak absorbance @ 230-260 nm (UVC) → Therefore → Component 1 expected to be stable in natural light

Terrestrial sunlight lacks UVC light (Diffey, 2002) → Therefore → Component 1 expected to be stable in natural light

"The levels of fluorescence intensity of [Component 1] …decreased with depth" (Yamashita et al., 2008)





"UVA incubation resulted in a net production [of Component 1] in the samples from all three sites" (Stedmon et al., 2007)

Component 1 behavior across studies suggests that Component 1 compounds are:

- **-photochemically produced**
- **-resistant to photodegradation**

Fluorescence/PARAFAC Strengths

Table 2 provides a summary of PARAFAC component tendencies. Spatial and temporal variability in PARAFAC components help predict changes in DOM behavior.

Table 2. Component trends based on consistent behavior across studies

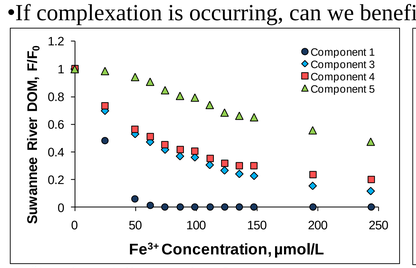
Category	Trends	Category	Trends
Terrestrial origin	1 > 3 > 2	Aluminum complexation	3 > 2 ~ 1
Conservatively mixed	1 > 3 > 2	Mercury complexation	2 > 3 ~ 1
Biologically degraded	2 > 3 > 1	Removal by coagulation	2 > 3 > 1
Biologically produced	2 > 3 > 1	Removal by ozonation	2 ~ 3 (1 unknown)
Photochemically degraded	2 > 3 > 1	Removal by BAC filtration	2 ~ 3 > 1
Photochemically produced	1 > 2 > 3	Removal by UV disinfection	3 ~ 2 (1 unknown)
Sediment sorption tendencies	2 > 3 > 1	Removal by chlorination	2 > 3 (1 unknown)
Iron complexation	2 > 3 > 1	Presence in finished water	2 ~ 3 > 1

Fluorescence/PARAFAC Weaknesses

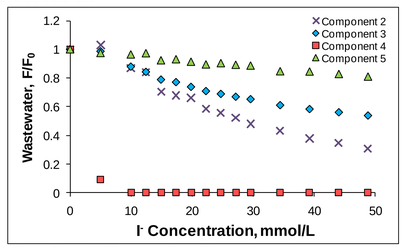
- **Component 3 behavior across studies is highly variable**
- **Previous PARAFAC studies do not acknowledge the effects of water quality on DOM properties**
  - -Water sample conditions, e.g., pH, ionic strength, dissolved oxygen, temperature, and metals content, must be held constant when characterizing DOM with PARAFAC
- **Existing PARAFAC research fails to recognize whether changes in DOM component fluorescence are due to:**
  - a) a chemical transformation,
  - b) a physical transformation, or
  - c) an addition/removal of DOM compounds
- **Caution should be exercised when comparing PARAFAC models**
  - -PARAFAC results only pertain to the spatial and temporal variability of the samples used to create the model

Future Research Needs

- Is fluorescence quenching of PARAFAC components indicative of complexation between a quencher and the DOM component?
- If complexation is occurring, can we benefit from it?



- Fe^{3+} preferentially quenches Component 1
- Will Component 1 be preferentially removed during Fe^{3+} coagulation?



- I^- preferentially quenches Component 4
- If Component 4 is removed during water treatment, will I^- also be removed as part of a iodide–DOM complex?