

Exploring aquatic organic matter fluorescence and biogeochemical spatiotemporal patterns using a combined approach of supplementary comparative PARAFAC models

Juliana D'Andrilli^{1,*}, Robert A. Payn^{1,2}

¹ Dept. of Land Resources & Environmental Sciences, Montana State University, Bozeman, Montana, USA

² Montana Institute on Ecosystems, Montana University System, Montana, USA

* Corresponding author email: Juliana@montana.edu

Characterization of organic matter (OM) offers a powerful means of understanding the source and fate of carbon in natural and managed environments. Dissolved OM (DOM) composition in aquatic ecosystems reflects an aggregation of biogeochemical imports or processing; thus, variations in DOM composition may inform understanding of the spatiotemporal organization of ecosystem connectivity and function. Excitation Emission Matrices (EEMs) have become a common tool for probing the composition, concentration, and dynamics of fluorescent OM from various source materials (Coble et al., 1998; Hudson et al., 2007; Coble, 2014; D'Andrilli et al., 2017). More and more researchers rely on the ease with which EEMs generate a wealth of data that can be analyzed with parallel factor (PARAFAC) decomposition techniques to provide objective interpretations of DOM composition and reactive nature (Stedmon et al., 2003; Murphy et al., 2013). PARAFAC analyses are typically applied to one, all-encompassing collection of EEMs per project, which allows hyperdimensional EEMs data to be decomposed into contributions from a limited number of fluorescent peak regions that explain variation in fluorescence intensities. While a considerable number of EEMs preprocessing steps are available for establishing objectivity in PARAFAC analyses, certain biases remain that can produce convoluted or masked signatures in modeled outputs (Figure 1a; C2). Using a supplementary comparative PARAFAC modeling approach, we have shown that convoluted signals from an overall PARAFAC model can be further resolved into separate fluorescent regions that provide more accurate DOM chemical interpretations (D'Andrilli et al., 2017).

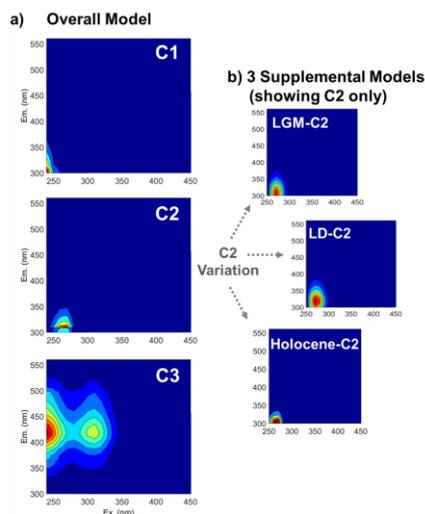


Figure 1. PARAFAC overall-to-supplementary comparative model examples from Antarctic ice core DOM with a) the three component (C1, C2, and C3) results from the overall model and b) three supplementary comparative climate period PARAFAC models as subsets of the overall model highlighting C2 for the Last Glacial Maximum (LGM), deglaciation (LD), and the Holocene (climate periods spanning 27,000-6,000 years ago) (D'Andrilli et al., 2017). Excitation (Ex) and emission (Em) wavelengths are provided on the x- and y-axis, respectively.

We explored the potential for DOM fluorescence signals to represent biogeochemical processing regimes and terrestrial-to-aquatic ecosystem connectivity in headwater streams and other watershed compartments (e.g., rain, glaciers, rivers). PARAFAC lists the components in decreasing order of explained fluorescent variation (C1 > C2 > C3). When combined with other PARAFAC models, a second level of organization emerges where components with similar properties are interpreted to reflect common DOM chemistries. Organizing models in a table format, where each model is in a

separate row and component order always starts from the left, creates a simple perspective for comparison among multiple models of the same watershed (Figure 2) or for different aquatic corridors. For effective comparison among varying fluorescent signatures, the components were categorized along a bioavailability continuum (lower to higher Ex/Em wavelengths) to combine more accurate interpretations of fluorescent signatures with groupings of compositions specific to spatial and temporal scales. For example, using this approach, DOM composition and bioavailability fluctuations in headwater streams were isolated spatially and temporally on diel, seasonal, and interannual scales. These general causal relationships are characterized by emerging fluorescent signatures and patterns that would have been masked using an overall PARAFAC model approach, alone (Figure 2- Overall model). Terrestrial DOM signatures (humic-like chemical species labeled ‘c’ and ‘e’) were observed continuously, describing a dominant hydrologic connection throughout this watershed (Figure 2- boxed data). This approach provides a way of isolating variables responsible for DOM processes that may be related to climate and land use change, human influences like nitrogen loading or metal contamination, or other naturally occurring processes. Analysis of results from a combined PARAFAC modeling approach with DOM from aquatic systems also has potential to separate coupling with adjacent terrestrial systems from *in situ* processing, which can be used to infer the response of biogeochemical regimes to a changing climate.

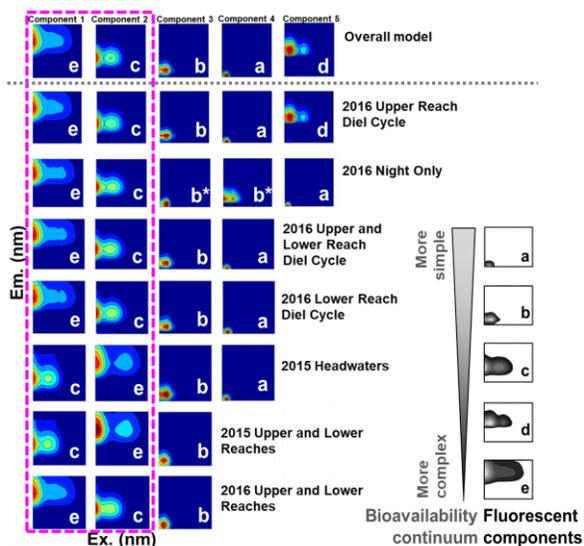


Figure 2. Eight individual PARAFAC models for one headwater stream ecosystem DOM dataset. Exemplary chemical species categories or DOM “types” are listed on the right (labeled a-e) and marked within each component for the models (left). The overall model is shown at the top, followed by seven supplementary comparative models defined by spatial and temporal scales. Note: b* encompasses an overlapping region closest to chemical species category ‘b’ character and may be attributed to different bioavailable chemistries. Dashed line boxed data (pink) indicate humic-like chemical species explaining the greatest variation in all PARAFAC models for this watershed.

References

- Coble, P.G., Del Castillo, C.E. and Avril, B. (1998) Distribution and optical properties of CDOM in the Arabian Sea during the 1995 Southwest Monsoon. *Deep-Sea Research Part II-Topical Studies in Oceanography* **45**, 2195-2223.
- Coble, P.G., Lead, J., Baker, A., Reynolds, D. M., Spencer, R. G. M. (eds) (2014) *Aquatic Organic Matter Fluorescence*. Cambridge University Press, Cambridge.
- D'Andrilli, J., Foreman, C.M., Sigl, M., Priscu, J.C. and McConnell, J.R. (2017) A 21 000-year record of fluorescent organic matter markers in the WAIS Divide ice core. *Clim. Past* **13**, 533-544.
- Hudson, N., Baker, A. and Reynolds, D. (2007) Fluorescence analysis of dissolved organic matter in natural, waste and polluted waters—a review. *River Research and Applications* **23**, 631-649.
- Murphy, K.R., Stedmon, C.A., Graeber, D. and Bro, R. (2013) Fluorescence spectroscopy and multi-way techniques. *PARAFAC. Analytical Methods* **5**, 6557-6566.
- Stedmon, C.A., Markager, S. and Bro, R. (2003) Tracing dissolved organic matter in aquatic environments using a new approach to fluorescence spectroscopy. *Mar. Chem.* **82**, 239-254.