Quantifying Spatial Heterogeneity in the Optical Properties of Surface Waters in a Semi-Enclosed Estuarine Basin

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Abstract

The optical properties of surface waters in estuarine systems can be characterized by a high degree of 'patchiness'. In this study, a custom flow-through system was used to collect data on fluorescent dissolved organic matter (fDOM) of surface waters in a semi-enclosed estuarine basin to quantify scales of spatial heterogeneity. Surface water samples were analyzed for chromophoric DOM absorbance and by Excitation Emission Matrix (EEM) spectroscopy to reveal factors driving heterogeneity.

Study Area and Methods

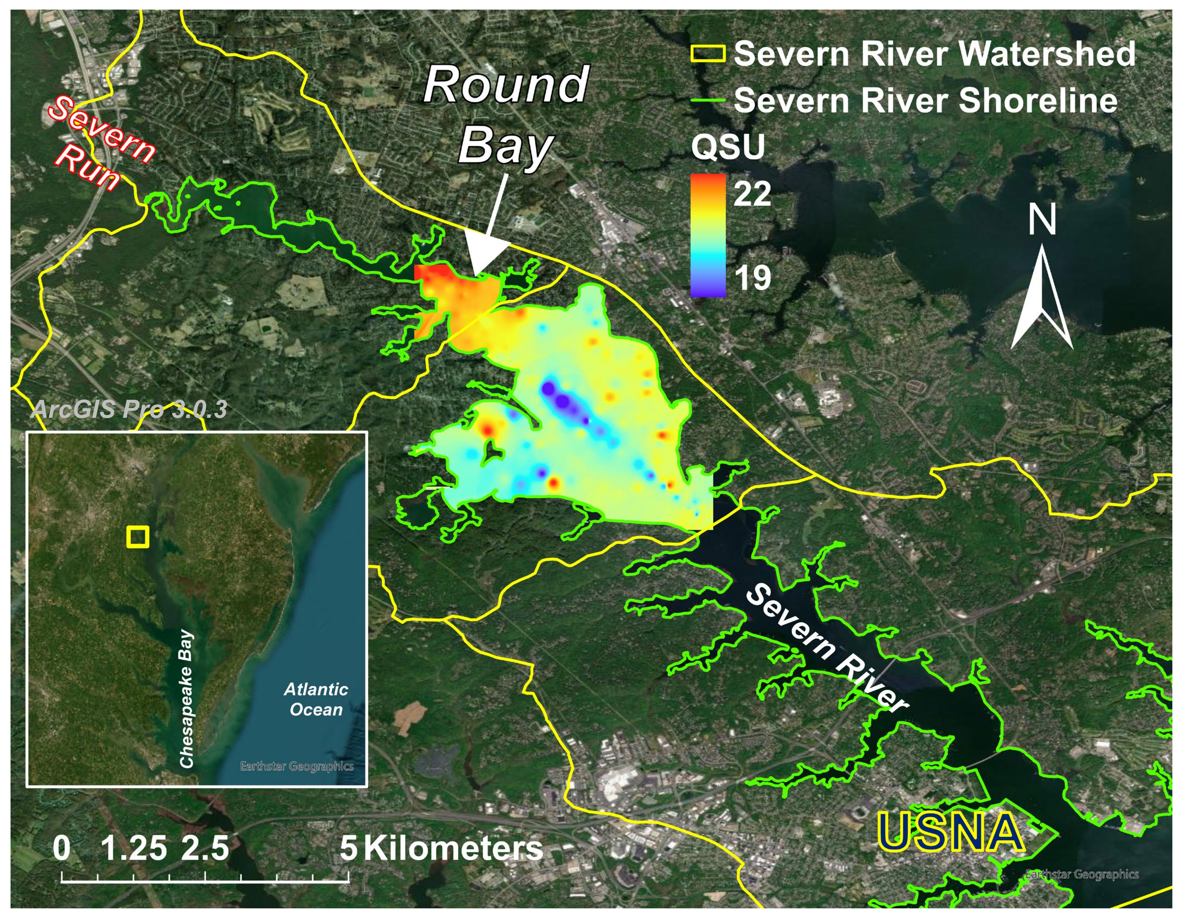

Figure 1. Round Bay is a semi-enclosed basin on the Severn River, a tidal tributary of the mesohaline Chesapeake Bay. Severn Run is a main freshwater source to Round Bay and the Severn River. On 14 November 2023, a custom flow-through (**Fig, 2b**) system equipped with a YSI EXO 1 multiparameter sonde with a SMART fDOM sensor was used to quantify the spatial heterogeneity in fDOM values in Round Bay**.**

Data on the optical properties of the surface waters of the Round Bay region of the Severn River (**Fig. 1**) were collected on 14 November 2023 using a custom flow-through system deployed off a small boat (**Fig. 2a**). The flow through system consists of a Flojet D21X005A duplex diaphragm sprayer pump which draws water into the system through an inlet at ~ 0.5 m depth. Water is pumped through a 2 µm pre-filter to a 3M Liqui-cel EXF Series membrane contactor to remove bubbles and then flows to a Sequoia LISST-200X submersible particle size analyzer and a YSI EXO1 multi-parameter sonde (www.ysi.com/exo1) with SMART sensors that measure salinity, temperature, turbidity, fluorescent dissolved organic matter (fDOM), and chlorophyll-a (**Fig. 2b**). Georeferenced data was logged every 2 seconds and averaged to 15 seconds using MATLAB R2023a. Data was then smoothed using inverse distance weighting and plotted using ArcGIS Pro 3.0.3. Results of the spatial distribution of fDOM from the 14 November 2023 survey were used to focus a follow-on survey of the upper part of Round Bay in the vicinity of Severn Run on 16 February 2024. In addition to flow-through data, a series of discrete water samples were collected along the estuarine salinity gradient at ~0.5m using a clean acrylic 3.2L Van-Dorn bottle (**Fig. 3**). A Sontek CastAway CTD (https://www.ysi.com/ castaway-ctd) was used to collect a vertical profile of salinity and temperature. Surface waters were syringe-filtered (0.2 µm) in the field into clean 40 ml amber borosilicate vials and analyzed in Hendrix Oceanography Laboratory for absorbance (250-600 nm) and excitation emission matrix (EEMs) acquisition 350-800 nm using a Horiba Aqualog spectrometer (https://www.horiba.com/ int/scientific/products/fluorescence-spectrometers/the-aqualog/). A 3-way, 3-component Parallel Factor Analysis (PARAFAC) model was performed on EEMs using Eigenvector Research SOLO software (https://eigenvector.com/software/solo/).

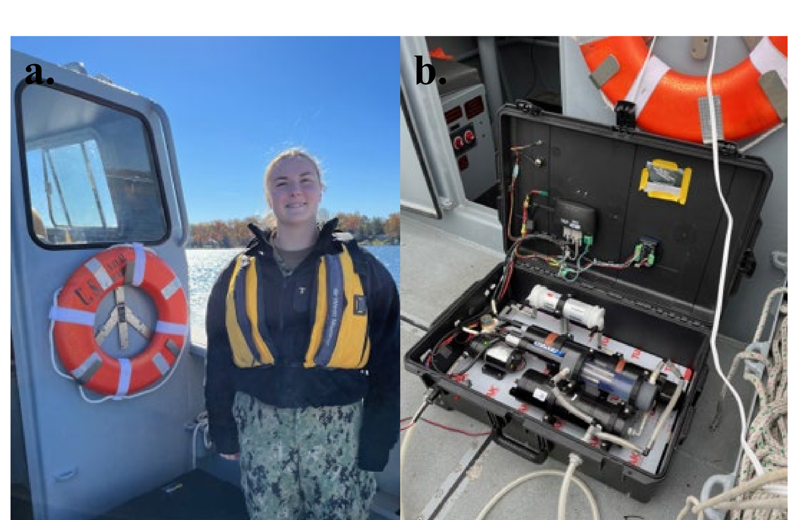

Figure 2. (**a**) Midshipman 1/C Cecelia Wheeler underway in Round Bay on 14 November 2023 collecting data on the optical properties of surface waters and (**b**) a custom flow-through system equipped with a YSI EXO 1 multiparameter sonde with SMART sensors that measure salinity, temperature, turbidity, fDOM, and chlorophyll-a.

References: Helms et al. (2008), *Limnol. Oceangr.* 53(3); Boyd et al. (2010), *JGR* 115: G00F13.

Results and Discussion

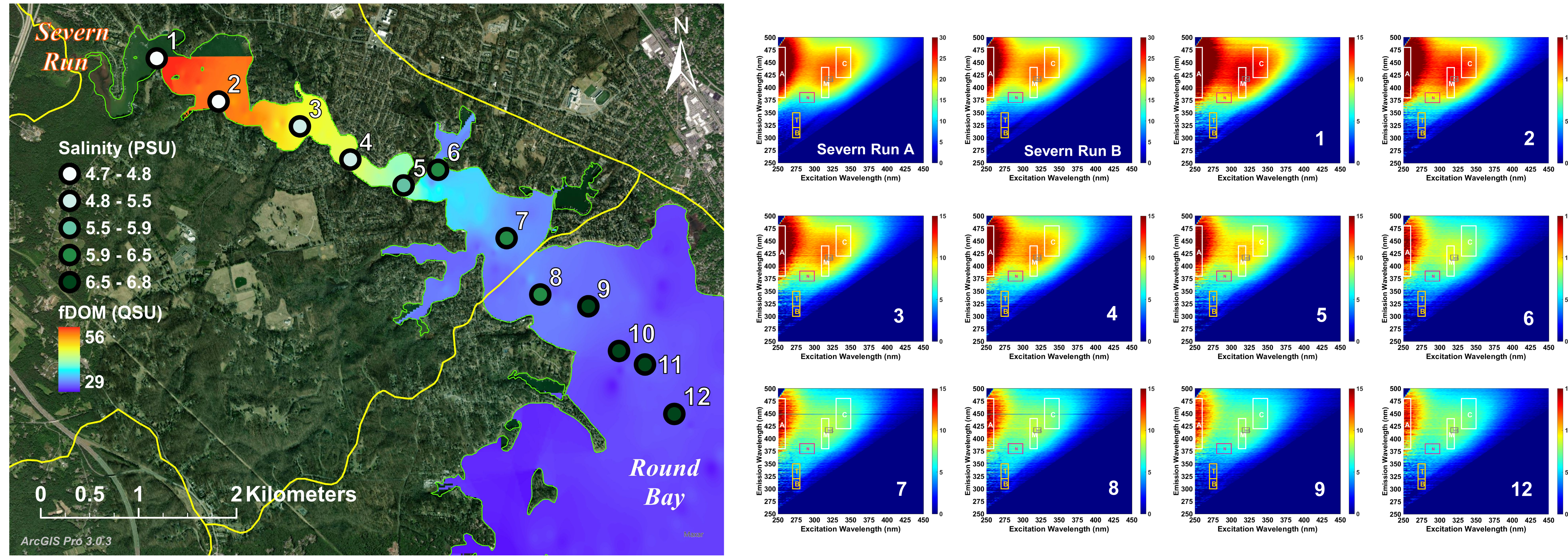

Figure 3. Smoothed contour plot of fDOM values measured using flow-through system and locations of CTD casts and discrete surface water sample collection sites along the estuarine salinity gradient in the upper part of Round Bay. A series EEMs plots show emission vs. excitation spectra (corrected and normalized fluorescence intensity) for waters collected on 16 February 2024 from Severn Run (Severn Run A and B; location not shown) and from sites (1-9 and 12). The highlighted regions of each EEM plot shows chromophoric dissolved organic matter (CDOM) component regions (from *Table 1, Boyd et al., 2010*): A & C = humics; M = marine humics; Int. = intermediate C-M; N = unknown; B = tyrosine protein-like; T = tryptophan protein, phenol-like. Note the scale shift between EEMs plots or Severn Run waters and EEMs plots derived from waters collected in Round Bay.

On 16 February 2024, higher fDOM values were measured at lower salinity values in the upper part of Round Bay where Severn Run discharges into Round Bay. Discharge from Severn Run is typically low with higher discharges associated with episodic high precipitation events. Discharge measured at the U.S. Geological Survey South Fork Jabez Branch (represents about 50% of total Severn Run flow) gauging station at Millersville, MD - 01589795 (https://waterdata.usgs.gov/monitoring-location/01589795) on 16 February 2024 was only 0.01 m^3/s, the long-term site average. The EEM spectra of Severn Run water suggests higher concentrations of dissolved organic matter (DOM), specifically terrestrial humics (region A and C), which are complex, heterogeneous mixtures of natural OM formed by biochemical processes such as decomposition. The EEMs spectra for Round Bay waters showed a decrease in the fluorescent fraction of DOM with increasing salinity from Severn Run into Round Bay (sites 1-12), most notably in the humic regions, suggesting Severn Run as the dominant source for OM export to the upper part of Round Bay (**Fig. 3**).

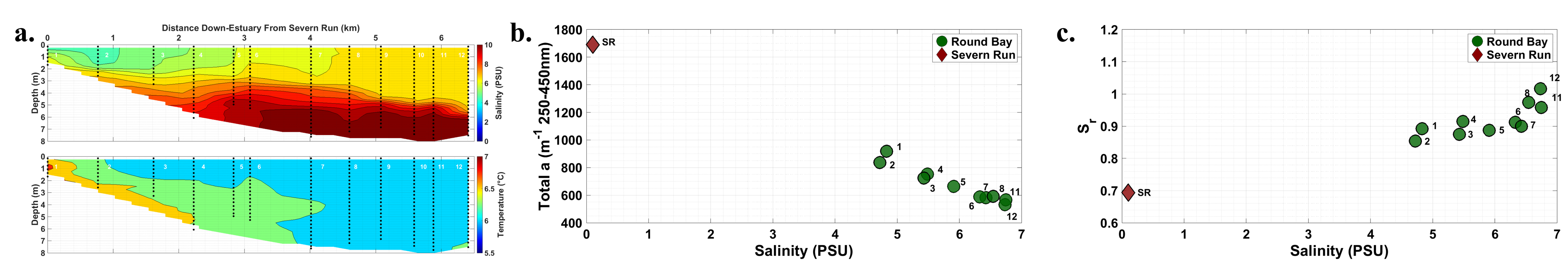

Figure 4. (**a**) Contoured salinity and temperature from sites 1-12; (**b**) Total absorption (Total a) from 250-450 nm and; (**c**) Spectral slope (S_r) vs. salinity from Severn Run into Round Bay vs. salinity. Total a is the sum of absorption coefficients from 250-450 nm (higher a indicates greater absorption in the CDOM range). Sr is the ratio of the slope of absorption in the shorter wavelength region (275–295 nm) to that of the longer wavelength region (350–400 nm). It provides a means to investigate the distribution of CDOM by molecular weight (MW) (*Helms et al., 2008*).

On 16 February 2024, the salinity of Severn Run water entering Round Bay was ~ 0.1 PSU. The upper reaches of Round Bay were slightly stratified with respect to salinity with a surface water gradient down estuary of roughly 3 PSU (**Fig. 4a**). Total CDOM absorption (Total a (250-450 nm)) was much higher (~2x) in Severn Run than in the waters of Round Bay (**Fig. 4b**) and the Spectral Slope (S_r) was significantly lower (**Fig. 4c**). Total a decreased and Sr increased along the salinity gradient in Round Bay suggesting a mixing of higher MW terrestrial CDOM from Severn Run with lower MW CDOM in Round Bay plus some potential photooxidation in surface waters (Helms et al., 2008). The 3-way, 3 component PARAFAC model analysis of EEMS plots revealed 2 major component differences between sites, both primarily in the terrestrial humic regions (A & C) with a potential marine contribution in component 2 (**Fig. 5a&b**). Both components showed a decreasing trend with increasing salinity (**Fig. 5c**) suggesting a rapid dilution of terrestrial CDOM from Severn Run with Round Bay waters in the upper reaches of Round Bay.

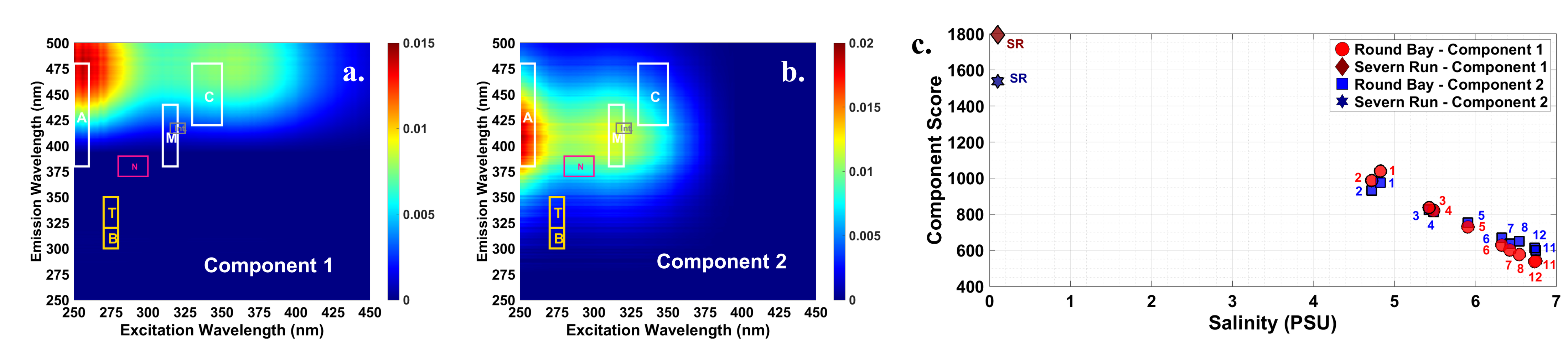

Figure 5. Results of PARAFAC model analysis of stacked EEMs plots showing: (**a**) loadings for Component 1 in the terrestrial humic region; (**b**) loadings for Component 2 in the terrestrial to marine humic region and; (**c**) weighted scores for Component 1 and 2 at Severn Run (SR) into Round Bay (sites 1-9, and 12) plotted against salinity.

- ***The surface waters of Round Bay exhibit some spatial 'patchiness' in fDOM values and CDOM concentrations, especially in the upper reaches near Severn Run***
- ***Analysis of CDOM absorption and EEMs intensities suggests rapid dilution of terrestrial CDOM along the salinity gradient that is largely limited to the upper reaches of Round Bay***

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