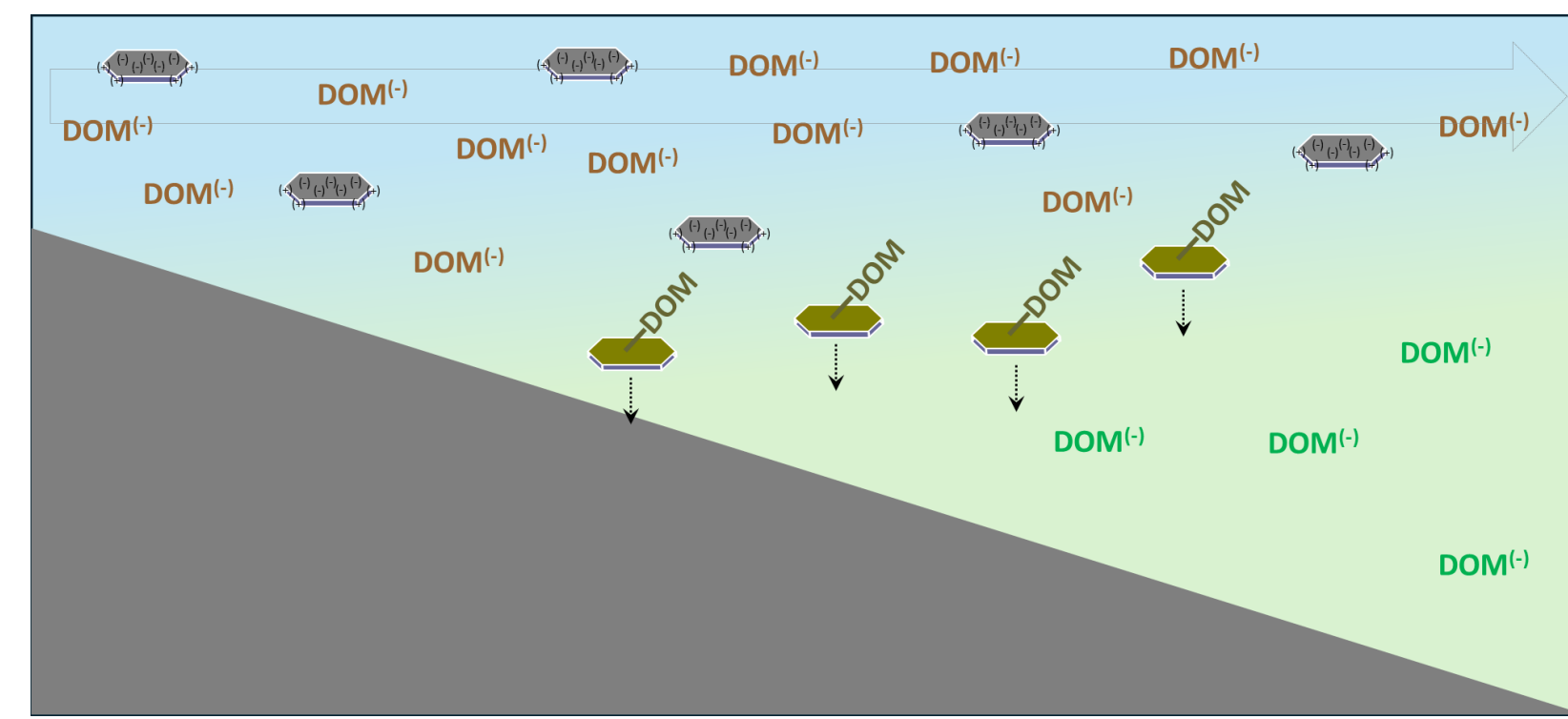


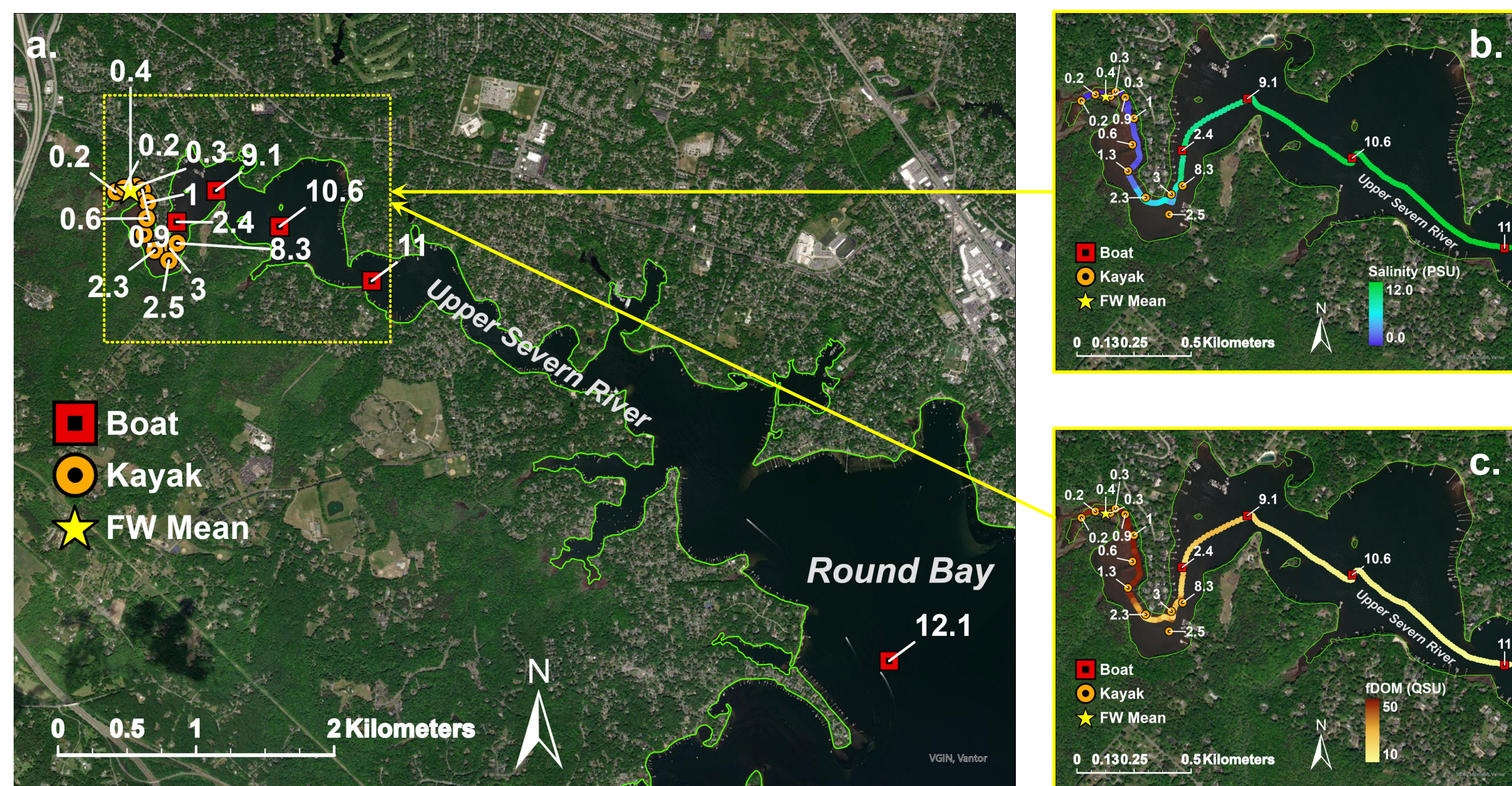
## Background and Objectives

The U.S. Naval Academy is sponsored by the U.S. Defense Threat Reduction Agency (DTRA) to conduct research to improve waterborne hazard mapping and tracking in shallow coastal systems. Salinity-induced flocculation is when increasing ionic strength promotes the aggregation of negatively charged dissolved organic matter (DOM) with other charged constituents to form larger flocs (Asmala et al., 2014). In this study, a conditional dissociation constant ( $K_d^*$ ) for clay (kaolinite) and DOM under increased ionic strength estimated by Daniel and Lambert (2026) was applied to predict the flocculation of natural OM in field observations along the salinity gradient of the upper Severn River, a micro-tidal estuary (Fig. 1).



**Figure 1.** Conceptual diagram for salinity-induced flocculation of between kaolinite and natural dissolved organic matter (DOM) along the salinity gradient of a microtidal-estuary.

## Study Area



**Figure 2.** (a) The Severn River is a micro-tidal estuary in the mesohaline Chesapeake Bay. The upper part of the estuary is narrow and shallow (depths < 1 – 6 m) and empties into a wide, deeper basin called Round Bay. The freshwater source to the Severn River is Severn Run, located at the head of the estuary. It is a small, groundwater-fed stream with low discharge (0.2 m<sup>3</sup>/s at baseflow conditions to >5 m<sup>3</sup>/s during pulsed, episodic high flow events). (b) The low freshwater discharge leads to a salinity gradient generally confined to the shallow reaches of the upper estuary. (c) Severn Run drains a ~ 104 km<sup>2</sup> forested sub-watershed resulting in significant inputs of terrestrial colored or fluorescent dissolved organic matter (fDOM) to the upper estuary. Locations for sample collection are shown and marked by salinity.

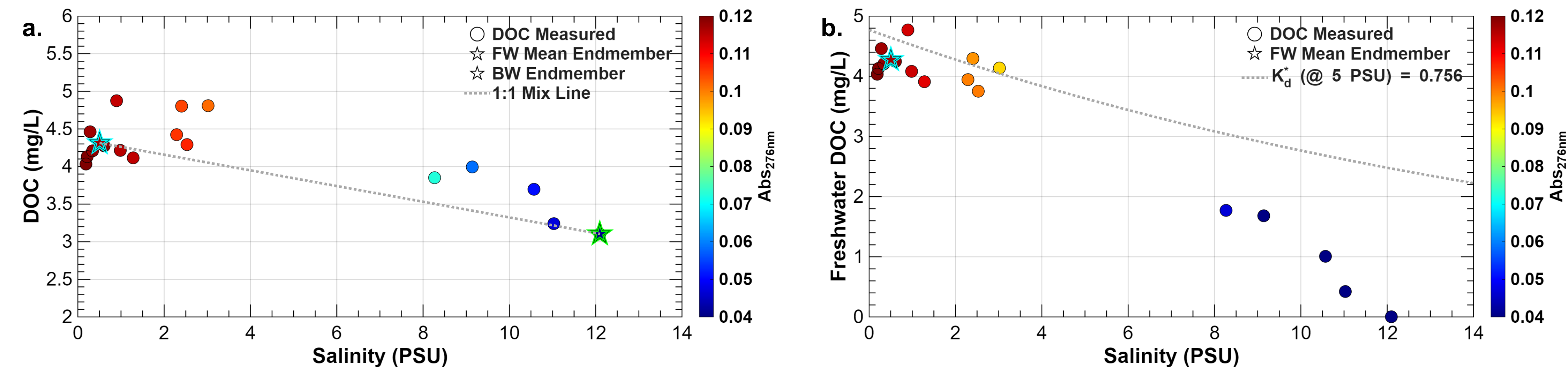
## Methods and Approach

On 16 March 2026, a field survey was conducted to investigate changes in the chemical and optical properties of surface waters (< 0.25 m) along the estuarine salinity gradient of the upper Severn River (Fig. 2a). Continuous measurements of temperature, salinity, and fluorescent dissolved organic matter (fDOM) were collected using a flow-through system equipped with a YSI EXO1 multi-parameter sonde ([www.ysi.com/exo1](http://www.ysi.com/exo1)) deployed off a small boat. In areas of the upper estuary too shallow for a boat, a YSI EXO 1 sonde was towed behind a kayak (Fig. 3). Discrete surface water samples were collected at intervals along the salinity gradient by dipping a pre-cleaned 500 mL or 1 L borosilicate glass Wheaton bottle off the side of the boat or kayak to a depth of ~ 0.2 m. After returning to the laboratory, waters were syringe-filtered (0.22 μm) into pre-baked 40 ml amber borosilicate vials for measurement of dissolved organic carbon (DOC) using a Shimadzu TOC-L Series Total Organic Carbon Analyzer ([www.ssi.shimadzu.com/products/total-organic-carbon-analysis/toc-analysis/toc-l-series/index.html](http://www.ssi.shimadzu.com/products/total-organic-carbon-analysis/toc-analysis/toc-l-series/index.html)). Absorbance (276 nm) and excitation emission matrix (EEMs) spectra were analyzed using a Horiba Aqualog spectrometer ([www.horiba.com/int/scientific/products/action/show/Product/aqualog-environmental-water-research-analyzer-3497/](http://www.horiba.com/int/scientific/products/action/show/Product/aqualog-environmental-water-research-analyzer-3497/)). Continuous measurement data collected from surface waters was pre-processed using MATLAB 2025, smoothed and plotted using ArcGIS Pro 3.5.1 to create contoured plots of salinity (Fig. 2b) and fDOM (Fig. 2c). Parallel Factor Analysis (PARAFAC) was used to organize EEMs into trilinear arrays in order to identify and model component (fluorophore) intensity variation in samples collected along the salinity gradient of the upper Severn River (Murphy et al., 2013). In this study, a 3-way, 3-component model was fit to the EEMs of samples. The drEEM toolbox ([www.dreem.openfluor.org/](http://www.dreem.openfluor.org/)) for MATLAB was used to perform PARAFAC analysis on the EEMs.

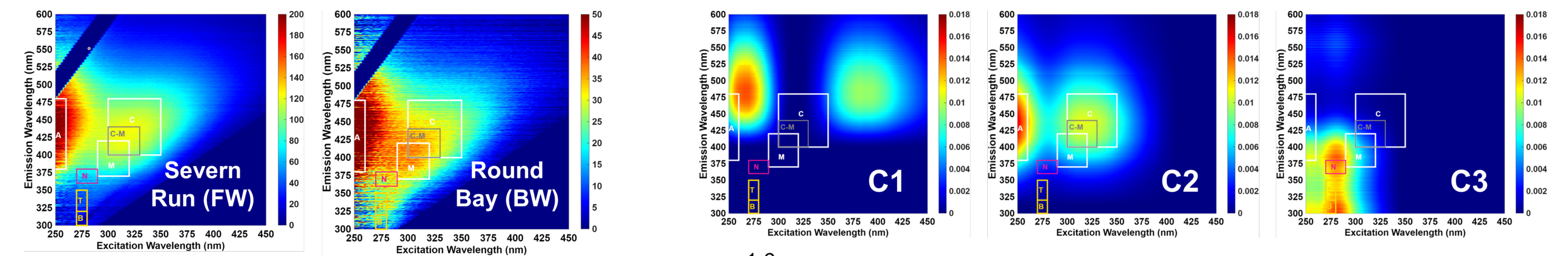


**Figure 3.** Midshipman I/C Alexis Lambert and Midshipman I/C Sofia Daniel collecting data and water samples in kayaks from the upper Severn River estuary on 16 March 2026.

## Results and Discussion

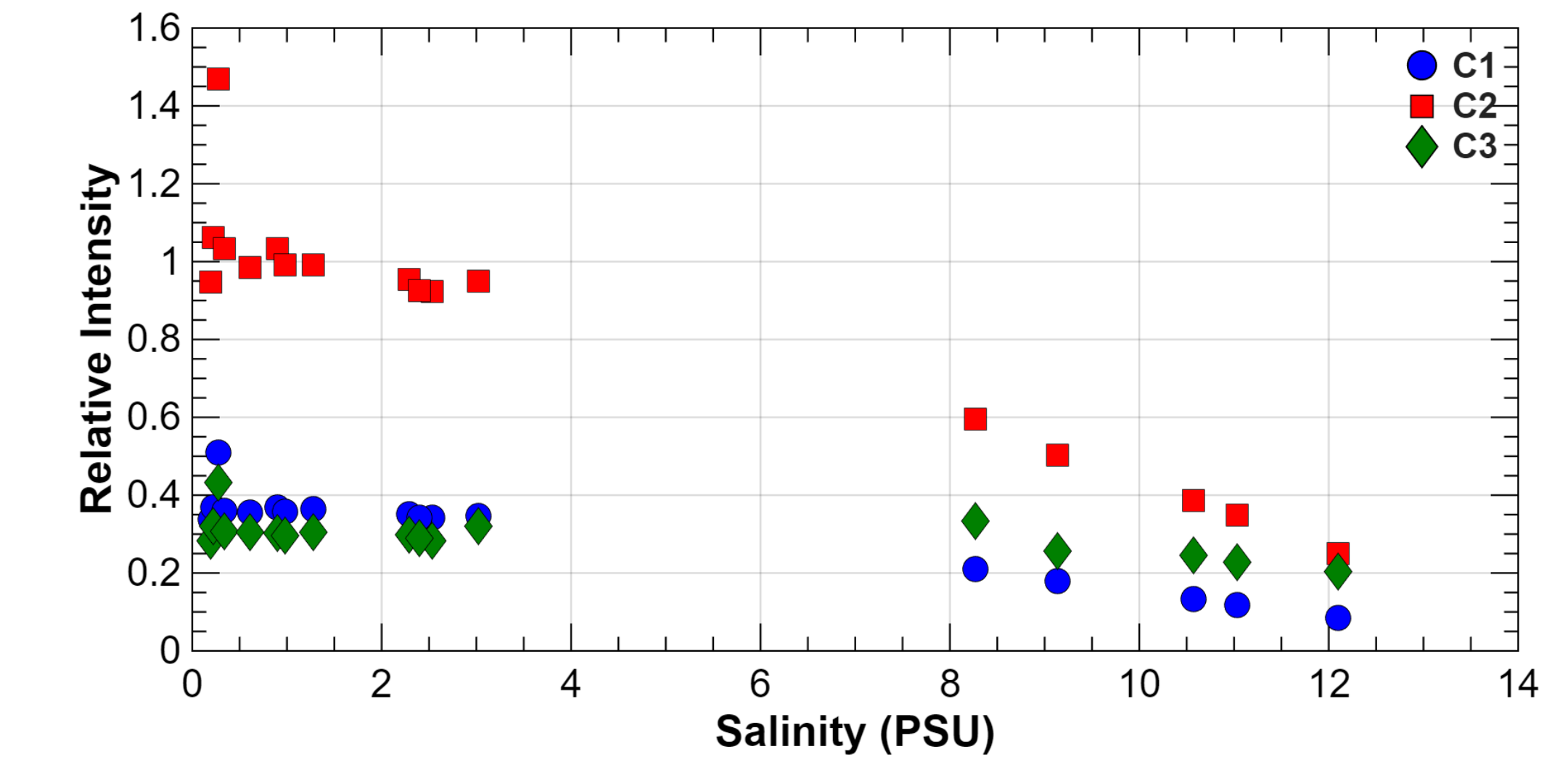


**Figure 4.** (a) DOC concentration (mg/L) contoured by relative absorbance at 276 nm ( $Abs_{276nm}$ ) vs. salinity (PSU) in samples collected from the upper Severn River. The gray dashed line represents a 1:1 mixing line between the mean freshwater (FW) end-member (cyan star) and the brackish water (BW) end-member in Round Bay (green star). (b) Freshwater DOC concentration (mg/L) adjusted for conservative mixing with brackish waters from Round Bay contoured by  $Abs_{276}$  vs. salinity. The fit line for a  $K_d^* = 0.756$  calculated by Daniel and Lambert (2026) at 5 PSU is shown for comparison (Jarmoskaite et al., 2020).



**Figure 5.** The fluorescent properties of the Severn Run freshwater (FW) end-member and the Round Bay brackish water (BW) end-member shown by excitation-emission matrices (EEMs). The contours represent units of (relative) fluorescent intensity. 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.

On 16 March 2026, DOC concentration decreased with increasing salinity in the upper Severn River (Fig 4a), as did  $Abs_{276nm}$  but DOC behaved non-conservatively with respect to salinity as evidenced by differences between observed values and the 1:1 mixing line between the mean freshwater (FW) end-member and the brackish water (BW) end-member. Assuming DOM in BW is charge neutral and not involved in flocculation in the upper estuary between 0-5 PSU (the salinity range for flocculation of DOM with clay particles like kaolinite (Sholkovitz, 1976)), the BW contribution to DOC can be removed leaving just reactive, FW-sourced DOC. Figure 4b shows corrected, FW-sourced DOC concentration and  $Abs_{276nm}$  vs. salinity. When compared to the fit line for a  $K_d^* = 0.756$  at 5 PSU calculated by Daniel and Lambert (2026) using laboratory organic matter with 20 mg/L kaolinite (a common clay), DOC concentration from 0-3 PSU generally behaves as predicted, indicating that significant salinity-induced flocculation of natural OM may be occurring. The lack of data between 3-8 PSU and low total suspended matter concentration (~ 6 mg/L) in the upper Severn River limits confidence in this result. Others have observed flocculation of terrestrial-sourced DOM at low salinities both in the laboratory and in the field (Asmala et al., 2014). In this study, the optical signatures of the FW and BW end-members as revealed by EEMs (Fig. 5) were similar and dominated by humics. PARAFAC was performed on sample EEMs to investigate what portion of the natural DOM pool might be involved in flocculation in the upper Severn River.



**Figure 6.** Component loadings (relative intensity) vs. salinity for a 3-component PARAFAC model run on EEMs for samples collected from the upper Severn River estuary. The EEMs spectrum for each component is shown above the plot. The highlighted regions of each component EEM shows CDOM component regions (Table 1, Boyd et al., 2010).

A 3-component PARAFAC model fit to EEMs from the upper Severn River explained 98% of the variance but with a core consistency of 65%. This suggests that the data is noisy or the 3-component model may be overfitting the data (Murphy et al., 2013). The C2 (humics) component had the highest relative intensity (Fig. 6). With the exception of a sample at 0.28 PSU, there was little variation in C2 or the C3, tryptophan, phenol-like protein component loading from 0-3 PSU which might be expected if significant flocculation of OM was occurring (Asmala et al., 2014).

## Conclusions and Future Work

- Field results are consistent with the  $K_d^*$  calculated for flocculation of OM with kaolinite in laboratory studies by Daniel and Lambert (2026)
- Continued research is required to further validate laboratory results under varying environmental conditions and suspended matter and OM loadings in microtidal systems like the upper Severn River and other estuarine systems before they can be applied to improve waterborne hazard mapping and tracking along the salinity gradient between freshwater and saltwater