Flocculation of Stream-Sourced, Natural Organic Matter Along an Estuarine Salinity Gradient

Midshipman First Class Kady Stigler, USN, Class of 2025

Advisor(s): Dr. Joseph P. Smith and Mr. Benjamin Hickman

Abstract

In this study, a series of field data collection surveys and laboratory experiments were conducted to investigate processes associated with salinity-induced flocculation of stream-sourced terrestrial dissolved organic matter in a micro-tidal estuary.

Study Area and Methods

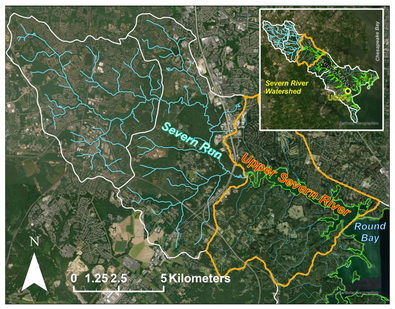

Figure 1. The Severn River estuary is a tidal tributary of the mesohaline Chesapeake Bay having a watershed area of ~ 350 km^2.The western, uppermost part of the estuary is narrow and shallow (depths < 1m – 6 m) and empties into the wider, deeper basin of Round Bay. Severn Run is a small, groundwater-fed stream draining a ~ 104 km^2 sub-watershed at the head of the upper estuary. Discharge through Severn Run ranges from 0.2 m^3/s at baseflow conditions to >5 m^3/s during pulsed, episodic high flow events following rainfall or snowmelt (*Murphy and Trevino, 2025*).

On 19 SEP 2024, high-resolution (1 Hz) measurements of the surface waters (~ 0.25 m) of the upper Severn River (**Fig. 1**) were collected along the estuarine salinity gradient (0 - 8 PSU) using a flow-through system deployed off a small boat (**Fig. 2a**). The system included a YSI EXO1 multi-parameter sonde (www.ysi.com/ exo1) to measure salinity, temperature, turbidity, and fluorescent dissolved organic matter (fDOM). In the shallow upper estuary, a YSI EXO 1 sonde was towed behind an inflatable kayak. Data was pre-processed using MATLAB 2023b, smoothed using inverse distance weighting, and plotted using ArcGIS Pro 3.0.3. Discrete surface water samples were collected along the salinity gradient using a 3.2 L Van-Dorn bottle. Waters were syringe-filtered (0.22 µm) in the field into 40 ml amber borosilicate vials for measurement of dissolved organic carbon (DOC) and absorbance (250-600 nm). Additional water was collected in 1L Wheaton bottles for measurement of turbidity and total suspended matter (TSM). On 20 SEP 2024, waters were collected from Severn Run (**Fig. 2b**) using these same methods along with measurement of discharge using a YSI SonTek FlowTracker2 handheld Acoustic Doppler Velocimeter (**Fig. 2c**; www.ysi.com/flowtracker2). A series of laboratory experiments to investigate salinity-induced flocculation were conducted using methods modified from *Asmala et al.* (2014). On 24 OCT, 06 NOV, and 03 DEC 2024, waters were collected from Severn Run in pre-baked 1L Wheaton bottles or in a clean 20 L glass carboy. Bulk (unfiltered) waters were used for the 24 OCT experiment whereas filtered (0.7 µm GF/F) water was used in the 06 NOV and 03 DEC experiments. The river samples were then spiked with a stock solution of artificial seawater (Instant Ocean) to salinities from ~ 0 PSU - 7 PSU plus a blank. Bottles were kept on a magnetic stir-plate at room temperature in the dark for 24 hours. After 24 hours, waters from each bottle were vacuum-filtered using a PALL magnetic filter tower through a pre-combusted, pre-weighed, 0.7 µm GF/F. Filtrate was then tested for DOC, TSM, turbidity, and total absorbance (Total-a; < 0.22 µm)). Analysis of DOC was performed 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), absorbance (250-600 nm) was measured using a Horiba Aqualog spectrometer (https://www.horiba.com/int/scientific/products/ fluorescence-spectrometers/the-aqualog/), and turbidity was measured using a Hach TU5200 Laboratory Laser Turbidimeter (www.hach.com/p-tu5200-benchtoplaser-turbidimeter/LPV442.99.01012). Spectral slope ratio (Sr) was determined from Total-a using methods described in *Helms et al.* (2008). Gravimetric analysis was used to determine TSM after vacuum filtration through pre-baked 0.7 µm GF/Fs (**Fig. 2d**).

Figure 2. (**a.**) Midshipman 1/C Kady Stigler collecting data in the upper Severn River; (**b.**) collecting waters from Severn Run; (**c.**) measuring discharge in Severn Run; (**d.**) and performing filtrations.

Field Data Collection – 19 September 2024

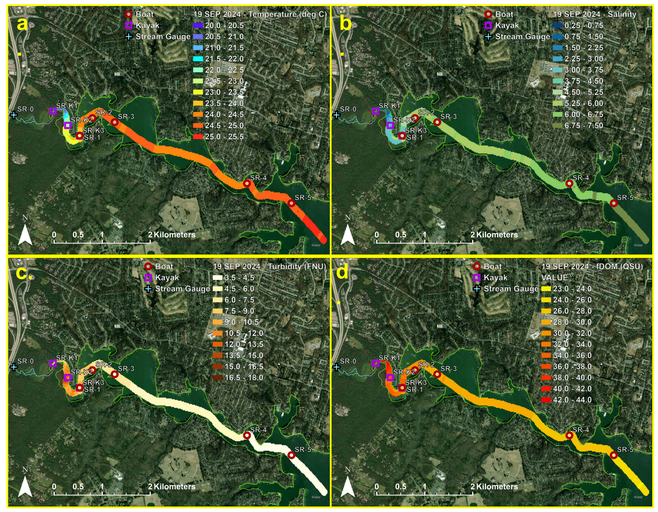

Figure 3. Contoured (**a.**) Temperature (°C); (**b.**) Salinity (PSU); (**c.**) Turbidity (FNU); and (**d.**) fDOM in the upper Severn River estuary (**Fig. 1**) on 19 SEP 2024. The SR-0 indicates the Severn Run gauging and sampling site. Locations for discrete sample collection are shown as purple (kayak) or red (boat) circles and labeled by site name. On 19 SEP 2024, Severn Run discharge on 19 SEP 2024 was at baseflow at ~0.2 m^3/s.

On 19 SEP 2024, surface waters in the upper Severn River increased down-estuary from Severn Run from 20 °C to 25 °C (**Fig. 3a**). Salinity quickly increased down estuary from near freshwater values (0.2 PSU) to over 6 PSU (**Fig. 3b**). Turbidity was at its highest (~18 FNU) near the mouth of Severn Run and was otherwise low (< 6 FNU) down estuary (**Fig. 3c**). Similarly, fDOM was high (> 42 QSU) near Severn Run and lower down estuary (**Fig. 3d**). Analysis of discrete samples vs. salinity showed a distinct increase in both TSM and turbidity (**Fig. 4a&b**), a slight decrease in DOC concentration (**Fig. 4c**), and a drop in Total-a and Sr (**Fig. 4d**) at 3 - 4 PSU.

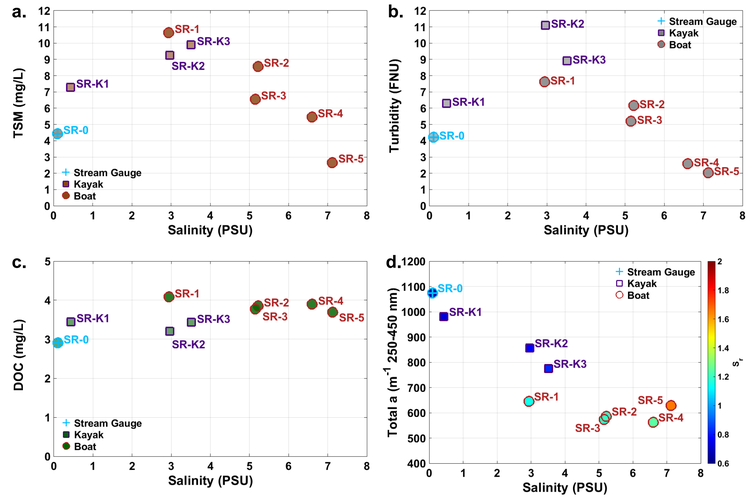

Figure 4. Plots of (**a.**) TSM (mg/L) (°C); (**b.**) Turbidity (NTU) (**c.**) DOC (mg/L); and (**d.**) Total-a (m-1 from 250 – 450 nm) contoured by Sr vs. Salinity (PSU) in discrete samples collected from the upper Severn River on 19 SEP 2024 and Severn Run on 20 SEP 2024 (**Fig. 3**). Samples collected by boat are plotted as circles and samples collected by kayak are plotted as squares. Samples indicated as '+" were collected from Severn Run.

Laboratory Experiments

A series of controlled experiments were conducted to investigate how increasing salinity from 0-5 PSU may induce flocculation of stream-sourced constituents and alter the properties of surface waters in the upper Severn River estuary. A 24-hour incubation of unfiltered waters collected from Severn Run on 24 OCT 2024 showed a distinct peak in both TSM concentration and turbidity from 2-3 PSU(**Fig. 5a&b**). There was an increase in DOC from 0 – 1 PSU followed by a slight decrease in DOC (**Fig. 5c**) at 3 PSU. Total-a increased from 0 – 1 PSU, then decreased gradually with increasing salinity while Sr decreased slightly from 0 - 3 PSU before increasing again (**Fig. 5d**). Incubations of pre-filtered water showed similar trends. In experiments on 06 NOV and 03 DEC 2024, TSM and turbidity increased from 1 – 3 PSU (**Fig. 5a&b**). Changes in DOC concentrations in pre-filtered waters was less clear but decreases in DOC concentration was found between 2 - 5 PSU (**Fig. 5c**). Total-a was not measured in experiments using water collected 06 NOV 2024, but in unfiltered water from 03 DEC 2024 there was a sharp decrease in Total-a as salinity increased from 0 - 1 PSU. Total-a then decreased with increasing salinity. Spectral slope (Sr) increased as salinity increased from 0 to1 PSU, but then decreased thereafter (**Fig. 5d**).

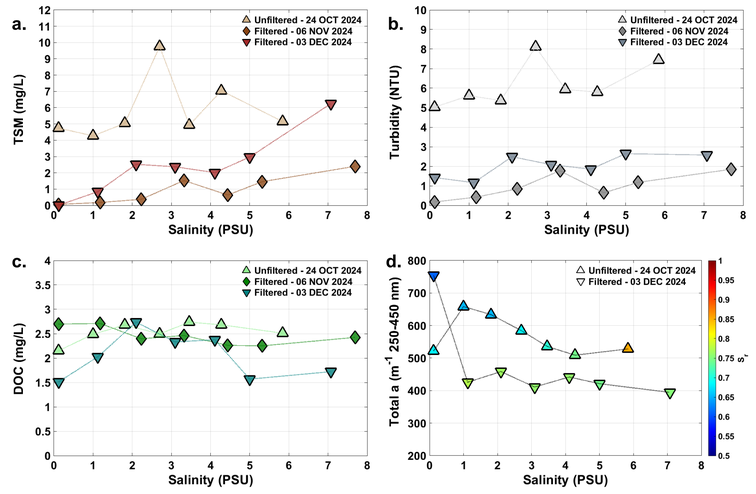

Figure 5. Plots of (**a.**) TSM (mg/L) (°C); (**b.**) Turbidity (NTU) (**c.**) DOC (mg/L); and (**d.**) Total-a (m-1 from 250 – 450 nm) contoured by Sr vs. Salinity (PSU) after 24-hour incubation of Severn Run waters spiked with Instant Ocean to create different salinities from 0-8 PSU. The experiment of 24 OCT 2024 was conducted using unfiltered water and the 06 NOV and 03 DEC 2024 experiments were conducted using filtered (0.7 µm) water.

Discussion

As freshwater mixes with higher salinity water, increasing ionic strength induces the flocculation of dissolved organic matter (DOM) and inorganic matter as fine-particles; this specifically occurs in the range of 0-5 PSU (*Sholkovitz, 1976*). Flocculation can alter the chemical and optical properties of waters entering an estuary by transferring dissolved constituents into the colloidal and particulate phases (*Virtasalo et al., 2023*), thereby increasing particle size and settling rates (*Abolfazli and Strom, 2023*), and altering DOM composition (*Asmala et al, 2014*). Field results from 19 SEP 2024 showa peak in TSM and turbidity and a dip in DOC concentration at 3 PSU and an increase in Sr and deceases in fDOM, turbidity, and Total-a from 3 - 6 PSU all which are consistent with salinity-induced flocculation occurring as Severn Run water mixes with the more saline upper Severn River water (**Fig. 3&4**). Experimental results support this, especially with unfiltered waters collected on 24 OCT 2024 (**Fig 5**). It is noteworthy that flow in the Severn Run was near baseflow between 19 SEP 2024 and 24 OCT 2024, with very low TSM (< 5 mg/L) and DOC concentrations (< 3 mg/L). This complicated the experimental results because there was a low-mass of dissolved OM and fine-grained inorganic particles available to interact and aggregate. Similarly, DOC concentrations were low (< 3.5 mg/L) on 06 NOV and 03 DEC 2024. Yet the general changes in TSM, DOC, and turbidity observed with increasing salinity supports that dissolved OM was aggregating to form colloids and larger particles as the salinity gradient increased from 0-5 PSU in the upper Severn River. The decrease in Total-a and increase in Sr suggest a shift in the OM pool, resulting in a change in the optical properties of the waters (*Helms et al., 2008*). To better understand the impact of flocculation, additional studies should be conducted under higher flow (stirring) regimes with increased TSM and DOC fluxes (*Bhattacharya and Osburn*, *2021*) and should include measurement of particle/floc size.

Conclusions

- ***Salinity induced-flocculation occurs between 0-5 PSU during mixing of Severn Run waters with the upper Severn River, altering chemical and optical properties***
- ***To better understand flocculation processes and the potential impact on the physiochemical and optical properties of surface waters, follow-up studies should be conducted under higher freshwater flow regimes and with higher TSM and DOC fluxes and should include measurement of particle/floc size***

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References: Sholkovitz (1976). *Geochim. Cosmochim. Acta* 40(7); Helms et al. (2008), *Limnol. Oceangr.* 53(3); Asmala et al. (2014). *J. Geophys. Res. Biogeosci.*: 119; Bhattacharya and Osburn,)2021). *Sci. Tot. Env.*: 760; Abolfazli and Strom (2023). *JGR Oceans*: 128; Virtasalo et al. (2023). *Biogeosci.*: 20; Murphy and Trevino (2025). USNA Capstone.