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Maximizing the Recovery of Dissolved Organic Matter from Saltwater Samples with Coupled ED and PPL Resin

Luke R. Chambers[1], Aron Stubbins[2], Ellery Ingall[1]
1Georgia Institute of Technology, Atlanta, GA 2Skidaway Institute of Oceanography, Savannah, GA

Abstract/Introduction

The Georgia coast is continually experiencing anthropogenic modifications. Dredging, shipping, and construction alters water and sediment properties which, in turn, influences cycles of nutrients key to biological production. A significant fraction of the nutrients in Georgia's coastal waters are associated with dissolved organic matter (DOM). Chemically characterizing the DOM is a first step to understanding how human influences change the nutrient cycling associated with DOM off the Georgia coast. Unfortunately, the lack of effective techniques to fully isolate DOM from natural samples with high salt concentrations have, thus far, hampered DOM characterization. Two techniques for DOM recovery were evaluated, electrodialysis (ED) and Bond Elut PPL exchange resin. Samples were collected near Savannah Georgia off the main dock of the Skidaway Institute of Oceanography at approximately one hour after high tide. The conductivity of the samples range from ~38 mS to ~47 mS. For ED studies a table-top system was constructed and optimized for the extraction of DOM from small volume (2 to 10 L) saltwater samples. With this system an average of 71.3% of the DOM present in saltwater samples is recovered. Processing samples with PPL resin recovered 38.1% of the DOM. Combing the PPL and ED techniques resulted in a recovery of 76.7% of the DOM. This combined recovery represents a major advancement relative to previously used DOM recovery methods such as tangential flow ultrafiltration or XAD resins which obtains DOM recoveries typically under 30%.

Most chemical and spectral characterizations of DOM in seawater are confounded by the high inorganic salt concentrations (~35g/L) and comparatively low DOM concentrations (~0.5-mg/L). Therefore, DOM must be concentrated and isolated before detailed characterizations can proceed. Over the past few decades many technologies have been developed to concentrate DOM from marine samples, each with their biases. Here two of the most efficient techniques were tested and combined.

Bond Elut PPL exchange resin

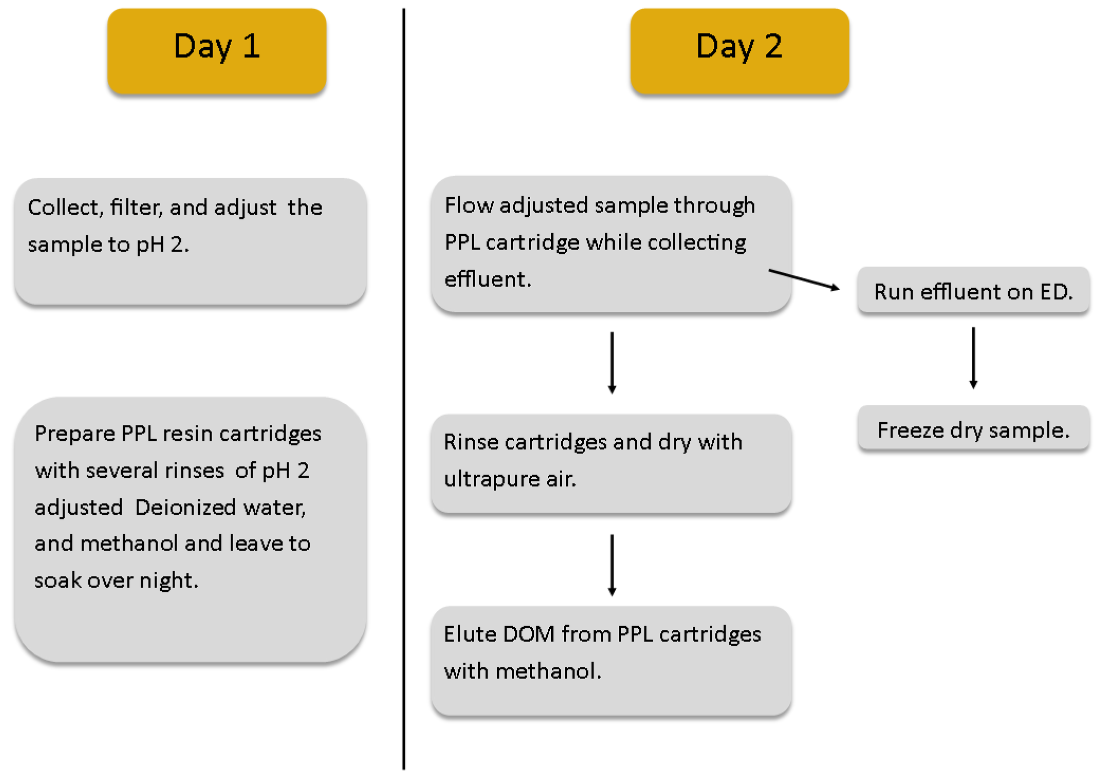

FIGURE 1: Procedure to isolate DOM from seawater using PPL.

- Samples were collected and filtered at the main dock of the Skidaway Institute of Oceanography approximately one hour after high tide.
- DOM was extracted using PPL according to the above diagram.
- To monitor DOM recovery during sample processing concentrations of dissolved organic carbon (DOC) as non-purgeable organic carbon (NPOC) and total dissolved nitrogen (TN), were determined using Shimadzu High Temperature Catalytic total organic carbon (TOC) analyzer.

Electrodialysis (ED)

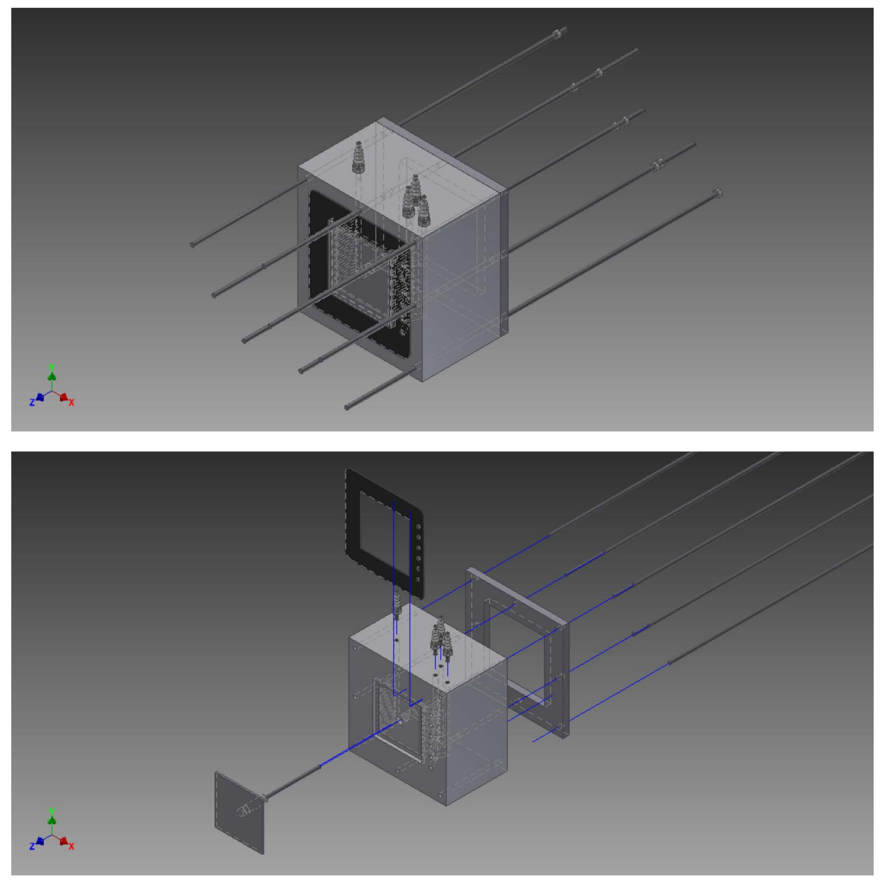

FIGURE 2: Computer drafted design of ED end blocks.

- 10 pairs of alternating cation (CMX) and anion membranes (AMX) are stacked between two end blocks.
- The membranes are separated by flexible turbulence promoting spacers which separate the concentrate and diluate (sample) channels.
- The respective end blocks house a cathode and anode which supplies an electrical potential across the stack.
- The electrical potential pulls anions and cations through the respective membranes, out of the sample channel, and into the "concentrate" channel where they are flushed out.
- Organic molecules are retained during the process in the sample channel.
- Note the separate alternating sample and concentrate channels.
- A sodium sulfate solution washes over the electrodes in separate channels in the end blocks.

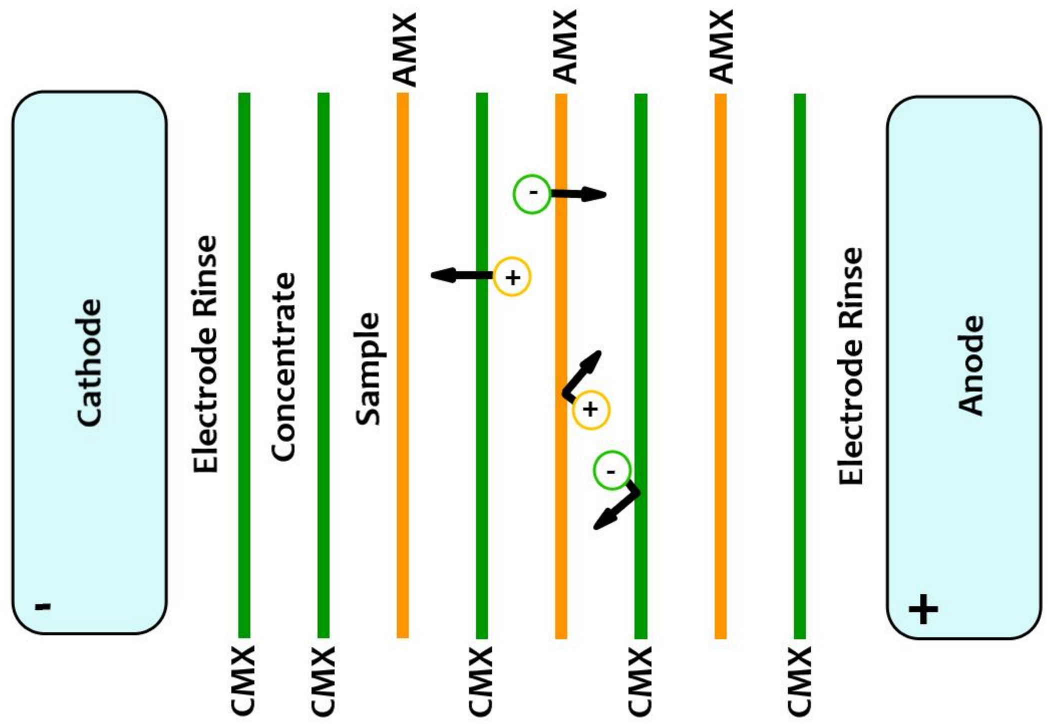

FIGURE 3: Diagram showing how ions would pass through exchange membranes.

Combining PPL and ED

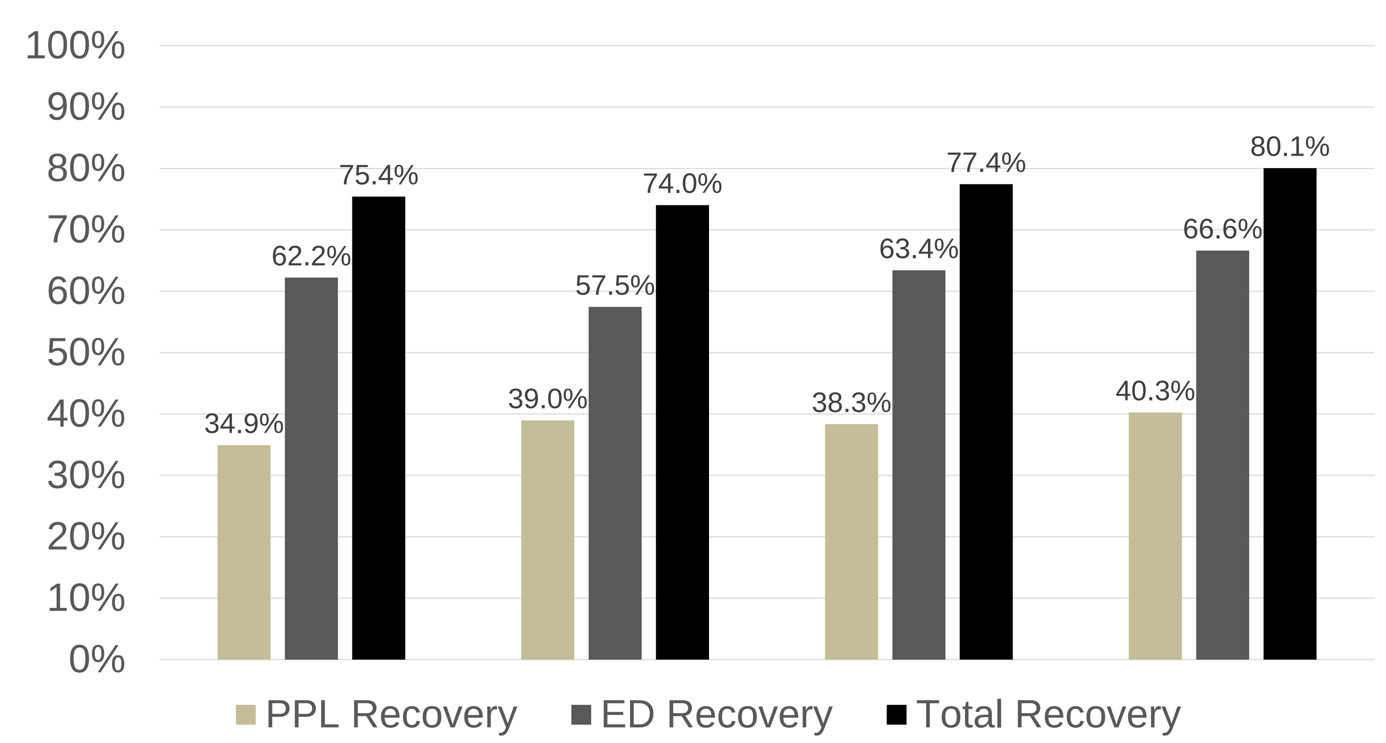

FIGURE 4: Replicate results of total DOM extractions for seawater samples using combined ED and PPL.

Biases

- Early experiments with standard compounds found a bias against small charged molecules.

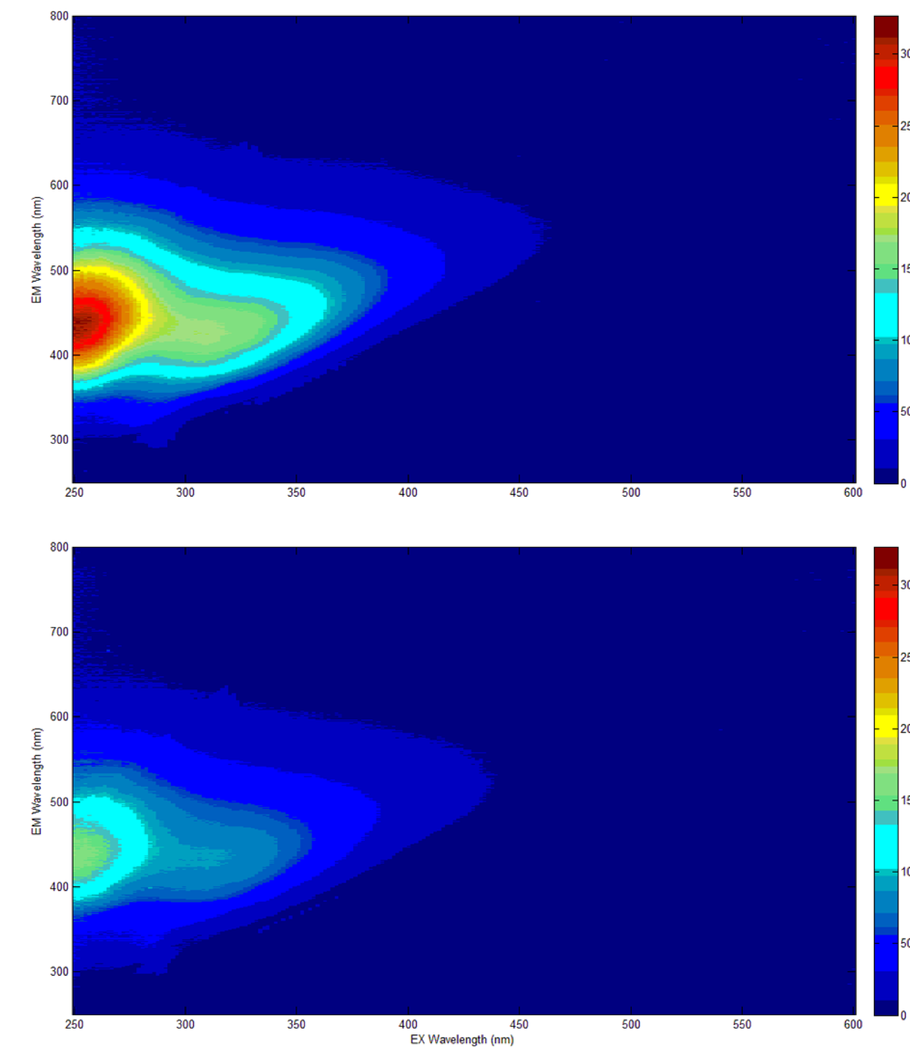

FIGURE : Average initial and final fluorescence excitation-emission matrix (EEM) for marine samples processed on ED.

- Peaks in EEM between 400-500 EM and 250-275 EX generally represent humic like DOM in the UV spectrum.
- Peaks in EEM between 400-450 EM and 300-400 EX generally represent humic like DOM in the visible spectrum.
- Noting the similar shapes and overall constant decrease in the intensity between the initial and final EEMs suggests a lack of bias in the fluorescent DOM species present in the marine sample.

TABLE 1: Initial and final C-N ratios for ED. (Dark Grey PPL & ED Processed)

Date	NPOC Recovery	Total Nitrogen Recovery	C/N Initial	C/N Final
9/26/2014	67.21%	39.92%	11.70	19.70
9/24/2014	75.92%	48.57%	11.39	17.81
9/22/2014	67.52%	42.90%	11.32	17.81
9/16/2014	64.20%	51.46%	12.90	16.10
9/12/2014	75.74%	53.99%	13.15	18.45
9/10/2014	77.32%	57.73%	13.18	17.66
9/5/2014	76.10%	61.64%	15.35	18.95
12/7/2014	65.47%	50.95%	25.29	32.50
12/3/2014	73.82%	56.87%	16.31	21.17
11/30/2014	73.87%	58.29%	14.97	18.97
11/24/2014	64.95%	49.97%	14.71	19.11
12/10/2014 (R1)	66.63%	37.79%	15.65	27.59
12/10/2014 (R2)	63.41%	40.88%	13.34	20.70
11/28/2014	57.45%	27.32%	15.65	32.91
11/26/2014	62.23%	34.95%	11.62	20.69

- Initial and final C/N ratios were calculated by dividing NPOC concentrations by the TN concentrations.
- Differences in the initial and final C/N ratios could occur due to the expected removal of inorganic nitrogen during the ED process.

Conclusion

- While biases against small charged particles were noticed with the ED system when processing standard compounds, natural saltwater samples show less biases.
- ED and PPL isolation techniques recover more DOM than their predecessors.
- Coupling PPL with ED increases the isolated DOM when compared to processing individually.
- On average 76.7% of DOM can be isolated when coupling PPL and ED.
- Isolating DOM can allow for a more complete understanding of marine nutrient cycling and help find accurate benchmarks for coastal areas.