# Multi-angle laser light scattering data of colloidal matter in field samples from the outer reaches of the Damariscotta River Estuary, Maine collected between October of 2017 and July of 2018.

**Website**: https://www.bco-dmo.org/dataset/811924
**Data Type**: Other Field Results
**Version**: 1
**Version Date**: 2020-05-19

**Project**
» Collaborative Proposal: Assessment of the Colloidal Iron Size Spectrum in Coastal and Oceanic Waters (Colloidal Metals)


| Contributors | Affiliation | Role |
|---|---|---|
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## Coverage

**Spatial Extent**: **N**:43.865 **E**:-69.577 **S**:43.761 **W**:-69.577
**Temporal Extent**: 2017-10-27 - 2018-07-08

## Dataset Description

These files contain the raw multi-angle laser light scattering data of colloidal matter in all of the project field samples in the outer reaches of the Damariscotta River Estuary on the mid-coast region of Maine collected between October of 2017 and July of 2018.

### Methods & Sampling

Methodology:
Flow field-flow fractionation (FlFFF) is a chromatography-like elution technique based on hydrodynamic principles, where colloid particles are separated due to their interaction with a cross-flow carrier liquid, applied over the cross section of a ribbon-like channel that is thin (~250 µm) and flat (~centimeter length). Here, the carrier solution was artificial seawater (ASW) that mimics the matrix of the sample solutions, such that the sample remains unaltered by the FlFFF processing. The ASW was first run through a column of Chelex resin (to remove metals) and then ultrafiltered (at 5 kDa nominal pore size, to remove any resin released during cleaning). This study is the first to use ASW as the carrier solution while coupling FlFFF to ICPMS, since previous studies worked only with lower salinity samples where 15 mmol L−1 NH4NO3 buffer (pH 7) was used as the carrier for freshwater and 55 mmol L-1 NH4Cl(aq) (pH 8) was used in saltier (estuarine) water to

resemble ~10% of sweater concentration to not clog the ICPMS cones.

The bottom wall of the FlFFF channel has a permeable (10 kDa) ultrafiltration membrane where the cross flow and soluble-sized material pass through to waste so that only the colloidal sized particles are retained within the channel. Two flows govern the FlFFF size exclusion chromatography elution: the (parabolic) sample flow and the cross flow. The sample in the ASW carrier solution flows tangentially to the ultrafiltration membrane, and a parabolic flow profile is created by a function of the thin, ribbon-like channel, as the walls drag the flow on the top and the bottom of the channel, producing a faster laminar flow in the center of the channel. The cross flow through the membrane creates an opposing diffusion force, where smaller compounds with higher diffusivities can diffuse against the cross-flow better and thus remain in the center of the chamber, while larger colloids remain lower towards the wall of the parabolic flow profile. The unequal velocities in laminar flow created by the parabolic flow profile down-channel, with constant Brownian motion based on diffusion, effectively separates the colloids in a 20 mL sample by producing a gradient of different size fractions (~eighteen 1.5 mL aliquots) that elute through the channel, with the smaller colloids eluting earlier than the larger colloids. Based on the diffusion coefficients of the separately eluted colloid size fractions, the hydrodynamic diameter, e.g. the diameter of a compact sphere, can be calculated using Stokes Law.

Sampling and analytical procedures:

The procedure for FlFFF includes three steps: sample loading and preconcentration, relaxation or focusing, and elution or colloid separation (Lyvén et al., 1997; Baalousha et al., 2011). The AF-2000 FlFFF instrument that was employed in this project has been modified to allow large volumes (in our case 20 mL) of ultrafiltered seawater to be back-loaded into the channel, where the accumulating colloids are focused at the head of the channel (into ~70-140 µL) during the first 50 minutes of run time. This small volume allows most colloids to start down the channel at the same time, which minimizes the issue of “blurring” of the size partitioning. We had some concern that the 286x pre-concentration at the channel head would allow a change in colloidal size and shape distribution during pre-concentration, though others have found that focusing even larger volumes of up to 500 ml does not appreciably alter the size distribution of organic colloids (Floge and Wells, 2007).

Next during the relaxation stage, the sample no longer experiences a large carrier focusing force pushing it up to the head of the channel. Then, the colloids balance the forces of Brownian diffusion and crossflow velocity, resulting in the separation of colloids along the membrane. This process of separation also occurs during preconcentration but is allowed to continue after for a short period after sample focusing but before the channel flow starts. The third phase, elution, begins when the channel flow pumps the carrier solution from the head of the channel, pushing the separated colloids through so that they elute out of the end of the channel. This channel outflow then passes through both the UVvis absorbance detector and the MALLS detectors online before being fraction collected into ~eighteen 1.5 mL aliquots. Each 1.5 mL fraction was acidified to pH 2 using Optima-grade hydrochloric acid (to 0.012 M HCl) in order to mitigate metal adsorption onto vial walls.

Prior to running each sample through the FlFFF, a daily FlFFF procedural blank was run through the system using the chelexed and ultrafiltered artificial seawater as the carrier and ultrapure water (18.2 MΩ-cm Milli-Q, MQ, Millipore) as the sample. The entire FlFFF run takes ~100 minutes with the channel outflow rate totaling 0.5 mL/min.

In addition, time was minimized between sample collection and FlFFF processing (<3 hours) to limit the potential bottle effects of storage, such as colloid sorption to bottle walls and colloidal instability (Fitzsimmons and Boyle, 2012). However, it has also been found that bottle storage for as long as 24 hours has minimal effects on colloid size distribution and that freezing does not affect the integrity of the organic colloidal size spectrum (Floge and Wells, 2007; Wells and Goldberg, 1994). Therefore, we minimized storage time and directly evaluated the effect of freezing (-20˚C) on the colloidal size distribution in fresh-frozen comparison tests on the same sample (see below).

Before each new sample run, the entire FlFFF-UVvis-MALLs system experienced a cleaning procedure of ~20 minutes each of flushing with 5% methanol (to wash out the trapped organics) and then MQ, and then dilute acid (trace metal grade 0.1M HCl) was loaded into the system and left overnight before final flushing with MQ until the pH was >6 and the MALLS detector angles read <1.5 for the scattering intensity values. Finally, the chelexed and ultrafiltered ASW was flushed through the system to prime it for the sample.

Matlab codes were written to 1) import the raw PostNova UV and MALLS data, and 2) process these data to generate colloidal size outputs. The importation code is run first and then the processing code. See Supplemental Documents for example m-files.

**Data Processing Description**

Matlab codes were written to 1) import the raw PostNova UV and MALLS data, and 2) process these data to generate colloidal size outputs. The importation code is run first and then the processing code.

BCO-DMO Data Manager Processing Notes:
* [Data files described here will be publicly accessible after the dataset restriction date has passed]
* Supplemental cruise sample table originally submitted as Excel file "Cruise Samples.xlsx" modified to combine two subtables separated by sampling season. Column Sampling_Season added. Exported as .csv and attached as a "Data File."
* Matlab m-file scripts submitted in word docuements "Matlab code - Import MALLS Blank.docx" and "Matlab code - Import MALLS Sample.docx" saved as import_MALLS_blank.m and import_MALLS_sample.m respectively.
* Zip file with MALLS data files added as a "Data File"

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## Related Publications

Baalousha, M., Stolpe, B., & Lead, J. R. (2011). Flow field-flow fractionation for the analysis and characterization of natural colloids and manufactured nanoparticles in environmental systems: A critical review. Journal of Chromatography A, 1218(27), 4078–4103. doi:10.1016/j.chroma.2011.04.063
*Methods*

Floge, S. A., & Wells, M. L. (2007). Variation in colloidal chromophoric dissolved organic matter in the Damariscotta Estuary, Maine. Limnology and Oceanography, 52(1), 32–45. doi:10.4319/lo.2007.52.1.0032
*Methods*

Lyvén, B., Hassellöv, M., Haraldsson, C., & Turner, D. R. (1997). Optimisation of on-channel preconcentration in flow field-flow fractionation for the determination of size distributions of low molecular weight colloidal material in natural waters. Analytica Chimica Acta, 357(3), 187–196. doi:10.1016/s0003-2670(97)00565-5 https://doi.org/10.1016/S0003-2670(97)00565-5
*Methods*

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## Parameters

*Parameters for this dataset have not yet been identified*

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## Instruments

| | |
|---|---|
| **Dataset-specific Instrument Name** | PostNova Flow Field Flow Fractionation Instrument |
| **Generic Instrument Name** | unknown |
| **Dataset-specific Description** | PostNova Flow Field Flow Fractionation Instrument equipped with UV detection and coupled to a PostNova Multi-Angle Laser Light Scattering (MALLS) detector, with collection at angles 35°, 50°, 75°, 90°, 105°, 130°, and 145°. |
| **Generic Instrument Description** | No relevant match in BCO-DMO instrument vocabulary. |

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## Project Information

**Collaborative Proposal: Assessment of the Colloidal Iron Size Spectrum in Coastal and Oceanic Waters (Colloidal Metals)**

**Coverage**: Coastal Maine

NSF abstract:

Bioavailable iron is arguably the most important nutrient for shaping the distribution and composition of marine primary productivity and, in turn, the magnitude of ocean carbon export. Iron exists in many phases throughout the world's oceans, and colloidal, or non-soluble, phases comprise a significant fraction of dissolved iron. However, the size and physical/chemical character of these phases is presently poorly understood. To better understand this key part of iron cycling, researchers will use new analytical chemistry methods to quantitatively separate the colloidal iron sizes present in a sample and measure the composition of these colloidal portions in shelf and oceanic waters. Results from this study will help hone future studies to better link the source and fate of iron in the marine environment. A postdoctoral researcher will serve as a principal investigator on the project, providing a unique professional development opportunity. In addition, the project will support the education and research training of one undergraduate student each year, and the researchers will conduct outreach activities to K-12 students and teachers.

The colloidal phase of iron may serve as a biological source of stored iron, a primary conveyance for stripping iron into sinking particulate matter (removing it from the pelagic biosphere), or, more likely, a dynamic balance of these roles that fluctuates with the source and character of iron input. The current methods to investigate marine colloidal matter involve operationally defining the bulk colloidal phase using single cutoff filters, a practical decision based on little or no evidence. More problematic, these methods homogenize the colloidal phase, obscuring what almost certainly is a reactivity spectrum of colloidal species tied to their size and compositional character. In this study, the researchers will use Flow Field-Flow Fractionation coupled to Multi-Angle Laser Light Scattering to make measurements of the uniformity or uniqueness of the colloidal size spectrum, and the physical/chemical character of these phases. The findings will have broad implications to the fields of marine ecology and biogeochemistry and, ultimately, to modeling studies of ocean-atmospheric coupling and climate change.

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## Funding

| Funding Source | Award |
|---|---|
| NSF Division of Ocean Sciences (NSF OCE) | OCE-1435021 |
| NSF Division of Ocean Sciences (NSF OCE) | OCE-1558722 |
| NSF Division of Ocean Sciences (NSF OCE) | OCE-1435008 |

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