Contrasting Effects of Marine and Terrestrial Dissolved Organic Matter on Mercury Cycling and Bioavailability

Amina Schartup[1], Udonna Ndu[2], Prentiss Balcom[2,3], Robert Mason[2], Elsie Sunderland[1,3]

1. Harvard University, TH Chan SPH. 2. University of Connecticut, Marine Sciences Department . 4. Harvard University, SEAS.

HARVARD School of Engineering and Applied Sciences

Summary

- **Quality of dissolved organic matter (DOM) changed across the salinity gradient**
- **Higher fractions of dissolved gaseous mercury (DGM) were found in waters with high marine DOM content**
- **Methylmercury (MeHg) in plankton increased linearly with decreasing terrestrial DOM fraction**
- **DOM composition is a critical driver of mercury (Hg) reactivity and bioavailability**

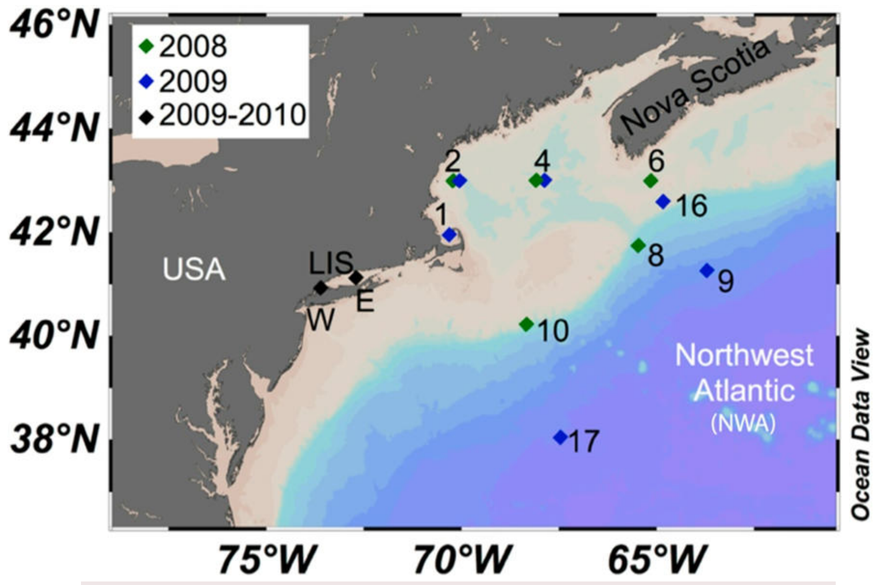

Figure 1: Map of sampling locations

Abstract

Methylmercury is the only species of Hg to biomagnify in aquatic food-webs to levels that are a widespread concern for human and ecological health. Here we investigate the association between DOM in seawater and Hg speciation and uptake using experimental data and field measurements from Long Island Sound (LIS) and the Northwestern Atlantic continental margin (NWA). We measured differences in DOM composition across sampling stations using excitation emission matrix (EEM) fluorescence spectroscopy and further separated DOM into terrestrial and marine components using Parallel Factor Analysis (PARAFAC). Highest MeHg concentrations were found in the estuarine stations (LIS) with highest DOM concentrations due to enhanced external inputs from the watershed and rivers. For stations on the shelf and slope, MeHg in plankton increased linearly with a decreasing fraction of fluorescence attributable to DOM components with a terrestrial rather than marine origin. These results are corroborated by experimental data showing higher MeHg uptake by cells in the presence of predominantly marine DOM compared to terrestrial DOM. Highest fractions of dissolved gaseous mercury were also found at stations with the highest marine DOM content, suggesting a greater reducible fraction of divalent inorganic Hg. These data suggest DOM composition is a critical driver of Hg reactivity and bioavailability in offshore marine waters.

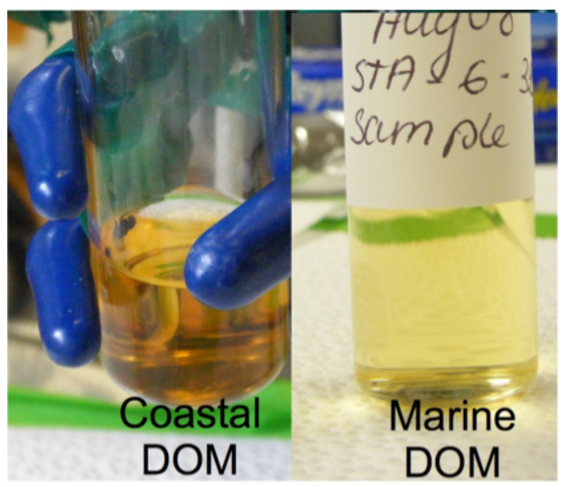

Figure 2: Dissolved organic matter extracts

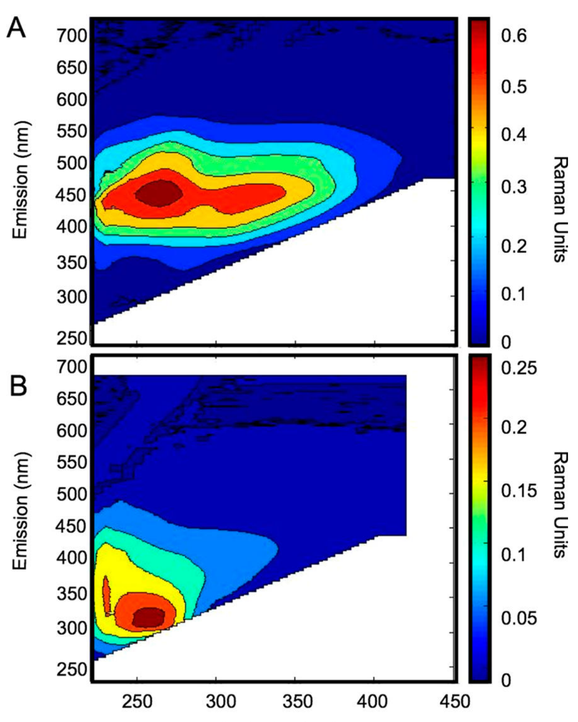

Figure 3: Three-dimensional excitation emission matrix for Panel A Suwannee River dissolved organic matter and Panel B marine DOM from Station 6

Table 1. Excitation and emission of each PARAFAC component and previously identified characteristics

	Excitation (nm)	Emission (nm)	Literature description	Classification for this work
C1	275-290	330-350	Protein-like, Tyrosine	Marine
C2	240-325	370-420	Humic-like, terrestrially-derived, microbial humic	Terrestrial
C3	250-380 (320-375)*	425-500	Humic-like, large molecular size, hydrophobic compounds, microbial humic	Terrestrial
C4	245-275	350-400 (280-300)	Protein-like, Tryptophan	Marine
C5	290-325	380-450	Humic-like and marine-like, medium size compounds	Terrestrial
C6	220-225 (270)	320-360	Protein-like	Marine
C7	230-240 (350-375)	435-500	Humic-like, Terrestrial, small molecular size compounds	Terrestrial

*Secondary peak locations ranges in parentheses.

Methods

Mercury analyses

Waters were collected in LIS and the NWA, Figure 1.

LIS water was analyzed for mercury species.

For the NWA, we used 2008-2009 data from Soerensen et al. on total Hg and DGM and 2008-2009 data from Hammerschmidt et al. on MeHg in seawater and MeHg in plankton.

Dissolved organic matter analyses

25 L of water from NWA were preconcentrated into 10 mL using the method described in Dittmar et al. 2008, Figure 2.

Composition of marine DOM in seawater using three-dimensional excitation-emission fluorescence spectroscopy (3D-EEM), Figure 3.

PARAFAC modeling was used to group fluorescence spectra (n=57) for samples from LIS and the NWA in 2008 into seven distinct components designated C1-C7 (Table 1) using the DOMFluor toolbox in MATLAB.

Complexation and uptake experiments

To examine the Hg binding sites of DOM, $Hg(NO_3)_2$ was added at concentrations between zero and 0.75 µM to a solution containing 30 mg L^{-1} DOM from Station 8 on the NWA (Figure 1), 0.04 M phosphate buffer (pH 6), and 0.1 N sodium chloride.

An Escherichia coli (E. coli) mer-lux biosensor was used to investigate the effects of terrestrial and marine DOM sources on cellular uptake. The biosensor produces light proportionally to the amount of MeHg inside cells. We incubated 5 nM MeHg solutions containing terrestrial (Suwannee River) or marine (NWA Station 10, Figure 1) DOM between 0 to 100 mg L^{-1} in 40 mL liquid scintillation vials for 24 hours in the dark and then added biosensor cells.

Results and Discussion

Figure 4A shows the seven DOM components identified in PARAFAC modeling for all sampling sites

Figure 4B shows results of our titration experiment that progressively added inorganic Hg to seawater containing DOM from NWA Station 8. Results illustrate that both the terrestrial and marine DOM components designated here bind to inorganic Hg, resulting in changes in fluorescence

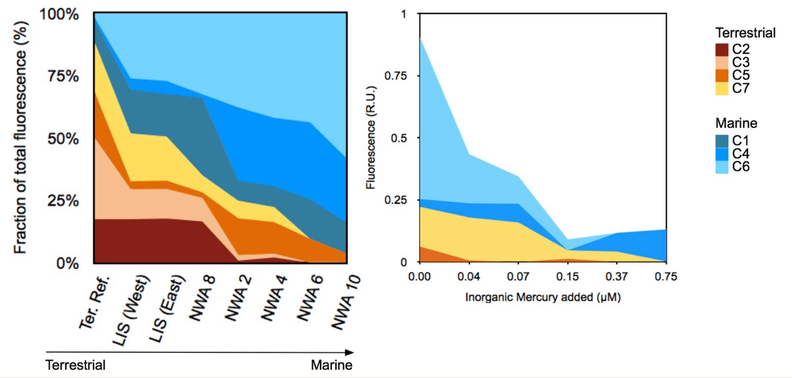

Figure 4: Panel (A) shows the fraction of fluorescence intensity attributable to terrestrial and marine DOM components. Panel (B) Experimental results showing change in DOM fluorescence intensity (NWA Station 8) with increasing inorganic Hg concentrations

Nearshore and offshore DOM concentrations to be similar (77 ± 13 µM) but carbon to nitrogen (C/N) molar ratios are suggestive of differences in terrestrial DOM (Figure 5A).

Increases in C/N ratios at offshore stations likely reflect aging of organic matter. %DGM in NWA seawater increases with a higher fraction of degraded terrestrial DOM indicated by the C5 component (Figure 5B).

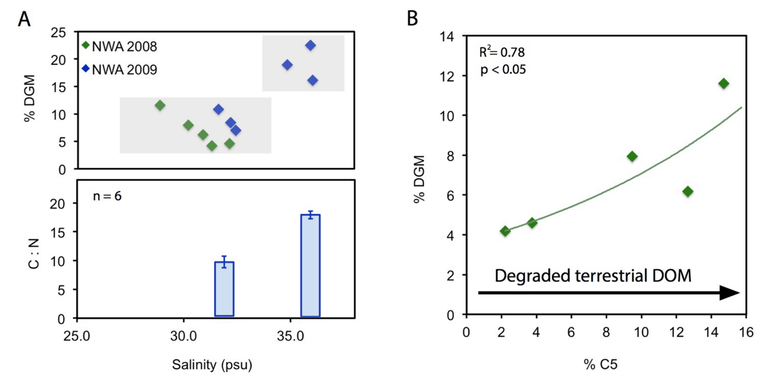

Figure 5: Relationship between DOM composition and dissolved gaseous mercury as a fraction of total mercury (%DGM) in offshore marine waters

MeHg in NWA and LIS plankton declines with decreasing contribution to total fluorescence from terrestrial DOM sources (Figure 6A).

Similar to field measurements, uptake of MeHg was less efficient in the presence of high terrestrial DOM concentrations, but unaffected by marine DOM. Both field and experimental results thus suggest marine DOM does not affect cellular uptake of MeHg but terrestrial DOM can inhibit uptake (Figure 6B).

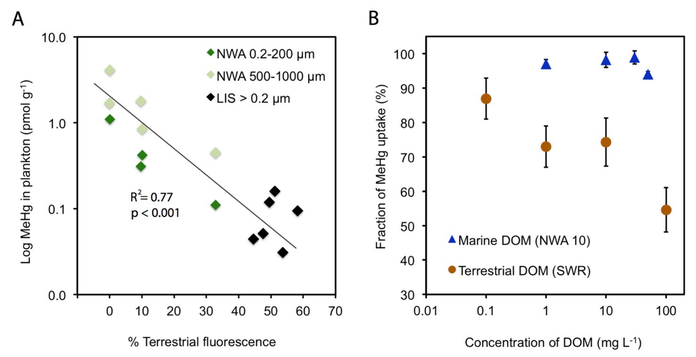

Figure 6: Field (Panel A) and experimental (Panel B) measurements of the effects of DOM composition on MeHg uptake by plankton

Differences in Hg reactivity and MeHg uptake in the presence of marine and terrestrial DOM help explain higher bioaccumulation factors often found in marine systems compared to terrestrial sites.

References

Waters were collected in Long Island Sound and the North West Atlantic Margin (NWA), Figure 1.