Coastal phytoplankton and mercury dynamics in watersheds along the U.S. East Coast from New Jersey to Maine assessed using particulate and dissolved samples collected in 2015 and 2016

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Project
» Collaborative Research: Transformations and mercury isotopic fractionation of methylmercury by marine phytoplankton (Phytoplankton MeHg)

Contributors	Affiliation	Role
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Abstract
Dissolved total mercury, dissolved methylmercury, dissolved organic carbon as well as different size fractions of coastal phytoplankton were measured in watersheds along the U.S. East Coast from New Jersey to Maine in 2015 and 2016. Chlorophyll and phaeopigment data and other parameters were also recorded. Samples were collected at different stages of the tide and over different months in the two years.

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Coverage

Spatial Extent: **N**:44.763 **E**:-68.791 **S**:38.928 **W**:-75.475
Temporal Extent: 2015-08 - 2016-07

Dataset Description

The data in each year are grouped by Location, Filter size, and measured parameters for each size fraction, as well as the measured dissolved parameters:

Location: state, site name and sub-location (in many instances these are sites with high (HOC) and low (LOC) organic carbon sediments), sampling month and sampling time in terms of tide (HT = high tide, LT = low tide, FL = falling and RS = rising tide; if more than one sample at a tide was collected, this is indicated, e.g. HT1, HT2), latitude and longitude

Filter size: Filtering protocols were not exactly identical between years. In 2015, samples were sequentially filtered so particulate samples are >20 µm (large fraction) and 0.2-20 µm (small fraction). In 2016, water was

sampled through filters independently so samples are >2 µm (bulk) and <20 µm (small fraction). For each filter, the following parameters were measured and are recorded: total suspended solids (TSS, mg/L), chlorophyll a (Chl a, µg/L) and phaeopigment (Pha, µg/L), particulate total Hg (part. HgT, pmol/g) and particulate methylmercury (part. MeHg, pmol/g).

Dissolved parameters: For each location, a filtered sample was analyzed for: dissolved total mercury (diss. HgT, pM), dissolved methylmercury (diss. MeHg, pM), and dissolved organic carbon (DOC, µM). Salinity and temperature (degrees C) were also recorded for each sample.

Methods & Sampling

Coastal phytoplankton measurements were taken from 22 sites wtihin watersheds along the U.S. East Coast, from New Jersey to Maine, in 2015 and 2016. Samples were collected from shore or small boat by hand using clean sampling techniques and processed within 12 hours of collection. Salinity and temperature were also measured, using a hand-held YSI sonde.

Water was filtered using either quartz filters combusted at 550 degrees C and 0.2 µm polycarbonate filters cleaned with 2% hydrochloric acid (2016) or sequentially filtered using 20 µm nylon filters and 0.2 µm polycarbonate filters cleaned with 2% hydrochloric acid (2015). The sequential filters in 2015 can be summed to calculate a bulk sample. The filters were stored frozen until analysis for particulate HgT and MeHg, and ancillary parameters.

Dissolved samples were collected after the filter (filtrate) into acid cleaned *iChem* bottles and preserved with 0.2% HCl if intended for HgT or combined MeHg and HgT analyses. Samples for only dissolved MeHg were preserved with 0.5% H2SO4. DOC samples were collected from the particulate Hg filtrate into muffled amber vials and nutrient samples into acid-cleaned plastic centrifuge tubes; both were preserved by freezing. Samples were collected at various tidal stages (as explained above in Description section).

Particulate and dissolved MeHg samples were analyzed on a Tekran 2700 Automated Methylmercury Analysis System following standard techniques (Hammerschmidt and Fitzgerald, 2006; Gosnell et al., 2017; Munson et al., 2014; Seelen et al., 2021). Briefly, particulate samples were digested in 4.5N nitric acid overnight, neutralized with potassium hydroxide and acetate buffer, and ethylated using sodium tetraethylborate before separation by gas chromatography and cold vapor atomic fluorescence detection with calibration against a standard curve (Alfa Aesar CAS: 115–09–3, LOT: 1791821 spike recovery= 103±14%). Dissolved MeHg samples were analyzed similarly except the seawater was digested overnight in 1% H2SO4, and 2.5% L-ascorbic acid was added prior to ethylation (Munson et al., 2014) (Alfa Aesar CAS: 115–09–3, LOT: 1791821 spike recovery= 86±34%). The samples were not corrected for spike recovery. The methods are a modified version of EPA method 1630.

HgT was analyzed on a Tekran 2600 by cold vapor atomic fluorescence spectrometry following EPA method 1631, refined by Hammerschmidt and Fitzgerald (2006). The particulate HgT (pHgT) sample filters were digested in 4.5N nitric acid with bromine monochloride (BrCl) for 16 hrs, followed by hydroxylamine hydrochloride and stannous chloride additions before analysis. Calibration was against a standard curve and the results were spike corrected (J.T.Baker CAS: 7732–16–5, Batch No: 0000127949 spike recovery= 121±2%). For some samples, the same filter was used for both pMeHg and pHgT, in which case the BrCl addition was made after the MeHg analysis was complete. Dissolved HgT (dHgT) analysis was similar to the particulate analysis, except only BrCl was added >16 hr for digestion prior to reduction for analysis. The samples were blank and spike corrected (J.T.Baker CAS: 7732–16–5, Batch No: 0000127949 spike recovery= 76±5%).

Total suspended solids (TSS) was determined using the dried filters, as they were pre-weighed prior to use. Chlorophyll a (chl a) and phaeopigment (pha) concentrations were quantified from wet filters using fluorescence techniques after 90% acetone extraction and acidification for pha. DOC was analyzed on a Shimadzu TOC/TN analyzer. Duplicate average RSD = 6.6% (pigments) and 2.8% (DOC); Seelen et al., 2021; Taylor et al., 2019).

Details of **filtering and other analytical methods** can be found in Seelen et al. (2021) and other publications covering these studies (Taylor et al., 2019; Seelen et al., 2018). Blanks and replicate samples were included in the sampling and analysis, and spike recoveries and other QA/QC included in the analysis (see Table1 in Supplemental Files below).

Data Processing Description

BCO-DMO processing:
- Combined datasets from years 2015 and 2016
- Joined watershed, site location, and subsite information to dataset
- Added a conventional header with dataset name, PI names, version date
- Adjusted parameter names to comply with database requirements
- Units removed and added to Parameter Description metadata section
- Missing data replaced with 'nd' (BCO-DMO's default missing data identifier)

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Data Files

File
coastal_phyto.csv (Comma Separated Values (.csv), 12.25 KB) MD5:59786a53addb8bd10049f6078d9f839e Primary data file for dataset ID 840578

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Supplemental Files

File
Table1_Mason_CoastalPhyto filename: Table1_Mason_CoastalPhyto.pdf (Portable Document Format (.pdf), 143.59 KB) MD5:f4d5a85c01b12f1393dae546b4a96ac3 Table 1: Quality assurance information for Mason coastal phytoplankton measurements

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Related Publications

Gosnell, K.J., Balcom, P.H., Tobias, C.R., Gilhooly, W.P., III and Mason, R.P. (2017), Spatial and temporal trophic transfer dynamics of mercury and methylmercury into zooplankton and phytoplankton of Long Island Sound. Limnol. Oceanogr., 62: 1122-1138. https://doi.org/10.1002/lno.10490
Methods

Hammerschmidt, C. R., & Fitzgerald, W. F. (2006). Bioaccumulation and Trophic Transfer of Methylmercury in Long Island Sound. Archives of Environmental Contamination and Toxicology, 51(3), 416–424. doi:10.1007/s00244-005-0265-7
Methods

Munson, K. M., Babi, D., & Lamborg, C. H. (2014). Determination of monomethylmercury from seawater with ascorbic acid-assisted direct ethylation. Limnology and Oceanography: Methods, 12(1), 1–9. doi:10.4319/lom.2014.12.1
Methods

Seelen, E. A., Chen, C. Y., Balcom, P. H., Buckman, K. L., Taylor, V. F., & Mason, R. P. (2021). Historic contamination alters mercury sources and cycling in temperate estuaries relative to uncontaminated sites. Water Research, 190, 116684. doi:10.1016/j.watres.2020.116684
Methods

Seelen, E. A., Massey, G. M., & Mason, R. P. (2018). Role of Sediment Resuspension on Estuarine Suspended Particulate Mercury Dynamics. Environmental science & technology, 52(14), 7736–7744. https://doi.org/10.1021/acs.est.8b01920
Methods

Taylor, V. F., Buckman, K. L., Seelen, E. A., Mazrui, N. M., Balcom, P. H., Mason, R. P., & Chen, C. Y. (2019).

Organic carbon content drives methylmercury levels in the water column and in estuarine food webs across latitudes in the Northeast United States. Environmental pollution (Barking, Essex : 1987), 246, 639–649. https://doi.org/10.1016/j.envpol.2018.12.064
Methods

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Parameters

Parameter	Description	Units
State	State location of sample collection	unitless
Watershed	Watershed name	unitless
Site_Location	Site location with the watershed	unitless
Site	Site name	unitless
Subsite	Subsite indicating presence of high or low organic carbon sediments	unitless
Latitude	Latitude of sample site	decimal degrees
Longitude	Longitude of sample site, west is negative	decimal degrees
Year	Year of sampling	unitless
Month	Month of sampling	unitless
Tide	Tidal state during the sampling	unitless
Part_fraction_small	Particulate fraction of filtered material (either 0.2-20 microns, or 0.45-20 microns)	microns (µm)
TSS_small	Chlorophyll a (smaller fraction)	milligrams per Liter (mg/L)
Chl_a_small	Phaeopigment (smaller fraction)	micrograms per Liter (µg/L)
Pha_small	Total suspended solids (smaller fraction)	micrograms per Liter (µg/L)
Part_MeHg_small	Particulate methylmercury (smaller fraction)	picomoles per gram (pmol/g)

Part_HgT_small	Particulate total mercury (smaller fraction)	nanomoles per gram (nmol/g)
Part_fraction_large	Particulate fraction of filtered material (larger fraction)	microns (µm)
TSS_large	Total suspended solids (larger fraction)	milligram per Liter (mg/L)
Chl_a_large	Chlorophyll a (larger fraction)	micrograms per Liter (µg/L)
Pha_large	Phaeopigment (larger fraction)	micrograms per Liter (µg/L)
Part_MeHg_large	Particulate methylmercury (larger fraction)	picomoles per gram (pmol/g)
Part_HgT_large	Particulate total mercury (larger fraction)	nanomoles per gram (nmol/g)
Diss_HgT	Dissolved methylmercury	picomoles (pM)
Diss_MeHg	Dissolved total mercury	picomoles (pM)
DOC	Dissolved Organic Carbon	micromoles (µM)
Salinity	Salinity of water at sample site	unitless
Temp	Temperature of water at sample site	degrees Celsius

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Instruments

Dataset-specific Instrument Name	Tekran 2700 Automated Methylmercury Analysis Systems
Generic Instrument Name	Automated Mercury Analysis System
Dataset-specific Description	Particulate and dissolved MeHg samples analyzed on a Tekran 2700 Automated Methylmercury Analysis System (which incorporates gas chromatography and cold vapor atomic fluorescence detection)\
Generic Instrument Description	Examples include Tekran Models 2600 and 2700

Dataset-specific Instrument Name	Tekran 2600 cold vapor atomic fluorescence spectrometer
Generic Instrument Name	Cold Vapor Atomic Fluorescence Spectrophotometer
Dataset-specific Description	Tekran 2600 cold vapor atomic fluorescence spectrometry used to measure HgT
Generic Instrument Description	A Cold Vapor Atomic Fluorescent Spectrophotometer (CVAFS) is an instrument used for quantitative determination of volatile heavy metals, such as mercury. CVAFS make use of the characteristic of mercury that allows vapor measurement at room temperature. Mercury atoms in an inert carrier gas are excited by a collimated UV light source at a particular wavelength. As the atoms return to their non-excited state they re-radiate their absorbed energy at the same wavelength. The fluorescence may be detected using a photomultiplier tube or UV photodiode.

Dataset-specific Instrument Name	YSI hand-held sonde
Generic Instrument Name	Salinity Sensor
Dataset-specific Description	Salinity and temperature were measured using a hand-held YSI sonde.
Generic Instrument Description	Category of instrument that simultaneously measures electrical conductivity and temperature in the water column to provide temperature and salinity data.

Dataset-specific Instrument Name	Shimadzu TOC/TN analyzer
Generic Instrument Name	Total Organic Carbon Analyzer
Dataset-specific Description	Shimadzu TOC/TN analyzer used to measure DOC
Generic Instrument Description	A unit that accurately determines the carbon concentrations of organic compounds typically by detecting and measuring its combustion product (CO2). See description document at: http://bcodata.whoi.edu/LaurentianGreatLakes_Chemistry/bs116.pdf

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Project Information

Collaborative Research: Transformations and mercury isotopic fractionation of methylmercury by marine phytoplankton (Phytoplankton MeHg)

Coverage: Antarctic Peninsula

NSF Award Abstract:
The accumulation of mercury (Hg) in seafood is a public health concern. The presence of Hg in seafood depends to a large degree on the air-sea exchange of Hg, with atmospheric deposition leading to accumulation of Hg in the ocean. The pathways to seafood start with the uptake of Hg by phytoplankton from seawater

where is has always been assumed to accumulate to be eaten by grazers and passed on to larger organisms. This project challenges this assumption with preliminary data that suggests certain phytoplankton species can transform Hg to volatile forms (mercury vapor & dimethylmercury) that are lost to the atmosphere, a processes that removes Hg from the ocean rather than simply concentrating it into the ecosystem and seafood. This process, which has not been studied before, could dramatically alter our view of the Hg cycle in the ocean. The researchers funded by this project will look for the specific phytoplankton species that are capable of volatilizing Hg and quantify the rates at which they do so. They will also examine the suspected role of associated sulfur and selenium compounds in the process, as well as quantifying the changes in the Hg isotopic values for potential use as chemical tracers of the source of Hg in the ecosystem and food supply. These results should allow oceanographers to better quantify and refine our knowledge of Hg cycling in the ocean. The project will support participation of graduate students, a postdoctoral scientist, and incorporation of new information directly into courses taught by the researchers. Funding will also support continuing activities by the participants in activities that disseminate information on mercury and its effect on public and environmental health.

Biogeochemical cycling of mercury (Hg) in the ocean may be more complex than previously assumed. New evidence has challenged the idea that methylmercury (MeHg) merely accumulates in phytoplankton and undergoes little to no transformation before being passed into the food web. This project aims to more fully elucidate the mechanisms behind the intracellular transformation of MeHg to volatile Hg and dimethylmercury (Me2Hg) that can be lost to the atmosphere, as well as to evaluate the range of algal taxa that can perform this transformation using directed culture work. Additionally, the PIs will investigate evidence that thiols, organic selenium (Se) compounds, and sulfides are required to facilitate these reactions within the phytoplankton, and specific pathways will be investigated and quantified through this research. Stable Hg isotopic data has been used to track Hg sources and pathways in marine systems and its fractionation during these MeHg transformations will also be quantified for future field study of marine Hg. The investigators hypothesize that coccolithophorids and other haptophytes capable of these intracellular reactions may account for a significant portion of the production of volatile Hg in the ocean. If this turns out to be the case, understanding and quantifying these volatilization processes may significantly alter our current understanding of the overall biogeochemical cycling of Hg in the ocean.

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Funding

Funding Source	Award
NSF Division of Ocean Sciences (NSF OCE)	OCE-1634048

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