Concentrations of mercury forms and ancillary parameters in size fractionated plankton samples and in water collected during 2014 from Long Island Sound and the adjacent shelf

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

Contributors	Affiliation	Role
Mason, Robert P.	University of Connecticut (UConn)	Principal Investigator
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Abstract
Concentrations of mercury forms and ancillary parameters were investigated in size fractionated plankton samples and in water from Long Island Sound and the adjacent shelf. Samples were collected in three separate seasons (Spring, Summer, Fall) during 2014 to research the temporal trophic transfer dynamics of mercury and methylmercury into zooplankton and phytoplankton.

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Coverage

Spatial Extent: **N**:41.263 **E**:-70.956 **S**:40.228 **W**:-73.56
Temporal Extent: 2014-05-20 - 2014-09-11

Acquisition Description

Sampling and analytical procedures:
Methods are described in detail in Gosnell et al. (2017).

Samples were collected to represent three separate seasons during 2014: Spring (May 20th-22nd), Summer (August 2nd-5th), and Fall (September 9th-11th). Plankton and water samples were collected from Western Long Island Sound (WLIS) and Eastern Long Island Sound (ELIS) stations in the spring and summer, while the fall collection included stations in Central Long Island Sound (CLIS), as well as along

the shelf break (SB) and mid-shelf (MS) region.

At each station, triplicate substations were sampled approximately one mile apart at each site during the spring and summer seasons, while duplicate substations were sampled during the fall. Water samples were collected using a trace-metal clean GoFlo bottle attached to a Kevlar line, or with a trace-metal clean rosette system. Water was kept cold and dark until processing. Water samples were filtered for particulate methylmercury (MeHg) and total mercury (HgT), total suspended solids (TSS) and chlorophyll a (Chl a). Filtrate was saved for dissolved mercury and methylmercury, nutrients, and dissolved organic carbon (DOC) measurements. A CTD was deployed concurrent with water collections, and recorded the vertical profiles of fluorescence, oxygen, temperature, and salinity. Separate phytoplankton (seston) fractions were obtained by sequentially filtering the seawater through polycarbonate filters of sizes 0.2 µm, 5 µm and 20 µm. Larger particulate material was excluded by initially passing water through a 200 µm mesh. Zooplankton were collected by attaching an opening/closing 200 µm net (Seatec) to the Kevlar line. Deployments were from 2 meters above the bottom up to 1 meter from the surface. Depths ranged from 11 meter in Long Island Sound, to 100 meter at the Mid-Shelf and Shelf Break stations. Zooplankton were separated into size fractions of 0.2–0.5 millimeters, 0.5–1 mm, 1–2 mm, and >2 mm via mesh screens.

Each sample was digested in 4.5 M HNO3 acid solution at 60 degrees C for at least 12 hours prior to analysis. For MeHg analysis, a subsample was neutralized with KOH, diluted to a final volume of 30 mililiters, buffered with acetate buffer (pH of 4.9), and ethylated with sodium tetraethylborate (Hammerschmidt et al. 2013). Water samples were analyzed without acid digestion (Munson et al., 2014). Samples were then analyzed using a Tekran 2700 methylmercury analyzer with cold vapor atomic fluorescence (CVAFS) detection, and an external calibration curve (r2 >0.998). For total Hg analysis (HgT), the remaining digest was diluted, bromine monochloride (BrCl) was added for a minimum 24 hours preceding analysis to decompose organic matter and convert all Hg into the ionic form. Hydroxylamine hydrochloride was added to degrade excess BrCl oxidant prior to analysis using a manual system with tin chloride (SnCl2) reduction, purging with N2 onto a trap containing gold-coated beads for quantification using a Tekran 2500 CVAFS detector, and an external calibration curve (r2 >0.999). For water samples, the acidified water was treated with BrCl and then processed as for biota digests. Chlorophyll and phaeopigment were analyzed using a Trilogy fluorometer, and DOC was analyzed using a Shimazdu TOC/TN instrument.

Additional information:
QA/QC information is given in Table 1. (see Supplemental Files section below)

Results of these data are shown in Figs 2-5 and Table 1 in Gosnell et al. (2017). Additional calculated information (%MeHg, bioconcentration factors) is included in the same paper in additional tables. Stable isotope data for C, N and S for zooplankton is also reported.

Problem report:
Not all size fractions of samples were collected at all locations because of biota variability. Missing information is indicated in the dataset as 'nd'. Additionally, Spring and Summer samples were collected only at two sites with additional Fall sampling at three other sites.

Processing Description

Data was processed using spreadsheets in Excel and no other post-analytical data processing occurred

BCO-DMO Processing:
- data was rearranged to list both Zooplankton and Phytoplankton species by season, location, and size
- values rounded to four decimal places for MeHg and HgT columns
- added fields for sample type, size ID, and description of depth
- replaced asterisk in standard deviation with 'nd' and created a column to list the number of samples
- dates and times joined to main data set

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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
Results

Hammerschmidt, C. R., Finiguerra, M. B., Weller, R. L., & Fitzgerald, W. F. (2013). Methylmercury Accumulation in Plankton on the Continental Margin of the Northwest Atlantic Ocean. Environmental Science & Technology, 47(8), 3671–3677. doi:10.1021/es3048619
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
Results

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Parameters

Parameter	Description	Units
Season	Season of sample collection (Spring, Summer, Fall)	unitless
Location	Location in Long Island Sound or on the associated shelf	unitless
Location_name	Western (WLIS), Central (CLIS), or Eastern (ELIS) Long Island Sounds; Mid-Shelf (MS); and Shelf Break (SB)	unitless
Latitude	Latitude of sampling	decimal degrees
Longitude	Longitude of sampling	decimal degrees
DateTime_Local_EDT	DateTime of sampling (yyyy-mm-dd hh:mm:ss) in Eastern time zone	unitless
Sample_type_size	Sample type (Zooplankton or Phytoplankton)	unitless
Sample_size_id	Size description of the sample (small, medium, large, x-large)	unitless
Sample_size	Size (in microns or millimeters) of the sample	unitless
Num_samples	Number of samples collected and used for calculating standard deviation	each
MeHg	Average methylmercury (MeHg) concentration in each seston size fraction on a wet weight basis	picomol per gram (wet weight)
MeHg_stdev	Standard deviation for the MeHg concentration for the size fraction. (If	picomol per gram (wet weight)
HgT	Average total mercury (HgT) concentration in each seston size fraction on a wet weight basis	picomol per gram (wet weight)
HgT_stdev	Standard deviation for the HgT concentration. (If	picomol per gram (wet weight)
Depth	Water depth for the water collections (mostly 2 per location)	meters (m)
Depth_description	Water column location	units
Diss_HgT	Dissolved total mercury (	picomol per liter
Diss_MeHg	Dissolved methylmercury (	picomol per liter
Part_HgT	Particulate total mercury on a dry weight basis	picomol per gram (dry weight)
Part_MeHg	Particulate methylmercury on a dry weight basis	picomol per gram (dry weight)
TSS	Total suspended solids	milligram per liter (dry weight)
DOC	Dissolved organic carbon (	micomol per liter (µM)
Chl_a	Chlorophyll a concentration	microgram per liter (µg/L)
ISO_DateTime_UTC	DateTime of sampling in UTC/GMT	unitless

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Instruments

Dataset-specific Instrument Name	Trilogy fluorometer
Generic Instrument Name	Fluorometer
Dataset-specific Description	Chlorophyll and phaeopigment were analyzed using a Trilogy fluorometer
Generic Instrument Description	A fluorometer or fluorimeter is a device used to measure parameters of fluorescence: its intensity and wavelength distribution of emission spectrum after excitation by a certain spectrum of light. The instrument is designed to measure the amount of stimulated electromagnetic radiation produced by pulses of electromagnetic radiation emitted into a water sample or in situ.

Dataset-specific Instrument Name	Shimadzu TOC/TN analyzer
Generic Instrument Name	Total Organic Carbon Analyzer
Dataset-specific Description	DOC was analyzed on a Shimadzu TOC/TN analyzer.
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

Dataset-specific Instrument Name	Tekran 2700 Automated Methylmercury Analysis System
Generic Instrument Name	Automated Mercury Analysis System
Dataset-specific Description	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 2500 Total Mercury Analysis System
Generic Instrument Name	Tekran 2500 CVAFS mercury detector
Dataset-specific Description	Tekran 2500 Total Mercury Analysis System (not automated; cold vapor atomic fluorescence spectrometry)
Generic Instrument Description	Tekran 2500 Total Mercury Analysis System (not automated; cold vapor atomic fluorescence spectrometry)

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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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