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# Effects of dissolved organic carbon on methylmercury bioavailability in stream ecosystems

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## Effects of dissolved organic carbon on methylmercury bioavailability in stream ecosystems

### Basic Information

<b>Title:</b>	Effects of dissolved organic carbon on methylmercury bioavailability in stream ecosystems
<b>Project Number:</b>	2016NH205G
<b>USGS Grant Number:</b>	
<b>Start Date:</b>	9/1/2016
<b>End Date:</b>	8/31/2018
<b>Funding Source:</b>	104G
<b>Congressional District:</b>	2nd Congressional district of New Hampshire
<b>Research Category:</b>	Water Quality
<b>Focus Categories:</b>	Surface Water, Geochemical Processes, Toxic Substances
<b>Descriptors:</b>	None
<b>Principal Investigators:</b>	Kathryn L Cottingham, Celia Y. Chen, James Shanley

### Publications

There are no publications.

## Effects of dissolved organic carbon on methylmercury bioavailability in stream ecosystems (2016NH205G)

**Problem:** Neurotoxic methylmercury bioaccumulates through aquatic food webs and is a primary cause for fish consumption advisories in the Northeast. The mobilization, transport and bioavailability of mercury in aquatic ecosystems is strongly tied to organic matter dissolved in the water, yet levels of methylmercury in watersheds, and that bioaccumulate in fish, are difficult to predict. Previous studies have noted that relationships between stream methylmercury and dissolved organic carbon (DOC) in streams changes over time. There is also a seemingly contradictory effect of DOC on uptake by the biota: at low concentrations of organic carbon, methylmercury bioaccumulation increases, whereas at higher concentrations, uptake into fish and invertebrates is attenuated. This project is testing the hypothesis that differences in the chemical structure of the DOC that is transporting MeHg in streams lead to the temporal changes and non-linearity in bioaccumulation noted in previous studies.

### Objectives:

- 1) Identify and characterize fractions of DOC that associate with MeHg and Hg in streams,
- 2) Determine the effects of DOC quality and quantity on MeHg uptake by primary producers at the base of the stream food web.

### Methods:

Field study: A spatial and temporal study of dissolved organic carbon quantity and quality, and water MeHg and Hg levels in the tributaries of Lake Sunapee was completed in the summer of 2017. Water samples were collected in April and August from 27 sites, as well as from three contrasting sites on a bi-weekly basis. Filtered water samples from field collection were analyzed by 3D excitation-emission fluorescence spectroscopy, and by ultraviolet spectroscopy within 48 h of collection. Whole and filtered water samples were also analyzed for total organic carbon, MeHg and Hg. Fluorescence excitation-emission matrix (EEM) data was analyzed in Matlab using the “Dr. EEM” toolbox, and corrected for instrument and inner filter effects. Components of organic carbon were identified from *a priori* fluorescence and UV indices, and PARAFAC analyses was performed on EEM matrices to identify organic carbon components specific to this watershed.

Our USGS collaborators collected samples from a reference watershed in Sleepers River, VT, to provide some comparison to the current watershed. Samples were analyzed for MeHg, Hg at Dartmouth, and for organic carbon quality and concentration by our USGS collaborators. Organic carbon quality data and MeHg/Hg concentrations from two other watersheds, collected during a previous study, were also provided by our USGS collaborators.

In August 2017, biofilm and invertebrate samples were collected from 11 streams at sites near the lake. Biofilm was analyzed for ash content, chlorophyll-a,  $\delta^{34}\text{S}$ . Biofilm and invertebrates were analyzed for MeHg, Hg,  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$ .

Biofilm growth: Our earlier attempts at biofilm growth gave us experience with managing nutrient regimes, but extremely heterogenous spatial distribution of biofilm thickness and algal taxa developed due to uneven flows in the cattle tanks that were originally adapted as artificial streams. We have constructed 4 artificial streams (2m x 0.5m) with paddles for water circulation, providing a more laminar flow to improve the homogeneity of biofilm growth. These streams will be used to complete the research on Hg uptake in biofilm under controlled conditions.

**Mapping:** Watershed landscape features for the Lake Sunapee watershed and three reference watersheds were assessed along stream buffer zones using high resolution aerial imagery and high-resolution lidar elevation models in ArcGIS.

**Principal findings and significance:** Modeling and statistical analysis of the fieldwork data from year 1 is in progress. Much higher levels of MeHg and Hg were present in the Lake Sunapee watershed than the reference watershed sites. Concentrations of MeHg were higher in the late summer than in the spring, and correlated spatially with % wetland in the watershed. Higher concentrations of both humic and protein-like organic matter occurred in streams that passed through wetlands, whereas spectral slope ( $S_R$ ), a proxy for molecular weight, was correlated with streams with open water (small lakes) upstream in the catchment. Concentrations of MeHg in the water column were weakly inversely correlated with  $S_R$ , and with the ratio of protein-like (microbially-mediated) to humic-like organic carbon fractions.

Methylmercury in biofilm was not correlated to MeHg in stream water, likely because of the variable composition of biofilm between streams, whereas % MeHg in biofilm was inversely related to % ash (inorganic material). Methylmercury in grazing invertebrates (caddisfly, mayfly) were correlated with MeHg and DOC in the water column at lower concentrations, but sites with the highest concentrations of DOC had lower uptake of MeHg in the biota.

Our preliminary findings suggest sites associated with wetlands export higher levels of MeHg, but bioavailability of MeHg associated with organic carbon from wetlands is lower than from streams without wetlands. The higher ratios of protein-like to humic-like organic matter originating from wetlands may reduce the availability of MeHg for uptake to the base of the foodweb. This hypothesis is being further tested under controlled mesocosm conditions using artificial streams.

**Publications and presentations:** Findings from the first year of research will be presented at the American Society of Limnology and Oceanography annual meeting in June 2018.

**Notable awards and achievements:** Co-PI Celia Chen and investigator Vivien Taylor received a CompX grant through the Neukom Institute at Dartmouth to compare findings from Lake Sunapee with other watersheds. The CompX grant has enabled us to improve our GIS and modeling capabilities.

Investigator Vivien Taylor received an NSF grant to study sources of methylmercury to fish in Lake Sunapee. This work will build on the current grant by comparing the isotopic ratios of mercury in the tributaries and in the lake, to determine whether bioavailable mercury is transferred from the watershed to the lake, or produced from in-lake processes.

**Outreach and information transferred:** We are in contact with the Lake Sunapee Protective Association and met with them later in May 2017 to talk with them about our prior studies on Lake Sunapee as well as the current research. In August 2017, three students associated with the project attended the Lake Sunapee Bass Derby and provided information to local fisherman about mercury in fish.

**Students supported:** (2)

Keith Kantack (Master's student), worked full time on the project for 2.5 months.

Paul Vickers (2<sup>nd</sup> year undergraduate), worked full-time on the project spring term, and part-time in the winter and summer terms.

**Faculty and staff supported: (5)**

Kathy Cottingham (Professor)

Celia Chen (Research Professor)

Vivien Taylor (Research Scientist)

Kate Buckman (Research Scientist)

Seth Roberts (Research Assistant)

**Special story and photo:**

"Being a part of the Dartmouth WRRRC team was a great opportunity to apply some of my GIS and watershed science skills, but also to learn hands on about aquatic ecology and environmental chemistry. My experience on the team made me a stronger applicant for the job I now have with a river restoration firm, where I work to improve riparian habitat in the New England and the Pacific Northwest."                      Keith Kantack, Dartmouth MSc Earth Science 2017



Keith joined the WRRC research team while finishing up his Master's degree in Earth Science, and applied his expertise in remote sensing and mapping to analyzing watershed landscape characteristics of Lake Sunapee and three reference watersheds. Keith also expanded his research skills by collecting and processing stream water samples for our field study, and learned to identify and collect biofilm and invertebrate samples for ecological assessment. Following the field season, he led a field laboratory session on stream invertebrates as part of the Dartmouth 'Stretch', an off-campus field program for Earth Science majors. Since gaining applied research experience on the WRRC Lake Sunapee project, Keith has started working for a river restoration company in New England, and is advancing his career in watershed research.