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ARTICLE

# Seasonal Mercury Dynamics in a New England Vernal Pool

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**Abstract** Mercury fluxes into and transformations within a small vernal pool in Massachusetts were investigated over a wet-dry-wet cycle. We measured the deposition of total mercury (HgT) and methyl mercury (MeHg) via litterfall between October 6 and December 2, 2010. Litterfall fluxes were 10 μg $m^{-2}$ and 80 ng $m^{-2}$, respectively, over that time period. Average HgT concentration in litterfall was 33±2 ng $gdw^{-1}$; 0.9 % was present as MeHg. The HgT content of the litter layer increased slightly throughout the year, reaching 55±20 ng $gdw^{-1}$ inside and 42±7 ng $gdw^{-1}$ outside the pool. Litter %MeHg increased only to 1.5 % on the forest floor, while it increased dramatically in the vernal pool after inundation in late November, reaching 9 % by early spring. Measurements in pool benthic invertebrates show that two types of shredders bioaccumulated MeHg 4–9-fold relative to the leaf litter substrate. Overall, our results indicate significant production and bioaccumulation of MeHg in this vernal pool. This *de novo* MeHg could impact resident amphibians or be exported to the surrounding forest.

**Keywords** Vernal pools · Total mercury · Methyl mercury · Litterfall · Seasonal forest pools

## Introduction

Mercury (Hg) is a toxic metal that is among the world's most widespread environmental contaminants. Inorganic Hg is transported to aquatic ecosystems via the atmosphere, and it is converted to methyl mercury (MeHg) under anaerobic conditions in water-logged soils and sediments. MeHg is more toxic than inorganic forms, and it is more readily bioaccumulated and biomagnified. The processes of MeHg production and subsequent bioaccumulation in aquatic organisms, particularly fish and piscivorous birds and mammals, has been the subject of intense research (reviewed in Mason and Benoit 2003). In the past several years, elevated concentrations of MeHg have also been measured in songbirds that live in the proximity of contaminated rivers and marshes (Cristol et al. 2008; Tsipoura et al. 2008) and even in montane environments (Rimmer et al. 2005). These studies suggest links between MeHg production in aquatic environments and bioaccumulation in avian insectivores, but further investigation is needed to identify sources of MeHg to terrestrial food webs (Evers et al. 2005; Cristol et al. 2008). Vernal pools, abundant features of New England forests (e.g. Brooks et al. 1998), represent potential "hot spots" for MeHg production in forested landscapes.

Seasonally-flooded forest pools, hereafter called vernal pools, share several characteristics: they occur in wooded areas, possess no permanent inlet or outlet, are small and shallow, are only seasonally filled, and lack established fish populations (Colburn 2004). Absence of fish predators allows vernal pools to support rich assemblages of invertebrates (Colburn et al. 2008) and to provide critical breeding habitat for amphibians, including salamanders and wood frogs (Semlitsch and Skelly 2008). Although Hg contamination has been suggested as a potential contributor to amphibian decline (Bank et al. 2006), limited information is available about Hg biogeochemistry in vernal pools (Brooks et al. 2012). However, they are likely sites of significant MeHg production due to the combination of high organic matter and inorganic Hg inputs (Benoit et al. 2003) and enhanced MeHg bioaccumulation caused by periodic inundation (Snodgrass et al. 2000; Hall et al. 2005). Vernal pools are

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linked to the surrounding forest through insects that use them as larval habitat, and insect emergence could represent a significant route of MeHg transfer into upland forests (Cristol et al. 2008).

In the current study, we investigated mercury biogeochemistry in a New England vernal pool with special attention to MeHg production over an annual wet-dry-wet cycle. We quantified the flux of total Hg (HgT) via litterfall and monitored changes in the MeHg content of the leaf litter layer in the pool and on the surrounding forest floor. These changes were used to calculate the *de novo* MeHg production rate in the vernal pool. We also determined the MeHg and HgT concentration profiles in soils beneath the vernal pool. Finally, we measured bioaccumulation factors for fauna living in the vernal pool litter layer to ascertain the extent to which MeHg is taken up at the base of the detrital food web.

## Materials and Methods

### Study Site

The pool chosen for the study is on the Wheaton College Campus (N41°57′49″,W71°11′00″) in Norton, Massachusetts. It is one of 98 vernal pools in the town of Norton certified by the Massachusetts Natural Heritage Program (http://www.mass.gov/dfwele/dfw/nhesp/nhesp.htm). The maximum area of this pool is approximately 121 $m^2$ and it occurs in a mixed-wood forest consisting primarily of black oak *(Quercus velutina),* American beech (*Fagus grandifolia*), red maple (*Acer rubrum),* Norway maple (*Acer platanoides*), white pine (*Pinus strobus*), red pine (*Pinus resinosa)* and Norway spruce (*Picea abies).* The pool typically fills in early fall, remains flooded through spring and dries out in mid- to late summer. The vernal pool lies within 11 m of a parking lot that is routinely used for storage of plowed snow. This proximity likely affects water quality due to runoff from the paved surface. In particular, dissolved chloride levels are elevated relative to more pristine pools. A study comparing the Wheaton vernal pool to two other local pools that are more distant from impervious surfaces found that the chloride concentration and conductivity were consistently about 5-fold higher in the Wheaton vernal pool compared to the other two (A. Demers, Honors Thesis, Wheaton College, 2002). The chloride level (see below) probably has little impact on Hg speciation, but may negatively affect the vernal pool diversity.

The pool has been the focus of study for Wheaton College's vernal pool research team of faculty and students since 1996. As of spring 2009 there were 329 individually documented yellow-spotted salamanders (*Ambystoma maculatum*) found in the pool during the spring migration. Wood frogs (*Rana sylvatica)* and spring peepers (*Pseudacris crucifer)* also frequent this ephemeral pool. Commonly found invertebrates include the following orders, Amphipoda, Bivalvia, Diptera, Gastropoda, Isopoda, Megaloptera, Odonata and Oligochaeta. Anion analysis of water samples collected in the fall and spring of the study indicated the following concentrations: chloride 60±10 mg $L^{-1}$, nitrate 1.9±0.5 mg $L^{-1}$, and sulfate 10±2 mg $L^{-1}$. These levels are consistent with earlier long-term water quality measurements taken in this vernal pool.

### Sample Collection and Preparation

Acid-cleaned polypropylene containers were used for all mercury samples. Trace-metal-free protocols were followed during all stages of sample collection, handling, storage and analysis. Freshly fallen leaves were collected on plastic mesh screens secured to the forest floor just outside the vernal pool from Oct 6 to Dec 12 in 2010. Fresh litterfall was removed from the screens approximately every week, transferred to plastic bags, and frozen until analysis. These collections were used to measure the flux of HgT and MeHg to the forest floor from litterfall.

Leaf litter directly from the forest floor was collected using gloved hands on six occasions between Jun 2010 and Mar 2011. Three sites within the pool boundary (dry or wet) and three sites around the perimeter were sampled on each occasion. The top layer of loose material (the Oi horizon), which consisted primarily of fresh or partially decomposed leaves, was gently scraped off and placed in a plastic bag. Care was taken not to include any of the underlying soil layers. Only large sticks (>1 cm diameter) were removed from the litter samples, whereas other materials, e.g., twigs or acorns, were included. Samples collected from inside the pool while it was inundated included any periphyton growing on the litter surface at the time of sampling. Our intention was to measure changes in MeHg and HgT in the surface litter layer over the course of the study in order to: 1) compare temporal changes inside and outside the pool, and 2) estimate MeHg production in the vernal pool after the dry-to-wet transition.

The vernal pool traversed a full flooding cycle (from wet to dry and back to wet again) over the course of the study period. The litter samples inside the vernal pool were always taken in the wet part of the pool, even if it was only partially filled. During the dry period (Aug sampling date) the samples were taken from within the area that typically is inundated each year. The litter layer was thin and highly broken down inside and outside the pool at this time. After leaves began to fall in October through the end of the study in March, the litter layer consisted of largely intact leaves and needles. The litter became darker in color and only somewhat more broken up throughout inundation.

Invertebrates were collected from separate leaf litter collections in the vernal pool in March and May 2011. The litter was scooped off of the bottom with a 500-μm mesh nylon net and delivered into a plastic bin. In the laboratory, portions of the

litter were examined under a dissecting microscope and macroinvertebrates were picked out and identified to the order level using a taxonomic guide (Vorshell and Bartle Wright 2002). Several individuals of the same order were placed together in plastic vials and frozen. A number of individuals were combined for analyses, as indicated in Table 1. For sow bugs, which were both large and abundant, replicate analyses were possible; these replicates indicate a variability of about 15 %. In order to assess bioaccumulation at the base of the detrital food web, bioaccumulation factors (BAF= $[MeHg]_{organism}/[MeHg]_{litter}$) were calculated for shredders (scuds and sowbugs) using the MeHg concentration in the leaf litter from which they were obtained. Two larval insects (mosquitoes and caddisflies) were included because of their potential to export MeHg upon emergence from the pool. For these invertebrates the MeHg concentrations of the diet was unknown, so BAFs could not be calculated.

In June 2012 three soil cores were taken from inside the vernal pool to determine subsurface MeHg accumulation. First, the surface litter layer was removed and then cores were inserted by hand into the soil. For this study, soil refers to everything below the loose litter layer on the surface, including the Oe and Oa horizons and underlying soil horizons. The cores were extruded in the laboratory and sectioned into 2-cm sections, which were placed in acid-cleaned polypropylene jars and frozen. Prior to analysis the sections were thawed and homogenized with a hand blender with a stainless-steel blade. Wet to dry weight ratios were determined in replicate samples, and the ratios were used to express concentrations on a dry weight basis.

All litter samples for HgT and MeHg analysis were dried for 24 h at 70 °C and ground in a glass blender with a stainless steel blade to provide a homogeneous powder. We verified that the drying method caused neither the loss nor gain of MeHg by running a comparison. One group of litter subsamples ($n$=5) was analyzed prior to drying and corrected for percent moisture, while a replicate group ($n$=5) was dried prior to analysis. The mean MeHg concentrations, 6.0±0.5 pg $gdw^{-1}$ for dried samples and 5.8±0.6 pg $gdw^{-1}$ for wet samples, were not significantly different between the two groups. Drying prior to analysis allowed for more thorough homogenization and provided better precision, so this method was chosen for the litter analyses. Invertebrate samples were dried and analyzed intact. Several organisms were used for each analysis in order to provide sufficient mass for detection of MeHg.

## Analytical Methods

Methods for mercury species were consistent with our previous work in other aquatic environments (e.g., Gilmour et al. 1998; Benoit et al. 2009). HgT concentrations were determined by acid digestion, $SnCl_2$ reduction, purge and trap on gold, thermal desorption and CVAFS detection (Gill and Fitzgerald 1987; Bloom and Fitzgerald 1988). This method measures all forms of Hg present in the sample. Since MeHg represents a small fraction of the total, HgT consists primarily of inorganic Hg species. MeHg concentrations were determined by distillation (Horvat et al. 1993), aqueous-phase ethylation, purge and trap, gas chromatographic separation of ethylated species, pyrolytic decomposition and cold-vapor atomic fluorescence (CVAFS) detection (Bloom 1989). Certified reference materials, MESS-3 (National Research Council of Canada) and IAEA-405 (International Atomic Energy Agency) were used to assess accuracy for HgT and MeHg, respectively. We measured an average ($n$=4) HgT concentration of 89.8±5.1 μg $g^{-1}$ in MESS-3, which is within the certified range of 82–100 μg $g^{-1}$. For IAEA-405, our measured average ($n$=4) MeHg concentration of 5.74±0.64 ng $g^{-1}$ also fell within the certified range of 4.96−6.02 ng $g^{-1}$. Analytical uncertainties were determined using triplicate sample measurements and expressed as % relative standard deviation; they were 6.5 % ($n$=4 triplicates) for HgT and 8.6 % ($n$=4 triplicates) for MeHg. Spike recoveries for MeHg were 1.02±0.11 ($n$=3). Detection limits, expressed on a dry-weight basis were 0.8 ng $g^{-1}$ for HgT and 0.04 ng $g^{-1}$ for MeHg. Excess inorganic mercury was added to samples in four of the distillation runs to check for artifactual MeHg formation, and none was detected. Dissolved chloride, nitrate, and sulfate in pool water were measured with a Dionex Ion Chromatogaph.

**Table 1** MeHg concentrations and bioaccumulation factors (BAF=$[MeHg]_{organism}/[MeHg]_{litter}$) in invertebrates collected from the litter layer in the Wheaton Woods vernal pool

| Common name | Order | # of individuals | MeHg conc. (ng $gdw^{-1}$) | BAF |
|---|---|---|---|---|
| Caddisfly larvae | Trichoptera | 4 | 17 | na |
| Mosquito larvae | Diptera | 6 | 34 | na |
| Scuds | Amphipoda | 8 | 21 | 4 |
| Sow bugs | Isopoda | 5 small | 52 | 10 |
| | | 5 small | 41 | 8 |
| | | 3 large | 46 | 9 |
| | | 3 large | 58 | 11 |

## Results

Cumulative HgT deposition via autumn litterfall is shown in Fig. 1. HgT concentration was remarkably constant over the course of the litter collections, with an average across all dates of 33±2 ng gdw$^{-1}$. Fresh litter also contained a relatively constant MeHg concentration of 0.27±0.05 ng gdw$^{-1}$, which corresponds to an average of 0.9±0.1 % MeHg in fresh litter. Leaf mass and HgT both showed the same trend of maximum flux between mid-October and mid-November with tapering off thereafter (Fig. 1).

HgT and MeHg concentrations were measured in surface leaf litter samples inside and outside the vernal pool between Jun 2010 and Mar 2011 (Fig. 2). Temporal trends in MeHg concentration in leaf litter were markedly different inside and outside the pool. On the first sampling date in June 2010, the pool was fully flooded. MeHg concentration in leaf litter averaged 5±1 ng/gdw inside the pool and 0.66±0.05 ng gdw$^{-1}$ on the surrounding forest floor. In August, after the vernal pool had dried up, these concentrations had not changed much, which suggests that MeHg in leaf litter is preserved when the pool dries up. As the pool began to fill in November, the concentrations inside and outside were the same, 0.29±0.03 ng gdw$^{-1}$ and 0.26±0.03 ng gdw$^{-1}$, respectively. These levels were indistinguishable from litterfall collected directly from the trees. The fresh litterfall buried the previous surface layer, thereby greatly reducing the MeHg concentration in the litter layer inside the pool. When the pool was fully flooded in January, MeHg in the pool litter layer had increased to 1.5±0.2 ng gdw$^{-1}$, but it had increased only slightly outside. By late May, the MeHg concentration inside the pool had increased to 4.7±0.2 ng gdw$^{-1}$, a level similar to what was observed in the previous June (Fig. 2a).

By comparison, changes in HgT were more subtle both inside and outside the pool (Fig. 2b). As was seen for MeHg, minimum HgT concentrations were observed in October after leaves began to fall, but before the pool was fully flooded. The HgT concentration increased through the winter and spring with a somewhat greater change inside the vernal pool than out. The observed increases in HgT likely resulted from loss of the leaf litter matrix as litter decomposed. The slight increase in MeHg concentration in leaf litter outside the pool might occur through the same mechanism. However, the large increase in MeHg in the pool leaf litter cannot wholly be explained in this way. Observed changes in %MeHg (Fig. 2c) indicate that the fraction of HgT in the form of MeHg increased by a factor of 10 after the pool flooded, indicating that net MeHg production occurred in the flooded leaf layer of the vernal pool.

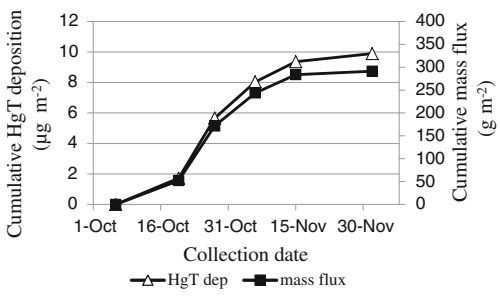


**Fig. 1** The cumulative deposition of total Hg and leaf mass at Wheaton's vernal pool from Oct 6 to Dec 2, 2010

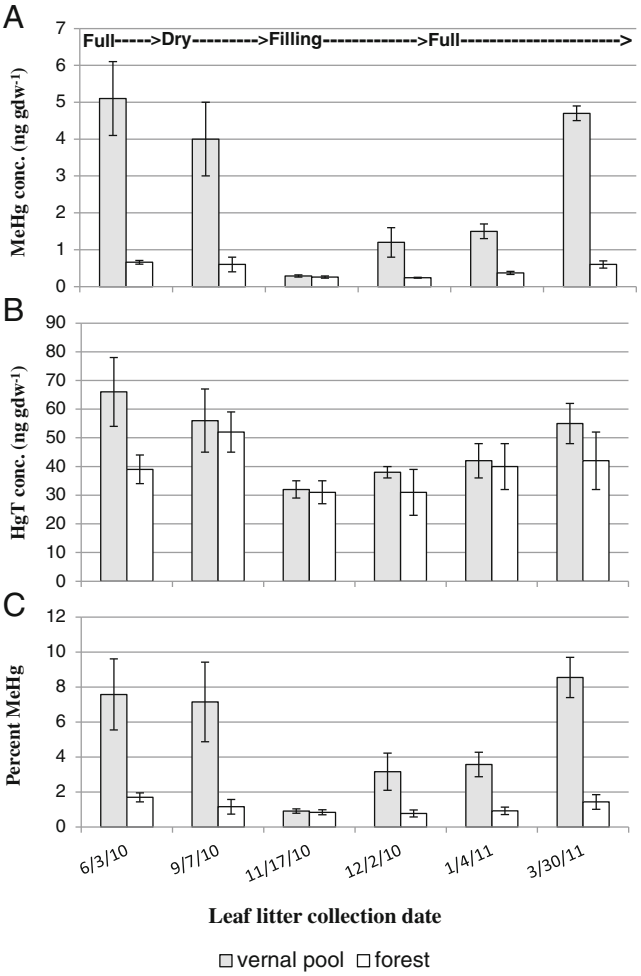


**Fig. 2** Changes in HgT and MeHg concentrations in the surface litter layer in and around Wheaton's vernal pool

Soil profiles showed a rapid decrease in MeHg concentration and %MeHg with depth below the soil surface (Fig. 3a). The average soil MeHg concentration declined from 2.3±0.2 ng gdw$^{-1}$ between 0 and 2 cm depth to 0.4±0.2 ng gdw$^{-1}$ between 8 cm and 12 cm depth. Litter MeHg concentration on the sampling date (5/3/2011) was 3.3±0.9 ng gdw$^{-1}$. On the other hand, HgT remained constant with soil depth at 220±30 ng gdw$^{-1}$ (not shown); therefore, the %MeHg decreased with depth. The organic matter content (%LOI; Fig. 3b) showed a trend with depth similar to MeHg concentration. The decline in organic matter is consistent with the observation that the soil column consisted of consolidated

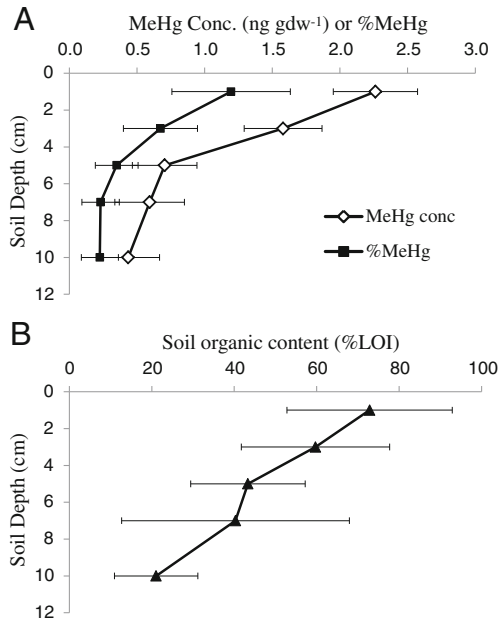


**Fig. 3** The average MeHg concentration (ng/gdw) and organic matter content (%LOI) in soil profiles collected 5/3/11 from inside the vernal pool. Error bars represent one standard deviation ($n$=3)

course organic material near the top that graded into a mix of fine particulate matter and clay below.

MeHg concentrations were measured in several types of invertebrates from the vernal pool leaf litter layer during inundation (Table 1). Sow bugs had the highest MeHg concentrations, which were independent of the size of the organism. Scuds had about half the MeHg concentration and BAF compared to sow bugs, and insect larvae MeHg concentrations were somewhat lower than sow bugs.

## Discussion

Deposition via litterfall provided a large source of HgT to the forest floor. The HgT deposition of 10 μg HgT $m^{-2}$ from October 6 to December 2, 2010 (Fig. 1) was twice the annual wet deposition of 5 μg HgT $m^{-2}$ measured at the nearest NADP Mercury Deposition Network station in Barnstable, MA (http://nadp.sws.uiuc.edu/). The HgT deposition rate from leaf litter in Wheaton Woods is quite similar to prior measurements in other northern forests, as shown in Table 2. The average %MeHg in litterfall, 0.9±0.1 %, falls within the range observed by Risch et al. (2012) in litterfall across fifteen eastern US states representing six forest cover types. Previous studies have shown that the bulk of Hg in forest foliage is derived from the atmosphere rather than uptake from soil water, indicating that litterfall represents a new source of HgT to the forest floor each year (Ericksen et al. 2003; Bushey et al. 2008). At our site, a load of litterfall is delivered to the pool as it fills, providing both fresh organic matter and HgT to fuel MeHg production.

The net change in MeHg burden inside the pool was 0.06 % per day between Oct 17 and Mar 30 (Fig. 2a). Mercury methylation in aquatic environments is largely a microbially-mediated process that occurs under anaerobic conditions (Benoit et al. 2003). Although sulfate-reducing bacteria have been indicated as the dominant Hg-methylators in a number of aquatic environments (Compeau and Bartha 1985; Gilmour and Henry 1991; Gilmour et al. 1998), the important methylators in vernal pools have not been identified. It is noteworthy that the sulfate concentration in the vernal pool, about 100 μM, falls within the range associated with high sediment %MeHg in lakes (Benoit et al. 1998). The suitability of leaf litter as a substrate for Hg methylation has also been previously demonstrated. For example, flux of MeHg from decomposing leaf litter due to *de novo* production and leaching has been observed in streams (Balogh et al. 2002), enclosure experiments (Hall et al. 2004), and laboratory incubations (Tsui et al. 2008). Mitchell et al. (2008) found that the concurrent addition of sulfate and leachate from deciduous and coniferous leaf litter substantially stimulated MeHg production in peatland mesocosms. In addition, recent or periodic flooding is known to stimulate Hg methylation. Enhanced production and/or bioaccumulation of MeHg have been associated with periodically-flooded wetlands (Snodgrass et al. 2000; Galloway and Branfireun 2004) and recently-flooded reservoirs (Hall et al. 1998). The combination of suitable sulfate concentration, Hg-laden litterfall loading and seasonal flooding, make this pool an efficient site for MeHg production.

There is undoubtedly considerable variability in MeHg production among vernal pools due to differences in physical and chemical characteristics. Given the role of leaf litter in Hg methylation, it's likely that the type of forest surrounding a vernal pool influences the amount of MeHg produced seasonally. Litterfall HgT concentration and annual deposition varies with different forest cover types (e.g., Risch et al. 2012). Also, it has been demonstrated that needles from softwoods produce more MeHg during decomposition than do leaves of hardwood species (Hall et al. 2004; Tsui et al. 2008). It also follows that the degree of canopy closure will control the amount of litterfall and HgT deposited to a vernal pool; therefore, it will influence the amount of MeHg produced. However, Brooks et al. (2012) found no significant relationship between canopy closure and MeHg concentrations in detrital and biotic components in twenty vernal pools. Finally, MeHg production in vernal pools is likely influenced by water quality characteristics, as has been observed in freshwater lakes (reviewed in Mason and Benoit 2003). In particular, Hg methylation is sensitive to pH, dissolved organic carbon, and sulfate concentration. Tsui et al. (2008) investigated the impact of water type on MeHg

**Table 2** Litterfall HgT concentrations and deposition rates at selected forest sites in the US and Canada

| Location | Forest type | Litterfall HgT concentration (ng $gdw^{-1}$) | Annual litterfall HgT deposition (μg $m^{-2}$) | reference |
|---|---|---|---|---|
| Wheaton Woods, MA | mixed | 33±2 | 10* | This study |
| Eastern USA (15 states) | mixed | 41.1 (21.4–62.7) | 12.3 (3.5–23.4) | Risch et al. 2012 |
| Acadia National Park, ME | mixed | 42±3 | 10 | Sheehan et al. 2006 |
| Adirondack region, NY | hardwood<br>softwood | 57±2<br>39±9 | 15<br>10 | Demers et al. 2007 |
| Lake Huron watershed, MI | hardwood | 33±8 | 11 | Rea et al. 2002 |
| Lake Champlain watershed, VT | mixed | 47±6 | 16 | Rea et al. 2002 |
| Experimental Lakes Area, Ontario | mixed | 42±19 | 14 | St. Louis et al. 2001 |

*Collections from Oct 6 to Dec 2, 2010; does not include chronic litter from softwoods

release by decomposing leaf litter in laboratory incubations. These authors found a 50-fold range in the amount MeHg released from maple leaf litter across a number of different stream water types. They also found that MeHg concentrations were positively correlated with dissolved sulfate, total suspended solids and chlorophyll-a concentrations in the incubation waters. Clearly, additional investigation is needed to ascertain the impact of these and other pool and forest variables on MeHg production in vernal pools.

High levels of MeHg in leaf litter in the bottom of the Wheaton Woods vernal pool present the possibility of bioaccumulation in the pool food web and export outside the vernal pool. Invertebrate shredders, represented by scuds and sow bugs, had MeHg concentrations of 21 and 49 ng $gdw^{-1}$, respectively. These organisms bioaccumulated MeHg 4–9 fold relative to the leaf litter. Shredders provide a link between detritus and organisms that prey upon them, so they could serve as a conduit for MeHg into higher levels of the vernal pool food web. Alternatively, trophic transfer of MeHg outside the vernal pool could occur through their predation by terrestrial animals that feed in the pool. Larval insects, caddisflies and mosquitoes, showed MeHg concentrations that were similar to levels reported in Massachusetts and Minnesota vernal pools with short hydroperiods (Brooks et al. 2012). Insects that spend their larval stages in vernal pools could export MeHg to the surrounding forest upon emergence, as has been previously demonstrated for reservoirs (Tremblay et al. 1998). Avian abundance and diversity tends to be greater at seasonal pools than at upland sites (McKinney and Paton 2009), so this export process could readily transfer MeHg into insectivorous birds.

Soil profiles provide evidence of the long-term fate of MeHg produced in the vernal pool. The sharp decline in %MeHg with depth (Fig. 3a) suggests that MeHg is preferentially lost over HgT as soil accumulates. As found in this study, Obrist (2012) observed higher MeHg concentration and %MeHg in litter compared to underlying soils in fourteen upland forests across the US. In contrast, profiles in estuarine sediments (Benoit et al. 2006; Hammerschmidt et al. 2004) and Everglades soils (Gilmour et al. 1998) typically show subsurface peaks in MeHg concentration. There are at least three possible mechanisms that could produce the observed vernal pool %MeHg soil profiles. First, loss of organic matter could lead to lower partitioning of MeHg to the solid phase relative to HgT. However, particle-water partition coefficients ($K_d$) measured in estuarine sediments ranged from $10^2$–$10^3$ L $kg^{-1}$ for MeHg and $10^3$–$10^5$ L $kg^{-1}$ for HgT, with $K_d$ decreasing in a similar manner for both species as sediment organic content decreased (Hammerschmidt et al. 2004). This observation suggests that lower organic matter content deeper in the soil cores (Fig. 3b) would not lead to preferential exchange of MeHg into soil pore waters while HgT remains on the solid phase. Second, MeHg may be demethylated as organic matter is remineralized during soil formation. The constant %MeHg below 6 cm could be explained as a recalcitrant MeHg fraction that neither exchanges readily nor is available for demethylation. Finally, MeHg may be lost from vernal pool soils via uptake into benthic organisms and trophic transfer to organisms that leave the vernal pool.

This study documents the production of MeHg in the leaf litter layer of a small, forested vernal pool. A ten-fold increase in the concentration and %MeHg occurred in the layer after it was flooded, while little change was observed in the same layer on the surrounding forest floor. These results provide further evidence that leaf litter is a potent substrate for MeHg production, and they suggest that Hg methylation may occur whenever leaf litter encounters waterlogged conditions. Although this study looks at a single vernal pool, seasonal Hg methylation is likely a feature of many other forested vernal pools in the northeastern US. Limited measurements of MeHg in benthic macroinvertebrates suggest that MeHg is transferred from leaf litter into the vernal pool food web. Further research is needed to ascertain how factors such as water chemistry, hydroperiod, canopy closure and cover type influence the timing and extent of MeHg production in vernal pools. Additional studies are also needed to determine the

factors that influence bioaccumulation, trophic transfer and export into the surrounding forest ecosystem.

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## References

Balogh SJ, Huang Y, Offerman HJ, Meyer ML, Johnson DK (2002) Episodes of elevated methylmercury concentrations in prairie streams. Environmental Science and Technology 36:1665–1670

Bank MS, Crocker JB, Davis S, Brotherton DK, Cook R, Behler J, Connery B (2006) Population decline of northern dusky salamanders at Acadia National Park, Maine, USA. Biological Conservation 130:230–238

Benoit JM, Gilmour CC, Heyes A, Mason RP, Miller CL (2003) Geochemical and biological controls on methylmercury production and degradation in aquatic ecosystems. In: Cai Y, Braids OC (eds) Biogeochemistry of Environmentally Important Trace Elements. ACS Symposium Series 835, pp 262–297

Benoit JM, Gilmour CC, Mason RP, Riedel GS, Riedel GF (1998) Behavior of mercury in the Patuxent River estuary. Biogeochemistry 40:249–265

Benoit JM, Shull DH, Harvey RM, Beal SA (2009) Effect of bioirrigation on sediment-water exchange of methylmercury in Boston Harbor, Massachusetts. Environmental Science and Technology 43:3669–3674

Benoit JM, Shull DH, Robinson P, Ucran LR (2006) Infaunal burrow densities and sediment monomethyl mercury distributions in Boston Harbor, Massachusetts. Marine Chemistry 102:124–133

Bloom NS (1989) Determination of picogram levels of methylmercury by aqueous phase ethylation, followed by cryogenic gas chromatography, with cold-vapor atomic fluorescence detection. Fresenius' Journal of Analytical Chemistry 46:1131–1140

Bloom NS, Fitzgerald WF (1988) Determination of volatile mercury at the picogram level by low-temperature gas chromatography with cold vapor atomic fluorescence detection. Analytica Chimica Acta 208:151–161

Brooks RT, Eggert SL, Nislow KH, Kolka RK, Chen CY, Ward DM (2012) Preliminary assessment of mercury accumulation in Massachusetts and Minnesota seasonal forest pools. Wetlands 32:653–663

Brooks RT, Stone J, Lyons P (1998) An inventory of seasonal forest ponds on the Quabbin Reservoir watershed, Massachusetts. Northeastern Naturalist 5:219–230

Bushey JT, Nallana AG, Montesdeoca MR, Driscoll CT (2008) Mercury dynamics of a northern hardwood canopy. Atmospheric Environment 42:6905–6914

Colburn EA (2004) Vernal pools: Natural history and conservation. McDonald & Woodward Publishing Co., Blacksburg, 426 pp

Colburn EA, Weeks SC, Reed SK (2008) Diversity and ecology of vernal pool invertebrates. In: Calhoun AJK, deMaynadier PG (eds) Science and conservation of vernal pools in Northeastern North America. CRC Press, Boca Raton, pp 105–126

Compeau GC, Bartha R (1985) Sulfate-reducing bacteria: Principle methylators of mercury in anoxic estuarine sediments. Applied and Environmental Microbiology 50:498–502

Cristol DA, Brasso RL, Condon AM, Fovargue RE, Friedman SL, Hallinger KK, Monroe AP, White AE (2008) The movement of aquatic mercury through terrestrial food webs. Science 320:335

Demers JD, Driscoll CT, Fahey TJ, Yavitt JB (2007) Mercury cycling in litter and soil in different forest types in the Adirondack Region, New York, USA. Ecological Applications 17:1341–1351

Ericksen JA, Gustin MS, Schorran DE, Johnson DW, Lindberg SE, Coleman JS (2003) Accumulation of atmospheric mercury in forest foliage. Atmospheric Environment 37:1613–1622

Evers DC, Burgess NM, Champoux L, Hoskins B, Major A, Goodale WM, Taylor RJ, Poppenga R, Daigle T (2005) Patterns and interpretations of mercury exposure in freshwater avian communities in northeastern North America. Ecotoxicology 14:193–221

Galloway ME, Branfireun BA (2004) Mercury dynamics of a temperate forested wetland. Science of the Total Environment 325:239–254

Gill GA, Fitzgerald WF (1987) Picomolar mercury measurements in seawater and other materials using stannous chloride reduction and two-stage gold amalgamation with gas phase detection. Marine Chemistry 20:227–243

Gilmour CC, Henry EA (1991) Mercury methylation in aquatic systems affected by acid deposition. Environmental Pollution 71:131–169

Gilmour CC, Riedel GS, Ederington MC, Bell JT, Benoit JM, Gill GA, Stordal MC (1998) Methylmercury concentrations and production rates across a trophic gradient in the northern Everglades. Biogeochemistry 40:327–345

Hall BD, Rosenberg DM, Wiens AP (1998) Methyl mercury in aquatic insects from an experimental reservoir. Canadian Journal of Fisheries and Aquatic Sciences 55:2036–2047

Hall BD, St. Louis VL, Bodaly RA (2004) The stimulation of methylmercury production by decomposition of birch leaves and jack pine needles. Biogeochemistry 68:107–129

Hall BD, St. Louis VL, Rolfhus KR, Bodaly RA, Beaty KG, Paterson MJ, Peech Cherewyk KA (2005) Impact of reservoir creation on biogeochemical cycling of methyl mercury and total mercury in boreal upland forests. Ecosystems 8:248–266

Hammerschmidt CR, Fitzgerald WF, Lamborg CH, Balcom PH, Visscher PT (2004) Biogeochemistry of methylmercury in sediments of Long Island Sound. Marine Chemistry 90:31–52

Horvat M, Bloom NS, Liang L (1993) Comparison of distillation with other current isolation methods for the determination of methyl mercury compounds in low-level environmental samples: Part 1. Sediments. Analytica Chimica Acta 281:135–152

Mason RP, Benoit JM (2003) Organomercury compounds in the environment. In: Craig PJ (ed) Organometallic compounds in the environment, 2nd edn. Wiley, New York, pp 57–99

McKinney RA, Paton PWC (2009) Breeding birds associated with seasonal pools in the northeastern United States. Journal of Field Ornithology 80:380–386

Mitchell CPJ, Branfireun BA, Kolka RK (2008) Assessing sulfate and carbon controls on net methylmercury production in peatlands: an in situ mesocosm approach. Applied Geochemistry 23:503–518

Obrist D (2012) Mercury distribution across fourteen U.S. Forests. Part II: patterns of methyl mercury concentrations and areal mass of total and methyl mercury. Environmental Science and Technology 46:5921–5930

Rea AW, Lindberg SE, Scherbatskoy T, Keeler GJ (2002) Mercury accumulation in foliage over time in two northern mixed-hardwood forests. Water, Air, and Soil Pollution 133:49–67

Rimmer CC, McFarland KP, Evers DC, Miller EK, Aubry Y, Busby D, Taylor RJ (2005) Mercury concentration in Bicknell's Thrush and other passerines in montane forests of northeastern North America. Ecotoxicology 14:223–240

Risch MR, DeWild JF, Krabbenhoft DP, Kolka RK, Zhang L (2012) Litterfall mercury dry deposition in the eastern USA. Environmental Pollution 161:284–290

Semlitsch RD, Skelly DK (2008) Ecology and conservation of pool-breeding amphibians. In: Calhoun AJK, deMaynadier PG (eds) Science and conservation of vernal pools in Northeastern North America. CRC Press, Boca Raton, pp 127–147

Sheehan KD, Fernandez IJ, Kahl JS, Amirbahman A (2006) Litterfall mercury in two forested watersheds at Acadia National Park, Maine, USA. Water, Air, and Soil Pollution 170:249–265

Snodgrass JW, Jagoe CH, Bryan AL Jr, Brant HA, Burger J (2000) Effects of tropic status and wetland morphology, hydroperiod, and water chemistry on mercury concentrations in fish. Canadian Journal of Fisheries and Aquatic Sciences 57:171–180

St. Louis VL, Rudd JWM, Kelly CA, Hall BD, Rolfhus KR, Scott KJ, Lindberg SE, Dong W (2001) Importance of the forest canopy to fluxes of methyl mercury and total mercury to boreal ecosystems. Environmental Science and Technology 35:3089–3098

Tremblay A, Cloutier L, Lucotte M (1998) Total and mercury and methylmercury fluxes via emerging insects in recently flooded hydroelectric reservoirs and a natural lake. Science of the Total Environment 210:209–221

Tsipoura N, Burger J, Feltes R, Yacabucci J, Mizrahi D, Jeitner C, Gochfeld M (2008) Metal concentrations in three species of passerine birds breeding in the Hackensack Meadowlands of New Jersey. Environmental Research 107:218–228

Tsui MTK, Finlay JC, Nater EA (2008) Effects of stream water chemistry and tree species on release and methylation of mercury during litter decomposition. Environmental Science and Technology 42:8692–8697

Vorshell JR, Bartle Wright A (2002) Guide to common freshwater invertebrates of North America. McDonald and Woodward Publishing Co, Blacksburg