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Mercury bioaccumulation in temperate forest food webs associated with headwater streams

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HIGHLIGHTS

- Small-scale spatial variation in Hg bioaccumulation in a forest was investigated.
- Soil chemistry was a good predictor of total Hg but not of MeHg bioaccumulation.
- Methylation of Hg was greater in upland areas compared to streamside environments.
- MeHg varied among taxa and was related to trophic position ($\delta^{15}N$) and location.
- MeHg and bioaccumulation are important issues for forests of eastern North America.

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ABSTRACT

The soils and food webs associated with mid to high elevation, forested, headwater streams in northeastern North America are potential hotspots for mercury (Hg) methylation and bioaccumulation, but are not well studied. Our goals were to quantify total Hg (THg) and methyl Hg (MeHg) concentrations in soils and terrestrial food webs associated with headwater streams of northern hardwood forests to identify predictors of small-scale spatial variation in Hg bioaccumulation. We sampled soil characteristics that promote Hg methylation including pH, sulfur and calcium content, and organic matter. To assess spatial variation, we sampled at high (~700 m asl) and mid elevations (~500 m asl), both adjacent to (<1 m) and away from (>75 m) three replicate headwater streams in each of two watersheds of the White Mountains region, New Hampshire, USA. Soils of these forested watersheds differed significantly in pH and the content of calcium, sulfur, organic matter and THg. Conditions for methylation were more favorable in the upland forest sites compared to streamside sites. Significant bioaccumulation of THg occurred in all measured components of the food web, including insects, spiders, salamanders, and birds. Trophic position, as determined by $\delta^{15}N$, was the best predictor of both THg and MeHg bioaccumulation across the sampled taxa and was also a better predictor than spatial location. However, the degree of bioaccumulation at which MeHg significantly affects animal behavior, reproduction or survival is unknown for most taxa in terrestrial habitats, particularly for invertebrates. These findings show that Hg methylation and bioaccumulation is not limited to areas traditionally classified as wetlands or to areas with exceptionally high THg inputs, but that it is a widespread and important phenomenon in the moist deciduous forests of eastern North America.

1. Introduction

Deposition of mercury (Hg) is high in the northeastern U.S.A. (Miller et al., 2005; Driscoll et al., 2007), and northern forest ecosystems can be sensitive to Hg inputs where damp, anoxic, acidic soils with high content of sulfur and organic matter favor methylation (Wiener et al., 2003; Scheuhammer et al., 2012). Inferential statistical models indicate that Hg deposition can be 2 to 5 times higher in montane areas than in surrounding low elevation areas (Miller et al., 2005) and recent observations show that bioaccumulation in high elevation, spruce-fir forest ecosystems is occurring (e.g., Rimmer et al., 2005; Townsend et al., 2014). These data contradict the general perception of Hg

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bioaccumulation as a lowland or strictly aquatic problem, and suggest that the regional extent of Hg contamination in ecosystems of the Northeast might be larger than previously thought (Shanley et al., 2008). Like in lowland systems (e.g., Chen et al., 2005; Pickhardt et al., 2002), information on both the abiotic conditions enhancing Hg bioaccumulation and the ecological pathways promoting biomagnification in upland forest food webs will be critical to understanding and projecting the spatial and temporal pattern of effects of Hg pollution, and to identifying mitigation strategies.

Montane hardwood forests in the Northeast are covered by a network of small streams that include many sites where conditions for Hg methylation are ideal, including seepage areas, debris dams, lateral seeps, saturated splash zones, saturated forest soils, etc. (Lee et al., 2000; Bernhardt et al., 2003; Likens and Buso, 2006). Drying and rewetting of the streamside also sustains high soil moisture associated with methylation; however, soil moisture content likely declines away from the stream channel (Likens, 2013; Naiman et al., 2005). Because of their small size, patchy distribution and upland location, headwater streams have seldom been sampled in surveys of MeHg contamination (Bank et al., 2005); hence, their contributions to regional contamination are not well known.

A growing body of evidence suggests that Hg bioaccumulation and biomagnification is occurring within the linked, terrestrial-aquatic food webs of headwater areas of the Northeast. Salamanders, web-building spiders and birds have been reported to bioaccumulate Hg and MeHg. Elevated levels of MeHg were found in both larvae and adults of the northern two-lined salamander (*Eurycea bislineata*) at two forested national parks with no point sources (Bank et al., 2005). In addition, web-building spiders of the family Araneidae bioaccumulate Hg through their diet of flying insects from both terrestrial and aquatic habitats (Collier et al., 2002; Rimmer et al., 2010; Wyman et al., 2011). Accumulation of Hg in terrestrial birds of the Northeast is also widespread (Evers and Duron, 2006; Townsend et al., 2014) and concentrations are particularly high for birds dwelling in areas with moist soils, such as near wetlands (Cristol et al., 2008; Brasso and Cristol, 2008) or in high elevation spruce-fir forests (Rimmer et al., 2005, 2010).

Food web structure, trophic position, and diet can enhance spatial variation in Hg concentrations (Vander Zanden and Rasmussen, 1996; Driscoll et al., 2007; Jones et al., 2013; Bartrons et al., 2015). More Hg is typically found in organisms occupying higher trophic levels of upland food webs (Cristol et al., 2008, Rimmer et al., 2010) and bioaccumulation in predators or prey may depend on their relative use of aquatic and terrestrial resources (e.g., Nakano and Murakami, 2001; Krell et al., 2015). Because of the many pathways linking the stream and terrestrial food webs associated with headwater streams (e.g., the dispersal of insects and amphibians with aquatic larvae), the influence of even small hotspots of Hg bioaccumulation may extend well beyond the stream boundary (Bank et al., 2005; Raikow et al., 2011; Muehlbauer et al., 2014; Howie et al., 2018).

The evidence presented above suggests that headwater systems in the Northeast might be important sites of Hg bioaccumulation and biomagnification. To assess whether headwaters were hotspots of Hg bioaccumulation in uplands of the Northeast (Vidon et al., 2010), and to examine the relative importance of abiotic conditions, including Hg availability and food web structure in causing variability in Hg concentrations, we tested the following two hypotheses. (1) Spatial variation in Hg bioaccumulation in upland taxa associated with headwater streams is explained by variation in soil characteristics promoting Hg methylation, including acidity (pH), organic matter, sulfur (S), and calcium (Ca) (Gabriel and Williamson, 2004). We tested three predictions of this hypothesis: (a) Hg bioaccumulation would be greatest at high elevations adjacent to headwater streams, and decreases away from streams, (b) Hg bioaccumulation would be greater where soil pH is lower and S and organic matter content greater at higher elevations, and (c) the lowest bioaccumulation of MeHg would occur where the buffering capacity of soils, as indicated by soil calcium content, was highest. We expected a positive relationship between THg and MeHg in forest soils and food webs (Obrist, 2012). Second, we hypothesized that trophic position in food webs would be an important determinant of Hg bioaccumulation in upland taxa, and tested these two predictions: (a) Hg and MeHg concentrations would be associated with trophic position in the food web, with highest bioaccumulation in top predators, and (b) predators sampled closer to streams would have greater Hg bioaccumulation, because of their greater dependence on prey from the stream community. Trophic position and carbon sources were determined by analysis of stable isotope tracers ($\delta^{15}N$ and $\delta^{13}C$, respectively).

2. Material and methods

2.1. Study sites and field sampling

To test the hypothesis that spatial variation in Hg bioaccumulation in the upland taxa associated with headwater streams was explained by variation in factors promoting Hg methylation, we sampled soils and focal animal taxa at locations (25 m × 25 m quadrats) along three replicate 1st-order streams within each of the Hubbard Brook (HB) and Jeffers Brook (JB) watersheds which are about 15 km apart in central New Hampshire, U.S.A. (Fig. 1). These watersheds are similar in elevation and slope, but known to differ in soil calcium (Ca) content and pH. Soils at HB are typically acidic and have lower Ca content (Likens, 2013) than those in the JB watershed (S. Baily, pers. comm.). Sampled plots were located between 450 m and 750 m above sea level (asl). This elevation band covers 2882 km^2 in both New Hampshire and Maine or 55% of the total area of the United States EPA White Mountains Ecoregion as determined from the Space Shuttle Radar Topography Mission (http://www2.jpl.nasa.gov/srtm/index.html).

Soils within the area are typically well-drained, coarse-textured spodosols (Likens, 2013). However, significant small scale spatial patterning occurs in the thickness of the O horizons, organic matter content, duration of water saturation, anoxia, and other features that can influence local biogeochemistry (Bailey et al., 2014; Gillin et al., 2015). These soils typically remain damp throughout most of the year, because mean annual rainfall, which is spread evenly throughout the year, averages 1400 mm (Campbell et al., 2007). However, the years sampled, 2008 and 2009, were atypically wet, with mean precipitation of 1630 mm at mid elevation (550 m asl) and 1690 mm at high elevation (750 m asl) (Campbell, 2018).

Because soil pH decreases with increasing elevation, and soil moisture usually declines away from streams, we also stratified sampling by elevation (low: 450–550 m asl vs. high: 650–750 m asl) and lateral position (streamside vs. forest). We sampled only reaches of streams with permanent flow of water and chose as the high elevation sampling location the highest elevation with permanent stream flow. Low elevation sites were located 1000 m downstream from the upper sites as measured along the stream channel. Streamside sites began at the bank-full channel edge and forest sites were located 75 m from the bank-full channel edge; the direction of the forest site from the stream was selected randomly. Data on stream water chemistry throughout the Hubbard Brook Watershed (Likens and Buso, 2006) were used to select replicate streams with typical pH gradients and that did not differ greatly in physical features. The same sampling regime was applied to the three streams in the Jeffers Brook watershed (Fig. 1). No known point-sources of mercury pollution occur in or near the study area and atmospheric deposition in this area is estimated to be lower than other parts of northeastern North America (Miller et al., 2005). Samples were collected between mid-July and early August in both 2008 and 2009 except where noted below. All samples were collected, frozen, lyophilized, and homogenized in I-CHEM™ certified mercury-free vials. Animal samples included the entire animal; egg samples included both the egg and shell, and tail-tips only were collected from

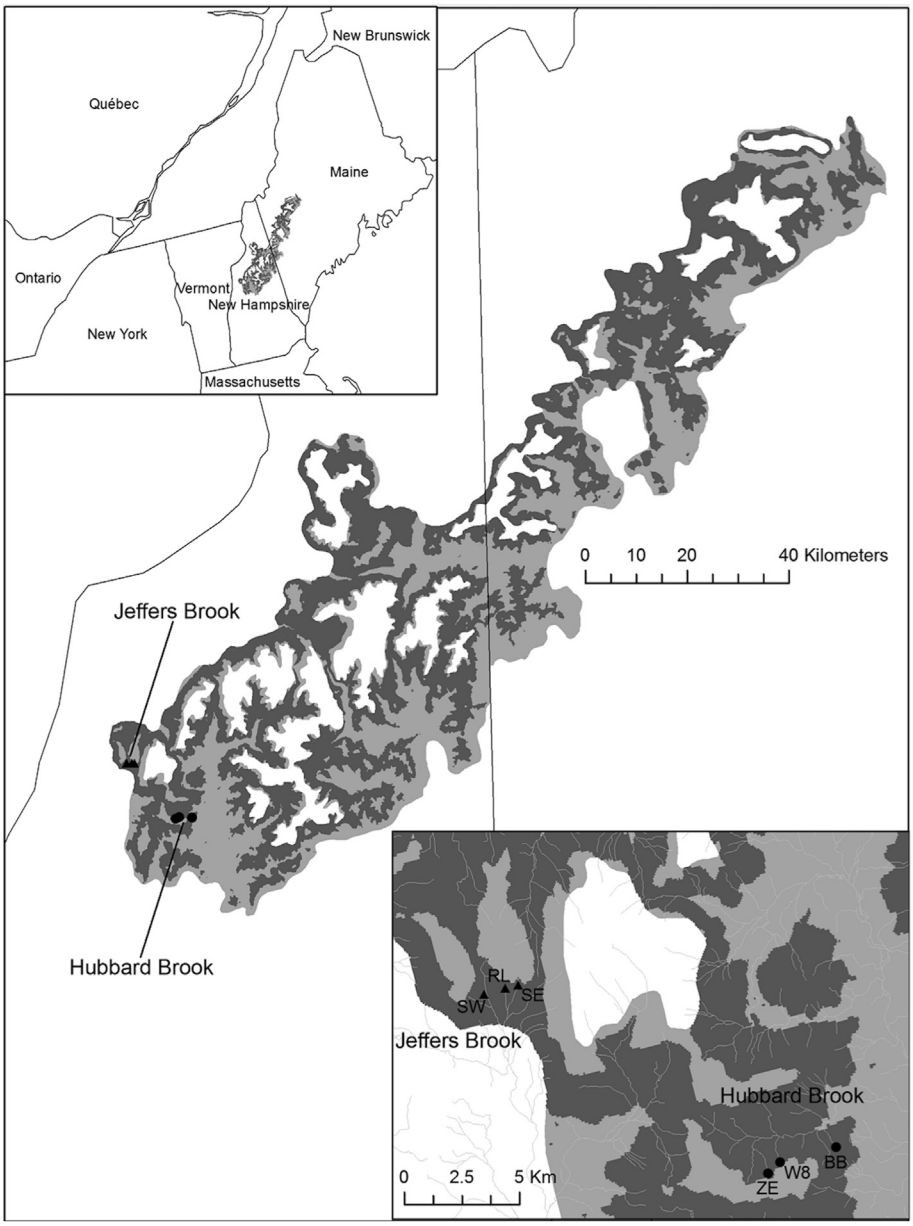

Fig. 1. Location of the watersheds (Jeffers Brook, Hubbard Brook) and streams sampled in 2008 and 2009 within the elevation band (450–750 m asl, dark gray region). Streams in Jeffers Brook watershed are labeled SW, SE and RL; in Hubbard Brook watershed: ZE, W8 and BB. The study area includes a high density of 1st-order streams and covers 54.9% of the White Mountains Ecoregion (region 58p, Level IV, Ecoregions of the Conterminous United States, U.S. Environmental Protection Agency) shown as the light gray region. Enclosed white areas are alpine zones higher than 750 m.

salamanders. Animal samples often included multiple individuals within a taxon that were homogenized together.

Soil characteristics for this study were determined from three composited, replicate 2.5cm diameter cores that included the Oe and Oa horizons. All soil samples were collected in July of 2009. Samples were air-dried, the roots removed, and the remaining material sieved (2 mm grid) before determining soil characteristics. Soil pH was measured by shaking 5 g of soil in deionized water for 24 h and then measuring the pH of the extracted solution with a Fisherbrand accumet AB 15 basic PH meter and electrode. To determine soil organic matter content, a sub-sample was dried at 85 °C for at least 24 h and then weighed before and after combustion at 550 °C for 12 h. Polarized energy dispersive X-ray fluorescence (pED-XRF) was used to determine the Ca and S content of soils (Spectro Xepos, Spectro Analytical, Kleve, Germany). pED-XRF achieved an analytical error of 0.66% for S and 0.37% for Ca ($n = 10$; standards bracketing each of 5 runs). Testing of all field-collected samples via pED-XRF was bracketed with National Institute of Standards and Technology 2709 Standard Reference Material. Measured concentrations of the elements tested remained within 15% of the accepted value for Ca; and within 15% of the mean value of the standards for S. Aliquots of 4 g of soil sample were prepared in XRF sample cups with 4 μm thick Mylar film windows. For each soil characteristic measured (pH, % organic matter, %Ca, %S), values used for analysis were means of two to five subsamples.

To test the hypothesis that trophic position in a food web would be an important determinant of Hg bioaccumulation and biomagnification in upland taxa, we sampled predators and their prey in the foliage and forest floor food webs. Taxa sampled in the foliar food web included web-spinning spiders (Aranea) and abandoned or unhatched eggs of the insectivorous, foliage-gleaning black-throated blue warbler (*Setophaga caerulescens*). Both araneid spiders (Wyman et al., 2011) and birds (Jackson et al., 2015) are known to bioaccumulate Hg in the Northeast. We sampled the insect prey of birds and spiders by using Malaise traps (Bioquip Products, Inc., Model 2875AG). These traps

captured a wide variety of flying insects, essentially all of which are foods of birds (Robinson and Holmes, 1982). We separated taxa within the Malaise samples into two groups: those emerging from aquatic habitats (Plecoptera, Trichoptera, Diptera: Tipulidae) and those emerging from the forest floor (Diptera only typically Muscidae, the larvae of which are detritivores). Lepidoptera were removed from the samples before analysis.

Samples from the forest floor food web included litter arthropods, litter spiders and tail-tips of red-backed salamander (*Plethodon cinereus*). Samples of litter arthropods and spiders were collected by visually searching the forest floor litter and picking out individual invertebrates with gloved hands (powder and mercury-free latex gloves) or tweezers washed between samples with ethanol. Forest floor invertebrates included a variety of arthropods, predominantly millipedes, beetles, centipedes, and unidentified larvae. All samples included a mixture of these taxa. Concentrations of Hg in salamander tail-tips are representative of total-body concentrations (Townsend and Driscoll, 2013), allowing us to sample them non-lethally. Bird eggs were collected in 2009 only.

2.2. Mercury analyses

Analysis for THg content was done by thermal decomposition, amalgamation, and atomic absorption spectrophotometry (EPA method 7473, US EPA, 1998) using a Milestone DMA-80 Direct Mercury Analyzer (Monroe, CT, USA), located at the Harvard School of Public Health Trace Metal Analytical Laboratory (Boston, MA, USA). Instrument level of detection for THg was 0.005 ng and the method detection limit was 0.22 ng/g. Instrument drift and inaccuracy were minimized by analyzing blanks and certified reference material (lobster hepatopancreas; TORT-2; National Research Council Canada, Ottawa, ON, Canada) between every 10 to 15 samples. Recovery of THg in reference material was between 97 and 112% of the certified value.

Methyl mercury (MeHg) analyses were performed at the Dartmouth College Trace Metals Analytical Laboratory (Hanover, NH, USA) on 2009 samples composited from samples of soil (Oe and Oa horizons) and each animal taxon (salamander, bird eggs, litter arthropods, litter spiders, aquatic emergents, forest floor emergents) collected in each watershed (HB, JB) and at each sampling location (high forest, high streamside, low forest, low streamside) according to the methods described by Bank et al. (2007). We were able to analyze only one composite sample from each taxonomic category (e.g., web spiders), so sampling sites showing the lowest variation (i.e., from low and high elevation) were combined for analysis. Replicate sampling for MeHg was not conducted due to the small amount of material available for analysis. Instrument level of detection for MeHg was 50 pg and the method detection limit was 1 ng/g. Recovery of reference material (mussel tissue; SRM 2976; National Institute of Standards and Technology, Gaithersburg, MD, USA) was between 97 and 115% of the certified value.

2.3. Stable isotope analyses

Stable isotope tracers ($\delta^{15}N$ and $\delta^{13}C$) are well-established tools for discerning trophic position ($\delta^{15}N$) and the relative contribution of prey from aquatic versus terrestrial sources ($\delta^{13}C$, e.g., Collier et al., 2002, McCutchan and Lewis, 2002). Because $\delta^{15}N$ increases by 3–4‰ from prey to predator, it can be used to determine the relative trophic position of consumers (Fry, 1991; Vander Zanden et al., 1999; Raikow et al., 2011). Differences in physiology and the carbon sources of terrestrial and aquatic plants at the base of the food web result in different $\delta^{13}C$ values in these environments. Consequently, $\delta^{13}C$ can be used to assess energy flow and the relative contributions of aquatic and terrestrial prey to consumers (Collier et al., 2002; Ogden et al., 2005).

Stable isotopes of $\delta^{15}N$ and $\delta^{13}C$ were measured using 2 mg of sample that were combusted in tin cups with an ECS 4010 CHNSO analyzer equipped with an auto sampler (Costech Analytical Technologies, Valencia, CA, USA) and linked with an isotope ratio mass spectrometer (Delta+, Finnagan, San Jose, CA, USA). Spinach and corn leaves were used as sample standards in order to adjust for instrumental drift. Carbon and nitrogen isotope ratios are expressed in the δ notation in parts per mil (‰) as: $\delta = (R_{sample} / R_{standard} - 1) \cdot 1000‰$ where R is the molar ratio of heavy to light isotopes ($^{15}N/^{14}N$, $^{13}C/^{12}C$). The standard is atmospheric air for nitrogen, and PDB for carbon.

2.4. Statistical analyses

We used Generalized Regression (SAS Institute, 2015) to test for spatial patterning of soil characteristics (Ca, S, pH, organic matter), THg and MeHg. Watershed (HB, JB), location (streamside, forest) and elevation (high, low) were considered fixed effects. Two-way, but not three way interactions were included in the initial model for all tests due to sample size constraints. Generalized regression is well suited for data sets with multiple potentially correlated independent variables (e.g., soil pH and Ca content), and this method functions well with a wide variety of distributions of the dependent variable (SAS Institute, 2015). We used it with the Adaptive Elastic Net technique (e.g., Park and Mazer, 2018) and AICc model validation to aid in reducing model dimensionality for final tests. Data were log transformed as needed to meet the assumptions of the tests used. All analyses were carried out by using JMP® Pro 13 statistical software (SAS Institute, Cary NC).

When simple linear regression was used (e.g., for testing biomagnification), residual plots were examined and robust fit regression (SAS Institute, 2015) was used to determine whether outliers affected the measured relationship. The Robust Fit in SAS JMP employs the Huber M-estimation method. In addition, we tested the relationship with and without the most variable taxon (i.e., the taxon with the greatest CV) to determine whether that particular taxon was obscuring a significant relationship. This approach was justified because limited funding for analyses necessitated the use of broad taxonomic categories, limited knowledge exists about the diet of most of the animals sampled, and multiple individuals often of different species were included in most taxa (e.g., Malaise-detritivores; see Table 2). We calculated trophic magnification slope (TMS) for the regression of $\delta^{15}N$ on either THg or MeHg (Lavoie et al., 2013). TMS represents average biomagnification across multiple trophic levels and is calculated using the following formula: $\log_{10}$ [Hg or MeHg] $= \delta^{15}N\ (b) + a$ where b is the reported slope of the linear regression as described in Lavoie et al. (2013). $b > 0$ indicates significant biomagnification across trophic levels.

3. Results

We hypothesized that spatial variation in Hg bioaccumulation associated with headwater streams could be predicted from variation in factors promoting Hg methylation, including soil acidity (pH), soil content of organic matter, sulfur (S), calcium (Ca), and THg availability. Significant spatial variation in these characteristics was detected between watersheds and location relative to headwater streams, but not between elevations (Table 1). The HB watershed had conditions considered more favorable for mercury methylation relative to the JB watershed: significantly lower pH, about 50% lower calcium content, more organic matter, and greater sulfur content (Fig. 2). Contrary to our expectation, soil characteristics were more favorable for methylation in the forest >75 m away from streams than at streamside sites (Fig. 2). Interestingly, THg in soil was greater where conditions for methylation were more favorable, that is at high elevation, forest sites in the HB watershed (Table 2, Fig. S1). Although there was no significant difference in soil characteristics (pH, S, Ca, organic matter) between low and high elevations (Table 2), THg was 43% more abundant in soils at the high versus low elevation sites (Table 2, Fig. S1).

Despite the strong spatial patterns in soil conditions, we found no evidence that bioaccumulation of THg in the forest food web matched the distribution of THg in soil. Significant differences between

Table 1
Final models for tests of soil characteristics that influence Hg methylation, including pH, % dry mass of Ca, S and organic matter. Samples represent the combined Oe and Oa horizons associated with three replicate headwater streams in two watersheds (Hubbard Brook, Jeffers Brook) in the White Mountains region of New Hampshire, USA. Samples were collected at two elevations (low [~500m asl] and high [~700m asl]) and two locations relative to the streams in each watershed (streamside [<1 m from the channel] and forest [75m away from the channel]) in 2008 and 2009. Results shown were generated by using Generalized Regression (SAS Institute, 2015) followed by the Adaptive Elastic Net technique to reduce model dimensionality and test model validity. Initial models included the main effects of watershed, elevation, and location, as well as all two-way interactions. The dependent variable was the mean of multiple samples per location; $N = 24$ for all tests except pH, which had 19. Nonsignificant effects were not included in the final model and hence are not shown. Test parameters were the following: distribution, normal; estimation method, Adaptive Elastic Net; validation method, AICc; model link, identity. Means ± SE are given in Fig. 2.

Source	pH[a]			Calcium[b]		Sulfur[c]		Organic matter[d]		LogTHg[e]	
	Wald			Wald		Wald		Wald		Wald	
	DF	ChiSq.	P	ChiSq.	P	ChiSq.	P	ChiSq.	P	ChiSq.	P
Watershed	1	13.78	<0.001	42.06	<0.001	4.90	0.03	6.65	0.01	11.42	0.001
Elevation	1									10.41	0.001
Location	1	24.17	<0.001	9.55	0.002			8.51	0.004	3.59	0.058

[a] Final model for pH: $R^2 = 0.72$.
[b] Final model for % Ca: $R^2 = 0.70$.
[c] Final model for % S: $R^2 = 0.26$.
[d] Final model for % organic matter: $R^2 = 0.42$.
[e] Final model for THg (ng/g dry mass): $R^2 = 0.52$.

watersheds, elevations or locations occurred for only two taxa and in each case the difference was opposite that expected based on soil conditions (Table 2). Likewise, the pattern of MeHg in soil did not follow the pattern of THg availability in soil or soil conditions favoring methylation. In fact, we found no spatial patterning in MeHg in soil or among the combined animal taxa (Table S1). It should be noted, however, that samples sizes for MeHg in soil were much smaller than for the animal taxa, and soil content of MeHg was much lower than for samples of biota (soil MeHg median = 0.46 ng/g dry mass, range 0.20–3.37 ng/g; Fig. 3a).

Essentially all of the variability in MeHg was among the animal taxa sampled, following the expected pattern of highest bioaccumulation in top predators: spiders, salamanders and bird eggs (Fig. 3a). The ratio of MeHg to THg differed greatly among predators. MeHg composed about 90% of the Hg in bird eggs, but there were much lower ratios of MeHg to THg in salamanders (56%), and considerably less in spiders (litter spiders 53% and web spiders 37%, Fig. 3b). Across all animal taxa, a significant positive relationship between THg and MeHg was detected (Fig. 4), suggesting that both THg and MeHg were being biomagnified.

Stable isotope analyses of nitrogen and carbon were performed, on all taxa, to quantify the relationship between THg, or MeHg and trophic position (Fig. 5). Linear regression revealed no significant relationship between $\delta^{15}N$ enrichment and THg or MeHg content when all animal taxa were included in the analyses (LogTHg: $F_{1,48} = 1.43$, $P = 0.24$, $R^2 = 0.03$; LogMeHg: $F_{1,43} = 1.24$, $P = 0.27$; $R^2 = 0.03$). However, when the highly variable Malaise-detritivores samples were excluded, $\delta^{15}N$ content predicted significantly both THg and MeHg (Fig. 6; LogTHg: $F_{1,40} = 34.5$, $P < 0.001$, $R^2 = 0.46$; LogMeHg: $F_{1,35} = 13.3$, $P = 0.001$,

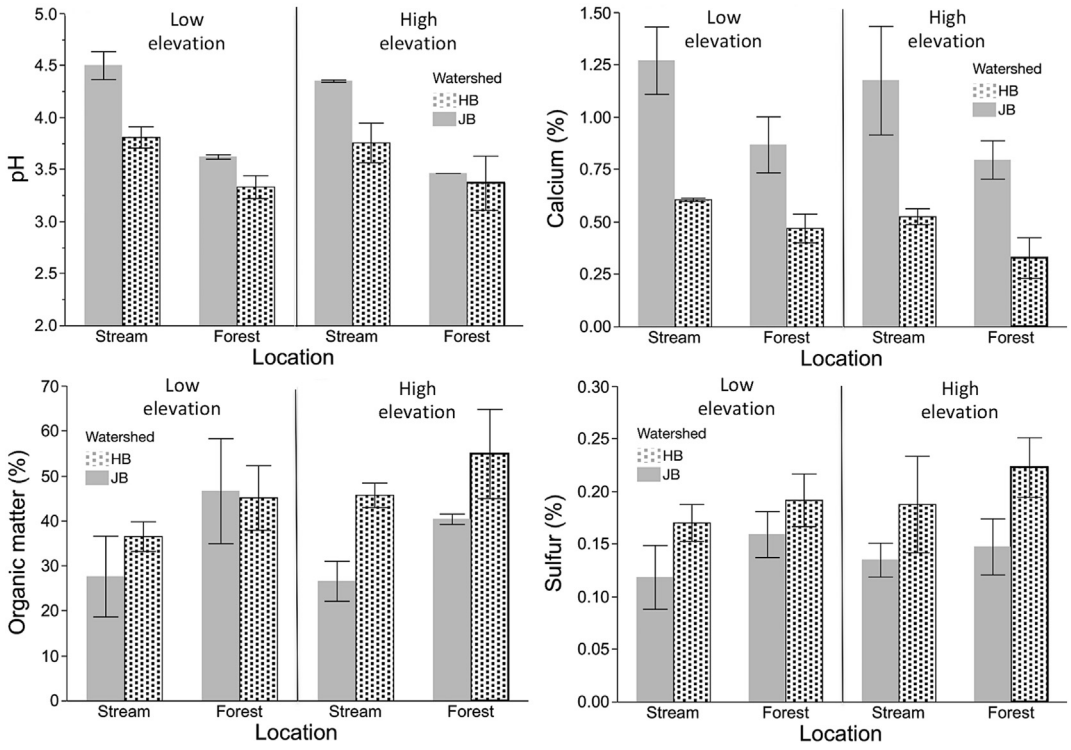

Fig. 2. Soil characteristics (mean ± SE) of three replicate 1st order streams in each of two watersheds (HB, JB), New Hampshire, USA, in 2008 and 2009. Samples were collected at two elevations (low [~500 m asl], high [~700 m asl]) and two locations relative the streams in each watershed (stream [<1m from the channel] and forest [75m away from the channel]). pH differed significantly between watersheds (HB < JB) and locations (forest < stream); calcium differed significantly between watersheds (HB < JB) and locations (forest < stream); percent organic matter in the Oa and Oe horizons differed significantly between watersheds (HB > JB) and locations (forest > stream); sulfur differed significantly between watersheds (HB > JB) only. Statistical results given in Table 1.

Table 2
THg (ng/g dry mass) in soils and multiple animal taxa from three replicate headwater streams in each of two watersheds (Hubbard Brook, Jeffers Brook) in central New Hampshire, USA, in 2008 and 2009. Taxa were sampled at two elevations (low [~500 m asl] and high [~700 m asl]) and two locations relative to the stream in each watershed (stream [<1 m from the channel] and forest [75m away from the channel]). Sample size (N) of means (±SE) are shown. Bold font indicates significant differences as determined using Generalized Regression tests[a] (SAS Institute, 2015) for differences in total mercury content between watersheds, elevations or location relative to the stream.

Taxon	Watershed				Elevation				Location			
	Hubbard Brook		Jeffers Brook		High		Mid		Stream		Forest	
	N[b]	Mean (SE)	N	Mean (SE)	N	Mean (SE)	N	Mean (SE)	N	Mean (SE)	N	Mean (SE)
Soil[c]	**12**	**195.5** (**19.9**)	**12**	**132.1** (**14.0**)	**12**	**192.7** (**18.9**)	**12**	**134.8** (**16.3**)	**12**	**145.4** (**15.1**)	**12**	**182.1** (**22.1**)
Malaise detritvores[d]	12	12.6 (1.7)	19	32.3 (5.2)	15	25.7 (5.4)	16	23.6 (5.1)	15	26.4 (6.2)	16	23.0 (4.2)
Litter arthropods[e]	23	**40.7** (**3.0**)	**20**	**56.0** (**12.5**)	22	39.8 (2.7)	21	56.3 (12.0)	21	58.3 (11.3)	22	37.8 (4.2)
Malaise aquatic[f]	8	38.9 (6.8)	15	78.2 (12.2)	12	63.1 (11.5)	11	66.0 (15.0)	15	68.3 (11.5)	8	57.4 (15.7)
Litter spiders[g]	22	200.9 (13.5)	20	195.5 (20.3)	22	206.0 (19.0)	20	189.9 (13.9)	20	184.7 (12.1)	22	210.7 (19.7)
Web spiders[h]	22	199.2 (10.7)	19	172.2 (9.5)	22	183.6 (10.1)	19	190.2 (11.3)	**20**	**200.9** (**8.9**)	**21**	**173.2** (**11.3**)
Salamanders[i]	23	86.3 (6.1)	18	76.1 (6.1)	21	74.5 (5.4)	20	89.4 (6.7)	19	86.1 (5.8)	22	78.0 (6.5)
BTBW eggs[j]	8	98.4 (26.1)	3	69.6 (23.8)	5	71.1 (13.8)	6	106.8 (34.6)	5	88.5 (39.3)	6	92.3 (20.3)

[a] The initial model included watershed, elevation and location as main effects and two-way interactions; additional statistical details in Material and methods.
[b] Maximum N was 48 but not all types of materials were sampled in each year (e.g., soils were collected in 2009 only) and some materials could not be found at some locations (e.g., emergent aquatic insects).
[c] The mean of two samples taken from composited material were analyzed; see Material and methods.
[d] Malaise detrivores were flying insects captured by Malaise traps with larval stages that feed on detritus (e.g. Muscidae, Rhagionidae).
[e] Litter arthropods were macroarthropods (excluding Chelicerata) common in the forest floor litter, often Diplopoda, Chilopoda, Isopoda, Coleoptera, Hymenoptera: Formicidae.
[f] Emergent adult forms of aquatic insects captured by Malaise traps; predominantly Plecoptera, Trichoptera and Diptera: Tipulidae.
[g] Spiders found in the forest floor litter (e.g., Lycosidae, Erigonidae, Opiliones).
[h] Primarily Araneidae.
[i] Salamanders were all red-backed salamanders (*Plethodon cinereus*). Tail tips only were collected for analysis.
[j] Eggs of black-throated blue warblers (*Setophaga caerulescens*); because so few samples were obtained, we tested only main effects of watershed, elevation and location.

$R^2 = 0.28$). Trophic magnification slopes (TMS) for these regressions (Fig. 6) indicated that the degree of biomagnification of THg (TMS = 0.14) and MeHg (TMS = 0.09) were relatively similar.

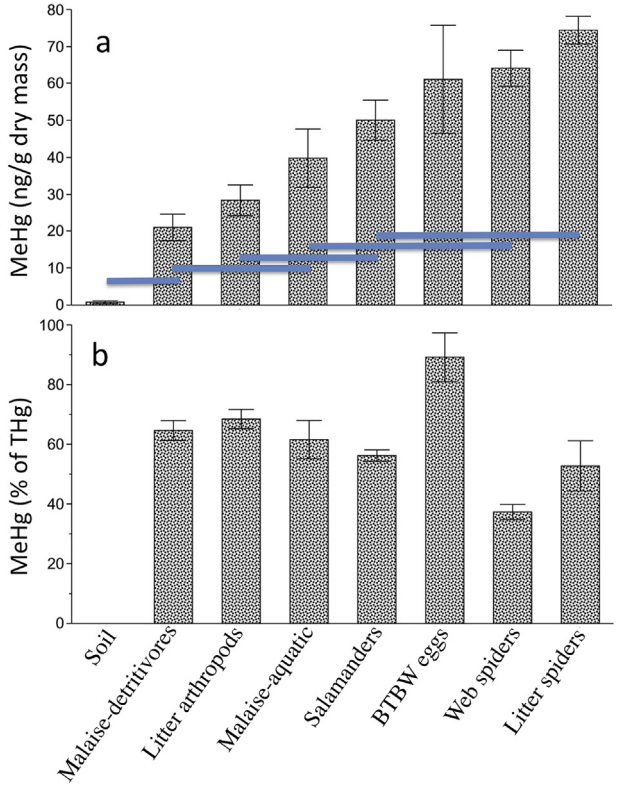

Fig. 3. Pattern of MeHg bioaccumulation (a) across seven taxa and soils (Oa and Oe horizons) sampled in two watersheds in New Hampshire, USA, in 2008 and 2009. Values are means (±SE); bars not connected by a line were significantly different at the 0.05 level according to Tukey's HSD test. Also shown (b) is the ratio of MeHg to THg (mean ± SE) found across all the taxa sampled. Samples from different watersheds, elevations and locations were combined for this analysis because these did not contribute significantly to the pattern of MeHg bioaccumulation (see Table S1).

Because we expected more methylation and bioaccumulation near streams, we tested whether fractionation and bioaccumulation MeHg differed significantly by location (streamside vs. forest). To conduct this test, we regressed $\delta^{15}N$ on LogMeHg for both streamside and forest sites. We included all taxa except Malaise-detritivores in this regression for the reason explained above. We found that $\delta^{15}N$ significantly predicted MeHg at streamside sites but not at forest sites (Linear regression: Streamside, $F_{1,16} = 15.5$, $P = 0.001$, $R^2 = 0.49$; Forest, $F_{1,17} = 2.26$, $P = 0.15$, $R^2 = 0.12$). In addition, TMS differed greatly between streamside and forest sites, with TMS at streamside sites about twice that at forest sites (Streamside TMS = 0.12; Forest = 0.06). This result suggests that fractionation, and hence bioaccumulation or biomagnification, of MeHg occurred more efficiently near streams even while soils away from streams contained more THg and had characteristics that seem more favorable for methylation.

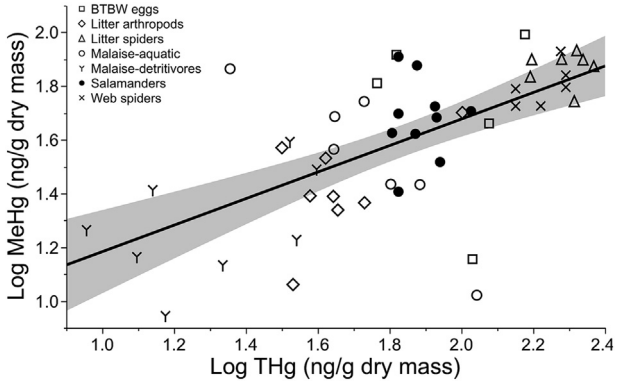

Fig. 4. Relationship between LogTHg and LogMeHg for animal taxa sampled in two watersheds of New Hampshire, USA, during 2008 and 2009 (Linear regression, $F_{1,49} = 34.0$, $P < 0.001$; $R^2 = 0.40$). Where multiple THg samples represented the same location as the composited MeHg samples, the mean of those THg samples was used for this test (see Material and methods for additional details). The gray band indicates the 95% confidence interval for the regression. THg and MeHg were determined from different samples and therefore were statistically independent.

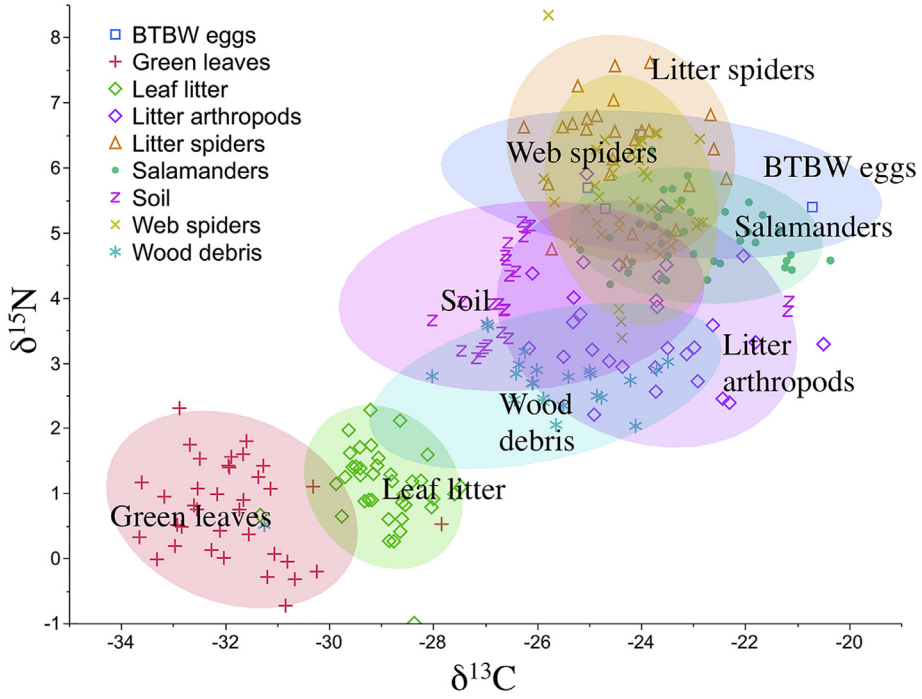

Fig. 5. Trophic position as determined by $\delta^{13}C$ and $\delta^{15}N$ of the materials and animal taxa sampled near three replicate streams in each of two watersheds (HB, JB), New Hampshire, USA, in 2008 and 2009. Ellipses include 90% of points for each group. See Table 2 for a description of what each taxon included.

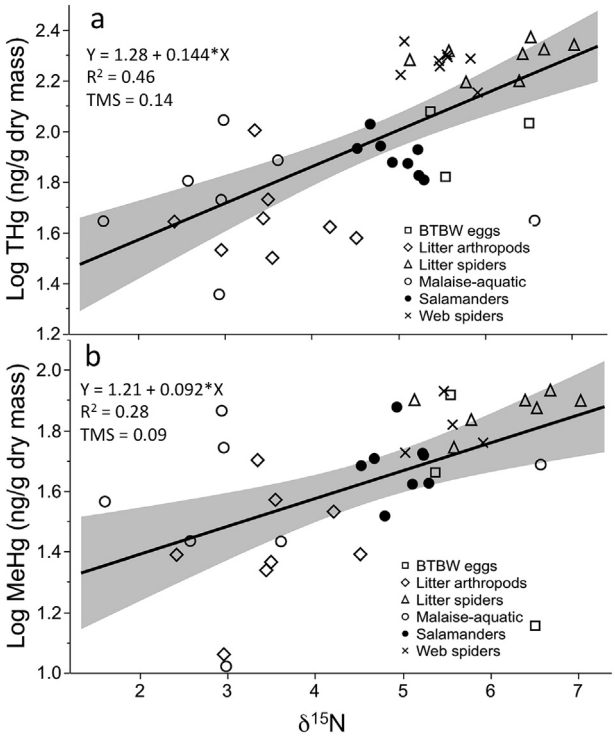

Fig. 6. $\delta^{15}N$ enrichment predicted Log(MeHg) and Log(THg) content across animal taxa sampled when highly variable Malaise-detritivore samples were excluded. Samples were collected from three replicate streams in each of two watersheds (HB, JB), New Hampshire, USA, in 2008 and 2009. Both regressions were highly significant (see text); the shaded area indicates the 95% confidence interval of the regression. The trophic magnification slope (TMS) was the slope of the regressions of Log(MeHg) or Log(THg) on $\delta^{15}N$.

4. Discussion

Our goal was to quantify the extent to which headwater streams and associated upland areas in montane regions of the northeastern U.S.A. are important sites of Hg bioaccumulation and biomagnification. Specifically, we tested the hypothesis that small-scale spatial variation in abiotic conditions associated with methylation and availability of Hg would predict spatial patterns in MeHg in two watersheds of the White Mountains Ecoregion. We found significant small-scale spatial variation in soil characteristics associated with mercury methylation and significant spatial variation the THg content of soils, but MeHg bioaccumulation and biomagnification were primarily dependent on food web structure.

Bioaccumulation of THg and MeHg was found throughout the area sampled, at low and high elevations, and at streamside and forest sites in watersheds that differed significantly in conditions for Hg methylation. These findings indicated that headwater areas in this region function, at least at times, like a wetland, probably due to the high density of first order streams, high precipitation, and low evapotranspiration rates at the sampled elevations. Throughout most of the year, soil moisture remained high and soil conditions for methylation were favorable. Our finding that soil conditions for methylation were more favorable at forest sites away from streams than at streamside sites supports this interpretation, suggesting that streams themselves are only a part of a broader headwaters area where Hg methylation and bioaccumulation occur.

THg content of soil measured in this study was comparable to that of others studies in which Hg was sampled broadly across the Northeast (e.g., Juillerat et al., 2012; Richardson et al., 2013) or sampled across an elevation gradient (Rimmer et al., 2010; Townsend and Driscoll, 2013; Townsend et al., 2014). This suggests that our results apply generally within the region. However, our samples may underestimate the maximum seasonal availability of THg since it typically peaks around snowmelt (e.g., Demers et al., 2010). MeHg seems to peak in July at about the time that we sampled (Gerson et al., 2017).

Soil characteristics favoring Hg methylation predicted THg content (see also Gruba et al., 2019), but not MeHg content. Soil THg content was two orders of magnitude greater than MeHg, and MeHg content

was highly variable in both soils and animal taxa, obscuring spatial patterns. We sampled in watersheds with soil characteristics that differed in ways that might enhance methylation, but these differences, although statistically significant, seem to have a negligible effect on the overall bioaccumulation and biomagnification regimes of the taxa sampled. Furthermore, the strong correlation between THg and MeHg across all taxa (i.e., from soils to bird eggs) and areas sampled suggests that methylation and biomagnification of both THg and MeHg were occurring throughout the sampled area, because our samples represented three replicate streams within two watersheds, as well as high and low elevation, and proximity to a headwater stream. A similar pattern between THg and MeHg has been reported by others (e.g., Shanley and Bishop, 2012), and suggests that even a low rate of methylation can sustain bioaccumulation and biomagnification to the levels observed despite significant differences in soil characteristics or Hg availability.

One spatial pattern in THg was prominent - soils at high elevation had greater content of THg. This matches the general pattern reported by Townsend and Driscoll (2013) and Townsend et al. (2014) from the Catskill Mountains, New York, and others (e.g., Driscoll et al., 2007). However, our data also show that much less change in soil THg content occurs with elevation within northern hardwood forest compared to the difference associated with the transition from hardwoods to spruce-fir (see: Townsend and Driscoll, 2013; Townsend et al., 2014). This transition represents not only a change in vegetation composition and structure, but also: an increase in precipitation inputs due to enhanced capture of cloud droplets by coniferous vegetation (Lovett and Reiners, 1986), increased atmospheric deposition of Hg (Driscoll et al., 2007), and soil characteristics conducive to retention of Hg (e.g., cool temperature, high organic matter content). It is also important to note that our values for THg in soils and salamanders are very similar to those reported by Townsend and Driscoll (2013).

Contrary to our expectation, THg content of soils was lower at streamside sites than at forest sites. At streamside sites, we sampled soils within 1 m of the channel, where periodic flooding is likely. A primary means of THg loss from northern hardwood forest is via streamflow during periods of high discharge (Shanley et al., 2008), which may explain this finding. Additionally, some loss of Hg near streams may occur via the movement of animals such as aquatic insects, salamanders, and birds (e.g., Greene et al., 2008). Although the physical flow of materials toward streams is obvious in areas like the Northeast, with >1400 mm of annual rainfall, a quantitative assessment of the redistribution of MeHg by animals from sources to sinks has not yet been done.

Results of stable isotope analyses for $\delta^{15}N$ indicated that bioaccumulation and biomagnification (i.e., increase in concentration of across tropic levels) of MeHg and THg is occurring in the food webs of headwater areas both near and away from streams, as has been reported in studies of wetlands (e.g., Coelho et al., 2013). Our TMS values were comparable to those from aquatic systems (see Lavoie et al., 2013), but surprising few TMS values for mercury in terrestrial systems exist (but see Speir et al., 2014). Our finding that $\delta^{15}N$ significantly predicted MeHg at streamside sites but not forest sites suggests that food web structure or diet (e.g., the proportion prey emerging from streams) are contributing to spatial variability in Hg bioaccumulation and biomagnification (Speir et al., 2014). Unfortunately, actual food web structure and diets are poorly known and highly variable for most organisms, particularly invertebrates, in northern hardwood forests (Rimmer et al., 2010). Indeed, we do not know the extent to which predators in our study (e.g., spiders) were preying on taxa at lower trophic levels (e.g., emergent aquatic insects), although such predation is highly likely (Cristol et al., 2008; Bartrons et al., 2015). Further complicating identification of hotspots of methylation and bioaccumulation is the lack of knowledge of the scale of movement for most invertebrate taxa. Although movement distances are likely short for nonflying invertebrates (e.g., millipedes), other taxa such as beetles are captured frequently in window traps (e.g., Maguire et al., 2014), indicating that they are flying for unknown distances above the forest floor. Recent studies suggest that movement distances can be well over 100 m, even in weakly flying invertebrates such as stoneflies (Macneale et al., 2005), but most may not move that far (Muehlbauer et al., 2014).

On a broader scale, our results provide the basis for predicting how ongoing environmental change in climate, forest composition, and atmospheric deposition will affect mercury bioaccumulation in montane areas of northern hardwood forests. For example, THg is likely to continue to accumulate in acidic soils rich in organic matter, such as are found in the Hubbard Brook watershed (Richardson et al., 2017). Net accumulation appears to be lower where soils are rich in calcium and less acidic, such as the Jeffers Brook watershed. Presently, montane deciduous forests of the northeast are becoming less acidic due to regulation of acid deposition (Likens and Buso, 2012), which might reduce THg accumulation. However, reduced duration of snow cover in winter and increased precipitation will keep soils unfrozen and moist longer during the leaf-off season (Groffman et al., 2012), potentially enhancing methylation in warmer soils (Gabriel and Williamson, 2004; Eklöf et al., 2018). Additionally, climate change is causing extreme precipitation and discharge events to increase in frequency, which may increase Hg movement from montane headwater areas into lowland sinks (Riscassi et al., 2011).

Despite years of study of Hg in linked terrestrial-aquatic systems, critical gaps in knowledge remain. Foremost is the near absence of Hg effect levels for most terrestrial and aquatic organisms (Gustin et al., 2016). Levels of Hg in this study seem well below those known to affect the behavior or reproductive success of birds (e.g., Varian-Ramos et al., 2014) and spiders (e.g., Wyman et al., 2011); however, effect levels are largely unknown for most arthropods and salamanders living in terrestrial habitats. In addition, validation of quantitative models of bioaccumulation and biomagnification of Hg in terrestrial environments is severely constrained by a lack of information on the rate of THg accumulation (net of deposition or bioaccumulation and loss) in forest soils (Richardson et al., 2017) and most free-living animals. Our findings add to a growing body of evidence showing the widespread occurrence of Hg methylation, bioaccumulation and biomagnification in terrestrial environments, including upland hardwood forests, and reinforce the importance of addressing these critical gaps in knowledge.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2019.02.151.

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