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RESEARCH ARTICLE

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Key Points:

- Post-harvest decreases in THg and dissolved organic carbon runoff concentrations were offset by more runoff, increasing solute mass yields
- Peat MeHg concentrations in adjacent peatland decreased post-harvest
- Harvesting had no significant impact on methylmercury accumulation in adjacent peatland invertebrates

Supporting Information:

Supporting Information may be found in the online version of this article.

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Effects of Clearcutting and Residual Biomass Harvesting on Hillslope Mercury Mobilization and Downgradient Mercury Accumulation

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Abstract Mercury (Hg) in forest runoff varies geographically and in relation to silvicultural practices. There is also considerable uncertainty about how forest management practices, such as residual biomass removal, affect Hg mobilization, and downgradient cumulative effects. In this study, total Hg, dissolved organic carbon (DOC), and sulfate (SO_4^{2-}) mobilization in runoff were compared among unharvested and harvested hillslopes with and without residual biomass removal, and peat soil and invertebrate methylmercury (MeHg) concentrations were assessed in a down-gradient peatland. Using a before-after-control-impact design, runoff from three adjacent hillslopes was monitored pre-harvest (2010–2011) and post-harvest (2012–2013) from snowmelt to freeze-up at the USDA Forest Service's Marcell Experimental Forest in northern Minnesota. Dilution, due to increased available hillslope soil water, led to decreased THg and DOC concentrations after harvest at both harvested hillslopes. Sulfate concentrations did not statistically change following harvest. Compared to its removal, leaving residual biomass significantly increased yields of all solutes but only DOC yields significantly increased when the residual biomass was removed. In the adjacent down-gradient peatland, peat MeHg concentrations decreased, whereas no change was observed in peat below the unharvested hillslope. There was no discernible change post-harvest in MeHg levels among several peatland macroinvertebrate taxa. This study provides a much-needed hillslope-scale understanding of Hg response to forest management practices, highlighting that increased solute yields from hillslopes do not necessarily stimulate Hg methylation or invertebrate bioaccumulation in down-gradient peatland systems.

Plain Language Summary The globally important pollutant, mercury, is usually stored in soils for long periods of time, lessening its toxic impact on ecosystems. Forestry operations, however, may disturb mercury storage in soils. This could, for example, result in higher concentrations of mercury in fish or insects within the nearby environment. In this field experiment, we use measurements of mercury and other chemicals in water moving from a forest into a wetland, as well as measurements of mercury concentrations in wetland soil and insects over a 4-year span. In the middle of this experiment, part of the forest was harvested using different approaches and therefore we compare pre-harvest observations with post-harvest observations. We found that after forest harvesting, mercury concentrations in water moving into the wetland went down but that the overall amount of mercury moving into the wetland went up because more water moved into the wetland. The amount of mercury that mainly accumulates in organisms, called methylmercury, went down in soils after forest harvest but levels in wetland insects did not change. This study shows that forestry operations do affect how mercury moves and transforms, but do not necessarily lead to effects in nearby organisms.

1. Introduction

Mercury (Hg) is a contaminant with global distribution that is deposited onto terrestrial landscapes via precipitation (wet deposition), gas exchange, and litterfall (dry deposition; Bishop et al., 2020; Zhang et al., 2019; Zhou et al., 2021). There is a concerted global effort to reduce Hg deposition by reducing Hg emissions through the Minamata Convention on Mercury (United Nations Environment, 2019). Still, the result of these deposition pathways is that terrestrial upland soils usually represent large stores of Hg (Bishop et al., 2020). Small fractions of the Hg stored in upland soils are transmitted to downgradient ecosystems via surface and subsurface runoff and sediment transport (Bishop et al., 2020), but these small fractions can have significant negative consequences

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in the receiving ecosystems, including adverse human health outcomes (O'Connor et al., 2019). Recent research has highlighted the importance of landscape disturbances, such as forest harvesting, to the mobilization of terrestrially stored Hg (Hsu-Kim et al., 2018). Yet, the linkages between mobilized upland Hg (predominantly as inorganic Hg), and cumulative effects in downgradient ecosystems under both disturbed and undisturbed conditions remains a critical gap in our knowledge.

Forest management and harvesting practices represent one relatively widespread anthropogenic disturbance that may negatively impact downstream water quality (Kuglerová et al., 2021). However, there has not been a consistent response in Hg concentrations or yields due to forest harvesting in downgradient surface waters or biota in the literature (Eklöf et al., 2016). Divergent findings stem from the inherent complexity of catchment-scale hydrochemical processes, time since harvest, ecohydrological flow paths, other solute mobilization, and landcover (e.g., wetland distribution; Bishop et al., 2020; Eklöf et al., 2016; Laudon et al., 2016; Skjellberg et al., 2009), coupled with different forest harvesting and silvicultural techniques (Eklöf et al., 2012, 2014; McCarter, Sebestyen, Eggert, Kolka, & Mitchell, 2021), as well as an incomplete understanding of Hg mobilization processes in terrestrial environments. Typically, changes to the hydrological and water quality conditions in lakes and rivers are used in assessing forest management impacts on Hg, however wetland and riparian areas directly adjacent to upland forestry operations can act as buffers for downgradient aquatic systems, intercepting and transforming upland-derived Hg (Mitchell et al., 2009). These intercepting wetlands can sequester or release both MeHg and inorganic Hg depending on changes to hydrology and the movement of other solutes such as nitrate, manganese, sulphate (SO_4^{2-}), or dissolved organic carbon (DOC; Branfireun et al., 1998; Bushey et al., 2008; Driscoll et al., 1998; Hintelmann et al., 2002; Jeremiason et al., 2006; Mitchell et al., 2009; Rudd, 1995; Skjellberg et al., 2009; St. Louis et al., 1994; Tjerngren et al., 2012). Changes in Hg and other solute mobilization can also drive changes in Hg bioaccumulation in downstream or down-gradient food webs (Lescord et al., 2019; Morel et al., 1998; Wu et al., 2018). Understanding the interplay between geochemical and hydrological conditions altered by forest management operations and Hg cycling in downgradient ecosystems is critical to contextualizing the variety of Hg responses to forest harvesting reported in the literature.

The bulk mobilization of Hg from upland forested hillslopes is thought to be controlled by the runoff processes on a given hillslope (Bishop et al., 2020; Haynes & Mitchell, 2012; McCarter, Sebestyen, Eggert, Kolka, & Mitchell, 2021; Sørensen et al., 2009a). Forest harvesting often increases the amount of runoff from a hillslope and the fraction of precipitation that is transmitted downgradient (Dung et al., 2012; McCarter, Sebestyen, Eggert, Kolka, & Mitchell, 2020; Oni et al., 2015). These changes in terrestrial runoff dynamics are also often expressed at larger catchment scales (Buttle et al., 2018; Ide et al., 2013; Monteith et al., 2006; Schelker, Kuglerová, et al., 2013; Sørensen et al., 2009b). However, specific forest harvesting practices can differentially alter the hillslope runoff response (Buttle et al., 2018; McCarter, Sebestyen, Eggert, Kolka, & Mitchell, 2020). For example, there has been ongoing interest in harvesting residual biomass such as branches, treetops, and other organic matter not suitable for timber or pulp production, also known as biomass harvesting (Dirkswager et al., 2011; Thiffault et al., 2011; Yemshanov et al., 2014). Compared to leaving substantial biomass on the forest floor of harvested sites, the removal of residual biomass can lessen the rainfall-runoff response by decreasing available soil water due to less surface shading and more solar radiation reaching the soil surface (Mazur et al., 2014).

Changes in the magnitude, timing, and routing of runoff can alter nutrient and DOC mobilization from hillslopes (Erdozain et al., 2021; Kim et al., 2017; Sebestyen, Funke, & Cotner, 2021; Verry & Timmons, 1982) and affect whether shallower or deeper soil stores of Hg are mobilized downslope to adjacent ecosystems (McCarter, Sebestyen, Eggert, Kolka, & Mitchell, 2021). The combined interactions between changes in the timing and magnitude of different DOC, nutrients and Hg mobilization may alter the production of MeHg in receiving peatlands, potentially creating Hg methylation hotspots at the interface between upland forests and peatlands (Mitchell et al., 2008b). However, how the interactions between forest harvest-mobilized Hg and other solutes from terrestrial uplands impacts Hg speciation (i.e., MeHg vs. inorganic Hg(II) compounds), concentration, and bioaccumulation in receiving peatlands is unknown. Therefore, our objective was to understand how both traditional clearcut harvesting and the harvesting of residual biomass after clearcutting impact the mobilization of Hg from a mineral soil hillslope, as well as to assess subsequent impacts on Hg speciation and accumulation in an adjacent downgradient peatland. Our specific objectives were to: (a) assess whether the removal of residual biomass post-harvest impacts the concentrations and yields of total Hg, DOC, and SO_4^{2-} in subsurface runoff relative to leaving the residual biomass on the hillslope and an unharvested hillslope; (b) determine if changes in

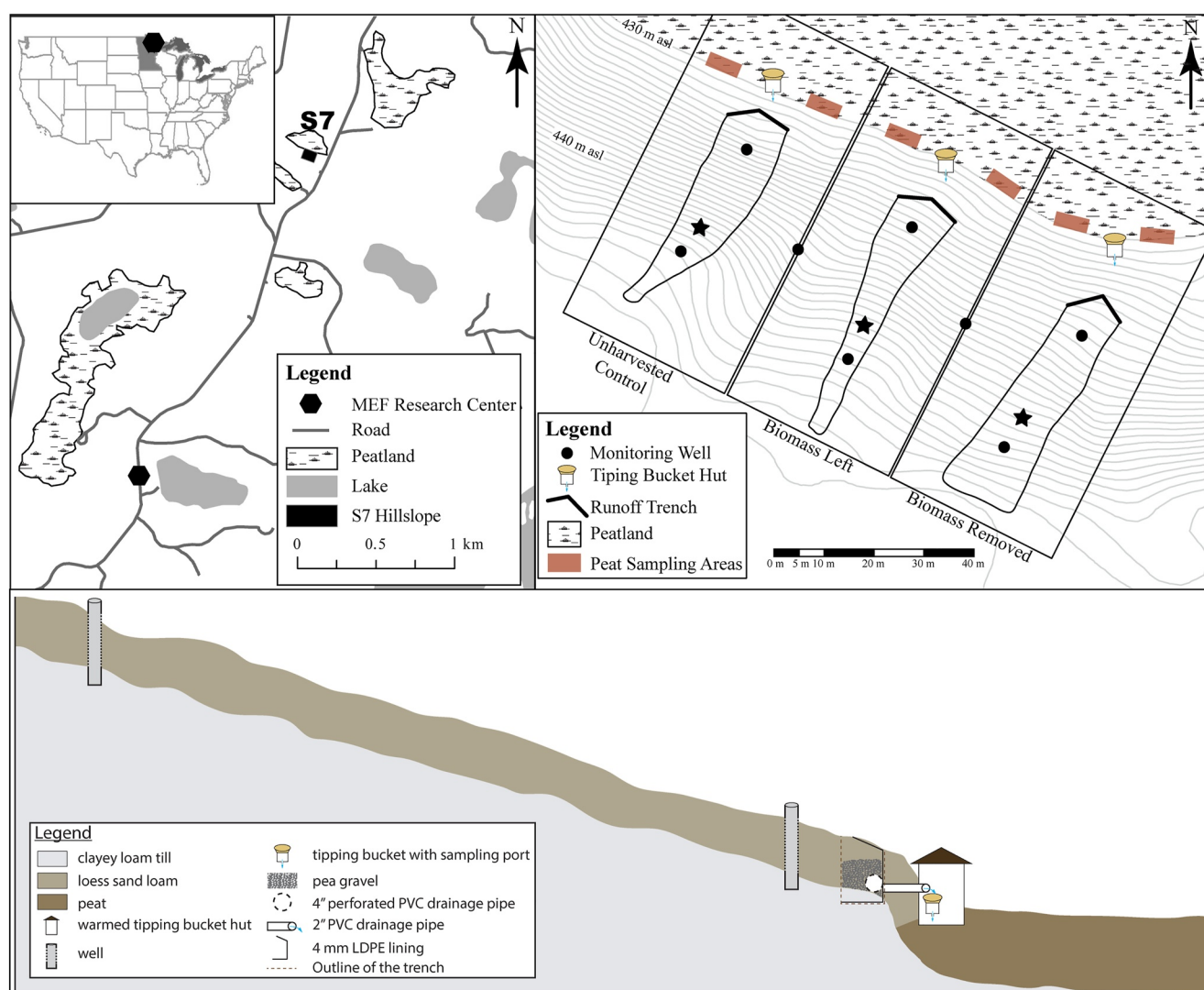


Figure 1. Site map and schematic representation of the hillslope (adapted from McCarter, Sebestyen, Eggert, Kolka, & Mitchell, 2020).

hillslope solute export impact Hg concentration, speciation, and potential methylation rate constants in peat soils within the upland-peatland interface; and (c) evaluate how different forestry practices impact MeHg concentrations in peatland macroinvertebrates within the upland-peatland ecotone.

2. Study Site

This study took place in the S7 headwater catchment at the USDA Forest Service's Marcell Experimental Forest (MEF) in north-central Minnesota (47° 31'21"N, 93°28'7"W; Sebestyen, Kolka, et al., 2011). The north-facing hillslope has a mean slope of 18° and drains into an adjacent ditched and treed (mainly black spruce, *Picea mariana*) *Sphagnum* peatland (Figure 1). The mean annual temperature is 4.2°C and annual precipitation is ~787 mm (Sebestyen, Lany, et al., 2021). On the hillslope there is a shallow organic horizon (generally <2 cm) with little litter persistence due to consumption by invasive earthworms (Hale et al., 2005; Holdsworth et al., 2008). Hillslope soils are composed of an upper, permeable sandy loam loess-derived horizon with a mean depth of 50 ± 27 cm that overlies a low-permeability Koochiching clay loam till (Mitchell et al., 2009; Verry et al., 2011). The low permeability till horizon significantly slows deep percolation of precipitation, resulting in the development of a transient shallow perched groundwater system (McCarter, Sebestyen, Eggert, Kolka, & Mitchell, 2020; Nichols & Verry, 2001). Prior to forest harvesting, the upland overstory vegetation was comprised primarily of

sugar maple (*Acer saccharum*), trembling aspen (*Populus tremuloides*), paper birch (*Betula papyrifera*), and balsam poplar (*Populus balsamifera*).

In 2009, three V-shaped subsurface runoff trenches were dug at the base of the hillslope with ~20 m of untrenched soil between each of them. Each trench extends from the surface to ~0.2 m into the low permeability Koochiching clay loam till and was lined with a 4 mm polyethylene sheeting to prevent leakage out of the trench (Figure 1; McCarter, Sebestyen, Eggert, Kolka, & Mitchell, 2020). Each trench was backfilled with pea gravel to about half depth and then with native soil to the original ground surface (Figure 1). All subsurface runoff was collected at the apex of the trench and routed by pipe to large (0.1 L) capacity tipping bucket runoff gauges (Figure 1). For further detail on trench design and hydrological function, see Haynes and Mitchell (2012) and McCarter, Sebestyen, Eggert, Kolka, and Mitchell (2020).

3. Methods

3.1. Experimental Design

Starting 1 April 2010, and ending 20 November 2013, subsurface runoff volume was continually measured, along with recurring sampling of the subsurface runoff for THg, SO_4^{2-} , and DOC concentrations. Peat Hg concentrations, both THg and methylmercury (MeHg), were determined three times per year (seasonally). The overall experimental design is a Before-After-Control-Impact (BACI) approach (Stewart-Oaten et al., 1986), wherein all hillslopes were simultaneously monitored for nearly 2 yr (March 2010–March 2012) before any harvest and again for ~1.75 yr (March 2012–November 2013) following harvest of two of the three hillslopes. During the “Before” portion of the BACI design, relationships among hillslopes for subsurface runoff rates and subsurface runoff chemistry measurements were established, along with Hg concentrations in the down-gradient peatland soils (herein referred to as peat) and macroinvertebrate community. Details of the hydrological measurements can be found in McCarter, Sebestyen, Eggert, Kolka, and Mitchell (2020).

In March 2012, two of the three hillslopes were mechanically clearcut harvested over frozen soils and relatively shallow snow cover, leaving one Unharvested Control hillslope. As inferred from the lack of change in the effective hydraulic conductivity profile post-harvest, harvesting did not impact the soil structure of the hillslopes (McCarter, Sebestyen, Eggert, Kolka, & Mitchell, 2020). On one of the harvested hillslope areas, ~85% of residual biomass was removed both by machine and then additionally by hand after forest harvesting (Biomass Removed). Residual biomass was left on the forest floor at the other harvested hillslope (Biomass Left). Mazur et al. (2014) observed an increase in woody debris at both harvested hillslopes post-harvest, with the largest increase at the Biomass Left hillslope. After harvesting, the hydrological and chemical relationships among hillslopes and within the peatland were again examined. Specifically, both harvested hillslopes were examined in relation to the Unharvested “Control” hillslope, leading to treatment ratios between “Impacted” hillslopes and the “Control” hillslope (McCarter, Sebestyen, Eggert, Kolka, & Mitchell, 2020). By examining differences in treatment ratios between Before (pre-harvest) and After (post-harvest) periods, impacts related to forest harvesting can be isolated from, for example, inter-annual variations in climate.

3.2. Water Sampling

Water sampling of the subsurface runoff occurred from the onset of snowmelt (mid-March–April) through to freeze-up in early November over a 4-yr period (from early 2010 to late 2013). Low sample volumes after August of each year often precluded analysis for solutes other than filter-passing THg concentrations. In 2013, sampling did not begin until late April due to a delayed snowmelt (Sebestyen et al., 2020). Sampling was conducted on a hybrid event-regular interval basis, where regular samples were taken weekly to bi-weekly when subsurface runoff was present. During snowmelt the regular sampling interval was increased (one to three times/day) to better capture the disproportionately high amount of the overall annual flux of Hg from catchments in the area (Mitchell et al., 2009). When possible, regular sampling was augmented to event-based sampling during or shortly following rainfall events.

All sampling was conducted using ultra-trace sampling protocols, often referred to as “clean hands-dirty hands” (United States Environmental Protection Agency, 1996). Powder-free nitrile gloves were worn when sampling and extreme care was taken to avoid contact between sample bottles and any other surface. Samples for Hg

analyses were collected in polyethylene tetraglycol bottles, preserved via the addition of trace metal-grade HCl to 0.5% by volume, and stored cold and in the dark in double zip-sealed plastic bags. All other chemical constituents were sampled into high-density polyethylene bottles and stored at 4°C until analysis (McCarter, Sebestyen, Eggert, Haynes, et al., 2021). All water samples were filtered through pre-ashed 0.7 µm glass microfiber filters. Due to low sample volumes, DOC was not analyzed during the snow-free period of 2010, while sulphate (SO_4^{2-}) analysis is missing from subsurface runoff samples retrieved from the Biomass Left hillslope during 2012.

3.3. Peat Sampling and Methylation Potential Assays

Peat was sampled to measure potential Hg methylation rate constants and to determine peat concentrations of both THg and MeHg. Peat was sampled once in 2010 (summer, $n = 9$ replicates per treatment) and three times per year (spring, summer, and fall, $n = 3$ replicates per depth, $n = 9$ per treatment) in the downgradient peatland of each hillslope in 2011 (pre-harvest), and 2012 (post-harvest). Samples were taken from the areas not directly downslope from the trench, but ~10 m on either side of the treatment to account for the interception of subsurface runoff in the trenches (Figure 1). No samples were taken within the 10 m buffer established at the edges of each treatment. To collect the samples, a 5 cm diameter rigid acrylic tube, with small silicone-sealed holes at 1 cm vertical intervals, was gently inserted into the peat to a depth of more than 8 cm and extracted by cutting the bottom of the peat. Samples were discarded if there was evidence of peat compression. The samples were then capped and sealed to prevent water drainage from cores. The cores were then placed in a dark cooler for transport.

To determine potential Hg methylation rate constants (K_{meth}), we followed the approach of Mitchell and Gilmour (2008) wherein enriched inorganic $^{201}\text{Hg}(\text{II})$ was injected at 1-cm intervals into each peat core and the turnover to Me^{201}Hg over a period of 5 hr was measured. Enriched isotopes were pre-equilibrated with native pore water for 1 hr prior to injections. The total mass of Hg injected was approximately equal to the mass of ambient Hg in each 1 cm depth interval of peat. Following the 5-hr incubation of injected cores at temperatures matching the ambient peat temperature at the time of core retrieval, peat was extruded at intervals of 0–2, 2–4, and 4–8 cm below the ground surface and immediately frozen to end the incubation. Frozen samples were then freeze dried under no light conditions, homogenized, and kept frozen until analysis. The calculation of K_{meth} uses the proportional turnover of enriched inorganic $^{201}\text{Hg}(\text{II})$ into Me^{201}Hg over the incubation time period t , and is given in units of day^{-1} .

3.4. Invertebrate Sampling

Macroinvertebrates were collected using numerous pitfall traps (acid-washed plastic cups, 64 cm² opening, which were ¼ filled with deionized water) placed into the peat in the down-gradient area of each experimental hillslope plot during May and June in 2010, 2011, and 2012 (Figure 1). Traps were emptied daily over several days each year. Some additional organisms were collected individually using clean forceps by turning over rotted logs. Trapped and hand-collected macroinvertebrates were composited by treatment area, sorted and identified to the lowest taxonomic level possible (family or genus). Some invertebrate genera and families were further composited to obtain enough biomass for MeHg analysis. Samples were ultimately transferred to clean polyethylene vials, frozen, freeze-dried, and homogenized for analysis.

3.5. Chemical Analysis

THg in water was analyzed with a Tekran 2600 automated Hg analysis system, which was hyphenated directly to an Agilent 7700 inductively coupled plasma mass spectrometer (ICP-MS). Research at this site has previously included additions of enriched Hg isotopes (different isotopes from those used in the K_{meth} assays) to this hillslope, the results of which have been separately reported (see McCarter, Sebestyen, Eggert, Haynes, et al., 2021). Hyphenation with ICP-MS was therefore necessary to correct for these mercury additions and to correctly quantify ambient THg concentrations. Briefly, water samples were first oxidized by reaction with 1% by volume bromine chloride (BrCl) overnight. By automation on the Tekran 2600 system, samples were mixed with SnCl_2 to reduce all Hg in the sample to volatile Hg^0 , Hg^0 was stripped from the mixture on a stream of clean argon gas and accumulated onto a gold-filled glass trap. This trap was thermally desorbed onto a second trap, which was again thermally desorbed. The Hg released was carried on a stream of clean argon gas into the ICP-MS where the Hg was quantified, including differentiation of its stable isotopes as discussed in McCarter,

Sebestyen, Eggert, Kolka, and Mitchell (2021). Calibration and isotope spike standards were run at least twice daily, and typical QA/QC included duplicates, analysis of certified reference materials, and matrix spikes every 10–15 samples (see McCarter, Sebestyen, Eggert, Haynes, et al., 2021 for QA/QC details). If references varied beyond 10%, the entire run was re-analyzed. Following regular analysis for MeHg concentrations in subsurface hillslope runoff water during the first 1.5 yr of the study with all samples below detection limits, MeHg analyses in the subsurface hillslope runoff were discontinued.

Freeze-dried and homogenized peat samples were analyzed for THg concentrations, including enriched isotopes relevant to methylation assays by first digesting in hot nitric acid (HNO_3) using a microwave digestion system (CEM, MARS 5) at 175°C under pressure for 30 min. Digestates were then diluted with deionized water and oxidized with BrCl overnight before introducing into the Tekran 2600 or Tekran 2600/ICPMS as outlined above for water samples.

The determination of peat MeHg concentrations was similar to MeHg in invertebrates, except for sample preparation. For peat, samples were first distilled with CuSO_4 , KCl, sulfuric acid, and an exact known quantity of enriched Me^{199}Hg . For invertebrates, MeHg was extracted using a KOH-methanol solution under heat, also with an exact known quantity of enriched Me^{199}Hg added. Aliquots of digestates or extracts were then added to gas washing bottles, pH was buffered and sodium tetraethylborate was added to ethylate MeHg. After 15 min of reaction time, pure nitrogen gas was bubbled through the gas washing bottles and the volatile ethylated MeHg was trapped onto Tenax traps. The traps were thermally desorbed on a stream of argon gas, species were separated through a gas chromatography column and introduced into the ICP-MS for quantification. ^{201}Hg as both T^{201}Hg and Me^{201}Hg in excess of natural abundance, as well as ambient THg or MeHg concentrations were determined using the isotope dilution/matrix methods outlined in Hintelmann and Ogrinc (2002), using the corrected ^{202}Hg signal for determination of ambient concentrations. See McCarter et al. (2022) for QA/QC details.

DOC concentrations (also filtered at 0.7 μm) were measured using a Shimadzu TOC V-CPH analyzer by high-temperature combustion using potassium hydrogen phthalate (KHP) for reference and check standards (McCarter, Sebestyen, Eggert, Haynes, et al., 2021). Sulfate was measured using suppressed conductivity detection (Standard Method 4110B, APHA, 1995) after injection through 20 (μm) filter caps on a Dionex DX-500 ion chromatograph with an IonPac AG14 pre-column and an AS14 column. All reference and check standard were within 10% of the reported value (McCarter, Sebestyen, Eggert, Haynes, et al., 2021).

3.6. Data Analysis

The solute yield of the subsurface runoff was determined through

$$S_{\text{yield}} = Q \cdot S_{\text{conc}}, \quad (1)$$

where, S_{yield} is the total yield of a given solute (g day^{-1} or $\mu\text{g day}^{-1}$), Q is the total daily subsurface runoff (L day^{-1}), and S_{conc} is the average concentration of a given solute taken between two sampling points (mg or ng L^{-1}). On sampling days, the measured S_{conc} value was used in the calculation of the daily S_{yield} . Given the short time between samples, typically <10 days, no time-weighted averaging was used. However, if the time between measurements was >10 days and the subsurface runoff fell to zero at any point in that time period, the flux calculation assumed a break in the continuous flow and the next S_{conc} value was used to determine the S_{yield} (McCarter, Sebestyen, Eggert, Kolka, & Mitchell, 2021). If no subsequent sample was taken, the last S_{conc} value was used to estimate S_{yield} . Daily subsurface runoff values were from McCarter, Sebestyen, Eggert, Kolka, and Mitchell (2020).

To assess the effect of forest harvesting treatment on the mobilization of THg, DOC and SO_4^{2-} , the treatment hillslopes (Biomass Removed and Biomass Left hillslopes, *Treatment*) were normalized to the corresponding temporal measurement from the Unharvested Control hillslope (*Unharvested*) by determining the treatment ratio (*TR*; Conner et al., 2016):

$$TR = \frac{\text{Treatment}}{\text{Unharvested}}. \quad (2)$$

Using a Biomagnification Factor (BMF), the degree of biomagnification of MeHg in the food web was examined between worms (Lumbriculidae) and peat (0–2 cm depth, where Lumbriculidae are most active). The BMF was

calculated as the ratio of the MeHg concentrations (ng g^{-1} dry weight) of the primary consumer Lumbriculidae (C_{PC}) and its likely food resource, peat (C_{FR} ; Gobas & Morrison, 2000).

$$BMF = (C_{\text{PC}}) / (C_{\text{FR}}). \quad (3)$$

3.7. Statistical Analysis

The natural logarithm treatment ratio was used as the dependent variable in mixed effect models using the emmean function in the Emmeans package in R (Lenth, 2020)

$$\log_e(TR) = \text{per} * \text{tre} + (1|Date), \quad (4)$$

where, *per* is the treatment period (pre- or post-harvest), *tre* is the treatment site (either Biomass Removed or Biomass Left) and *Date* is the date of measurement. The resultant least-squares means were then compared using the post-hoc Tukey test (Lenth, 2016) to determine the statistical differences among treatment sites (Biomass Removed and Biomass Left hillslopes), and treatment periods (pre- and post-harvest).

To determine if the slope of the THg-DOC relationship changed due to the different hillslope harvesting treatments, an analysis of covariance was performed between the pre- and post-harvest THg-DOC relationships for each treatment hillslope. For all analysis of covariance, THg was $\log_{10}$ transformed.

To assess changes in the summertime peat Hg concentrations and K_{meth} , mixed effect models were developed following

$$\log_e(PM) = \text{per} * \text{tre} + (1|Depth), \quad (5)$$

where, *PM* is the peat Hg measurement of interest on a $\log_{10}$ scale (THg, MeHg, %MeHg, or K_{meth}), *per* is the treatment period (pre- or post-harvest), *tre* is the treatment site (either Biomass Removed, Biomass Left, or Unharvested Control), and *Depth* is the sampling depth range of a given sample. To ensure a balanced experimental design, only the 2011 (pre-harvest) and 2012 (post-harvest) summertime values were compared in this particular statistical analysis. The resultant least-squares means were then compared using the post-hoc Tukey test (Lenth, 2016) to determine the statistical differences among treatment sites (Biomass Removed, Biomass Left, and Unharvested Control hillslopes), and treatment periods (pre- and post-harvest). All statistical analysis was performed in R Statistical Software (R Development Core Team, 2021).

Differences in MeHg concentrations among treatments and years within entire food webs (pooled peat, primary consumer, and secondary consumer data) were examined using ANOVA. Data were transformed ($\log_{x+1}$) prior to analysis to meet conditions of normality and equal variance.

4. Results

4.1. Total Mercury in Subsurface Runoff

Total mercury concentrations decreased and THg yields increased in subsurface runoff from pre-to post-harvesting periods on both Biomass Removed and Biomass Left hillslopes (Figure 2, Table S1 in Supporting Information S1). Annual average THg concentrations in subsurface runoff pre-harvest varied from 19 to 32 ng L^{-1} on all hillslopes (Table 1), with no difference across all three hillslopes in annual average THg concentrations or yields (Figure 2, Table 2). Post-harvest, THg concentrations in subsurface runoff were lower, but more variable (8–24 ng L^{-1}) across all three hillslopes (Figure 2, Table 1). Total Hg concentrations in subsurface runoff also decreased between the first (2012) and second (2013) years following harvest, though these differences did not noticeably impact THg yields in 2013 versus 2012 (Table 2). Unlike the harvested hillslopes, THg concentrations and yields on the Unharvested Control hillslope remained similar across all four study years (Tables 1 and 2).

In addition to comparisons of totals and averages across years, examining treatment ratios provides a greater ability to ascribe changes specifically to harvesting practices, particularly with respect to controlling for natural, climatic driven inter-annual differences (Conner et al., 2016). At both harvested hillslopes, the THg concentration treatment ratios decreased post-harvest ($p < 0.001$), while the THg yield treatment ratios increased (Figure 3, Table S2 in Supporting Information S1). However, the observed increase in THg yield treatment ratios post-harvest was

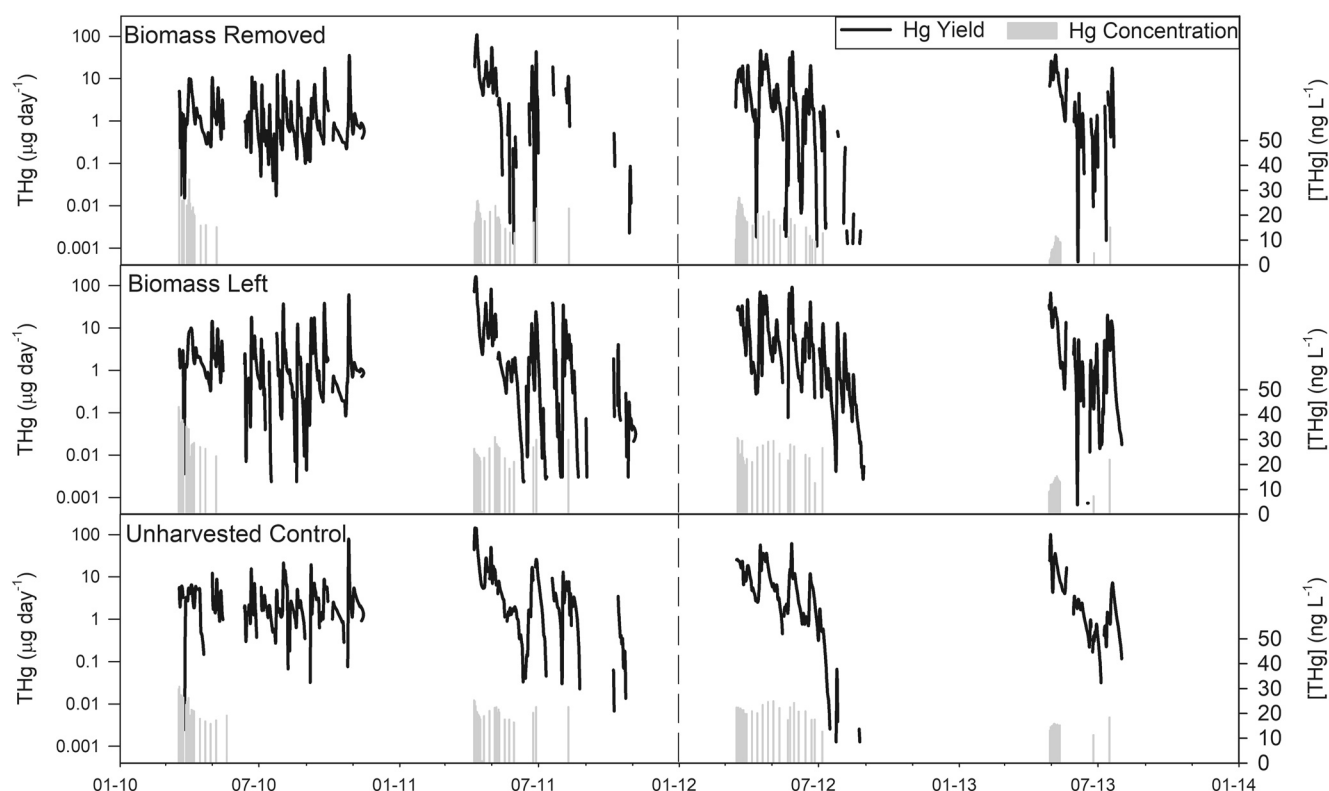


Figure 2. Timeseries of mercury concentrations (gray bars) and yields (black lines) in subsurface runoff. The dashed vertical line delineates pre-harvest (left) from post-harvest (right) periods.

only significant ($p < 0.001$) at the Biomass Left hillslope (Figure 3, Table S2 in Supporting Information S1). At both harvested sites there was a noticeable decrease in THg concentration treatment ratio below the pre-harvest estimated marginal mean, with greater decreases in 2013 compared to 2012 (Figure 3). These treatment impacts were driven by changes on both treatment hillslopes and not variations at the Unharvested Control hillslope (Figure 2).

Table 1
Annual Average (± 1 SD) Subsurface Runoff Concentrations

Site	Years	THg [ng L ⁻¹]	DOC [mg L ⁻¹]	SO ₄ ²⁻ [mg L ⁻¹]
Biomass removed	2010	23.95 (7.19)	20.18 (4.00)	4.38 (0.81)
	2011	19.32 (3.92)	19.80 (6.90)	2.56 (0.48)
	2012	18.48 (5.02)	18.14 (3.05)	3.97 (1.27)
	2013	8.00 (3.36)	12.98 (2.03)	1.51 (1.35)
Biomass left	2010	31.91 (6.30)	23.95 (2.04)	3.78 (0.91)
	2011	24.89 (3.22)	21.71 (3.15)	2.28 (0.46)
	2012	24.31 (4.20)	22.30 (4.51)	3.19 (0.55)
	2013	12.95 (3.19)	15.15 (1.82)	2.29 (0.99)
Unharvested control	2010	22.43 (6.47)	19.29 (4.71)	3.25 (0.84)
	2011	20.48 (2.46)	17.26 (2.63)	2.16 (0.20)
	2012	20.90 (2.51)	17.99 (3.30)	2.58 (0.45)
	2013	14.94 (1.47)	16.14 (2.87)	2.05 (1.12)

Note. The average DOC Concentration in 2010 only represents the spring freshest due to limited sampling volumes. DOC, dissolved organic carbon.

4.2. DOC in Subsurface Runoff

Annual average DOC concentrations in subsurface runoff were relatively stable at the Unharvested Control hillslope across all 4 yr (Figure 3, Table 1, Figure S1 in Supporting Information S1). Harvesting noticeably decreased DOC concentrations in subsurface runoff at both harvested hillslopes in 2013 (2 yr post-harvest) but no change was observed in 2012 (Figure 3, Table 1). The overall treatment effect was similar to that of THg, where post-harvest, there were significant decreases in DOC concentration treatment ratios (Table S1 in Supporting Information S1) and significant increases in DOC yield treatment ratios (Table S2 in Supporting Information S1) at both harvested hillslopes (Figure 3).

4.3. Sulfate in Subsurface Runoff

There was no systematic change in annual average SO₄²⁻ concentrations in subsurface runoff or yields at either harvested hillslope post-harvest (Figure S2 in Supporting Information S1, Table 1). Nor were the SO₄²⁻ concentration treatment ratios significantly different post-harvest at either hillslope (Figure 3). During the post-harvest spring freshet, there were high SO₄²⁻

Table 2

Annual Average (± 1 SD), Total Subsurface Runoff Yields, and Mass Fluxes. The Square Brackets, [], Indicate the Ratio to the Unharvested Control Hillslope

Site	Years	THg			DOC			SO ₄ ²⁻		
		Average [$\mu\text{g day}^{-1}$]	Total [μg]	Yield [$\text{ng m}^{-2} \text{ day}^{-1}$]	Average [g day^{-1}]	Total [g]	Yield [mg $\text{m}^{-2} \text{ day}^{-1}$]	Average [g day^{-1}]	Total [g]	Yield [mg $\text{m}^{-2} \text{ day}^{-1}$]
Biomass Removed	2010	1.8 (3.2)	374	6.1 [0.5]	—	—	—	0.37 (0.65)	77	1 [0.6]
	2011	9.0 (16.7)	764	23.4 [1.1]	6.90 (19.26)	706	21.5 [1.3]	1.35 (2.11)	82	2.3 [1]
	2012	5.7 (8.5)	761	13.1 [0.7]	3.05 (8.68)	783	13.5 [0.9]	1.39 (1.46)	108	1.7 [0.9]
	2013	5.6 (7.8)	328	12.1 [1]	2.03 (11.81)	488	18 [1.4]	0.99 (1.77)	61	1.7 [1]
Biomass left	2010	2.6 (5.4)	511	11.6 [1]	—	—	—	0.49 (1.04)	96	1.8 [1.1]
	2011	7.6 (21.8)	1,144	26.2 [1.2]	3.15 (27.19)	1,014	20.9 [1.2]	1.24 (3.5)	116	2.8 [1.2]
	2012	7.9 (13.8)	1,244	23.5 [1.3]	4.51 (14.99)	1,331	20.3 [1.3]	1.98 (2.31)		2.7 [1.4]
	2013	5.6 (10.5)	458	13.9 [1.1]	1.82 (9.91)	487	13.5 [1]	1.09 (2.29)	104	2 [1.2]
Unharvested control	2010	3.3 (5.5)	595	11.1 [-]	—	—	—	0.47 (0.76)	85	1 [-]
	2011	8.7 (21.1)	1,206	22.2 [-]	2.63 (23.03)	931	17.1 [-]	1.23 (2.5)	107	2.3 [-]
	2012	7.7 (10.5)	1,049	17.6 [-]	3.30 (9.39)	901	15.2 [-]	1.43 (1.35)	109	1.7 [-]
	2013	6.0 (13.0)	495	12.4 [-]	2.87 (14.92)	523	13.1 [-]	0.92 (1.92)	82	1.7 [-]

Note. DOC, dissolved organic carbon.

concentrations at both harvested hillslopes that were not observed at the Unharvested Control hillslope (Figure S2 in Supporting Information S1). The magnitude of the increased springtime SO₄²⁻ concentrations was $\sim 1.4\times$ greater for the Biomass Removed hillslope than the Biomass Left hillslope (Figure 3). Despite increased subsurface runoff at both harvested hillslopes (McCarter, Sebestyen, Eggert, Kolka, & Mitchell, 2020), SO₄²⁻ yields increased at both harvested hillslopes, but only significantly at the Biomass Removed hillslope (Figure 3, Table S2 in Supporting Information S1).

4.4. Interactions Among Subsurface Runoff Chemistry and Hydrology

On these same hillslopes, McCarter, Sebestyen, Eggert, Kolka, and Mitchell (2020) observed significant annual and event-scale subsurface runoff changes at the harvested hillslopes, where the Biomass Left hillslope produced more runoff than observed at the Biomass Removed hillslope (Table S3 in Supporting Information S1). Significant negative linear correlations were observed between annual subsurface runoff ratio and annual average concentrations of THg, DOC, and SO₄²⁻ in subsurface runoff (Figure 4). Correlations were generally positive between annual subsurface runoff ratios and yields, though not significant for DOC yields and only significant for THg yields if 2013 ($R^2 = 0.90$, $p < 0.001$) data were excluded (Figure 4a, dashed black line).

There were also strong, positive linear relationships between DOC and THg concentrations in subsurface runoff at all hillslopes, though the relationships differed across hillslopes (Figure 5). There was no change in the DOC-THg relationship between pre- and post-harvest conditions at the Unharvested Control and Biomass Left hillslopes, while the slope of the DOC-THg relationship increased marginally ($p = 0.09$) at the Biomass Removed hillslope post-harvest.

4.5. Mercury in Peat

Summertime Hg concentrations and K_{meth} in peat down-gradient of the experimental hillslopes generally decreased following harvesting, though not always significantly. In contrast, inter-annual differences were generally not observed down-gradient of the Unharvested Control hillslope (Figure 6; pair-wise comparisons in Table S4 in Supporting Information S1). Despite an increase in the total mass of THg entering the upland-peatland interface, THg concentrations did not change in any of the downgradient peat following harvest (Figure 6). Conversely, mean peat MeHg concentrations decreased ($p < 0.05$) down-gradient of the Biomass Removed and Biomass Left hillslopes following harvest, whereas the inter-annual change in peat MeHg concentrations down-gradient

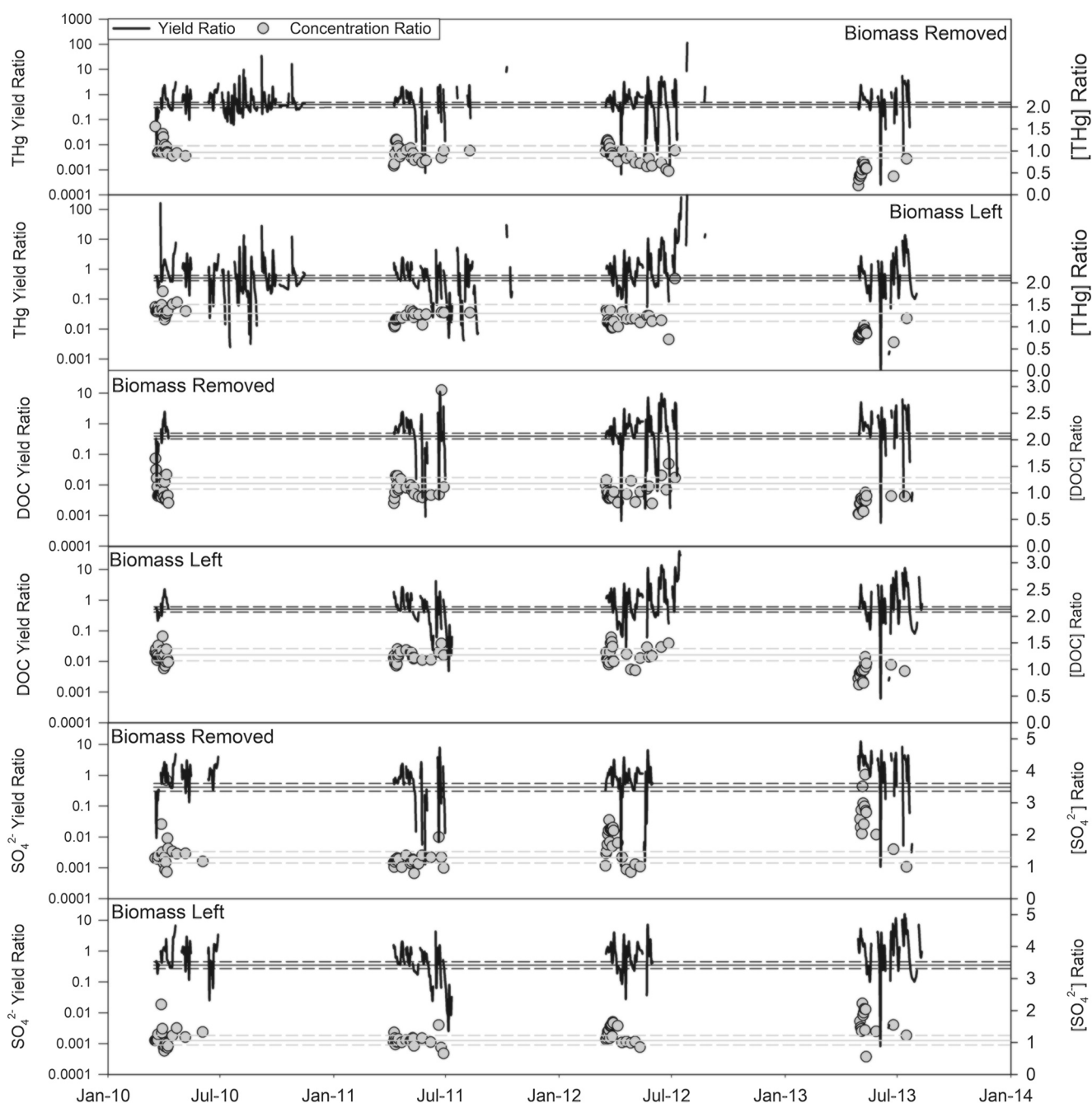


Figure 3. Timeseries of the yield (primary y-axis; black lines) and concentration (secondary y-axis; gray dots) treatment ratios (treatment hillslope values/control hillslope values) for THg, DOC, and SO_4^{2-} at the Biomass Removed and Biomass Left hillslopes. The solid and dashed lines are the estimated marginal mean and 95% confidence intervals of the treatment ratio during the pre-harvest period. *Note.* Yields are plotted on a $\log_{10}$ scale whereas concentrations are on a linear scale.

of the Unharvested Control hillslope was insignificant (Figure 6, Table S4 in Supporting Information S1). The changes in MeHg concentrations drove decreases in %MeHg in the receiving peatland on the Biomass Removed ($p < 0.001$) and Biomass Left ($p = 0.07$) hillslopes, while no change in %MeHg was observed at the Unharvested Control hillslope. Pre-harvest, K_{meth} was not different among the three hillslopes ($p > 0.1$), while post-harvest, K_{meth} decreased ($p < 0.0001$) in all downgradient peat, regardless of treatment (Figure 6, Table S4 in Supporting Information S1). Relative to the Unharvested Control, K_{meth} was higher in the peatland interface of both harvested hillslopes but were not different between harvested hillslopes (Figure 6, Table S4 in Supporting Information S1).

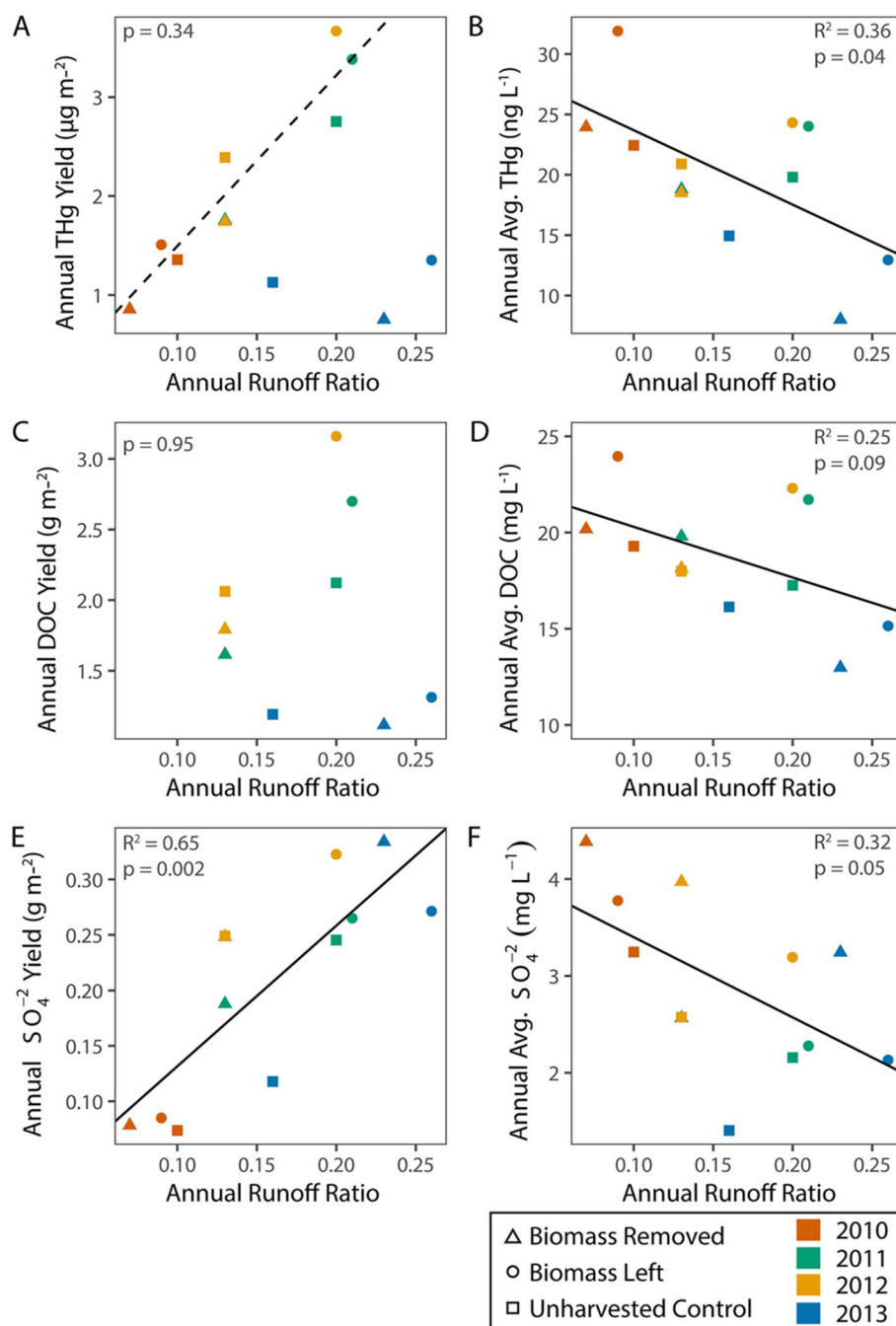


Figure 4. Linear regressions between annual hillslope runoff ratios and THg, DOC, and SO_4^{2-} yields (a, c, and e) and concentrations (b, d, and f). Note. For THg yield (a), the displayed dashed black line is a linear regression that does not include 2013 values (in blue); when 2013 was included, the regression was not significant. Due to limited DOC samples in 2010, no annual yield estimates were available for regression.

Seasonally, peat MeHg concentrations and %MeHg were greatest in the summer and least in the fall (Figure S3 in Supporting Information S1). There was no clear seasonal trend in K_{meth} (Figure S3 in Supporting Information S1).

4.6. Peatland Invertebrate Methylmercury

Methylmercury concentrations within the peatland interface food web increased from the lowest to highest assumed trophic levels across all hillslopes during all years. During the spring, which coincided with the

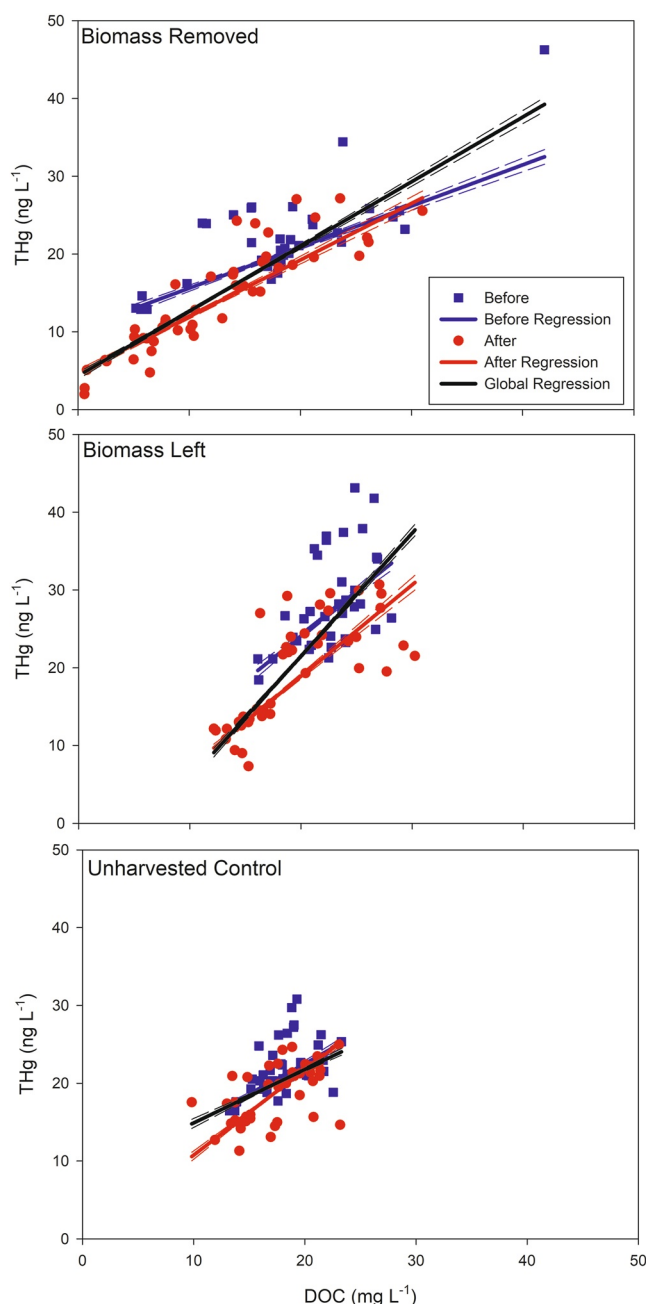


Figure 5. Linear regressions between DOC and THg concentrations in subsurface runoff of each of the three hillslopes.

macro-invertebrate sampling, concentrations of MeHg in the 0–2 cm depth peat, the basal food resource of the peatland interface for Lumbriculidae, ranged from 2.0 ng g⁻¹ below the Biomass Left hillslope prior to harvesting to 8.3 ng g⁻¹ below the Unharvested Control hillslope during the first pre-harvest year (Figure S3 in Supporting Information S1). Primary consumers that feed on detritus such as peat, including Lumbriculidae (worms) and *Polydesmus* spp. (millipedes), had lower levels of MeHg (Lumbriculidae: 7.4–26.3 ng g⁻¹; *Polydesmus* spp. 22.6–37.5 ng g⁻¹) compared to the other macroinvertebrates, with no clear differences among treatments or years (Figure 7).

Biomagnification of MeHg by worms from peat was not apparent after harvest below the Biomass Left hillslope but was elevated below the Biomass Removed hillslope after harvesting when compared to the BMF for the Unharvested Control (Figure 8). Patterns of MeHg concentrations found for predaceous *Pholcidae* (cellar spiders: 7.433.3–54.9 ng g⁻¹), *Carabidae* (ground beetles: 19.9–94.2 ng g⁻¹), mixed Araneae (mixed spiders: 44.9–133.6 ng g⁻¹), and *Lycosidae* (wolf spiders: 78.1–224.9 ng g⁻¹) below both harvested hillsides were similar to those found below the Unharvested Control hillside (Figure 7). Within the pooled taxa of the food webs examined here, we found no significant differences in MeHg concentrations among treatments (ANOVA, $p = 0.816$), years (ANOVA, $p = 0.349$), or the treatment by year interaction (ANOVA, $p = 0.878$) suggesting little impact of harvest treatments on MeHg levels within the peatland interface food web.

5. Discussion

5.1. Mobilization of Mercury and DOC From Harvested Hillslopes

Recent research at this study site (McCarter, Sebestyen, Eggert, Kolka, & Mitchell, 2020) has demonstrated that after harvest (2012 and 2013), both subsurface runoff and runoff ratios at both harvested hillslopes significantly increased, but there was a differential response between harvesting treatments (Table S3 in Supporting Information S1). Leaving the residual biomass resulted in significantly greater runoff generation than harvesting the residual biomass (McCarter, Sebestyen, Eggert, Kolka, & Mitchell, 2020). On the Biomass Removed hillslope, the difference in runoff generation created hydrological conditions that were more similar to the Unharvested Control hillslope, though still impacted (McCarter, Sebestyen, Eggert, Kolka, & Mitchell, 2020). These differences in runoff generation between the harvested hillslopes were likely driven by differences in soil evaporation, where the removal of residual biomass increased water loss to the atmosphere relative to leaving the residual biomass (McCarter, Sebestyen, Eggert, Kolka, & Mitchell, 2020). On both harvested hillslopes, there was also a shift in the routing of runoff toward a greater proportion of near-surface preferential flow at the expense of deeper saturated throughflow (McCarter, Sebestyen, Eggert, Kolka, & Mitchell, 2021).

The forest harvest-driven increases in THg yields at first appear contrary to the observed decreases in subsurface runoff THg concentrations at both harvested hillslopes. However, this seeming dichotomy is because of harvest-driven increases in subsurface runoff volumes observed by McCarter, Sebestyen, Eggert, Kolka, and Mitchell (2020) that more than compensated for the lower concentrations observed post-harvest. Oswald and Branfireun (2014) observed similar concentration and yield responses in stream waters diluted by large precipitation events. This response was less apparent for THg on the Biomass Removed hillslope post-harvest, where the relatively smaller increase in subsurface runoff (McCarter, Sebestyen, Eggert, Kolka, & Mitchell, 2020) was not enough to offset the dilution effect, leading to a smaller and insignificant increase in THg yield in subsurface

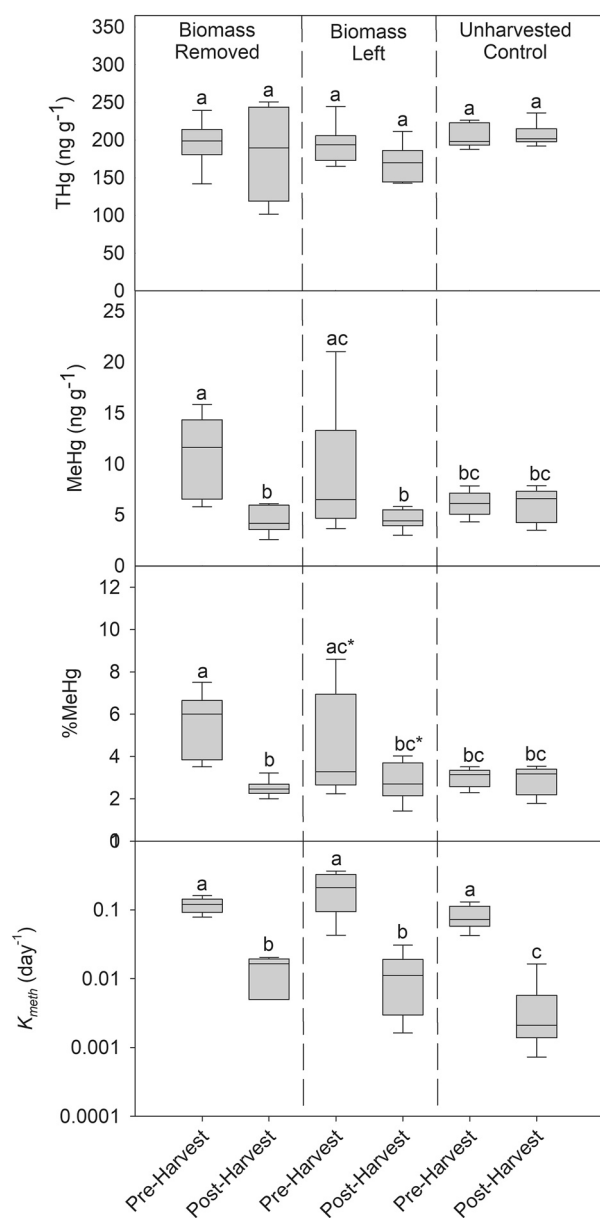


Figure 6. THg and MeHg concentrations, %MeHg, and K_{meth} in peat down gradient of all sites during the summer in 2011 and 2012. The different letters represent significance at $p < 0.05$, with pairwise difference statistics available in Table S4 in Supporting Information S1. * $p = 0.07$. Seasonal and seasonal $\times$ sampling depth plots of these peat parameters can be found in the Supporting Information (Figure S3 in Supporting Information S1).

runoff. On the Biomass Left hillslope, the larger increase in subsurface runoff post-harvest (McCarter, Sebestyen, Eggert, Kolka, & Mitchell, 2020) significantly increased THg yields because it offset the dilution effect. When the efficiency with which precipitation was converted into subsurface runoff (i.e., the runoff ratio) was high, subsurface water was rapidly shuttled downhill, decreasing the THg concentrations and partly driving the observed dilution effect. However, in 2013, the lower but more consistent precipitation amounts per event coupled with harvesting resulted in a breakdown of the runoff ratio-THg yield relationship. This breakdown was likely driven by changes in the routing of water between near-surface preferential flow and deeper flowpaths, which has been shown to alter the mobilization of different THg pools from these hillslopes (McCarter, Sebestyen, Eggert, Kolka, & Mitchell, 2021) and the dilution effect observed in this study. Here, we postulate that the more consistent precipitation decreased the proportion of near-surface preferential flow, while maintaining greater downslope hydrological connectivity and thus higher runoff ratios (McCarter, Sebestyen, Eggert, Kolka, & Mitchell, 2020). Since there was a greater proportion of water that flowed through the deeper and lower Hg concentration soils relative to the near-surface soils (Haynes & Mitchell, 2012), there were lower THg concentrations in the subsurface runoff despite the high runoff ratios (Haynes & Mitchell, 2012). Although the increased total gaseous Hg flux during the leaf-out period observed at this study site by Mazur et al. (2014) could have further impacted the THg concentrations, the overall impact of this process was likely minor relative to the hillslope soil Hg pool. In any case, it is evident that the hydrological changes due to the different harvesting practices play a critical role in regulating the mobilization of Hg from harvested hillslopes.

The hydrological processes (i.e., runoff ratio) that governed THg yields and concentrations also governed DOC yield and concentrations. Relative to THg, the dilution effect on DOC concentrations post-harvest was more subtle, resulting in significantly greater DOC yields from both harvested hillslopes. Beyond the hydrological impacts that impact both THg and DOC, the addition of fresh litter (residual biomass) to the hillslope can further alter DOC patterns because of the decomposition of the residual biomass (Dai et al., 2001; Kalbitz et al., 2004; Schelker, Grabs, et al., 2013), potentially explaining the poorer relationship between runoff ratio and DOC concentration relative to THg. Schelker, Grabs, et al. (2013) determined that DOC mobilization post-harvest was due to changes in both hydrological flow paths and warming soils (due to enhanced sunlight exposure when trees were removed), which increased the decomposition of organic matter and residual biomass. The results of Schelker, Grabs, et al. (2013) are consistent with the enhanced DOC yield at the Biomass Removed hillslope, where the lack of residual biomass increased the solar radiation and soil temperature relative to the Biomass Left hillslope (Mazur et al., 2014), potentially increasing the decomposition of remaining organic matter (either residual soil organic matter or woody and vegetal harvesting debris that was not removed) and

decreasing the magnitude of the aforementioned dilution effect. On the Biomass Left hillslope, shading of the surface by residual biomass resulted in a smaller increase in soil temperatures (Mazur et al., 2014), potentially moderating decomposition rates even though a significantly larger pool of residual biomass was on the surface. The potential differences in decomposition rates coupled with the greater dilution effect on the Biomass Left hillslope likely drove the lower DOC concentrations. These contrasting post-harvest conditions suggest a delicate balance between hydrological and biogeochemical changes that govern the response in DOC mobilization from harvested hillslopes, at least over relatively short periods (2 yr).

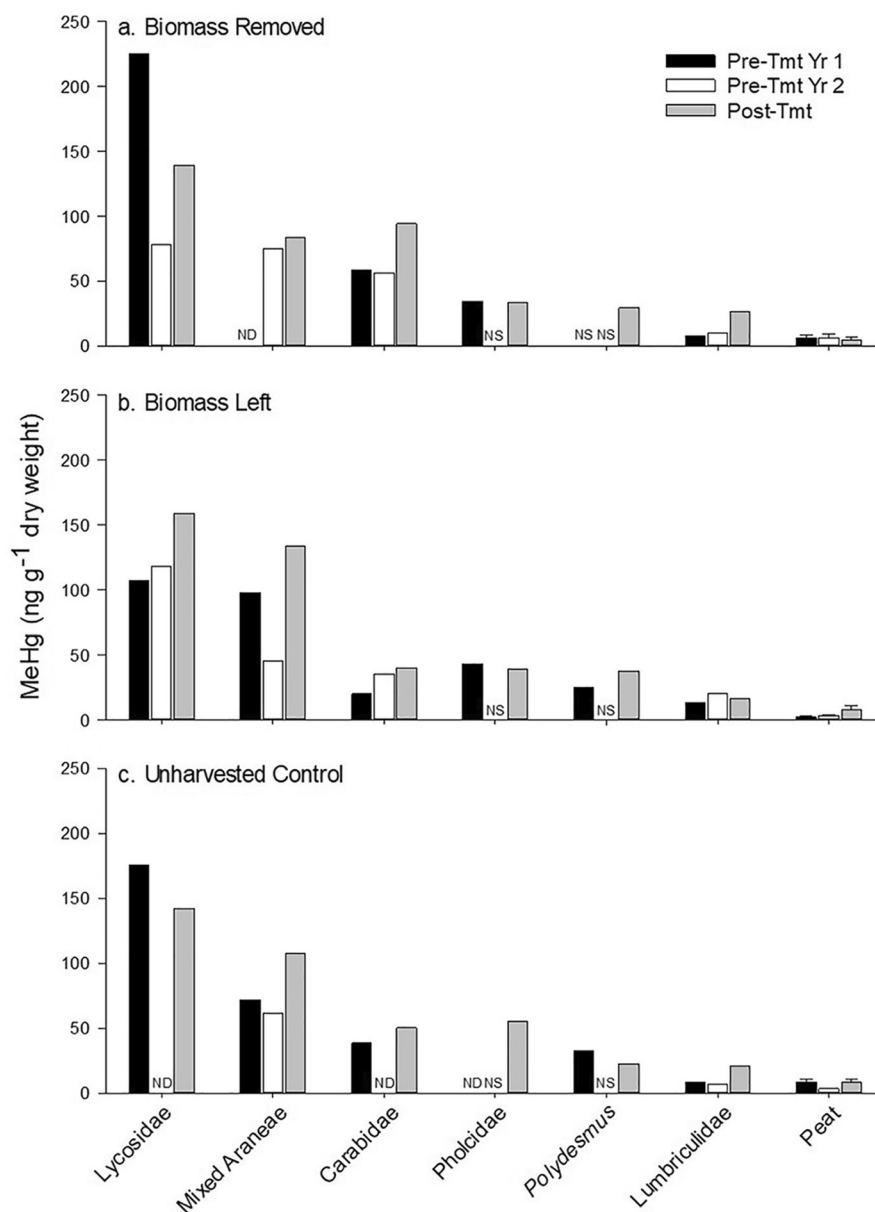


Figure 7. Methylmercury concentrations by dry weight in invertebrates and peat pre- (Pre-Tmt Yr1 and Pre-Tmt Yr2) and post-harvest (Post-Tmt). Peat values are $M + 1\ SD$ ($n = 3$ or 6). Other data points represent a composite sample ($n = 1$). NS, no sample collected; ND, sufficient sample material collected but data lost.

There was a differential response between harvesting practices on the co-mobilization of THg and DOC. The drier conditions at the Biomass Removed hillslope likely altered the production and consumption of DOC in the pore waters (Schelker, Grabs, et al., 2013) and the hydrological flow pathways (McCarter, Sebestyen, Eggert, Kolka, & Mitchell, 2021), resulting in a shift in the DOC-THg relationship. This shift was potentially due to changes to the dominant source of THg or DOC on this hillslope. For instance, McCarter, Sebestyen, Eggert, Kolka, and Mitchell (2021) observed an increase in the proportion of an enriched Hg isotope tracer relative to the ambient THg (at times $>40\%$), driven by alterations to hydrological flowpaths and preferential near-surface flow. Such as shift in the routing of subsurface runoff may disproportionately change the DOC-THg relationship on the drier Biomass Removed hillslope. In contrast, leaving the residual biomass only decreased the concentrations of THg and DOC, indicating an overall dilution effect but likely no functional change, as any changes in the production and consumption of DOC in the pore waters and the hydrological flow pathways were offset by the dilution effect. The response in the DOC-THg relationship is not consistent throughout the literature (Eklöf

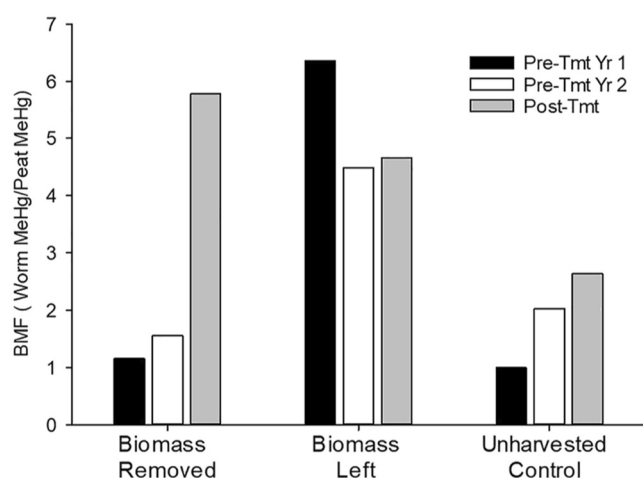


Figure 8. Biomagnification Factor (BMF) of methylmercury in Lumbricidae from peat (0–2 cm depth) for each treatment during spring 2010 (pre-harvest year 1), 2011 (pre-harvest year 2), and 2012 (post-harvest year 1).

et al., 2016). Eckley et al. (2018) observed changes in both the intercepts and overall slopes of DOC-filtered/particulate Hg relationships in western USA harvested catchments, while Skjellberg et al. (2009) observed an increase in Hg-DOC ratio in streamwater draining clearcut Swedish boreal forests within 0–4 yr. Conversely, de Wit et al. (2014) observed no change in the DOC-THg relationship in a boreal Norwegian forest catchment. It is likely that these divergent responses were due to the different local catchment physiography, such as slope, soil type, or hydrological flowpath length. The complex interaction between changes in subsurface runoff dynamics and the mobilization of Hg and ancillary solutes, such as DOC, has contributed to the conflicting Hg response to forestry operations.

5.2. Sulfate Response

Forestry operations often result in limited changes to SO_4^{2-} mobilization from uplands to lakes and rivers (Kronberg et al., 2016; Piirainen et al., 2004, 2009). However, small changes in SO_4^{2-} concentrations can have profound downgradient impacts on Hg cycling by fueling microbial SO_4^{2-} reduction and subsequent Hg methylation, particularly in peatlands (Branfireun et al., 1999; Mitchell et al., 2008a, 2009; Pierce et al., 2022). On these hillslopes, there was not a clear change in SO_4^{2-} concentration treat-

ment ratios due to either harvesting practice but there was more inter- and intra-annual variability post-harvest. Although there was no statistically significant increase in SO_4^{2-} concentration at either harvested hillslope, leaving residual biomass appears to have created subtle but unclear conditions that may have been more favorable to SO_4^{2-} mobilization. These more favorable mobilization conditions were strongly related to the changes in the efficiency with which precipitation generates subsurface runoff (i.e., runoff ratio), where the increase in runoff ratio increased both SO_4^{2-} yields and concentration. A key difference between these hillslopes and those studied by Kronberg et al. (2016) and Eklöf et al. (2018) is the lack of relatively saturated organic soils on these hillslopes. Given the relatively rapid draining of these hillslope soils (McCarter, Sebestyen, Eggert, Kolka, & Mitchell, 2020), microbial SO_4^{2-} reduction, and subsequent Hg methylation as observed by Kronberg et al. (2016) and Eklöf et al. (2018), would be limited (Bishop et al., 2020; Mitchell et al., 2009). Regardless of the exact mechanism that governs SO_4^{2-} mobilization from undisturbed and harvested hillslopes, the increased subsurface runoff, particularly during summer on the Biomass Left hillslope (McCarter, Sebestyen, Eggert, Kolka, & Mitchell, 2020), mobilized more SO_4^{2-} than pre-harvest, driving the increased SO_4^{2-} yields at both sites. Given that leaving residual biomass on the hillslope is a common forestry practice (Dirks-wager et al., 2011), investigating the co-mobilization of THg, DOC, and SO_4^{2-} from harvested hillslopes may illuminate some of the variability in Hg response to forest harvesting in the literature.

5.3. Cumulative Downgradient Impacts of Harvesting

There was no change in the THg bound to the peat post-harvest due to either harvesting practice, likely because the mass of THg entering the peatland was several orders of magnitude lower than what is bound within the upper few decimeters of peat directly adjacent to the hillslope. Given the much larger store of Hg in the peat versus the subsurface runoff and the relatively short study length, the impact from forest harvesting would have to be on a much longer time scale or magnitude than commonly observed to appreciably change peat THg concentrations (Bishop et al., 2009; de Wit et al., 2014; Skjellberg et al., 2009). As the changes in hillslope hydrology were a significant factor in the differential mobilization of Hg, the return of pre-harvest subsurface runoff dynamics will ultimately limit the length of any overall impact. The regeneration of the forest and the associated decrease in subsurface runoff would likely decrease the impact over time and be limited to ~ 10 yr (Buttle et al., 2018, 2019; Sebestyen, Verry, & Brooks, 2011; Skjellberg et al., 2009). When coupled with the minimal surface disturbance in this study (i.e., limited, if any, overland flow and erosion; McCarter, Sebestyen, Eggert, Kolka, & Mitchell, 2020), the regeneration of the forest would likely offset any longer-term impacts to THg from these particular forestry operations.

Post-harvest, it was expected that MeHg production in the receiving peatland would be stimulated during the warmer summertime because of the increase in the mass of THg, SO_4^{2-} , and, what is assumed to be relatively labile dissolved organic matter in the subsurface runoff (Mitchell et al., 2008b). Such an increase in methylation did not occur in the peatland area down-gradient of either harvested hillslope relative to pre-harvest conditions. In 2012 (post-harvest), K_{meth} significantly decreased across all three hillslopes but the decrease in K_{meth} was significantly smaller at both the harvested hillslopes relative to the Unharvested Control hillslope post-harvest. Given that there was no difference in K_{meth} prior to harvest between any site, the smaller decrease in K_{meth} relative to the Unharvested Control hillslope suggests that harvesting could stimulate methylation in the upland-peatland interface, but only to a relatively small degree. However, the large inter-annual decrease in K_{meth} , including in peat below the Unharvested Control hillslope, pre- to post-harvest suggests that other factors governed the overall magnitude of K_{meth} in these particular interfaces. For instance, during peat sampling the water table in the peatland was ~5 to 15 cm lower in 2012 than 2011 (McCarter et al., 2020a, 2020b), which would drive lower peat moisture contents of the sampled peat (Waddington et al., 2015). Given these changes in K_{meth} , but much clearer experiment-related decreases in peat MeHg concentrations, we suggest that the observed decrease in summer peat MeHg concentrations post-harvest was driven by demethylation, which may have been stimulated by inputs of more energetic electron acceptors (Branfireun et al., 2020; Todorova et al., 2009; Vlassopoulos et al., 2018). Since we did not directly measure demethylation (i.e., K_{demeth}), we are limited in our capacity to interpret how important the stimulation of demethylation might be. In any case, these results highlight the complexity in unraveling cumulative Hg impacts from forest harvesting. Determining the specific interaction between harvesting and the downgradient decrease in peat MeHg concentration post-harvest is critical to properly assessing the overall impacts of hillslope forestry operations. These processes remain uncertain and are a critical research gap in Hg forestry research.

The lack of significant differences in MeHg concentrations within the peatland invertebrates below each hillslope treatment does not match with the observed changes in MeHg concentrations within the peat nor with the observed increases in THg mass flux from the experimental hillslopes. Though we observed an increase in BMF in the receiving peatland below the Biomass Removed hillslope, this was clearly driven by the decreased peat MeHg concentration rather than an increase in Lumbricidae MeHg concentration. Instead, patterns of MeHg concentrations in detritivores and invertebrate predators collected below each hillslope were similar to patterns of MeHg concentrations in organisms of similar trophic levels from other studies (Bartrons et al., 2015; Rimmer et al., 2010; Wyman et al., 2011). The biomagnification of MeHg from lower to upper trophic levels can lead to negative consequences as MeHg eventually reaches very large concentrations in avian and other mammals in adjacent food webs (Cristol et al., 2008). Although we did not have enough sample biomass to run MeHg analyses on every organism type found in these food webs (Batzer et al., 2016), concentrations of MeHg in the dominant organisms found inhabiting the peatland interface below both harvest treatments were below or similar to those reported in other forest soils (Rieder et al., 2011) and *Sphagnum* peatlands and heathlands (Bartrons et al., 2015). Results from a previous study demonstrating low levels of MeHg in predaceous juvenile shrews (*Sorex cinereus*) from this same peatland pre-harvest (Tavshunsky et al., 2017), along with the current study results, suggest that biomass harvesting in peatland dominated landscapes similar to those studied here likely will not result in large transfers of Hg to higher trophic levels at this particular spatial scale or timeframe.

5.4. Linkages to Catchment-Scale Studies

The measurement of Hg at the catchment scale is an integrated measurement of all the processes impacting Hg along hydrological flowpaths (Åkerblom et al., 2015; Woerndle et al., 2018). For instance, Hg-total organic carbon ratios are highest in precipitation and subsequently decline along the flowpath from soil water to stream-water (Åkerblom et al., 2015) due to covarying changes in organic matter composition and adsorption of Hg or Hg-DOC complexes to the soils (Demers et al., 2013; Jiskra et al., 2017; Kolka et al., 2001; O'Connor et al., 2019). Relative to catchment-scale studies, there are few studies that investigate the mobilization of Hg from hillslopes, and fewer from harvested hillslopes. Linking the hillslope and catchment scales is challenging due to the differences in measurements used to assess forest harvest impacts, beyond only concentrations, which do not account for water volume. For instance, many hillslope studies report elevated Hg concentrations in pore water or tire-rut surface water (Eklöf et al., 2012, 2018; Haynes & Mitchell, 2012; Kronberg et al., 2016), while catchment studies often report Hg yields along with concentrations, though again, the directionality of these changes is not consistent throughout the literature (Bishop & Lee, 1997; Eckley et al., 2018; Eklöf et al., 2012, 2014; Oswald &

Branfireun, 2014; Porvari et al., 2003; Skjellberg et al., 2009; Sørensen et al., 2009a; Ukonmaanaho et al., 2016). In this study, we take a component of the integrated catchment measurement, hillslope subsurface runoff derived THg, and because of the experimental design are able to report not only the THg concentration that is commonly reported, but also the THg yields. On the unharvested hillslopes (treatment hillslopes in 2010–2011 and all years of the Unharvested Control hillslope), there was a large difference in the annual mass of THg mobilized among the three different hillslopes (374–1,206 μg). The annual mass of THg leaving the undisturbed hillslopes was controlled by the effectiveness of the hillslope to convey water (i.e., annual runoff ratios). As the annual runoff ratio increased, there was proportionally more mass of Hg leaving the hillslope. However, the THg yields observed from these unharvested hillslopes (6–26 $\text{ng m}^{-2} \text{day}^{-1}$) were often 2–3x higher than observed in stream waters at catchment scales (0.8–10 $\text{ng m}^{-2} \text{day}^{-1}$; Bishop et al., 2009; de Wit et al., 2014; Eckley et al., 2018; Eklöf et al., 2014; Porvari et al., 2003). Similar to the unharvested yields on these hillslopes, the post-harvest THg yields (12.1–23.5 $\text{ng m}^{-2} \text{day}^{-1}$) were consistently higher than those reported in the broader catchment literature (1.3–14.5 $\text{ng m}^{-2} \text{day}^{-1}$; Bishop et al., 2009; de Wit et al., 2014; Eckley et al., 2018; Eklöf et al., 2014; Porvari et al., 2003). Post-harvest, the highest catchment THg yields from the literature were from organic-soil dominated boreal forests in Europe (de Wit et al., 2014; Eklöf et al., 2014; Porvari et al., 2003), while the lowest were from the more mineral-soil dominated and steep forests of the western USA (Eckley et al., 2018). Despite this broader trend in mineral versus organic/humus-rich soil hillslopes, the THg yields measured from these mineral-soil dominated hillslopes were much higher than any of the catchment yields, suggesting that the routing of water through ecosystems (ecohydrological flowpaths) between the surface waters and the hillslopes are critical in modulating adverse impacts from forestry operations on downgradient Hg dynamics.

6. Conclusions

In this study, we elucidated complicated interactions that govern the response of Hg due to differing forest harvesting practices, as well as the complexity in assessing cumulative impacts of Hg in receiving ecosystems and biota. The cumulative impacts of forest harvesting on Hg were strongly governed by the routing of precipitation and the mobilization of other solutes, such as DOC and SO_4^{2-} . On these hillslopes, there was a greater maintained water surplus post-harvest that created a dilution effect, decreasing both THg and DOC concentrations at both harvested hillslopes. This dilution effect was proportional to the subsurface runoff response (i.e., greater at Biomass Left than Biomass Removed). Concurrently, this increased amount of subsurface runoff mobilized more THg and DOC from both harvested hillslopes. The increase in subsurface runoff also increased the SO_4^{2-} yield at both sites but only significantly at the Biomass Left hillslope. Harvest operations led to smaller decreases in peat K_{meth} relative to the Unharvested Control hillslope, but much larger, experiment-specific declines in peat MeHg concentration and %MeHg during the warmer summertime below both harvested hillslopes were observed. The changes in peat MeHg concentrations post-harvest were not expressed in the peatland macroinvertebrate community. The disparate impacts of forestry operations on Hg bioaccumulation and mobilization across the literature is, at least partly, explained by variations in physiographic hillslope features (e.g., soil type and slope) and harvesting practice. The differential response in Hg mobilization between harvesting residual biomass versus leaving residual biomass on the ground after clearcutting highlights the necessity to tailor mitigation measures to varying forest harvesting practices and illustrates situations where harvesting has little to no impact on downgradient MeHg accumulation.

Data Availability Statement

All data used in this publication can be found in McCarter, Sebestyen, Eggert, Haynes, et al. (2020), McCarter, Sebestyen, Eggert, Haynes, et al. (2021), and McCarter et al. (2022).

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