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New Insights on Ecosystem Mercury Cycling Revealed by Stable Isotopes of Mercury in Water Flowing from a Headwater Peatland Catchment

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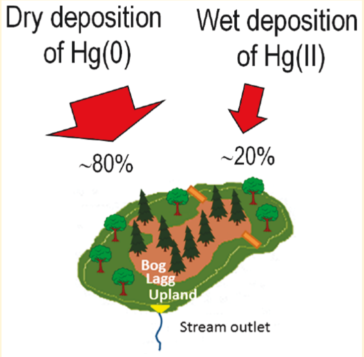
Supporting Information

ABSTRACT: Stable isotope compositions of mercury (Hg) were measured in the outlet stream and in soil cores at different landscape positions in a 9.7-ha boreal upland-peatland catchment. An acidic permanganate/persulfate digestion procedure was validated for water samples with high dissolved organic matter (DOM) concentrations through Hg spike addition analysis. We report a relatively large variation in mass-dependent fractionation (δ^{202}Hg; from −2.12 to −1.32‰) and a smaller, but significant, variation of mass-independent fractionation (Δ^{199}Hg; from −0.35 to −0.12‰) during two years of sampling with streamflow varying from 0.003 to 7.8 L s^{-1}. Large variations in δ^{202}Hg occurred only during low streamflow (<0.6 L s^{-1}), which suggest that under high streamflow conditions a peatland lagg zone between the bog (3.0 ha) and uplands (6.7 ha) becomes the dominant source of Hg in downstream waters. Further, a binary mixing model showed that except for the spring snowmelt period, Hg in streamwater from the catchment was mainly derived from dry deposition of gaseous elemental Hg (73−95%). This study demonstrates the usefulness of Hg isotopes for tracing sources of Hg deposition, which can lead to a better understanding of the biogeochemical cycling and hydrological transport of Hg in headwater catchments.



INTRODUCTION

Peatlands, a particular type of wetland, store vast amounts of carbon in deep organic soil and are important landscape features in boreal and northern environments.[1] Peatlands are substantial sinks of mercury (Hg) from atmospheric deposition and sources of dissolved organic matter (DOM) and Hg to surface waters.[2,3] Peatlands are also important sources of methylmercury (MeHg) because saturation at and below peatland water tables maintains anaerobic conditions, under which extensive Hg methylation can occur.[4,5] Several factors affect how Hg is transported downstream from upland/peatland headwaters. First, DOM movement in flowing water is important because Hg strongly binds with reduced thiol groups on DOM.[6] Second, although peatlands are important areas of Hg cycling and transport, uplands are only intermittent sources of water, DOM, nutrients, and Hg to peatlands.[7] Uplands are sources of water and Hg when shallow subsurface stormflow occurs along lateral flow paths through mineral soils on upland hillslopes.[8] Although couplings between upland and peatland sources and transport processes drive the downstream movement of water, DOM, and Hg, little is known about how atmospheric Hg deposition relates to Hg processing in upland-peatland catchments.[9,10] In other words, we know little about how various atmospheric Hg sources (either as Hg(0) in dry deposition or as Hg(II) in wet deposition)[11] are directly or indirectly linked to downstream aqueous Hg transport. It is particularly important to differentiate between these two deposition pathways because we currently only monitor wet deposition of Hg through the Mercury Deposition Network of the National Atmospheric Deposition Program (URL: http://nadp.sws.uiuc.edu/mdn).[12] However, recent studies have suggested that dry deposition may be the dominant pathway of Hg deposition in vegetated landscapes.[13−15] Thus, an in-depth understanding of dry deposition will be required to fully understand and predict effects of atmospheric deposition of Hg at landscape and regional scales. Atmospheric Hg may be the substrate for MeHg formation in downstream habitats, and leads to extensive MeHg bioaccumulation and biomagnification in food webs.

New insights into Hg cycling in the environment have been gained through stable Hg isotope studies.[16] Mercury can

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undergo both mass-dependent fractionation (MDF; expressed as δ^{202}Hg) and mass-independent fractionation (MIF; expressed as Δ^{199}Hg or Δ^{201}Hg), with large-magnitude MIF (>0.4 ‰) of odd-mass isotopes (^{199}Hg and ^{201}Hg) being produced mainly through photoreduction of inorganic Hg and photodegradation of MeHg.[17] Subtle MIF associated with even-mass isotopes (^{200}Hg and ^{204}Hg) has also been recently observed for samples linked to atmospheric origins.[18−20] A number of recent studies have successfully demonstrated that natural-abundance Hg isotopes can help distinguish sources (e.g., natural vs anthropogenic)[20−22] and transformations (e.g., gaseous Hg oxidation; MeHg photodegradation)[23,24] of Hg in the environment.

A few previous studies have analyzed natural-abundance Hg isotopes in water samples with relatively low DOM levels (such as rain, snow, and lake waters) to examine isotopic variations of Hg in these environmental pools.[13,18,19,21,25−27] A recent study used ultrafiltration to collect Hg associated with DOM to measure Hg isotope ratios in streams in a boreal forest catchment where DOM is elevated.[28] This method is feasible but requires large volumes of water (e.g., 50 L) and cumbersome subsequent separation of Hg from DOM and other matrices in the water samples.[28] To make the processing more efficient we validated and used an acidic permanganate/persulfate digestion procedure, used previously for surface water with high solid loads and wastewater samples,[29,30] and followed by subsequent purge and trap of Hg to transfer it to a small volume of trapping solution.[13,18,21] With this approach we removed matrix interferences in water samples (i.e., DOM), which allowed investigation of the isotopic composition of Hg in various Hg source areas (uplands or peatlands) in a well-studied catchment in northern Minnesota. We chose this catchment because previous investigations have provided a foundational knowledge of ecosystem and hydrological processes, and the DOM and Hg source areas and transport are well-known within the watershed.[31−33] Our goal was to examine whether Hg isotopes could be used in peatland catchments to determine the relative importance of different sources of Hg (wet and dry deposition) and elucidate ecosystem processes within the catchment that affect the downstream export of Hg.

■ MATERIALS AND METHODS

Study Site and Sample Collection. The study site is a 9.7-ha upland-peatland catchment (S2) in northern Minnesota at the USDA Forest Service's Marcell Experimental Forest (MEF) (see Supporting Information (SI) Figure S1). The 3.2-ha peatland has a central 3.0-ha, ombrotrophic, raised-dome bog with Histosol soil. The bog is surrounded by a 0.2-ha lagg (wet zone on the perimeter of the peatland). There are no inlet streams to the peatland, and the outlet stream originates from the lagg at the area of lowest elevation in the peatland. The bog has a black spruce (*Picea mariana*)-*Sphagnum* community. The uplands have Alfisol soils with a ~0.5 m sandy loam layer overlying a loamy clay aquitard. The upland forest is a stand with mature aspen (*Populus tremuloides*), white birch (*Betula papyrifera*), balsam fir (*Abies balsamea*), and jack pine (*Pinus banksiana*) in the overstory. Meteorological and hydrological data (streamflow, air temperature, and precipitation amount) have been monitored for more than a half century in catchment S2 as part of a long-term research monitoring program.[34] Site information and field measurements are described in detail in SI Part I. We collected streamwater every 2 weeks during 2014 and 2015 at a v-notch weir on the outlet stream of the catchment when the stream flowed (see SI Part II). Streamflow was measured at the v-notch weir, and we apportioned streamflow into slow flow and quick flow components.[35] We consider quick flow to be streamflow that occurs in response to a rainfall or snowmelt event. Occasionally, we collected upland runoff samples (that included upland runoff above frozen soils and near surface flow through the forest floor) and subsurface stormflow samples as well as porewater samples at the lagg. In spring 2015, we collected soil samples (50 cm long cores of bog, lagg and upland soils) and vegetation samples (needles of black spruce (bog), grass litter of *Eriophorum* spp., needles of tamarack (bog), and leaf litter (aspen and white birch)) to represent different Hg sources that may have affected stream Hg concentrations and isotopic compositions. All samples were shipped on ice overnight to the analytical laboratory at the University of North Carolina at Greensboro and refrigerated or frozen until processed.

Sample Processing and Analyses. Two bottles of streamwater were collected at each sampling time for general water chemistry (cations and total organic carbon (TOC) in an HDPE bottle) and both Hg concentration (total-Hg and MeHg) and Hg isotopic analyses (in an acid-cleaned 2 L Teflon bottle). Soil and vegetation samples were collected, acid-digested, and analyzed for total-Hg (see SI Part III). Recent sampling and analyses of streamwater have shown TOC and DOC to be equivalent measurements for stream, porewater, and upland runoff water samples from the S2 catchment.[36] Herein, we report TOC, as that is what we actually measured, but we consider TOC and dissolved organic carbon (DOC) concentrations to be equivalent.

Since many of the water samples (except upland runoff and subsurface flow) had high TOC concentrations (range for all aqueous samples: 8−116 mg L^{-1}), we added an acidic mixture of permanganate and persulfate to the aqueous samples in the Teflon bottle. Per 1 L of water samples, we added 10 mL of acidic digestant (20 HNO_3:1 H_2SO_4) and 10 mL of oxidizing reagents (5% (w/v) of $KMnO_4$ and 2.5% (w/v) of $K_2S_2O_8$ dissolved in high-purity water) followed by heating in an oven at 95 °C overnight,[29,30] which has been previously shown to result in full recovery of Hg from water samples with very high TOC and/or high suspended solid concentrations. We compared this method with the traditional method of BrCl oxidation of water samples followed by complete UV oxidation,[37] which we assumed to result in complete breakdown of DOM and Hg and which should result in Hg not being associated with any binding sites after the treatment (see SI Part IV). The use of UV oxidization is known to be much more effective in completely breaking down organic matter than adding BrCl alone, but we were concerned that UV photochemical reactions might fractionate Hg isotopes in the samples.[38] We determined that the acidic permanganate and persulfate approach released >92% of Hg from water samples. Standard addition analyses of the digested samples led to an average of 99.5% recovery of Hg (SI Table S1).

To collect Hg from aqueous samples for isotopic measurements, we used a purge and trap setup to extract Hg from each ~1 L of fully digested and neutralized water sample by continuous $SnCl_2$ reduction, and we concentrated the released Hg into a small trap (6−7 g) solution of 1% $KMnO_4$ in 10% H_2SO_4 solution over 3−4 h (see detailed procedures in SI Part V and illustrated setup in Figure S2). For solid samples, we combusted the homogenized samples in a two-stage furnace

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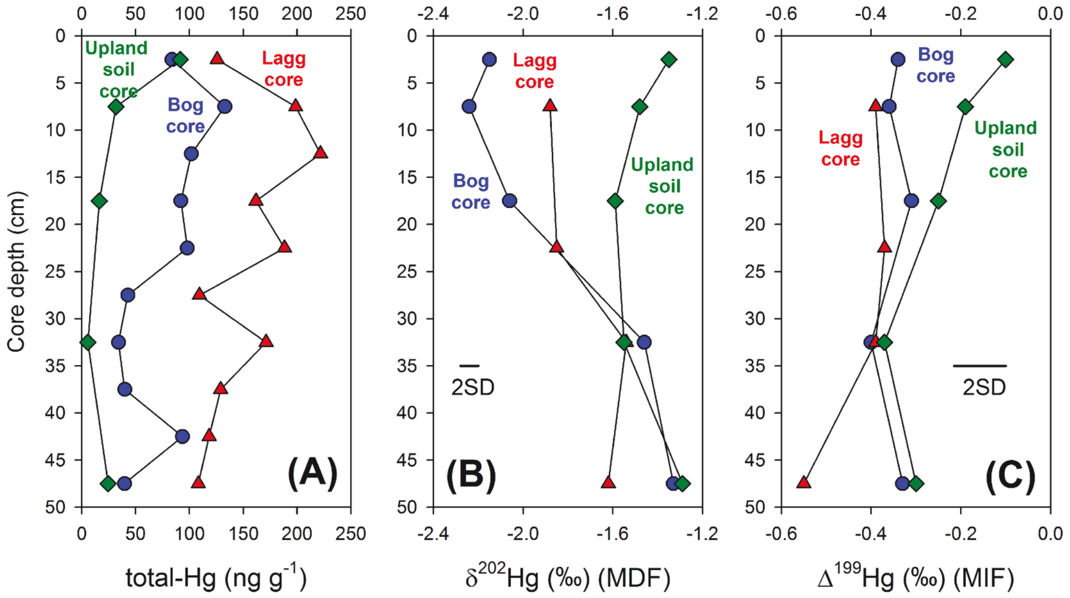

Figure 1. (A) Total-mercury concentrations (total-Hg), (B) mass-dependent fractionation (MDF; as δ^{202}Hg) and (C) mass-independent fractionation (MIF; as Δ^{199}Hg) of 50 cm cores collected at the peatland, lagg and upland forest in April, 2015. Only selected layers (4−5 per core) were analyzed for stable mercury isotopes. For (B) and (C), error bars represent external analytical reproducibility (2 SD) of our isotope measurements.

over 6 h with subsequent sample matrix removal and concentration of Hg into a final 1% $KMnO_4$ trap solution (see SI Part V). All final sample solutions were measured for total-Hg content, and the concentrations were adjusted to match within 5% the concentration of the isotopic bracketing standard (SRM NIST-3133). Mercury isotope ratios of samples were analyzed using a multicollector-inductively coupled plasma-mass spectrometer (MC-ICP-MS) (see SI Part VI) at the Biogeochemistry and Environmental Isotope Geochemistry Laboratory, University of Michigan (Ann Arbor, MI).

Quality Control and Data Analyses. Quality control and assurance for Hg isotopic analysis were performed through analyzing a secondary isotope standard solution throughout the study (UM-Almadén), and spiking of a Hg isotope standard (NIST-3133) through the entire sample processing procedure for water sample analysis, as well as analyses of standard reference materials of solid samples, that is, SRM NIST-1515 (Apple Leaves) and SRM MESS-3 (Marine Sediment). Detailed information can be found in SI Part V and Part VI, and isotopic results for solid SRMs are summarized in SI Table S2. Linear regression analyses were performed using SigmaPlot 12.5 (Systat) and the significance level for all statistical analyses was $\alpha = 0.05$.

■ RESULTS AND DISCUSSION

Streamflow and Mercury Levels. Streamflow was highly variable within and between the two years of the study. The largest amounts of stormflow occurred during late spring and summer in 2014, and during spring, fall and early winter in 2015 (SI Figure S3). Snowmelt during spring is typically a period of extended high flow, and often includes the largest flow event of the year.[7,31] However, during the winter of 2014/2015 there was little snowfall leading to much less snowmelt and streamflow during late winter and early spring of 2015 (SI Figure S3).

Over the two years of study, we collected 24 streamwater samples (2 L each, $n = 12$ per year) under variable streamflow from 0.003 to 7.8 L s^{-1} (SI Table S4). Concentrations of TOC varied from 37 to 116 mg L^{-1}, (unfiltered) total-Hg varied from 4.6 to 25.0 ng L^{-1}, and (unfiltered) MeHg varied from <0.04 to 1.47 ng L^{-1} (SI Table S4). In contrast to many other stream studies,[3,39,40] we did not observe a significant relationship between TOC and total-Hg or MeHg among the stream samples ($p > 0.05$). We also combined total-Hg, MeHg, and % MeHg data from our study with previously published studies at the S2 catchment during 1993, 1994, 1995, and 2005 (SI Figure S4).[41,42] We observed a weak positive correlation ($r^2 = 0.03$; $p = 0.07$) between $\log_{10}$-transformed total-Hg and $\log_{10}$-transformed streamflow. Interestingly, both $\log_{10}$-transformed MeHg and $\log_{10}$-transformed %MeHg exponentially decreased (both $p < 0.0001$) with $\log_{10}$-transformed streamflow, showing streamwater MeHg concentrations were highest when flow declined in this small upland-peatland catchment. The results are within our expectations because as streamflow increases we expect to see more upland runoff with lower MeHg levels, and this increased upland runoff should contribute a higher fraction of water to streamflow. Thus, a dilution effect occurred when MeHg in water from the bog was mixed with upland runoff.

In addition to stream waters, we also analyzed other water types including upland runoff ($n = 2$) and subsurface stormflow through upland soils ($n = 3$), as well as lagg porewater ($n = 2$) (SI Table S6). Upland runoff samples had higher total-Hg (18.3−56.8 ng L^{-1}) but lower MeHg (0.04−0.06 ng L^{-1}) relative to other sample types, whereas lagg porewater samples had the lowest total-Hg (10.4−13.1 ng L^{-1}), but with the highest MeHg (0.27−0.33 ng L^{-1}) and %MeHg (2.1−3.2%). These results are consistent with previous findings that the lagg is a hotspot of microbial Hg methylation in this catchment.[5]

Stable Mercury Isotopes. As shown in Figure 1A, the lagg core had the highest total-Hg concentrations (108−222 ng/g, $n = 10$), with less in the peat (bog) core (34−133 ng/g, $n = 10$), and much less in the upland soil (5.6−92 ng/g, $n = 5$) (SI Table S3), which consists of mineral soil except for the higher total-Hg concentrations in the top 5−10 cm of the forest floor.

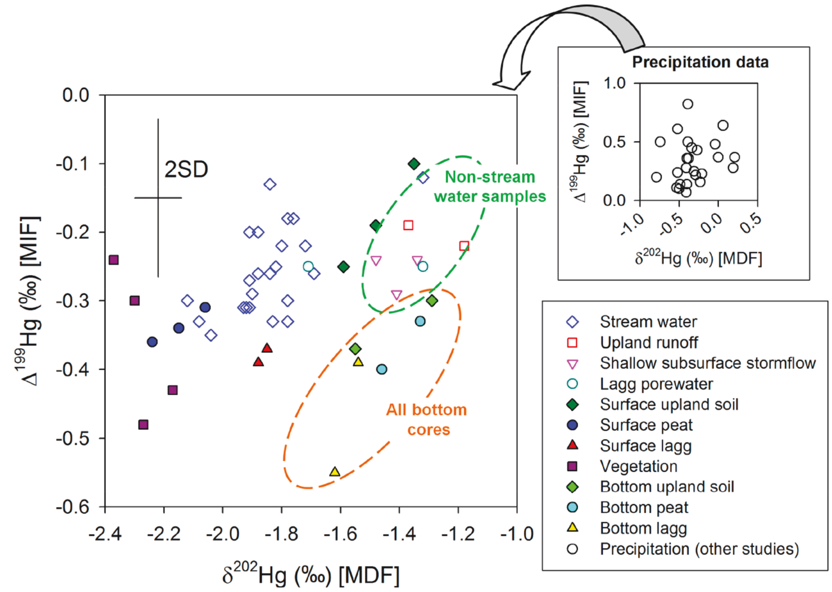

Figure 2. Stable Hg isotope compositions of all samples in this study, showing mass-dependent fractionation (MDF; as δ^{202}Hg) and mass-independent fractionation (MIF; as Δ^{199}Hg); the inset shows isotopic data of Hg in previous precipitation studies in the Great Lakes region.[13,18] Error bars show typical external analytical reproducibility (2SD) of our stable Hg isotope measurements in this study.

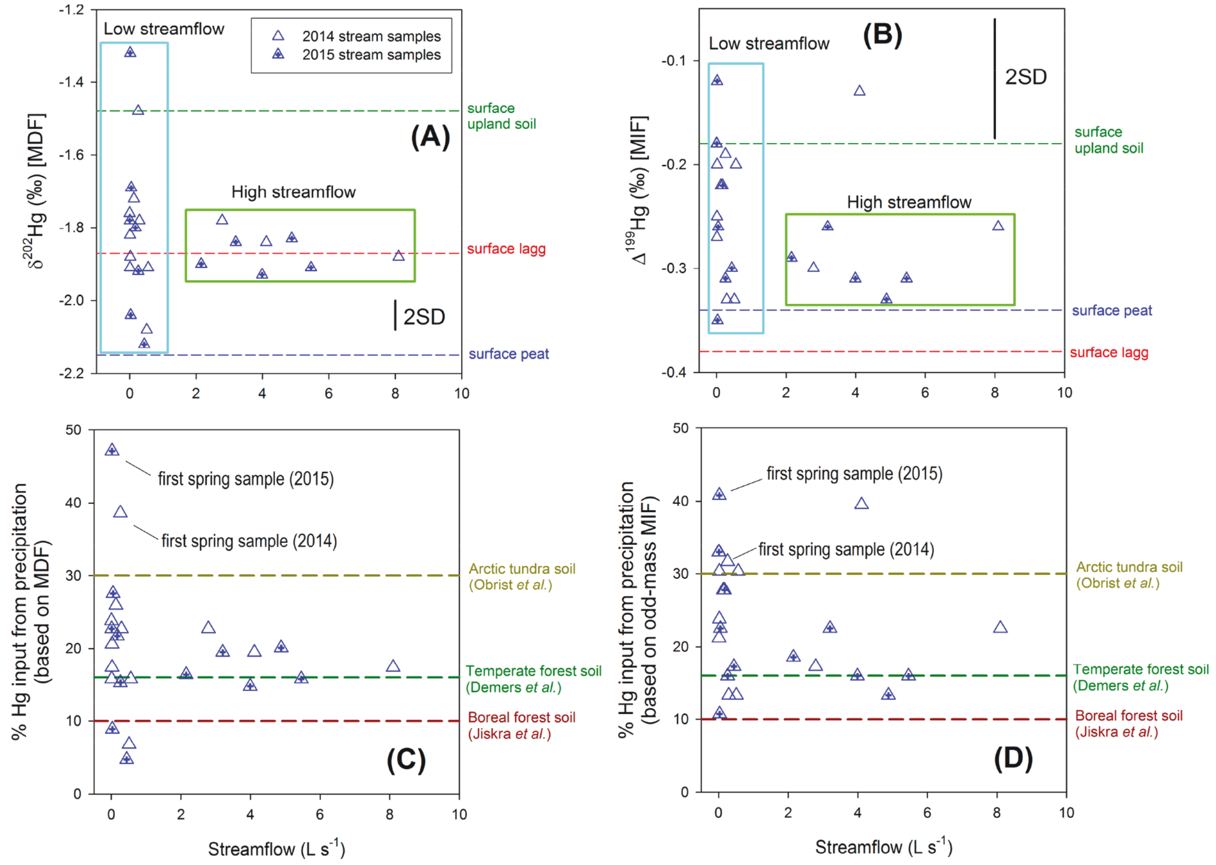

Figure 3. (A) Mass-dependent fractionation (MDF; as δ^{202}Hg) and (B) mass-independent fractionation (MIF; as Δ^{199}Hg) of Hg in streamwater as a function of streamflow at the S2 catchment; for (A) and (B), horizontal dashed lines represent the mean values in the top layer (0−20 cm) of different cores collected; error bars represent external analytical reproducibility (2 SD) of our isotopic measurements. Results of binary mixing model estimating the percent Hg contributed from wet deposition to Hg in streamwater at the S2 catchment based on (C) MDF; as δ^{202}Hg, and (D) odd-mass MIF; as Δ^{199}Hg.; horizontal dashed lines indicate the average percentage contribution of wet deposition to Hg deposition in different landscape types.[13−15]

All three cores had a narrow range of δ^{202}Hg (MDF) values (from −1.60 to −1.30 ‰) at the bottom (30−50 cm), but we found a wider range in δ^{202}Hg in the top 20 cm of the cores (from −2.30 to −1.30‰); the δ^{202}Hg value was highest in the top 20 cm of upland soil core (−1.48 to −1.35‰), lowest in the top 20 cm of peat core (−2.24 to −2.06‰), and intermediate in the top 20 cm of lagg core (−1.88‰) (Figure 1B; SI Table S3). It is noteworthy that the top 20 cm of the upland soil had the highest Δ^{199}Hg (MIF) values (−0.25 to −0.10‰) while the top 20 cm of the peat core (−0.36 to −0.31‰) and lagg core (−0.39‰) both had slightly lower Δ^{199}Hg (MIF) values (Figure 1C; SI Table S3). Nevertheless, the differences in Δ^{199}Hg values were relatively small compared to δ^{202}Hg values. These Hg isotope results for the cores also suggest that geogenic sources of Hg, which have near-zero Δ^{199}Hg (MIF) values,[16,43] are not a dominant source of Hg in these soils. The top layers of the upland soil core had the highest Δ^{199}Hg (closest to zero; Figure 1C) but we speculate that this may be due to the relatively higher inputs of Hg from wet deposition (precipitation) (see below).

Overall, there were relatively large ranges in Hg isotopic composition among streamwater samples, with δ^{202}Hg ranging from −2.12 to −1.32 ‰ and Δ^{199}Hg ranging from −0.35 to −0.12 ‰ over the two years of sampling (Figure 2 and SI Table S4). The lowest values of both δ^{202}Hg and Δ^{199}Hg in streamwater samples were similar to surficial peat (top 20 cm of core) while the highest values of both δ^{202}Hg and Δ^{199}Hg for water samples were similar to surficial upland soil (top 20 cm of core) (Figure 2). Surface lagg cores had δ^{202}Hg values similar to many water samples but their Δ^{199}Hg values were slightly lower than water samples, although the differences were within the analytical uncertainty (2SD) (Figure 2). As expected, isotopic compositions of Hg in vegetation samples collected in upland and peatland areas (δ^{202}Hg: −2.37 to −2.17 ‰; Δ^{199}Hg: −0.48 to −0.24 ‰; $n = 4$) (SI Table S5) were also similar to those collected elsewhere in North America, e.g., Wisconsin (δ^{202}Hg: −2.53 to −1.79 ‰; Δ^{199}Hg: −0.40 to −0.23 ‰; $n = 18$)[13] and across multiple forests (δ^{202}Hg: −2.67 to −2.08 ‰; Δ^{199}Hg: −0.47 to −0.06 ‰; $n = 84$).[44] The δ^{202}Hg values of vegetation were among the lowest values we observed in all samples collected from the S2 catchment (Figure 2).

For nonstreamwater samples collected within the catchment (i.e., upland runoff, subsurface stormflow, and porewater at the lagg), δ^{202}Hg values were mostly higher than streamwater samples while their Δ^{199}Hg values were also near the high range of streamwater samples (Figure 2; SI Table S4 and SI Table S6). It is interesting to note that these nonstreamwater samples had a smaller range of both δ^{202}Hg and Δ^{199}Hg values (δ^{202}Hg: −1.71 to −1.18‰; Δ^{199}Hg: −0.29 to −0.19‰) than streamwater samples, suggesting that Hg in lagg porewater was derived from the upland through subsurface stormflow, since there were no significant differences in Hg isotopic compositions (both δ^{202}Hg and Δ^{199}Hg) between the top 20 cm of the upland soil core and the lagg porewater samples ($p > 0.05$). Moreover, we found that the δ^{202}Hg values, but not Δ^{199}Hg values, matched well between these nonstreamwater samples and the bottom sections of all three soil cores we collected (Figure 1 and Figure 2).

Isotopic Variations with Streamflow and Mixing Model Calculation. Among the streamwater samples we found that streamflow strongly influenced both δ^{202}Hg and Δ^{199}Hg values (Figure 3A and B). We can group the isotopic data into "low streamflow" (<0.6 L s^{-1}) and "high streamflow" (2.2−7.8 L s^{-1}), and most of the variations in δ^{202}Hg and Δ^{199}Hg values were found in samples grouped as low streamflow. However, it should be noted that even during low streamflow there may have been some "quick flow" from saturated areas of the peatland that allowed event waters to be rapidly transmitted to the stream (SI Table S4). During high streamflow conditions there was only a narrow range of δ^{202}Hg (mean ± S.D.: −1.86 ± 0.05 ‰; $n = 8$) and Δ^{199}Hg (mean ± S.D.: −0.27 ± 0.06 ‰; $n = 8$), with one obvious outlier for Δ^{199}Hg under high streamflow (Figure 3B).

Stream water samples with the lowest δ^{202}Hg values only occurred when streamflow was entirely slow flow (i.e., there was no quick flow, SI Table 2) and during which all the water in the stream originated from the peatland (SI Figure S5). We also note that streamwater samples with higher δ^{202}Hg values only occurred when there was quick flow (>0%), showing a streamflow response to upland sources and/or precipitation (e.g., snow) events. Alternatively, in situ Hg transformations such as photoreduction of Hg(II) may become more important and shift both MDF and MIF signatures during the lowest of streamflows when the residence time of water in the channel may be substantially increased.

It has been found that Hg accumulated in foliage as a result of dry deposition of Hg(0) has much lower δ^{202}Hg and slightly lower Δ^{199}Hg value[13,44] than aqueous Hg found in wet deposition.[13,18,19,21] This isotopic contrast has allowed the quantification of the proportion of Hg derived from dry deposition (as elemental Hg) vs wet deposition (as oxidized Hg) in different ecosystems by analyzing Hg isotopes in forest floor or vegetation substrates.[13−15,45] Following this approach, we estimated the percent contribution of dry vs wet deposition to Hg in streamwater collected at the outlet of the S2 catchment using a binary mixing model. Since there is a much wider range of δ^{202}Hg than Δ^{199}Hg values, we first use MDF values for the mixing model because it provides better accuracy for the model output (i.e., %Hg from wet deposition). For the dry deposition endmember, we used the average δ^{202}Hg value of foliage samples in the S2 catchment (mean ± S.D.: δ^{202}Hg: −2.19 ± 0.15‰; $n = 4$). For the wet deposition endmember, we used the average δ^{202}Hg values in precipitation samples from the Great Lakes region published previously (mean ± S.D.: −0.32 ± 0.25‰; $n = 25$).[13,18,26]

One common consideration when using precipitation Hg isotope data is that aqueous Hg would likely be adsorbed to particles (e.g., organic matter, soil minerals) before being exported as streamflow.[6,46] A previous Hg isotope study used an average MDF shift due to adsorption of −0.4‰ to account for the inputs of precipitation Hg into the water column and binding to particles in the Great Lakes.[20] However, in our study catchment if precipitation Hg directly contributes to Hg in streamflow, then it is likely that most, if not all, precipitation Hg would quickly bind to DOM in the surface water within the peatland, and thus this would cause negligible or no MDF of Hg isotopes. This presumption is supported by a recent field study demonstrating no significant MDF of Hg isotopes between bulk soil and surface water samples in a boreal forest ecosystem,[28] implying that Hg desorbed from soil or decomposed litter may still be well bound to DOM. Therefore, these results imply that in this situation we may directly compare Hg isotope ratios in streamwater with those in bulk materials (e.g., foliage and soil) without considering secondary processes, that is, a shift of δ^{202}Hg.[28]

From our mixing calculation based on MDF values in stream samples we found an average of 18 ± 3% (±SD; $n = 8$) of wet deposition contributing to streamwater Hg under high streamflow conditions, and from ∼5% to ∼47% of wet deposition contributing to streamwater Hg under low streamflow conditions (Figure 3C). Second, we used odd-mass MIF values (Δ^{199}Hg) for the binary mixing models as MIF can be advantageous because it is not influenced by nonphotochemical processes such as adsorption to particles.[17] We obtained a similar estimate if our mixing model was based on Δ^{199}Hg values (Figure 3D). Although they do not follow one another exactly, the two estimation methods (based on δ^{202}Hg vs Δ^{199}Hg) yielded reasonable agreement with each other (SI Figure S6); it should be noted that the smaller range of odd-mass MIF values in streamwater samples may imply lower resolution and power in estimation of Hg input from precipitation. However, even-mass MIF values (Δ^{200}Hg and Δ^{204}Hg) were not observed to have a large enough magnitude (e.g., > 0.20 ‰) to show variation that might be related to sample types (refer to SI Tables S3, S4, S5, and S6). We note that while Δ^{204}Hg is generally negative in precipitation, Δ^{204}Hg in Hg(0) has been shown to be slightly positive.[13,47] Therefore, in mixtures of Hg deposited as both wet and dry deposition the even-mass MIF signal can be canceled out, especially if dry deposition is greater than wet deposition inputs as we have found to be the case in this study. Notably, the two stream samples with the highest % Hg contribution from wet deposition were each the first spring samples collected during low streamflow conditions. At those times, streamwater and Hg originated from snowmelt directly to the stream at a time when the (frozen) bog was not yet contributing water to the stream. These data, along with a few recent studies analyzing Hg isotopes in soils or vegetation samples,[13−15,45] demonstrate the importance and dominance of dry deposition (i.e., foliage uptake of Hg) to Hg accumulation in forested ecosystems and to the ultimate export of Hg to aquatic ecosystems. These results are in contrast to earlier studies using Hg concentration analyses alone, that suggested much higher proportions of Hg accumulation in forests due to wet deposition.[3,48] Atmospheric Hg deposition is most widely and consistently measured in the USA by the Mercury Deposition Network (URL: http://nadp.sws.uiuc.edu/mdn), including the MN16 MDN site at the MEF. This network measures Hg in wet precipitation (rain and snow) but not dry deposition. With recent studies showing that dry deposition of Hg(0) is a dominant process of Hg deposition in forested watersheds, we presume that our general knowledge of Hg deposition as based on wet deposition monitoring represents a systematic bias toward underestimation of Hg deposition in forested landscapes. Additional work will be needed to quantify dry deposition of Hg on regional scales, in addition to wet deposition.

Our current results also raise an important question regarding the ultimate fate of Hg from wet deposition. It is possible that this pool of aqueous Hg could be more susceptible to photoreduction and could be volatilized as gaseous elemental Hg back to the atmosphere. Alternatively, it is possible that this pool of aqueous Hg is more readily methylated than Hg that is dry deposited to foliage.[9] Additional research will be needed to resolve these complexities.

Interpretation of Results in the Context of Catchment Hydrology. We interpret the data presented here within the well-established hydrological setting of this headwater peatland catchment. Laggs occur at a landscape position that receives runoff from the central raised-dome bog and the surrounding forest uplands. The lagg yields water to the outlet stream whenever there is streamflow.[7,31] In contrast, uplands intermittently yield water to the lagg and stream, but only during the wettest conditions, when upland soils become saturated and water flows laterally downslope as subsurface stormflow.[49] Upland runoff does occasionally occur on upland hillslopes, but it is quantitatively unimportant relative to the effects of subsurface stormflow on seasonal or annual TOC yields.[2,7,31] The high total-Hg content and intermediate δ^{202}Hg values of lagg peat shows the lagg to be a zone where Hg from upland subsurface stormflow accumulates on organic matter. The correspondence of δ^{202}Hg values between streamwater and surface (0−20 cm) lagg peat shows that the majority of Hg in streamwater is derived from the lagg zone, which itself is a mixture of Hg from the bog and uplands during high streamflow. We also examined whether the variation in δ^{202}Hg values for low flow samples was related to redox sensitive elements such as iron (Fe), but we did not find a significant relationship between total Fe and δ^{202}Hg values of Hg in streamwater (SI Figure S7).

The lagg, despite its small area (0.2 ha) compared to the bog (3.0 ha), has been identified as a hydrological and biogeochemical hotspot in this and other peatland catchments at the MEF.[5,7,32] Our Hg isotope data corroborate that perspective and suggest that the lagg was most crucial in determining the stream Hg isotopic composition as the lagg zone is the most proximal hydrological connection to the stream outlet and is consequently biogeochemically important as a hotspot that affects stream chemistry (SI Figure S1). In most cases, especially during stormflow, the isotopic composition of Hg in stream waters resembled those of surface (0−20 cm) lagg peat. However, since the surface upland soil and bog peat had a Hg isotopic composition at the opposite end of the range of δ^{202}Hg values, simple mixing of Hg from these two sources[41] could also produce the δ^{202}Hg values of Hg isotopes that we observed in stream waters (Figure 1B). Another important caveat of the data interpretation is that Hg derived from precipitation could potentially be mixed with surface upland soil, and thus stream Hg isotope compositions (MDF and MIF) may reflect inputs from both upland soil (derived from previous precipitation and dry deposition) and recent precipitation, which we are unable to apportion in streamwater based on our current data set.

Overall, this study demonstrates the versatility of stable Hg isotopes for revealing how sources, transport processes, and biogeochemical transformations affect the variation of streamwater Hg over time in this small peatland/upland catchment. Using acidic permanganate/persulfate chemical digestion of waters to eliminate possible interferences from high DOM concentrations and followed by purge and trap pre-enrichment of Hg, it was feasible to determine the natural-abundance isotopic compositions of dissolved and/or particulate Hg in peatland ecosystems. This approach is especially important because headwater peatlands are widespread in northern latitudes, crucial atmospheric sinks of Hg, hotspots of MeHg production, and sources of downstream DOM, inorganic Hg and MeHg. Our results provide insight into the interplay and effects of distinct source areas on stream Hg dynamics beyond previous Hg studies in this catchment.[2,3,5,8,41,42] Our results also demonstrate the dominant role of dry deposition in Hg accumulation in forests and Hg export via streamflow.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.7b04449.

Detailed information on site description, sample collection, mercury concentration analyses, validation of sample digestion method, sample processing and mercury isotopic analysis. Complete data set of validation of sample digestion method, mercury concentrations and mercury isotopic ratios of all samples. Additional data on weather during the study period. Relationship between stream mercury concentrations and streamflow in the study site (PDF)

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Notes

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