

Legacy mercury and stoichiometry with C, N, and S in soil, pore water, and stream water across the upland-wetland interface: The influence of hydrogeologic setting

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[1] Mechanisms influencing retention, biogeochemical cycling, and release of legacy mercury within soils of forests and wetlands remain poorly understood. We quantified mercury pool size and stoichiometry with carbon, nitrogen, and sulfur across forest-wetland transects and among wetlands of different hydrogeologic settings in the Adirondack region of New York State. Average total mercury pool size in soils (to 50 cm depth) was greater in forests (17.5 mg/m²) than in wetlands (6.1 mg/m²; $p < 0.010$). The average mercury pool size (to 50 cm depth) in shallow-peat riparian wetlands (9.3 mg/m²) was greater than in deep-peat riparian (5.4 mg/m²; $p = 0.099$) or headwater wetlands (3.6 mg/m²; $p = 0.046$). Accumulation of mercury was enhanced at the forest-wetland interface. In mineral horizons of the forest soil and in shallow-peat riparian wetlands, mercury was positively correlated with carbon ($r^2 = 0.73$ – 0.96) and nitrogen ($r^2 = 0.82$ – 0.93), but not sulfur. In contrast, mercury and sulfur were strongly correlated in headwater wetland peat ($r^2 = 0.73$). Dissolved mercury was correlated with dissolved organic carbon (DOC) in pore water and stream water of deep-peat and shallow-peat riparian wetlands ($r^2 = 0.46$ – 0.73), but not in headwater wetland pore water. In headwater outlet streams, dissolved mercury was correlated with DOC ($r^2 = 0.62$), but the slope was only one third that in riparian streams. Hydrogeologic setting influences decomposition processes, biogeochemical cycling of mercury, and hydrologic transport that in turn, govern the size and stoichiometry of mercury pools across the upland-wetland interface and among different wetland types. Ultimately, mobilization of legacy mercury into aquatic ecosystems from forest soils and wetlands likely depends upon decomposition dynamics and hydrologic flow paths.

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1. Introduction

[2] The current rate of mercury deposition in the north-eastern U.S. is about 3.5 times greater than it was during the mid-1800s, prior to industrialization [Lorey and Driscoll, 1999]. This elevated rate of mercury deposition has led to a large legacy of mercury accumulation in forest and wetland soils [e.g., Benoit *et al.*, 1994; Grigal, 2003]. As legislative efforts to decrease anthropogenic emissions of mercury into

the atmosphere are intended to reduce surface water mercury contamination and bioaccumulation in fish and wildlife, the potential release of legacy mercury from soils becomes critically important. Where there is limited terrestrial influence on aquatic ecosystems, surface water recovery may be rapid; however, chronic accumulation of mercury in forest and wetland soils may moderate recovery of connected aquatic ecosystems as large repositories of historically deposited mercury may be exported to surface waters [e.g., Lorey and Driscoll, 1999; Kamman and Engstrom, 2002; Wiener *et al.*, 2006; Engstrom *et al.*, 2007; Harris *et al.*, 2007; Bookman *et al.*, 2008]. Thus, connectivity between terrestrial and aquatic ecosystems has emerged as an important characteristic influencing mercury supply to surface waters. However, because complex biogeochemical cycling involving organic matter and mercury:element interactions also likely influence the retention and release of mercury accumulated in forest and wetland soils, the ultimate fate of legacy mercury is difficult to predict.

[3] Wetlands function as ecological and biogeochemical linkages between terrestrial and aquatic ecosystems. Although wetlands are traditionally defined by their hydrology,

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physicochemical environment, and biota [Mitch and Gosselink, 2000], hydrogeologic setting has been recognized as a primary factor influencing wetland structure and function [Winter, 1988, 1992; Brinson, 1993; Bedford, 1996, 1999]. Hydrogeologic setting of a wetland links landscape position and surficial geology to the resulting hydrologic regime, water chemistry, and the chemistry and accumulation of wetland soils [Winter, 1988, 1992; Winter and Woo, 1990; Bedford, 1996, 1999; Hill and Devito, 1997]. Specifically, hydrogeologic setting influences water table level and fluctuation and thus the duration of soil saturation, as well as the supply of nutrients and electron acceptors. Together, these hydrological and geochemical factors influence the rate of production and decomposition of organic matter. For example, soil saturation results in anoxic conditions that retard decomposition. Also, the availability of alternate electron acceptors influences which anaerobic decomposition pathways dominate (e.g., denitrification, sulfate reduction). Given the importance of organic matter in the retention and transport of mercury [Meili, 1991; Mierle and Ingram, 1991; Yin et al., 1997; Kolka et al., 2001; Grigal, 2002; Shanley et al., 2002; Grigal, 2003], these hydrogeologically linked factors likely influence the fate of mercury within different wetland types. In a 3 year study comparing fluxes of mercury and methylmercury from catchments containing uplands, basin wetlands, and valley-bottom wetlands, St. Louis et al. [1996] found that the basin wetlands had the greatest flux of methyl mercury and suggested that differences in wetland type stemmed from differences in the internal hydrology of the wetlands. Importantly, hydrogeologic setting places a large emphasis on the placement of a wetland within the landscape and the hydrologic connectivity between the upland and the wetland [Bedford, 1996, 1999]. Thus, not only does hydrogeologic setting enable one to consider wetlands within the context of the broader landscape, but also the influence of hydrogeologic setting on the biogeochemical cycling of mercury may provide a more mechanistic framework within which to interpret and predict the role of varying wetland types in mediating upland-surface water connectivity and the retention and release of mercury accumulated in forest and wetland soils.

[4] Decomposition dynamics could also influence mercury retention and release in forest soils, as carbon is lost via respiration and mercury is concentrated in organic residues [Grigal, 2003; Hall and St. Louis, 2004; Demers et al., 2007]. Dissolved organic matter (DOM), along with complexed mercury, can be hydrologically transported into mineral soil horizons where it is immobilized through the process of podzolization [e.g., Deconinck, 1980; Driscoll and Postek, 1995], or may short circuit the soil profile by moving laterally down-gradient through shallow interflow into adjacent wetland and stream ecosystems [e.g., Kolka et al., 2001; Dittman et al., 2007; Mitchell et al., 2009; Demers et al., 2010].

[5] The chemical properties of mercury influence the mode of its transport and retention. Mercury is a soft acid (a type B metal) and bonds strongly with soft ligands such as thiol ($-SH$) and sulfide (S^{2-}), and organic S (e.g., cysteine) and N (e.g., lysine, histidine) [Stumm and Morgan, 1995]. Thus, mercury transport and retention are often closely linked to organic matter [e.g., Meili, 1991; Mierle and Ingram, 1991], although specific mechanisms for the retention of mercury in natural soils might vary across hydrologic gradients.

[6] In well-drained, predominantly oxic soils, Hg(II) is predominantly bound to particulate and dissolved organic matter [e.g., Khwaja et al., 2006, and references therein]. Direct evidence from x-ray absorption spectroscopy (XAS) and extended x-ray absorption fine structure spectroscopy (EXAFS) shows that humic acids derived from forest soil organic horizons form bidentate complexes with mercury, with Hg(II) coordinating with one reduced sulfur (e.g., thiol) and one oxygen or nitrogen heteroatom [Xia et al., 1999; Skyllberg et al., 2000].

[7] In poorly drained or saturated anoxic soils, equilibrium calculations involving inorganic ligands predict that mercury sulfide complexation and precipitation should dominate the distribution of mercury between the aqueous and solid phase, thus limiting the mobility of mercury [Hurley et al., 1998b; Benoit et al., 1999, 2003; Drexel et al., 2002]. However, studies from the Florida Everglades have demonstrated that strong Hg(II) binding sites in peat actually compete with inorganic sulfide species [Drexel et al., 2002]. At environmentally relevant concentrations of mercury and realistically low Hg:DOM ratios, Hg-DOM complexes have greater conditional stability constants than Hg-inorganic sulfide complexes [Skylberg et al., 2000; Drexel et al., 2002; Haitzer et al., 2002; Ravichandran, 2004]. Moreover, DOM has been shown to enhance the dissolution of cinnabar (HgS) [Ravichandran et al., 1998, 1999; Reddy and Aiken, 2001; Waples et al., 2005]. Based on the strength of estimated Hg-DOM stability constants and the results of dissolution experiments of HgS by DOM, it appears that organic matter is capable of outcompeting sulfide for mercury in anoxic environments. Thus, the retention and transport of mercury can be mechanistically coupled to organic matter in both uplands and wetlands of different hydrogeologic settings.

[8] The objective of this study was to quantify mercury pool size and examine mechanisms of mercury retention through field investigations of mercury stoichiometry with carbon, nitrogen, and sulfur in forest soils and wetlands of different hydrogeologic settings. We compare forest soils with ombrotrophic headwater bogs influenced primarily by precipitation and riparian wetlands that were strongly influenced by groundwater and surface water. By quantifying differences in mercury pool size across upland-wetland transects, we also assess the role of upland-wetland connectivity and the importance of mercury delivery to the accumulation of mercury in wetland soils. We expected that upland soils would have accumulated the largest pools of mercury (deposition to forested ecosystems is greater than to non-forested sites) and that most of that mercury would be retained in mineral soils in association with residual organic matter. We also expected that connectivity between uplands and wetlands would increase mercury pool sizes within wetlands. We hypothesized that organic carbon dynamics might be more important to retention dynamics in more aerated oxidizing settings (i.e., the uplands and shallow-peat riparian wetlands in this study), resulting in high Hg:C ratios and strong correlations between mercury and carbon, and that sulfur might exhibit stronger influence on mercury retention in more permanently saturated anoxic reducing environments (e.g., the headwater wetlands in this study), resulting in strong correlations between mercury and sulfur. Finally, we hypothesized that Hg:DOC stoichiometry of waters emanating from wetlands of different hydrogeologic settings

Table 1. Water Table Level Maximum, Minimum, and Range (Max-Min) Across Wetland Transects in Different Wetland Types of the Sunday Lake Watershed in the Western Adirondack Region of New York State, USA^a

Wetland Type	Transect Distance (m)	Water Table Relative to Ground Surface			Hydraulic Conductivity (K) (m d ⁻¹)
		Max (cm)	Min (cm)	Max-Min (cm)	
Shallow-peat riparian wetland	1	0.6	-14.3	14.9	0.15 (0.13, 3)
	5	-0.7	-19.2	18.5	
	10.5	-7.5	-30.0	22.5	
	Stream	-13.3	-39.8	26.5	
Shallow-peat riparian wetland	1	-10.6	-49.8	39.2	1.42 (0.57, 3)
	9	-8.8	-35.5	26.7	
	18	-2.4	-33.0	30.6	
	Stream	-5.8	-38.8	33.0	
Deep-peat riparian wetland	1	-13.9	-33.6	19.7	0.02 (0.02, 3)
	30	-8.6	-30.7	22.1	
	60	-0.5	-26.6	26.1	
	Stream	-5.6	-33.1	27.5	
Deep-peat riparian wetland	1	-5.3	-19.5	14.2	1.54 (1.35, 3)
	40.5	1.0	-20.7	21.7	
	81	5.2	-4.7	9.9	
	Stream	-11.3	-20.1	8.8	
Headwater wetland	1	8.5	-6.6	15.1	5.38 (0.26, 2)
	37.5	6.9	-9.4	16.3	
	75	8.3	-7.5	15.8	
	Outlet	-6.7	-29.6	22.9	
Headwater wetland	1	0.9	-16.8	17.7	2.08 (1.26, 5)
	45	2.7	-4.9	7.6	
	60	5.5	-6.9	12.4	
	80	2.2	-6.4	8.6	
	100	5.7	-0.3	6.0	
	Outlet	9.2	-0.3	9.5	

^aAverage hydraulic conductivity (K, m d⁻¹) measured in the top 50 cm of substrate across each wetland transect is also reported; values in parentheses show (1SE, n).

would reflect the stoichiometry of the soil environments from which they were derived.

2. Methods

2.1. Site Description

[9] This research was conducted in the Sunday Lake watershed located near the Stillwater Reservoir along the southwestern boundary of the Adirondack region of New York, USA (43°51'40"N, 74°06'07"W). Average precipitation is ~1300 mm/yr (1971–2000 mean), with about 30% delivered as snow (data from Big Moose Station and available online at <http://climod.nrc.cornell.edu>). Sunday Lake has two inlets, with combined watershed area of ~1273 ha. Vegetation cover is typical north temperate mixed deciduous and coniferous forest, with the coniferous forests predominantly surrounding ponds, wetlands, and stream corridors. The upland soils of this watershed are mostly well-drained spodosols (Typic Haplorthods) with a sandy loam to loamy sand texture overlying glacial till or glacial outwash [Demers et al., 2007]. Eskers are a distinctive feature of the landscape in the vicinity of Sunday Lake and provide a complex series of ridges and depressions resulting in numerous wetlands and wetland types, which reflect differences in hydrogeologic setting. The highest density of wetlands occurs amidst the esker terrain; however, wetlands also occur in areas of the watershed underlain by glacial till, especially along stream corridors and in the headwaters of each subwatershed.

[10] We selected six wetlands that spanned a gradient in hydrogeologic setting and thus differed in wetland structure and function. Two were headwater wetlands perched in depressions formed by eskers. In terms of the physiographic settings framed by *Winter* [1988, 1992], these were depressional wetlands typical of Wisconsinian age glacial terrain of the north central and northeastern United States. Both headwater wetlands were elevated above the lower stream valleys within the watershed; thus, they have no inlet streams and very small watersheds that influence only the edges of the wetlands, where weak upwelling gradients are associated with the break in slope. Away from the edges, these headwater wetlands are ombrotrophic bogs with strong recharge gradients and hydrologic inputs dominated by precipitation (see the supporting information). Both headwater wetland sites are dominated by sphagnum moss (*Sphagnum* spp.); one headwater wetland site has an open central pond and a scrub-forest fringe dominated by red spruce (*Picea rubens* Sarg.), black spruce (*Picea mariana* Mill.), and American larch (*Larix laricina* Du Roi), whereas the second headwater wetland site is more densely forested. The water table is near the surface of the peat in both headwater wetlands throughout the year, resulting in permanently saturated conditions, with peat pore water pH averaging ~4.1 within the top 50 cm of the peat profile, and total peat accumulation that has reached ~7 m in depth.

[11] Four sites were riparian wetlands located at the transition between uplands and first-order streams; we further differentiated between two deep-peat riparian and two shallow-

peat riparian wetlands. In the terms of *Winter* [1988, 1992], these riparian wetlands occur in a physiographic setting of steep slopes adjacent to narrow lowlands, typical in mountainous terrain but common at both large and small scales. Thus, the riparian wetlands result from discontinuities in the slope of the water table and land surface and can be influenced by groundwater, surface water, and precipitation inputs. Stratigraphy within the riparian wetlands differentiated the shallow-peat and deep-peat riparian wetlands and influenced the flow of water through them. Both the shallow-peat and deep-peat riparian wetlands are influenced by local upwelling (discharge) zones at the break in slope at the upland-wetland interface (see the supporting information). However, movement of subsurface water across the deep-peat riparian wetlands is limited by the low hydraulic conductivity of the peat (Table 1), especially at depths greater than 50 cm. Within the top 50 cm, peat pore water pH was ~4.8, on average. The deep-peat riparian wetlands ranged from ~5 to 6 m maximum peat depth and were dominated by sedges (*Carex* spp.), broadleaved deciduous shrubs (e.g., *Myrica gale*), and occasional occurrence of spruce and larch. In the shallow-peat riparian wetlands, subsurface water movement across the wetland is less restricted, and underflow of subsurface water originating from both the adjacent slope and the adjacent stream likely interacts with the shallow peat. The shallow-peat riparian wetlands seldom exceeded peat depths of ~35cm, but were also dominated by sedge species, with speckled alder (*Aldus rugosa*) present in dense patches, and occasional occurrence of red spruce and American larch. Within the top 50 cm, pore water pH was ~5.5 on average. The water table fluctuates more in the riparian wetlands than in the headwater wetlands, episodically rising to the surface of the peat and seasonally dropping more than 50 cm below the surface of the peat in shallow-peat riparian wetlands.

2.2. Wetland Transects and Instrumentation

[12] An upland-wetland transect was established across the entirety of each of the six study wetlands. Transect length ranged ~10–20 m in the shallow-peat riparian wetlands, ~60–80 m in the deep-peat riparian wetlands, and ~75–135 m in the headwater wetlands. Along each transect, at least six wetland soil sampling points were established between the upland-wetland interface and the outlet or riparian stream (a greater number of cores were taken from longer transects). An upland soil sampling point was located 1 m upslope of the upland-wetland interface of each wetland.

[13] Nested clusters of water table wells and piezometers were placed along upland-wetland transects established for wetland peat coring. In riparian wetlands, one nested well cluster was placed 1 m into the wetland from the upland-wetland interface, a second nested well cluster was placed midway between the upland-wetland interface and the stream channel, and a third nested well cluster was placed 1 m from the edge of the stream. In headwater wetlands, additional clusters were used to quantify the influence of open water and changes in overstory vegetation along each transect. Each nested well cluster comprised two water table wells and two piezometers. Each water table well extended to 50 cm depth and was slotted along its entire length from the surface of the peat to its tip. One water table well was made of Teflon, for sampling pore water chemistry. The

second water table well was used for hydrological measurements. The two piezometers were at different depths: the tip of one piezometer was placed at the midway point between the peat surface and the underlying mineral soil and the tip of the second piezometer was placed into the mineral soil below the accumulation of organic peat in each wetland. Each piezometer was slotted along a 10 cm segment at its tip. A staff gauge was installed at each headwater outlet and in each stream to monitor water level.

2.3. Hydrologic Measurements

[14] Water table wells, piezometers, and staff gauges were surveyed in order to determine their relative elevation in each wetland. During each sampling period, water level heights were recorded in water table wells, piezometers, and at staff gauges. Water level data were used to determine water table elevation and to calculate piezometric gradients within each wetland. Hydrologic data were summarized in cross sections of each wetland transect and flow nets were constructed in order to characterize hydrologic flow through each wetland. Hydraulic conductivity was measured at each nested well cluster with a Horslev piezometer test (i.e., bail tests) [Freeze and Cherry, 1979].

2.4. Soil Sampling Procedures and Analysis

[15] Wetland soil cores were obtained with a stainless-steel hemispherical peat corer (5.5 cm diameter) in order to minimize compaction of peat samples. The top 50 cm of each wetland core was sectioned into 5 cm increments. An additional 10 cm increment of each peat core was sampled at a depth of 90–100 cm and at each additional meter of depth throughout the entire wetland peat profile. Upland soil cores were obtained with acid-washed split PVC cores (5.2 cm diameter), horizons (forest floor, A, B) were delineated in the field and the depth of each horizon was verified by in situ measurements. All soil samples were double bagged in Ziploc bags, frozen immediately upon return from the field, and freeze dried in preparation for analysis.

[16] Soil samples were analyzed for total mercury using a hot refluxing nitric:sulfuric (3:7) acid digestion, followed by dilution and analysis with a Tekran 2600 Cold Vapor Atomic Fluorescence Spectrophotometer (CVAFS; Tekran, Toronto, Ontario, Canada). Soil carbon, nitrogen, and sulfur were analyzed with an Elemental Combustion System, Model ECS 4010 (Costech Analytical Technologies, Valencia, California, USA). Samples were analyzed in batches with quality control, and a detailed summary of the quality control results for each analyte has been provided (see the supporting information).

2.5. Water Sampling Procedures and Analysis

[17] Peat pore water, headwater outlets, and streams associated with riparian sites were sampled seasonally (April, June, August, September, November/December). Peat pore water samples were pumped from Teflon water table wells at each well cluster in each wetland. Samples were pumped through Teflon tubing into a borosilicate glass reservoir, and then transferred to Teflon bottles in the field, using clean procedures [United States Environmental Protection Agency (USEPA), 1996]. Separate tubing and reservoir equipment were used for each wetland. All tubing and reservoirs were thoroughly rinsed with ultrapure

de-ionized water and cleaned in a 20% hot nitric acid bath between seasonal sampling campaigns. Glass reservoirs were stored with 1% hydrochloric acid, rinsed with ultrapure de-ionized water prior to sampling campaigns, and additionally rinsed with sample water in the field. Outlet and stream water samples were collected directly into Teflon bottles, using clean procedures [USEPA, 1996]. Samples for analysis of dissolved organic carbon (DOC) were collected in high-density polyethylene sample bottles and filled to minimize headspace. Samples were packed in coolers with frozen-water ice packs and returned to the laboratory for processing. Sample filtering and preservation occurred upon arrival at Syracuse University within 48 h of sampling.

[18] Samples for analysis of mercury were filtered through a clean 0.45 μm Teflon membrane. For outlet and stream water samples, both filtered and unfiltered aliquots were acidified to 0.4% with hydrochloric acid and stored in the dark at 4°C until analysis. For pore water samples, only the filtered fraction was preserved and stored for analysis. The concentration of total mercury (all forms of mercury) was determined for filtered (THg_d) samples. Prior to analysis for THg, samples were subjected to UV light treatment to remove measurement interferences (i.e., high concentrations of DOC) [Olson et al., 1997]. Mercury concentrations were quantified according to EPA Method 1631 using automated CVAFS (Tekran, Toronto, Ontario, Canada) [USEPA, 1998]. DOC concentrations were determined for filtered samples (0.7 μm glass fiber filter, pre-baked at 450°C) with a Dohrmann Phoenix 8000 Analyzer using the persulfate-ultraviolet oxidation method [APHA, 1998]. Samples were analyzed in batches with quality control and a summary of the quality control results for each analyte have been provided (see the supporting information).

2.6. Pool Size and Stoichiometric Calculations

[19] Total pool size of mercury, carbon, nitrogen, and sulfur in the top 50 cm of soils was based on measured concentrations, cross-sectional area of the core, and total dry soil weight (accounting for differences in bulk density of each core segment). In the wetland soils, pool size calculations were made separately for each 5 cm increment and then summed over a depth of 50 cm. Wetland soil pool size beyond 50 cm in depth was determined by averaging pool size estimates at the top and bottom of each additional 1 m segment and then extrapolating that value to each additional 1 m segment. In the upland soils, pool size calculations were made separately for each soil horizon and then summed over a depth of 50 cm.

[20] Molar ratios of mercury with carbon, nitrogen, and sulfur were calculated based on the total pool size of each element within the top 50 cm of soil in the headwater and deep-peat riparian wetlands. In the upland and shallow-peat riparian soils, molar ratios were calculated separately for the organic and mineral soil horizons. Additionally, within the top 50 cm of each core, we assessed elemental correlations of mercury with carbon, nitrogen, and sulfur within individual wetland soil core segments and upland soil horizons.

2.7. Statistical Procedures

[21] Statistical procedures were performed with SAS [SAS Institute Inc, 1999]. Differences in total mercury pool size

between upland and wetland soils and among wetland types were analyzed using fixed effects models (PROC GLM) [SAS Institute Inc, 1999]. All wetland soil cores across each individual wetland transect were averaged to obtain a single estimate of pool size for each wetland; thus, differences among wetland types were more difficult to detect because of a low number of replicate wetlands ($n=2$ for each wetland type) and p -values < 0.1 were interpreted to indicate statistically significant differences. Differences between the pool size of mercury at the upland-wetland edge of each wetland and the average pool size across the wetland transect were assessed with a paired t test (PROC Means) [SAS Institute Inc, 1999]. Differences in the Hg:C, Hg:N, and Hg:S ratio between upland mineral and organic soil horizons, mineral soil horizons in the uplands and shallow-peat riparian wetlands, upland organic horizon and peat at the wetland edge, and among wetland types were also determined using fixed effects models (PROC GLM) [SAS Institute Inc, 1999]. The relationship between mercury and carbon, mercury and nitrogen, and mercury and sulfur concentrations in individual samples, as well as the relationship between mercury and DOC in pore water and surface water, was assessed using regression techniques (PROC GLM) [SAS Institute Inc, 1999]. Assumptions of linearity, normality, and homoskedacity were satisfied for all results presented; outliers were assessed using estimates of leverage and Cook's distance to determine influence.

3. Results

3.1. Hydrologic Characteristics of Wetlands of Different Hydrogeologic Setting

[22] Headwater wetlands were characterized by a consistently high water table and strong recharge gradients. The water table remained near the surface of the peat throughout the year, rising above the surface during winter, spring, and fall (mean maximum = 5.7 cm, SE = 2.3 cm), but falling below the surface of the peat during summer (mean minimum = -7.4 cm, SE = 0.4 cm; Table 1). Thus, nearly the entire peat profile of the headwater wetlands remained saturated throughout the year. Piezometric head potential measurements showed that recharge gradients dominated the hydrology of headwater wetlands during all seasonal sampling periods; only at the upland edges did we detect a weak discharge gradient (see the supporting information).

[23] In contrast, both the deep-peat and shallow-peat riparian wetlands were characterized by a dynamic, seasonally fluctuating water table and patterns of piezometric head potential that were dominated by discharge (Table 1 and the supporting information). Notably, the water table in the shallow-peat riparian wetlands remained below the surface of the peat during all seasonal sampling periods (mean maximum = -4.9 cm, SE = 2.4 cm), falling to a mean depth of -30.4 cm (SE = 9.1 cm) below the surface of the peat during summer. Thus, the water table in the shallow-peat riparian wetlands declined into the underlying mineral soil, exposing the entire peat profile to unsaturated, oxidizing conditions (Table 1 and the supporting information). Nevertheless, observations of sand and gravel deposited throughout shallow-peat riparian soil profiles and on the surface of organic horizons are indicative of occasional overbank flooding. In the deep-peat riparian wetlands, weak discharge

Table 2. Mercury Pool Size in Soil Substrates of Uplands and Different Wetland Types in the Sunday Lake Watershed in the Western Adirondack Region of New York State, USA^a

	Generalized Transect Distance (m)	n	Organic Horizon Hg Within 50 cm Depth (mg/m ²)	Mineral Horizon Hg Within 50 cm Depth (mg/m ²)	Total Hg Within 50 cm Depth (mg/m ²)	Total Hg Within Entire Profile to Mineral Interface (mg/m ²)
Upland	~	6	6.3 (2.4)	11.1 (2.7)	17.5 (3.4)	6.3 (2.4)
Shallow-peat riparian wetlands	1	2	3.2 (1.8)	6.4 (1.4)	9.5 (3.2)	3.2 (1.8)
	3	2	3.1 (0.6)	6.4 (2.0)	9.6 (1.4)	3.1 (0.6)
	5	2	3.3 (1.8)	6.4 (1.5)	9.7 (3.3)	3.3 (1.8)
	7	2	3.8 (2.7)	6.6 (1.7)	10.3 (1.0)	3.8 (2.7)
	9	2	2.4 (0.04)	7.4 (2.7)	9.8 (2.7)	2.4 (0.04)
	11	2	3.4 (0.7)	4.3 (1.3)	7.7 (0.5)	3.4 (0.7)
Deep-peat riparian wetlands	1	2	7.7 (1.1)	0.8 (0.8)	8.5 (0.3)	11.6 (4.9)
	11	2	6.1 (1.9)	~	6.1 (1.9)	17.7 (2.0)
	24	2	3.2 (0.5)	~	3.2 (0.5)	20.0 (0.4)
	35	2	5.1 (2.6)	~	5.1 (2.6)	18.6 (0.6)
	47	2	4.6 (1.3)	~	4.6 (1.3)	19.6 (5.6)
	59	2	4.6 (0.5)	~	4.6 (0.5)	24.0 (5.1)
	71	2	5.3 (1.5)	~	5.3 (1.5)	17.2 (8.2)
Headwater wetlands	1	2	7.0 (2.5)	~	7.0 (2.5)	11.5 (4.8)
	14	2	3.4 (1.7)	~	3.4 (1.7)	16.2 (11.2)
	28	2	3.2 (2.1)	~	3.2 (2.1)	13.7 (6.3)
	41	2	2.1 (1.5)	~	2.1 (1.5)	14.2 (9.0)
	51	2	1.9 (1.4)	~	1.9 (1.4)	9.8 (8.8)
	72	2	2.7 (1.9)	~	2.7 (1.9)	15.2 (3.2)
	86	2	4.1 (1.9)	~	4.1 (1.9)	19.7 (3.2)
	111	1	1.7	~	1.7	12.0
	130	1	2.4	~	2.4	3.3

^aMean mercury pool size is shown for the organic horizon within 50 cm depth, the mineral horizon within 50 cm depth, the total soil profile within 50 cm depth, and within the entire peat profile down to the mineral soil interface in each wetland type. Values in parentheses show 1SE.

zones were common at the streamside and at the upland-wetland interface during spring and fall, whereas recharge gradients dominated the central portions of the deep-peat riparian wetlands, especially during summer. In the shallow-peat riparian wetlands, piezometric head potentials were difficult to detect, in part due to the shallow placement of piezometers relative to the water table; thus, shallow-peat riparian wetlands tended to lack clear recharge and discharge gradients. Nonetheless, we detected discharge gradients far more frequently than recharge gradients in shallow-peat riparian wetlands (71% overall, 86% at upland edge, 78% at the center, and 40% at stream edge; see the supporting information).

3.2. Mercury Pool Size in Forest Soil and Wetland Peat

[24] We focused on quantifying mercury pools at shallow soil depths and in organic horizons, from which mercury is more likely to be mobilized. In forest soils, we quantified mercury pools to a depth of 50 cm, differentiating between mineral and organic horizons (Table 2 and Figure 1). In headwater wetlands and deep-peat riparian wetlands, we quantified mercury pools in the top 50 cm of peat, a depth estimated to include the less dense and more microbially active layer of the peat profile, the acrotelm. This depth also encompasses the zone of water table fluctuation (Table 1). In shallow-peat riparian wetlands, we quantified mercury pools to a depth of 50 cm, differentiating between mineral and organic horizons; however, a lot of organic matter was mixed into the upper mineral soil layers in these shallow-peat riparian wetlands. Thus, we present both total mercury pool size to a depth of 50 cm, as well as mercury pool size in the organic and mineral horizons alone (within 50 cm depth) to provide a detailed comparison of mercury

accumulation in these very different substrates. We also provide total mercury pool size of the entire peat profile to mineral soil interface in each wetland (Table 2).

[25] Total mercury pool size was greater in upland soils than in wetland soils on an areal basis to a depth of 50 cm (~90–400% greater, on average, as calculated from data in Table 2) (Figure 1; $p < 0.010$, $n = 12$). Among wetland types, shallow-peat riparian wetlands had a greater mercury pool size (to a depth of 50 cm) than deep-peat riparian wetlands (~70% greater, on average) or headwater wetlands (~160% greater, on average), with the smallest pools occurring in the headwater wetlands (Figure 1; $p = 0.099$, $p = 0.046$, respectively; $n = 2$ for each wetland site).

[26] Much of the mercury pool in uplands and shallow-peat riparian wetlands was associated with mineral soil horizons that had been enriched with organic matter from the overlying forest floor and wetland sedge peat, respectively. In contrast, there was no evidence of mineral soil in the top 50 cm of the deep-peat riparian and headwater wetlands. The accumulation of mercury in the organic horizon alone (to a depth of 50 cm) did not differ among sites; however, including the entire peat profile mercury pool from deep-peat riparian and headwater wetlands increased total wetland mercury pool size (Table 2). Mineral soil horizon samples from the uplands and shallow-peat riparian wetlands were high in mercury concentration (44.1 ng/g, SE=11.3, $n = 6$; 26.6 ng/g, SE=2.3, $n = 11$; respectively) relative to mercury concentration of mineral soils underlying deep-peat riparian and headwater wetland sites (2.3 ng/g, SE=0.8, $n = 9$; 5.6 ng/g, SE=2.0, $n = 7$; respectively), likely indicative of enrichment by organic residues.

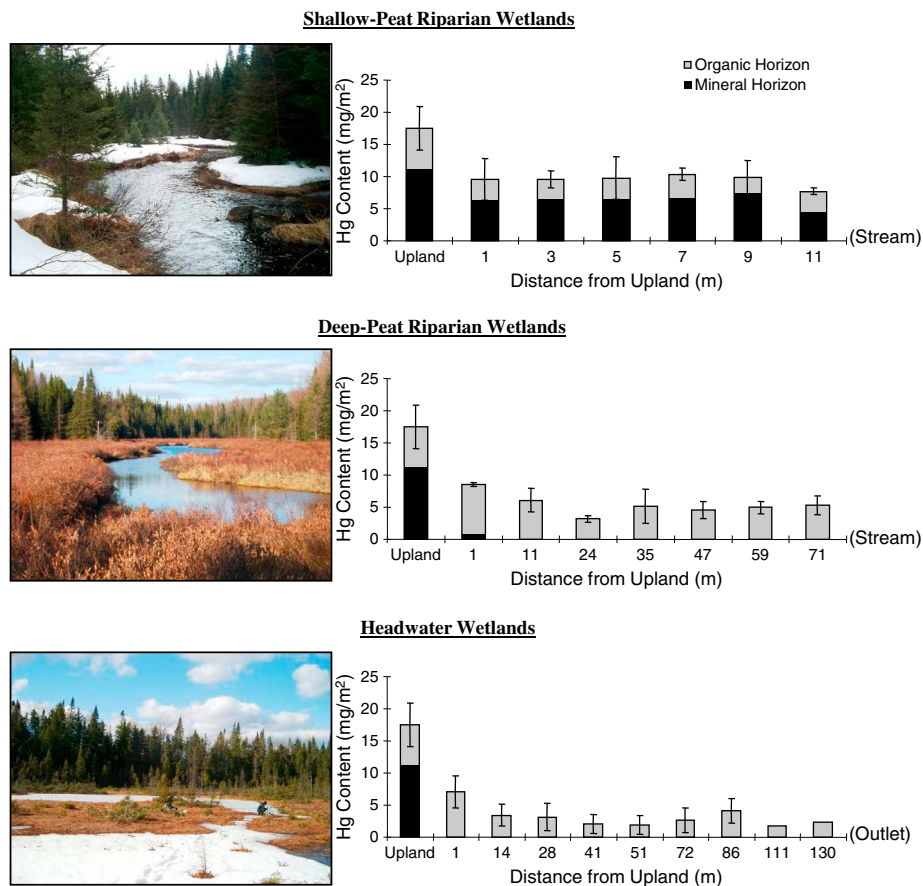


Figure 1. Mercury pool size in soil substrates along transects across different wetland types of the Sunday Lake watershed located in the western Adirondack region of New York State. Bars show the mean total Hg (THg) pool in the top 50 cm of soil ($n=6$ for upland; $n=2$ for each wetland type). Error bars associated with uplands show ± 1 SE of THg pool in upland soils; whereas error bars associated with wetlands show the range of THg pool size along transects in individual wetlands. Distances along these generalized transects are approximate.

[27] The accumulation of mercury in wetland soils (to a depth of 50 cm) varied across wetland transects, with a greater accumulation of mercury occurring at the upland-wetland interface in deep-peat riparian (~75% greater on average) and headwater wetlands (~130% greater on average; Table 2 and Figure 1; $p=0.008$; $n=4$). In contrast, there was no difference in the mercury pool size at the edge of shallow-peat riparian wetlands in comparison to the rest of the wetland transect, as the edge effect apparent in other wetland types appeared to extend across the entire transect in the (narrow) shallow-peat riparian wetlands.

[28] Differences in mercury pool sizes among wetlands of a single wetland type, or within an individual wetland could be further explained qualitatively by differences in groundwater hydrology and vegetation. Differences in mercury accumulation within deep-peat riparian wetlands coincided with differences in groundwater hydrology. Transect points within the deep-peat riparian wetlands that were associated with discharge gradients (i.e., upwelling) accumulated more mercury in surficial peat substrates than transect points with recharge gradients (i.e., downwelling; see the supporting information). Differences in mercury pool size in peat substrates of the headwater wetlands coincided with differences in vegetation, with the sphagnum-dominated

bog accumulating less mercury than its forested counterpart. Also, greater mercury accumulation in headwater wetland peat appeared to coincide with increases in forest canopy cover along an individual transect.

3.3. Stoichiometry of Hg, C, N, and S in Forest Soil and Wetland Peat

3.3.1. Molar Ratios in Bulk Soil Pools

[29] Molar ratios of mercury with carbon, nitrogen, and sulfur were initially quantified using total elemental pools in the top 50 cm of upland soil and within each wetland type. The molar ratio of mercury to carbon (Hg:C) varied between mineral and organic soil horizons and among wetland types (Figure 2). Within the upland soils, Hg:C ratio was almost 2 times greater in the mineral horizon than in the organic horizon ($p=0.0464$, $n=6$ for each soil horizon), coinciding with the accumulation of more recalcitrant carbon pools in the mineral soils subsequent to oxidative carbon losses, leaching, and immobilization (see section 4.1) [e.g., Grigal, 2003]. There was no difference in Hg:C between the mineral soils of the upland versus that in shallow-peat riparian wetlands. There was also no difference between the Hg:C ratio in the upland organic horizon and peat at the wetland edge in all

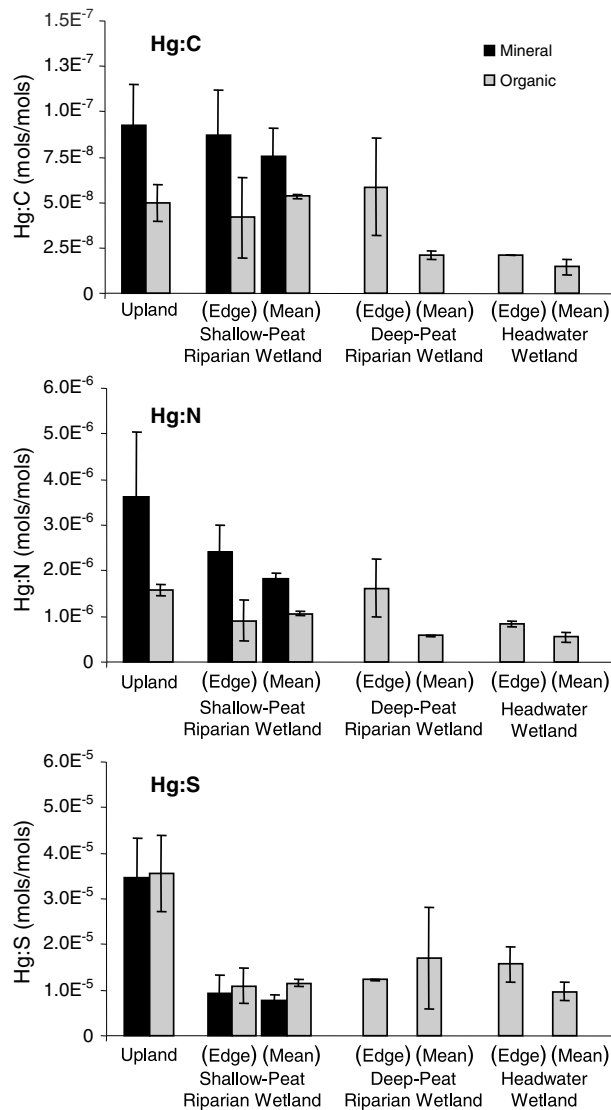


Figure 2. Elemental ratios showing the mean accumulation of Hg per unit C, Hg per unit N, and Hg per unit S in the top 50 cm of organic and mineral soil substrates of uplands and different wetland types in the Sunday Lake watershed located in the western Adirondack region of New York State. Upland samples were taken 1m from the wetland edge, wetland edge samples were taken 1m from the upland edge, wetland mean shows the mean elemental ratio in the top 50 cm of organic and mineral soil substrates across wetland transects. Error bars associated with uplands show ± 1 SE ($n=6$) of the mean elemental ratio; whereas error bars associated with wetlands show the range in the mean elemental ratio along transects of individual wetlands ($n=2$).

wetland types; however, the Hg:C ratio in the upland organic horizon was greater than the mean Hg:C ratio across the entire wetland transect, with or without edge effects ($p=0.0172$, $n=12$; $p=0.0181$, $n=12$). Among wetlands, the Hg:C molar ratio in organic peat from across the entire shallow-peat riparian transect was greater than the mean Hg:C molar ratio in organic peat across deep-peat riparian and headwater wetland transects, also regardless of edge effects ($p=0.0011$, $p=0.0116$, with and without edge,

respectively; $n=2$ for each wetland type). Differences in Hg:C among wetland types could reflect differences in mercury delivery and retention, as well as rates of oxidative loss of carbon in wetlands across a gradient of hydrogeologic setting (see section 4.2).

[30] The spatial patterns of Hg:N across the study sites were similar to those for Hg:C, with the Hg:N molar ratio also varying in organic versus mineral soil horizons and among wetland types (Figure 2). Within upland soils, the Hg:N ratio was greater in the mineral soil horizon than in the organic soil horizon ($p=0.090$, $n=6$ for each soil horizon). The only exception to the similarity of spatial patterns of Hg:N and Hg:C was that on average, the Hg:N ratio in the upland organic horizon was greater than in peat at the upland-wetland interface (i.e., the wetland edge; $p=0.070$, $n=12$), as well as across the entire wetland transect ($p=0.0004$, $n=12$). Among wetland types, and similar to Hg:C patterns, the mean molar ratio of Hg:N across shallow-peat riparian wetlands was greater than the mean molar ratio of Hg:N across deep-peat riparian and headwater wetlands, regardless of edge effects ($p=0.0177$, $p=0.0035$, with and without edge, respectively, $n=2$ for each wetland type).

[31] In contrast to Hg:C and Hg:N, the molar ratio of mercury to sulfur (Hg:S) in bulk soil pools did not vary between organic and mineral soil horizons within the uplands. However, similar to Hg:N, the Hg:S ratio in the upland organic horizon was greater than in peat at the upland-wetland interface (i.e., the wetland edge; $p=0.0121$, $n=12$) and across the entire wetland transect ($p=0.0130$, $n=12$). Additionally, the Hg:S in the upland mineral soil was greater than Hg:S in the mineral soil at the upland-wetland interface and across the entire wetland transect of the shallow-peat riparian wetland ($p=0.0787$, $n=8$; $p=0.0662$, $n=8$; respectively). Among wetland types, the Hg:S molar ratio did not vary significantly.

3.3.2. Elemental Correlations Within Individual Samples

[32] Scatterplots of Hg and C, Hg and N, and Hg and S concentrations in individual horizon and depth increments from uplands and wetland transects (Figure 3) revealed patterns within stoichiometric relationships that were not evident based on average molar ratios of the bulk soil pools (Figure 2).

[33] In the uplands, mercury in the A horizon and the B horizon of mineral soils showed strong positive relationships with carbon (Figure 3a; $p=0.0016$, $r^2=0.73$, $n=10$, slope = 3.95×10^{-8} , SE = 8.41×10^{-9} ; and $p < 0.0001$, $r^2=0.96$, $n=8$, slope = 4.63×10^{-8} , SE = 3.91×10^{-9} , respectively) and with nitrogen (Figure 3a; $p=0.0003$, $r^2=0.82$, $n=10$, slope = 1.30×10^{-6} , SE = 2.14×10^{-7} ; and $p=0.0004$, $r^2=0.90$, $n=8$, slope = 1.50×10^{-6} , SE = 3.03×10^{-7} , respectively), but not with sulfur (Figure 3a; $p=0.14$, $r^2=0.25$, $n=10$; and $p=0.48$, $r^2=0.08$, $n=8$, respectively). Note that the correlation with sulfur in the A horizon became statistically significant when one outlier was removed (Figure 3a; $p=0.016$, $r^2=0.59$, $n=9$, slope = 1.81×10^{-5}), but still explained much less of the variability in mercury concentration than did either carbon or nitrogen.

[34] In contrast, in organic horizons of the upland soils, mercury showed no statistically significant correlation with carbon ($p=0.3380$, $n=8$), nitrogen ($p=0.6256$, $n=8$), nor sulfur ($p=0.8570$, $n=8$) (Figure 3a). When all of the upland organic and mineral soil data were considered together, the strong correlation between mercury and carbon and between mercury

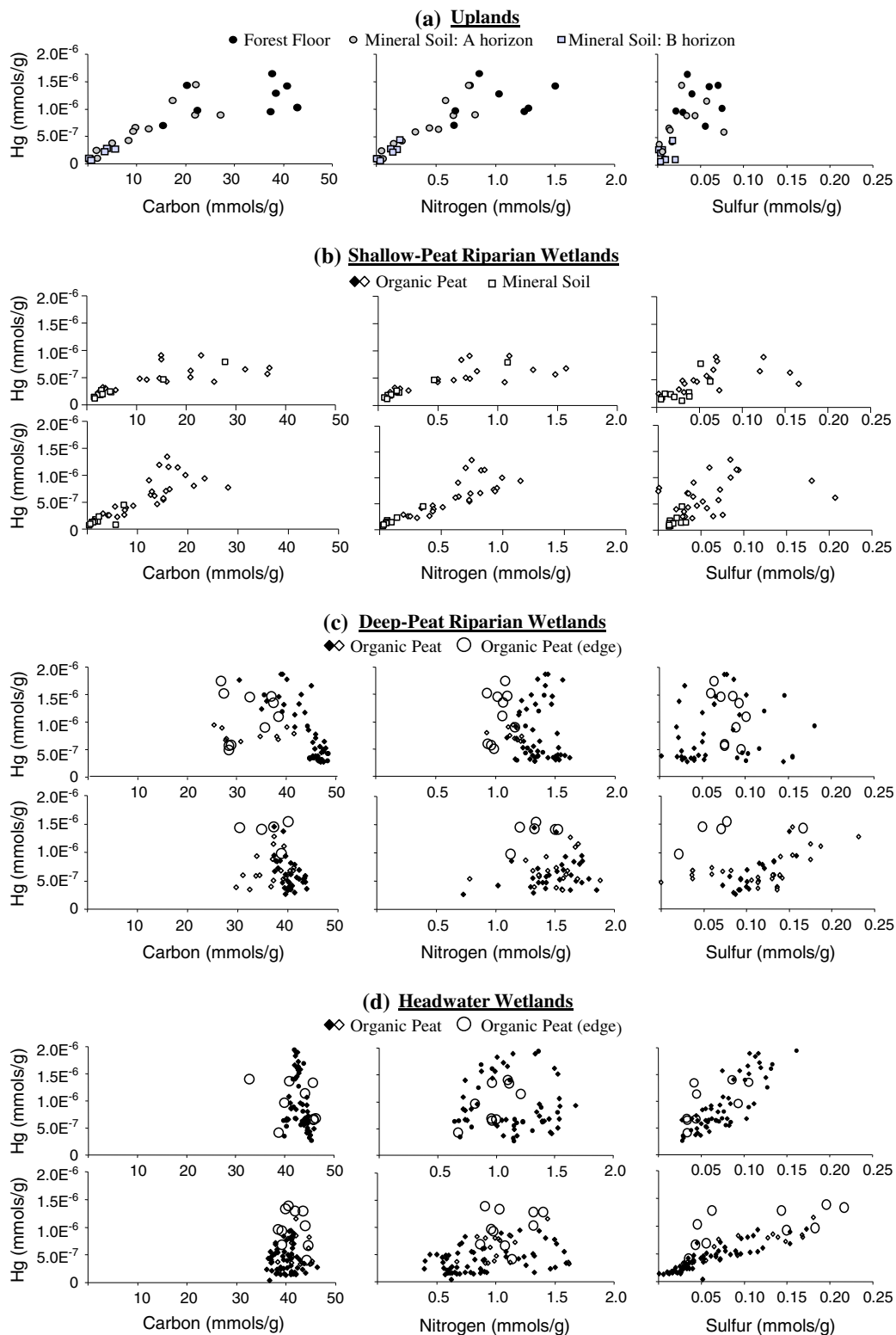


Figure 3. Scatterplots showing the relationship between Hg and C, N, and S concentrations in soil substrates of (a) uplands, (b) shallow-peat riparian wetlands, (c) deep-peat riparian wetlands, and (d) headwater wetlands in the Sunday Lake watershed in the western Adirondack region of New York State. The upland panels include soil data associated with the uplands adjacent to each of the six wetlands studied. The data for each wetland type are shown in two rows of panels, with each row showing the data for an individual wetland. Data points are shown for each individual depth section of each core in each wetland. Wetland symbols that are closed represent areas not influenced by groundwater; open symbols represent areas influenced by groundwater.

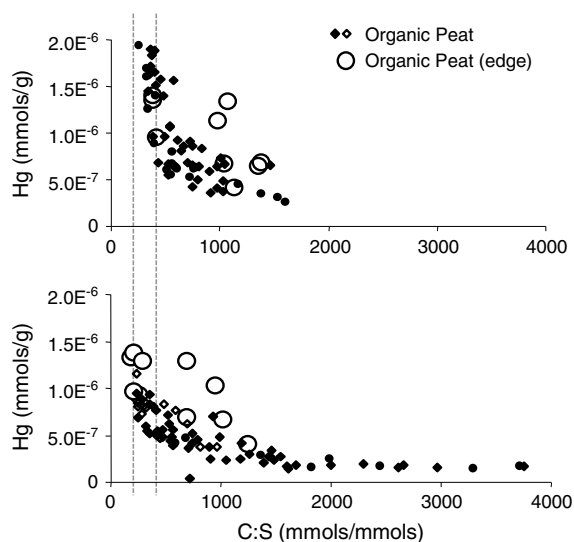


Figure 4. Scatterplots showing the relationship between Hg and the C:S ratio in headwater wetland peat in the Sunday Lake watershed in the western Adirondack region of New York State. Wetland symbols that are closed represent areas not influenced by groundwater; open symbols represent areas influenced by groundwater. Vertical dashed lines show the C:S ratio at 200 and 400, below and above which, respectively, sulfur mineralization and sulfur immobilization should dominate (see section 3.3.2).

and nitrogen was lost at approximately ~ 15 – 20 mmol/g carbon and ~ 0.75 – 1.0 mmol/g nitrogen (Figure 3a).

[35] In the shallow-peat riparian wetlands, the relationships between mercury and carbon, nitrogen, and sulfur (Figure 3b) in both mineral and organic soils were similar to those reported for the upland mineral soils (Figure 3a). Mercury in the mineral soils of the shallow-peat riparian wetlands was strongly correlated with carbon (Figure 3b; $p < 0.0001$, $r^2 = 0.87$, $n = 20$, slope = 2.45×10^{-8} , SE = 2.26×10^{-9}) and nitrogen (Figure 3b; $p < 0.0001$, $r^2 = 0.93$, $n = 19$, slope = 8.26×10^{-7} , SE = 5.64×10^{-8}) but not with sulfur (Figure 3b; $p = 0.1030$, $r^2 = 0.16$, $n = 18$). Whereas there was no statistically significant correlation of mercury with carbon, nitrogen, nor sulfur in the organic horizon of the upland forest soils (Figure 3a), mercury in the organic soils of the shallow-peat riparian wetlands was weakly correlated with carbon (Figure 3b; $p < 0.0011$, $r^2 = 0.23$, $n = 43$) and nitrogen (Figure 3b; $p < 0.0001$, $r^2 = 0.32$, $n = 43$) and only very weakly correlated with sulfur (Figure 3b; $p = 0.0502$, $r^2 = 0.09$, $n = 43$). Note that the slope of both the mercury to carbon relationship and the mercury to nitrogen relationship differed between sites (comparison of regression lines for carbon: $p = 0.0034$; slope = 1.02×10^{-8} , SE = 4.18×10^{-9} ; and slope = 3.68×10^{-8} , SE = 7.54×10^{-9} ; comparison of regression lines for nitrogen: $p = 0.0009$; slope = 2.79×10^{-7} , SE = 9.33×10^{-8} ; and slope = 9.35×10^{-7} , SE = 1.59×10^{-7}). When this site-specific difference was accounted for, the amount of the variability in mercury concentration explained by carbon, and nitrogen, nearly doubled ($r^2 = 0.48$, 0.57 , respectively). Also, the relationship between mercury and carbon, and mercury and nitrogen, in one of the two shallow-peat riparian wetlands did not plateau; however, in the range of carbon and nitrogen concentrations measured at that site

(< 20 mmol/g C, < 1 mmol/g N; Figure 3b), it remained consistent with the elemental relationship described for upland soils (Figure 3a).

[36] The two deep-peat riparian wetlands behaved differently. Overall, there were no statistically significant positive correlations between mercury and carbon, nor between mercury and nitrogen (Figure 3c). However, in one of the deep-peat riparian sites, the C:N ratio was weakly correlated with mercury concentration ($p = 0.0020$, $r^2 = 0.16$, $n = 69$, slope = -3.59×10^{-8} , SE = 1.1×10^{-8}), such that mercury concentration increased with decreasing C:N ratio. In the other deep-peat riparian wetland, only sulfur was significantly correlated with mercury ($p = 0.0120$, $n = 68$, $r^2 = 0.02$, slope = 2.18×10^{-6} , SE = 8.45×10^{-7}), with explanatory power increasing to 26% when edge sites were excluded ($p = 0.0001$, $n = 59$, slope = 3.19×10^{-6} , SE = 7.11×10^{-7} ; Figure 3c). Overall, elemental correlations with mercury explained much less of the variability in mercury concentrations in deep-peat riparian wetlands as compared to either shallow-peat riparian or headwater wetlands.

[37] There was a strong correlation between mercury and sulfur in the peat of the headwater wetlands (Figure 3d; $p < 0.0001$, $r^2 = 0.45$, $n = 157$). However, the slope of the relationship between mercury and sulfur differed among the two headwater wetland sites ($p < 0.0001$); there was more mercury per unit sulfur in the forested headwater wetland (slope 1.19×10^{-5} , SE = 1.16×10^{-6}) as compared to the nonforested headwater wetland (slope 5.08×10^{-6} , SE = 3.72×10^{-7}). When these site differences were taken into account, sulfur explained much more of the variability in mercury concentration ($r^2 = 0.73$). When edge sites were excluded from the analysis, the variability in mercury concentration explained by sulfur alone increased modestly ($p < 0.0001$, $r^2 = 0.80$, additional $r^2 = 0.07$, $n = 138$).

[38] We tested two additional models that investigated the interaction between sulfur and carbon in the headwater wetland peat. First we tested a model that included carbon, sulfur, and a carbon-sulfur interaction; including the carbon variable and the carbon-sulfur interaction in the model explained little additional variability (additional $r^2 = 0.02$). We also tested a simple regression model that used only the C:S ratio to explain variability in mercury concentration; however, it explained less variability than did sulfur alone ($p < 0.0001$, $r^2 = 0.68$, $n = 150$). Nevertheless, peak mercury concentrations occurred at a C:S ratio of ~ 200 – 400 (Figure 4), which coincides with the break-even point between net microbial sulfur mineralization and immobilization reported by *Germida* [2005]. Although these values were based on decomposition studies using crop residues, and thresholds may vary somewhat depending on the type of decomposers and the C:S ratio of substrate [*Germida*, 2005], this generally suggests that decomposition dynamics may also be important controls on mercury retention and stoichiometry in saturated wetland peat soils, as Hg concentrations increase with microbially mediated sulfur retention and oxidative carbon losses that increase sulfur concentration and decrease the C:S ratio of the peat (see section 4.2.2).

3.4. Stoichiometry of Hg and C in Pore Water and Stream Water

[39] The relationship between total dissolved mercury (THg_d) and dissolved organic carbon (DOC) in both peat

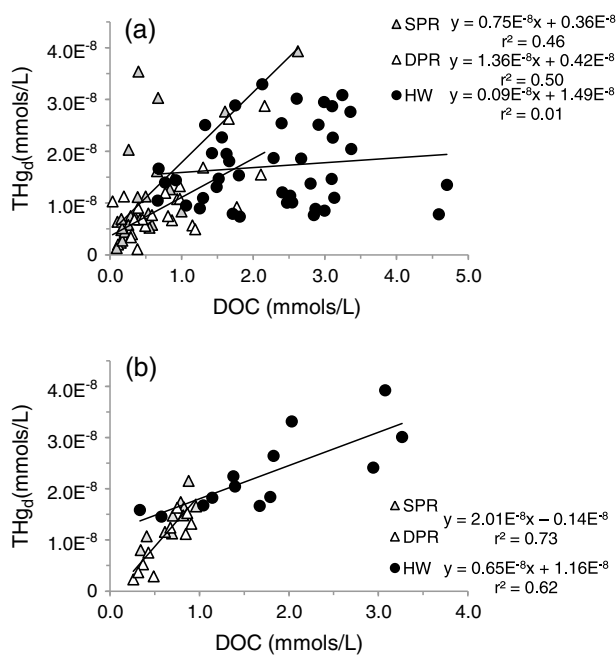


Figure 5. Scatterplots showing the relationship between total dissolved mercury (THg_d) and dissolved organic carbon (DOC) in (a) pore water of shallow-peat riparian (SPR), deep-peat riparian (DPR), and headwater (HW) wetlands, and (b) riparian streams and headwater wetland outlets in the Sunday Lake watershed in the western Adirondack region of New York State. In Figure 5b, note that there was no significant difference in the slope and intercept of the deep- and shallow-peat riparian regression lines; thus, all riparian stream data were combined. Statistical results of regression analyses are reported in the results (see section 3.4).

pore water and stream water differed among wetland types (Figure 5). In the pore water of both the deep-peat and shallow-peat riparian wetlands, THg_d was correlated with DOC ($p=0.0004$, $r^2=0.46$, $n=23$, slope= 0.75×10^{-8} , SE= 0.18×10^{-8} ; $p<0.0001$, $r^2=0.50$, $n=28$, slope= 1.36×10^{-8} , SE= 0.26×10^{-8} ; Figure 5); note that a comparison of regression lines showed that the slope of these two lines differed at nearly the alpha 0.05 level ($p=0.0668$, $n=51$). In the pore water of the headwater wetlands, in contrast, the slope of the relationship between THg_d and DOC was not significantly different from zero ($p=0.4547$, $n=42$; Figure 5).

[40] In stream water of the deep-peat and shallow-peat riparian wetlands, together, THg_d was strongly correlated with DOC ($p<0.0001$, $r^2=0.73$, $n=20$, slope= 2.01×10^{-8} , SE= 0.29×10^{-8} ; Figure 5), with an intercept not significantly different from zero ($p=0.4910$, intercept= -0.14×10^{-8} , SE= 0.20×10^{-8}); note that a comparison of regression lines showed that the slopes and intercepts of these two sample sets were not different ($p=0.6177$, $p=0.8650$, respectively). Based on a comparison of regression lines, the slope and intercept of the relationship between THg_d and DOC in the headwater wetland stream both differed from that of the riparian stream water ($p=0.0018$, $p=0.0008$, $n=33$). In the headwater wetland outlets, THg_d was correlated with DOC, but the slope of the relationship was only one third of that measured in

the riparian stream water ($p<0.0013$, $r^2=0.62$, $n=13$, slope= 0.65×10^{-8} , SE= 0.15×10^{-8} ; Figure 5), and had a nonzero intercept ($p=0.0024$, intercept= 1.16×10^{-8} , SE= 0.29×10^{-8}).

4. Discussion

4.1. Forest Soil Mercury: Stoichiometric Convergence and Possible Binding Site Limitation

[41] The greater pool size of mercury in the top 50 cm of the forest soils as compared to the wetland soils agrees with our understanding that atmospheric deposition of mercury is greatly enhanced by the forest canopy [St. Louis et al., 2001; Rea et al., 2002; Miller et al., 2005]. For example, in the Sunday Lake watershed, mercury inputs are roughly 3 to 6 times greater to the forest floor than into open sites, depending on forest type [Demers et al., 2007]. Furthermore, inputs to the forest floor are approximately 1.5 to 3 times greater than mercury export from the forest floor, and more than an order of magnitude greater than leaching losses from mineral soil horizons [Demers et al., 2007]. Mercury entering the forest floor via leaf fall or throughfall is associated with particulate or dissolved organic matter. During decomposition of organic matter in forest organic horizons, the concentration of mercury increases [Hall and St. Louis, 2004; Demers et al., 2007]. Eventually, decomposition of organic matter in the forest floor releases dissolved organic matter (along with its complexed mercury), which is hydrologically transported into the mineral soil where dissolved organic matter is immobilized during the process of podzolization [e.g., Deconinck, 1980; Driscoll and Postek, 1995]. Thus, the distribution of mercury in forest soils results from the interaction of multiple processes: decomposition, hydrologic transport, and the physicochemical fractioning of organic matter between the dissolved and adsorbed phases.

[42] Mercury concentrations measured in the forest floor (mean= 235 ng/g , SE= 22 ng/g , $n=8$), A horizon (mean= 135 ng/g , SE= 27 ng/g , $n=10$), and B horizon (mean= 52 ng/g , SE= 14 ng/g , $n=8$) in the Sunday Lake watershed were about 2 times greater than the mean mercury concentration in the forest floor (140 ng/g) and mineral soils (20 ng/g) reported for the north-central U.S., and greater than the mode for natural and arable soils from Europe [Grigal, 2003]. Whereas Hg concentrations decreased with depth in the forest soil profile, the mean stoichiometric ratio of Hg:C increased from the organic forest floor ($4.0 \times 10^{-8} \text{ mol Hg per mol C}$; SE= 5.2×10^{-9}) to the A horizon ($6.4 \times 10^{-8} \text{ mol Hg per mol C}$, 8.2×10^{-9}) and into the B horizon ($10.3 \times 10^{-8} \text{ mol Hg per mol C}$, SE= 2.9×10^{-8}). These data compare well with the review by Grigal [2003], who reported that the average ratio for surface organic horizons was $4.2 \times 10^{-8} \text{ mol Hg per mol C}$, increasing to $9.0 \times 10^{-8} \text{ mol Hg per mol C}$ in the A horizon, to $15.0 \times 10^{-8} \text{ mol Hg per mol C}$ in the B horizon, and $22.8 \times 10^{-8} \text{ mol Hg per mol C}$ in the C horizon. Therefore, despite the greater accumulation of mercury in the soils of the Sunday Lake watershed, the increase in the Hg:C ratio from the forest floor to the mineral soil (A and B horizons) compares well to that reported for Hg:C and Hg:SOM in soils from the north-central U.S. and Sweden [Lindqvist et al., 1991; Grigal, 2003]. Thus, despite regional and depthwise differences in soil

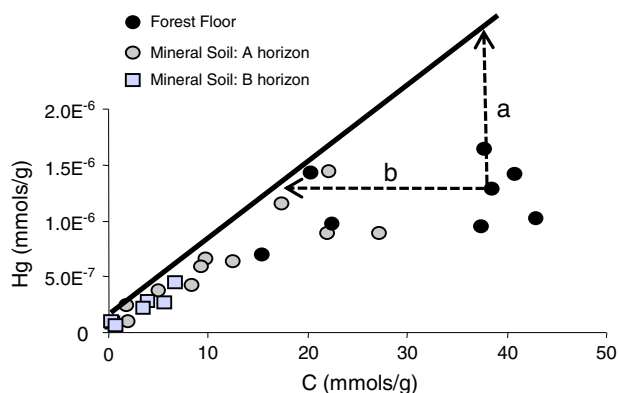


Figure 6. Conceptual diagram showing the relationship between Hg and C in upland forest soil. The Hg:C ratio in a soil sample may approach the apparent stoichiometric limit (the solid diagonal line) by either (a) gaining mercury or (b) losing carbon.

mercury concentrations, (1) the amount of mercury per unit carbon or organic matter is typically greater in mineral horizons than in overlying organic horizons and (2) the relative differences in Hg:C stoichiometry among horizons in forest soil profiles appear to be somewhat consistent.

[43] The increase in Hg:C and Hg:SOM ratios with depth in forest soils may occur for several reasons. Differences in the relative amount of reduced sulfur associated with SOM in each soil horizon could promote differences in Hg:SOM through the forest soil depth profile. Data from the north-central U.S. show a more constant relationship between Hg and S than between Hg and SOM, and Hg:S stoichiometry of the organic and mineral soil horizons was similar, implying that differences in Hg concentration simply reflected changes in S concentration [Grigal, 2003]. In our study, the bulk forest soil pool data also showed similar average Hg:S stoichiometry in the upland organic and mineral soils (see section 3.3.1 and Figure 2); however, mercury and sulfur were not correlated at the scale of individual samples in either the organic or mineral soils of the uplands (see section 3.3.2 and Figure 3). This lack of correlation between Hg and S in the forest soils from our study could, in part, result from the limited range in soil sulfur concentrations represented in our forest soil data set, or may simply be suggestive of greater mechanistic complexity. Although reduced sulfur groups in organic matter are known to bind mercury, only a fraction of the total sulfur in organic matter is reduced sulfur [e.g., Xia *et al.*, 1999; Skyllberg *et al.*, 2000; Ravichandran, 2004]. Moreover, research suggests that mercury is involved in bidentate complexation with one reduced sulfur and one nitrogen heteroatom [e.g., Skyllberg *et al.*, 2000; Hesterberg *et al.*, 2001] and that the quantity of reduced sulfur binding sites actually occurring in close proximity to reduced nitrogen binding sites may significantly reduce the quantity of strongest binding sites available to complex with mercury [e.g., Skyllberg *et al.*, 2000]. Obrist *et al.* [2009] also found that mercury was correlated with nitrogen in forest soil pools in Sierra Nevada forest sites. Thus, it should not be altogether surprising that mercury was not well correlated with total sulfur in the forest soils in this study.

[44] It appears more likely in our case that decomposition dynamics may play a crucial role in the observed stoichiometric differences among forest soil horizons. We know that decomposition of leaf litter concentrates mercury in the forest floor as mercury is gained [Hall and St. Louis, 2004], perhaps by fungal translocation [Demers *et al.*, 2007], and carbon is lost as CO₂ via microbial respiration [Grigal, 2003], thus increasing the concentration of mercury relative to carbon. Hence, DOC with a large Hg:C ratio is leached downward, becoming immobilized in mineral horizons lower in the soil profile during the process of podzolization.

[45] Numerous calculations over the past decade have demonstrated that the quantity of binding sites present in organic matter is multiple orders of magnitude greater than environmentally relevant concentrations of mercury [Ravichandran, 2004]. Nonetheless, the distinct pattern in elemental stoichiometry (Hg:C, Hg:N; see section 3.3.2 and Figure 3) observed in the upland forest soils challenges the notion that the binding capacity of organic matter cannot be saturated under natural environmental conditions. In the upland forest organic soil horizon, there was no correlation between mercury and carbon, nitrogen, or sulfur. However, the correlation between mercury and carbon (and mercury and nitrogen) became significant upon the transition from the organic horizon to the underlying mineral soil (A and B horizons), with the strongest correlations occurring within the mineral B horizon.

[46] The lack of elemental correlation in the organic horizons does not necessarily mean that mercury retention is not associated with organic matter, but perhaps that the overabundance of available binding sites poses no apparent limit on the amount of mercury bound with the organic matter [Hurley *et al.*, 1998a]; that is, the supply of mercury is limited relative to the numerous potential binding sites for mercury. Applying similar logic to the mineral soil horizon leads us to the opposite conclusion that the quantity of potential binding sites for mercury in the mineral soil horizon is limited relative to the supply of mercury. As previously discussed, mercury accumulating in the mineral horizon is likely transported to depth along with DOM, with which it was already complexed in the organic soil horizon. As decomposition proceeds, the concentration of mercury associated with the dissolved organic matter that is produced and released from the organic soil horizon appears to converge upon a Hg:C and Hg:N ratio that serves as an upper limit to Hg:C and Hg:N ratios throughout the forest soil profile (Figure 6).

4.2. Wetland Soil Mercury Pool and Stoichiometry: Importance of Wetland Type and Hydrogeologic Setting

[47] Our results further showed that hydrogeologically driven differences in the mode of decomposition in different wetland types influenced the stoichiometry of mercury retention and mobility in wetland soils.

4.2.1. Shallow-Peat Riparian Wetlands

[48] Patterns of mercury retention within the shallow-peat riparian wetlands resembled patterns of retention within the forest soils, that is, much of the mercury pool within shallow-peat riparian wetlands was within mineral material underlying the organic peat soils. As in many riparian areas, the hydrology is seasonally and episodically dynamic, and much of the organic horizon is not permanently saturated,

thus promoting fast, efficient aerobic decomposition that results in oxidative losses of carbon and a shallow peat deposit. Furthermore, upwelling groundwater provides a supply of alternate electron acceptors (e.g., nitrate, sulfate, iron) such that when anoxic conditions do occur, the fluctuating water table provides a mechanism for the recycling of electron acceptors between their reduced and oxidized forms [Demers, 2009]. Thus, we suggest that organic matter decomposition produces dissolved organic carbon and associated mercury that can be transported to the underlying mineral soil horizons or to the stream channel. The coarse matrix of mineral material below the shallow riparian peat is enriched in organic matter contributed from the overlying peat, and mercury associated with this organic matter may be more hydrologically mobile than the mercury retained in podzolized upland soils.

[49] Additionally, elemental stoichiometry in the shallow-peat riparian wetlands was similar to elemental stoichiometry observed in the upland forest soils, as mercury was well correlated with carbon and nitrogen concentrations within the mineral soil. Although there was no statistically significant correlation between mercury and sulfur in the upland forest soils, Hg:S followed similar patterns as Hg:C and Hg:N in the shallow-peat riparian wetlands; albeit, the correlation with sulfur was weaker than with carbon and nitrogen. Thus, similar mechanisms might control the distribution of mercury in upland forest soils and shallow-peat riparian wetlands: predominantly aerobic decomposition of organic matter and subsequent transport and retention of decomposition products and associated mercury into the mineral horizon.

4.2.2. Headwater Wetlands

[50] That the smallest pool size of mercury occurred in the headwater wetlands (to a depth of 50 cm) is consistent with slow rates of organic matter decomposition. Deep peats form as a result of slow decomposition relative to primary production, as consistently high water table levels maintain saturated, anoxic conditions within the peat that promotes slow, inefficient anaerobic decomposition [Mitch and Gosselink, 2000]. Moreover, headwater wetlands are separated from groundwater, and thus they do not benefit from a supply of alternate electron acceptors, further limiting microbial decomposition. Thus, the hydrogeologic setting of headwater wetlands provides a fundamentally different environment for the biogeochemical cycling of elements that influences both the inferred relative rate and mode of decomposition, and perhaps the biogeochemical cycling of mercury.

[51] Elemental stoichiometry of mercury with carbon, nitrogen, and sulfur in the headwater wetlands was distinctly different from elemental stoichiometry in upland forests and shallow-peat riparian wetlands; that is, there was a strong correlation between mercury and sulfur in the headwater wetlands. This could suggest co-deposition of sulfur and mercury from the atmosphere, which are subsequently immobilized together within the peat. Benoit *et al.* [1994] suggested that, on the basis of inorganic mercury speciation, mercury was immobile within the peat profile; however, more recent isotopic evidence indicates that sulfur is not immobile within the peat profile, migrating vertically down through the peat subsequent to deposition [Novak *et al.*, 2005]. Thus, a simple model of co-deposition and immobilization as inorganic mercury sulfide alone may not be a

complete explanation for the strong correlation between mercury and sulfur in the headwater peat.

[52] Another possible mechanism for the strong correlation between mercury and sulfur in headwater wetland peat may be the biogeochemical cycling of sulfur that results in the incorporation of mercury with organic sulfur, rather than sulfide. The proportion of total sulfur as organic sulfur in sphagnum peat wetlands typically exceeds 90%, with 90% of the organic sulfur typically involved in carbon-sulfur bonds. Inputs of inorganic sulfate fuel microbial sulfate reduction, but in peat soils, organic S is the major product rather than reduced mineral sulfides [Wieder and Lang, 1988]. Turnover of the smaller sulfate and inorganic sulfur pool is rapid (i.e., hours and days, respectively), whereas the turnover of the larger carbon-bonded sulfur pool is slow (i.e., years). Thus, most inorganic additions of sulfur are eventually incorporated into the organic sulfur pool, and mercury may follow. Moreover, recent research shows that peat substrates and dissolved organic matter can compete with inorganic sulfur species (including cinnabar, HgS_(s)) in binding mercury species (see section 1) [e.g., Drexel *et al.*, 2002] and that much of the mercury in organic-rich environments may indeed be associated with the organic sulfur pool, even in the presence of sulfides.

[53] We found that mercury concentration increased exponentially with decreasing C:S ratio (Figure 4 and see section 3.3.2). As C:S ratio decreases, mercury binding-site density increases, possibly increasing the likelihood of bidentate coordination between mercury and sulfur; not surprisingly then, mercury concentration is highest where C:S is lowest. Also, note that the rate of increase in mercury concentration became markedly greater between C:S ratios of 200–400, with an asymptote as the C:S ratio approached 200. In sulfur cycling studies, net sulfur immobilization dominates when the substrate molar ratio of C:S > 400, whereas net sulfur mineralization dominates when the substrate molar ratio of C:S < 200 [Germida, 2005]. Thus, the mercury concentration was maximized within a range of C:S values at which sulfur immobilization was relatively balanced with sulfur mineralization. Microbially mediated retention of sulfur, as well as oxidative losses of carbon, would decrease the C:S ratio of the substrate. Retention and mobility of mercury in hydrologically saturated wetland peat likely involve complex cycling between inorganic and organic pools of sulfur, and further experimental work quantifying this cycling of mercury between inorganic and organic sulfur pools is a critical next step for understanding the fate of large pools of legacy mercury stored in saturated peat-wetland environments.

4.3. Edge Effects and Evidence of Upland-Wetland Connectivity

[54] Differences in mercury pool size across upland-wetland transects are suggestive of wetland retention of mercury inputs derived from the uplands. The accumulation of mercury at the forest-wetland interface is likely the result of a combination of different mercury fluxes including increased atmospheric deposition along the forest-edge [e.g., Weathers *et al.*, 2000, 2001], direct inputs of litter from the forest canopy to the adjacent wetland [St. Louis *et al.*, 2001], shallow lateral interflow from forested hillslopes into wetlands [Branfireun *et al.*, 1996, 1998; Kolka *et al.*, 2001; Mitchell *et al.*, 2008, 2009; Richardson

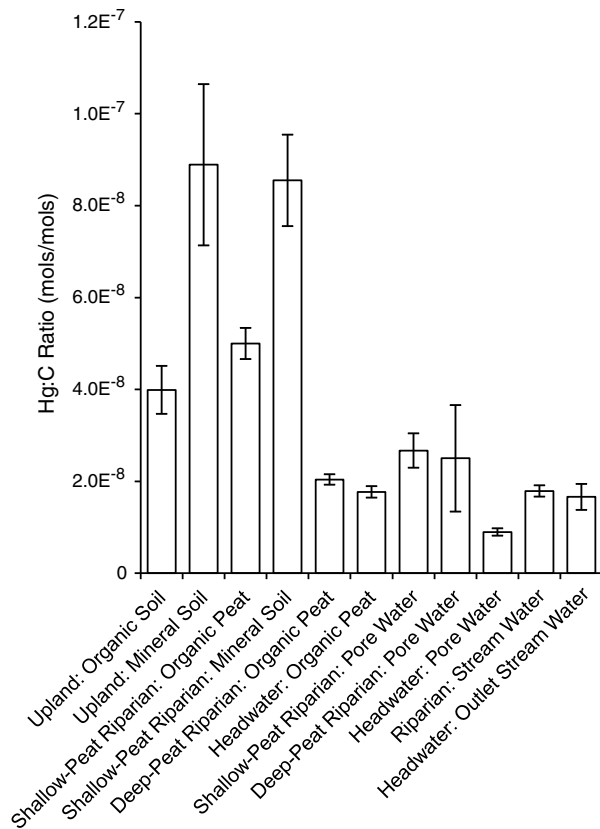


Figure 7. A summary comparison of mean Hg:C molar ratios in soil substrates, pore water, and stream water associated with uplands and different wetland types of the Sunday Lake watershed located in the western Adirondack region of New York State. Error bars show ± 1 SE.

et al., 2010], and upwelling of groundwater at the break in slope at the upland-wetland interface [e.g., *Winter*, 1988, 1992] that may contribute DOC and associated mercury, although perhaps only in small amounts [*Krabbenhoft and Babiartz*, 1992]. Mercury accumulation at the upland-wetland interface was most evident in the deep-peat riparian and headwater wetlands, possibly due to low hydraulic conductivity and resulting low hydrologic flux through these zones that could limit the mobility of deposited mercury. In the shallow-peat riparian wetlands, the total pool size at the upland-wetland interface was similar to the mercury pool size across the rest of the wetland transect, whereas mercury concentrations at shallow depths alone (dominated by organic matter rather than mineral soil) were greater at the upland-wetland edge. This pattern reflects that pool sizes in the shallow-peat riparian wetland were strongly influenced by the mineral soil horizon. Whereas shallow lateral interflow and upwelling groundwater would likely have a strong influence on the mineral soil mercury pool throughout the wetland, the edge effect apparent in the uppermost organic horizon is more likely influenced by increased deposition of throughfall and litterfall at the forest edge.

[55] Edge effects also influenced elemental stoichiometry. In the shallow-peat riparian wetlands where apparent edge effects influenced most of the narrow wetland corridor, the elemental stoichiometry of edge samples was similar to the stoichiometry in samples from across the remainder of

the wetland. However, in deep-peat riparian and headwater wetlands, the stoichiometry of samples from edges tended to be outliers, implying differences in both inputs (delivery) of mercury as well as differences in the processes resulting in mercury retention and storage. Thus, edge effects further illustrate the influence of hydrology and upland-wetland connectivity on the pattern and process of mercury accumulation in wetlands of different hydrogeologic setting.

4.4. Mercury Release and Transport: Comparing Stoichiometry of Soil, Pore Water, and Surface Water

[56] Mercury research in stream ecosystems has demonstrated strong correlations between dissolved mercury and DOC, particulate mercury and POC, and total mercury and TOC [e.g., *Meili*, 1991; *Mierle and Ingram*, 1991; *Shanley et al.*, 2008; *Dittman et al.*, 2010]. However, it appears that the strong correlation between mercury and carbon weakens considerably away from the stream channel, especially where highly organic sources such as forest floor organic horizons and leachates, and wetland peat soils and peat pore waters are considered.

[57] For example, the lack of strong correlation between Hg and C in both pore water and outlet streams from headwater wetlands in this study reflected the peat environment from which they were derived (Figures 3 and 5). Given that mercury was correlated with sulfur (not carbon) in the headwater peat, it is possible that mercury may also be better correlated with (reduced) sulfur in the headwater wetland pore water and outlet streams. However, whereas there was no correlation between mercury and carbon in the pore water, there was a weak relationship between mercury and carbon in the headwater outlet streams. This slight slope in the Hg:DOC relationship may simply indicate that the source of mercury to the outlets does not reflect average wetland pore water. For example, a disproportionate fraction of mercury and DOC at the outlet could be derived from the upland-forest impacted lag zone [e.g., *Kolka et al.*, 2001]. It is also possible that only a fraction of DOC in the headwater wetland pore water is mobile, or that the fraction that reaches the outlet has been processed to a greater extent or has been exposed to aerobic decomposition processes that may have begun to alter its stoichiometric composition. Overall, the observed lack in correlation between mercury and DOC in the peat pore water of the headwater wetlands (see section 3.4 and Figure 5a), in addition to the low slope of the mercury:DOC relationship in the headwater outlet stream water (see section 3.4 and Figure 5b), may suggest that export of mercury from the headwater wetlands is limited by the supply of mercury rather than by the availability of Hg-DOC binding sites. In contrast, the quantity of mercury transported in riparian streams is more limited by DOC binding and mobilization (see section 3.4 and Figure 5b) and reflects the strong correlation between mercury and carbon observed in the upland mineral soil horizons and shallow-peat riparian wetlands (see section 3 and Figure 3), likely derived from decomposition products leached from organic horizons.

[58] Using Hg:C stoichiometry to connect headwater outlet and riparian stream water mercury back to their terrestrial and wetland sources may be challenging. Whereas the strength of the correlation between mercury and carbon in riparian stream water does resemble that of the upland

mineral and shallow-peat riparian soil, a comparison of average Hg:C ratios (Figure 7) shows distinct differences in Hg:C stoichiometry between soil and stream water. That is, the Hg:C ratio in riparian stream water appears to most closely resemble that of riparian pore water and headwater wetland outlets; this makes some sense in that the riparian pore water and headwater outlets represent mobile fractions. Also, this may suggest that riparian stream water is a mixture of sources originating in more organic soil pools (e.g., headwater wetlands, riparian pore water, shallow interflow from upland organic forest soil horizons) and mineral soil horizons in the adjacent upland and riparian soils. Note that *Canham et al.* [2004] used inverse modeling to demonstrate that allochthonous DOC in Adirondack lakes was contributed by both forested uplands and wetlands and that a large proportion of DOC transported in streams between lakes was consumed in transit. In their study, the proportion of DOC derived from different sources varied dramatically by watershed depending upon the quantity, type, and distribution of wetlands across the landscape [*Canham et al.*, 2004]. For example, in representative low-DOC and high-DOC lakes with 0.3% and 29.8% of their watershed area as wetlands, respectively, the contribution of DOC from forested uplands ranged from 98% down to 34% (calculated from data in *Canham et al.* [2004]). *Schelker et al.* [2011] found that Hg:C stoichiometry was altered upon transit through open water bodies, likely by photochemical processes. Thus, not surprisingly, it appears that mercury in down-watershed riparian streams is likely a composite of multiple sources and that Hg:C stoichiometry may be additionally modified during in-stream transport (e.g., loss of carbon due to respiration or UV oxidation, or loss of mercury by photoreduction and volatilization).

5. Conclusions and Implications

[59] The accumulation and elemental stoichiometry of mercury in soils of uplands and wetlands are influenced by hydrogeologic setting, which governs the rate and mode of decomposition by influencing the extent and duration of saturation, and the supply of nutrients and alternate electron acceptors. Hydrogeologically driven differences in decomposition dynamics and associated differences in the biogeochemical cycling of mercury likely control the retention and mobility of mercury, influencing the size and distribution of mercury pools across the upland-wetland interface, and among different wetland types. Differences in Hg stoichiometry with C, N, and S in soils across the upland-wetland interface of forests and wetlands of different hydrogeologic setting likely reflect mechanistic differences in mercury retention within these hydrologically contrasting soil environments. In the upland forest soils and shallow-peat riparian wetlands, predominantly aerobic decomposition of organic matter followed by transport and retention of organic residues into the mineral soil along with associated mercury results in strong correlations between Hg and C, and Hg and N. In contrast, headwater wetlands provide a fundamentally different environment for the biogeochemical cycling of mercury that results in strong correlations between Hg and S. Thus, hydrogeologic setting may provide a framework for better understanding mechanisms of mercury retention in varying environmental settings, and

this framework could provide guidance for the quantification of the mobile fraction of legacy mercury in soils of forests and wetlands across the landscape. Ultimately, decomposition dynamics and hydrology influence the production of dissolved organic matter and its mobilization to surface waters along with associated mercury.

[60] In a recent cross-site synthesis, *Riscassi and Scanlon* [2011] showed that Hg:DOC ratios in stream water varied widely among watersheds across the Northern Hemisphere and suggested that soil organic carbon content was a primary factor influencing the amount of Hg per unit organic carbon transported by streams, possibly because locations higher in organic matter content had lower Hg:DOC ratios due to biodilution [*Meili*, 1991; *Riscassi and Scanlon*, 2011]. Secondary factors included Hg deposition, soil mineral composition, water chemistry, and DOC quality (aromatic moieties have higher Hg:DOC ratios) [*Riscassi and Scanlon*, 2011]. Other studies investigating mercury transport during high flow events have demonstrated that increases in stream water Hg concentrations resulting from changes in contributing source area [*Demers et al.*, 2010] or particulate mobilization [e.g., *Shanley et al.*, 2002] typically coincided with changes in Hg:C stoichiometry, suggesting that various sources of Hg within the watershed had distinct Hg:C ratios. Thus, both this study and previous research suggest that disparate observations of Hg:C stoichiometry in stream water from across complex landscapes may, in part, be explained by linking stream water stoichiometry back to the chemistry of soils and pore water of the forests and wetlands that serve as sources of the Hg:C relationships observed in stream water. In some situations, Hg:C stoichiometry may be a valuable way to distinguish sources and to hypothesize about the processing of mercury both before and after it reaches the stream channel. However, it is important to note that Hg:element stoichiometry is by no means a conservative tracer, likely changing along the flow path from terrestrial and wetland sources to streams and down-gradient aquatic ecosystems [e.g., *Schelker et al.*, 2011; *Burns et al.*, 2012], and thus should be interpreted with caution. Nonetheless, stoichiometry should help guide us toward a more mechanistic understanding of the sources and fate of mercury retained within and transported through terrestrial and aquatic ecosystems.

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