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Latent Effect of Soil Organic Matter Oxidation on Mercury Cycling within a Southern Boreal Ecosystem

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The focus of this study is to investigate processes causing the observed spatial variation of total mercury (THg) in the soil O horizon of watersheds within the Superior National Forest (Minnesota) and to determine if results have implications toward understanding long-term changes in THg concentrations for resident fish. Principal component analysis was used to evaluate the spatial relationships of 42 chemical elements in three soil horizons over 10 watersheds. Results indicate that soil organic carbon is the primary factor controlling the spatial variation of certain metals (Hg, Tl, Pb, Bi, Cd, Sn, Sb, Cu, and As) in the O and A soil horizons. In the B/E horizon, organic carbon appeared to play a minor role in metal spatial variation. These characteristics are consistent with the concentration of soil organic matter and carbon decreasing from the O to the B/E horizons. We also investigated the relationship between percent change in upland soil organic content and fish THg concentrations across all watersheds. Statistical regression analysis indicates that a 50% reduction in age-one and age-two fish THg concentration could result from an average 10% decrease in upland soil organic content. Disturbances that decrease the content of THg and organic matter in the O and A horizons (e.g., fire) may cause a short-term increase in atmospherically deposited mercury but, over the long term, may lead to decreased fish THg concentrations in affected watersheds.

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Mercury is an element of concern due to the harmful effects it poses to humans and wildlife. Freshwater marshes are of particular interest in mercury-related investigations because they harbor reduced soil conditions that can promote efficient production of methylmercury (CH_3Hg^+), a highly toxic form of mercury (St. Louis et al., 1996; Hall et al., 2008). The North American boreal ecosystem, which stretches from Canada to the United States Great Lakes Region, is an area of focus in mercury-related investigations because of its abundant peatlands and freshwater marshes. Several studies show elevated total mercury (THg) and methyl-mercury (MeHg) concentrations in soils, surface water, fish, and periphyton biofilm in forest stretches of this region (Wren et al., 1991; Grigal, 2002; Porvari et al., 2003; Sorenson et al., 2005; Wiener et al., 2006; Desrosiers et al., 2006; Gabriel et al., 2009) and that atmospheric mercury deposition to remote lakes in eastern North America has increased over the last century (Woodruff et al., 2009). Despite significant gains in quantifying the sensitivity of the boreal ecosystem to mercury contamination, there is a need to understand the factors that control the spatiotemporal dynamics of mercury within boreal watersheds and adjacent ecoregions (Snodgrass et al., 2000; Roué-Le Gall et al., 2005; Wiener et al., 2006; Simonin et al., 2008). Having this information will allow resource managers to plan for events (e.g., prescribed burning and logging [Porvari et al., 2003; Allen et al., 2005]) that can affect mercury's fate, transport, and bioaccumulation.

Many studies have identified forest floor carbon and soil organic matter (SOM) as strong adsorbents for metals, including mercury (Schuster, 1991; Nater and Grigal, 1992; Jackson, 1998; Kolka et al., 1999; Reddy and Aiken, 2001; Drexel et al., 2002; Grigal, 2003; Amirbahman et al., 2004; Biswas et al., 2007; Munthe et al., 2007; Jing et al., 2007). Spatial changes in soil THg concentrations are typically attributed to variation in SOM concentrations (Grigal, 2003; Engle et al., 2006; Perry et al., 2006); thus, SOM can have a major impact on mercury transport and bioavailability in a forest system (Kolka et al., 1999; Munthe et al., 2007; Amirbahman et al., 2004). Organic

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Abbreviations: MeHg, methyl mercury; PCA, principal component analysis; SNF, Superior National Forest; SOM, soil organic matter; THg, total mercury.

matter, specifically humic substances, is a strong trace metal adsorbent because (i) it has a large, negatively charged molecular surface area (Jackson, 1998; Jing et al., 2007), (ii) it has a relatively high cation exchange capacity (Jackson, 1998; Jing et al., 2007), and (iii) it forms strong bonds between humic matter ligand functional groups (e.g., -SH, -COOH) and metals, in particular ionic forms of mercury (Jackson, 1998; Turetsky et al., 2006).

Recent research indicates that concentrations of THg in the O horizon of upland soil play an important role in the spatial variability of THg in young-of-year yellow perch for lakes within the Superior National Forest in northeastern Minnesota (Spearman $\rho = 0.80^{****}$) (Gabriel et al., 2009). This study demonstrated that the accumulation of fish mercury in the region is not solely related to impacts from direct atmospheric deposition to lakes but is also related to upland soil THg concentration. The intent of this research was (i) to investigate what natural system processes are causing the observed spatial variability of THg concentration in the soil O horizon and (ii) to determine if the results from (i) have implications toward understanding long-term changes in THg concentrations for resident fish across the studied region.

Methods and Materials

Study Setting

Upland soil and fish samples were collected from 10 watershed-lake systems within the Superior National Forest (SNF) and Boundary Waters Canoe Area Wilderness in northeastern Minnesota (Fig. 1). The region surrounding SNF is part of a transition zone between the boreal ecosystem to the north and northern hardwood forests to the south. The region is blanketed with numerous seepage lakes and wetlands. We studied 10 watersheds that each included a lake. From west to east, the studied lakes were: Wolf, Merritt, Mud, Ella Hall, Thelma, Everett, Lum, Lizz, Ball Club, and Dislocation. Soils in the region are classified as shallow Inceptisols and Entisols developed on thin deposits of loamy till (Cummins and Grigal, 1981). According to the Carlson Index, the trophic status of the study lakes is mesotrophic (chlorophyll-a [trophic status index] TSI = 41.6; total phosphorus TSI = 46.6; secchi depth TSI = 45.7). Gabriel et al. (2009) provide information on surface water chemistry for each lake and the physical properties of each watershed.

Soil Sampling and Analysis

Upland soil samples from the O, A, and B/E horizons within each watershed were collected for analysis. Sampling took place over a 2-yr period (2004 and 2005). Eight of the 10 study lakes' watershed soils (Wolf, Merritt, Mud, Ella Hall, Everett, Lum, Lizz, and Ball Club) were sampled in September 2004. In September 2005, soils from the watersheds of Dislocation and Thelma lakes were sampled. Ten soil samples were collected per horizon, totaling 30 soil samples per watershed. All soils were collected by volume and weighed in the field. Where present, soil O horizon was collected after removal of fresh litter, woody debris, and living plants. The O horizon collected at each site

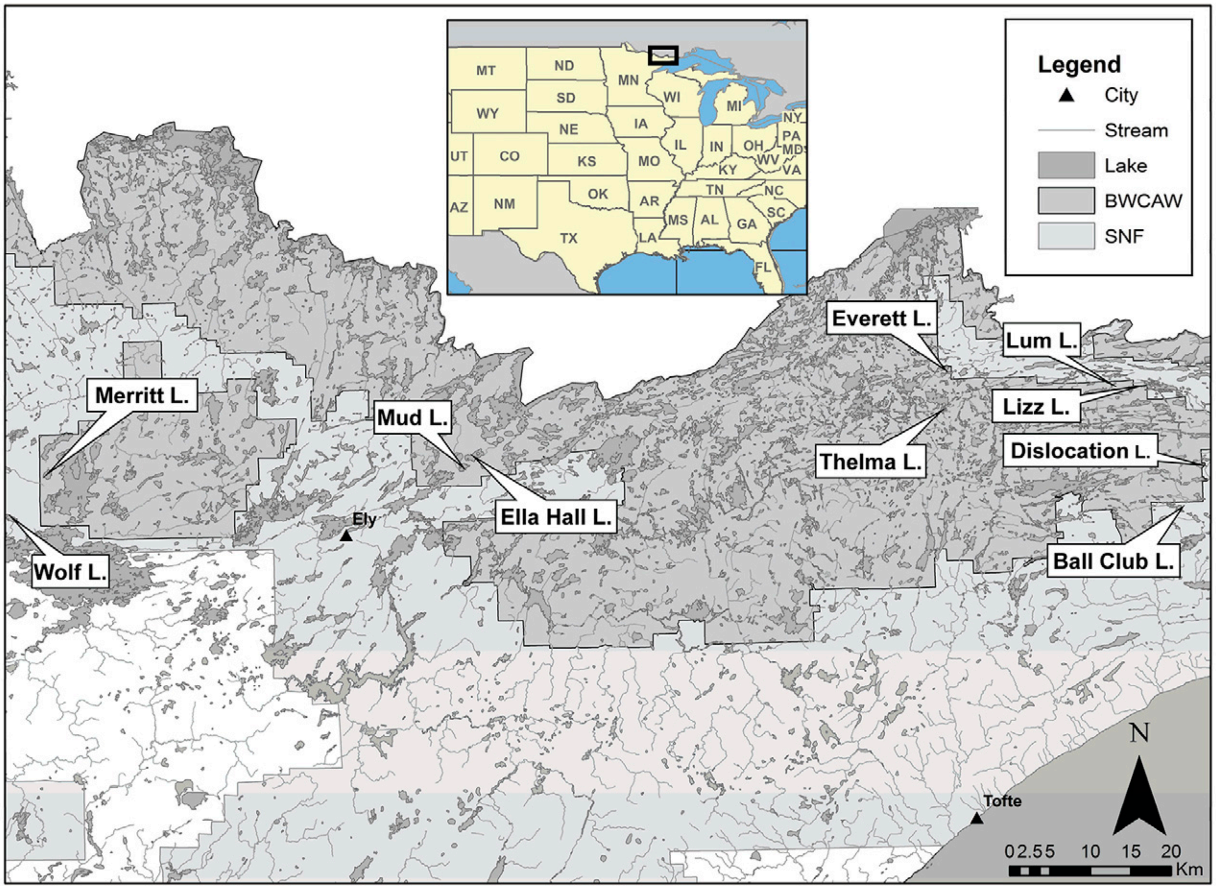

Fig. 1. The study lakes within the greater Superior National Forest of northeastern Minnesota. BWCAW, Boundary Waters Canoe Area Wilderness; SNF, Superior National Forest.

was moderately decomposed matter (Oe) and more highly decomposed matter (Oa). The thickness of the O horizon was highly variable, ranging from 0 to 20 cm in depth, across the study area because of vegetation type. In areas easily accessible to people (e.g., portages and lakes close to entry points), some sites had no O horizon because earthworms had completely consumed the organic matter and incorporated it into the underlying A-horizon mineral soil. In contrast, at some watersheds, the O horizon was intact and up to 10 cm thick.

In the laboratory, soils were air-dried at 20°C and sieved to <2 mm before analysis. All samples were analyzed for 42 elements by a combination of inductively coupled plasma–atomic emission spectrometry and inductively coupled plasma–mass spectrometry (PerkinElmer, Waltham, MA) (with the exception of carbon, organic matter, mercury, and selenium) (Table 1). Analyses were performed on each mineral soil sample (A and B horizons) and the ashed portions of the organic soils (O horizons). Each sample was digested using a mixture of hydrochloric, nitric, perchloric, and hydrofluoric acids at low temperature. An aliquot of the digested sample was then aspirated into the inductively coupled plasma–atomic emission spectrometry and the inductively coupled plasma–mass spectrometry for element level quantification. The analytical methods used are described in detail by Taggert (2002). Carbon from mineral soils was measured with a total C analyzer. For the O horizons (forest floor), carbon was estimated using methods described in Schumacher (2002). Organic matter content for the O horizons was determined using the loss-on-ignition method. For the mineral soils, organic matter content was not determined.

For selenium analyses, mineral and unashed organic soil were mixed with nitric, hydrofluoric, and perchloric acids and heated. After the solution cooled, hydrochloric and nitric acids were added, and heating followed. Once cooled, the solution was analyzed by atomic adsorption spectrometry for selenium detection.

Analytical methods for mercury analyses of soils followed procedures described in Taggert (2002). Mineral and unashed organic soils were dissolved in a mixture of nitric and hydrochloric acids. Potassium permanganate, sulfuric acid, and potassium persulfate were added to each solution, followed by the addition of NaCl-hydroxylamine. Mercury in solution was measured by cold vapor atomic adsorption spectroscopy (Flow Injection Mercury System FIMS-100; PerkinElmer). This instrumentation was routinely calibrated using standards containing 0, 0.5, 2.0, 5.0, and 10 μg g^{-1} mercury (Woodruff and Cannon, 2010). For the O horizon, the mean relative standard deviation for analytical duplicates was ±3.07 and ±11.6% for the A horizon.

Fish Collection, Analysis, and Standardization

Detailed methods of the fish collection and analysis used in this study can be found in Gabriel et al. (2009). Briefly, fish sampling took place during 4-d periods shortly after ice-out in early May of 2004 through 2008. Yellow perch (*Perca flavescens*), bluegill (*Lepomis macrochirus*), and pumpkinseed fish (*Lepomis gibbosus*) were collected using electroshock methods. These fish species were targeted because they are good indicators of MeHg in food webs (Greenfield et al., 2001; Wiener et al., 2006) and are the preferred prey for a number of fish-eating species in the SNF.

For each year, a minimum of 10 fish were caught per lake and analyzed for THg. In total, over all 5 yr, 881 fish were collected and analyzed for THg. Measurements were taken for fish length, weight, and age, and the fish were double bagged and put on ice. For THg detection, we placed the entire fish in a Teflon digestion bomb and added 10 to 20 mL of concentrated nitric acid (depending on the size of the fish). The bomb was sealed and digested overnight in an oven at 70°C, after which the digest was diluted and analyzed using cold vapor atomic fluorescence spectroscopy (using double amalgamation), as outlined in Bloom and Crecelius (1983), along with a Brooks Rand AFS Model III (Brooks Rand Labs, Seattle, WA) and Mercury Guru software (Brooks Rand Labs), which was used for THg detection within fish tissue. We used one or two NIST standard reference materials for these analyses (dogfish muscle and leaf tissue). All fish THg concentrations were quantified based on wet weight. Two or three analytical duplicates were run for each lake per year. The average relative percent difference for routine and analytical duplicates were 6.8% for 2004, 6.5% for 2005, 8.0% for 2006, 7.5% for 2007, and 4.2% for 2008.

Age-one and age-two yellow perch were the primary fish category considered for interpretation because they were the most predominant fish type and age caught over each year (Gabriel et al., 2009). Data from age-two fish were only used for 2007 and 2008 because there was sufficient sample size for these years. Fish THg concentrations were further standardized (divided) by length. The above filtering and standardization processes were performed so that fish THg variation was evaluated only on the basis of surrounding environmental processes. After filtering and standardization, data from certain lakes were not included in the correlations due to lack of data ($n < 4$). Table 2 provides a list of average THg concentrations for fish used in the regression analyses. For the studied lakes, there is a clear geographical trend in fish THg concentration (Fig. 2), which is largely linked to levels of THg in the soil O horizon, watershed size, and percent upland wetlands (Gabriel et al., 2009).

Statistical Methods and Applications

An investigation of terrestrial natural system processes affecting the spatial variation of THg in the O horizon began with evaluating spatial relationships between the 42 chemical constituents for all soil horizons using principal component analysis (PCA). The geochemical properties of each soil horizon were considered the primary factors controlling THg composition because all other influential landscape factors (e.g., mercury sources, land cover, and land use) were relatively uniform across the studied region. Principal component analysis addresses all possible linear combinations between variables by generating loadings (correlation or covariance values). The size of the loading indicates the level a variable had on the development of a component. This process then ranks the factors that explain the most variance in the data. Principal component analysis is commonly used to identify sources for contaminants or solutes in surface water (Vaidya et al., 2000). In this case, PCA was used to help identify the processes influencing the spatial variation of the 42 soil constituents. Typically, the Kaiser Criterion is used in PCA analysis to help decide which components to retain for analysis. Under this criterion, components are retained that have eigenvalues >1. We looked at the first two components so as to only focus on the most influential processes affecting soil THg variation.

Nonparametric and parametric statistical methods were used for data set comparisons. The Spearman or Pearson method was used for all correlations depending on data distribution and symmetry. Linear least-squares regression analysis was used for empirical model development. All normality tests were evaluated using the Anderson-Darling method (adjusted). Significance was considered ≥95% confidence. All statistical analyses were performed using MINITAB 14.0 (Minitab, Inc., State College, PA). Principal component analyses were performed using SigmaStat 2.03 (Systat, San Jose, CA). All graphical exercises were performed using ArcView 9.0 (Esri, Redlands, CA), ArcGIS (Esri), and SigmaPlot 8.0 (Systat).

Table 1. Soil constituent concentrations for the study watersheds.

Variable	O horizon	A horizon	B/E horizon
		mg kg^{-1}	
C†	367,400 (37,900)‡	218,500 (106,766)	40,000 (36,900)
Ca	102,184 (47,424)	13,000 (4976)	17,365 (8042)
Al	49,030 (12,541)	37,300 (15,124)	63,357 (11,245)
Fe	32,871 (12,493)	21,400 (12,000)	41,865 (20,873)
K	21,260 (4269)	9000 (4702)	14,493 (5131)
Mg	15,226 (5539)	5500 (2882)	9861 (4193)
Na	12,256 (6018)	10,800 (6643)	19,869 (7117)
Mn	9441 (6171)	1307 (1360)	938 (959)
P	8939 (4020)	718 (233)	470 (303)
S	8423 (4467)	800 (350)	250 (87.0)
Ti	2836 (1942)	2600 (1780)	4800 (2610)
Ba	1306 (511)	424 (174)	508 (147)
Zn	904 (603)	85.4 (47.4)	76.5 (35.2)
Sr	717 (255)	222 (133)	358 (158)
Pb	103 (74.6)	39.6 (20.0)	16.5 (5.34)
Rb	91.5 (30.8)	37.3 (18.6)	52.3 (23.7)
%Org. matter	84.4 (8.72)	–	–
Cu	84.1 (65.9)	18.1 (17.0)	26.2 (32.1)
V	76.1 (35.9)	59.3 (33.5)	104 (45.2)
Ce	41.4 (35.5)	23.0 (11.4)	31.6 (12.7)
Cr	41.0 (16.3)	38.1 (18.5)	65.3 (30.3)
Ni	40.3 (20.2)	20.3 (9.09)	32.2 (16.3)
La	23.3 (30.1)	11.9 (6.01)	15.0 (5.07)
Li	16.9 (4.61)	10.4 (6.32)	18.7 (7.44)
Co	16.3 (7.70)	9.32 (6.00)	16.8 (12.5)
Y	12.3 (15.8)	6.02 (3.75)	8.45 (2.70)
Ga	10.8 (3.07)	9.11 (3.27)	16.4 (2.72)
Sc	7.14 (2.50)	5.40 (2.29)	9.82 (3.36)
As	7.12 (3.60)	4.00 (1.62)	3.19 (1.95)
Cs	5.96 (3.83)	1.79 (0.67)	2.06 (0.98)
Cd	5.94 (3.17)	0.53 (0.31)	0.17 (0.10)
Nb	4.80 (1.87)	4.18 (2.16)	5.85 (2.72)
Th	4.53 (1.32)	2.93 (1.16)	3.96 (1.68)
Sn	3.04 (1.61)	1.36 (0.48)	1.33 (0.60)
Mo	2.78 (1.03)	8.85 (0.34)	0.78 (0.58)
Sb	1.54 (1.00)	0.51 (0.24)	0.21 (0.09)
U	1.43 (0.47)	0.87 (0.33)	1.15 (0.44)
Be	1.07 (0.34)	0.66 (0.27)	1.01 (0.24)
Tl	0.94 (0.52)	0.24 (0.13)	0.34 (0.12)
W	0.90 (0.33)	0.39 (0.12)	0.33 (0.18)
Bi	0.57 (0.35)	0.27 (0.31)	0.15 (0.13)
Se	0.42 (0.13)	0.44 (0.21)	0.22 (0.13)
Hg	0.13 (0.06)	0.16 (0.09)	0.04 (0.01)

† Estimated carbon for soil O horizon (%Org. matter/2.3) (Schumacher, 2002); carbon for the A and B/E horizons was analytically quantified.

‡ Values are averages with ±1 SD in parentheses.

Results and Discussion

Spatial Variability of Geochemical Soil Constituents

For the O horizon data, the first PCA component explained 45% of the total variation in all parameters, and the second explained 22% (Table 3). A distinct feature of the O horizon is that many of the poor or basic metals and border transition metals (Hg, Tl, Pb, Bi, Cd, Sn, Sb, Cu, As) load highly (all loadings/ r values are >0.80) on component #1 and thus are highly spatially correlated. Constituents that also load highly on component #1 are organic matter and carbon (r = 0.927; listed as %Org. matter in Table 3). Similar to results for the O horizon, data for the A horizon samples show high importance of carbon (C) and some of the same metals (Hg, As, Sb, Pb) on the loading of component #1 (Table 3). The importance of soil C (the majority of SOM mass) on element variability in the B horizon is nonexistent (r = 0.062), and there is considerable scatter of loadings for all elements (Table 3). The metals listed above (Hg, Tl, Pb, Bi, Cd, Sn, Sb, Cu, As) in elemental state have similar electronegativity (1.26 ± 0.55) and ionic radii (1.5 Å [radius for a 6-coordination, octahedral] ± 0.35) (Krauskopf and Bird, 1995; Jing et al., 2007) and therefore share similar binding affinity for a particular soil constituent. The lower the concentrations of soil C and SOM in each horizon, the more distribution/spread there is in factor loadings for all elements, indicating that both play a large role in controlling the spatial structure of the data (Tables 1 and 3). Percent ash, the inverse of organic content, has a strong negative correlation with soil O horizon THg ($\rho = -0.75^{****}$, Spearman). This level of correlation between SOM and soil THg is similar to values found by Rodrigues et al. (2006) in urban soils (r = 0.41–0.65) and by Grigal (2003) (r = 0.84; r = 0.51). Therefore, consistent with other studies, the above PCA analyses suggest SOM is a major controlling factor for the spatial variation of THg in the A and, particularly, O horizons.

Relationship between Soil Organic Matter and Fish Tissue Total Mercury Concentrations

As demonstrated by Gabriel et al. (2009), the most significant physicochemical watershed factor controlling THg concentration in young-of-year yellow perch out of 45 watershed properties for these lakes was soil O horizon THg concentration (Spearman

Table 2. Average length-standardized age-one and age-two fish mercury concentrations used in the regression analyses. All data are yellow perch except for Wolf lake, which is bluegill.

Lake name	2004 (n)	2005 (n)	2006 (n)	2007 (n)	2008 (n)	2004–2008 avg.†
	ng g^{-1} mm^{-1}					
			Age-one fish			
Lum	2.26 (5)		2.39 (8)	1.97 (20)	1.80 (5)	2.10
Everett		1.32 (5)	1.86 (10)	1.20 (8)	1.26 (36)	1.41
Thelma	1.13 (13)	1.06 (10)	1.85 (10)	1.09 (5)	1.46 (13)	1.32
Ball Club		0.64 (10)	1.58 (6)	0.63 (16)	0.60 (19)	0.86
Dislocation		0.86 (10)	1.08 (9)	2.04 (28)	1.76 (4)	1.43
Lizz			0.90 (6)			0.90
Ella Hall	0.38 (8)	0.49 (10)	0.54 (10)	0.36 (3)		0.44
Mud		0.73 (10)	0.39 (10)	0.43 (7)	1.00 (16)	0.64
Merritt	0.55 (7)	0.83 (3)	0.44 (10)		0.68 (23)	0.62
Wolf		0.81 (10)	0.60 (6)	0.91 (5)	0.85 (29)	0.81
			Age-two fish			
	2007 (n)	**2008 (n)**	**2007–2008 avg.†**			
Lum	1.48 (3)	1.50 (4)	1.49			
Everett	1.03 (5)	1.01 (15)	1.02			
Thelma	0.72 (5)	1.18 (4)	0.95			
Ball Club	0.71 (3)		0.71			
Dislocation	0.87 (8)	0.92 (12)	0.89			
Lizz						
Ella Hall	0.26 (3)		0.26			
Merritt	0.30 (14)	0.54 (11)	0.42			
Mud	0.28 (12)	0.45 (6)	0.36			
Wolf	0.37 (9)	0.40 (3)	0.37			

† Weighted average (the number of samples is the weight).

$\rho = 0.80$**** for 2005 and 2006). United States Geological Survey researchers also found a positive spatial correlation between mercury content of soils and game fish within the nearby Voyageurs National Park (USGS, 2007). In the previous PCA discussion, SOM was shown to play a major role in controlling THg concentration in upland soils for these studied watersheds. Thus, a valuable next step is to evaluate the spatial relationship between upland SOM and fish THg concentrations. The importance of this investigation is reinforced because boreal surface soils can be high in SOM (Turetsky et al., 2006), which can change in mass over time from natural system processes. Accordingly, for each year of data (2004–2008), average SOM content for the O horizon of each watershed was correlated with average THg concentrations in age-one and age-two yellow perch from all lakes. For each year, there is a positive relationship between watershed SOM and yellow perch THg except for age-one data in 2008 (Fig. 3). These positive relationships are expected due to the positive relationship between yellow perch THg and soil O horizon THg; however, this provides a first glance into the SOM–yellow perch THg relationship and hence how changes in watershed SOM may affect fish THg concentrations. An analysis of data for all years (Fig. 4, right plot) illustrates that a 50% reduction in resident fish THg concentration may be associated with an average 10% reduction in O horizon SOM for these watersheds, thus demonstrating that fish THg concentrations may be fairly sensitive to changes in O horizon SOM. The cause for the less-than-perfect relationship between fish THg and %SOM is the result of several other influential environmental factors (watershed area, lake water pH, vegetation type, nutrient levels, etc.) on fish THg concentration, as defined in Gabriel et al. (2009). For comparative purposes, the right plot in Fig. 4 excludes Lum Lake, where anomalously high yellow perch THg concentrations were found for both fish age groups (Lum Lake also contained the highest standardized residuals [errors] among all other data points). In addition, both plots incorporate Wolf Lake, where only bluegill data were available for both years. Wolf Lake was included to develop a more complete spatial observation despite there being statistical differences between fish species across all lakes (Gabriel et al., 2009). Due to the lack of other fish species for Wolf Lake, it is not possible to compare interspecies THg differences for this lake. Interestingly, there are no statistically significant relationships (all $p > 0.30$, Pearson r correlation) between fish THg concentration and total SOM mass (SOM mass m^{-2}) for each soil horizon separately (O, A, B/E) and cumulatively (O+A, O+B/E, A+B/E, O+A+B/E; data not shown), thus establishing that spatial variation in fish THg is not related to total mass of organic matter but rather to the relative proportion of organic matter.

Because these analyses reveal that the spatial variation of fish THg concentration is a function of upland O horizon SOM concentration for these study lakes, a valuable investigation is to assess system processes that can affect changes in SOM concentration. The next sections provide a literature review on forest floor disturbances and how they can alter upland SOM and soil and fish THg content for resident lakes and put into perspective the relevance of this literature review with regard to the data collected in this study and, hence, forest fire management practices for the studied region.

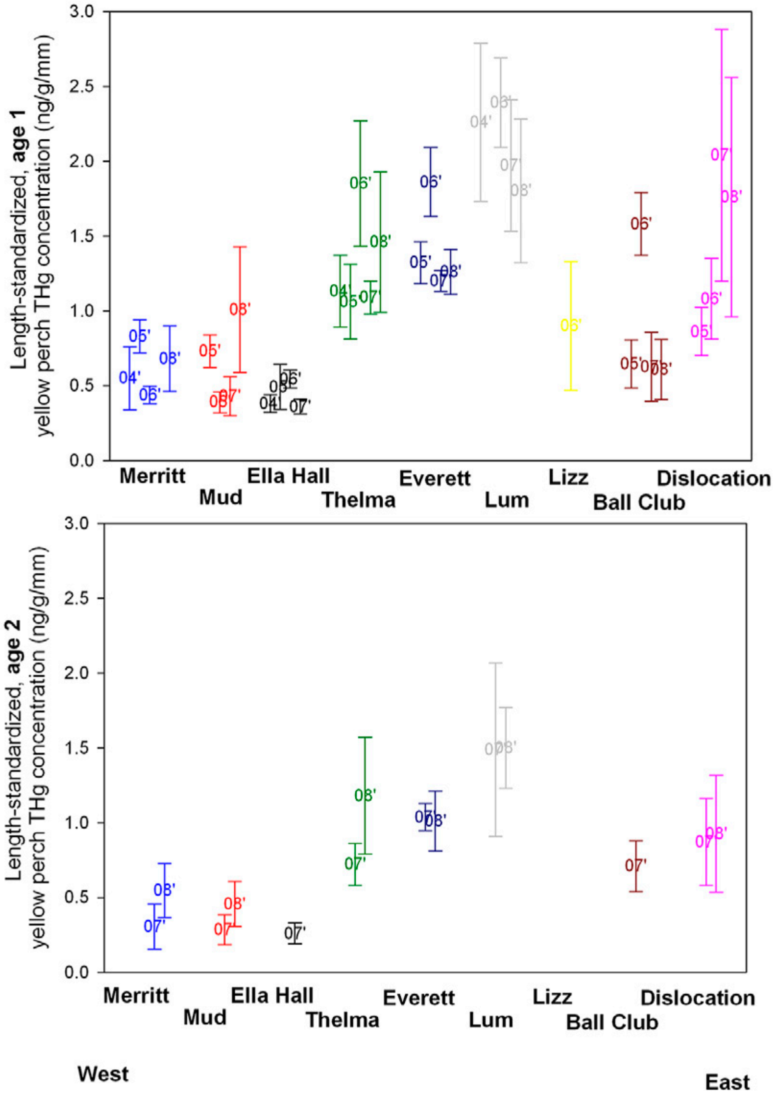

Fig. 2. Length-standardized yellow perch total mercury (THg) concentrations for the studied lakes. Results display average ±1 SD.

Forest Fire Effects on Concentrations of Organic Matter and Total Mercury in Upland Soil

In boreal ecosystems, the following processes largely control the loss of upland SOM: watershed runoff, forest fire, physical and biological soil subsidence and oxidation, and earthworm activity. Of these mechanisms, forest fire typically exhibits the sharpest reduction of SOM per event. In addition, due to the oxidation process of combustion, SOM that is reduced by forest fire to CO_2 and other volatile compounds can be transported out of the watershed system. Soil organic matter that is reduced by fire heavily affects the speciation and transport of mercury throughout the watershed environment (Amirbahman et al., 2004). Storm-driven runoff after forest fire has been shown to enhance mobilization of the remaining mercury and organic matter through transport of charred and partially combusted material (Caldwell et al., 2000). This organic material provides a fresh carbon source for MeHg production in sediment (Caldwell et al., 2000). Forest fire dramatically reduces THg concentration in upland soil because combustion typically releases >95% of all mercury bound to organic litter to the atmosphere (Friedli et al., 2001, Woodruff et al., 2009; Mailman and Bodaly, 2005, 2006; Engle et al., 2006; Turetsky et al., 2006; Smith et al., 2011). Field observations by Amirbahman et al. (2004) showed that mercury in the O horizon of a burned watershed was significantly lower than an unburned watershed, with no change in the mineral horizons. Biswas et al. (2008) revealed a positive relationship between percent mercury and SOM loss for several soil horizons in a conifer forest after forest fire under varying intensity. Laboratory investigations by Friedli et al. (2001) demonstrate that combustion of litter (which included various types of coniferous litter and green vegetation) results in near complete release of mercury stored in fuel (between 98 and 99.8%). Temperatures applied were >650°C, which is within the range of natural vegetation fires (650–1100°C); however, most prescribed fires involve low-severity burning conditions in which the O horizon is only partially consumed (DiCosty et al., 2006). Laboratory combustion of vegetation indicates mercury is almost completely mobilized from organic matter in elemental form (Hg^0) (Friedli et al., 2001, 2003a, 2003b), although some airborne measurements of smoke plumes show that up to 13% of the volatilized mercury in smoke is in particulate form (Friedli et al., 2001; Turetsky et al., 2006; Biswas et al., 2008). Estimates show there is an approximate one-to-one relationship between total mass and THg loss for coniferous litter with combustion (Friedli et al., 2001, 2003a; Engle et al., 2006; Mailman and Bodaly, 2005). This is not the case during the combustion of organic soil, which yields 27% soil mass loss vs. 79% THg mass loss (Mailman and Bodaly, 2005). The difference between total mass and THg loss from organic soil could be a function of soil heating and associated volatilization of Hg^0. Forest fire can have a lasting effect on soil SOM and THg content. A recent study by Woodruff and Cannon (2010) showed positive correlations between years since last stand-replacing watershed fire, soil mercury, and carbon concentrations in the O and A horizons for watersheds within the Boundary Waters Canoe Area Wilderness. They indicated that extended periods of time are required for THg and SOM to rebound in forest soil after fire, taking approximately 100 yr to increase in soil THg and carbon mass per area by 50%. Between the years approximately 1950 and 1980, atmospheric mercury deposition was at its peak for the upper Midwest region in the United States (Engstrom and Swain, 1997). With a drop in atmospheric mercury deposition since this period due to regulatory emission standards, the time to increase to similar pre-burn soil THg levels may be even longer.

Potential Impacts of Forest Fire on Fish Mercury Concentrations in Hydrologically Connected Lakes

Given that forest fire can greatly alter soil Hg concentrations, it is implicit that fire can also affect fish mercury concentrations for these watersheds. For any system, forest fire can affect fish mercury concentrations in adjacent water bodies by (i) enhancing direct atmospheric mercury deposition, (ii) restructuring food webs, and (iii) increasing soil mineralization (McEachern et al., 2000; Carignan and Steedman, 2000; Allen et al., 2005; Kelly et al., 2006; Orihel et al., 2006; Witt et al., 2009). Effects associated with fire-induced soil mineralization that can lead to changes in MeHg dynamics include transient eutrophication (due to increases in chlorophyll-a, dissolved organic carbon, inorganic nitrogenous compounds [e.g., ammonium and nitrate], and phosphorous), increased soil pH, and a shift in algal community toward cyanobacteria (McEachern et al., 2000; Carignan and Steedman, 2000; Spencer et al., 2003; Arocena and Opio, 2003; Allen et al., 2005; Kelly et al., 2006). In some cases, phosphorous and nitrogen can increase 60-fold in watershed runoff after fire (Spencer et al., 2003). Kelly et al. (2006)

Table 3. Factor loadings (with Varimax rotation; $\gamma = 1.00$). Two factors were extracted per soil layer.

Variable	O horizon		A horizon		B/E horizon	
	Factor 1	Factor 2	Factor 1	Factor 2	Factor 1	Factor 2
C	0.927†	–0.143	0.872†	–0.480	0.062	0.693‡
Ca	0.277	–0.761	–0.474	–0.243	–0.924	–0.234
Al	–0.229	0.665‡	–0.897	0.355	–0.334	–0.788
Fe	0.381	0.734‡	0.814†	0.205	–0.655	0.707‡
K	0.449	0.030	–0.711	0.624‡	0.887†	–0.414
Mg	0.072	–0.412	–0.447	0.044	–0.873	0.099
Na	–0.854	–0.019	–0.928	0.181	0.030	–0.834
Mn	0.723‡	–0.018	–0.181	0.638‡	–0.130	0.535‡
P	0.921†	–0.373	0.663‡	0.418	0.363	0.660‡
S	0.842†	–0.275	0.836†	–0.386	–0.066	0.879†
Ti	0.223	0.672‡	0.897†	0.009	–0.681	0.623‡
Ba	0.612‡	0.136	–0.740	0.529‡	0.854†	–0.402
Zn	0.335	0.134	0.402	0.626‡	–0.062	0.957†
Sr	–0.230	–0.878	–0.885	–0.051	0.049	–0.795
Pb	0.909†	0.310	0.849†	0.030	0.933†	0.187
Rb	0.540‡	–0.091	–0.640	0.737‡	0.908†	–0.131
%Organic matter	0.927†	–0.143	–	–	–	–
Cu	0.883†	0.040	0.783‡	–0.202	–0.496	0.706‡
V	0.334	0.738‡	0.826†	0.216	–0.655	0.654‡
Ce	0.339	0.517‡	–0.107	0.895†	0.669‡	0.436
Cr	–0.273	0.554‡	–0.449	–0.005	–0.781	–0.173
Ni	0.403	0.171	–0.081	–0.248	–0.921	0.166
La	0.586‡	0.391	0.164	0.891†	0.757‡	0.395
Li	–0.035	0.786‡	–0.412	0.816†	0.249	0.747‡
Co	0.406	0.153	0.224	0.461	–0.708	0.491
Y	0.708‡	0.381	0.617‡	0.413	–0.147	0.840†
Ga	–0.123	0.965†	–0.287	0.664‡	–0.414	0.621‡
Sc	0.320	0.853†	0.511‡	0.048	–0.618	0.642‡
As	0.915†	0.323	0.925†	–0.261	–0.315	0.635‡
Cs	0.777‡	–0.025	0.072	0.972†	0.427	0.529‡
Cd	0.879†	–0.007	0.656‡	0.272	0.099	0.842†
Nb	0.484	0.635‡	0.915†	0.266	0.185	0.511‡
Th	0.556‡	0.622‡	–0.123	0.846†	0.879†	0.349
Sn	0.887†	0.394	0.603‡	0.718‡	0.786‡	–0.237
Mo	0.843†	0.413	0.872†	0.411	0.165	0.612‡
Sb	0.939†	0.287	0.939†	–0.134	0.434	0.350
U	0.689‡	0.666‡	0.347	0.858†	0.675‡	0.666‡
Be	0.456	0.587‡	–0.588	0.794‡	0.882†	0.006
Tl	0.886†	0.388	0.204	0.870†	0.918†	–0.085
W	0.919†	0.338	0.759‡	0.394	0.686‡	0.044
Bi	0.928†	0.322	0.518‡	–0.514	–0.147	0.241
Se	0.732‡	0.188	0.924†	0.022	–0.286	0.840†
Hg	0.869†	0.287	0.946†	–0.200	0.120	0.931†
Percent of total	44.86	22.11	43.69	26.72	35.43	33.85
Explained variation	20.19	9.951	18.35	11.22	14.88	14.22
Eigenvalue	21.73	8.412	18.53	11.04	16.03	13.07

† Loadings > 0.8

‡ Loadings > 0.5.

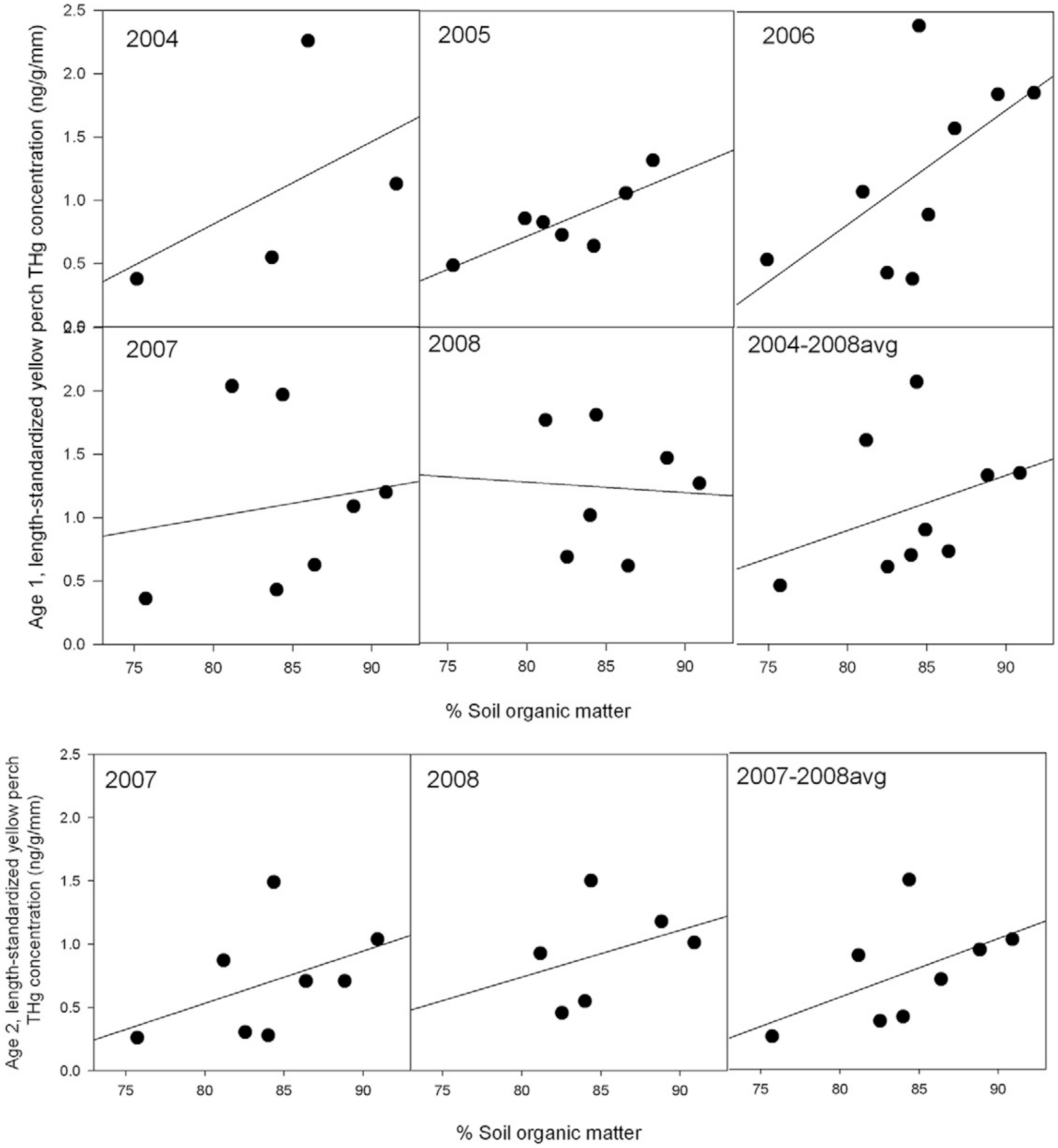

Fig. 3. Linear relationships between soil organic matter and yellow perch total mercury (THg) concentrations for the studies lakes from 2004 through 2008. Results display average concentration. Weighted averages are used for the 2004–2008 and 2007–2008 plots. All data sets are normally distributed (all *p* > 0.3, Anderson Darling test).

note a 5-fold increase in fish mercury accumulation in a partially burned catchment in Moab Lake as a result of two mechanisms: food web restructuring and increased MeHg production from mercury inputs, with the former being more important. It is suspected that forest fire effects on aquatic food web restructuring are subtler at higher trophic levels (Carignan and Steedman, 2000). Results from Garcia and Carignan (1999, 2000), however, showed no difference in MeHg concentrations of biota between burned and unburned lakes in Boreal Shield lakes. Similarly, Woodruff et al. (2009) found no statistical difference in young-of-year yellow perch between one burned watershed and three unburned (control) watersheds. Allen et al. (2005) suggest that increased algal productivity, as induced by forest fire, can decrease MeHg concentrations in phytoplankton and fish via growth dilution, whereby the increase in the volume of algal cells dilutes the bioavailable pool of MeHg. In parallel with Kelly et al. (2006), Harris et al. (2007) indicate that changes in deposition will not affect the relative magnitudes of biogeochemical pathways competing for mercury in littoral environments of lakes. In all, fire intensity, proportion of catchment burned, timing and intensity of runoff, and watershed shape and slope (which affect erosion patterns) are factors controlling nutrient runoff and hence MeHg production after forest fire (Allen et al., 2005; Kelly et al., 2006; Smith et al., 2011).

Mercury Elimination from Fish after Forest Fire

Forest fire and soil mineralization can increase lake MeHg production and fish THg; however, this increase may be short lived because research studies indicate that accumulated mercury in fish can decrease relatively quickly after an abrupt decrease in source (Allen et al., 2005; Munthe et al., 2007; Berardelli 2007; Harris et al., 2007; Van Walleghem et al., 2007). Specifically, the METALLICUS study, where mercury was added directly to the lake in one pulse, showed that lake-labeled mercury declined in biota after 3 yr (Munthe et al., 2007). Three months after a fire at another site, Allen

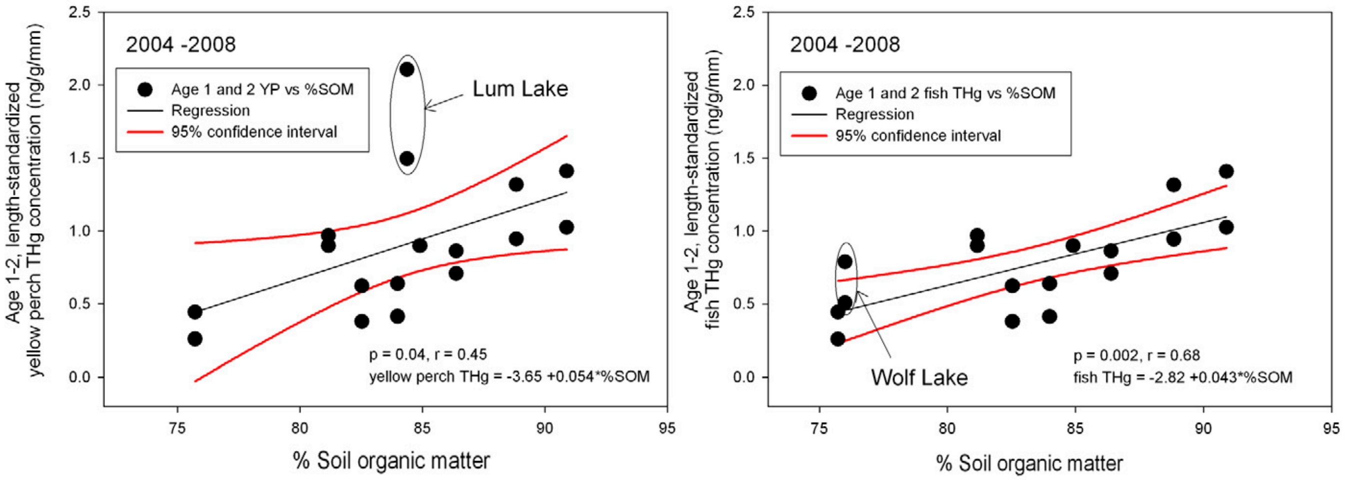

Fig. 4. Regression plots between age-one and age-two fish total mercury (THg) concentration and associated O horizon soil organic matter (SOM) (%). Results display averages. Both plots contain Wolf Lake, which only includes bluegill THg data due to the unavailability of yellow perch. All other fish species are yellow perch. For comparative purposes, the left plot does not contain data for Lake Lum due to the high standardized residuals in regression with percent SOM. Both data sets are normally distributed (*p* > 0.15, Anderson-Darling normality test).

et al. (2005) demonstrated that biota MeHg concentrations decreased between 30 and 50% relative to the previous year. Van Walleghem et al. (2007) monitored the loss of spiked THg in yellow perch in a treated lake and saw rapid losses (~90 d) from the liver and visceral tissues. They estimated the half-life of spike THg to be 489 d in the field, which is cited as slower than other estimates for whole fish. Trudel and Rasmussen (1997) infer the half-life of MeHg in fish to be between 130 and 1030 d after acute exposure (e.g., forest fire). A study by Harris et al. (2007) indicated that fish MeHg concentrations responded rapidly to changes in mercury deposition over the first 3 yr of a study. After 2 mo, MeHg lake-spike was found in several fish species, including young-of-the-year perch. They predicted that mercury emission reductions will yield rapid (years) reductions in fish MeHg. A bioaccumulation model investigation by Knightes et al. (2009) showed rapid THg losses in young-of-the-year yellow perch after a decrease in atmospheric mercury deposition (i.e., a 40% reduction in fish THg after 5 yr after a 50% reduction in atmospheric mercury deposition). Their study also indicated a delayed response in fish THg loss after source reduction for watersheds that received a large fraction of their mercury inputs from the watershed (as opposed to direct deposition to the lake), which is similar to the lakes in this study. For such watersheds, local forest fire may, however, present a more rapid response in fish THg decline due to reductions in closely linked soil THg and organic carbon dynamics. Overall, the above studies suggest that mercury spikes in fish caused by fire-related atmospheric mercury deposition should decrease fairly rapidly (<5 yr) to near pre-event levels.

Similar to atmospheric deposition, the impacts of soil mineralization on MeHg production and accumulation in fish may be short lived or, in some cases, nonexistent (McEachern et al., 2000; Carignan et al., 2000). Increases in lake nutrient concentrations, algal growth, and soil nitrogen mineralization rates for several studies indicate a decline to preburn levels and conditions within 1 to 5 yr (Hauer and Spencer, 1998; Carignan and Steedman, 2000; McEachern et al., 2000; Wan et al., 2001; Wilson et al., 2002; Allen et al., 2005; Kelly et al., 2006), with periodic increases during spring runoff (Hauer and Spencer, 1998; Spencer et al., 2003). Smith et al. (2011) note suspended sediment yields following the first year after a fire generally decline as vegetation cover is re-established and fire impacts on soil and hillslope hydrological properties decline to pre-event levels. Carignan et al. (2000) reported that wildfire did not cause a statistically significant increase in dissolved organic carbon stream exports for burned catchments within Quebec Boreal forests. Overall, the amount of time required to return to pre-burn lake nutrient conditions depends on several factors, namely, fire severity, proportion of catchment burned, watershed slope, riparian and upland plant succession, and timing and intensity of runoff (McEachern et al., 2000; Kelly et al., 2006).

Potential Impacts of Forest Fire on Fish Mercury Concentrations for the Studied Region

The previous review of the literature demonstrates that forest fire is a prominent process in boreal ecosystems that can reduce organic matter and THg concentrations in surface soils including, over the long-term, fish THg concentrations. The statistical regression formulas provided in Fig. 4 could potentially be used to determine the long-term drop in fish THg as a result of local forest fire by observing average percent reduction in SOM for the upland soil O horizon across the entire watershed. Generally speaking, Fig. 4 is applicable to any SOM reduction process (e.g., biological subsidence); however, the focus here is forest fire due to forest management implications. The literature suggests that local forest fire should produce a short-term spike in fish THg concentration, followed by a decrease in concentration that is lower than pre-fire event levels. Therefore, in the case of forest fire, the regressions in Fig. 4 would be applied after post-fire THg spikes in fish have subsided. A post-forest fire drop in fish THg levels should persist for several years because SOM requires decades or centuries to rebound to near pre-burn concentrations in boreal ecosystems, depending on fire severity (Kimble et al., 2003; USGS, 2007; Tessler et al., 2007; Woodruff and Cannon, 2010). This is supported by Woodruff et al. (2009), who found no measureable rebound in soil mercury and carbon concentrations

2 yr after forest fire with various intensities. A lengthy period of time is required for SOM to rebound in the O horizon due to slow reduction processes of forest floor litter in boreal systems. In addition, severely burned areas can have lower rates of Hg accumulation due to burning of aboveground vegetation that captures dry deposition and a reduced ability of the soil to retain previously accumulated mercury (Biswas et al., 2007; Woodruff and Cannon, 2010), which would further prolong mercury accumulation in fish after a forest fire event.

Summary

Principal component analyses indicated that SOM is a major controlling factor for THg spatial variation within the soil A horizon and, particularly, in the O horizon in the 10 studied watersheds. With these results, continued investigation involved correlating fish THg with upland SOM content. Overall, there was a positive relationship between yellow perch THg and watershed O horizon SOM concentrations. After pooling data for all years, results show that a 50% reduction in resident fish THg concentration may result from an average 10% reduction in O horizon SOM for these watersheds. Forest fire, through natural and prescribed activities, is a prominent process controlling SOM levels in the upland environment. Review of the literature suggests that local forest fire within these studied watersheds should produce a short-term spike in yellow perch THg concentration followed by a decrease in concentration that is lower than pre-fire event levels. The lower post-fire THg level in fish may be postulated from the statistical regression formulas developed in this study after obtaining the average percent change in SOM for the upland watershed.

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