

Yellow Perch (*Perca flavescens*) Mercury Unaffected by Wildland Fires in Northern Minnesota

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Abstract

Wildland fire can alter mercury (Hg) cycling on land and in adjacent aquatic environments. In addition to enhancing local atmospheric Hg redeposition, fire can influence terrestrial movement of Hg and other elements into lakes via runoff from burned upland soil. However, the impact of fire on water quality and the accumulation of Hg in fish remain equivocal. We investigated the effects of fire—specifically, a low-severity prescribed fire and moderate-severity wildfire—on young-of-the-year yellow perch (*Perca flavescens*) and lake chemistry in a small remote watershed in the Boundary Waters Canoe Area Wilderness in northeastern Minnesota. We used a paired watershed approach: the fire-affected watershed was compared with an adjacent, unimpacted (reference) watershed. Prior to fire, upland organic horizons in the two study watersheds contained 1549 $\mu\text{g Hg m}^{-2}$ on average. Despite a 19% decrease in upland organic horizon Hg stocks due to the moderate severity wildfire fire, fish Hg accumulation and lake productivity were not affected by fire in subsequent years. Instead, climate and lake water levels were the strongest predictors of lake chemistry and fish responses in our study lakes over 9 yr. Our results suggest that low- to moderate-severity wildland fire does not alter lake productivity or Hg accumulation in young-of-the-year yellow perch in these small, shallow lakes in the northern deciduous and boreal forest region.

Core Ideas

- The study investigated wildland fire impact on fish mercury and lake chemistry.
- A paired watershed approach was used in the investigation.
- Wildland fire decreased upland organic soil carbon and mercury stocks.
- There was no impact of wildland fire on fish mercury or lake productivity.
- Lake chemistry and fish mercury varied with climate and lake water levels.

MERCURY (Hg) is a pollutant that negatively affects human and wildlife health, commonly through fish consumption. Understanding the factors that influence elevated fish Hg concentration is of importance to regulatory agencies monitoring Hg conditions in lakes. Landscape disturbances, such as fire, are known to disrupt the cycling of Hg in the environment (Wiedinmyer and Friedli, 2007; Bishop et al., 2009; Gabriel et al., 2012). However, it is unclear what fire conditions and subsequent watershed alterations lead to significant changes in the concentration of Hg in fish. In the northern boreal and deciduous forests of the Great Lakes region, understanding the relationship between wildland fire and Hg cycling is particularly important. Lakes in this region are used extensively for both recreational and subsistence fishing (Imm et al., 2005; Madsen et al., 2008). Furthermore, fire is an integral component of ecosystem functioning in this region, with both wild and prescribed fires occurring regularly (Heinselman, 1973).

Mercury accumulation in fish is influenced by terrestrial upland Hg loads (Gabriel et al., 2009), the movement of Hg from terrestrial to aquatic environments (Garcia and Carignan, 1999), lake chemistry (e.g., lake pH and nutrient status; Dittman and Driscoll, 2009), and food web dynamics (e.g., fish diet and body condition; Greenfield et al., 2001). Wildland fires can have widespread immediate and long-term effects on both the upland terrestrial and aquatic environments and, consequently, may affect Hg cycling and bioaccumulation in fish. Specifically, wildland fire may influence fish Hg bioaccumulation both directly, by changing lake Hg concentrations and/or availability, and indirectly, by altering methylation rates (Amirbahman et al., 2004), lake nutrient status, and food web dynamics (Kelly et al., 2006).

Forest fires can directly affect Hg concentrations in aquatic food webs by enhancing concentrations of Hg in the lake. Wildland fires that consume forest litter and upland soil organic matter release previously stored Hg to the atmosphere (Wiedinmyer and Friedli, 2007). This can result in reduced Hg stocks within the burn perimeter (Woodruff and Cannon, 2010). However, a portion of the Hg released to the atmosphere,

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Abbreviations: LOI, loss on ignition; NIST, National Institute of Standards and Testing; O horizon, organic horizon; TOC, total organic carbon.

specifically atmospheric particulate Hg, is redeposited locally via fire smoke, where it could be available for uptake into the aquatic food chain (Friedli et al., 2003; Witt et al., 2009). In addition to altering immediate local atmospheric redeposition of Hg, wildland fires also result in increased watershed runoff and erosion from recently exposed and/or disturbed soils that could enhance the availability of Hg in adjacent water bodies (Spencer et al., 2003; Burke et al., 2010; Smith et al., 2011; Eklöf et al., 2016).

Forest fires can also indirectly affect Hg concentrations in aquatic food webs, particularly higher-trophic-level organisms, via indirect means by affecting methylation rates, bioaccumulation, and/or otherwise altering the food web. Fires can lead to increased carbon (C) and nutrient runoff into lakes and their adjacent wetlands, a hotspot for Hg methylation (St. Louis et al., 1994). Fire effects on lake nutrient status can also alter lake productivity, aquatic food chain structure, and the bioaccumulation of Hg in fish. For example, Kelly et al. (2006) found that increased lake nutrient concentrations after wildland fire were associated with increased lake productivity, food web restructuring (including increased piscivory and food chain length), and ultimately, increased concentration of Hg in lake rainbow trout (*Oncorhynchus mykiss*). Alternatively, increased lake productivity in response to wildland fire can also decrease fish Hg concentrations via growth dilution (Karimi et al., 2007), whereby fast-growing, energy-efficient species have lower tissue Hg concentrations per unit mass (Laarman et al., 1976; Dittman and Driscoll, 2009).

Previous research on the effects of forest fire on fish Hg concentration has been equivocal. Whereas some studies have observed a significant increase in fish Hg after forest fires (Kelly et al., 2006), others observe no significant effect of wildland fire on fish Hg (Garcia and Carignan, 2000; Allen et al., 2005; Woodruff et al., 2009). A clear understanding of when and why wildland fire significantly alters Hg bioaccumulation in fish is lacking. Specifically, how do wildland fire severity and watershed characteristics influence whether fish Hg bioaccumulation is affected by wildland fire? The objective of this study was to quantify the immediate effects of wildland fire on Hg cycling using a paired watershed approach. Specifically, we examined the effects of wildland fire on soils, lake chemistry, and Hg in young-of-the-year yellow perch (*Perca flavescens*) in two geographically colocated lakes in northern Minnesota in the years after fire events. During the 9-yr study period, one of the lake watersheds was fire-affected in 2004 and 2007, whereas the other was not. We hypothesized that the immediate and direct effects of fire—specifically, increased transport and redeposition of Hg to the lake—would increase yellow perch Hg bioaccumulation.

Materials and Methods

Study Sites

We investigated the effects of wildland fire on two small, shallow drainage lakes in the Boundary Waters Canoe Area Wilderness (Superior National Forest, MN). Thelma Lake (48.02935° N, 90.87459° W) is located ~5 km directly south of Everett lake (48.07548° N, 90.87697° W) (Supplemental Fig. S1). Both lakes drain surrounding watersheds with mixed forest and wetland cover, gradual slopes, and shallow soils over bedrock (Supplemental Table S1, Supplemental Text S1). During the study period (2004–2012), mean annual air temperature

was 3.25°C and mean annual precipitation was 714 mm yr⁻¹ (Supplemental Text S2). On average, ~69% of the precipitation occurred during spring and summer (April–September).

Fire History and Severity

We compiled the fire history of the Thelma and Everett Lake watersheds from USDA Forest Service records of recent (1916–present) wildland fires (unpublished data). For the fires that occurred during the study period, fire severity within the watershed area was calculated using the differenced Normalized Burn Ratio (dNBR)—an estimate of burn severity (low, moderate, and high) calculated from pre- and post-fire Landsat reflectance imagery (Bobbe et al., 2001; USDA Forest Service, 2016).

Two wildland fires affected the Everett Lake watershed during the study period: a low-severity, 854.7-ha prescribed fire (Tuscarora, 9 Sept. 2004) and a moderate-severity, 30,695.8-ha wildfire (Ham Lake, 5–15 May 2007) (Supplemental Fig. S1). The Tuscarora prescribed fire burned 11% (7.1 ha) of the Everett Lake watershed. The burn severity of the area affected by fire within the watershed was predominately low (92% of burned area). On the day of and day after the Tuscarora fire, the winds were predominantly from the south (Supplemental Table S3), likely dispersing the fire smoke to the north and not over the unaffected Thelma Lake watershed to the south.

The Ham Lake wildfire burned 99% (63.3 ha) of the Everett Lake watershed. The severity of the burn within the Everett Lake watershed was predominantly moderate (63% of burned area), followed by low (19%) and high (18%). The wildfire ignited east of Everett on 5 May 2007 and burned the Everett lake watershed on 9 May 2007 (Fites et al., 2007). During the first days of the fire, when it was closest to the study lakes, winds were predominantly easterly and southerly (Supplemental Table S3); again, this likely caused smoke to disperse to the west and north, not over the Thelma lake watershed. The Thelma lake watershed was unaffected by fire during the study period; the most recent wildland fire to affect the lake watershed was a stand-replacing fire that occurred circa 1875 (Heinselman, 1973).

Soil Sampling

Soils were sampled from eight or nine randomly located plots within each lake's watershed at the beginning of the study (Everett Lake: 2004 [prior to the Tuscarora fire], Thelma Lake: 2005). At each location, a 0.093-m² plot was established where the upland surficial organic horizon (O horizon) was sampled in two parts: an upper part, which consisted of relatively loose, low-density, moderately decomposed organic materials, and a lower portion that consisted of more compacted, higher-density, relatively more decomposed organic materials typically held together by fine roots of trees and other vegetation. These two samples were sieved to <2 mm, dried, and weighed. The upper O horizon subsamples were analyzed for C content via loss on ignition (LOI), and the lower subsamples were analyzed for total C content by combustion in an oxygen atmosphere at 1370°C, followed by infrared detection on a LECO solid state detector. Organic matter (%) content determined via LOI was converted to percentage C by multiplying organic matter content by a factor of 0.61, which assumes that 61% of the O horizon organic matter is organic C (Grigal and Ohmann, 1992). The total Hg

content of both subsamples was determined following the analytical and quality control methods described by Taggart (2002). Briefly, soils were digested in a mixture of nitric and hydrochloric acids, followed by addition of potassium permanganate, sulfuric acid, potassium persulfate, and NaCl-hydroxylamine. A continuous-flow, cold-vapor, atomic absorption Hg analyzer measured Hg in solution (0.02 mg kg⁻¹ detection limit).

After the 2007 Ham Lake wildfire, Everett plots were resampled in 2008 following the procedures described above. The Ham Lake fire burned all or part of the upper part of the O horizon but generally did not consume the lower part of the O horizon. The 2004 Tuscarora prescribed fire did not affect the Everett watershed areas sampled for soil; consequently, the 2008 post-fire resampling reflects the impact of the 2007 fire only, and not the combined effects of the 2004 and 2007 fires.

Lake Sampling

Lake water samples were collected from Everett and Thelma Lakes yearly in 2004 to 2012. Each lake was visited three times per year during the growing season (~June–September), except in 2004 (Thelma: one visit, Everett: two visits), 2009 (Thelma: four visits, Everett: five visits), and 2011 (Thelma: two visits). During each sampling trip, lake parameters were recorded at an index station located over the deepest spot of the lake in the main basin, accessed via canoe. Specifically, water pH, dissolved oxygen concentration, and temperature were measured at 1-m depth with a water quality sonde meter. Secchi depth was also recorded. At the same location, water samples were collected for chemical analyses at 1-m depth using a Van Dorn sampler. Nonacidified water samples were analyzed for dissolved and suspended iron (Fe) and sulfur (S) via inductively coupled plasma atomic emission spectrometry (ICP–AES). Additionally, samples were analyzed for nutrients (total phosphorus [P] and total Kjeldahl nitrogen [N]), total suspended solids, and other organics (total organic C [TOC] and chlorophyll- α) (relevant methods: EPA 365.3, EPA 351.2, USGS I-3765-85, SM 5310C, and SM 10200, respectively). In 2008 to 2012, additional unfiltered samples were preserved in the field with bromine monochloride (BrCl) for total Hg analysis. Prior to analysis, the BrCl-preserved samples were heated at 70°C overnight to digest dissolved organic C. An aliquot of the digestate was added to a bubbler flask and excess BrCl was reduced with hydroxylammonium hydrochloride. Total Hg analysis was subsequently performed using the double gold amalgamation method of Bloom and Creclius (1983) (similar to USEPA Method 1631) with a Brooks Rand Model III cold vapor atomic fluorescence spectroscopy analyzer and Mercury Guru software (Brooks Rand Instruments, 2009). Standard curves were run at the initiation of each analysis (mean $R^2 = 0.9994$). The limit of detection was 0.049 ng (mean plus three times the standard deviation of the analytical blanks). Average recovery of National Institute of Standards and Testing (NIST) Reference Material 1515 (apple leaves), matrix spikes, and analytical standards were 99.8, 96.9, and 98.9%, respectively. The average relative percentage difference between analytical duplicates was 6.5%.

The lake water level was recorded in relation to a fixed reference (i.e., a marked rock) during each sampling trip by measuring the vertical distance between the reference mark and the lake surface. We used the known depth and volume of each lake

to normalize these measurements across lakes. Specifically, the maximum lake level recorded at each lake during the entire study period was assigned the known maximum lake storage volume (m³) of that lake; we used the deviation in recorded level from that observed lake maximum to convert all measurements to lake water storage volume (m³). Finally, we divided the lake storage volume by the lake's maximum lake water storage and multiplied by 100 to yield lake water level expressed as percentage of lake maximum. We also calculated annual mean, minimum, and maximum water levels at each lake. At both lakes, the mean, minimum, and maximum annual water levels were strongly positively correlated (Supplemental Table S4). Consequently, we used mean lake level only in all subsequent analyses.

Fish Sampling

Each spring in 2005 to 2012, yellow perch were sampled via electroshock once the lakes were accessible and ice free (Supplemental Table S5). Upon collection, fish mass and length were measured and fish scale subsamples were extracted. Fish were digested whole for total Hg analysis with concentrated nitric acid at 70°C overnight in polytetrafluoroethylene (PTFE) bombs. An aliquot of the digest was analyzed as described above for lake water samples. Standard curves were run at the initiation of each analysis (mean $R^2 = 0.9994$) and the limit of detection was 0.045 ng. The average relative percentage difference between analytical duplicates (two to three duplicates per lake per year) was 4.17%. Average recovery of NIST reference material 2976 (freeze-dried mussel tissue), matrix spikes, and analytical standards were 101.8, 97.6, and 101.1%, respectively.

Fish sample age was calculated using the observed fish size (length vs. weight) distributions within each lake during each year. When clear separations among age classes were not evident, age was verified using scale data (Schneider et al., 2000; Schneider, 2001). Of the age classes, the age one (hereafter, young-of-the-year) yellow perch samples were the most complete across all years and lakes and are reported here.

Statistical Analyses

All analyses were performed in R (R version 3.0.1) (R Core Team, 2013) at a significance level of $\alpha = 0.05$. We used a two-sample t test to identify significant differences between the burned (Everett) and unburned (Thelma) watersheds' upland soil O horizon Hg and C stocks before wildland fire (O horizon subsamples were pooled for the statistical analyses). Additionally, we used a student's t test for paired samples to identify significant differences between soil samples collected before (2004) and after (2008) the Ham Lake wildfire at Everett.

To identify significant differences in lake and fish metrics between the burned (Everett) and unburned (Thelma) lakes before and after wildland fire, we used two-way ANOVA. Specifically, we examined the effects of lake identity and year on lake parameters, fish mass (g), fish Hg concentration (ng Hg g⁻¹ fish), and individual fish Hg mass (fish Hg concentration \times fish mass, ng Hg fish⁻¹). Lake identity, year, and the lake \times year interaction were included as fixed effects (Type II ANOVA, *car* package) (Fox and Weisberg, 2011). Regression model assumptions of normality and homogeneity of variance were checked by plotting the model residual values versus fitted values, as well as examining quantile-quantile residual plots.

Non-normally distributed response variables were log transformed when needed. When there were significant interactions present in the ANOVA model, post hoc pairwise comparisons were performed using the *lsmeans* package (Lenth, 2014); *p*-values were Bonferroni corrected for multiple comparisons.

Finally, we identified potential drivers of temporal variation in fish responses by calculating the bivariate Pearson correlation coefficients between fish mass, fish Hg concentration, and fish Hg mass and mean annual climate and lake variables with at least 8 yr of data (*Hmisc* package) (Harrell, 2014). Again, *p*-values were Bonferroni corrected for multiple comparisons. Since yellow perch were collected at the beginning of their second growing season (i.e., 1 yr after hatching), Hg accumulation in sampled young-of-the-year yellow perch reflect conditions experienced by the fish during the previous year. Consequently, we examined the relationships between fish variables and lake chemistry variables the *previous* year (i.e., the year the fish hatched). For all temperature-based climate metrics (Supplemental Text S2), we examined the metrics occurring the full year prior to the sampling date because this encompassed the first year of growth. Lake water level metrics reflect cumulative climate effects on the landscape; consequently, we examined the relationship between fish responses and mean annual lake water level the year the fish were sampled.

Results

Temporal and Spatial Variation in Soil C and Hg Stocks

At the initiation of the study, pre-fire upland soil O horizon C stocks were 3031 g C m⁻² (range 2215–4324 g C m⁻²) and 3173 g C m⁻² (range 1646–47312 g C m⁻²) on average in the Thelma and Everett Lake watersheds, respectively (overall mean: 3106 g C m⁻²). Mercury stocks in the upland soil O horizon were 1315 μg Hg m⁻² on average (range 933–1947 μg Hg m⁻²) at Thelma and 1756 μg Hg m⁻² on average (range 745–3121 μg Hg m⁻²) at Everett (overall mean: 1549 μg Hg m⁻²). Pre-fire soil C and Hg stocks in the upland soil O horizon did not differ between the lake watersheds (*p* > 0.1). However, there was a significant difference between the pre-fire (2004) and post-fire (2008) soil C stock at Everett: after the 2007 wildfire, O horizon C stocks decreased by 821 g C m⁻² (26%) on average (*p* = 0.02) (Fig. 1a). Mercury stocks in the O horizon

also decreased after the 2007 wildfire by 332 μg Hg m⁻² (19%) on average (*p* = 0.04) (Fig. 1b).

Temporal and Spatial Variation in Lake Parameters

Before and after the watershed fires, observed fluctuations in the concentration of lake total suspended solids (Fig. 2a–2b), lake productivity (i.e., chlorophyll-*α* and TOC; Fig. 2c–2d), and lake nutrients (i.e., total Kjeldahl N and total P) were similar in both study lakes (Supplemental Fig. S5). Over the whole study period, the following seasonal mean lake water parameters were significantly higher in Thelma than in Everett: total suspended solids, total Kjeldahl N, total P, chlorophyll-*α*, Fe, and total Hg (Fig. 2e–2f, see Supplemental Tables S6–S7 for lake variable ANOVA results and data). Other parameters were statistically significantly lower in Thelma than in Everett, including lake Secchi depth, dissolved oxygen concentration, and pH. Lake S concentration and lake water temperature did not differ significantly between the lakes. There was a significant effect of year on lake total Kjeldahl N, chlorophyll-*α*, S, Fe, Secchi depth, and dissolved oxygen in both lakes. Total Kjeldahl N, chlorophyll-*α*, and S were highest in 2007 and 2012, and lake Fe was highest in 2007 compared with all other remaining years, whereas lake Secchi depth was lowest in 2007 and 2012.

There was a significant interactive effect of lake identity and year on seasonal mean lake water TOC (interaction: *p* < 0.0001). The concentration of TOC was higher in Thelma than in Everett across all years; the difference between lakes was significant in all years except 2006. In both lakes, the concentration of TOC was higher in 2007 (fire year) compared with either the previous year (2006) or subsequent (2008) year, although the inter-year difference was significant at Thelma only. In addition to the observed increase in both lakes in 2007, in Thelma, the concentration of TOC increased significantly in 2012 relative to 2010. Finally, there was also a significant interactive effect of lake identity and year on lake water level (interaction: *p* = 0.0002). On average, lake water levels (normalized to each lake's maximum) were higher in Everett than in Thelma, although the difference was only significant in 2012 (Bonferroni corrected pairwise lake comparison, *p* < 0.0001).

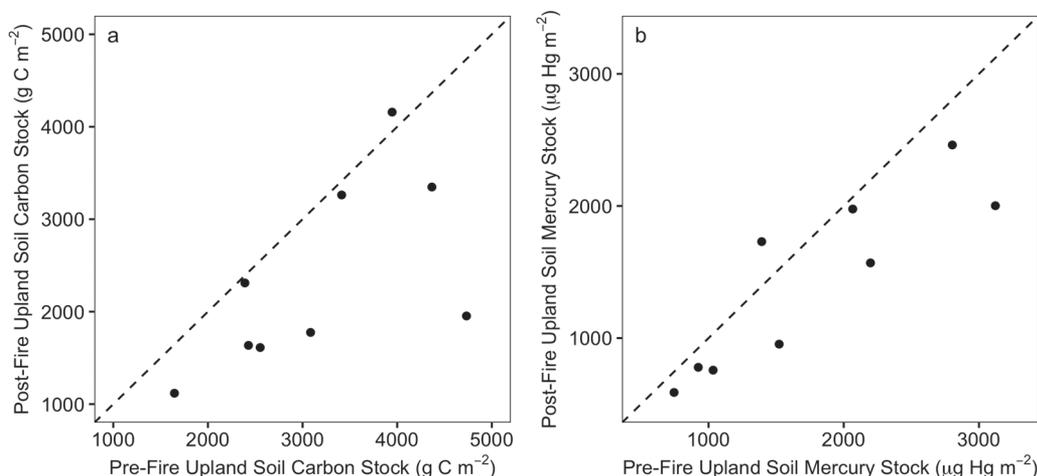


Fig. 1. (a) Upland organic horizon soil carbon and (b) mercury stocks in the Everett Lake watershed before and after wildland fire. Each point is a plot sampled before (2004) and after (2008) wildland fire. The dotted 1:1 line indicates identical values between sampling years.

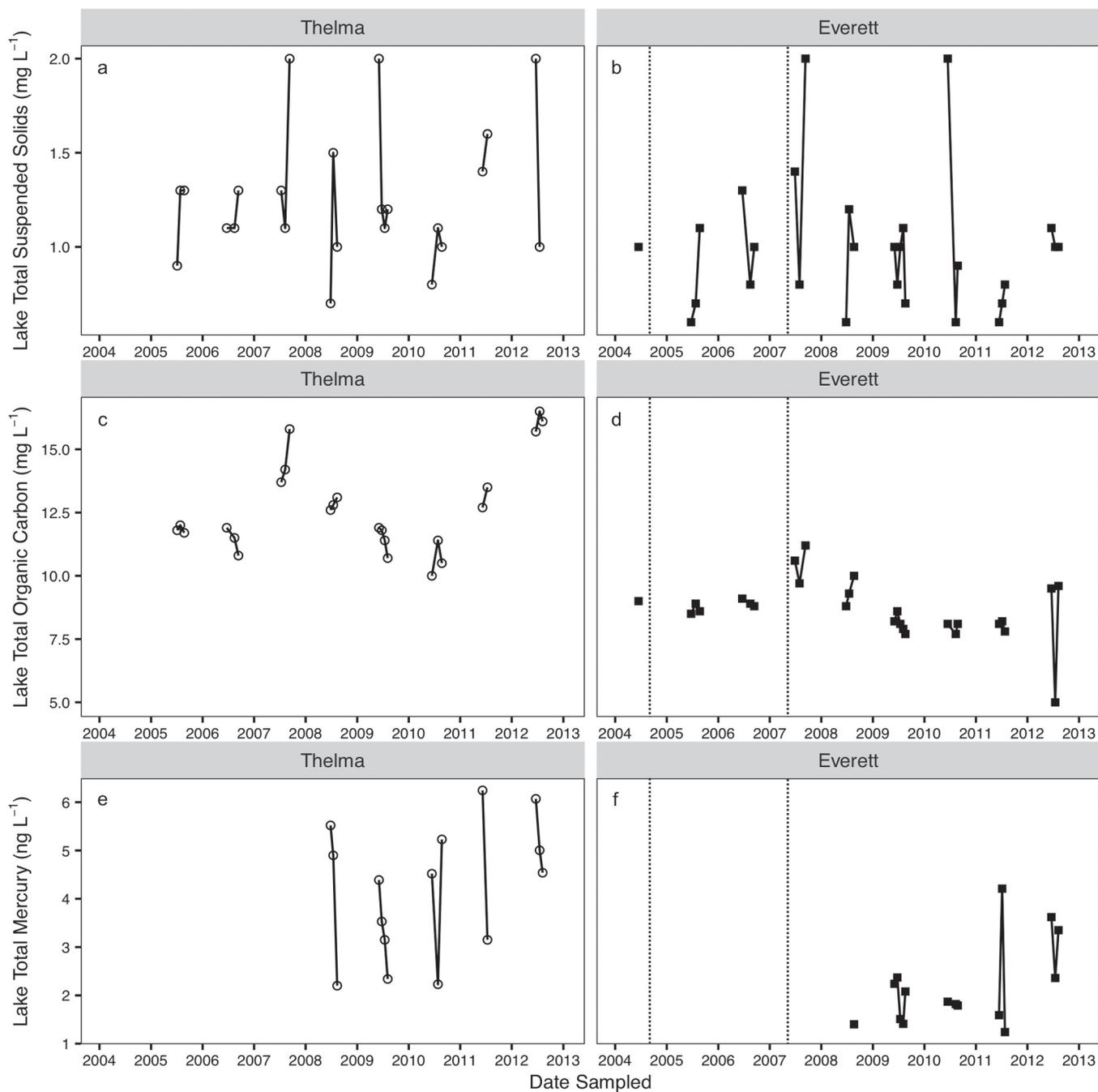


Fig. 2. (a, b) Lake water total suspended solids, (c, d) total organic carbon, and (e, f) total mercury concentrations in Thelma (open circle) and Everett (filled square) Lakes. All panels show individual measurements taken at each lake during sampling visits. Dashed vertical lines show dates of fires in Everett watershed (September 2004: Tuscarora prescribed fire; May 2007: Ham Lake wildfire).

Temporal and Spatial Variation in Fish Mass, Hg Concentration, and Hg Mass

There was a significant interactive effect of lake identity and year on the mass of young-of-the-year yellow perch (Fig. 3a, see Supplemental Tables S8–S10 for fish parameter ANOVA results and post hoc pairwise lake and year comparisons). Mean fish mass was greater in Everett than Thelma across all years (overall lake means: 2.45 g in Everett, 1.66 g in Thelma), although the difference in fish mass between lakes was only significant in 2006, 2008, 2011, and 2012 (Bonferroni corrected pairwise lake comparisons, $p < 0.05$). Year-by-year differences in weight within each lake were also significant (Supplemental Table S10).

There were significant interactive effects of lake identity and year on fish Hg concentration (ng Hg g⁻¹ fish, Fig. 3b) and fish Hg mass (ng Hg fish⁻¹, Fig. 3c), although the within-year differences between lakes varied. Fish Hg concentration was significantly higher in Everett compared with Thelma in 2007 and 2010 and was significantly lower in Everett than Thelma in 2011 and 2012 (Bonferroni corrected pairwise lake comparisons, $p < 0.05$). Fish Hg mass was significantly greater in Everett than in Thelma in 2006, 2007, 2008, 2010, and 2011 (Bonferroni corrected pairwise lake comparisons, $p < 0.05$). At Everett, fish Hg concentration and mass were highest in 2010 and 2006 and lowest in 2012. Fish sampled from Thelma in 2010 also had the highest mean annual fish Hg mass, but fish sampled in 2012 had the highest fish Hg concentration.

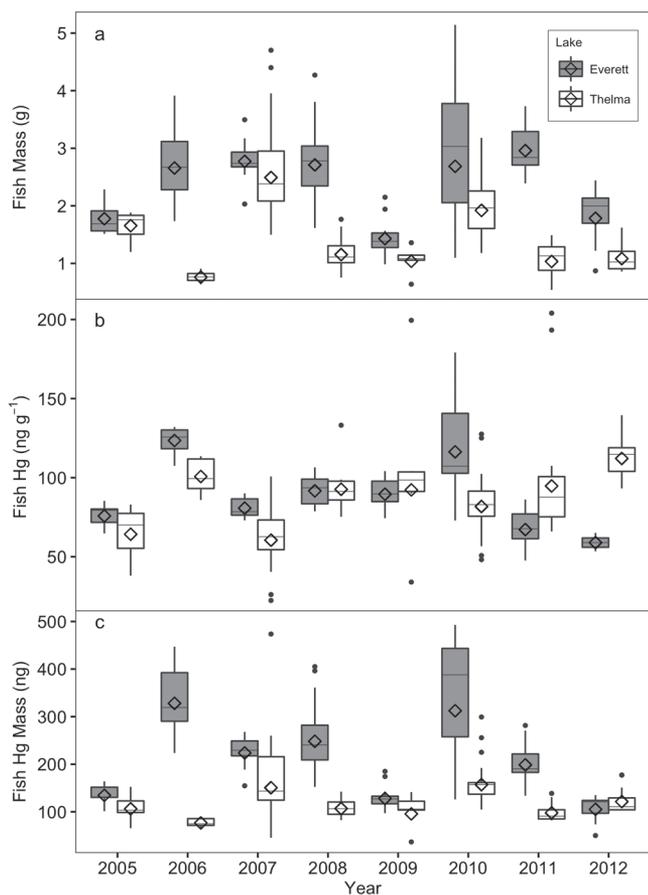


Fig. 3. (a) Annual variability in fish mass, (b) fish mercury (Hg) concentration, and (c) individual fish Hg mass in Everett and Thelma Lakes. All panels show geometric means (diamond symbol) and ranges of fish sampled in 2005 to 2012 at both lakes. Lake codes: Everett = gray boxes, Thelma = open boxes. See Supplemental Table S5 for sample numbers and Supplemental Tables S9–10 for post hoc pairwise lake and year comparison results.

Compared with Everett, there was less interannual variation in fish Hg mass in Thelma, despite the year-to-year fluctuations in fish mass and fish Hg concentration. This reflects the negative exponential relationship between fish mass and Hg concentration at Thelma (fish Hg concentration $\sim 102.71 - 40.14 \times \log(\text{fish mass})$, $R^2 = 0.38$, model p -value < 0.0001 , Supplemental Fig. S6). There was no significant relationship between fish mass and Hg concentration in Everett.

Potential Drivers of Fish Temporal Variability

We examined the relationships between fish responses (weight, Hg concentration, and Hg mass) and potential lake and climatic predictors. Across all years, lakes responded independently: no single variable had the strongest correlation with fish mass, Hg concentration, or Hg mass at both lakes (Table 1). There was a significant positive correlation between fish mass and lake dissolved oxygen concentration during the growing season in Thelma ($r = 0.64$, $p < 0.0001$; Supplemental Fig. S7) and a significant positive correlation between fish mass and air temperature during spring of fish hatching in Everett ($r = 0.60$, $p < 0.0001$; Supplemental Fig. S8). In Thelma, the best correlate with fish Hg concentration was mean lake water level ($r = -0.37$, $p = 0.005$), whereas in Everett, it was lake Fe concentration during the growing season ($r = 0.69$, $p < 0.0001$), although mean lake water level was

also significantly correlated with fish Hg concentration in that lake ($r = -0.42$, $p = 0.0002$; Supplemental Fig. S9–S10). Finally, there was a significant but weak positive correlation between lake dissolved oxygen concentration and fish Hg mass in Thelma ($r = 0.45$, $p < 0.0001$) and a significant negative correlation between growing season lake Secchi depth and fish Hg mass in Everett ($r = -0.58$, $p < 0.0001$; Supplemental Fig. S11). The exclusion of the 2010 fish data, which were sampled later in the season (Supplemental Table S5), had no impact on which climate and lake variables best correlated with fish mass and fish Hg, except for Everett fish Hg mass. When 2010 was excluded, mean lake water level became the strongest predictor of fish Hg mass in Everett ($r = -0.72$, $p < 0.0001$; Supplemental Table S11).

Discussion

Wildland Fire Decreased Soil Hg and C Stocks in Upland Soils

After the Ham Lake wildfire, upland soil O horizon Hg and C stocks decreased by 19 and 26% on average, respectively. The magnitude of O horizon Hg loss was comparable with the loss observed by Woodruff et al. (2009) in the high-severity burn areas in nearby Voyageurs National Park (332 vs. 220 $\mu\text{g Hg m}^{-2}$, respectively). Fires are known to decrease the pools of C and Hg in upland soils (Amirbahman et al., 2004; Woodruff and Cannon, 2010; Miesel et al., 2012) due to the combustion of these materials during fire and atmospheric release of CO_2 and gaseous and particulate Hg species (Friedli et al., 2003), as well as the subsequent erosion and runoff from fire-disturbed soils (Eklöf et al., 2016). In addition to fire occurrence, the severity of the fire affects the size of C and Hg stocks remaining in upland soils: more severe fires release more previously stored C and Hg to the atmosphere, leading to less remaining soil C and Hg, compared with less severe fires (Certini, 2005; Mitchell et al., 2012). The impact of the Tuscarora fire on the Everett lake watershed was minimal, as it burned only 11% of the lake watershed area and was predominantly a low-severity burn. Consequently, while we did observe decreases in the O horizon C and Hg stocks after the Ham Lake wildfire, we expect that the impact of the much less severe Tuscarora prescribed fire on upland soil stocks was minimal.

No Significant Effect of Wildland Fire on Lake Chemistry and Fish Hg

Despite the significant effect of the Ham Lake wildfire on the Everett watershed upland soil C and Hg stocks, we did not find evidence to support our hypothesis that direct fire impacts (local redeposition of particulates and runoff of soil particles into the lake) led to altered lake productivity and fish Hg bioaccumulation immediately after the fire. First, we did not observe post-fire increases in lake total suspended solids in Everett after the Tuscarora and Ham Lake fires; both inter- and intra-annual fluctuations in total suspended solids in Everett were paralleled in Thelma. Additionally, the observed increase in lake productivity (e.g., lake TOC, lake chlorophyll- α) and nutrients (e.g., total Kjeldahl N) in 2007, the summer immediately after the Ham Lake wildfire, occurred in both the fire-affected lake, as well as in the reference lake.

Table 1. Pearson correlation coefficients between mean annual lake and climatic variables (predictors) and fish mass, mercury (Hg) concentration, and Hg mass (response) at Everett and Thelma Lakes. Pearson correlation coefficients in italics indicate significant ($p \leq 0.05$) Bonferroni corrected p -values.

Variable	Fish Mass		Fish Hg		Fish Hg Mass	
	Everett	Thelma	Everett	Thelma	Everett	Thelma
	g		ng g ⁻¹		ng	
Lake temperature†	0.17	<i>-0.45</i>	<i>-0.34</i>	0.12	-0.06	<i>-0.43</i>
Lake pH†	-0.26	-0.10	<i>0.34</i>	-0.06	-0.01	-0.17
Lake dissolved oxygen†	-0.14	<i>0.64</i>	0.02	<i>-0.35</i>	-0.10	<i>0.45</i>
Lake total organic carbon†	-0.02	-0.27	0.28	0.18	0.14	-0.16
Lake total suspended solid†	<i>0.37</i>	-0.08	0.07	0.11	<i>0.32</i>	0.00
Lake total Kjeldahl nitrogen†	0.15	-0.07	0.18	0.18	0.22	0.09
Lake total phosphorus†	-0.01	<i>-0.42</i>	<i>0.36</i>	<i>0.35</i>	0.19	-0.18
Lake chlorophyll- α †	0.09	-0.28	<i>0.40</i>	0.12	0.29	-0.22
Lake Secchi depth†	-0.28	-0.14	<i>-0.63</i>	-0.10	<i>-0.58</i>	-0.27
Lake sulfur†	0.03	0.22	0.11	-0.21	0.08	0.07
Lake iron†	0.21	0.04	<i>0.69</i>	-0.06	<i>0.55</i>	-0.01
Lake water level	<i>-0.31</i>	<i>0.38</i>	<i>-0.42</i>	<i>-0.37</i>	<i>-0.47</i>	0.10
Air temperature, spring	0.02	<i>0.33</i>	0.16	-0.12	0.10	0.29
Air temperature, winter	-0.10	-0.08	-0.09	0.26	-0.13	0.14
Air temperature, previous fall	0.22	0.00	<i>-0.41</i>	0.05	-0.06	0.05
Air temperature, previous summer	0.14	-0.28	-0.24	0.22	-0.03	-0.14
Air temperature, previous spring	<i>0.60</i>	0.05	-0.09	-0.10	<i>0.41</i>	-0.03
Freezing degrees	-0.03	-0.02	0.08	-0.16	0.02	-0.17
Freezing degree days	0.15	0.01	-0.10	-0.17	0.06	-0.15
Growing degrees‡	<i>0.37</i>	-0.20	-0.20	0.13	0.17	-0.12
Growing degree days‡	0.28	<i>-0.47</i>	0.08	0.26	0.26	-0.32

† Mean annual lake variables from fish first growing season (1 yr prior to fish sampling year).

‡ Growing degrees and growing degree days from fish first growing season (1 yr prior to fish sampling year).

Second, we did not find evidence to support our hypothesis that wildland fire affected fish Hg bioaccumulation in Everett Lake in the years after either the Tuscarora or Ham Lake fires. After the fall 2004 Tuscarora prescribed fire, Hg concentration significantly increased in Everett fish sampled in 2006 (hatched in spring 2005, several months after the Tuscarora prescribed fire) relative to fish sampled in 2005 (hatched in spring 2004, prior to the fire) and 2007 (hatched in spring 2006, 1+ years after fire). However, this post-fire increase in fish Hg concentration occurred in unburned Thelma as well. Furthermore, prior to and after the spring 2007 Ham Lake wildfire, there was no significant change in fish Hg concentration at Everett (fish sampled in 2007–2009 were statistically identical). It was only in the 2010 samples, three growing seasons after the Ham Lake fire, that there was a statistically significant increase in fish Hg concentration compared with the prior years. However, a fire effect is unlikely, since both Thelma and Everett had significantly greater fish Hg concentrations in 2010 samples compared with the pre-fire-period (2007) samples. Alternate factors (e.g., mean lake water level or lake Fe concentration in concert with the late sampling date), likely explain the relatively high fish Hg concentrations in the 2010 samples.

Our results are congruent with other studies that have found no impact of fire on lake chemistry and fish Hg in the short term. Although a number of studies have observed increased nutrient concentrations and fish Hg bioaccumulation immediately after wildland fire (Kelly et al., 2006), forest fires do not always result in increased runoff to the adjacent aquatic ecosystem and/or altered Hg cycling. For example, in shallow, high-nutrient-status

lakes in the Alaskan boreal forest, the concentrations of total P, total N, and chlorophyll- α did not change after a moderate-severity forest fire (Lewis et al., 2014). Furthermore, despite positive correlations with fire for some lake chemistry parameters (e.g., aqueous nitrate, SO_4^{2-} , and chlorophyll- α), Garcia and Carignan found that fire had no effect on the Hg concentration of zooplankton (Garcia and Carignan, 1999) or northern pike (Garcia and Carignan, 2000) in a lake located in a boreal forested watershed. Likewise, Allen et al. (2005) reported no impact of forest fire on Hg concentration in fish, nor in most zooplankton groups surveyed, in Canadian boreal plains lakes. Additionally, Woodruff et al. (2009) found no effect of fire on fish growth or fish Hg concentration in northern Minnesota lakes located in boreal forested watersheds similar to those studied here.

Why might there have been no impact of wildland fire on fish Hg in this and other studies? One potential explanation is fire severity. As discussed above, the impact of fire on upland soil chemical, physical, and biological properties varies with fire severity. For example, compared with low- to moderate-severity burns, watersheds that burn more severely have more potential for post-fire runoff and erosion (Certini, 2005; Mitchell et al., 2012) and, consequently, altered lake nutrient and Hg loads (although in cases of very severe fire and complete organic matter volatilization, Hg export can decrease and fire may ultimately reduce Hg loads in biota; Bank et al., 2005). We may not have observed fire impacts on fish Hg due to the low- and moderate-severity impact of the Tuscarora and Ham Lake fires, respectively, on our experimental watershed. Unfortunately, fire severity is infrequently reported in the literature, making

it difficult to assess the extent to which this factor explains the difference in reported effects among studies.

The burn extent and topographical characteristics of the watershed could also explain fire impact (or lack thereof). For example, a larger burn impact ratio—the ratio of burned catchment area to lake area (Allen et al., 2005)—suggests that relatively more material from the upland was exported into the lake after the fire. Indeed the Ham Lake fire burn impact ratio in the Everett catchment was much smaller (~4:1) than the burn impact ratio observed in the Kelly et al. (2006) study (~12:1). Additionally, the characteristics of the watershed affected by fire may also be relevant. For example, Woodruff et al. (2009) hypothesized that the “subdued” topography of the surrounding upland in their study could have led to minimal catchment inputs to the lake, thus explaining the lack of fire impact on fish Hg. Gentle topography is likely relevant in our study system as well; the average slope of the Everett catchment was relatively low (15.5%).

The timing of the fire event relative to subsequent precipitation events and in-lake processing could also explain the occurrence and magnitude of fire impact. For example, Allen et al. (2005) suggested that the dry conditions after their study’s fire limited soil erosion and export into the lake and potentially explained the lack of impact they observed. This is unlikely the case in our study lake, as the summer after the Ham Lake fire (2007) was relatively wet compared with the mean precipitation. However, we do not have good information on the hydrologic connectivity of the watershed, which could have been limited despite the higher-than-average precipitation. In addition, observed changes to lake chemistry will also depend on the timing of the fire event and sampling. The earliest annual water samples were collected after lake stratification at Everett (data not shown); consequently, lake particulates that resulted from increased post-fire runoff may have settled in the hypolimnion prior to sample collection.

Climate and Lake Parameters, Not Wildland Fire, Explain Interannual Variation in Lake Productivity and Fish Hg Bioaccumulation

If wildland fire was not driving change in lake productivity and fish Hg bioaccumulation at Everett Lake, what alternate factors may explain the temporal variation observed at both study lakes? First, the increase in lake productivity (e.g., TOC) observed in 2007 at both lakes could reflect the positive effects of increased precipitation and/or temperature on lake production. The summer of 2007 was relatively wet compared with the preceding and following years (summer total precipitation, 2007: 354 mm; overall mean: 250 mm), as well as relatively warm (growing degrees and degree days, 2007: 969°C and 147 d; overall mean: 875°C and 134 d). Climate could be an important driver of fish productivity as well; mean air temperature during spring of fish hatching was the strongest predictor of fish mass in Everett Lake during the study period.

Despite similar interannual fluctuations in lake productivity and nutrients in Thelma and Everett, there was not a single climate metric that explained lake productivity variability across both of the lakes (Supplemental Table S12). Given the morphological differences between the study lakes and their respective

watersheds, it is unsurprising that the relationship between climate and lake productivity differed between them. For example, the watershed:lake area ratio and watershed wetland cover is larger at Thelma than at Everett (Supplemental Table S1), which suggests that the influence of the surrounding upland area on lake chemistry is also greater at Thelma. Consequently, the influence of climate on the surrounding upland area (e.g., runoff events during high precipitation), as well as on the lake itself (e.g., via in-lake processes), likely differs between the lakes.

Second, in lieu of a fire impact, mean lake water level was a strong predictor of fish Hg at both lakes; fish Hg was lower when mean annual lake water level was higher. Relationships between water level fluctuations and the concentration of Hg in yellow perch are well established, especially in systems where water levels are managed (e.g., in reservoirs; Willacker et al., 2016). For example, Sorensen et al. (2005) found that Hg concentration in young-of-the-year yellow perch was strongly positively correlated with annual lake water level fluctuations in northern Minnesota lakes (including mean and maximum water level, water level range, and change in water level relative to the previous year). The authors hypothesized that large fluctuations in lake water level (specifically, increases over time) lead to greater Hg accumulation in fish because drying and rewetting of sediments and nearby wetlands can increase sulfate levels, thereby increasing methylmercury production (Coleman Wasik et al., 2015).

Interestingly, while Sorensen et al. (2005) found strong positive correlations between fish Hg and mean lake water level, we found that the relationship between fish Hg and mean lake water level was negative. It is important to note that interannual differences between lake water level measurements observed in our study were sometimes greater than intra-annual differences (Supplemental Fig. S12), and that mean lake water level correlated significantly with both seasonal minimum and maximum lake water levels at both lakes (Supplemental Table S4). Consequently, the observed relationship between mean lake water level and fish Hg may be a stronger indicator of the effects of differences between years, rather than lake water level within a year.

Conclusion

Overall, we found that low- to moderate-intensity wildland fire did not significantly alter Hg accumulation in young-of-the-year yellow perch or lake productivity using a paired watershed approach that evaluated potential direct fire effects. Our results are consistent with other studies performed in the northern boreal and deciduous forest region that found no significant effect of fire on fish Hg (Garcia and Carignan, 2000; Allen et al., 2005; Woodruff et al., 2009). Instead, climate metrics and lake water levels were the best predictors of fish size and Hg accumulation, respectively, in both lakes. Despite a significant impact of fire on upland soil Hg and C stocks, our results suggest that low- to moderate-severity wildland fire does not directly alter lake chemistry or the accumulation of Hg in young-of-the-year yellow perch in these small, shallow lakes in northern Minnesota during the years immediately after fire.

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