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Evaluating the spatial variation of total mercury in young-of-year yellow perch (*Perca flavescens*), surface water and upland soil for watershed–lake systems within the southern Boreal Shield

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ABSTRACT

The primary objective of this research is to investigate relationships between mercury in upland soil, lake water and fish tissue and explore the cause for the observed spatial variation of THg in age one yellow perch (*Perca flavescens*) for ten lakes within the Superior National Forest. Spatial relationships between yellow perch THg tissue concentration and a total of 45 watershed and water chemistry parameters were evaluated for two separate years: 2005 and 2006. Results show agreement with other studies where watershed area, lake water pH, nutrient levels (specifically dissolved NO_3^--N) and dissolved iron are important factors controlling and/or predicting fish THg level. Exceeding all was the strong dependence of yellow perch THg level on soil A-horizon THg and, in particular, soil O-horizon THg concentrations (Spearman $\rho = 0.81$). Soil B-horizon THg concentration was significantly correlated (Pearson $r = 0.75$) with lake water THg concentration. Lakes surrounded by a greater percentage of shrub wetlands (peatlands) had higher fish tissue THg levels, thus it is highly possible that these wetlands are main locations for mercury methylation. Stepwise regression was used to develop empirical models for the purpose of predicting the spatial variation in yellow perch THg over the studied region. The 2005 regression model demonstrates it is possible to obtain good prediction (up to 60% variance description) of resident yellow perch THg level using upland soil O-horizon THg as the only independent variable. The 2006 model shows even greater prediction ($r^2 = 0.73$, with an overall 10 ng/g [tissue, wet weight] margin of error), using lake water dissolved iron and watershed area as the only model independent variables. The developed regression models in this study can help with interpreting THg concentrations in low trophic level fish species for untested lakes of the greater Superior National Forest and surrounding Boreal ecosystem.

1. Introduction

A major focal point in environmental pollution research is the bioconcentration of mercury in fish tissue as elevated levels can pose severe impacts to wildlife and human health. For the protection of piscivorous avian and mammalian wildlife, the U.S. Environmental Protection Agency (USEPA) has placed a criterion of 77 ng/g (total mercury [THg], wet weight) and 346 ng/g for trophic levels 3 and 4 fish, respectively (USEPA, 1997). Likewise, the U.S. Fish and Wildlife Service (USFWS) list a predatory protection criterion of 100 ng/g for prey species (Eisler, 1987). Currently, many regions throughout the United States and adjacent Canadian provinces show widespread fish tissue THg levels above these criteria. Northeastern Minnesota is of particular concern because of the shallow, low buffering capacity, organic rich soils and the abundant seepage lakes and wetlands. As of 2004, Minnesota's Impaired Waters List included 808 lakes because of elevated mercury levels in resident fish. Many of these impaired lakes are located within the Boundary Waters Canoe Wilderness (BWCAW) of the Superior National Forest in northeastern Minnesota.

Quantifying the spatial variation of THg in fish is a critical step toward forecasting mercury bioaccumulation potential. The concentration of mercury in fish is a function of a wide array of biological and ecological variables (Vaidya and Howell, 2002; Wiener et al., 2003). In natural systems the dietary uptake of methylmercury (MeHg) is a function of fish size, diet, and trophic position (Wiener et al., 2003); however, equally important are biogeochemical characteristics of the surrounding watershed–lake system. With spatial differences in physical and biogeochemical controls of the watershed, subsequent

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spatial changes in fish THg levels follow. Previous research has shown THg concentrations in northern pike (*Esox lucius*), largemouth bass (*Micropterus salmoides*), and various sunfish species can vary nearly ten-fold among small lakes over relatively short distances (tens of kilometers) (Rencz et al., 2003; Sonesten 2003; Rumbold and Fink 2006; Simonin et al., 2006; Wiener et al., 2006). The processes causing the observed spatial variation in mercury levels are difficult to quantify and typically vary with each system (Sorenson et al., 1990; Desrosiers et al., 2006b; Wiener et al., 2006). It is unlikely that atmospheric loading of mercury to the landscape can account for the observed variation in MeHg production and fish tissue levels (Vaidya and Howell, 2002; Wiener et al., 2006); therefore, investigation is needed on potential watershed influences.

There are several studies that explore the inter- and intra-relationships between mercury in various natural media (e.g. soil, water, fish tissue), landscape features, and water chemistry to better understand the fate and transport of mercury. Regarding fish THg concentration, thus far, some of the most important parameters controlling tissue accumulation appear to include the following: fish trophic position, weight, age (Grieb et al., 1990; Sorenson et al., 1990; Sonesten, 2003; Belger and Forsberg, 2006), surface water pH (Sorenson et al., 1990; Winfrey and Rudd, 1990; Greenfield et al., 2001; Rencz et al., 2003; Chen et al., 2005; Belger and Forsberg, 2006; Simonin et al., 2006; Wiener et al., 2006; Simonin et al., 2008), dissolved organic carbon (Sorenson et al., 1990; Snodgrass et al., 2000; Rencz et al., 2003; Sorenson et al., 2005; Belger and Forsberg, 2006), acid neutralizing capacity/alkalinity (Lange et al., 1993; Chen et al., 2005; Simonin et al., 2006, 2008), wetland area/hydrologic connectivity, (Greenfield et al., 2001; Castro et al., 2007; Hall et al., 2008; Simonin et al., 2008), eutrophic condition (Lange et al., 1993; Cleckner et al., 1998; Gilmour et al., 1998; Sonesten, 2003), lake and watershed size (Greenfield et al., 2001; Ethier et al., 2008) hydroperiod, (Snodgrass et al., 2000; Sorenson et al., 2005; Belger and Forsberg, 2006) water depth, (Snodgrass et al., 2000, Sorenson et al., 2005), water temperature (Bodaly et al., 1993; Ethier et al., 2008) and sulfate reducing bacteria activity (Cleckner et al., 1998; Gilmour et al., 1998; Chen et al., 2005; Wiener et al., 2006; Ethier et al., 2008). Most of the above parameters are important to fish THg level because they regulate mercury methylation. With the relative importance of each parameter varying for each system there is ultimately a need to quantify a discrete subset of parameters that best predict fish THg concentration (Simonin et al., 2008), particularly for those systems that contain or are near water bodies where predatory protection criteria have been exceeded and/or human consumption advisories have been issued. Using these parameters in empirical based models can help environmental resource managers better identify water bodies which may require mercury-related human and natural wildlife consumption advisories (Wren et al., 1991; Greenfield et al., 2001).

The primary objective of this research is to (1) explore the cause for the observed spatial variation of THg in yellow perch (*Perca flavescens*) for ten lakes within the Superior National Forest and (2) investigate relationships between mercury in three watershed media (upland soil, lake water, fish tissue), physical watershed properties and lake water chemistry.

2. Methods and materials

2.1. Study area

The Boundary Waters Canoe Area Wilderness (BWCAW) of the Superior National Forest in northeastern MN was the setting for this study. The BWCAW is located inside a geographic triangle lying south of the Pigeon and Rainy Rivers and extending southward to Lake Superior. This triangle is frequently referred to as the Minnesota Arrowhead Country. Geologically, the 415,716 ha BWCAW is underlain by rocks of the Precambrian Canadian Shield. Pleistocene glaciation shaped the bedrock surface and resulted in a myriad of lakes. The landscape for the BWCAW is characterized by thin soils, abundant outcrops of metamorphic and igneous bedrock and is largely forest-covered. The numerous lakes of this region are primarily hydrologically isolated seepage lakes formed from ice scouring during the last glacial event. The plants and animals of the BWCAW are representative of a southern boreal forest biome. Average annual precipitation ranges from 50 to 90 cm with approximately 75% occurring in snow-free period and average temperatures are 5.5 °C in spring 17.7 °C in summer 7.2 °C in fall and −11 °C in winter.

Data were collected on fish, surface water chemistry, upland soil THg and watershed characteristics for ten lake–watershed systems for this study (Table 1). From west to east the lakes were as follows: Wolf, Merritt, Mud, Ella Hall, Thelma, Everett, Lum, Lizz, Ball Club and Dislocation (Fig. 1). Surface lake area varied from 9.3 ha (Lizz Lake) to 155 ha (Ella Hall) and watershed sizes ranged from 61.4 ha (Everett) to 512 ha (Mud Lake).

2.2. Lake water sampling

All surface water sampling took place during the ice free periods (May to September) in 2005 and 2006. Grab samples were retrieved once per month for the analysis of 25 water quality parameters including total mercury (ng/L) (Table 1). A trace level Teflon *Van Dorn* sampler was used to collect water from lakes that had definable hypolimnion and epilimnion layers. Epilimnion water was sampled

Table 1
Summary of lake water parameters and wetland components for all study lakes over both years.

	Median	25th-percentile	75th-percentile
Alkalinity (as $CaCO_3$ mg/L)	10.0	8.00	19.7
Secchi depth (m)	2.70	2.29	3.00
Chlorophyll-a (µg/L)	3.00	2.00	4.00
Total organic carbon (mg/L)	9.00	7.50	11.6
[b]pH ($-\log[H^+]$)	6.44	6.20	6.90
Total phosphorous (mg/L)	0.02	0.01	0.02
TSS (mg/L)	1.30	1.00	2.00
Specific conductance (µs/cm)	33.0	30.0	42.0
Dissolved $SO_4^{2-}S$ (mg/L)	3.12	2.59	3.54
Dissolved iron (mg/L)	0.15	0.09	0.26
[b]Dissolved oxygen (mg/L)	7.13	2.31	8.05
Color (PTCO)	31.0	12.7	50.0
Acid neut. capacity (mg/L)	11.0	9.00	14.8
Kjeldahl-N (mg/L)	0.40	0.30	0.60
Dissolved NO_3^-N (mg/L)	0.02	[a] 0.01	0.04
Dissolved manganese (mg/L)	1.56	1.19	1.81
Dissolved sodium (mg/L)	1.65	1.53	1.88
Orthophosphate (mg/L)	[a]0.001	[a]0.001	0.002
Dissolved chloride (mg/L)	0.38	0.33	0.42
Dissolved potassium (mg/L)	0.32	0.25	0.44
Pheophytin (mg/L)	0.50	*0.05	0.80
Dissolved calcium (mg/L)	3.12	2.54	3.88
Diss. organic carbon (mg/L)	8.90	7.42	11.5
[b]Water temperature (°C)	21.9	19.8	23.4
	Median	**Minimum**	**maximum**
Watershed area (ha)	319	61.4	512
Lake (ha, %[c])	49.2, 19.7	9.25, 4.55	155, 34.7
Total wetlands (ha, %[c])	87.6, 30.0	14.9, 16.8	221, 43.3
Total lacustrine wetlands (ha, %[c])	52.5, 19.7	9.25, 7.19	155, 34.7
Total palustrine wetlands (ha, %[c])	35.0, 9.81	3.19, 3.68	150, 29.3
PFO wetlands (ha, %[c])	22.7, 6.57	0.65, 0.86	131, 25.7
L1UBH wetlands (ha, %[c])	41.2, 15.8	9.21, 5.97	103, 25.4
PUB wetlands (ha, %[c])	0.75, 0.18	0.04, 0.01	3.50, 1.00
L2UBH wetlands (ha, %[c])	25.6, 6.87	4.24, 1.22	52.1, 11.6
PEM wetlands (ha, %[c])	1.61, 0.62	0.01, 0.01	10.7, 2.66
PSS wetlands (ha, %[c])	2.52, 0.97	0.79, 0.24	15.2, 3.79

[a] Detection limit.
[b] Transect data: values were averaged over the vertical transect (1-m increments) for each lake.
[c] Percentage of watershed area.

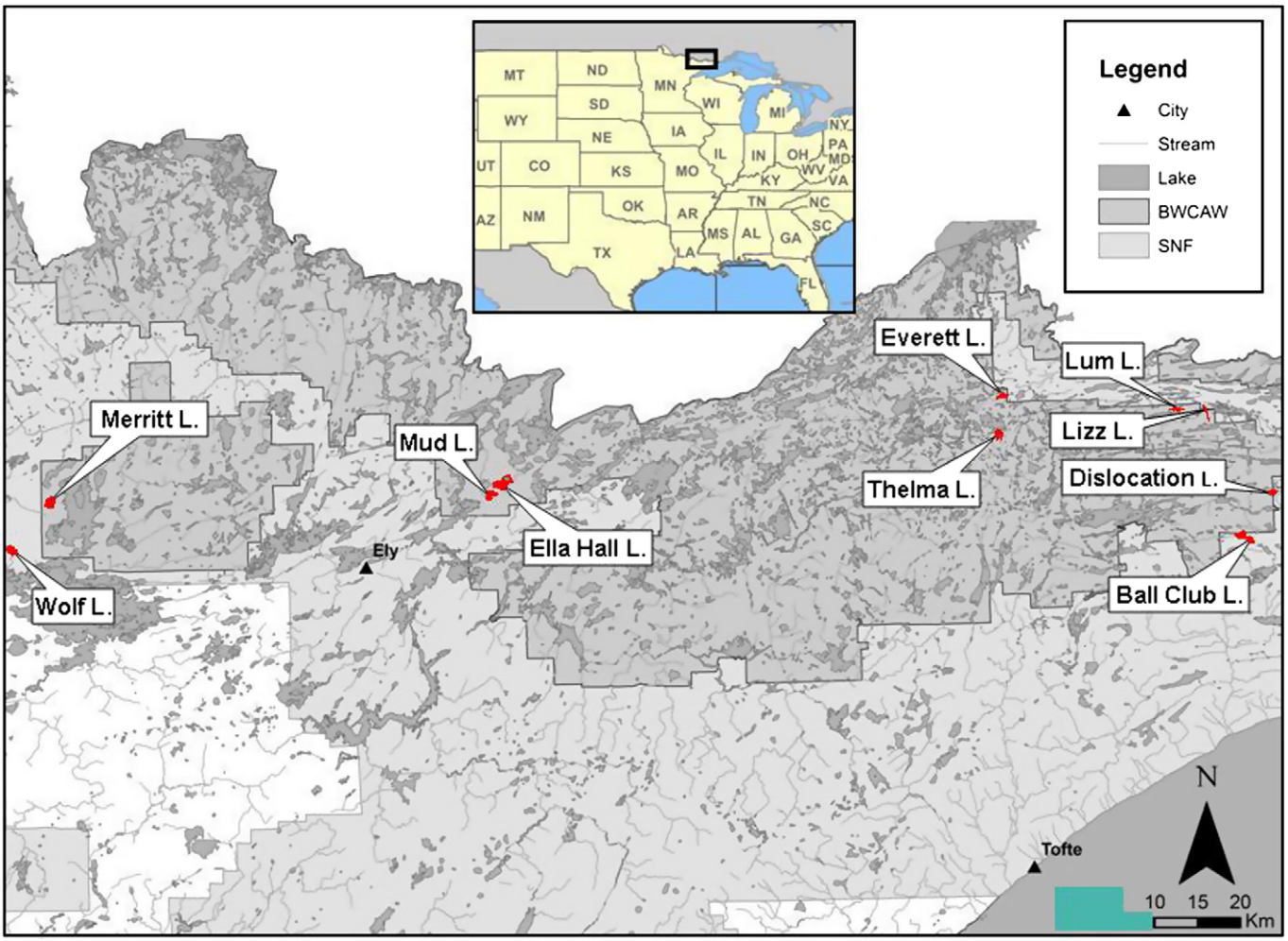

Fig. 1. Lakes and surrounding watersheds used for evaluating the spatial variation of total mercury in age 1 yellow perch, upland soil and lake water.

1 m below the surface and hypolimnion water was sampled mid-way between the thermocline and the lake bottom. Samples were obtained 1 m below the water surface for lakes that had no definable thermocline. Water samples for chlorophyll-a analysis were only retrieved from the epilimnion. All cations were analyzed using a ThermoElemental® inductively coupled plasma-optical emission spectrometer and all anions on a Dionex® ion chromatograph. Cation:anion ratios were used to evaluate the analytical error of instrumentation. For our data sets, ratios were typically between 0.85 and 1.15, which is acceptable (Wren et al., 1991). USEPA methods 351.2, 415.1, 150.1, 365.2, 120.1 and 200.7 were used to quantify Kjeldahl-N, dissolved NO_3^--N, TOC, DOC, pH, orthophosphate, conductivity, total phosphorous, dissolved iron, sodium, potassium, magnesium and calcium. Standard methods 2320-B, 10200H, 2120B, and 4110C were used to quantify acid neutralizing capacity, pheophytin, chlorophyll-a, color, dissolved sulfate, phosphate, nitrate, and chloride. USGS methods 1–37 was used for total suspended solids analysis. Temperature, dissolved oxygen and additional pH and specific conductivity measurements were collected over vertical in-lake transects with a HydroLab Quanta®. Acid neutralizing capacity was determined using a Mettler-Toledo Auto-Titrater with a Gran Plot.

2.3. Soil sampling

Upland soil samples from the O, A and B/E horizons within each watershed were collected for THg analysis. Sampling took place over a two year period (2004 and 2005). Eight of the ten study lakes' watershed soils (Wolf, Merritt, Mud, Ella Hall, Everett, Lum, Lizz, 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 lake watershed for each soil horizon.

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 quantity of an O horizon was dependent on landscape factors, such as forest type and the presence or absence of earthworms. Following collection of an A-horizon soil, the topmost 5 cm of the B-horizon, occasionally mixed with the E-horizon, was collected. In the laboratory, all soils were air-dried and sieved to <2 mm prior to analysis.

2.4. Fish collection and analysis

Fish sampling took place during four-day periods shortly after ice-out in early May 2005 and 2006. Yellow perch (*P. flavescens*), bluegill (*Lepomis macrochirus*), and pumpkinseed fish (*Lepomis gibbosus*) were collected using electroshock methods. Yellow perch, bluegill and pumpkinseed are secondary predatory fish with an average lifespan of four to seven years in the wild. These fish were targeted as they are good indicators of MeHg in food webs (Greenfield et al., 2001; Wiener et al., 2006). Due to their low trophic position, THg variation in these fish reflects ecosystems processes and factors influencing the abundance of MeHg. Bluegill, pumpkinseed and yellow perch are widespread in natural surface waters and are the preferred prey for a

Table 2
Fish physiological characteristics for 2005 and 2006 combined.

	Weight (g)		Length (mm)		Specie (*n*)			Age (n)		
Lake name	Mean	SD	Mean	SD	YP[a]	BG[b]	PD[c]	1	2	3
Wolf	2.98	2.04	58.6	12.0		20		17	3	
Merritt	2.52	0.92	77.9	18.5	20			20		
Mud	1.91	1.33	57.4	9.39	20			20		
Ella Hall	0.46	0.12	37.8	3.20	20			20		
Thelma	1.34	0.45	56.8	6.23	20			20		
Everett	2.31	0.70	64.4	5.49	20			15	5	
Lum	3.02	2.05	63.3	12.6	20			10	8	2
Lizz	1.76	2.75	41.7	17.6	10		10	13	7	
Ball Club	2.71	0.71	67.3	5.53	20			16	4	
Dislocation	0.87	0.42	45.9	5.29	20			20		

[a] Yellow perch.
[b] Bluegill.
[c] Pumpkinseed.

number of fish-eating species in the BWCAW; therefore, these species may also be an indicator of mercury exposure to wading birds and other fish-eating wildlife. For each year at least 10 fish were caught per lake and analyzed for THg (Table 2). Once fish were caught they were double bagged and put on ice. At the laboratory, measurements were taken for fish length, weight and age.

2.5. Total mercury analysis

For total mercury in lake water, all samples were collected in pre-cleaned acid washed Teflon bottles using the clean-hands/dirty-hands method. Prior to use, each bottle was soaked in concentrated HNO_3, rinsed using milli-RO H_2O (Millipore Mill-RO® water system) and 5 mL of high purity HNO_3 was added to each bottle. Bottles were tightly capped then stored in two zip-loc bags. At the sampling site, each bottle was emptied and rinsed with lake water before sample retrieval. Once the sample was collected the bottle was re-sealed in a zip-loc bag, stored in a cooler then shipped to the analytical laboratory. Double amalgamation cold vapor atomic fluorescence spectroscopy (as outlined in USEPA method 1631, Revision C) in concert with a gold coated sand trap pre-concentration unit was used for total mercury analysis. In the laboratory total mercury in each sample was first oxidized with BrCl. Bromine mono-chloride sample ratios were between 1:10 and 1:20 depending on the amount of organic material present in the sample. Remaining BrCl was neutralized with hydroxylamine. Oxidized mercury was reduced to Hg^0 with $SnCl_2$ overnight at 65 °C. Produced Hg^0 was then purged from each sample and delivered to the sand traps, thermally desorbed, then directed to a Brooks–Rand AFS Model III (detection limit = 10 pg) for detection. Mercury Guru software was used in line with the detection unit for user application. Standard curves were run prior to each day's analysis. One field blank was collected and one analytical duplicate was analyzed per lake for 2006. The average field blank was 1.05 ng/L (±0.02 ng/L) and the average percent difference between the routine and analytical duplicates was 7.2%.

For THg detection in fish, the entire fish was digested in 10 to 20 mL of nitric acid (depending on the size of the fish) overnight at 70 °C. Cold vapor atomic fluorescence spectroscopy (using double amalgamation) as outlined in USEPA method 1631, Revision C along with a Brooks–Rand AFS Model III and Mercury Guru software was used for THg detection within fish tissue. The working detection limit for this method is 0.01 µg/L. Two to three analytical duplicates were run for each lake per year. The average %RPD (relative percent difference) for routine and analytical duplicates was 6.5% and 8.0% for 2005 and 2006, respectively.

Analytical methods described by Taggert (2002) were used for total mercury analysis of soils. Mineral and unashed organic soils were first 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 using a cold vapor atomic adsorption spectroscopy mercury analyzer (Perkin-Elmer Flow Injection Mercury System, FIMS-100 [0.02 ppm detection limit]). This instrumentation was routinely calibrated using standards containing 0, 0.5, 2.0, 5.0 and 10 ppb Hg.

2.6. Wetland delineations

For each watershed–lake system, wetland area and type were delineated using the National Wetlands Inventory (NWI) Database; a national program sponsored by the US Fish and Wildlife Service. Each watershed was divided into three main components: upland (non-wetlands), lacustrine and palustrine wetlands. Lacustrine and palustrine were further divided into several subsystems (e.g. limnetic, littoral, river based). In all, the NWI aerial coverage (as hectare and percentage of entire watershed) of the following nine wetland and lake compartments was considered: total wetlands, lacustrine, palustrine, PFO (palustrine, forested), L1UBH (lacustrine, limnetic, unconsolidated bottom, permanently flooded), PUB (palustrine, unconsolidated bottom freshwater ponds), L2UBH (lacustrine, littoral, unconsolidated bottom, permanently flooded), PEM (palustrine, emergent), and PSS (palustrine, scrub shrub).

2.7. Statistical and graphical applications

Both non-parametric and parametric statistical methods were used for data set comparisons. All associated post-hoc data comparisons were performed using either the Dunn's or Tukey method. Spearman or Pearson correlation was used for all correlations depending on data distribution and symmetry. 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, SigmaStat® 2.03. and SyStat® 10.2.02 was used for all ANCOVA analyses. All graphical exercises were performed using ArcView® 9.0, ArcGIS® and SigmaPlot® 8.0.

3. Results and discussion

3.1. Total mercury variability in all media

All media demonstrate typical total mercury concentration ranges for the western Lake States (Sorenson et al., 1990; Greenfield et al., 2001; Wiener et al., 2006), nearby Canadian Shield and lower Ontario lakes (McMurty et al., 1989; Bodaly et al., 1993; Vaidya et al., 2002; Rencz et al., 2003; Roue'-Le Gall et al., 2005; Paterson et al., 2006) (Table 3). For 2005 there were statistically significant differences in

Table 3
Total mercury in all media types for 2005 and 2006.

	Fish THg[a] (ng/g)		Lake water[b] THg (ng/L)		Upland soil horizons (mg/kg)[c]					
					O		A		B	
Lake name	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
Wolf	40.6	9.60	2.55	1.84	0.06	0.02	0.07	0.05	0.03	0.01
Merritt	44.5	18.4	1.91	1.10	0.12	0.03	0.12	0.04	0.02	0.01
Mud	30.8	7.50	2.55	1.06	0.08	0.03	0.1	0.04	0.02	0.02
Ella Hall	19.2	3.09	3.03	3.12	0.07	0.04	0.09	0.05	0.03	0.02
Thelma	79.5	20.0	2.84	1.29	0.17	0.06	0.15	0.06	0.03	0.01
Everett	98.7	25.4	2.40	1.70	0.20	0.06	0.16	0.07	0.03	0.01
Lum	116	36.0	3.30	2.60	0.18	0.06	0.23	0.08	0.04	0.01
Lizz	56.4	42.1	2.32	0.80	0.19	0.04	0.23	0.08	0.04	0.01
Ball Club	74.6	36.0	3.43	2.95	0.12	0.03	0.23	0.08	0.05	0.01
Dislocation	42.7	10.5	4.95	3.21	0.20	0.06	0.27	0.08	0.06	0.02

[a] Fish muscle tissue wet weight; resulted are for both years combined.
[b] Data from 2006.
[c] Dry weight, data from 2004 and 2005.

fish THg among all lakes (Kruskal Wallis; $H=76$; $df=9$; $p<0.001$). Pairwise comparisons demonstrated fish from Lum lake and Everett lake had higher THg levels than most other lakes (Dunn's method; $p<0.05$). For 2006 there were also statistically significant differences in fish THg among all lakes (Kruskal Wallis; $H=93$; $df=9$; $p<0.001$). Pairwise comparisons showed similar results from 2005 where fish from Lum Lake and Everett Lake had higher THg levels (Dunn's method; $p<0.05$). Average THg fish levels varied 5-fold across all lakes in 2005 [19 ng/g (min) to 89 ng/g (max)] and 7 fold in 2006 [19 ng/g (min) to 124 ng/g (max)]. Despite 6 of the 10 lakes showing an average 60% increase in THg fish concentration in 2006, after pooling all data, there was no statistical difference between both years (Mann–Whitney; $p=0.414$). The within-lake variability of fish THg for both years combined (average SD = 19.2 ng/g) was less than the among-lake variability (SD = 31.0 ng/g), therefore hinting at the importance of spatial location on THg levels in fish. The observed spatial variation in fish THg is moderate as some studies have shown more spatial variation (Greenfield et al., 2001; Wiener et al., 2006), less variation (Bodaly et al., 1993) while others have demonstrated similar spatial variance (Sorenson et al., 1990) (Fig. 2).

In 2005 18% of all fish collected (from Thelma, Everett, Lum and Lizz Lakes) exceeded the USEPA criterion of 77 ng/g (for trophic level 3 species [USEPA, 1997]). Yellow perch, bluegill and pumpkinseed can be regarded as trophic level 3 species (Loftus et al., 1998). In this same year, 4% of all fish exceeded the USFWS criteria of 100 ng/g (Eisler, 1987). In 2006, 43% of all fish collected exceeded the USEPA criterion and 33% exceeded the USFWS criterion. The lakes exceeding the USEPA criterion were again Lum, Thelma, Everett, Lizz with the addition of Ball Club Lake. All fish from Everett and Lum and nearly all from Ball Club were above the USFWS criterion.

Total mercury levels in lake water were similar to other data sets collected in the same region (Sorenson et al., 1990; Greenfield et al., 2001; Wiener et al., 2006) (Table 3). For lake water THg, there was no statistical difference among all lakes (Kruskal Wallis; $H=7.1$, $df=9$; $p=0.620$). For upland soils, there were statistical differences in THg by horizon ($p<0.001$) and concentrations for each horizon were statistically different among lake watersheds. Overall, A-horizon soils had higher THg concentrations than O-horizon soils. Soils collected as B-horizon samples had the overall lowest Hg concentrations. The spatial variance in THg was highest for the O-horizon. There are strong and consistent correlations between upland soil THg levels, in particular O-horizon soils, and fish THg (Table 4). Total mercury in lake water shows a strong correlation with soil B-horizon THg, indicating the signature of dissolved mercury in lake water may be influenced by subsurface interflow from upland soils.

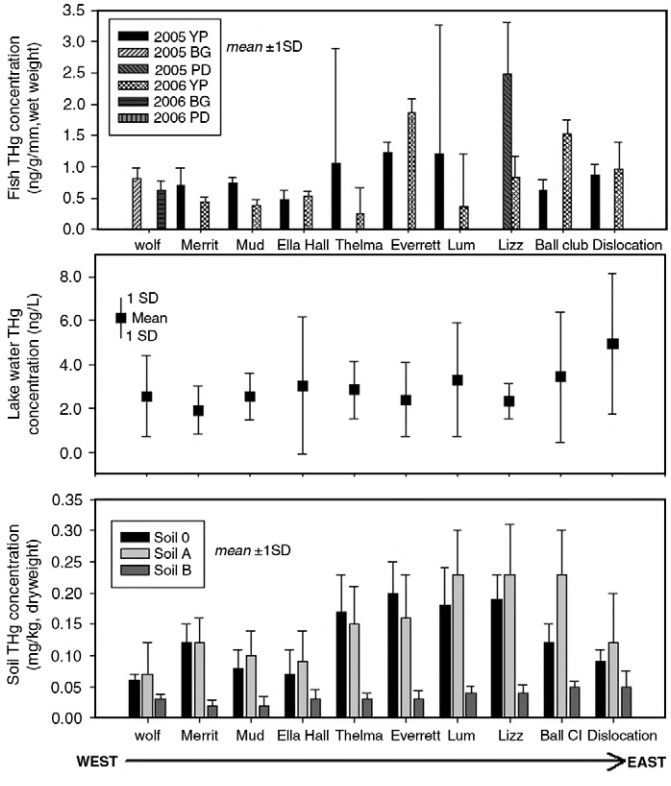

Fig. 2. Spatial representation of THg levels in lake water, upland soil and all fish species (PD = pumpkinseed fish, BG = bluegill and YP = yellow perch) for both years.

Table 4
Regressions between THg in all media (Pearson *r* upper cell, *p-value* lower cell).

2005				2006				
	Soil O	Soil A	Soil B		Soil O	Soil A	Soil B	Lakewater
Soil A	**0.75**			Soil A	**0.75**			
	0.01				***0.01***			
Soil B	0.15	0.57		Soil B	0.15	0.57		
	0.67	*0.08*			*0.67*	*0.08*		
Fish[a]	**0.90**	**0.63**	0.04	Lake water	−0.23	0.06	**0.75**	
	<0.001	***0.04***	*0.91*		*0.51*	*0.86*	***0.01***	
				Fish[a]	**0.68**	**0.65**	0.38	0.151
					0.02	***0.04***	*0.26*	*0.678*

Data pooled across all lakes.
[a] Includes an average of all fish types, sizes and ages.

3.2. Fish THg variation as a function of physiology and location

It is well known that THg levels in fish vary as a function of species, length, weight and age (e.g. Grieb et al., 1990). After pooling data across all lakes for 2005, fish THg concentration was significantly correlated with length (Spearman rank; $\rho=0.44$; $p<0.001$) and weight (Spearman rank; $\rho=0.38$; $p<0.001$). After standardizing (dividing) concentrations by length and only considering age-1, THg levels were significantly different among the three fish species (Kruskal–Wallis; $H=15.1$; $df=2$; $p\leq0.001$), with pumpkinseed fish having higher THg than both yellow perch and bluegill (Dunn's method, $p<0.05$). There was no statistical difference in THg concentration between bluegill and yellow perch. These results are surprising considering these fish reside within same trophic level (3–4) and hence have similar diet (phytoplankton, zooplankton; switching to benthic macro-invertebrates and smaller fish in adulthood) (Ethier et al., 2008). For 2006, THg levels in fish were correlated with length (Spearman rank; $\rho=0.23$; $p=0.02$) and weight (Spearman rank; $\rho=0.21$; $p=0.03$). After following the same length and age-1 standardization, there was no significant difference (Mann–Whitney; $p=0.12$) in THg concentrations between the two fish species (yellow perch, bluegill) caught that year (Table 2). For 2005 there was a significant difference in THg concentration with fish ages, 1 and 2, with the latter being higher (Mann–Whitney; $p\leq0.001$; only considering yellow perch).

If not filtered out, physiological factors may mask the impacts of spatial location on fish THg level. For both years, the most important co-variant for THg was fish length. Considering this, attempts were made to use ANCOVA to remove the relative impact of fish length on THg variation. For 2005, with length as the co-variant, THg concentration as the dependant variable and location (lake) as the independent variable results indicated an insignificant interaction between the co-variant and the dependent variable (lake*length, $p=0.09$, $df=9$, $F=1.7$) thus permitting an assessment of the dependent-independent variable interaction (Zar, 1996). Results show that fish THg did not vary with location after removing the effect of fish length ($p=0.15$ between THg and location). For 2006, due to the significant interaction between lake and length (lake*length, $p=<0.001$, $df=9$, $F=6.8$) ANCOVA could not be used.

Considering the differing ANCOVA results by year, a secondary and more robust method was to manually standardize by physiological attributes. After standardizing by length and only considering age 1 yellow perch, one-way ANOVA shows significant spatial variation in yellow perch THg for 2005 ($F=18$, $df=6$, $p<0.001$) and Kruskal–Wallis one-way ANOVA on ranks shows significant spatial variation for 2006 ($H=67$, $df=6$, $p<0.001$). For 2005, Tukey's method of pairwise comparisons showed yellow perch THg concentrations for lakes Lum and Everett were greater than all other lakes ($p<0.05$). For 2006, lakes Lum, Thelma and Everett were all greater than lakes Mud, Merritt and Ella Hall (Dunn's method; $p<0.05$).

3.3. Evaluating spatial trends in yellow perch THg

We used two methods to evaluate the spatial variance in fish THg across the study area: (1) assessing water chemistry and watershed correlates that best described the variation and (2) developing a multi-regression model based on the best set of correlates. Multi-regression was chosen for model development as it is a fairly robust method for spatial analysis when applied appropriately (homoscedasity of data distributions and model residuals are required).

To examine the impacts of watershed–lake system processes on fish THg variation it is important to remove fish physiological influences. Therefore, we began the modeling process by first screening all fish for only age-1 yellow perch as this was the most predominant fish type for both years. These data were further screened by the inner quartile ranges (between the 25th and 75th percentiles) of weight and length: 45–65 mm and 0.7–1.87 g for 2005 and 48–69 mm and 0.76–3.0 g for 2006. Following the screening procedures, the time series lengths varied considerably for each year ($n=28$ for 2005 and $n=42$ for 2006). Despite smaller data sets for particular lakes, statistical differences in yellow perch THg among all lakes still existed (2005 one-way ANOVA, $F=93.5$, $df=6$, $p<0.001$), (2006 one-way ANOVA, $F=18.5$, $df=4$, $p<0.001$).

3.3.1. Correlations

Spearman correlations were developed between a total of 48 correlates and yellow perch THg for each lake for both years (Table 5). Correlations were developed over two separate years to identify any consistent relationships and thus to strengthen any hypotheses.

For both years, there is a strong negative relationship between watershed size, lake size and yellow perch THg (Table 5). Several other studies have shown similar results (Bodaly et al., 1993; Greenfield et al., 2001) whereas others have shown the opposite (McMurty et al., 1989; Suns and Hitchin, 1990; Chen et al., 2005). Munthe et al. (2007) suggest watershed size and watershed-to-surface water ratios are the most important determinants for mercury delivery to aquatic systems. As watershed size increases, yields of mercury per unit area typically decline because large watersheds are less efficient in sediment and solute transport. The inverse relationship between lake size and fish THg is also suggested to result from smaller lakes having the ability to increase in temperature faster and to higher levels. Warmer temperatures promote bacterial activity including MeHg production (Desrosiers et al., 2006a). In addition, warmer temperatures increase metabolic rates in fish including feeding rates and gill ventilation (Bodaly et al., 1993). However, we show a clear inverse relationship in our study between THg and water temperature (Table 5). Reduction in lake size may also increase the effect of allochthonous inputs of organic matter by increasing the proportionate influx of wetland-derived materials (e.g. organic compounds) compared to the total lake volume (Greenfield et al., 2001). However, in this study we found inverse relationships between fish THg and DOC (discussed in detail below) and TOC.

Several previous studies have reported significant positive relationships between percent wetlands and fish THg (yellow perch, brook trout) (Hurley et al., 1995; Shanley et al., 2005; Simonin et al., 2006, Belger and Forsberg, 2006; Castro et al., 2007). This relationship largely exists due to wetlands being the primary center for MeHg production (Rudd, 1995; Shanley et al., 2005; Selvendiran et al., 2008). In this study, however, nearly all wetlands types were negatively correlated with perch THg which may be due to a lake/watershed–wetland size relationship. In most cases large lakes contained large sized wetlands. Over both years, consistent exceptions were for %PSS and %L1UBH wetlands. Lakes with greater percentages of PSS and L1UBH wetlands had higher fish issue THg levels, thereby suggesting these two watershed compartments are main areas for mercury methylation.

Table 5
Spearman correlations between water chemistry, watershed correlates (independent variables) and yellow perch THg (dependent variable): correlates in bold font demonstrate statistically significant ($p<0.05$) correlations for individual years and correlates in bold font + shaded were statistically significant for both years.

2005			2006		
Parameter	ρ	p	Parameter	ρ	p
Dis Ca	−0.698	<0.001	PFO wetls. area (ha)	−0.916	<0.001
Water temp.	−0.636	<0.001	PFO wetls. area (%)	−0.901	<0.001
Kjeld-N	−0.621	<0.001	Dis Na	−0.829	<0.001
ANC	−0.620	<0.001	Palus. wetls. area (%)	−0.824	<0.001
PUB wetls. area (ha)	−0.605	0.006	Non-uplands area (ha)	−0.800	<0.001
PUB wetls. area (%)	−0.605	0.006	Palus. wetls. area (ha)	−0.792	<0.001
PFO wetls. area (ha)	−0.594	0.001	Watershed area (ha)	−0.677	<0.001
Specific conductivity	−0.592	<0.001	PEM wetls. area (ha)	−0.654	<0.001
Total-*P*	−0.571	0.001	Dis O	−0.644	<0.001
Watershed area (ha)	−0.532	0.003	Dis SO_4^{2-}	−0.593	<0.001
PFO wetls. area (%)	−0.504	0.006	Water temp.	−0.589	<0.001
pH	−0.477	0.010	Lake area (ha)	−0.580	<0.001
[b]Non-uplands area (ha)	−0.455	0.015	Lacus. wetls. area (ha)	−0.580	<0.001
Lake area (ha)	−0.439	0.019	L1UBH wetls. area (ha)	−0.580	<0.001
[a]Lacus. wetls. area (ha)	−0.439	0.019	Kjeld-N	−0.538	<0.001
L1UBH wetls. area (ha)	−0.439	0.019	Chlor-A	−0.536	<0.001
Palus. wetls. area (ha)	−0.413	0.029	Total-*P*	−0.519	<0.001
[c]Dis O	−0.373	0.050	Non-uplands area (%)	−0.502	<0.001
Chlor-A	−0.294	0.128	Dis Cl	−0.481	0.001
Palus. wetls. area (%)	−0.264	0.174	TOC	−0.334	0.030
Non-uplands area (%)	−0.188	0.335	Dis Ca	−0.329	0.033
[d]Dis OC	−0.185	0.343	ANC	−0.274	0.079
Dis Mg	−0.183	0.347	PEM wetls. area (%)	−0.273	0.112
Dis Na	−0.162	0.408	L2UBH wetls. area (ha)	−0.269	0.303
L2UBH wetls. area (ha)	−0.132	0.637	L2UBH wetls. area (%)	−0.269	0.303
L2UBH wetls. area (%)	−0.132	0.637	TSS	−0.232	0.138
TOC	−0.131	0.503	PSS wetls. area (ha)	−0.161	0.347
TSS	−0.111	0.572	PUB wetls. area (ha)	−0.105	0.627
Lake water THg	−0.077	0.693	PUB wetls. area (%)	−0.105	0.627
Color	−0.017	0.928	pH	−0.102	0.519
Ortho-P	0.037	0.849	Dis Mg	−0.066	0.675
Soil B-horizon THg	0.050	0.797	Ortho-P	−0.023	0.883
Dis SO_4^{2-}	0.093	0.634	Pheophytin	0.128	0.418
PEM wetls. area (ha)	0.096	0.634	Lacus. wetls. area (%)	0.178	0.258
Lacus. wetls. area (%)	0.190	0.330	Lake depth	0.187	0.234
Secchi depth	0.194	0.320	Specific conductivity	0.193	0.219
PSS wetls. area (%)	0.254	0.228	Dis K	0.223	0.155
PSS wetls. area (ha)	0.298	0.157	Color	0.234	0.136
L1UBH wetls. area (%)	0.260	0.180	Lake water THg	0.298	0.055
Dis Fe	0.440	0.019	PSS wetls. area (%)	0.342	0.041
Dis Cl	0.460	0.013	L1UBH wetls. area (%)	0.414	0.006
Dis K	0.461	0.013	Soil B-horizon THg	0.543	<0.001
Pheophytin	0.516	0.005	Dis NO_3^-N	0.544	<0.001
PEM wetls. area (%)	0.539	0.003	Dis Fe	0.646	<0.001
Lake depth	0.557	0.002	Soil O-horizon THg	0.815	<0.001
Soil A-horizon THg	0.586	0.001	Soil A-horizon THg	0.847	<0.001
Dis NO_3^-N	0.615	<0.001			
Soil O-horizon THg	0.812	<0.001			

Secchi depth or DOC is not included for 2006.
[a] Lacustrine wetlands.
[b] All palustrine and lacustrine wetlands.
[c] Dissolved oxygen.
[d] Dissolved organic carbon.

Both years demonstrate a strong relationship between yellow perch THg, soil O- and A-horizon THg concentrations. This is one of the first studies to display a close link between THg in upland surface soils and fish for background/un-impacted areas. Overall, the strongest correlation was with soil O-horizon THg (Spearman $\rho = 0.812$, $p<0.001$ [2005], Spearman $\rho = 0.815$, $p<0.001$ [2006]) indicating near-surface watershed runoff processes have a large role in fish tissue THg burdens. The next informative step would be to investigate the factors or natural system processes that can alter upland soil O-horizon THg levels, such as landscape disturbances including forest fire, logging and invasive earthworms. The basis for soil O-horizon as an important THg source for fish is further supported by the finding that lake water THg shows no relationship with fish THg burden (Tables 4 and 5) and lake water THg is positively correlated with soil B-horizon THg (Table 4). All together, these relationships suggest (1) mercury in near-surface runoff may be in a form that is more prone to methylation than mercury that enters the lake by subsurface flow and/or (2) the upland is an important source for MeHg.

Similar to Lange et al. (1993) our results show a positive relationship between fish THg and lakewater NO_3^-; however, we found a reverse relationship for total phosphorous (Table 5). In the Florida Everglades Cleckner et al. (1998) and Gilmour et al. (1998) also reported a negative relationship between fish THg and bioaccumulation factor (fish THg /MeHg surface water) as the eutrophic condition increased. In South Florida wetlands Vaithiyanathan et al. (1996) found no relationship between eutrophication and potential for net MeHg production in sediment after relating methylation/demethylation ratio to phosphorus concentrations.

In contrast to data presented by Bodaly et al. (1993), we found a negative relationship between yellow perch THg and lake water temperature. It is, however, difficult to surmise the significance of this relationship, including that for DO, because of the high spatiotemporal variability of these two parameters and the vertical water column averaging that was performed. It is clear from previous laboratory and field mesocosm studies that temperature and DO impact mercury methylation and MeHg partitioning. A two-fold increase in MeHg partitioning to algae can be seen with a doubling in temperature (20 °C to 40 °C) (Moye et al., 2002).

Wren et al. (1991) and Lange et al. (1993) found negative relationships between fish THg and lake water conductance while McMurty et al. (1989) showed a positive relationship for largemouth bass. In this study we found a significant (Spearman $\rho = -0.59$, $p<0.001$) negative relationship for 2005 and insignificant (Spearman $\rho = 0.19$, $p = 0.21$) positive relationship for 2006. It is possible that increases in dissolved ions will reduce the biological availability of neutral Hg species (e.g., $Hg(HS)_2$, $HgCl_2$, $Hg(OH)_2$, HgS) that are important in mercury methylation (Benoit et al., 1999; Kelly et al., 2003; Mehrotra et al., 2003; Drott and Skyllberg, 2007).

It is becoming increasingly apparent that sulfate reducing bacteria are primary methylators of mercury in aquatic systems. Sulfate reduction and mercury bioaccumulation are two very distinct biological processes, thus attempting to find a relationship between fish THg and surface water sulfate could prove difficult; however, some studies have shown positive relationships (Gilmour et al., 1998; Harmon et al., 2005; Jeremiason et al., 2006; Wiener et al., 2006). A recent study by Selvendiran et al. (2008) shows decreasing sulfate levels during the vegetative growing season is attributed to sulfate reduction (Selvendiran et al., 2008); therefore, a decrease in sulfate could also indicate biological sulfate reduction activity. The sulfate levels for our study lakes (2–3 mg/L) are low enough to assume there is little methylation inhibition from sulfide. It is highly possible that sulfate reduction is the driver for methylation, but what is limiting methylation may involve other important aspects, such as type and amount of labile organic carbon, redox potential or other competing mercury methylation pathways (e.g. iron reduction).

In this study, there was a strong positive relationship between THg in fish and dissolved iron. Two previous studies found the same relationship: Wren et al. (1991) for walleye and northern pike and McMurty et al. (1989) for lake trout. Two potential reasons for the positive relationship are (1) the production of MeHg by iron-reducing bacteria (Warner et al., 2004) and (2) the similar transport pathways of mercury and iron from upland watershed soils to lake water due to their high affinity for organic compounds.

Two of the most documented water chemistry parameters associated with mercury biogeochemistry are pH and DOC. We found negative correlations between TOC (unfiltered) and fish THg concentrations although only the relationship in 2006 was significant. The literature indicates mixed results regarding the influence of DOC on fish THg accumulation. For example, Grieb et al. (1990), Snodgrass et al. (2000) and Greenfield et al. (2001) all found a negative correlation between THg in several different fish species and lake water DOC while several studies have documented a positive correlation (McMurty et al., 1989; Wren et al., 1991; Rencz et al., 2003; Belger and Forsberg, 2006; Driscoll et al., 2007). The negative relationship is suspected to result from long-chain carbon compounds binding to mercury forms thereby reducing bioavailability (Snodgrass et al., 2000; Benoit et al., 2001). In addition, DOC is suspected to reduce bioavailability by enhancing photoreduction of Hg^{2+} to Hg^0 (O'Driscoll et al., 2003; Hall et al., 2008). Conversely, increased DOC may increase bioavailability by transporting Hg to areas where methylation is efficient. For example, Nilsson and Hakanson (1992) suggest Hg in the presence of humic material increases Hg deposition to the sediment–water interface, an area of where most Hg methylation occurs. In addition, DOC can provide a carbon substrate that enhances Hg methylation by sulfate- and/or iron-reducing bacteria in sediment (Hall et al., 2008). Simonin et al. (2008) found DOC to be unimportant in yellow perch or bass THg accumulation. The vegetation and soil type can have a large influence on surface water DOC characteristics (e.g. extent of short chain carbon compounds) which may provide one explanation for the previously reported mixed results.

The inverse relationship between fish THg levels and pH is well documented (Suns and Hitchin, 1990; Wren et al., 1991; Bodaly et al., 1993; Lange et al., 1993; Sonesten 2003; Wiener et al., 2006; Driscoll et al., 2007). Studies indicate that lakes with low buffering capacity typically have higher fish THg levels (McMurty et al., 1989; Grieb et al., 1990; Wren et al., 1991; Lange et al., 1993). There appears to be multiple factors related to fish metabolism and molecular Hg bioavailability that can produce this relationship. Some studies document the following at high lake water pH: (1) increased volatilization of Hg^0 from the water column (Wiener et al., 2006) (2) production of highly volatile di-MeHg ($(CH_3)_2Hg$) (Lange et al., 1993) and (3) decreased MeHg accumulation across fish gill membranes (Lange et al., 1993). Methylation is most efficient at lower pH as this is the condition where methylation efficient species (e.g. HgS) are chemically stable and thus more abundant (Kelly et al., 2003; Mehrotra et al., 2003; Miller et al., 2007). In this study we found similar inverse relationships between pH and fish THg although only the relationship in 2005 was significant.

3.3.2. Regression modeling

For regression model development, best predictors for 2005 and 2006 were selected based on Spearman ρ values (Table 5). To provide a basis for interpretation, only the five best predictors were chosen for 2005 and best eight for 2006. These discrete sets were selected based on the principle that the number of observations should be at least 5 times the number of predictors ($n \geq 5k$, where n is number of observations and k is number of predictors (Kleinbaum et al., 1988). The following five were chosen for 2005: soil O-horizon THg, water temperature, Dis NO_3^--N, Dis Ca, and Kjeldahl-N; and the following eight for 2006: PFO wetlands

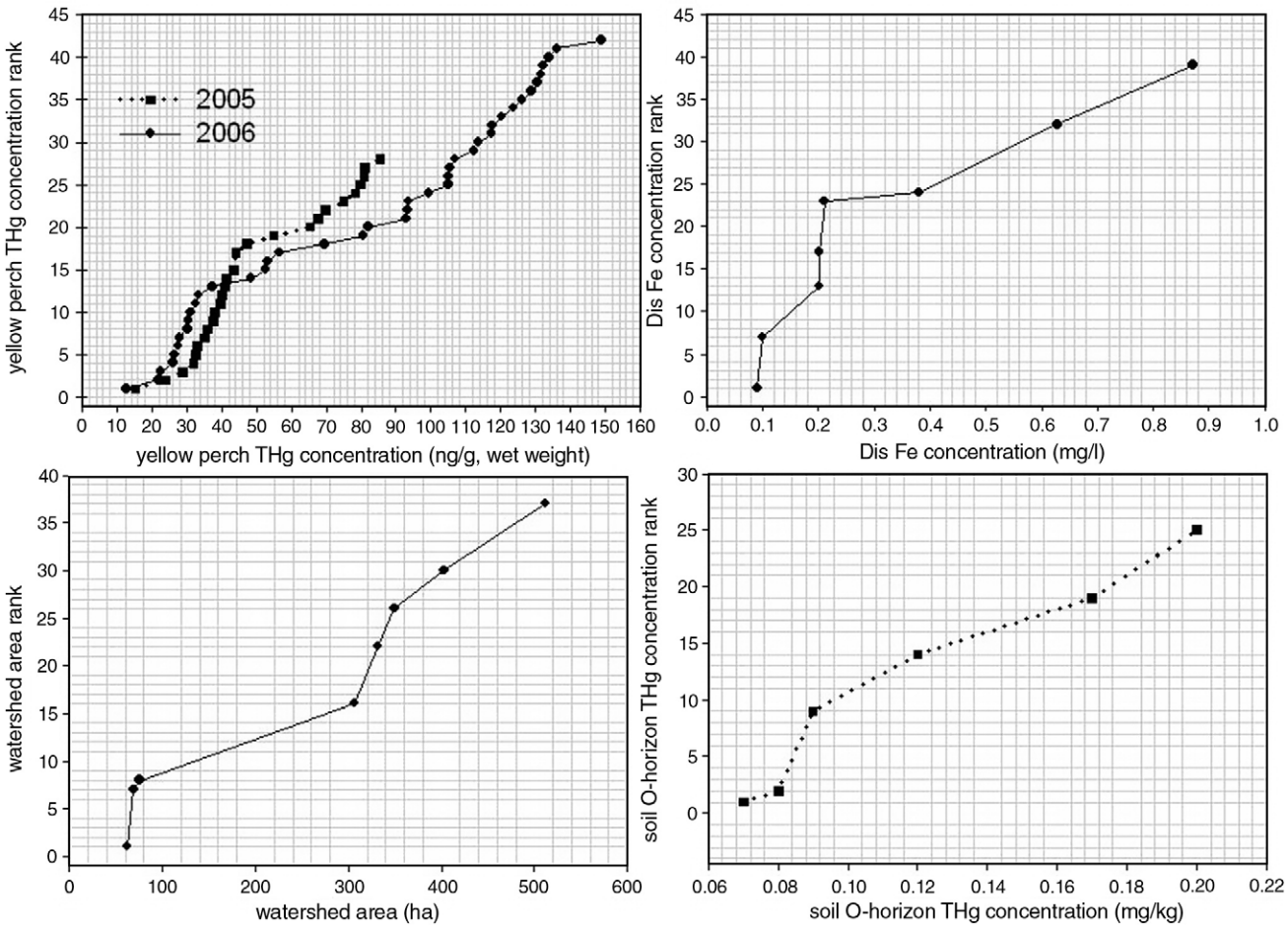

Fig. 3. Concentrations, watershed areas and associated ranks for the 2005 and 2006 models.

(%), PFO wetlands (ha), soil O-horizon THg, non-uplands (ha), palustrine wetlands (ha), watershed area (ha), soil A-horizon THg and Dis Fe. Following the initial selection of 13 parameters, we whittled the list of predictors to five for the regression analysis. Co-linearity criteria were considered as well as the utility or ease of measurement of each parameter. To start, soil O-horizon THg was chosen as a result of its consistent high correlation for both years. Soil A-horizon THg was not chosen due to its co-linearity with soil O horizon THg for both years. In addition, field volume measurements for the soil O horizon are typically much less labor intensive than for the A-horizon. All of the selected wetland components (Non-upland area [ha], PFO wetland area [%, ha], palustrine wetlands [ha]) were replaced with watershed area because these wetland components were highly correlated with watershed and lake area. Dissolved NO_3^--N was chosen over Kjeldahl-N for its less intensive analytical measurement. Finally, Dis Fe and Dis Ca were chosen as they show high correlations for both years and their concentrations are generally stable for lake systems. Therefore based on the above evaluations on the above thirteen, the following final set was chosen for the stepwise regression process: soil O-horizon THg, Dis Ca, watershed area (ha), Dis Fe and NO_3^--N.

Statistical models were developed for each year using stepwise regression. The forward-and-backward selection method was used to select the best subset of parameters from the pre-defined list. Model performance criteria and residual analyses were then used to compare candidate models. In all cases the stepwise alpha-to-enter was 0.10 and *F*-to-enter was 4. For 2005, the stepwise procedure selected soil O-horizon THg as the only significant predictor out of the five: (yellow perch ng/g rank = 4.65 + 0.799 * SoilO-horizon THg rank) ($r^2 = 0.59$, $p = <0.001$) (df[1] = 1, F[2] = 47.81, DW[3] = 2.23, PRESS[4] = 736.0) with residual homoscedasity ($p = 0.537$; Anderson–Darling) (Fig. 3). For 2006, stepwise selected soil O-horizon THg, Dis Fe and watershed area (ha) as the best predictors for spatial variation of yellow perch THg (yellow perch ng/g rank = 14.2 + 0.314 * SoilO-horizon THg rank + 0.447 * DisFe rank − 0.370 * watershed area rank) ($r^2 = 0.74$, $p = <0.001$). Model performance criteria for this model also looked promising; $df = 3$, $F = 45.17$, VIF[5] = 1.4 to 4.4, DW = 1.62, PRESS = 1601), with residual homoscedasity ($p = 0.751$; Anderson–Darling). High VIFs for 2006, however, indicate multi-colinearity between predictors. Re-running with the only two parameters that were not co-linear, Dis Fe and watershed area ($p = 0.333$, $r = 0.153$ on ranks), produced better results: yellow perch ng/g rank = 22.8 + 0.544 * FeDis rank − 0.612 * watershed area rank, $r^2 = 0.73$, $p = <0.001$, $df = 2$, $F = 61.3$, VIF = 1.0, DW = 1.58, PRESS = 1687, (residuals) $p = 0.973$; Anderson–Darling. The weakest part of the 2006 model was predicting high fish concentrations. The difference in parameters chosen under the stepwise regression procedures is likely a major function of contrasting variability or structure of each data set. The trade-off for obtaining better prediction by using the 2006 model is the need for obtaining two parameters (watershed area + Dis Fe [2006 model] vs. soil O-horizon THg [2005 model]). The selection and utility of each

[1] Degrees of freedom.
[2] *F*-statistic.
[3] Durban Watson statistic.
[4] Predicted residual sums of squares.
[5] Variance inflation factor.

model is ultimately a judgment call by the scientist. Overall, the developed regression models and concentration-rank plots (Fig. 3) in this study can help with interpreting THg concentrations in yellow perch and similar trophic level fish species for untested lakes of the greater Superior National Forest and surrounding boreal ecosystem.

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