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Mercury in streams at Grand Portage National Monument (Minnesota, USA): Assessment of ecosystem sensitivity and ecological risk

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HIGHLIGHTS

- GRPO is an ecosystem that is sensitive to mercury contamination.
- MeHg values in GRPO streams and food webs are elevated relative to the region.
- Mercury enrichment may be due in part to historic local trading activity.
- GRPO fish pose a dietary risk to sensitive piscivores, but not to humans.

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ABSTRACT

Mercury (Hg) in water, sediment, soils, seston, and biota were quantified for three streams in the Grand Portage National Monument (GRPO) in far northeastern Minnesota to assess ecosystem contamination and the potential for harmful exposure of piscivorous fish, wildlife, and humans to methylmercury (MeHg). Concentrations of total Hg in water, sediment, and soil were typical of those in forest ecosystems within the region, whereas MeHg concentrations and percent MeHg in these ecosystem components were markedly higher than values reported elsewhere in the western Great Lakes Region. Soils and sediment were Hg-enriched, containing approximately 4-fold more total Hg per unit of organic matter. We hypothesized that localized Hg enrichment was due in part to anthropogenic pollution associated with historic fur-trading activity. Bottom-up forcing of bioaccumulation was evidenced by MeHg concentrations in larval dragonflies, which were near the maxima for dragonflies sampled concurrently from five other national park units in the region. Despite its semi-remote location, GRPO is a Hg-sensitive landscape in which MeHg is produced and bioaccumulated in aquatic food webs to concentrations that pose ecological risks to MeHg-sensitive piscivores, including predatory fish, belted kingfisher, and mink.

1. Introduction

The Great Lakes region of North America contains abundant aquatic and forest resources, including parks and forests managed by national, state, and provincial agencies. The aquatic resources of this region are contaminated with Hg of primarily atmospheric source (Evers et al., 2011; Wiener et al., 2012a), that poses a threat to fish and wildlife because of the bioavailability, toxicity, biomagnification, and reproductive effects of MeHg (Scheuhammer et al., 2007, 2012; Tan et al., 2009; Lavoie et al., 2013). Aquatic food webs are important pathways for biotic exposure to MeHg, and exposure levels in many lakes in the Great Lakes region are high enough to adversely affect the reproduction and health of piscivorous fish and wildlife (Burgess and Meyer, 2008; Evers et al., 2011; Sandheinrich et al., 2011; Wiener et al., 2012b). In humans, the consumption of fish is the primary pathway for exposure to MeHg (Mergler et al., 2007). Most recreational fishing in the Great Lakes region is done in inland lakes and streams (Evers et al., 2011), and frequent consumers of sport fish are at risk to adverse effects of MeHg exposure (Imm et al., 2005; Knobeloch et al., 2006, 2007; McCann, 2011).

Wet and dry atmospheric depositions are the primary pathways for the entry of Hg into watersheds and inland waters in northeastern Minnesota, and the broader Great Lakes Region (Wiener et al., 2006; Woodruff and Cannon, 2010; Risch et al., 2012a, 2012b), and analyses of lacustrine sediment show that most of this deposited Hg is from

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anthropogenic sources (Engstrom and Swain, 1997; Engstrom et al., 2007; Drevnick et al., 2011). Moreover, studies of inland lakes indicate that atmospheric deposition is the primary source of Hg accumulating as MeHg in fish and other biota in aquatic food webs (Wiener et al., 2006; Munthe et al., 2007; Orihel et al., 2007; Harris et al., 2007).

The majority of the Hg in wet and dry atmospheric depositions is inorganic (Hall et al., 2005). Methylmercury, the organic compound that bioaccumulates and biomagnifies in food webs, is produced by methylating bacteria in anaerobic environments in bed sediments, hydric soils, wetlands, and perhaps even water columns (Benoit et al., 2003; Branfireun et al., 2005; Gilmour et al., 2013). Water bodies and landscapes can differ markedly in their sensitivity to atmospheric Hg loadings, depending on the extent to which inorganic mercury is transformed by microbes to MeHg at the base of the food web (Wiener et al., 2003; Munthe et al., 2007).

Mercury was quantified in selected physical and biotic components from three streams in Grand Portage National Monument, a national park unit in northeastern Minnesota on the north shore of Lake Superior. We hypothesized that, despite its semi-remote location, landscape factors, biogeochemical cycling, and historic anthropogenic activity have resulted in risks to resident piscivorous biota and humans. Objectives of this study were (1) to quantify total Hg and MeHg in unfiltered and filtered stream water, suspended particles (seston), bed sediment, riparian soil, larval dragonflies, and fish; (2) to assess potential risks of MeHg in the food webs in these streams to fish, wildlife, and humans; and (3) to assess the sensitivity of these stream ecosystems to Hg. This study was part of a larger effort to quantify bioaccumulative contaminants in aquatic food webs in US national park units across the western Great Lakes region (Route et al., 2011, 2014; Wiener et al., 2013).

2. Material and methods

2.1. Study area

Grand Portage National Monument (Monument or "GRPO") is located near the United States-Canada border. The Monument, situated within the Grand Portage Indian Reservation, was established to commemorate and protect a premier site of the 18th century fur trade (White, 2005) and to assist the Grand Portage Band of Lake Superior Chippewa in preserving and interpreting the culture of Ojibwe people. The Monument's namesake is the 14-km Grand Portage between Lake Superior and the western terminus at Fort Charlotte on the Pigeon River. The portage intersects the watersheds of three streams (Grand Portage Creek, Poplar Creek, and Snow Creek) that span the Monument from east to west (Lafrancois and Glase, 2005; Fig. 1).

The present study focused on reaches of Grand Portage Creek, Poplar Creek, and Snow Creek within the boundaries of the Monument (Table 1). Grand Portage Creek flows directly into Lake Superior, whereas Poplar Creek and Snow Creek flow into the Pigeon River.

Water in these streams during our study (2009–2012) had low to circum-neutral pH (range 6.2–8.1), high concentrations of dissolved organic carbon (DOC, 15–26 mg/L), low to moderate dissolved sulfate (0.5–7.5 mg/L) and conductivity (55–139 μS/cm), and low hardness (42–80 mg/L) and alkalinity (31–65 mg/L), values characteristic of the dystrophic waters of boreal ecosystems (Lafrancois et al., 2009) (Supplementary Data (SD) Table 1).

The landscape is topographically complex with two principal geologic formations. The Pigeon River diabase dikes are basaltic intrusions cut through Rove formation shales and siltstones (Green et al., 1987; Morey, 1969). Glacial processes have deposited till in valleys between the dikes where clayey soils of lacustrine origin are often mantled with silty to loamy deposits (Gafvert, 2009) (Fig. 1).

The watersheds are composed primarily of second-growth forest (Winterstien, 2002), including Spruce–Fir–Aspen and Aspen–Birch/Boreal Conifer forest associations (Hop et al., 2010). The principal land cover classes in the three drainage basins are deciduous forest, evergreen forest, mixed forest, shrub/scrub, and woody wetlands (Table 1). These five cover classes together accounted for 94% to 97% of the basin area upstream of our stream-sampling stations. The three streams in this study are influenced by beaver-impounded wetlands (Moen and Moore, 2011), which can be active sites of methylmercury production and export to downstream reaches (Roy et al., 2009). Emergent herbaceous wetlands accounted for about 1.6% of the upstream basin area in Grand Portage and Poplar creeks and 4.6% of the upstream area in Snow Creek (Table 1).

Most of the Poplar Creek watershed and the entire Snow Creek watershed are within the Swamp River Till Plain, whereas the Grand Portage Creek watershed is entirely within the North Shore Till Plain (Miller et al., 2001). These till plains are differentiated by glacial landforms, bedrock types, topographic roughness, lake and stream distributions, wetland patterns, depth to ground water table, soil parent material, and pre-European settlement vegetation (Minnesota DNR, 2014). The climate of the North Shore Till Plain is significantly affected by Lake Superior, which increases annual snowfall, summer precipitation,

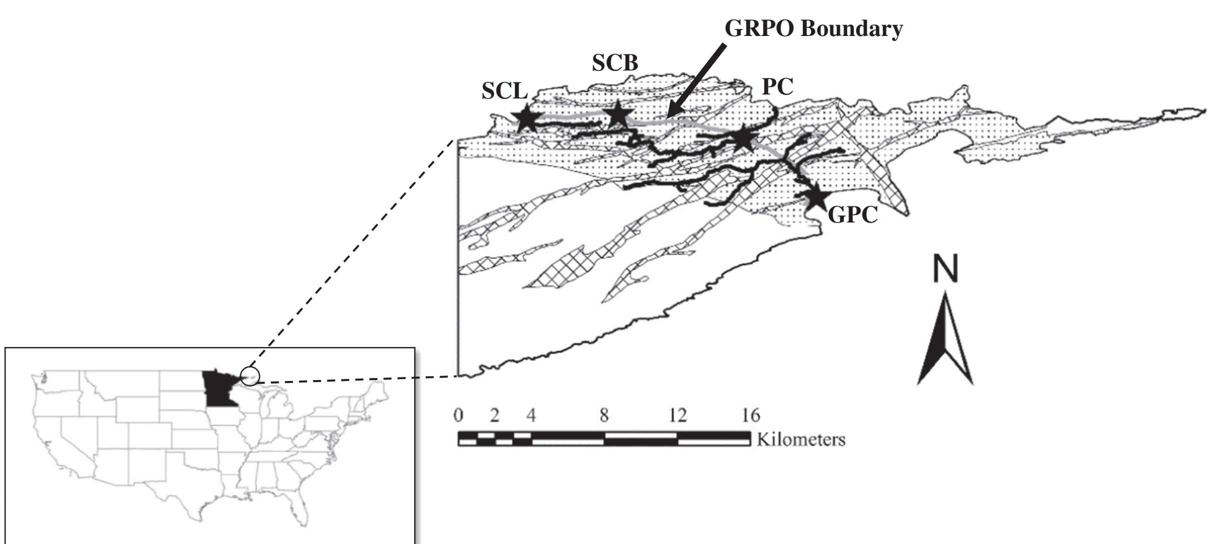

Fig. 1. Schematic map of the Grand Portage National Monument region of far northeastern Minnesota (USA). Our four sampling locations are denoted by stars: "GPC" = Grand Portage Creek, "PC" = Poplar Creek, "SCB" = Snow Creek Beaver Pond, "SCL" = Snow Creek Lower Reach. GRPO monument area is shown in gray. Two regional geological formations are shown: rove formation shales and siltstones (stippled areas) and Pigeon River diabase dikes (cross-hatched areas) (2 column figure).

Table 1
Characteristics and percent land cover of specific vegetation of sampled stream sites and watersheds at Grand Portage National Monument.

Variable[a]	Grand Portage Creek	Poplar Creek	Snow Creek
Stream order	2	2	1
Total length of stream, km	13.6	12.1	2.2
Elevation, m (min–max)	186–534	299–534	382–451
Drainage area, km^2	18.13	11.43	4.05
National land cover class, % of area			
Deciduous forest	19.2	11.2	13.0
Evergreen forest	32.4	38.0	34.2
Mixed forest	16.7	16.4	26.0
Shrub/scrub	12.6	8.2	9.4
Woody wetlands	13.5	23.6	11.7
Emergent herbaceous wetlands	1.7	1.6	4.6
Other	3.9	1.1	1.2

[a] Drainage area attributes represent the portion of each basin upstream from the most downstream sampling station in each stream. Estimates of basin drainage area were derived with high resolution (1 m) LiDar data from MNGEO, a database from the State of Minnesota. Land cover data were derived from the US Geological Survey National Land Cover Database (Fry et al., 2011).

and the length of growing season, whereas the Swamp River Till Plain has a cool continental climate that is less affected by Lake Superior (University of Minnesota, 1981).

2.2. Sample collection, processing, and Hg determinations

Sampling was done at four sites: the lower reach of Grand Portage Creek, the south branch of Poplar Creek, and at two sites in Snow Creek, including the lower reach and a beaver pond in the upper reach. All sampling was done during late May through early June. In 2010–2012, we sampled and analyzed bed sediment, stream water, and seston from each stream. Soil from the forest floor was sampled near stream margins during 2012. In 2009–2012 we sampled larval dragonflies and prey fish as biosentinel organisms for detecting spatiotemporal patterns in the concentration of MeHg in aquatic food webs (Wiener et al., 2007; Haro et al., 2013).

Surficial soils were collected between 2 and 3 m from the margin of each stream. A stainless steel corer equipped with acid-washed plastic sleeves was used to collect the top 5–10 cm of soil from five randomly selected locations, and these subsamples were then composited (typically a mixture of the O and A horizons). Two such composite samples were collected along each stream, and stored frozen in zip-seal bags until processing. Bed sediments were collected with an acid-washed plastic corer from three locations in each streambed where larval dragonflies were also obtained. Both soils and sediments were stored frozen until processing and analysis in the laboratory. Soils and sediments were lyophilized, sieved, and homogenized with a mortar and pestle. Total Hg in soil and sediment was determined by direct combustion analysis (US Environmental Protection Agency; EPA Method 7473; US EPA, 2007). Methylmercury was determined on a MERX-M Autoanalyzer (Brooks-Rand, Inc.) with an adaptation of EPA Method 1630 (US EPA, 2001), which consisted of steam distillation followed by cold vapor atomic fluorescence spectrophotometry (CVAFS; see detailed methods in the Supplementary Data). Measures of air-dried sediment and soil organic matter were taken by percent mass lost on ignition in aluminum pans at 550 °C for 5 h.

Unfiltered and filtered stream water was sampled at mid-depth about 1–2 m from the stream margin, typically within 1 m of the channel center. Water was collected in acid-washed Teflon bottles with a peristaltic pump and filtered with in-line acid-washed 0.45-μm polyethersulfone filters. Samples to be analyzed for dissolved sulfate (Dionex IC-90 ion chromatograph) and DOC (Shimadzu TOC-V-CSH analyzer) were collected concurrently with the samples for Hg determinations. Aqueous pH, temperature, dissolved oxygen, and conductivity were measured in situ with a multi-parameter probe (Thermo-Fisher Orion 5-Star). Water samples were promptly acidified to 0.5% (v/v) HCl and stored in a refrigerator until analysis. Total Hg in water was determined by an adaptation of EPA Method 1631 (US EPA, 2002), and MeHg by an adaptation of the steam distillation-CVAFS method (EPA Method 1630).

Seston (suspended particulate matter) was collected by pumping 1 to 2 L of stream water onto ashed, quartz-fiber filters held in an acid-washed filter pack. Filters were removed from the packs and stored frozen in plastic petri dishes until analysis. Seston filters for total Hg analysis (collected during 2011–2012) were oxidized in small Teflon vials containing deionized water and analyzed by a modification of EPA Method 1631. Seston filters for MeHg analysis (collected 2010–2012) were steam distilled and analyzed by the modification of EPA Method 1630.

Larval dragonflies (Insecta: Odonata: Anisoptera) were sampled with dip nets from the streambed and from woody structure along the stream margins. We focused on larger larvae (late instars), which were expected to emerge soon as winged adults. In the field, larvae were handled with stainless steel forceps and held in zip-seal bags with stream water. Larvae were held overnight in aerated water at room temperature to allow egestion of gut contents, and then placed into plastic vials and stored in a domestic freezer until further processing. In the laboratory, larvae were thawed, identified to species, photographed, measured (body length and wet weight), lyophilized whole, weighed (dry weight), homogenized, and analyzed individually for total Hg and MeHg. Methods for processing and analysis of larvae have been described elsewhere (Haro et al., 2013; Wiener et al., 2013).

Fish were captured with a DC-pulse backpack electrofisher. Fish were collected from flowing reaches of Grand Portage and Poplar creeks. In Snow Creek, all but one fish were obtained from two beaver ponds impounding the stream; one of these beaver ponds was in the upper reaches (near the Grand Portage boardwalk), and the second was in the lower reaches of Snow Creek. Each fish was identified to species, measured (total length and wet weight), lyophilized, homogenized, and analyzed individually for total Hg by direct mercury analysis with EPA Method 7473 on a Milestone DMA-80 analyzer (US EPA, 2007). Total Hg accumulates almost entirely as MeHg in both whole fish (Drysdale et al., 2005; Greenfield and Jahn, 2010; Van Walleghem et al., 2007) and axial fillets (Grieb et al., 1990; Bloom, 1992). We analyzed 454 whole prey fish of 7 species from the three streams; these included blacknose dace (*Rhinichthys atratulus*), longnose dace (*Rhinichthys cataractae*), creek chub (*Semotilus atromaculatus*), central mudminnow (*Umbra limi*), fathead minnow (*Pimephales promelas*), slimy sculpin (*Cottus cognatus*), and brook stickleback (*Culaea inconstans*). Skinless fillets (axial muscle tissue) were dissected and analyzed from 47 additional fish, including 35 rainbow trout (*Oncorhynchus mykiss*) from Grand Portage Creek and 12 creek chub from Poplar Creek; no rainbow trout or large creek chub were captured from Snow Creek. Detailed methods for sampling, processing, dissection, and analysis of fish have been described elsewhere (Wiener et al., 2013) or are provided in the Supplementary data.

2.2.1. Quality assurance

The precision and accuracy of total Hg and MeHg determinations were estimated by the analyses of (1) analytical and procedural blanks, (2) replicate samples, (3) spiked samples, and (4) reference materials from the National Institute of Standards and Technology (NIST; NIST-2976) and the National Research Council of Canada (NRCC; TORT-2, DORM-3, DOLT-4). Determinations of percent mass loss on ignition for sediment and soils were replicated and analyzed concurrently with blanks. Quality-assurance metrics during analyses of each sample matrix are documented in detail in the Supplementary Data (Table SD 2).

2.3. Assessment of risk

2.3.1. Risk to fish

To assess the potential for direct effects of MeHg exposure on fish, we compared Hg concentrations in whole fish from the streams to a threshold concentration (200 ng/g wet weight in whole fish) associated with sublethal and reproductive effects (Beckvar et al., 2005). Concentrations below this threshold value are not expected to adversely affect the health or reproduction of freshwater fish. To assess the ecological risk of MeHg to piscivorous fish in the streams, we compared Hg concentrations in whole prey fish to the estimated dietary threshold (40 ng/g wet weight) for reproductive effects of MeHg on piscivorous fish (Depew et al., 2012a, 2013).

2.3.2. Risk to piscivorous wildlife

Both piscivorous birds and mammals occur in or near the park unit. Avian piscivores include osprey (*Pandion haliaetus*), common merganser (*Mergus merganser*), hooded merganser (*Lophodytes cucullatus*), red-breasted merganser (*Mergus serrator*), common tern (*Sterna hirundo*), belted kingfisher (*Ceryle alcyon*), American bittern (*Botaurus lentiginosus*), cattle egret (*Bubulcus ibis*), great blue heron (*Ardea herodias*), and little blue heron (*Egretta caerulea*). The avian species considered most likely to feed on small fish in the streams and associated wetlands at GRPO include belted kingfisher, great blue heron, American bittern, and little blue heron. Mammalian piscivores in the area include mink (*Mustela vison*) and river otter (*Lontra canadensis*).

We used the belted kingfisher and the mink as model piscivores to assess potential ecological risks of MeHg in fish in the streams at GRPO to fish-eating wildlife. Each of these species is distributed across much of the United States and Canada, and each forages in a diverse array of aquatic habitats, with small fish typically composing half (mink) or most (belted kingfisher) of their diet (Salyer and Lagler, 1949; Davis, 1982; Evers et al., 2005; Basu et al., 2007; Kelly et al., 2009). The belted kingfisher and mink are both considered highly sensitive to MeHg, and each has been used in assessments of ecological risks of MeHg in aquatic food webs (Lazorchak et al., 2003; Basu et al., 2007; Scheuhammer et al., 2007; Walters et al., 2010). Belted kingfishers establish feeding territories along streams, with the length of the territory dependent upon reproductive status of the birds and inversely related to density of prey (Davis, 1982). The mean stream length of the territory ranges from about 0.4 km for non-breeding kingfishers (Davis, 1982) to about 2.2 km for breeding pairs (Brooks and Davis, 1987). The home range of mink along streams ranges from about 1 to 5 km (Gerrell, 1970). Information on diet, home range, and other pertinent biological information on these species can be found in US EPA (1993).

We used Wildlife Values derived by Lazorchak et al. (2003) as screening-level, dietary benchmarks to assess potential risks of MeHg in fish on the health and reproduction of these two model piscivores. The screening dietary benchmark (Hg concentration in whole prey fish) was 30 ng/g wet weight for the belted kingfisher and 70 ng/g wet weight for mink.

2.3.3. Risk to fish-eating humans

Fish consumption is the primary pathway for exposure of humans to MeHg (Mergler et al., 2007; McKelvey and Oken, 2012). To assess the potential for harmful MeHg exposure in humans consuming stream fish, we compared Hg concentrations in axial muscle of rainbow trout from Grand Portage Creek to the EPA tissue residue criterion for MeHg (300 ng/g wet weight), which was established to protect the health of humans who eat noncommercial fish (Borum et al., 2001). Nearly all of the Hg in the fillets of fish is MeHg (Grieb et al., 1990; Bloom, 1992), hence the total Hg concentrations measured in rainbow trout are valid estimates of MeHg concentrations. We also compared Hg concentrations in rainbow trout to the fish-consumption guidelines recommended by the Great Lakes Fish Advisory Workgroup (2007), which has substantial expertise on bioaccumulative contaminants in fishery resources of the Great Lakes Region and their health risks to humans who consume wild fish. Specifically, we used the Workgroup's recommended fish-consumption guidelines for MeHg-sensitive groups, which include pregnant women, women who may become pregnant, and children under 15 years of age. The guidelines, expressed in ng/g of Hg in edible fish tissue on a wet-weight basis, are as follows: ≤50 ng/g-Unrestricted fish consumption; 51–110-Limit fish consumption to 2 meals per week; 111–220-Limit fish consumption to 1 meal per week; 221–950-Limit fish consumption to 1 meal per month; and >950-No fish consumption.

3. Results

3.1. Hg in ecosystem components

Surficial soils sampled from the four stream sites in 2012 had mean concentrations of total Hg ranging from 62 to 164 ng/g dry weight (dw) (Table 2). Mean MeHg in soils ranged from 1.6 to 2.9 ng/g dw, representing 1.0% to 2.6% of total Hg. Total Hg in soil correlated well with percent mass loss on ignition (LOI), a surrogate measure of organic matter content ($r^2 = 0.92$; Fig. 2, upper panel). The slope between total Hg and LOI in GRPO soils was more than 3-fold that for soils sampled in 2012 from five other park units in the western Great Lakes region and from the Experimental Lakes Area in northwestern Ontario (K. Rolfhus, unpublished data).

Mean total Hg in surficial bed sediments sampled from the four stream sites at GRPO during 2010–2012 ranged from 37 to 141 ng/g dw (Table 2). Mean MeHg in sediment varied from 0.81 to 1.82 ng/g dw, accounting for 1.2% to 2.2% of total Hg, a range similar to that in soils. Total Hg in sediment exhibited a similar relation to percent LOI (Fig. 2, lower panel), and the four stream sites at GRPO exhibited a slope approximately 4.5-fold that in sediment from five other national park units (data combined) in the western Great Lakes region. The total Hg/LOI slope for GRPO soil was 1.5-fold that of GRPO sediment.

Mean concentrations of total Hg in water ranged from 8.7 to 16.9 ng/L in unfiltered samples and from 5.4 to 8.3 ng/L in filtered (0.45 μm) samples, with filter-passing mercury averaging 62% (range 49–75%) of the total Hg present in unfiltered samples (Table 3). Mean concentrations of MeHg ranged from 0.57 to 2.7 ng/L in unfiltered samples and from 0.35 to 1.9 ng/L in filtered samples, with filter-passing MeHg accounting for 63% (range 45–74%) of the total MeHg present in unfiltered water. Methylmercury accounted for 15% (range 4.5–28%) of the total Hg in unfiltered samples and for 14% (range 6.4–33%) of the total Hg in filtered samples. The Beaver Pond site on the upper reaches of Snow Creek had the highest concentrations of MeHg and %MeHg, while Poplar Creek was highest for total Hg.

In seston, mean concentrations ranged from 50 to 241 ng/g dry weight for total Hg and from 1.2 to 16.2 ng/g dry weight for MeHg, which accounted for 5.3% ± 2.1% of the total Hg in seston (Table 3). Seston from the Beaver Pond at Snow Creek had the highest concentration of MeHg.

3.2. Bioaccumulation of MeHg in streams

Larvae of the families Aeshnidae and Corduliidae were the most widely distributed dragonflies collected at GRPO, inhabiting all four stream sites and accounting for 64% of the 201 larvae sampled and analyzed (Table 4). Larvae from three other dragonfly families, including 22 cordulegastrids, 1 gomphid, and 50 libellulids, were found at one or two of the four sites. Mean concentrations of MeHg in larval dragonflies from the four stream sites ranged from 118 to 190 ng/g dry weight in aeshnids and from 136 to 185 ng/g in corduliids. Methylmercury accounted for more than 90% of the total Hg in dragonfly larvae for most taxa and stream sites. For example, mean %MeHg in larvae from the four stream sites ranged from 91% to 97% in corduliids and from 81% to 94% in aeshnids.

Mean whole-body concentrations of Hg in individual prey-fish species varied from 24 to 58 ng/g wet weight in Grand Portage Creek (two species), from 49 to 91 ng/g in Poplar Creek (five species), and from 50 to 63 ng/g in the lower reach of Snow Creek (four species)

Table 2
Total mercury, methylmercury (MeHg), percent MeHg, and percent loss on ignition (LOI) in surficial soils (upper 5 cm) and sediments (upper 5 cm) near streams in Grand Portage National Monument. For soils, two composited samples, each composed of subsamples of surface soil collected in 2012 from five locations along each stream site, were analyzed.

Stream		Total Hg (ng/g dry weight)		MeHg (ng/g dry weight)		MeHg (%)	LOI (%)	
	n	Mean	Range	Mean	Range	Mean	Mean	Range
Soil								
Grand Portage Creek	2	–[a]	–[a]	2.26	1.99–2.54	–[a]	7.2	4.9–9.4
Poplar Creek	2	62	58.2–65.5	1.58	1.58–1.59	2.6	6.7	6.6–6.7
Snow Creek (beaver pond)	2	152	150–154	1.58	1.58–1.59	1.0	19.2	18.9–19.5
Snow Creek (lower reach)	2	164	152–178	2.90	2.65–3.16	1.8	17.4	17.0–17.8
Sediment								
Grand Portage Creek	6	37	–[b]	0.81	0.40	2.2	5.8	4.9–6.7
Poplar Creek	7	61	6	0.90	0.10	1.5	10	7.2–15
Snow Creek (beaver pond)	7	141	40	1.70	0.42	1.2	27	22–36
Snow Creek (lower reach)	7	132	16	1.82	0.34	1.4	18	8.8–22

[a] These samples were not analyzed for total Hg.
[b] Total Hg in Grand Portage Creek samples are reported for 2011 and 2012 only.

(Table 5). In the beaver pond at upper Snow Creek, the concentration of Hg averaged 35 ng/g in the central mudminnow, the only species obtained from that site in sufficient numbers for statistical estimation. Species means for whole fish within individual stream sites ranged from 24 ng/g wet weight in slimy sculpin to 91 ng/g in blacknose dace and longnose dace. In axial fillets, concentrations of total Hg averaged 40 ng/g wet weight in rainbow trout from Grand Portage Creek, ranging from 23 to 69 ng/g in individual fish (Table 5). Concentrations were higher in fillets of creek chub from Poplar Creek, averaging 91 ng/g and ranging from 54 to 168 ng/g.

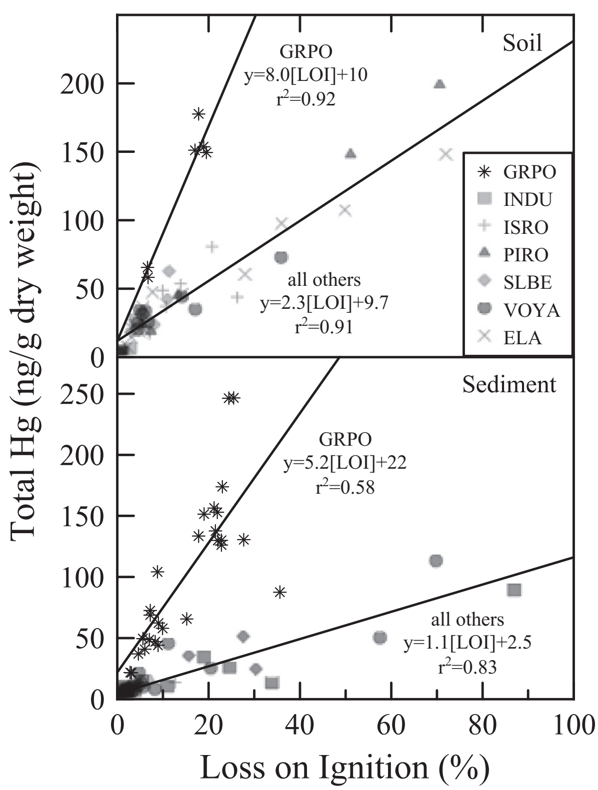

Fig. 2. Relation of total mercury in surficial soil (upper panel) and sediment (lower panel) to percent loss on ignition (LOI), a surrogate measure of organic matter content. Mercury levels in samples from GRPO are shown in relation to mercury in samples from five other US national park units in the Great Lakes region and from the Experimental Lakes Area (ELA) in northwestern Ontario. Other park units were Voyageurs National Park (VOYA), Isle Royale National Park (ISRO), Pictured Rocks National Lakeshore (PIRO), Sleeping Bear Dunes National Lakeshore (SLBE), and Indiana Dunes National Lakeshore (INDU) (K. Rolfhus, unpublished data). Soil samples from the ELA were sampled in 2012 with the same methods as those used in the US national park units (1.5 column figure).

3.3. Assessment of risk

3.3.1. Risk to fish

Only 4 of the 454 prey fish analyzed had whole-body concentrations of Hg exceeding 200 ng/g wet weight, an estimated tissue threshold associated with sublethal and reproductive effects in fish. These include 2 longnose dace from Grand Portage Creek, 1 blacknose dace from Poplar Creek, and 1 central mudminnow from Snow Creek. Mercury concentrations in most (99%) of the prey fish analyzed would not be expected to adversely affect health or reproduction. Stream-specific, mean concentrations of total Hg exceeded 40 ng/g wet weight, an estimated dietary threshold associated with diminished reproduction of piscivorous fish, in six of the seven species of prey fish analyzed (Table 5). Only slimy sculpin from Grand Portage Creek (24 ng/g) and central mudminnows from Snow Creek (beaver pond; 35 ng/g) contained a mean concentration less than the 40 ng/g threshold value for reproductive effects on piscivorous fish.

3.3.2. Risk to piscivorous wildlife

The screening-level dietary benchmark for the belted kingfisher (30 ng/g wet weight) was exceeded in 79% of the whole fish analyzed from the three streams (Table 5). The dietary benchmark for belted kingfisher was exceeded in 61% of the fish from Grand Portage Creek, 97% from Poplar Creek, and 84% from Snow Creek. If we excluded data for slimy sculpin, which was found only in Grand Portage Creek and had substantially lower concentrations than the other fishes analyzed, 83% of the fish from Grand Portage Creek (all longnose dace) had concentrations exceeding the screening benchmark for belted kingfisher. Mean concentrations of Hg in all species except slimy sculpin exceeded the dietary benchmark for belted kingfishers (Table 5).

The screening-level benchmark for Hg in the diet of mink (70 ng/g wet weight) was exceeded in 23% of the whole fish analyzed from the three streams (Table 5). The dietary benchmark for mink was exceeded in 11% of the fish from Grand Portage Creek, 47% of the fish from Poplar Creek, and 17% of the fish from Snow Creek. In Poplar Creek, mean concentrations of Hg in three species of fish (blacknose dace, longnose dace, and brook stickleback) exceeded the estimated dietary benchmark for mink.

3.3.3. Risk to fish-eating humans

None of the fillets of rainbow trout or creek chub had a Hg concentration exceeding the US Environmental Protection Agency fish-tissue criterion of 300 ng/g wet weight for MeHg (Table 5). Concentrations in 31 of the 35 rainbow trout were less than 50 ng/g; no restrictions

Table 3
Total mercury (Hg) and methylmercury (MeHg) in unfiltered water, 0.45-μm filtered water, and seston sampled from streams in Grand Portage National Monument. For seston, total Hg is reported for samples collected during 2011–2012, and MeHg is for samples collected during 2010–2012.

Sample type and stream									
Water	Total Hg (ng/L)					MeHg (ng/L)				
		Unfiltered		Filtered			Unfiltered		Filtered	
	n	Mean	SE	Mean	SE	n	Mean	SE	Mean	SE
Grand Portage Creek	6	8.65	1.11	5.43	0.64	6	0.57	0.16	0.35	0.04
Poplar Creek	5	16.9	–[b]	8.25	1.76	5	0.77	0.03	0.57	–[a]
Snow Creek (beaver pond)	6	9.47	0.29	5.82	0.70	6	2.70	0.22	1.90	0.25
Snow Creek (lower reach)	6	9.81	1.85	7.39	1.80	5	1.89	–[a]	0.85	0.20

Seston	Total Hg (ng/g dry weight)			MeHg (ng/g dry weight)			MeHg (%)
	n	Mean	Range	n	Mean	SE	Mean
Grand Portage Creek	2	50.2	40–61	6	1.20	0.04	2.4
Poplar Creek	2	74.3	16–133	6	1.21	0.51	4.2
Snow Creek (beaver pond)	2	138	77–200	6	16.2	4.56	11.4
Snow Creek (lower reach)	2	241	134–348	5	8.65	3.46	3.3

[a] Samples are reported for 2010 and 2012 only due to bottle leakage.
[b] Samples are reported for 2011 and 2012 only due to bottle leakage.

on fish consumption by humans are recommended by the Great Lakes Fish Advisory Workgroup (2007) for fish with concentrations less than 50 ng/g. Concentrations in the other 4 rainbow trout ranged from 51 to 69 ng/g, values in the lower end of the range (51–110 ng/g) for which the Workgroup recommended that fish consumption be limited to 2 meals per week. Concentrations in axial muscle of creek chub were higher than those in rainbow trout (Table 5), presumably due to differences in trophic position between these two species. The diet of creek chub often includes small prey fish, such as shiners, whereas rainbow trout are primarily invertivorous (Becker, 1983).

4. Discussion

4.1. Ecosystem contamination and sensitivity to Hg

Overall, the lower reach and beaver pond sites along Snow Creek consistently exhibited the greatest MeHg concentrations in soil, sediment, water, and seston. These sites consistently had a higher DOC, lower pH, lower DO, and a slightly higher percentage of emergent herbaceous wetland cover relative to the other streams. Each of these factors has been associated with enhanced MeHg production in aquatic ecosystems (Wiener et al., 2003; Munthe et al., 2007).

Concentrations of total Hg and MeHg in unfiltered water from streams at GRPO were at the upper end of the range of base-flow concentrations measured in non-urban rivers and streams in the western Great Lakes region (Hurley et al., 1995; Balogh et al., 2002, 2004; Chasar et al., 2009; Brigham et al., 2009; Tsui and Finlay, 2011; Babiarz et al., 2012), and far exceeded median values for 337 non-mining impacted streams in a national assessment by the USGS (MeHg 0.11 ng/L, total Hg 1.90 ng/L, Scudder et al., 2009). The percentages of filter-passing MeHg and total Hg in GRPO waters (60–65%) were similar to values reported for regional streams. However, the fraction of total Hg present as MeHg at GRPO streams (mean 15%, range 4.6 to 29%; often considered a proxy for relative Hg methylation potential) generally exceeded values reported for the western Great Lakes Region (range 0.2 to 17%; Hurley et al., 1995; Balogh et al., 2004) and the national assessment by USGS (median 5.4%; Scudder et al., 2009), indicating that the landscape at GRPO is highly conducive to Hg methylation. Concentrations of total Hg and MeHg in GRPO seston (ranges 74 to 241 ng/g and 1.2 to 16.2 ng/g dw, respectively) were generally similar to values reported for Minnesota streams (ranges 54 to 514 ng/g and 0.5 to 39 ng/g dw, respectively; Tsui and Finlay, 2011).

Total Hg concentrations in GRPO bed sediment and adjacent soil were typical of the region, whereas MeHg values were substantially higher. Concentrations of total Hg were highest at Snow Creek by a factor of about 2, likely due to its greater organic matter content. Total Hg concentrations in these sediment were less than the median Hg level in surficial or modern lacustrine sediments from 20 lakes in forest landscapes of northeastern Minnesota (Engstrom et al., 2007), yet both total Hg and MeHg in GRPO sediment were greater than the median values for 257 stream sediments across the US (MeHg 0.51 ng/g dw,

Table 4
Total mercury, methylmercury (MeHg), and percent MeHg in families of larval dragonflies collected from streams in Grand Portage National Monument during 2009–2012.

Stream	Family	Total Hg[a] (ng/g dry weight)			MeHg[a] (ng/g dry weight)			MeHg (%)	
		n	Mean	SE	n	Mean	SE	Mean	SE
Grand Portage Creek	Aeshnidae	10	162	13	10	143	14	87	2.7
	Cordulegastridae	10	168	7.5	10	159	6.2	95	2.2
	Corduliidae	8	149	20	9	136	15	91	4.9
Poplar Creek	Aeshnidae	19	129	9.6	19	118	8.9	94	5.0
	Cordulegastridae	12	126	7.0	12	118	8.1	95	6.5
	Corduliidae	31	194	14	32	185	15	96	2.1
	Libellulidae	1	177	–	1	111	–	63	–
Snow Creek (beaver pond)	Aeshnidae	7	142	14	7	129	13	92	4.5
	Corduliidae	30	140	7.4	30	136	7.9	96	2.0
	Gomphidae	1	70	–	1	54	–	77	–
	Libellulidae	58	134	6.0	58	124	6.3	92	1.9
Snow Creek (lower reach)	Aeshnidae	11	233	11	11	190	20	81	7.1
	Corduliidae	16	168	4.5	16	163	5.8	97	1.6

[a] Dry-weight concentrations presented here can be converted to wet-weight values by multiplying by 0.203, given that the moisture content of larval dragonflies sampled from six regional national park units averaged 79.7% (95% CI, 79.5–79.9%); R. Haro, unpublished data.

Table 5
Total length, weight, and concentration of total mercury (Hg) in whole body and axial muscle tissue (skinless fillets) of fish collected from streams in Grand Portage National Monument during 2009–2012, with percentages (%) of whole fish exceeding screening dietary benchmarks for the belted kingfisher (30 ng/g wet weight) and mink (70 ng/g) ("na" indicates not applicable).

Fish tissue analyzed and stream	Species	n	Total length (mm)		Wet weight (g)		Hg (ng/g wet weight)			Percent of fish exceeding benchmarks	
			Median	Range	Median	Range	Mean	SE	Range	30 ng/g	70 ng/g
Whole prey fish											
Grand Portage Creek	Longnose dace	110	77	49–107	3.9	0.93–13.2	58	4	21–355	83	18
	Slimy sculpin	68	58	41–83	2.7	0.84–7.9	24	1	8–54	26	0
Poplar Creek	Creek chub	49	78	56–105	5.2	1.5–14.3	49	3	29–118	92	12
	Blacknose dace	43	74	46–89	5.0	1.1–8.6	91	6	43–242	100	74
	Longnose dace	16	71	64–97	4.3	2.3–8.5	91	9	50–194	100	75
	Central mudminnow	14	47	32–77	1.2	0.65–5.6	67	6	37–123	100	50
	Brook stickleback	7	47	44–55	1.2	0.80–1.8	73	10	47–112	100	43
Snow Creek (beaver pond)	Central mudminnow	40	47	33–88	1.2	0.32–5.2	35	2	15–69	50	0
	Fathead minnow	1	77	–	4.7	–	75	–	–	100	100
	Brook stickleback	1	50	–	1.4	–	27	–	–	0	0
Snow Creek (lower reach)	Central mudminnow	83	69	36–124	3.4	0.5–19.5	63	2	25–204	99	28
	Fathead minnow	10	72	61–83	4.4	2.6–7.6	50	4	29–65	90	0
	Brook stickleback	7	55	49–62	1.7	1.4–2.8	53	4	39–74	100	43
	Creek chub	5	102	90–144	9.4	7.5–33.6	51	3	43–60	100	0
Axial muscle tissue											
Grand Portage Creek	Rainbow trout	35	111	75–308	15.5	4.5–278.6	40	2	23–69	na	na
Poplar Creek	Creek chub	12	130	99–168	23.6	9.8–48.5	91	11	54–168	na	na

total Hg 30.3 ng/g dw; Scudder et al., 2009). Total Hg in GRPO surficial soils were similar to those measured at nearby Voyageurs National Park, MN (A-horizon range, 58 to 256 ng/g dw; Wiener et al., 2006), while both MeHg concentration and the fraction of total Hg present as MeHg were similar to or higher than those measured in soils of other forest ecosystems (Tabatchnick et al., 2011; Obrist, 2012). As with the streamwater samples, our analyses of GRPO sediments and soils are indicative of an ecosystem with active, substantial Hg methylation.

Concentrations of total Hg in soil and sediment at GRPO, relative to organic matter content (%LOI), were about 4-fold those sampled concurrently from six other regional sites and are particularly striking. The ratios of total Hg to %LOI for the other five national parks in the western Great Lakes region were remarkably similar, yielding soil Hg:C molar ratios of about 3.8×10^{-8}, assuming that labile organic matter in the region is about 40% carbon by mass (K. Rolfhus, unpublished data). Soils at GRPO, in contrast, had a Hg:C molar ratio of 12×10^{-8}. This pattern was also evident for bed sediment, with GRPO exhibiting much greater Hg:C ratios (3.1×10^{-8}) than the other regional sites combined (6.7×10^{-9}). While elevated relative to regional sites, the GRPO [total Hg]/%LOI value of 5.2 ng/(g·%) (regression slope in Fig. 2, lower panel) was similar to the median value of 5.91 ng/(g·%) observed in the national assessment of US streams compiled by Scudder et al. (2009). Several other studies have indicated strong relations between soil organic matter and total Hg concentration in forest soils (Grigal, 2003; Munthe et al., 2007). Moreover, Gabriel et al. (2012) showed a relation between Hg concentrations in the O and A soil horizons to those in yellow perch (*Perca flavescens*) in 10 northeastern Minnesota watersheds. The sites at Voyageurs National Park and the Experimental Lakes Area are both within 150 km of GRPO, yet their ratios of soil Hg to %LOI were similar to those in other national park units across the broader western Great Lakes region (K. Rolfhus, unpublished data). The linear relations between total Hg and organic matter content (%LOI) in both soil and sediment at GRPO suggest a dispersed local/regional source of Hg that has supplemented the inputs from atmospheric deposition. Wet and dry depositions are the dominant pathways for entry of Hg into the forest-covered landscapes of northeastern Minnesota and the western Laurentian Great Lakes region, an area where on-site geologic sources of Hg are small (Wiener et al., 2006; Engstrom et al., 2007; Woodruff and Cannon, 2010; Drevnick et al., 2011; Risch et al., 2012a, 2012b).

It is possible that the enrichment of Hg in GRPO sediment and soil is related to historic fur trade activity. Vermilion, a synthetic mercuric sulfide pigment derived from cinnabar ore (Gettens et al., 1972) was a principal trade item and gift in the 18th century fur trade (Hanson, 1971). An account of English customs records indicates that Holland was a dominant exporter of vermilion until 1760, when Chinese and German exports began influencing the market (Harley, 1970). By the late 18th century, the majority of Chinese vermilion supplying the fur trade likely originated from Kwei-chow province of China (Hanson, 1971). The Northwest Fur Company supply of vermilion at Grand Portage was voluminous enough that one 1797 inventory of their goods left over from a season of trade found more than 100 lb (White, 2004). Indeed, total Hg concentrations in C-horizon soils at three locations along the historic trail were 1.7 to 2.1-fold those in A-horizon soils, with no apparent local geogenic source (Laurel Woodruff, US Geological Survey, St. Paul, MN, pers. commun.).

Complex transformations have recently been documented for Hg cycling in forest ecosystems with the use of stable isotopes (Demers et al., 2013), indicating potential pathways for soil re-emission of gaseous Hg and recycling via stomatal uptake, oxidation, and litterfall processes. It is also possible that the microbial methylation is enhanced by the enriched Hg on organic matter, leading to enhanced MeHg production. If the regional Hg:LOI slope observed in Fig. 2 is representative of the typical "preferred" ligand concentration on organic matter (e.g., thiols), excess Hg may be more weakly bound and reactive (Skyllberg et al., 2003; Qian et al., 2002).

4.2. Bioaccumulation of MeHg

The bioaccumulation of MeHg in GRPO streams, expressed as the logarithm of the bioaccumulation factor (BAF = [food web component] / [unfiltered aqueous methylmercury], units L kg^{-1}), was compared to that in other water bodies within and beyond the western Great Lakes region (Fig. 3). For this comparison, we used data from 20 water bodies (19 lakes and 1 wetland complex) in five other national park units within the region (K. Rolfhus, unpublished data), as well as published data for 46 streams across the western Great Lakes region and the southeastern US (Babiarz et al., 2001, 2012; Brigham et al., 2009; Chasar et al., 2009; Tsui and Finlay, 2011). Bioaccumulation factors for prey fish from GRPO and 5 regional national park units were calculated with whole-body dry weight concentrations of total Hg in small prey fishes within narrow total-length intervals for each species.

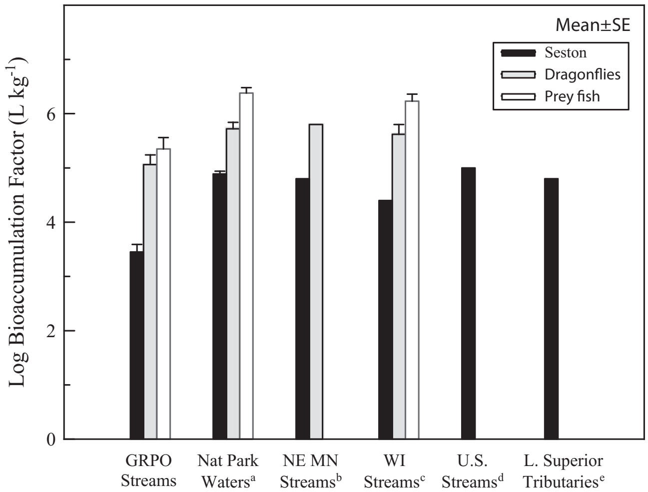

Fig. 3. Logarithm of bioaccumulation factors (BAFs) for components of aquatic food webs in GRPO streams relative to (a) 19 lakes and one wetland complex in five other US national park units in the western Great Lakes region (K. Rolfhus, unpublished data), including Indiana Dunes National Lakeshore, Isle Royale National Park, Pictured Rocks National Lakeshore, Sleeping Bear Dunes National Lakeshore, and Voyageurs National Park, (b) 8 streams from northeastern Minnesota (Tsui and Finlay, 2011), (c) 3 streams from Wisconsin (Brigham et al., 2009; Chasar et al., 2009), (d) 15 streams from Wisconsin, Minnesota, Michigan, Georgia, and Florida (Babiarz et al., 2001), and (e) 20 tributaries to Lake Superior in the US and Canada (Babiarz et al., 2012). The seston:water BAF is analogous to the partition coefficient, K_d. Bars represent means and standard errors (1.5 column figure).

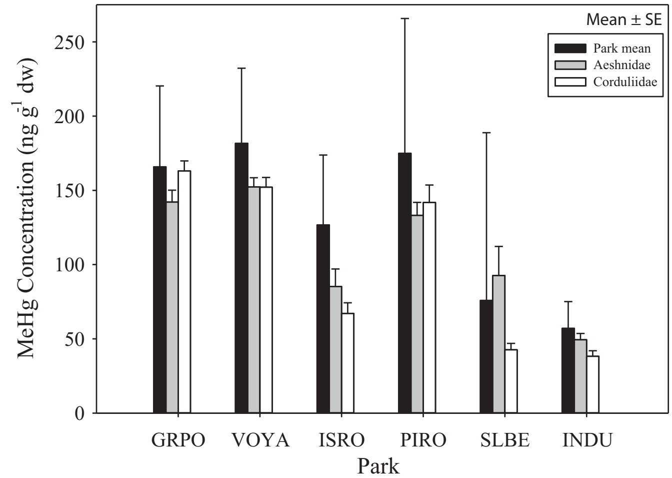

Fig. 4. Mean concentrations of methylmercury in larval dragonflies in streams at GRPO in relation to larvae sampled from water bodies at five other national park units in the western Great Lakes region (R. Haro, unpublished data), including Voyageurs National Park (VOYA), Isle Royale National Park (ISRO), Pictured Rocks National Lakeshore (PIRO), Sleeping Bear Dunes National Lakeshore (SLBE), and Indiana Dunes National Lakeshore (INDU). Park means are weighted by abundance in analyzed samples, and simple geometric means are shown for each family of dragonflies (1.5 column figure).

Measures of the trophic transfer of MeHg, as indicated by bioaccumulation factors relative to unfiltered water, suggest that GRPO was less efficient than other regional lakes and streams at transferring MeHg to seston. The BAF for seston:water, which is analogous to the partition coefficient (K_d), was about one $\log_{10}$ unit lower at GRPO than at the other lakes and streams. In addition to the high aqueous concentrations of MeHg in GRPO streams, this may be the result of high concentrations of dissolved organic matter in stream water (DOC 15–26 mg/L), which can suppress seston:water bioaccumulation factors because of the competitive sorption of MeHg to dissolved organic matter possessing strong ligands (Rolfhus et al., 2011; Tsui and Finlay, 2011). Bioaccumulation factors for dragonfly larvae and prey fish from GRPO streams also appear to be lower than those for other lakes and streams of the Great Lakes Region (Fig. 3).

Even with the lower BAFs at GRPO, our analyses of larval dragonflies indicated that MeHg was bioaccumulating to high concentrations in the food webs of these streams (Fig. 4). In larval aeshnids and corduliids, the two most widely distributed dragonfly taxa in the stream sites sampled at GRPO, mean concentrations of MeHg equaled mean concentrations in larvae from two other national park units in the western Great Lakes region and substantially exceeded concentrations in larvae from three others (Fig. 4). Our findings for streams at GRPO indicate the utility of larval dragonflies as biosentinels of MeHg in lotic and lacustrine food webs (Haro et al., 2013).

4.3. Risks to piscivorous fish and wildlife

Mercury concentrations in whole prey fish from the streams at GRPO exceeded the estimated dietary threshold (40 ng/g wet weight) associated with reproductive effects of MeHg on piscivorous fish (Depew et al., 2012a). Moreover, belted kingfishers and mink feeding on fish from streams at GRPO could also be exposed to harmful concentrations of dietary MeHg. For mink, risks would be greatest for animals feeding on fish from Poplar Creek, where the dietary benchmark (70 ng/g wet weight) was exceeded in almost half of the fish analyzed.

The avian species used in our risk assessment, the belted kingfisher, is considered to be highly sensitive to MeHg. Another avian piscivore, the common loon (*Gavia immer*), nests and feeds on many lakes and reservoirs near the present study area, but does not feed in small streams such as those studied at GRPO. Egg-injection experiments show that the common loon is moderately sensitive to MeHg (cf. Heinz et al., 2009; Kenow et al., 2011); thus, toxicological benchmarks for the common loon can be used to gage the potential risks to fish-eating birds that have moderate sensitivity to MeHg. The estimated dietary threshold for adverse behavioral impacts of MeHg in adult loons is 100 ng/g wet weight in prey fish, whereas a Hg concentration of 180 ng/g in prey fish adversely affects reproductive success of adult loons (Depew et al., 2012b, 2013). Mean concentrations of Hg in the seven species of fish sampled from the streams at GRPO were less than these dietary benchmarks for loons, suggesting that ecological risks of MeHg would be small for moderately sensitive, avian piscivores that forage in the streams at GRPO.

4.4. Risk to humans

Concentrations of Hg in fillets of small rainbow trout sampled from Grand Portage Creek were below levels considered harmful to sensitive groups of humans who eat fish, such as women of childbearing age and children (Great Lakes Fish Advisory Workgroup, 2007). In general, the small streams at Grand Portage National Monument do not contain resident populations of long-lived piscivorous fish that would be expected to accumulate high concentrations of MeHg in axial muscle tissue.

5. Conclusions

Our findings indicate that the GRPO streams are in a Hg-sensitive landscape, with unusually high concentrations of MeHg and high %MeHg in water, soil, and sediment relative to other regional lakes and streams. Elevated MeHg concentrations in the lower food web are biomagnified to high levels in resident biota (dragonfly larvae and prey fish), but the bioaccumulation factors at GRPO are similar to or lower than other studies for other areas in the region. The soil and sediment at GRPO contain about 4-fold more total Hg per unit of organic matter than other forested sites in the western Great Lakes region. The cause of this enrichment is unclear, but the available data suggest possible contamination from the historic fur trade in addition to atmospheric deposition. Mercury concentrations in prey fish were high enough to pose sublethal and reproductive risks to MeHg-sensitive piscivores, but were not high enough to pose significant risks to the prey fish or to fish-consuming humans. This study adds to the growing body of evidence that landscape susceptibility (poorly buffered soils, low-mid pH, cold and oligotrophic boreal conditions) significantly affects methylmercury bioaccumulation in lakes and streams, even in regions far removed from emissions sources.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.scitotenv.2015.01.079.

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