Mercury in streams at Grand Portage National Monument: Evidence of ecosystem sensitivity and ecological risk

Prepared for Brandon Seitz, Grand Portage National Monument

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Project description. In 2008, the University of Wisconsin-La Crosse began quantifying mercury in aquatic food webs in six national park units in the western Great Lakes region, including Grand Portage National Monument (GRPO). Initial funding (2008-2009) for this project was provided by the National Park Service, Great Lakes Inventory and Monitoring Network. Intensified monitoring during 2010-2012 is supported by the Great Lakes Restoration Initiative. Principal objectives are (1) to identify parks and water bodies where concentrations of methylmercury are high enough to adversely affect fish and wildlife, and (2) to assess spatiotemporal patterns in methylmercury contamination of aquatic food webs. Methylmercury is a highly toxic compound that readily bioaccumulates in exposed organisms and can biomagnify to harmful concentrations in organisms in upper trophic levels of aquatic food webs (Scheuhammer et al. 2007, Sandheinrich and Wiener 2011, Evers et al. 2011, 2012).

Monitoring at GRPO. We sampled and analyzed water, seston (suspended particulate material, including algae), sediment, fish, and larval dragonflies from three streams that collectively span the park unit from east to west. Study sites at GRPO include Snow Creek (beaver pond in upper reaches and lower reaches), Poplar Creek (south branch), and Grand Portage Creek (lower reach). Analytical results reveal elevated concentrations of both total mercury and methylmercury in these stream systems.

High mercury levels in streamwater. Concentrations of total mercury and methylmercury in streamwater from GRPO are substantially higher than concentrations typically found in lakes and streams in the western Great Lakes region (e.g., Rolfhus et al. 2011). In 2010, for example, methylmercury in unfiltered streamwater averaged 1.5 ng/L (nanogram per liter, equivalent to parts per trillion), ranging from 0.55 to 2.3 ng/L, and total mercury averaged 7.8 ng/L (range 6.5-9.3 ng/L). For comparison, mean concentrations in unfiltered water from 17 lakes in Voyageurs National Park (Minnesota), a national park containing game fish with high concentrations of mercury, ranged from <0.04 to 0.30 ng/L for methylmercury and from 0.45 to 3.3 ng/L for total mercury (Wiener et al. 2006).

GRPO—a mercury-sensitive ecosystem. On average, methylmercury accounted for 13% of the total mercury in filtered stream water, indicating that much of the inorganic mercury in these stream systems is available for microbial conversion to methylmercury. These results indicate that these streams and their basins are mercury-sensitive ecosystems in which environmental conditions are favorable for conversion of inorganic mercury—the

dominant form in wet and dry deposition—to methylmercury, which readily accumulates in lotic food webs.

Sources. In the Great Lakes region, atmospheric deposition is the dominant source of mercury, and geologic (i.e., natural) sources of mercury are small (Wiener et al. 2006, Woodruff and Cannon 2010, Evers et al. 2011, Drevnick et al. 2012). It can be reasonably inferred from these recently published regional studies that (1) nearly all of the mercury present in streams and forest soils at GRPO is from wet and dry deposition, (2) that most of this atmospherically deposited mercury is from anthropogenic emissions, and (3) that most of the mercury bioaccumulating as methylmercury in streams at GRPO is from anthropogenic sources.

Bioaccumulation and ecological risk. In 2010, prey fish were sampled from three streams in the park and analyzed whole for total mercury, which accumulates in fish as methylmercury. Mean concentrations were highest, exceeding 100 ng/g wet weight (nanograms per gram, equivalent to parts per billion) in blacknose dace (*Rhinichthys atratulus*) and longnose dace (*Rhinichthys cataractae*) from Poplar Creek. These mean concentrations in dace substantially exceed the estimated dietary threshold (40 ng/g wet weight in prey fish) associated with reproductive effects of mercury on piscivorous fish that feed on prey fish (Depew et al. *in press*). Mean concentrations of mercury in most of the other prey fishes analyzed also exceeded the 40 ng/g threshold for reproductive effects on piscivorous fish; these included creek chub (43 ng/g) and central mudminnow (56 ng/g) from Poplar Creek, fathead minnow (58 ng/g) and central mudminnow (55 ng/g) from Snow Creek, and longnose dace from Grand Portage Creek (67 ng/g). The maximal concentrations in individual fish were 242 ng/g in blacknose dace and 211 ng/g in longnose dace. These maximal values exceed dietary thresholds associated with adverse effects of methylmercury on the health and reproduction of fish-eating birds (Evers et al. 2011).

Mean concentrations of methylmercury (145 ng/g dry weight) and total mercury (151 ng/g dry weight) in larval dragonflies from the streams at GRPO substantially exceeded those in larvae from the five other park units (Table 1). In addition, the fraction of total mercury present as methylmercury (95%) in larval dragonflies from GRPO exceeded that in larvae from the other five park units (Table 1).

The high concentrations of methylmercury in larval dragonflies may indicate significant risks for insectivorous songbirds that forage and nest near streams at GRPO. Studies in eastern North America have documented unexpectedly high concentrations of mercury (present as methylmercury) in certain terrestrial invertivores, including passerine songbirds (Evers et al. 2012). Most songbirds with elevated concentrations of mercury are linked trophically to mercury-methylating environments—such as wetlands, streams, or lakes—and feed on spiders or emergent insects with aquatic larval stages (Brasso and Cristol 2008, Cristol et al. 2008, Evers et al. 2012). Methylmercury in the diet of reproducing female birds is transferred rapidly to the developing egg, and the embryo is the most sensitive life stage (Scheuhammer et al. 2007, Heinz et al. 2009). Methylmercury

exposure and its potential effects on reproductive success of invertivorous songbirds at GRPO has not been assessed but merits critical evaluation.

Table 1. Mean total mercury (Hg), methylmercury (MeHg), and percent methylmercury in larval dragonflies sampled from six park units during 2008-2009. Mean values were calculated from data for all species from each park unit. Sample size (n) indicates the number of dragonflies analyzed individually for both total mercury and methylmercury.

Park unit	n	MeHg (ng/g dry weight)	Total Hg (ng/g dry weight)	Percent MeHg
GRPO	59	145	151	95
INDU	16	53	66	91
ISRO	139	57	73	74
PIRO	101	63	92	73
SLBE	119	51	64	77
VOYA	117	98	119	85

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