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Mercury in aquatic forage of large herbivores: Impact of environmental conditions, assessment of health threats, and implications for transfer across ecosystem compartments

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HIGHLIGHTS

- Macrophyte community composition may mediate generalist herbivore mercury exposure.
- Many abiotic factors were poor predictors of macrophyte MeHg concentrations.
- Macrophyte MeHg was not higher for lakes expanded by beaver than for glacial lakes.
- Macrophytes bioconcentrated MeHg in inverse proportion to ambient concentrations.
- Beaver may be vulnerable to sub-lethal neurological effects of Hg in some areas.

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ABSTRACT

Mercury (Hg) is a leading contaminant across U.S. water bodies, warranting concern for wildlife species that depend upon food from aquatic systems. The risk of Hg toxicity to large herbivores is little understood, even though some large herbivores consume aquatic vascular plants (macrophytes) that may hyper-accumulate Hg. We investigated whether total Hg and methylmercury (MeHg) in aquatic forage may be of concern to moose (*Alces alces*) and beaver (*Castor canadensis*) by measuring total Hg and MeHg concentrations, calculating sediment–water bioconcentration factors for macrophyte species these herbivores consume, and estimating herbivore daily Hg consumption. Abiotic factors impacting macrophyte Hg were assessed, as was the difference in Hg concentrations of macrophytes from glacial lakes and those created or expanded by beaver damming. The amount of aquatic-derived Hg that moose move from aquatic to terrestrial systems was calculated, in order to investigate the potential for movement of Hg across ecosystem compartments by large herbivores. Results indicate that the Hg exposure of generalist herbivores may be affected by macrophyte community composition more so than by many abiotic factors in the aquatic environment. Mercury concentrations varied greatly between macrophyte species, with relatively high concentrations in *Utricularia vulgaris* (>80 ng g^{-1} in some sites), and negligible concentrations in *Nuphar variegata* (~6 ng g^{-1}). Macrophyte total Hg concentration was correlated with water pH in predictable ways, but not with other variables generally associated with aquatic Hg concentrations, such as dissolved organic carbon. Moose estimated daily consumption of MeHg is equivalent to or below human reference levels, and far below wildlife reference levels. However, estimated beaver Hg consumption exceeds reference doses for humans, indicating the potential for sub-lethal nervous impairment. In regions of high moose density, moose may be ecologically important vectors that transfer Hg from aquatic to surrounding terrestrial systems.

1. Introduction

1.1. The mercury concern for generalist mammalian herbivores

As a leading contaminant of U.S. water bodies, mercury (Hg) has been extensively studied within algae-based aquatic food webs (Boening, 2000; Ullrich et al., 2001; United States Environmental Protection Agency [USEPA], 2011; Wang et al., 2004). Comparatively, little is known about Hg transfer between aquatic vascular plants (macrophytes) and herbivores. Nonetheless many macrophyte species are hyper-accumulators of Hg and other metals, maintaining toxic metal levels hundreds of times greater than the water columns in which they grow (Vardanyan and Ingole, 2006), and removing over 99% of Hg in water over a period of 16 days (Kamal et al., 2004). Thus, it is important to know if macrophyte Hg concentrations

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may be of concern for herbivores that rely on aquatic vascular plants as a major component of their diets. Mercury toxicity impairs nervous, cardiovascular, and reproductive systems, among others, with potential effects that include motor and sensory debilitation and depressed reproductive success (Tchounwou et al., 2003; World Health Organization, 2008). Vertebrate herbivores may be particularly vulnerable due to the absence of mechanisms to restrict or detoxify Hg (Klaassen et al., 1986; Wren et al., 1980). Species such as moose (*Alces alces*) and beaver (*Castor canadensis*) consume macrophytes as an estimated 14–37%, and 55–80% of summer and annual diets, respectively (Tischler, 2004; Milligan and Humphries, 2010; Severud et al., 2013). These mammals may be directly affected by chronic Hg ingestion, and could serve as vectors for Hg transfer between aquatic and terrestrial ecosystem compartments.

1.2. Variation of mercury concentrations in macrophytes

Macrophyte species vary in rates of metal uptake and accumulation, and in metal partitioning between roots, rhizomes, and shoots (Ohlson and Staaland, 2001; Rai, 2009). For example, maximum Hg concentrations of 8 macrophyte species in the same water body varied by 2 orders of magnitude (Cajander and Ihantola, 1984). The extent to which specific macrophyte species accumulate or exclude Hg is unknown or poorly understood for many of the macrophyte species that moose and beaver consume, including widely eaten *Utricularia vulgaris*, a non-rooted, insectivorous plant; and *Nuphar variegata*, the yellow water lily.

N. variegata may be particularly important to beaver diets year-round where it occurs, because beaver include *N. variegata* rhizomes in their winter food cache, and can acquire additional rhizomes throughout the winter (Milligan and Humphries, 2010; Slough, 1978). Recent stable isotope analyses of claws, hair, and muscle found that beaver consume an equal or greater amount of aquatic forage in winter as in summer, indicating a high rate of rhizome consumption (Milligan and Humphries, 2010; Severud et al., 2013). Extensive rhizome consumption may be of concern because rhizomes and roots of some macrophyte species accumulate more Hg than aboveground portions do (Afrous et al., 2011; Moreno et al., 2008), and are "hot spots" where methylation rates exceed those of surrounding sediments (Blaabjerg and Finster, 1998; Mauro et al., 2002). The Hg accumulation of *Nuphar* rhizomes remains understudied, and is not readily predicted by how the taxon accumulates other metals (Campbell et al., 1985).

Within a given species, macrophyte concentration of Hg is affected by chemical and physical conditions of the aquatic environment (Rai, 2009), largely because these conditions influence Hg speciation (Brooks and Robinson, 1998). In particular, factors found to affect methylmercury (MeHg) availability include dissolved organic carbon (DOC), sulfate and sulfide, temperature, pH, light, and oxygen availability (Ullrich et al., 2001). These abiotic influences on Hg availability and speciation may help to explain why bioconcentration factors (ratio of metal concentration in organisms to exposure metal concentrations) do not follow a predictable pattern for Hg as for many other metals (McGeer et al., 2003). Macrophyte bioconcentration can vary greatly for the same species based on conditions. For example, bioconcentration in *Schoenoplectus californicus* varied by a factor of 11 between two constructed wetland systems (Sundberg-Jones and Hassan, 2007).

1.3. Potential effect of large herbivores on mercury speciation and distribution

Beaver may alter the speciation and bioavailability of Hg on the landscape by creating water bodies that have distinct chemical and physical characteristics, such as high DOC (which is generally associated with higher total Hg concentrations, Selvendiran et al., 2008; Ullrich et al., 2001), low dissolved oxygen (DO), and low pH (which tend to increase methylation rates, Margolis et al., 2001; Palmer et al., 2000; Snodgrass and Meffe, 1998). Meanwhile, moose may particularly affect Hg movement between aquatic and terrestrial systems by eating Hg-rich aquatic plants and subsequently excreting excess Hg on land. In contrast to beaver, moose spend the majority of their time on land when not consuming macrophytes (Belovsky and Jordan, 1978).

1.4. Present study

The extent to which Hg concentrations in aquatic forage may be of concern to moose and beaver was investigated by measuring total Hg (Hg_t) and MeHg concentrations, calculating bioconcentration factors in macrophyte species these herbivores are known to consume, and estimating herbivore daily Hg_t and MeHg consumption from aquatic sources. The amount of aquatic-derived Hg that moose move from aquatic to terrestrial systems was calculated in order to assess transfer across ecosystem compartments. Whether macrophyte Hg concentrations could be predicted by environmental conditions was assessed by (1) correlation analyses between macrophyte Hg_t and MeHg concentrations versus water and sediment conditions (water Hg_t, MeHg, conductivity, DO, DOC, light, N, oxidation reduction potential [ORP], pH, temperature; sediment Hg_t, MeHg, Ca, K, Mg, P, SO_4), and (2) determination of the extent to which Hg in macrophytes varied between glacial lakes, and lakes created or expanded through beaver damming. We hypothesized that moose and beaver Hg consumption levels would fall below toxic thresholds for wildlife, particularly in lakes of low-Hg ecosystems; and that that lakes expanded by beaver would host plants with higher MeHg concentrations due to environmental conditions that promote Hg accumulation and methylation. If true, recovering beaver populations in North America (Collen and Gibson, 2000) may increase the availability of toxic Hg to macrophyte-consuming herbivores on the landscape.

2. Material and methods

2.1. Study area

All study sites were inland water bodies of two national protected areas: Isle Royale National Park, MI, USA, and Grand Portage National Monument, MN, USA. These parks are located within ~35 km of one-another in the Lake Superior watershed (Fig. 1), but have displayed notably different levels of Hg in recent years. Isle Royale lakes recently had among the lowest concentrations of water Hg_t and MeHg in national parks of the upper Midwest U.S., while ponds in Grand Portage had among the highest concentrations (Rolfhus, K.R., *unpublished data*). Isle Royale is a ~536 km^2 island wilderness area with 43 named inland lakes. Copper mining occurred at restricted sites on the island over a century ago (Kerfoot et al., 2009), but our study sites are removed from these disturbed locations. On Isle Royale, types of water bodies studied include "damned lakes": lakes created or expanded through beaver damming over a continuous period of at least 25 years ($n = 6$), "glacial lakes": lakes formed by glacial carving, with no expansion of the littoral zone from beaver dams ($n = 9$), and "riverine ponds": ponds established by beaver damming of stream outflow ($n = 1$). Grand Portage National Monument is a ~14 km^2 reserve on the Northwest shore of Lake Superior, which contained two riverine ponds that were sampled during this study (details not shown, Fig. 1).

2.2. Sample collection and analysis

2.2.1. Sample collection

Mercury clean techniques were applied for sample collection, processing, and analysis (USEPA, 1996). Polyvinyl gloves were worn at all stages of sample collection and handling. Water samples were collected from 5 locations of each water body at a depth of 50 cm, and compiled into at least 2 composite samples per water body. Composite water