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The influence of avian biovectors on mercury speciation in a bog ecosystem

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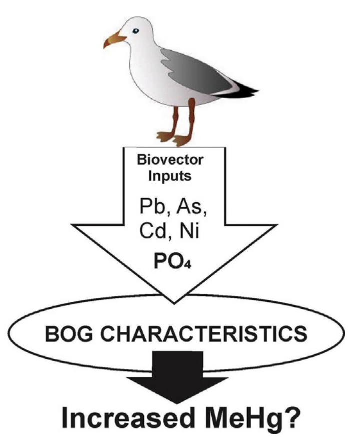
HIGHLIGHTS

- Hg speciation was examined in a bog ecosystem with avian biovector colonization.
- Avian-impacted bog had elevated dissolved TOC, phosphate (PO_4^{3-}), and several metals including methylmercury.
- Avian biovector subsidies may influence net Hg methylation.

GRAPHICAL ABSTRACT



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ABSTRACT

Methylmercury (MeHg) is a neurotoxin and endocrine disruptor that bioaccumulates and biomagnifies through trophic levels, resulting in potentially hazardous concentrations. Although wetlands are known hotspots for mercury (Hg) methylation, the effects of avian biovectors on these processes are poorly understood. We examined Hg speciation and distribution in shallow groundwater and surface water from a raised-bog with over 30 years of avian biovector (herring gulls *Larus argentatus* and great black-backed gulls *Larus marinus*) colonization and guano input. Compared to the reference site, the avian-impacted bog had elevated concentrations of total dissolved organic carbon (TOC), total Hg, MeHg, phosphate (PO_4^{3-}), and other trace metals, notably Pb, As, Cd and Ni. Spatial interpolation showed that the densest area of gull nesting was co-located with areas that had the highest concentrations of PO_4^{3-}, MeHg, As and Cd, but not total mercury (THg), and models suggested that Mn, PO_4^{3-}, and dissolved TOC were strong predictors of MeHg. Our findings suggest that while these gulls may not be a significant source of Hg, the excess of PO_4^{3-} (a well recognised component of guano) and the subsequent changes in water chemistry due to avian biovector subsidies may increase net Hg methylation.

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1. Introduction

Mercury (Hg) is a neurotoxic trace metal that occurs naturally in the environment, but has increased in concentration in the atmosphere due to anthropogenic activities such as fossil fuel combustion (Crump and Trudeau, 2009; Gustin et al., 2008; Sunderland and Chmura, 2000). The three main types of Hg relevant to mercury cycling in food webs are: elemental (Hg(0))—the most prevalent species in air, divalent (Hg(II))—the most prevalent species in water, and methylmercury (MeHg)—the most prevalent species in upper trophic level species (O'Driscoll et al., 2005). When Hg(0) is emitted into the atmosphere it can be transported long distances, primarily due to air currents, to areas far from the initial emission source (O'Driscoll et al., 2005). During transport, Hg(0) can undergo oxidation and conversion into Hg(II), and can move via wet and dry deposition into aquatic and terrestrial environments, and further migrate via sediment movement or water currents. Additionally, Hg(II) from terrestrial and aquatic environments can be reduced to Hg(0), re-volatized back into the atmosphere, bound to sediment, or subject to bacterial methylation and conversion to MeHg that is available to biota (Gochfeld, 2003; O'Driscoll et al., 2005). MeHg can bioaccumulate and biomagnify through food webs, and can result in hazardous concentrations in higher trophic level species and cause neurological damage and endocrine disruption (Crump and Trudeau, 2009; Gochfeld, 2003; Singh et al., 2011). Due to increasing risk of Hg exposure and its negative repercussions on human and wildlife health, an international agreement to reduce Hg emissions (the Minimata Convention, http://mercuryconvention.org) was ratified in August 2017, and countries now need to implement protocols to monitor Hg levels in the environment (Evers et al., 2016).

Sulfate-reducing bacteria (SRB), and to a lesser degree iron-reducing bacteria (IRB), are responsible for converting Hg bound to organic matter into MeHg (Branfireun et al., 1999; Fleming et al., 2006; Gilmour et al., 1992; Jeremiason et al., 2006). While the Hg cycle is complex, the processes that result in Hg methylation hinge directly upon the activity of SRB and IRB, and these bacteria are primarily influenced by pH levels (Branfireun et al., 1999; Miskimmin et al., 1992), sulfur and iron speciation (Regnell et al., 2001), and dissolved organic carbon (DOC) concentrations (Mazrui et al., 2016; Miskimmin, 1991) of an ecosystem. Wetlands, such as bogs, frequently have high DOC and anoxic conditions, and are often ideal environments for SRB (Jeremiason et al., 2006; Munthe et al., 2007).

The controls on these chemical factors in the most current Hg models (e.g. Regional Mercury Cycling Model and the Quantitative Water Air Sediment Interaction -QWASI model) are based on a number of physical, chemical and microbiological processes and partitioning mechanisms, or use Hg species concentration ratios based on elemental Hg as the key species driving transport (Knightes and Ambrose Jr, 2007; Ethier et al., 2008). However, organisms can alter these processes by acting as biovectors, which transport contaminants through the food web, within an ecosystem, or between ecosystems (Blais et al., 2007). Hereafter, this paper will refer to biovectors on the scale of movement among ecosystems. Because MeHg is a contaminant of concern, and wetlands are hotspots for Hg methylation as well as critical, sensitive ecosystems, it is important to consider the impacts that biovectors can have on the Hg cycle in wetlands. Avian biovectors can contribute significant levels of nutrients, in the form of phosphate (PO_4^{3-}) and nitrate (NO_3^-), and contaminants, such as cadmium (Brimble et al., 2009a, 2009b; Cederholm et al., 1999; Foster et al., 2011) to mercury-sensitive ecosystems due to the gregarious nature of some avian species such as gulls.

In this paper, we provide new insights into the impacts of avian biovector colonization on Hg speciation in bogs by comparing the water chemistry in a relatively pristine reference bog and a nearby degraded bog, called Big Meadow Bog, which hosts a large colony of gulls. To determine Hg speciation, both total mercury (THg) and MeHg were analysed in ground and surface water samples and mapped using geographic information system (GIS) techniques. We predicted that concentrations of these Hg species and nutrients would be higher in Big Meadow Bog due to avian biovector inputs.

2. Methods

2.1. Description of study sites

Big Meadow Bog (BMB; UTM: 710167 4902099, zone 19) and the Reference Bog (RB1; UTM: 709982 4903582, zone 19; Fig. S1) are both located on Brier Island, Nova Scotia, Canada, near the Bay of Fundy. BMB is the largest raised bog on the island (60 ha; 350,450 m wide × 1800 m long). Bogs are characterized by acidic waters, low nutrients (ultraoligotrophic), sphagnum moss and heath family-dominated plant communities, and are mostly dependent upon precipitation for a water source (Reddy and DeLaune, 2008; Wells, 1996). The annual mean temperature for Brier Island is 6.6°C, and the average annual precipitation is 1146 mm; August is typically the driest month and October is the wettest month (climate data available for 1988—1992; Environment Canada, 2016).

RB1 is approximately 750 m to the northwest of BMB, and is similar in length and aspect, but is narrower than BMB (width 100–200 m). RB1 and BMB are in similar geological settings, and RB1 features a fen-lagg and raised bog wetland community similar to what is thought to have been present at BMB before it was ditched in 1958 (Cameron and Leverin, 1949). RB1 is low shrub peatland characterized by low pH levels and the ombrotrophic indicator herb *Rubus chamaemorus*, which is also known to have been common in BMB before ditching. The lagg-fens have higher pH and nutrient levels due to the runoff from basalt, and consequently support calcium-indicating plants (such as *Dasiphora fruticosa*, *Thalictrum pubescens*, *Menyanthes trifoliolata*, *Carex livida*; Wells and Pollett, 1983).

Prior to being ditched, BMB was a typical raised-bog overlaying a woody layer of organic material, similar to RB1, and had a natural drainage system along the northeast and southwest margins of the bog (Spooner et al., 2017). Most of its original raised central profile still remains but is now less pronounced. The northeastern section of BMB drains into the Grand Passage (section of the Bay of Fundy), and the southwestern section drains into Big Pond (a freshwater pond on the southern tip of Brier Island which drains into the Bay of Fundy). BMB has always received inflow from basalt-based slope swamps along its east and west margins. These swamp inputs, coupled with the precipitation input on the central raised bog, mix together in a marginal fen-lagg zone (Kennedy and Drage, 2015). The fen-lagg hydrological inputs historically drained north and south through a system of small streams and pools until 1958 when a series of three, north-south oriented ditches were dug at depths ranging from 1—2 m (Supplementary Material Fig. S1; Kennedy and Drage, 2015). Unsuccessful agricultural trials were conducted for two years (1960—1962) in the north-east section, and subsequently abandoned.

The intensive drainage activities resulted in significant increases in surface water drainage, and further modifications were made to the central bog area throughout the 1960s which caused additional drainage from the edges of the bog to the central ditch (Kennedy et al., 2015). This caused drying in the central dome of the bog, and a shift in vegetation from typical bog plants (such as pitcher plants [*Sarracenia purpurea*], heather [Ericaceae] and sphagnum moss [*Sphagnum spp.*]) to plants that thrive in disturbed sites such as raspberries (*Rubus spp.*) and fireweed (*Epilobium spp.*; Environment and Climate Change Canada, 2016). Between 1988 and 2011, areas of BMB became isolated due to the encroachment of black and white spruce (*Picea mariana*; *P. glauca*; Kennedy and Drage, 2015) trees, while the northern central area became dominated by raspberries and fireweed (Environment and Climate Change Canada, 2016). This change in hydrology also caused the bog surface to dry enough to provide suitable nesting conditions for herring (*Larus argentatus*) and great black-backed gulls