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Methylmercury in water, sediment, and invertebrates in created wetlands of Rouge Park, Toronto, Canada

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ABSTRACT

Thousands of hectares of wetlands are created annually because wetlands provide beneficial ecosystem services. Wetlands are also key sites for production of the bioaccumulative neurotoxin methylmercury (MeHg), but little is known about MeHg production in created systems. Here, we studied methylmercury in sediment, water, and invertebrates in created wetlands of various ages. Sediment MeHg reached 8 ng g^{-1} in the newest wetland, which was significantly greater than in natural, control wetlands. This trend was mirrored in several invertebrate taxa, whose concentrations reached as high as 1.6 μg g^{-1} in the newest wetland, above levels thought to affect reproduction in birds. The MeHg concentrations in created wetland invertebrate taxa generally decreased with increasing wetland age, possibly due to a combination of deeper anoxia and less organic matter accumulation in younger wetlands. A short-term management intervention and/or improved engineering design may be necessary to reduce the mercury-associated risk in newly created wetlands.

1. Introduction

Wetlands are key features for mercury (Hg) transformations within landscapes, particularly for the methylation of inorganic Hg that has accumulated within these systems (St. Louis et al., 1994). Methylmercury (MeHg) is the main bioaccumulative form of Hg. It is biomagnified through the food chain and as a result of chronic exposure through diet, can have detrimental health effects for both wildlife and humans at relatively low levels (Mergler et al., 2007; Scheuhammer et al., 2007). The load of MeHg transported to aquatic systems as well as the accumulation of Hg by aquatic biota has been linked to the area of wetlands within watersheds (Driscoll et al., 2007; Hurley et al., 1995; Wiener et al., 2006). However, given the different biogeochemical environments of different wetland types, MeHg production rates and concentrations vary widely (Mitchell and Gilmour, 2008; Tjerngren et al., 2012).

Outside of the propensity for MeHg production in wetlands, wetlands perform numerous beneficial ecological services within ecosystems. These ecological services may include flood attenuation, the removal of overabundant nutrients, metals, and pesticides, and the provision of important habitat for semi-aquatic organisms and birds (Mitsch and Gosselink, 2007). Historically, enormous expanses of wetlands have been destroyed due to drainage and conversion to farmland, stream channelization, dam construction, mining, filling for development, and sedimentation (van der Valk, 2006), but within the last few decades, the importance of the ecological services provided by wetlands has become better understood. To compensate for historic wetland losses and to protect against further loss of wetland habitat, wetland construction, creation, restoration, and compensatory mitigation projects have more popularly been implemented since the early 1980s (Brix, 1994). Approximately 20,000 ha of wetlands in the United States are created annually as a result of the U.S. Army Corps of Engineers Section 404 dredge-and-fill permit program alone (Mitsch and Gosselink, 2007).

Research on MeHg production within constructed, created, or restored (collectively "artificial") wetlands has been relatively sparse compared to the existing literature on MeHg production in

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natural wetlands like peatlands and marshes, but a few published studies have demonstrated the potential for artificial wetlands to produce MeHg (e.g. Chavan et al., 2007; Rumbold and Fink, 2006). This literature has largely been based on hydrological mass balances and demonstrated that effluent waters or waters within the wetlands are elevated, often by several orders of magnitude, over influent waters (Chavan et al., 2007; Rumbold and Fink, 2006). Particularly for created wetlands, which by definition are created for habitat restoration purposes (Brix, 1994), the potential for biotic uptake of MeHg has not been characterized. Thus, although the potential for a "pollution trade-off" has been recognized between water quality improvement and MeHg production in artificial wetlands (Stamenkovic et al., 2005), the relative risk from MeHg production in wetland creation projects is currently unknown.

The purpose of this research was thus to assess the importance of MeHg production in several created wetlands in Rouge Park, a 47 km^2 protected greenspace located in Toronto, the major urban center of Canada. To assess the potential risk from MeHg due to wetland creation, we measured MeHg and THg concentrations and other biogeochemical variables in multiple matrices (water, sediment, invertebrates) of five wetlands created between one and nine years before sampling, as well as a local (urban) natural wetland and a more distant (rural) natural wetland. We designed our observations around a gradient in created wetland age because we expected that younger created wetlands would constitute a different biogeochemical environment than older created wetlands due to differences in productivity and organic matter accumulation (Ballantine and Schneider, 2009). Our hypothesis was that these differences would manifest as differences in MeHg production in sediment and accumulation in wetland invertebrates.

2. Materials and methods

2.1. Site description

Six of the seven studied wetlands (five created wetlands and one natural wetland) were located within Rouge Park (43°50′N 79°10′W), a 47 km^2 park located within the city boundaries of Toronto, Canada (Fig. 1). As in Brix (1994), we distinguish created wetlands from constructed wetlands. The purpose of a created wetland is to provide habitat whereas the purpose of a constructed wetland is generally to treat water effluent. Rouge Park is currently administered at the municipal/regional level, but is slated to become a Canadian urban national park. Thus there is currently both considerable local and national interest about the environmental characterization of the area. Rouge Park is mainly a mix of forest and agricultural land cover. The wetlands we studied within Rouge Park were all located on former (naturally regenerating) agricultural land or immediately adjacent to agricultural land. For comparison to these wetlands, we also studied a natural, rural wetland located within the Minesing Wetlands complex (44°23′N 79°52′W), approximately 15 km west of Barrie, Ontario or 85 km northwest of Rouge Park. All of the wetlands were similar in that they all were small, shallow, open water wetlands with emergent littoral vegetation (mostly *Typha* spp.), neutral to slightly basic pH, and with mildly reducing surface waters (Table 1). The five created wetlands were built across a nine-year range, between 2001 and 2010. Four of the wetlands were created through winter berming with local soil, which blocked most drainage, allowing the areas to flood. Each has a well defined, but hydrologically unmonitored inlet and outlet. One (Wetland #10) was created by excavating into the existing soil, which resulted in a narrower, ditch-like wetland, without a defined outlet or inlet.

2.2. Water, sediment, and invertebrate sampling

Surface water sampling from the littoral zone of each wetland was conducted on three separate occasions during the summer of 2011, in mid-June, mid-July, and early August. Strict "clean hands–dirty hands" methods were followed for surface water sample collection (Gill and Fitzgerald, 1985). Samples were collected by gloved hand using PETG bottles after rinsing the bottles three times with sample. Bottles were double-bagged and transported in a cooler, on ice, immediately back to the laboratory. In the laboratory, half of each water sample was filtered using an acid-washed, Teflon filtration tower and ashed 0.7 μm glass fiber filters. The other half of the water sample was kept for determination of unfiltered concentrations. Small aliquots of the filtered sample were also collected in separate bottles for the determination of major anions and dissolved organic carbon (DOC). All water

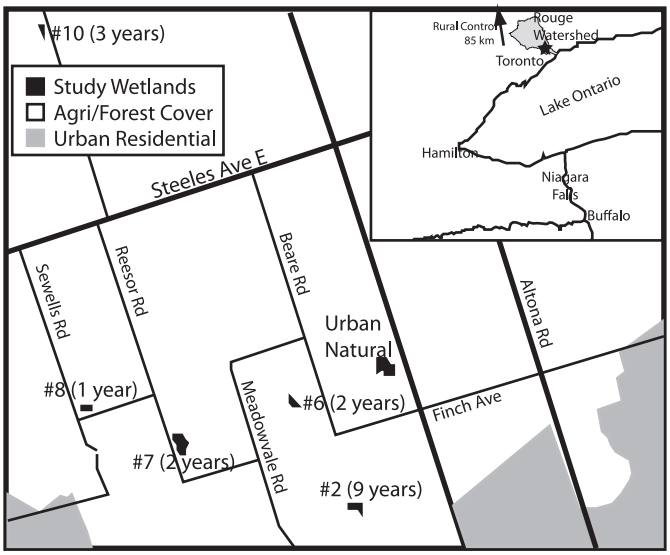

Fig. 1. Location of study wetlands within Rouge Park, Toronto and location of the Rouge River watershed where the park is located (inset). Note the location of the rural natural/control wetland, approximately 85 km north of Rouge Park.

samples for THg and MeHg analysis were preserved through the addition of concentrated trace metal free HCl, to 0.5% concentration in the sample, and then refrigerated in dark bags until analysis.

Multiple sediment cores were obtained once during the summer, from the littoral zone of each wetland during mid-July 2011. Cores were obtained by hand using 5 cm diameter cylindrical polycarbonate tubes. In the laboratory, triplicate sediment cores from each wetland were extruded at three depth intervals (0–2 cm, 2–4 cm and 4–8 cm) and sub-sampled for determination of THg, MeHg, 0.5M HCl-extractable iron, and sediment physical characteristics (organic matter content, bulk density, and porosity). Samples were immediately frozen and later lyophilized prior to analysis. Additional cores obtained immediately adjacent to cores for sediment analysis were similarly extruded and multiple samples from each respective depth interval were vacuum filtered using acid-washed 0.2 μm Nalgene filter units to obtain one composite pore water sample for each depth in each wetland. Samples for THg and MeHg analysis were stored in PETG bottles and preserved with trace metal free HCl, as previously explained. If sample volume was sufficient, additional separate samples for major anions and DOC were also bottled. pH was immediately measured on all pore water samples.

Wetland invertebrates were collected once during the summer from the littoral zone of the wetlands during early to mid-July 2011. To ensure consistent collection across the different wetlands, a D-frame net was utilized by one person at each wetland holding the net firmly on the wetland bottom and sweeping inwards ten times. Invertebrates were collected at 4 different, randomly chosen locations in each wetland. Samples were transferred back to the laboratory in bags and immediately sorted by hand. Invertebrates were sorted to family level, then placed in vials of deionized water and left in a refrigerator overnight to allow the invertebrates to purge their guts. Samples were then drained, frozen, and later lyophilized prior to analysis for THg and MeHg concentrations. Where enough biomass was obtained, samples from the 4 sites in each wetland were analyzed separately as replicates. However, obtaining enough biomass for replicate samples at the family level was difficult and some compositing of samples from the 4 sites within each wetland was often required. The reduction in replication due to sample compositing affected our ability to undertake certain statistical analyses. Where necessary, we thus used individual samples within families as replicates in analysis among orders. The number of replicate samples for MeHg analysis are noted in Table S1 of Supporting Information.

2.3. Analytical methods

Total Hg concentrations in water samples were determined by cold vapor atomic fluorescence spectroscopy (CVAFS) on a Tekran 2600 automated Hg analysis system, as described in US EPA Method 1631 Revision E (USEPA, 2002). Sediment and invertebrate samples for THg analysis were microwave digested in concentrated HNO_3, diluted, and then analyzed the same as water samples. Methylmercury analysis in all samples was conducted by isotope dilution–gas chromatography–inductively coupled plasma mass spectrometry (ID–GC–ICPMS; Hintelmann and Evans, 1997). A known amount of $Me^{199}Hg$ was added to all samples as an internal standard. Prior to quantification, water and lyophilized sediment samples were distilled in a H_2SO_4–KCl–$Cu(SO_4)$ mixture. Methylmercury in invertebrate samples was extracted by gentle boiling in a 25%