Seasonal Patterns of Total and Methyl Mercury Concentrations in Ground and Surface Waters in Natural and Restored Freshwater Wetlands in Northern New York

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Abstract

Among mercury species, methylmercury (MeHg) strongly bioaccumulates and biomagnifies in aquatic food chains, generally controlling the exposure that threatens human and wildlife health. Wetlands are important environments for biogeochemical transformations of Hg, as reducing conditions and wetting/drying cycles promote the production of MeHg. In recent years, nearly half of freshwater wetlands have been lost. In response, there has been an effort to restore freshwater wetlands to improve the ecosystem services they provide. Although wetlands are important landscape features that supply MeHg to downstream aquatic ecosystems, there have been few studies comparing the processing of Hg in restored wetlands with natural wetlands. I measured concentrations of Hg species and ancillary parameters in ground waters and surface waters of four natural and 16 restored wetlands in northern New York for six months, investigating the factors contributing to the differences in concentrations in Hg species among wetlands. I hypothesized that there would be no difference in Hg dynamics between restored and natural wetlands based on concentrations of THg, MeHg and ancillary measurements. Indeed, I found no obvious differences in concentrations of THg and MeHg in surface waters between natural and restored wetlands. Similar seasonal patterns of THg and MeHg concentrations were evident in both natural and restored wetlands, with higher concentrations in late spring and summer, and lower values in early spring and fall. THg concentrations in pond waters were greater than those in ground waters. Ground water stage was generally greater than pond stage, except for the low flow summer period, suggesting the flow of ground waters from the watershed into the surface waters. This pattern coupled with higher concentrations of THg in pond waters than ground waters suggests that Hg in pond waters is partly derived from direct atmospheric deposition or by mobilization from near-wetland shallow sediments, in addition to
groundwater inflows. Higher concentrations of THg in pond water than ground water could also be due to loss of water associated with evapotranspiration. The percent MeHg (%MeHg) at the study wetland sites were high in both surface (43.4 ± 25.6%) and ground waters (38.8 ± 27.6%), suggesting that these wetlands are relatively efficient in converting ionic Hg to MeHg regardless if restored or natural. I observed weak or non-existent relations between concentrations of dissolved organic carbon and THg and MeHg. However, large increases in dissolved organic carbon concentrations in pond waters compared to groundwater suggest that dissolved organic matter is important in the supply of Hg to pond waters. Drying and rewetting cycles during summer in both restored and natural wetlands likely promote methylation rates and contribute to relatively high fractions of THg as MeHg. Although the %MeHg values were generally high in study wetlands, in ground waters with high concentrations of SO₄²⁻ (> 10 mg S/L) and NO₃⁻ (> 0.5 mg N/L) MeHg concentrations and %MeHg were uniformly low, suggesting some chemical limitation on methylation.
Seasonal Patterns of Total and Methyl Mercury Concentrations in Ground and Surface Waters in Natural and Restored Freshwater Wetlands in Northern New York

by

Ting Wang

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1. Introduction

Wetlands are the interfaces between uplands and surface waters, where soils, sediments, water and biota closely interact (Zillioux et al., 1993). The United States Environmental Protection Agency (EPA) defines wetlands as areas where water covers soil or is present at or near the surface of the soil for all or varying periods during the year (https://www.epa.gov/wetlands/what-wetland). Although wetlands only occupy less than 9% of the land area of the Earth, they provide a disproportionate amount of ecosystem services (Zedler and Kercher, 2005). Wetlands are important sites of biogeochemical transformations (Lacerda and Fitzgerald, 2001; Galloway and Branfireun, 2004; Mitchell et al., 2008). Due to water storage and support of reducing environments, wetlands can experience wetting and drying periods under varying hydrologic conditions which facilitate alternating redox cycles (Driscoll et al., 1998; Feng et al., 2014; Wasik et al., 2015; Strickman and Mitchell, 2017).

Wetland loss is a significant environmental issue (National Research Council, 2001). It is estimated that nearly half of global wetland area has been lost over the last two centuries, with the remaining highly degraded (Zedler and Kercher, 2005). Similarly, in the United States, nearly 47% of the total wetland area has been lost since the 1780s (Dahl, 2011; National Research Council, 2001). Wetland disturbance is largely associated with human activities, such as agriculture, residential development, silviculture and other land use conversions (Dahl, 2011; Zedler and Kercher, 2005) Conservation programs including Public-Private Partnerships (PPP) have helped conserve and restore wetlands in the Great Lakes watershed. The restored wetlands investigated in this study were restored as a PPP within the St. Lawrence River watershed in New York State.
Wetlands are important landscape areas for transformations of mercury (Hg). They serve as net sinks for total mercury (THg), and are critical environments for methyl mercury (MeHg) formation and supply to downstream aquatic ecosystems (Galloway and Branfireun, 2004; Driscoll et al., 2007; Selvendiran et al., 2008). Atmospheric deposition is the main source of Hg to most remote aquatic ecosystems (Benoit et al., 2003; Driscoll et al., 2007, 1998; Feng et al., 2014; Fitzgerald et al., 1998). Besides natural sources, Hg is emitted directly to the atmosphere from human activities associated with power plants, smelting and other industrial processes, and artisanal and small-scale gold mining (ASGM) (UNEP, 2013). Moreover, Hg previously deposited to the Earth’s surface can be subsequently reduced and remitted back to the atmosphere (Driscoll et al., 2013). Mercury pollution is a global problem, because gaseous elemental mercury emitted to the atmosphere has a long atmospheric residence time (0.5 to one year), before deposition to the Earth’s surface (Driscoll et al., 2013; Morel and Amyot, 1998).

In wetlands, the accumulation of organic matter and saturated soils promote reducing conditions which allows for the conversion of ionic Hg to MeHg through obligate anaerobic sulfate and iron reducing bacteria and archaea (Benoit et al., 2003; Fleming et al., 2006; Mehrotra and Sedlak, 2005; Podar et al., 2015; Selvendiran et al., 2008). In contrast to THg, only a small amount of MeHg is derived from atmospheric deposition; most is transformed from ionic Hg within ecosystems. In situ production of MeHg in fresh water wetlands has been shown to be related to temperature, pH, microbial activity, sulfate, nitrate and dissolved organic carbon concentrations and hydrologic conditions (Zillioux, et al., 1993; Benoit et al., 2003; Selvendiran et al., 2008; Todorova et al., 2009). MeHg strongly bioaccumulates and biomagnifies in the aquatic food chains, and generally drives human and wild life exposure (Wasik et al., 2015; Lacerda and Fitzgerald, 2001; Selvendiran et al., 2008; Zillioux et al., 1993). MeHg is a neurotoxic substance,
which is especially problematic for young children and women of child-bearing age (Benoit et al., 2003; Driscoll et al., 2007; Galloway and Branfireun, 2004; Lacerda and Fitzgerald, 2001). Minamata disease is caused by elevated exposure to MeHg, primarily through consumption of fish and to a lesser extent contaminated MeHg rice (Kwon et al., 2018; Li et al., 2010; Zhang, Feng et al., 2010; Wasik et al., 2015).

Freshwater wetlands are sensitive to Hg pollution (Driscoll et al., 2007). Understanding the biogeochemical processing and cycling of Hg in wetlands is critical to assessment of the risk of Hg in polluted areas (Lacerda and Fitzgerald, 2001). Many studies have demonstrated the function of restored wetlands, such as providing water storage, facilitating carbon sequestration and improving water quality (Hogan et al., 2004; Verhoeven et al., 2006; Woltemade, 2000). However, fewer studies have examined Hg cycling and MeHg production in restored wetlands (Gilmour, 2011; Hogan et al., 2004; Park et al., 2012; Zedler and Kercher, 2005). In this thesis, I measured the chemical and hydrological characteristics of both surface and ground waters from 16 restored wetlands and four natural wetlands near St. Lawrence River in New York State. I compared concentrations of total (THg) and methyl Hg (MeHg) from surface and ground waters in these natural and restored wetlands.

2. Materials and Methods

2.1 Site Description

Twenty wetland sites along St. Lawrence River in New York State (Figure 2.1, Table 2.1) were selected for this study. The St. Lawrence River is one of the largest rivers in the world, and an important water resource for both the United States and Canada. Among these wetland sites, four are natural wetlands and the remaining 16 are restored wetlands, of varying age and characteristics. The latitude and longitude ranges of the study wetlands is from 44.1 to 45.0°N
and 74.5 to 76.0°W, respectively. The climate is humid continental. Meteorological data were obtained for five regional sites from Climate Data Online (CDO) of the National Oceanic and Atmospheric Administration (NOAA) National Centers for Environmental Information website (http://www.ncdc.noaa.gov/cdo-web/) for the period 1989-2010. The average temperature in winter (from December to February) is -6.4 °C, in summer (from June to August) is 19.4°C, in spring (from March to May) is 5.6°C, and in fall (from September to November) is 8.6°C.

Annual average precipitation from five nearby weather stations is 961 ± 79 mm. The highest quantity of precipitation over the annual cycle occurs in fall.

The historical data suggest that the temperature of the study region is cool, with abundant precipitation.

Table 2.1 Characteristics of the 20 wetland study sites in the St. Lawrence River Valley.

<table>
<thead>
<tr>
<th>Site</th>
<th>Latitude (deg N)</th>
<th>Longitude (deg W)</th>
<th>Pond Area (ha)</th>
<th>Watershed Area (ha)</th>
<th>Wetland Type</th>
<th>Pond Depth (m)</th>
<th>Wetland Age (years)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BAR</td>
<td>44.2603</td>
<td>75.9297</td>
<td>3.09</td>
<td>653.3</td>
<td>Restored</td>
<td>0.69</td>
<td>24</td>
</tr>
<tr>
<td>BRA</td>
<td>44.8661</td>
<td>74.7189</td>
<td>4.18</td>
<td>578.5</td>
<td>Natural</td>
<td>2.09</td>
<td>NA</td>
</tr>
<tr>
<td>BUC</td>
<td>44.2053</td>
<td>75.6519</td>
<td>3.33</td>
<td>65.8</td>
<td>Restored</td>
<td>0.73</td>
<td>11</td>
</tr>
<tr>
<td>CUT</td>
<td>44.5889</td>
<td>75.3397</td>
<td>0.17</td>
<td>16.3</td>
<td>Restored</td>
<td>1.01</td>
<td>7</td>
</tr>
<tr>
<td>FIC</td>
<td>44.4978</td>
<td>75.5789</td>
<td>3.99</td>
<td>13.9</td>
<td>Natural</td>
<td>0.60</td>
<td>NA</td>
</tr>
<tr>
<td>GAR</td>
<td>44.3094</td>
<td>75.9500</td>
<td>3.45</td>
<td>6.5</td>
<td>Restored</td>
<td>0.79</td>
<td>NA</td>
</tr>
<tr>
<td>HMP</td>
<td>44.7208</td>
<td>74.9453</td>
<td>3.46</td>
<td>512.4</td>
<td>Restored</td>
<td>1.21</td>
<td>NA</td>
</tr>
<tr>
<td>JAC</td>
<td>44.5236</td>
<td>75.5022</td>
<td>0.12</td>
<td>18.0</td>
<td>Restored</td>
<td>3.40</td>
<td>NA</td>
</tr>
<tr>
<td>JBN</td>
<td>44.5700</td>
<td>75.6488</td>
<td>0.21</td>
<td>8.7</td>
<td>Restored</td>
<td>0.92</td>
<td>NA</td>
</tr>
<tr>
<td>JEW</td>
<td>44.6817</td>
<td>75.0275</td>
<td>2.73</td>
<td>32.8</td>
<td>Restored</td>
<td>0.87</td>
<td>9</td>
</tr>
<tr>
<td>KOG</td>
<td>44.6405</td>
<td>75.0558</td>
<td>3.14</td>
<td>126.8</td>
<td>Restored</td>
<td>0.88</td>
<td>11</td>
</tr>
<tr>
<td>LSB</td>
<td>44.4294</td>
<td>75.6544</td>
<td>4.05</td>
<td>35.9</td>
<td>Natural</td>
<td>1.27</td>
<td>NA</td>
</tr>
<tr>
<td>MEI</td>
<td>44.9633</td>
<td>74.4644</td>
<td>0.07</td>
<td>5.5</td>
<td>Restored</td>
<td>0.99</td>
<td>NA</td>
</tr>
<tr>
<td>MON</td>
<td>44.8564</td>
<td>74.5306</td>
<td>0.24</td>
<td>82.9</td>
<td>Restored</td>
<td>1.46</td>
<td>NA</td>
</tr>
<tr>
<td>PHI</td>
<td>44.2092</td>
<td>76.0136</td>
<td>0.84</td>
<td>26.1</td>
<td>Restored</td>
<td>1.19</td>
<td>NA</td>
</tr>
<tr>
<td>POO</td>
<td>44.6306</td>
<td>75.4086</td>
<td>0.89</td>
<td>5.4</td>
<td>Restored</td>
<td>0.75</td>
<td>NA</td>
</tr>
<tr>
<td>SIM</td>
<td>44.5437</td>
<td>75.6906</td>
<td>0.44</td>
<td>7.2</td>
<td>Restored</td>
<td>1.22</td>
<td>8</td>
</tr>
<tr>
<td>SMI</td>
<td>44.0725</td>
<td>75.9703</td>
<td>0.91</td>
<td>7.8</td>
<td>Restored</td>
<td>0.99</td>
<td>22</td>
</tr>
<tr>
<td>SPE</td>
<td>44.5379</td>
<td>75.1407</td>
<td>3.58</td>
<td>48.0</td>
<td>Natural</td>
<td>0.94</td>
<td>NA</td>
</tr>
<tr>
<td>ZUF</td>
<td>44.7914</td>
<td>75.2597</td>
<td>1.49</td>
<td>22.6</td>
<td>Restored</td>
<td>1.14</td>
<td>NA</td>
</tr>
</tbody>
</table>
Figure 2.1 Map showing the location of 20 wetland study sites along St. Lawrence River. Circles showed natural wetlands and triangles showed restored wetlands.

Wetland enhancement involved placement of a berm for stage control and increased area. Wetlands were also “enhanced” by reversing agricultural drainage “improvements” such as drainage ditches. Berms were generally constructed from excavated material. The impoundments typically have a control structure for outlet. Most wetlands have first order streams unless they are bank overflow sites adjacent to a stream/river. All wetland ponds are shallow (1.15 ± 0.59 m) with a small surface area (2.39 ± 1.61 ha) (Table 2.1). From water column temperature observations, these wetlands were under well-mixed throughout the year (Hwang, 2018).
The dominant land cover of the watersheds adjacent to the wetlands includes agriculture (pasture/hay and cultivated crops) (36.6% ± 28.1%), and forest (deciduous, evergreen and mixed) (35.3 ± 26.9%) and wetlands (13.3 ± 11.0%) (Figure 2.2). For natural wetlands, the main land cover is forest, ranging from 39.8% to 84.7% (mean = 65.1%, n = 4). In contrast, the main land cover for restored wetlands is agriculture, although the fraction of agriculture watershed land cover is highly variable, ranging from 12.4% to 89.3% (mean = 43.9%, n = 16) (Figure 2.2).

![Figure 2.2 The fractional distribution of land cover characteristics for watershed of the 20 wetland study sites (Hwang, 2018).](image)

### 2.2 Pond waters and ground waters sampling

Measurements of both surface waters and ground waters were conducted at the 20 wetland sites for water stage and water quality conditions. Ground water wells made of 5cm diameter PVC pipes were installed in the upland adjacent to the wetlands. Wells were placed upslope of the wetlands to represent ground water contributions to the wetlands and were used to understand change in ground water stage, flux into or out of the associated wetland and sample for water
chemistry. The average depth of the wells from soil surface to the bottom pipe is 1.11 ± 0.35 m; the depths for natural and restored wetlands ranged from 1.08 to 2.01, and from 0.38 to 1.40, respectively (Hwang, 2018). Levels of surface and ground water were measured hourly using gauge pressure sensors (U20 HOBO data loggers, Onset Computer Corporation, Bourne, MA, USA), which were placed at the bottom, and approximately deepest location of wetland ponds and in the upslope groundwater wells.

Each wetland was sampled on five dates from May to October in 2015. Teflon bottles were used to collect water samples, which were double bagged and contained 0.4% HCl prior to collection. The “clean hands/dirty hands” technique was used for sample collection (EPA, 2002, Method 1631, Version E). The dirty-hands person opened the outside bag, and the clean-hands person opened the inside bag, removing the sample bottle from inside the bag. The acid solution in the sample bottle was deposited into a waste-carboy. Before collecting pond waters, Teflon bottles were rinsed three times with the water to be sampled. When collecting pond samples, bottles were submerged completely beneath the water surface, making sure no air was entrained in the sample container. Nearly all pond sample sites were located near the wetland outlet.

Ground water samples were collected by pumping water from piezometers. The collection flask and tubing were rinsed with about 10 mL samples of water three times before sample collection. On occasion the quantity of ground water was limited at some sites, especially during the dry season (from July to September). During these periods, Milli-Q water was used to rinse the flask and tubing twice before collection, with the third and final rinse conducted with sample water. Similar to surface water collections, the “clean hands/dirty hands” technique was used to sample groundwater. During the dry season, from June to August, on some sampling dates there was inadequate water in the piezometers to collect samples.
Water samples were kept in coolers with ice after collection, then transported to the laboratory at Syracuse University for analysis. Half of the water samples were filtered within 48 hours of collection, using the 0.45μm Millipore Express PLUS PES membrane filter for analysis of concentrations of total and methyl Hg. The filtered samples were placed into 250 mL Teflon bottles, and 0.4% HCl was added as a preservative. The unfiltered remaining sample was poured into polypropylene bottles for analysis of major solutes and nutrients. All samples were stored at 4°C until analysis.

2.3 Chemical analyses

The methods used for chemical analysis of collected water samples are summarized in Table 2.2. Quality control was applied through duplicate sampling, instrument detection limits, initial and ongoing precision recovery, initial calibration verification (ICV), continuous calibration verification (CCV), initial calibration blank (ICB), continuous calibration blank (CCB), method blanks (MB), matrix spike (MS), and matrix spike duplicates (MSD). Before analyzing samples, standard calibration curves were performed. All blanks were less than the method detection limit, 0.2 ng/L for THg and 0.002 ng/L for MeHg respectively. Nearly all recoveries of standards and spikes were in the range of acceptance criteria (Table 2.3).

2.3 Data analyses

All results are presented as a mean ± standard error. Statistical comparisons of Hg variables among surface and ground waters, wetland types, seasonal change, well depths and wetland ages were made with a mixed - model analysis of variance (ANOVA). All statistically significant relationships and differences were determined at α ≤ 0.05. Relationships between Hg concentrations and ancillary variables were performed with linear regression. All statistical
analyses were conducted using R, package version 2.0.6 (R Core Team, 2017) and Mini Tab 17 (Minitab, Inc. 2014).

Table 2.2 Methods used for chemical analysis in this study.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Method</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>THg</td>
<td>Tekran 2600 Automated Total Mercury Analyzer, Oxidation, purge and trap, desorption, and cold-vapor atomic fluorescence spectrometry (CVAFS) Tekran model 2500</td>
<td>U.S. EPA. Method 1631, Revision E, 2002</td>
</tr>
<tr>
<td>MeHg</td>
<td>Distillation, aqueous methylation, purge and trap, desorption, and cold-vapor atomic fluorescence spectrometry (CVAFS)</td>
<td>U.S. EPA. Method 1630, 2001</td>
</tr>
<tr>
<td>Dissolved Organic Carbon (DOC)</td>
<td>UV-enhanced persulfate oxidation on a Tekmar-Dohrmann Phoenix 8000 (5310C)</td>
<td>APHA/AWWA/WEF, 1998</td>
</tr>
<tr>
<td>SO₄²⁻, NO₃⁻</td>
<td>Ion Chromatography with chemical suppression of eluent conductivity (4110B)</td>
<td>APHA/AWWA/WEF, 1998</td>
</tr>
</tbody>
</table>

Table 2.3 Quality Control of THg and MeHg analysis.

<table>
<thead>
<tr>
<th>Quality Control (QC)</th>
<th>THg-%Recovery</th>
<th>MeHg-%Recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mean</td>
<td>Std</td>
</tr>
<tr>
<td>Continuing Calibration Verification (CCV)</td>
<td>97.6%</td>
<td>6.7%</td>
</tr>
<tr>
<td>Quality Control Sample (QCS)</td>
<td>94.4%</td>
<td>10.0%</td>
</tr>
<tr>
<td>Matrix Spike/Matrix Spike Duplicate sample (MS/MSD)</td>
<td>94.0%</td>
<td>9.2%</td>
</tr>
<tr>
<td>Ongoing Precision and Recovery (OPR)</td>
<td>99.4%</td>
<td>12.6%</td>
</tr>
</tbody>
</table>

3. Results

3.1 Mercury concentrations in surface and ground waters

The average concentrations of total mercury (THg) and methyl mercury (MeHg) in surface waters (THg = 1.11 ± 0.77 ng/L; MeHg = 0.51 ± 0.50 ng/L) were approximately two and three
times higher, respectively, than values in ground waters (THg = 0.38 ± 0.35 ng/L; MeHg= 0.13 ± 0.19 ng/L; Table 3.1). Although the variability in concentrations of Hg species was large across the study sites, the differences between surface and ground waters were statistically significant for each sampling event (p < 0.001). The values of %MeHg ((MeHg/THg)*100) in the study wetland sites were high in both surface (43.4 ± 25.6%) and ground waters (38.8 ± 27.6%), with no differences between these types of waters (p > 0.1).

3.2 Mercury in natural and restored wetlands

For surface waters, the mean concentrations of THg and MeHg in restored wetlands were not significantly different from values in natural wetlands (p > 0.1) (Table 3.1). In ground waters, however, the average concentration of THg in restored wetlands was higher than natural wetlands (p = 0.003) (ANOVA), with significant differences occurring in each month during the study period. While the mean concentration of MeHg ground waters of restored wetlands was around three times higher than in natural wetlands, this difference was not statistically significant (p = 0.064). The mean values of %MeHg in natural and restored wetlands were similarly high, without significant differences (Table 3.1). As the wetlands exhibited high fractions of THg occurring as MeHg (%MeHg), there were relatively strong relationships between concentrations of MeHg and THg, except for ground waters in natural wetlands (Figure 3.2).

Seasonal patterns of THg and MeHg concentrations and %MeHg in natural and restored wetlands were similar. In surface waters, THg and MeHg concentrations increased from May to June and then decreased during the low flow period in August. Concentrations increased again in September and then decreased from September to October. %MeHg values in surface waters were higher in May and September, and lower in October. In ground waters, THg concentrations increased from May to June and gradually decreased from June to October. %MeHg and MeHg
concentrations in ground waters exhibited no obvious seasonal change (ANOVA) (Figure 3.1).

Table 3.1 Mean concentrations and standard deviations of THg (ng/L), MeHg (ng/L), %MeHg, DOC (mg C/L), SO$_4^{2-}$ (mg S/L) and NO$_3^-$ (mg N/L) in natural and restored wetlands in both surface (SW) and ground waters (GW). Statistically significant differences in concentrations are indicated.

<table>
<thead>
<tr>
<th>Water Type</th>
<th>Wetland Type</th>
<th>THg(ng/L)</th>
<th>MeHg(ng/L)</th>
<th>%MeHg</th>
</tr>
</thead>
<tbody>
<tr>
<td>SW</td>
<td>Natural</td>
<td>0.98±0.62(A**)</td>
<td>0.44±0.58(A)</td>
<td>36.7±27.5(A)</td>
</tr>
<tr>
<td></td>
<td>Restored</td>
<td>1.14±0.81(A**)</td>
<td>0.53±0.48(A)</td>
<td>45.1±25.0(A)</td>
</tr>
<tr>
<td>GW</td>
<td>Natural</td>
<td>0.18±0.14(B*)</td>
<td>0.06±0.04(B)</td>
<td>36.8±24.0(A)</td>
</tr>
<tr>
<td></td>
<td>Restored</td>
<td>0.44±0.38(A*)</td>
<td>0.15±0.21(A)</td>
<td>39.5±28.8(A)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Water Type</th>
<th>Wetland Type</th>
<th>DOC(mg C/L)</th>
<th>SO$_4^{2-}$(mg S/L)</th>
<th>NO$_3^-$ (mg N/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SW</td>
<td>Natural</td>
<td>12.6±3.2(A**)</td>
<td>0.68±1.23(B**)</td>
<td>0.25±0.27(A*)</td>
</tr>
<tr>
<td></td>
<td>Restored</td>
<td>11.8±3.7(A*)</td>
<td>2.22±2.58(A**)</td>
<td>0.25±0.25(A*)</td>
</tr>
<tr>
<td>GW</td>
<td>Natural</td>
<td>2.7±1.5(A)</td>
<td>3.71±2.17(B**)</td>
<td>0.08±0.08(B**)</td>
</tr>
<tr>
<td></td>
<td>Restored</td>
<td>3.5±3.2(A)</td>
<td>8.44±7.74(A**)</td>
<td>0.37±0.45(A**)</td>
</tr>
</tbody>
</table>

Note: A** and B**: there was statistically different between natural and restored wetlands; A** and A**: there was difference, but the difference was not significant; A* and A*: there was no obvious difference.
Figure 3.1 Boxplots showing seasonal concentrations of a) THg in surface waters, b) THg in ground waters, (c) MeHg in surface waters, d) MeHg in ground waters, e) %MeHg in surface waters, and f) %MeHg in ground waters. The median is represented by the middle line of each box, hinges represent the 0.25 and 0.75 quartiles, and whiskers represent the minimum and maximum values, the outliers represent the extremely high values. Natural wetlands are shown by green, and restored wetlands are shown by orange.
Figure 3.2 Relationships between concentrations of MeHg and THg in a) surface waters (SW) (NW: slope=0.76, r²=0.68, p<0.001; RW: slope=0.42, r²=0.52, p<0.001), and b) ground waters (GW) (NW: slope=0.09, r²=0.11, p>0.1; RW: slope=0.45, r²=0.40, p<0.001). Natural wetlands (NW) are represented by green dots, and restored wetlands (RW) are represented by orange triangles.

3.3 Relations with chemical parameters

The average concentration of dissolved organic carbon (DOC) in surface waters (11.38 ± 3.61 mg C/L) was significantly higher than in ground water (3.33 ± 2.89 mg C/L) (p < 0.001), while the differences in DOC between natural and restored wetlands were not evident (Table 3.1).

Unlike many studies in the literature, there were not strong relations between concentrations of THg or MeHg and DOC in pond or ground waters. In ground waters, at lower DOC concentrations (≤ 8 mg C/L) there was weak a positive relationship with THg (r² = 0.25, p<0.001). This relation deteriorated at higher DOC concentrations (≥ 8 mg C/L) possibly suggesting limitations to THg supply at higher DOC (Fig. 3.3 a). There was a weak relation between MeHg and %MeHg with DOC in surface waters of restored wetlands (r² = 0.24, p
<0.001; $r^2 = 0.22$, p < 0.001, respectively) (Fig. 3.3 c and d).
Figure 3.3 Relationships between concentrations of THg and DOC in a) surface waters (SW) (NW: $r^2 = 0.21$, $p = 0.040$; RW: $r^2 = 0.07$, $p = 0.019$), b) ground waters (GW) (NW: $r^2 = 0.06$, $p > 0.1$; RW: $r^2 = 0.11$, $p = 0.008$; RW – DOC < 8 mg C/L: $r^2 = 0.31$, $p < 0.001$), between MeHg and DOC in c) surface waters(RW – DOC > 8 mg C/L: $r^2 = 0.18$, $p = 0.002$), and d) ground waters (RW – DOC < 8 mg C/L: $r^2 = 0.08$, $p = 0.042$); and between %MeHg and DOC in e) surface waters (RW: $r^2 = 0.22$, $p < 0.001$; RW – DOC > 8 mg C/L: $r^2 = 0.27$, $p < 0.001$), and f) ground waters. Natural wetlands (NW) are represented by green dots, and restored wetlands (RW) are represented by orange triangles.

Previous studies have demonstrated that DOC is a significant carrier in the transport of Hg (Mitchell et al., 2008). Ratios of THg:DOC and MeHg:DOC were used to examine sources of THg and MeHg relative to DOC inputs in natural and restored wetlands. The mean value of THg:DOC ratios in ground waters was significantly higher than in surface waters ($p = 0.04$). In surface waters, THg:DOC ratios values in restored wetlands were higher, but not significantly higher than natural wetlands ($p > 0.1$) (Table 3.2). In ground waters the THg:DOC ratios values in restored wetlands were significantly higher than natural wetlands ($p = 0.014$), suggesting that the supply of THg per unit DOC was greater in ground waters draining into restored wetlands than natural wetlands (Table 3.2). The mean value of MeHg:DOC ratio in the ground waters of
restored wetlands was more than two times higher than in natural wetlands, but the difference was not statistically significant (p = 0.106).

Seasonal patterns of THg:DOC and MeHg:DOC ratios in natural and restored wetlands were similar to seasonal patterns for THg and MeHg, with increases from May to June and lower values in August (Figure 3.4).

The mean concentration of SO$_4^{2-}$ in ground waters ($7.32 \pm 7.12$ mg S/L) was more than three times higher than surface waters ($1.90 \pm 2.44$ mg S/L) (p < 0.001) and mean concentrations of SO$_4^{2-}$ in restored wetlands was greater than in natural wetlands for both surface (p < 0.01) and ground waters (p < 0.01) (Table 3.1). Note that the variability in SO$_4^{2-}$ concentrations among wetlands was high. MeHg concentrations in ground waters showed a crude relationship with SO$_4^{2-}$ concentration, which was more evident for restored wetlands due to their greater range of concentrations. Under low SO$_4^{2-}$ concentrations ($\leq 10$ mg S/L) there was a wide range of MeHg concentrations and %MeHg values, and MeHg concentrations in restored wetlands were significantly higher than in natural wetlands (p = 0.046). With increases in concentrations of SO$_4^{2-}$ (> 10 mg S/L), the concentrations of MeHg and %MeHg decreased, and %MeHg values were significantly lower at high SO$_4^{2-}$ concentrations (> 10 mg S/L) (p = 0.010). Note that a similar pattern was not evident for surface waters.

Table 3.2 Mean of THg:DOC and MeHg:DOC in natural and restored wetlands in both surface (SW) and ground waters (GW).

<table>
<thead>
<tr>
<th>Water Type</th>
<th>Wetland Type</th>
<th>THg:DOC</th>
<th>MeHg:DOC</th>
</tr>
</thead>
<tbody>
<tr>
<td>SW</td>
<td>Natural</td>
<td>8.97E-08 ±7.69E-08(A*)</td>
<td>4.27E-08 ±7.04E-08(A*)</td>
</tr>
<tr>
<td>SW</td>
<td>Restored</td>
<td>1.07E-07 ±7.46E-08(A*)</td>
<td>4.57E-08 ±3.69E-08(A*)</td>
</tr>
<tr>
<td>GW</td>
<td>Natural</td>
<td>8.14E-08 ±6.11E-08(A**)</td>
<td>2.48E-08 ±1.97E-08(A**)</td>
</tr>
<tr>
<td>GW</td>
<td>Restored</td>
<td>1.47E-07 ±1.09E-07(B**)</td>
<td>5.15E-08 ±6.78E-08(A**)</td>
</tr>
</tbody>
</table>

Note: A**, and B**: there was statistically different between natural and restored wetlands; A** and A**: there was difference, but the difference was not significant; A* and A*: there was no
obvious difference.

Figure 3.4 Boxplots showing seasonal patterns of a) THg:DOC in surface waters, b) THg:DOC in ground waters, (c) MeHg:DOC in surface waters, d) MeHg:DOC in ground waters. The median is represented by the middle line of each box, hinges represent the 0.25 and 0.75 quartiles, and whiskers represent the minimum and maximum values, the outlies represent the
extremely higher values. Natural wetlands are shown by green, and restored wetlands are shown by orange.

The average concentrations of nitrate (NO$_3^-$) in surface waters ($0.25 \pm 0.25$ mg N/L) was similar to values in ground waters ($0.30 \pm 0.41$ mg N/L). In surface waters, the average concentration of NO$_3^-$ in natural wetlands was similar to the mean concentration in restored wetlands. In contrast, the mean NO$_3^-$ concentrations of ground waters in restored wetlands was significantly higher than natural wetlands ($p < 0.01$) (Table 3.1). Similar to the pattern for SO$_4^{2-}$ and MeHg in ground waters, at low NO$_3^-$ concentrations ($\leq 0.5$ mg N/L) the concentrations of MeHg and values of %MeHg were varied, and these values decreased with increases in NO$_3^-$ concentration ($> 0.5$ mg N/L). %MeHg values were lower at high NO$_3^-$ concentrations ($> 0.5$ mg N/L) than at low NO$_3^-$ concentrations ($\leq 0.5$ mg N/L), but the difference was not significant ($p = 0.122$).

### 3.4 Physical Factors

The mean monthly temperature and precipitation were calculated based on the monthly values of five nearby weather stations during the study period, from May to October in 2015. The average temperature increased from May, reaching a maximum monthly value in August ($19.3 \pm 0.4^\circ$C), and decreased successively in September and October ($8.2 \pm 0.7^\circ$C). Monthly precipitation was relatively uniform over the study period. The lowest monthly precipitation occurred in May and the greatest precipitation in September and October, showing a gradual increase from May to October 2015. Peak snowmelt occurred in March and April.

In general, ground water stage exceeded pond stage over the study period, suggesting downslope flow of water from the upslope well direction to the pond. Ground water stage showed considerable variability in response to snowmelt and precipitation events. As a result, ground
water stage was generally higher in May and June, and again in September and October. Ground water stage generally decreased starting in late June and recovered in early September (Figure 3.6). Pond stage showed a similar seasonal pattern as ground water stage, but variations were more muted. During the period of low ground water stage, ground water stage values periodically decreased below pond stage, suggesting limited or no inflow to the ponds under this condition. The season patterns of ground water and pond stage were generally similar for restored and natural wetlands, ground water stage decreased below pond stage to a lesser degree during the summer low stage period and ground water stage recovered more rapidly in the fall. Indeed, ground waters in some restored wetland sites became completely dry for several days during the summer low stage period. An important characteristic of the wetlands was the marked changes in groundwater stage, demonstrating drying and rewetting events over the study period in response to precipitation events. In my study, changes in groundwater level closely corresponded with amount of precipitation during an event in both natural and restored wetlands (natural wetlands, $r^2 = 0.71$, $p < 0.001$; restored wetlands, $r^2 = 0.56$, $p < 0.001$).

Previous research has demonstrated that the age of restored wetlands may influence the concentrations of Hg due to changes in the production and accumulation of organic matter (Ballantine and Schneider, 2014; Sinclair et al., 2012; Strickman and Mitchell, 2017). Most of these restored wetlands were constructed less than 20 years ago (Table 2.1). I did not observe any obvious influence of wetland age on pond water chemistry, including THg, MeHg or %MeHg.

Even though previous research demonstrated the importance of land cover and land use on controlling of Hg in freshwater ecosystems (Driscoll et al., 2013), there were not obvious
patterns of differences in Hg speciation in wetlands dominated by forest cover compared with agriculture cover at my study sites.

Figure 3.5 Patterns of MeHg and %MeHg with SO$_4^{2-}$ and NO$_3^-$ concentrations in ground water (GW). a) The relationship between MeHg and SO$_4^{2-}$; b) the relationship between %MeHg and
SO$_4^{2-}$; c) the relationship between MeHg and NO$_3^-$; d) the relationship between %MeHg and NO$_3^-$. Green dots – natural wetlands (NW), orange triangles – restored wetlands (RW).

Figure 3.6 Daily average water tables (hydraulic heads) of a) 4 natural wetlands, and b) 14 restored wetlands (sensors in two of the restored wetland did not adequately function); as well as average daily precipitation of nearby weather stations. Blue lines showed water table in ground waters, and red lines showed water tables in surface waters, green bars showed precipitation based on nearby weather station.
4. Discussion

4.1 Factors influencing mercury concentrations in natural and restored wetlands

Concentrations of THg, and MeHg, and %MeHg values in the St. Lawrence wetlands were generally similar to the low end of values reported in other wetland studies (Table 4.1). In contrast %MeHg values seem higher than other values reported for wetland studies in the literature.

Table 4.1 Comparison of concentrations of THg (ng/L), MeHg (ng/L) and %MeHg (%) in this study with values reported in other studies. Shown are ranges of values and mean values and standard deviation.

<table>
<thead>
<tr>
<th>Year</th>
<th>Location</th>
<th>Water type</th>
<th>THg (ng/L)</th>
<th>MeHg (ng/L)</th>
<th>%MeHg</th>
<th>Citation</th>
</tr>
</thead>
<tbody>
<tr>
<td>2015</td>
<td>St. Lawrence County, US</td>
<td>SW</td>
<td>1.11 ± 0.77</td>
<td>0.51 ± 0.50</td>
<td>43.4 ± 25.6</td>
<td>This study</td>
</tr>
<tr>
<td></td>
<td></td>
<td>GW</td>
<td>0.38 ± 0.35</td>
<td>0.13 ± 0.19</td>
<td>38.8 ± 27.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>SW</td>
<td>3.18 ± 2.33</td>
<td>0.17 ± 0.15</td>
<td>1.6 - 10</td>
<td></td>
</tr>
<tr>
<td>2004-2006</td>
<td>Central Adirondack Mountain, US</td>
<td>GW</td>
<td>-</td>
<td>-</td>
<td>29 (Average); 70 (Maximum)</td>
<td>Selvendiran et al., 2008</td>
</tr>
<tr>
<td>2000</td>
<td>Southern Ontario, Canada</td>
<td>SW</td>
<td>0.01 - 7.37;</td>
<td>0.01 - 0.47</td>
<td>-</td>
<td>Galloway and Branfireun, 2004</td>
</tr>
<tr>
<td></td>
<td>North-central Minnesota, US</td>
<td>GW</td>
<td>6.2 ± 1.8</td>
<td>0.89 ± 1.3</td>
<td>-</td>
<td>Mitchell et al., 2008</td>
</tr>
<tr>
<td>2005</td>
<td>Everglades, FL, US</td>
<td>SW</td>
<td>0.9 - 8.3</td>
<td>0.035 - 3.8</td>
<td>2 - 52</td>
<td>Liu et al., 2008</td>
</tr>
<tr>
<td>2008</td>
<td>Northeastern Alberta, Canada</td>
<td>SW</td>
<td>27.2 ± 2.19</td>
<td>0.43 ± 0.19;</td>
<td>4.4 ± 1.3</td>
<td>Oswald and Carey, 2016</td>
</tr>
<tr>
<td>2012-2013</td>
<td></td>
<td>GW</td>
<td>-</td>
<td>0.02 - 4.3</td>
<td>20 (Average)</td>
<td></td>
</tr>
</tbody>
</table>

In pond waters of my study wetlands, there was no obvious difference in the Hg chemistry between natural and restored wetlands. THg and MeHg in surface waters were higher than ground waters. My hydrologic analysis of ground water and pond stage indicate that through most of the study period the adjacent wetlands supplied ground water to the ponds (Figure 3.6).
An exception to this pattern occurred during the low flow summer largely in August and early September, and this change was more pronounced for restored than natural wetlands. The inflow of ground water to surface wetlands, coupled with the increase in THg concentration in wetland surface water compared to ground water suggests that the surface waters received Hg inputs from multiple pathways. In addition to groundwater, the ponds also likely received THg from direct atmospheric deposition and/or mobilization from surface wetland soils. The higher concentrations of THg in ground waters of the restored wetlands may be evidence of the greater supply of THg at shallower soil depth, as the depth of ground water is less than those for natural wetlands (Figure 4.1).

![Figure 4.1 Depth of ground water wells from soil surface. Green color shows the boxplot of well depth for natural wetlands, while orange depicts values for restored wetlands. The labeled numbers are average values, and the average well depths of restored wetlands was significantly deeper than natural wetlands.](image)

Note that DOC concentrations were elevated in pond water relative to ground waters (Table 3.1; Figure 3.3), suggesting the mobilization of DOC from surface deposits in the wetlands to surface waters. This supply of DOC could facilitate the transport of higher THg concentrations in pond
waters. Many previous studies have demonstrated the important function of DOC in the transport and bioavailability of Hg, concentrations of DOC typically have a close positive relationship with particularly THg and to a lesser extent MeHg in aquatic ecosystems (Dennis et al., 2005; Dittman and Driscoll, 2009; Driscoll et al., 1998; Liu et al., 2008; Selvendiran et al., 2008; Ullrich et al., 2001). However, in my study, relationship between DOC and THg was weak (Fig. 3.3 a and b). The THg:DOC ratios were highly variable across the study sites (Figure 3.5; Table 3.2). This variable pattern could indicate different rates of DOC and/or THg supply across these wetlands with different landscape settings and land use histories or differences in the quality of dissolved organic matter with a range of binding affinity for THg. It may be noteworthy that there was no difference in the THg:DOC ratio between restored and natural wetlands, suggesting that pond restoration does not strongly influence the supply of DOC relative to the supply of THg. Previous studies have indicated a dual role of DOC in the transport and bioavailability of Hg (Dittman and Driscoll, 2009; Driscoll et al., 1994; Feng et al., 2014). When DOC is low ($\leq 8$ mg C/L), it has important role of THg supply and a positive relation is evident with MeHg and Hg in biota; when DOC is higher ($> 8$ mg C/L), the relationships with MeHg and mercury in biota is diminished, suggesting that higher concentrations of dissolved organic matter binds with ionic Hg reducing the bioavailability (Driscoll et al., 1995; Selvendiran et al., 2008). There was no evidence in my study that the bioavailability of ionic Hg was altered by DOC, as I did not observe any significant relation of %MeHg with concentrations of DOC.

Similar to THg, there was no obvious difference in MeHg concentrations between natural and restored wetlands in surface or ground waters. The most distinctive feature of Hg dynamics from this study is the relatively high %MeHg values, indicating that these wetlands are efficient in the conversion of ionic Hg to MeHg (Table 4.1; Figure 3.2). It is not clear why these wetlands are so
effective in the production of MeHg. One possible explanation is the marked wetting and drying cycles of the wetlands associated with precipitation events and the subsequent drying of the wetland soils (Figure 3.6). Drying of wetlands or sediments allows for the mineralization of organic matter and release of associated ionic Hg (Chen et al., 2012). Re-wetting of wetland sediments following precipitation events allows for the development of reducing conditions and promotes methylation of the mineralized ionic Hg. Successive wetting and drying cycles over the summer season in wetlands allows for the efficient production of MeHg. The high %MeHg values could also be explained by strong binding between Hg and DOC leading to a greater partitioning of Hg in the water column and increases in Hg methylation (Liu et al., 2008). Values of %MeHg were similar for both natural and restored wetlands, which suggests the function of MeHg production in restored wetlands was similar to natural wetlands (Strickman and Mitchell, 2017). The close positive relationship between THg and MeHg (Figure 3.3) indicates that the main control on MeHg production in the study wetlands is ionic Hg supply (Dennis et al., 2005).

Concentration of SO$_4^{2-}$ and NO$_3^{-}$ in ground waters seemed to have some influence on MeHg production. Sulfate has a complex relationship with MeHg production (Benoit et al., 2003; Gilmour and Henry, 1991; Gilmour, 2011). Sulfate reducing bacteria are important in the production of MeHg (Podar et al., 2015). Under low SO$_4^{2-}$ concentrations methylation may be SO$_4^{2-}$ limited; increases in SO$_4^{2-}$ concentrations can stimulate production of MeHg. At high SO$_4^{2-}$ concentrations under reducing conditions, the production of sulfide can form aqueous complexes or precipitate ionic Hg limiting its availability for methylation. The result is an optimum concentration of SO$_4^{2-}$ for the production of MeHg, whose value varies with environmental conditions such as DOC and iron concentrations (Gilmour, 2011). The patterns of MeHg
and %MeHg in groundwater are suggestive of this relationship with \(\text{SO}_4^{2-}\). Concentrations of \(\text{SO}_4^{2-}\) are elevated in some of groundwater in restored wetlands. The source of this \(\text{SO}_4^{2-}\) is likely due to interaction of saline geologic deposits and groundwater during excavation of the wetlands (Franzi et al., 2000), resulting in elevated concentrations of \(\text{SO}_4^{2-}\) in some of the ground waters in the restored wetlands. I observed lower %MeHg values in these high \(\text{SO}_4^{2-}\) (> 10 mg S/L) ground waters. In contrast, the lower \(\text{SO}_4^{2-}\) ground waters had higher and more variable MeHg concentrations and %MeHg values.

A similar pattern appears to be manifested for \(\text{NO}_3^-\). In ground waters, \(\text{NO}_3^-\) concentrations were statistically higher in restored wetlands than natural wetlands, while the differences were not evident in surface waters. The source of this \(\text{NO}_3^-\) is likely runoff from agricultural lands adjacent to the restored wetlands. It has been observed that elevated \(\text{NO}_3^-\) can limit MeHg production (Matthews et al., 2013; Shih et al., 2011; Todorova et al., 2009). The mechanism for this effect is not clear. Nitrate is a strong oxidant. In its presence sediment iron will oxidize and ferric oxide can effectively adsorb Hg limiting methylation and transport in water. Alternatively, \(\text{NO}_3^-\) can limit the activity of \(\text{SO}_4^{2-}\) reducing bacteria and MeHg production from this pathway (Matthews et al., 2013; Strickman and Mitchell, 2018; Todorova et al., 2009). Like \(\text{SO}_4^{2-}\), I observed a curvilinear relationship between concentrations of MeHg and \(\text{NO}_3^-\) in ground waters. At low concentrations of \(\text{NO}_3^-\), MeHg and %MeHg values were variable; and MeHg concentrations and %MeHg decreased with increases in \(\text{NO}_3^-\) at concentrations above 0.5 mg N/L.

### 4.2 Seasonal change of mercury concentrations

The seasonal pattern of THg in both surface and ground waters may be related to meteorological conditions and water table depth. In the absence of local industrial activity, atmospheric
Deposition is likely the main source of THg to the study area (Driscoll et al., 2007; Yu et al., 2013). Temperature is likely an important factor driving seasonal variation in THg.

Concentrations of THg often increase during the low flow summer period due to the release of THg from mineralization of organic matter and concentration due to water losses associated with increases in evapotranspiration (Selvendiran et al., 2008). As a result, the overall seasonal pattern of lower THg and MeHg during the late spring and fall and generally higher concentrations during summer are expected. Superimposed on this pattern was lower concentrations in August.

Two factors may have contributed to the lower THg and MeHg during this period. First, I observed a marked decrease in groundwater stage in late summer (Figure 3.5) suggesting a decrease in groundwater flow to the ponds and possibly a decrease in THg inputs. Second, the longer hydrologic residence time associated with lower inflows to the ponds may have allowed for greater photoreduction of THg and loss by evasion. Evasion has been shown to be an important loss mechanism for THg in some lakes (Denkenberger et al., 2012; Ullrich et al., 2001).

High nutrient inputs to wetlands likely promote plant production (Lacerda and Fitzgerald, 2001; Mitchell et al., 2008). This carbon input coupled with, modest SO\textsubscript{4}\textsuperscript{2-} in the study sites could promote microbial activity to produce more MeHg (Driscoll et al., 1998; Gilmour et al., 1998; Ullrich et al., 2001). However, this study and others suggest that elevated NO\textsubscript{3}\textsuperscript{-} can limit methylation (Matthews et al., 2013; Todorova et al., 2009). A likely contributing factor for the high MeHg production efficiency is the wetting and drying cycles occurring in wetland sediments throughout the summer season which continuously promotes MeHg formation. (Driscoll et al., 2007; Feng et al., 2014; Strickman and Mitchell, 2017). Note that the highest %MeHg was
observed in September (Figure 3.1), a month which is the transition between the dry summer and wet fall season, but is characterized by warmer temperatures that allow for MeHg formation. Although these wetlands exhibit high %MeHg values, I see little difference in the ability of the restored and natural wetlands in this region to process Hg. Investigators have indicated concern for MeHg production in different stages of constructed wetlands. Sinclair et al. (2012) observed elevated concentrations of MeHg sediments and invertebrates in newly created wetlands for stormwater management compared to natural control wetlands but concentrations decreased with wetland age. Strickland and Mitchell (2017) found that recently created wetlands for stormwater were low in organic matter and had low rates on MeHg production and low sediment MeHg concentrations, while MeHg production and accumulation increased with wetland age. In contrast, the variability I observed across the restored wetlands masked any effect of wetland age on THg, MeHg or %MeHg. However, the youngest pond of those I studied was seven years old, so the fact that I did not have the opportunity to investigate a recently restored pond likely limits evaluation of pond age on Hg dynamics.

5. Conclusions

In this project, I found no obvious differences in concentrations of Hg species in surface waters between natural and restored wetlands. Seasonal patterns of THg and MeHg concentrations were similar in both natural and restored wetlands, with higher concentrations under warmer conditions in late spring and early fall, and lower values under cooler conditions in early spring and late fall. Lower concentrations also occurred during the low flow summer condition, likely due to decreases in water inflows and increases losses associated with increased hydraulic residence time. Concentrations of THg and MeHg were higher in pond waters than ground water inflows. This pattern suggests that in addition to ground water inputs, surface water Hg was
supplied by atmospheric deposition and the mobilization of Hg from near-surface sediments. I observed relatively high MeHg/THg ratios (%MeHg) in the study wetlands indicating that these systems are effective in converting ionic Hg to MeHg, in both restored and natural wetlands. Drying and rewetting cycles, which occurred throughout the summer in response to precipitation events likely contribute to the high methylation efficiency. While methylation efficiency was high in the study wetlands, there was some evidence that methylation may have been limited in ground waters of restored wetlands due to high concentrations of \( \text{SO}_4^{2-} \) (> 10 mg S/L) and/or \( \text{NO}_3^- \) (> 0.5 mg N/L). Relationships between DOC and THg and MeHg were weak across sites, but high concentrations of dissolved organic matter likely was important in the transport of Hg to surface waters.

Wetlands provide valuable services. The wetlands I studied were restored to improve habitat for fisheries and wildlife. Wetlands are critical zones of the landscape for the production of MeHg and its transport to downstream aquatic ecosystems. Indeed, these wetlands were very effective in converting ionic Hg to MeHg, although no difference was evident in %MeHg between restored and natural wetlands. The results of my study suggest that management of MeHg production in restored wetlands should focus on the ultimate source of this Hg, atmospheric deposition.
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