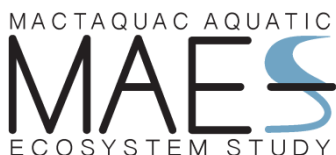


**Mactaquac Aquatic Ecosystem Study
Report Series 2018-063**



**MERCURY IN SEDIMENTS OF THE
MACTAQUAC AND BEECHWOOD
RESERVOIRS**

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DISCLAIMER

Intended Use and Technical Limitations of this report: This report summarizes the sediment mercury assessments for the both the Mactaquac and Beechwood head ponds. The data reflect the mercury levels in surface sediments from grab samples and don't reflect a full spatial sampling of sediments in the head ponds. The Canadian Rivers Institute, University of New Brunswick does not assume liability for any use of the included data or analyses outside the stated scope.

1. Introduction

Mercury is a toxic element that occurs naturally in soils and rocks but is increasing in the atmosphere because of human activities such as gold mining, burning of fossil fuels and chlor-alkali processes (Pacyna et al., 2006; UNEP, 2013). These processes emit inorganic mercury directly to the atmosphere, where it is either deposited locally to land or water or is transported distances up to 1000's of kilometers before deposition (Mason et al., 1994). Once in the water, this metal may evaporate back to the atmosphere or it may bind with other material and settle into the sediment layer (Mason et al., 1994). The conversion of inorganic mercury to an organic and more toxic form (methylmercury) primarily takes place in this sediment layer, and from here it can be incorporated into the food web (Compeau and Bartha, 1985; Wiener et al., 2003). The purpose of this study was to collect and analyze surface sediments from the Mactaquac and Beechwood reservoirs / head ponds for both the inorganic and organic forms of mercury to understand their concentrations and spatial patterns.

2. Methods

The top five cm of sediment were collected from the Mactaquac Generating Station's headpond (Mactaquac) in August 2017 and from the Beechwood Generating Station's headpond (Beechwood) in November 2017 using an Ekman dredge ($n = 3/\text{site}$) and clean techniques. Sediments were also collected from Beechwood in November 2016 ($n = 1/\text{site}$). Sampling locations for each dam can be seen in Figure 1 and Figure 2. Sampling upstream of the Beechwood Dam was not as comprehensive because the Beechwood substrate was difficult to dredge. Samples were frozen in plastic freezer bags, returned to the laboratory, before being freeze dried, homogenized and analyzed.

Methylmercury analysis was done for the Mactaquac sediments at the Environmental Biogeochemistry Lab at Acadia University (Wolfville, NS) using gas chromatography-atomic fluorescence analysis (Brooks Rand automated MERX system with a Model III fluorescence detector). Sediments were digested using 1.5 M KBr in 5% H_2SO_4 and 1 M CuSO_4 and extracted into dichloromethane (DCM). The MeHg in the DCM phase was then released into Milli Q water by heating and bubbling with high purity argon. The MeHg in the water phase was then analyzed through aqueous-phase ethylation, purge-and-trap gas chromatography prior to pyrolysis and atomic fluorescence spectrometry. Quality control included the analysis of certified reference material for sediment (ERMCC580, European Reference Materials) for extract recoveries and 50 pg standards for analytical recoveries, with average recoveries of 45% ($n = 5$) and 104% ($n = 9$), respectively. All sediment methylmercury concentrations were corrected for certified reference material recoveries. Average precision (measured as %RSD of triplicate samples) was 49% ($n = 9$) due to the low concentrations of MeHg in the samples, with an overall method detection limit (DL) of 0.023 ppb (3 times the standard deviation of blanks, $n=6$). Some samples (6) were below method detection limits so these samples were assigned values of $\frac{1}{2}$ the DL for reporting purposes (0.0115 ppb). Methylmercury analysis was not done for the Beechwood sediments owing to challenges with sediment quality and costs.

Total mercury (both organic and inorganic forms) in sediments (Mactaquac and Beechwood) was analyzed at the University of New Brunswick Saint John using a Milestone Direct Mercury Analyzer. This analysis was done using 30 mg of dried sediment. Quality control

included blanks, duplicates, and various standards/standard reference materials (intra-lab standard of Saint John Harbour sediments, 10 ng liquid Mercury standard and SRM2702 from National Institute of Standards and Technology). The mean percent recovery of the SRM2702 was $107 \pm 8\%$ ($n = 6$), the intra-lab standard was $70 \pm 11\%$ ($n = 6$), and the 10 ng liquid mercury standard was $92 \pm 3\%$ ($n = 6$). The mean concentration of total mercury in method blanks, assuming a 30 mg sample, was <0.001 ppb ($n = 6$). Average precision was within 6% ($n = 5$) for duplicate samples, with an overall method detection limit of 3.75 ppb, which is the lowest point on the calibration curve used. All concentrations are reported in dry weight. The % methylmercury (percentage of total mercury in the form of methylmercury) was also calculated for Mactaquac sediments by dividing the methylmercury concentration by the total mercury concentration for each sample. All mercury levels are reported on a parts per billion (ppb; ng/g) dry weight (dw) basis and as mean $\pm$ SD unless otherwise indicated.

The mass of sediment lost on ignition (LOI) was used to infer organic content of the sediments. Around four grams of each pre-dried sample was weighed into a ceramic crucible (dw1), burned at 550°C, and weighed again (dw2). LOI (%) was calculated using the following equation.

$$\text{LOI} = ((\text{dw1} - \text{dw2}) / \text{dw1}) * 100$$

3. Results and Discussion

3.1 Mactaquac Reservoir Sediments

Average total mercury in the Mactaquac sediments was 77 ± 33 ppb dw and the range was 11 to 133 ppb across sites. Figure 3 shows a general increase in total mercury concentrations moving downstream from the Meduxnekaeg River towards the Mactaquac Generating Station. These concentrations were very similar to those reported in Kidd et al. (2015, 2016) for the headpond, with ranges of 12.9 to 154 ppb, and lower than those found in nearby lakes (121 to 236 ppb). In comparison, total mercury concentrations in sediments upstream of the younger Three Gorges Reservoir in China (opened in 2003) were lower and ranged from 10 to 45 ppb (Ma et al., 2017), while surface sediments from older reservoirs sampled in Ontario had concentrations up to 300 ppb (opened in 1915 – 1969; Rodgers, Dickman, and Han, 1995). Total mercury in stream sediments from New Brunswick collected between 1960 and 2008 ($n = 7,413$) had an average of 81.6 ppb (Nasr and Arp, 2017). Overall, the concentrations were not elevated compared to historical data for the province.

Average methylmercury in the Mactaquac sediments was much lower at 0.19 ± 0.16 ppb. Figure 4 shows similar and low concentrations of methylmercury among sites 1 to 12. These concentrations are also similar to Reinhart et al. (2018) in 2016 in the Saint John River in Long Reach closer to the City of Saint John, where sediments had an average methylmercury of 0.34 ± 0.17 ppb. The average methylmercury in sediments from the younger Three Gorges Reservoir in China ranged from 0.3 to 1.1 ppb (Ma et al., 2017). Mercury in sediments is typically comprised of 0.2 – 2.8 % methylmercury (Marvin-Dipasquale et al., 2009; Ma et al., 2017), and the current Mactaquac mercury levels were comparable at 0.3% methylmercury. The % methylmercury also shows a slight decreasing spatial trend from upstream toward the Mactaquac Generating Station (Figure 5). This data suggests that while there may be an increase in total mercury concentrations near the station, there is no increase in the form of the metal most toxic for animals (methylmercury) at these sites.

Similar to the spatial trend in total mercury (Figure 3), the organic content, represented by LOI (%), in the Mactaquac sediments increased from upstream to downstream (Figure 6). Mercury is often found to be associated with organic matter in aquatic systems (Nasr and Arp, 2017; Mason and Lawrence, 1999). Therefore, the increase in organic material may be driving the increase in sediment mercury levels toward the Mactaquac Generating Station. Despite this increase, all LOI values were lower than the average LOI found in New Brunswick stream sediments from 1960 to 2008 ($n = 7,413$; Nasr and Arp, 2017).

3.2 Beechwood Reservoir Sediments

Total mercury in sediments upstream of the Beechwood Dam were lower than those just upstream of the Mactaquac Dam, on average. The average above Beechwood was 33.9 ± 19.9 ppb in 2016 ($n = 5$) and 16.9 ± 3.9 ppb in 2017 ($n = 12$). Figure 7 shows the range in concentrations among sites. While there does not seem to be a spatial trend from upstream (site 5) to downstream (site 14 nearest the dam) in 2017, total mercury increases - from 12 ppb to 58 ppb - in 2016 towards the dam, though sample sizes were low ($n=1/\text{site}$). The concentrations of total mercury in sediments from the Beechwood headpond are low in general compared to other older reservoirs (Rodgers, Dickman, and Han, 1995).

Similar to total mercury, there was no spatial trend observed in the organic content (LOI) of Beechwood sediments in 2017 (Figure 8). The Beechwood sediments, too, were low in both total mercury and organic content compared to those measured in stream sediments (Nasr and Arp, 2017).

Travers (1976) measured total mercury concentrations in Saint John River sediments and these are compared to the results of the current study in Table 1. Concentrations at Beechwood are five times lower in 2017 (than 1976), while Meduxnekaeg River concentrations are 2 times lower in 2017. Nackawic and Long's Creek concentrations were similar between years (within 30% change between years). However, 2017 concentrations at Mactaquac are twice as high.

4. Conclusion

Trends in the total mercury in the Mactaquac reservoir sediments indicated higher levels closest to the station, but this is likely associated with the increased organic content in the sediments near the station. A similar trend wasn't apparent in the Beechwood sediments. The trend in total mercury over time from 1976 to present day suggests a decrease in the Beechwood sediments and an increase in Mactaquac sediments. Such results are difficult to interpret given the difference in methodologies. Overall, the concentrations of total mercury and methylmercury found in the sediments in the Mactaquac and Beechwood reservoir sediments were low and comparable to historical data from other streams in the province (Nasr and Arp, 2017).

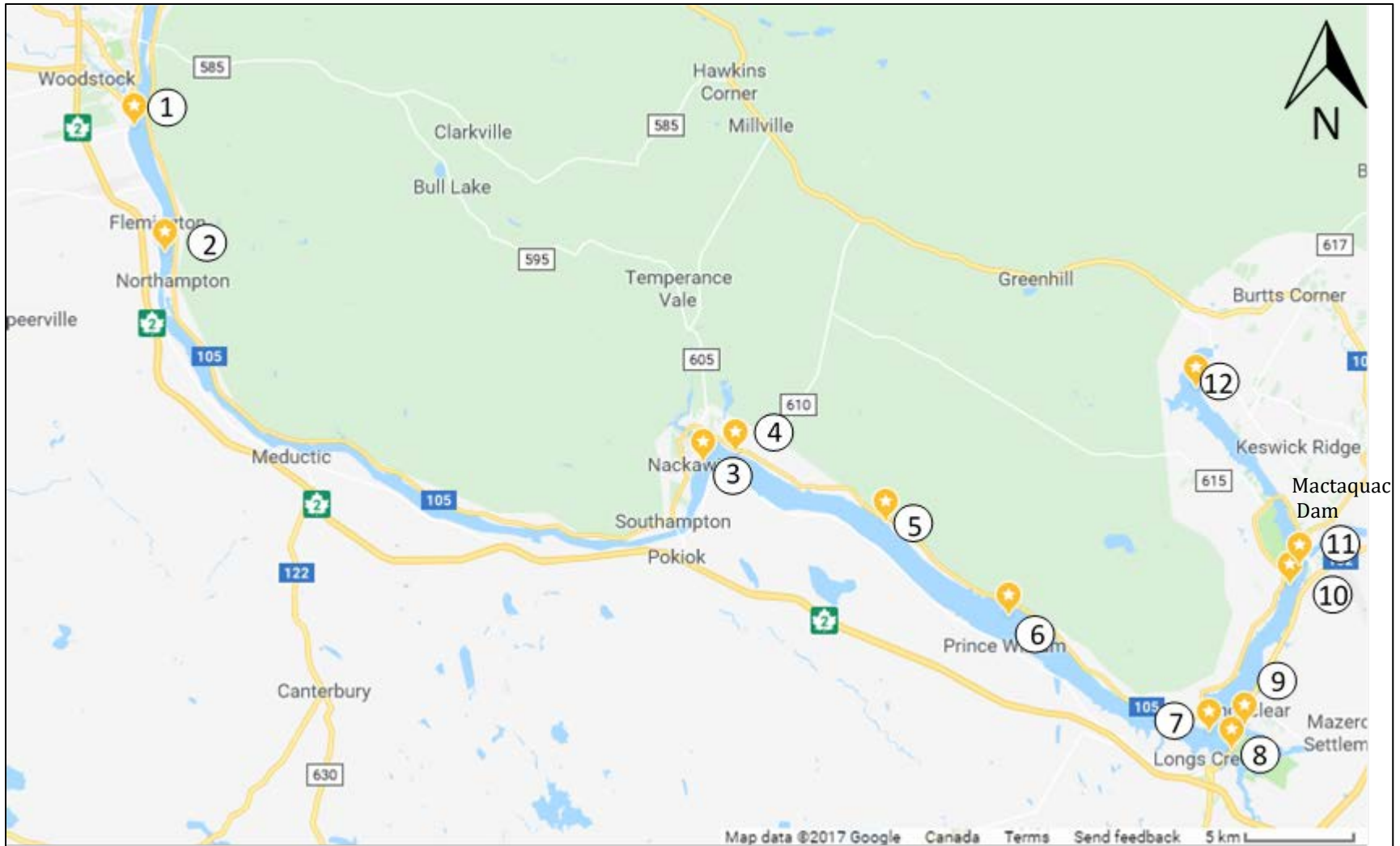


Figure 1: Sediment collection sites upstream of the Mactaquac Generating Station on the Saint John River, New Brunswick in 2017.

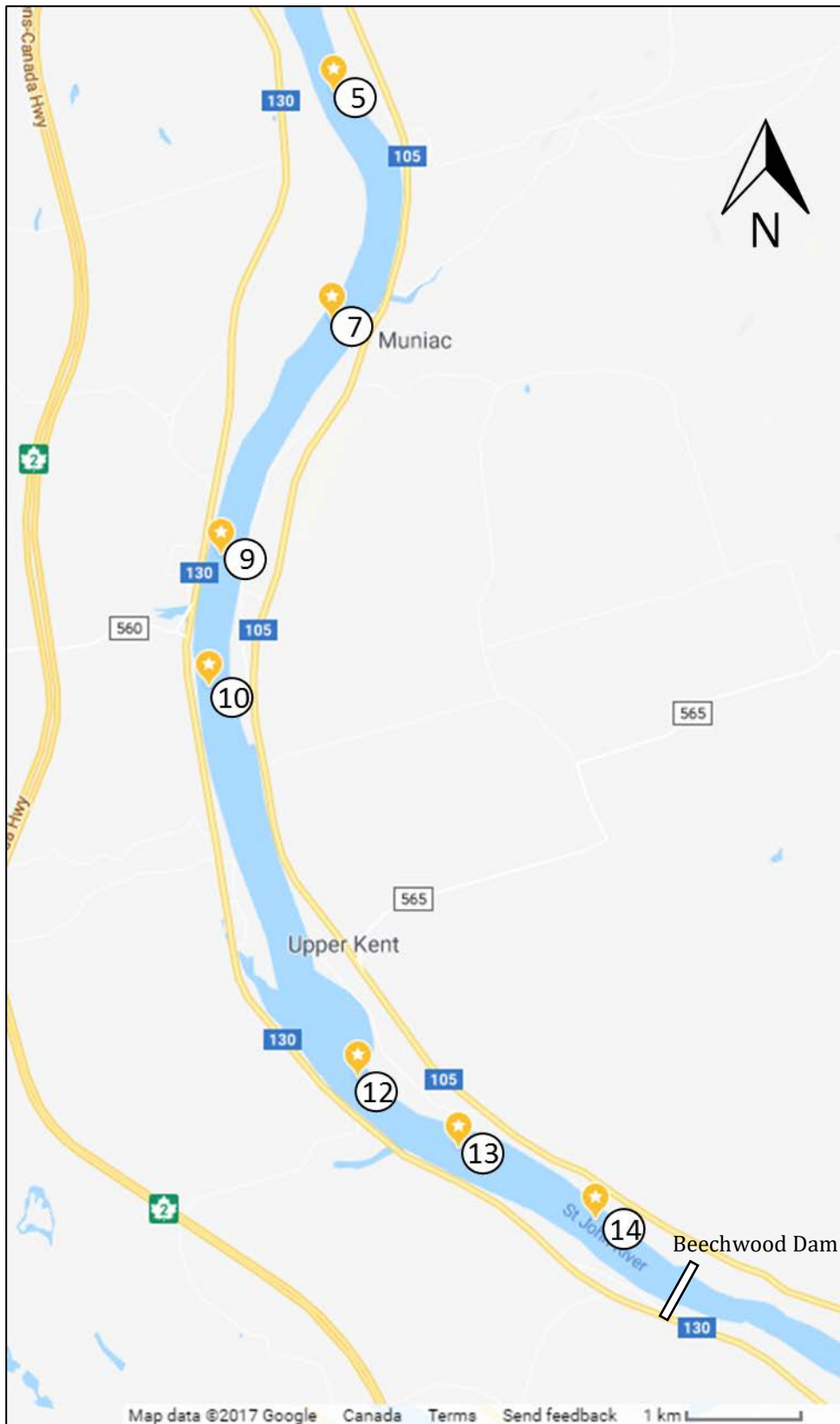


Figure 2: Sediment collection sites upstream of the Beechwood Dam on the Saint John River, New Brunswick, Canada from 2016 (sites 5, 7, 10, 12, and 14) and 2017 (9, 12, 13, and 14).

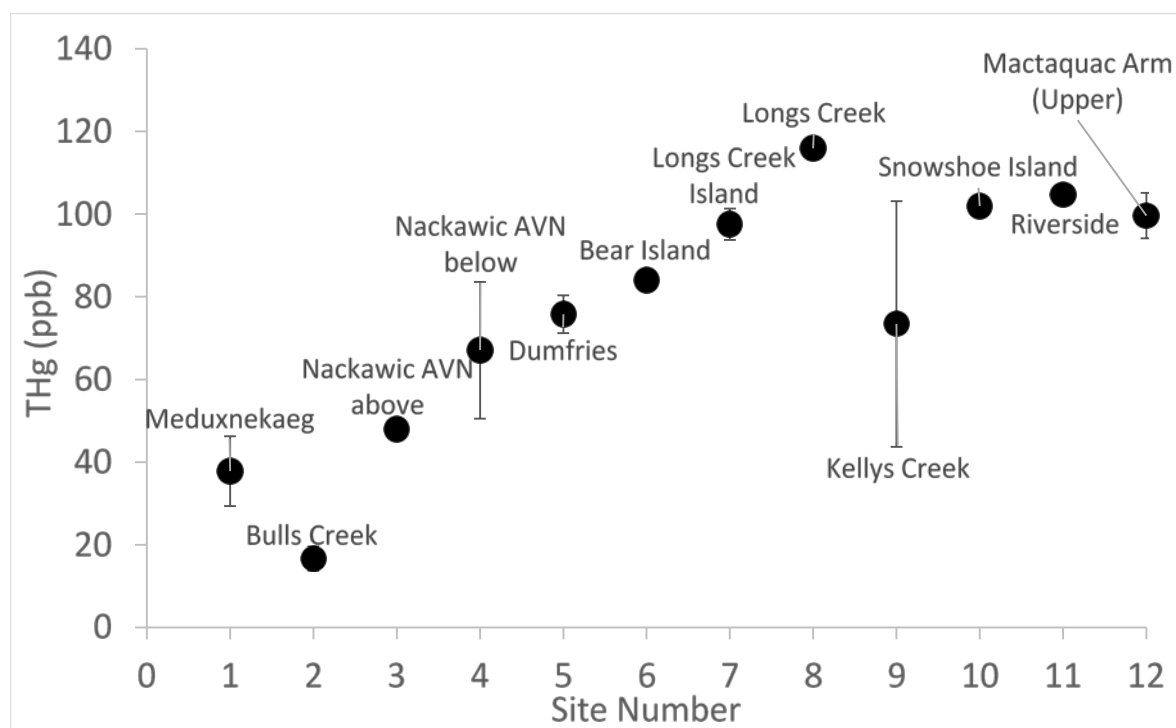


Figure 3. Mean total mercury $\pm$ 1 standard error in sediments upstream of the Mactaquac Generating Station in 2017 ($n = 3/\text{site}$).

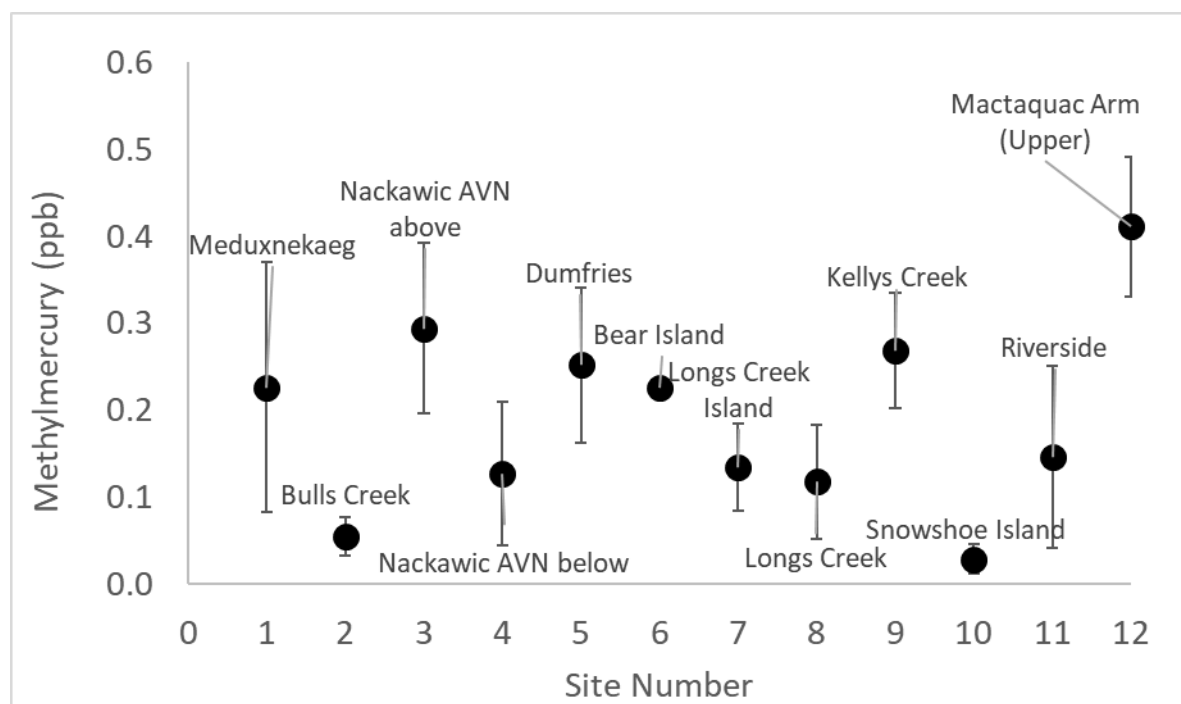


Figure 4. Mean methylmercury $\pm$ 1 standard error in sediments upstream of the Mactaquac Generating Station in 2017 ($n = 1-3/\text{site}$).

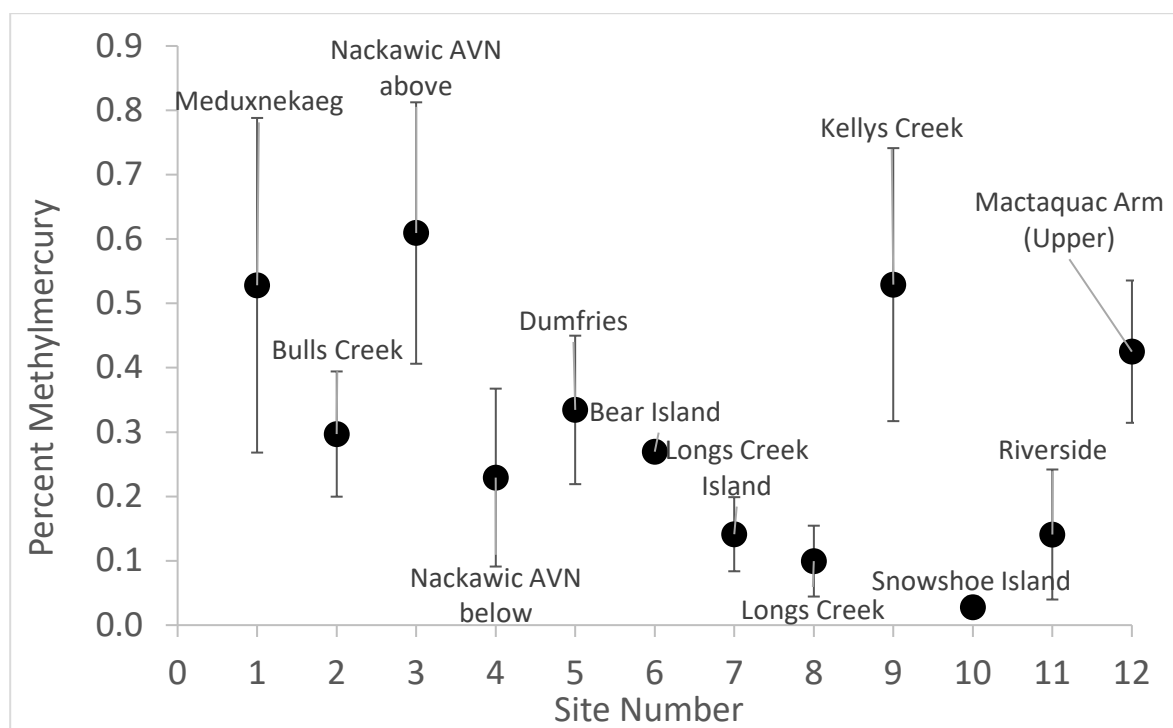


Figure 5. Mean percent methylmercury $\pm$ 1 standard error in sediments upstream of the Mactaquac Generating Station in 2017 ($n = 3/\text{site}$).

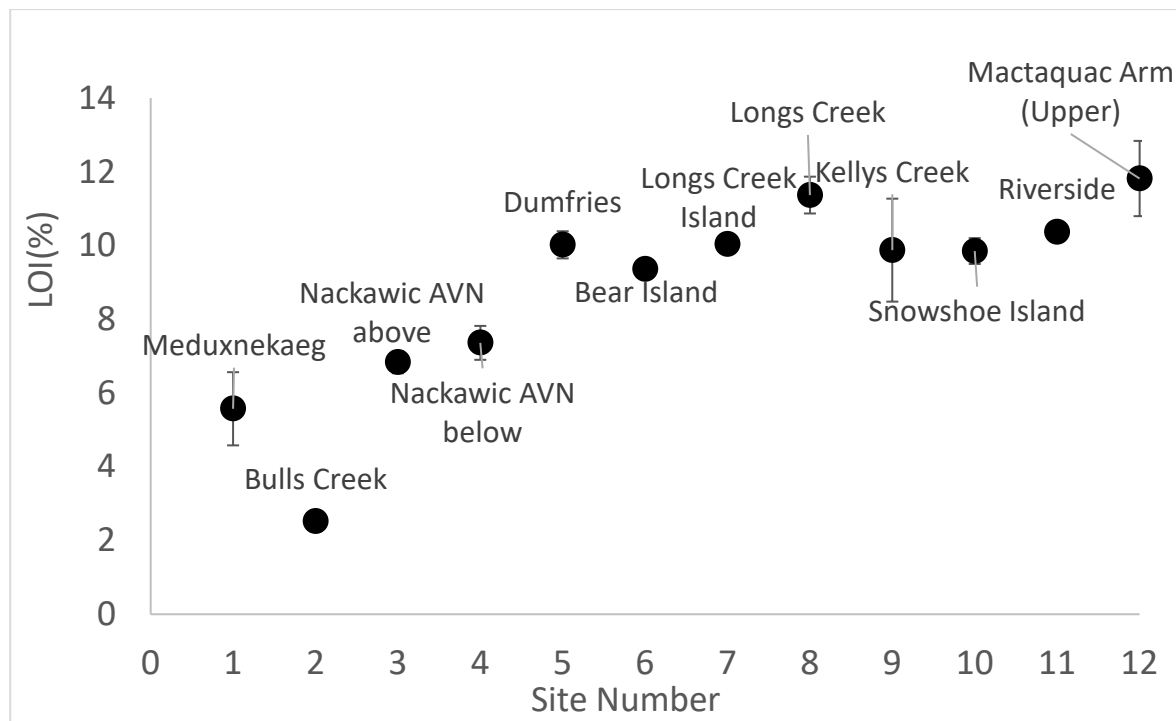


Figure 6. Mean loss on ignition (LOI %) $\pm$ 1 standard error measured in sediments upstream of the Mactaquac Generating Station in 2017 ($n = 3/\text{site}$).

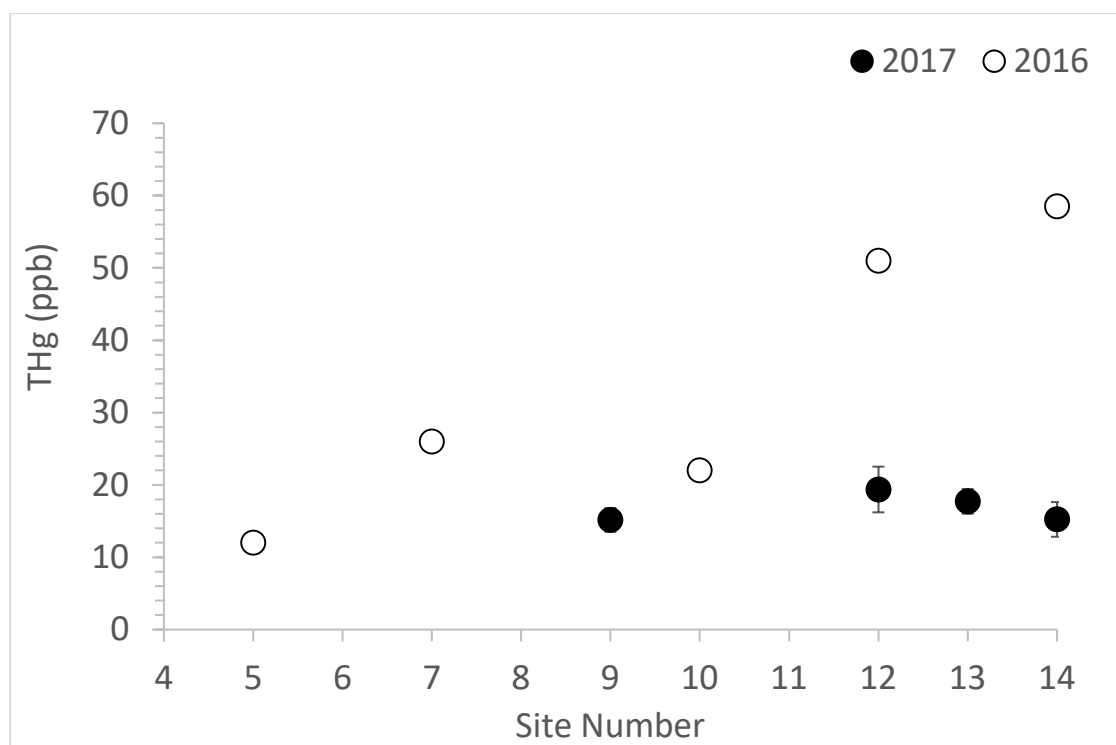


Figure 7. Mean total mercury ± 1 standard error measured in sediments from upstream of the Beechwood Generating Station in 2016 ($n = 1/\text{site}$) and 2017 ($n = 3/\text{site}$).

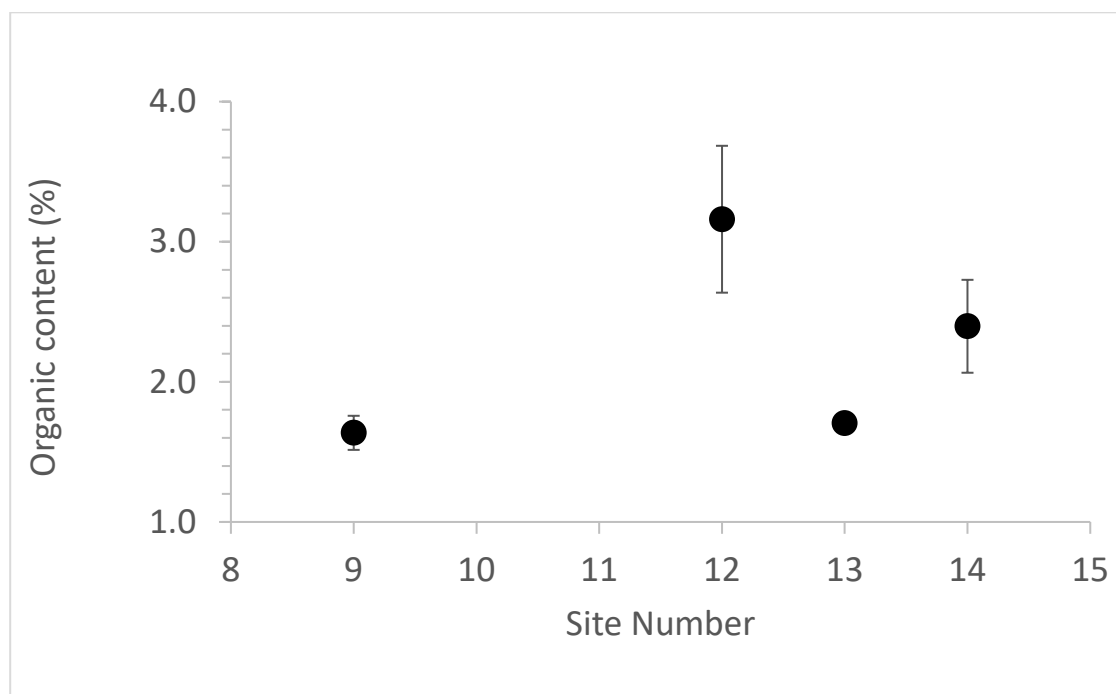


Figure 8. Mean loss on ignition (LOI %) ± 1 standard error measured in sediments from upstream of the Beechwood Generating Station in 2017 ($n = 3/\text{site}$).

Table 1. Concentrations of total mercury in Saint John River sediments from Travers (1976) compared to average concentrations from one or multiple sites in the same region in 2017.

Travers (1976) sites	2017 sites used for average	1976 total mercury (ppb)	2017 total mercury (ppb)
Beechwood	All Beechwood sites	81	16.9
Meduxnekaeg	1	74	37.8
Nackawic	4 and 3	66	57.5
Long's Creek	9, 8, and 7	70	95.6
Mactaquac	10 and 11	45	103.4

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