

Supplementary Information for:

Mercury methylation in stormwater ponds at different stages in the management lifecycle

Strickman, R.J. and Mitchell, C.P.J.

Supplementary Text S1: Additional Chemical Analysis Information

Distillation was used to prepare samples for analysis of MeHg. In brief, sediment samples were spiked with a known concentration of Me¹⁹⁹Hg as an internal standard, and distilled using a similar method to that described by Horvat et al. (1993)¹ in 8M H₂SO₄ and 20% KCl. Acid-cleaned Teflon vessels were used for the distillations. All mercury species, inclusive of MeHg, were ethylated with sodium tetraethylborate, purged from solution by bubbling with high-purity nitrogen, and concentrated into a glass trap filled with Tenax[®]. The mercury held in these traps was thermally desorbed into a stream of mercury-free argon gas, separated in a chromatographic column, and introduced directly to an Agilent 7700x ICP-MS. Isotope ratios and the concentration of the internal Me¹⁹⁹Hg standard were used to determine the concentrations of both ambient MeHg, and newly formed “excess” Me²⁰⁰Hg (that which is attributable to the added enriched isotope). This approach and detailed calculations are described by Hintelmann and Evans (1997)². The calculation method of Drott et al. (2008)³ was used to determine K_{meth} values for each sample.

Quality control of mercury determinations was assessed through the use of blanks, duplicate samples, certified reference materials (MESS-3 for THg; ERM CC580 for MeHg sediment samples, Dorm-3 for MeHg invertebrate samples) and matrix spikes (THg only).

Method detection limits were calculated as three times the standard deviation of blank results. Blank concentrations were assessed using the average mass of sample digested. Limits of detection for K_{meth} were determined on a per-sample basis using the calculation method of Hintelmann et al. 1997, and represented the minimum Me^{200}Hg concentration that allowed the newly formed Me^{200}Hg to be distinguished from that naturally present. These data can be found in Table S1.

Table S1: Quality control data for MeHg and THg determinations

| | Ambient MeHg (based on Me^{202}Hg) | Me^{200}Hg | K_{meth} | Ambient THg (based on T^{202}Hg) | T^{200}Hg |
|---------------------------------|---|--------------------------------|---|---|--------------------------------|
| Certified reference material | CC580 | | | MESS-3 | |
| CRM average recovery (%) | 94.4 ± 13.1 (n = 14) | | | 101.4 ± 6.9 (n = 7) | |
| Average duplicate RSD (%) | 5.3 ± 6.0 (n = 12 pairs) | 7.9 ± 6.3 (n = 9 pairs) | | 4.1 ± 5.2 (n = 7 pairs) | 7.6 ± 5.7 (n = 7 pairs) |
| Spike recovery (%) | | | | 107.2 ± 8.3 (n = 6) | |
| Ongoing procedural recovery (%) | | | | 96.5 ± 7.5 (n = 15) | |
| Detection limit | 0.049 ng g^{-1} | 0.009 ng g^{-1} | $0.01\text{--}0.45$ ng g^{-1} | 0.04 ng g^{-1} | 0.01 ng g^{-1} |

Table S2: Summary of the MeHg and IHg concentrations in the sediments of stormwater retentions ponds or stormwater treatment wetlands, with basic information on wetland type and location. Inventory is based on peer-reviewed studies for which both MeHg and IHg sediment concentrations are available. Unless otherwise indicated, numbers represent the mean or range of means of the relevant variable. A dash indicates data were not available.

| | Location | Reference | Notes | Sediment MeHg (ng/g) | Sediment IHg (ng/g) | K_{meth} (day ⁻¹) |
|-----------------------------------|---------------------------------|--------------------|---|----------------------|---------------------|--|
| Functional stormwater wetlands | Greater Toronto Area (Brampton) | This publication | new | 0.04–0.34 | 4.18–8.18 | 0.020–0.22 |
| | | | dredged | 0.12–1.97 | 10.40–24.51 | 0.004–0.096 |
| | | | mature | 0.34–1.25 | 21.07–33.53 | 0.033–0.069 |
| Functional stormwater pond | Greater Toronto Area (Brampton) | Strickman 2017 | Stormwater wetland | 0.29–0.88 | 47.15 | 0–0.016 |
| Experimental stormwater wetland* | Reno, Nevada, USA | Gustin et al 2006 | sediment at outlet with contaminated sediment- | 0.5 | c.300 | – |
| | | | contaminated water clean sediment, | 0.3 | c. 50 | – |
| | | | contaminated water contaminated sediment, clean water | 0.9 | C. 220 | – |
| | | | clean sediment, clean water | 0.5 | c. 50 | – |
| Experimental stormwater mesocosms | Savannah, Georgia, USA | Harmon et al. 2004 | control | 1.4–1.5 | 20–30 | – |
| | | | low-sulfate treatment | 1.5–2.4 | 30–34 | – |
| | | | high-sulfate treatment | 0.9–1.5 | 29–32 | – |

Table S3: Wetlands for comparison with the present study. These wetlands were selected based on their location (Southern Ontario), size (small to mid-size sites) and simple hydrology (sites must have a defined inflow and outflow, and have an area of open water; marshes or peatlands were not included, nor were large wetland complexes).

| | Location | Reference | Notes | Sediment MeHg (ng/g) | Sediment IHg (ng/g) | K_{meth} (day ⁻¹) |
|------------------|-----------------------------------|-----------------------------|---|----------------------|---------------------|---------------------------------|
| Habitat wetlands | Greater Toronto Area (Rouge Park) | Sinclair et al. 2012 | one year old wetland | 8 | 53 | – |
| | | | two year old wetlands | 2.8–3 | 35 | – |
| | | | three year old wetlands | 2 | 55 | – |
| | | | nine year old wetland | 1.5 | 22 | – |
| Natural wetland | | | urban control wetland | 2.8 | 50 | – |
| Natural wetland | | | rural control wetland | 2 | 63 | – |
| Habitat wetlands | Greater Toronto Area (Rouge Park) | Strickman and Mitchell 2017 | | 0.83–2.77 | 41.28 | 0–0.03 1 |
| Natural wetland | Philips Lake (Richmond Hill) | He et al. 2007 | Data from surface to 10 cm depth; small, rural lakes with forested watersheds | 1–2.4 | 110–190 | – |
| Natural wetland | St. George Lake (Richmond Hill) | | | 1.2–3 | 120-190 | – |

* In Gustin et al. 2006, data were collected at both the inlet and the outlet of the experimental ponds; data from near the outlet are reported here. In addition, data on the IHg concentrations are approximations, as they are estimated from a graphical presentation of the data that did not allow better estimations of the true values.

Table S4: Summary of sediment chemistry and mercury variables from the new, dredged, and mature stormwater pond. Data are presented separately for seasons (Early Summer, Peak Summer, and Fall) and zones within the pond (L: littoral, P: pelagic). Where applicable, data is summarized as mean \pm standard deviation.

| | | Sediment Chemistry | | | | Sediment Mercury Variables | | | | |
|----------------|--------------|--|---|---------------------------------------|---------------------------------------|--------------------------------|-------------------------------|-------------------|-------------------|-------------------|
| | | Ferrous iron ($\mu\text{g g}^{-1}$) | Ferric iron ($\mu\text{g g}^{-1}$) | Nitrate-N ($\mu\text{g g}^{-1}$) | Ammonia-N ($\mu\text{g g}^{-1}$) | MeHg (ng g^{-1}) | IHg (ng g^{-1}) | %MeHg | K_{meth} | |
| Sample Size | | 3 | 3 | 3 | 3 | 1-3 | 1-3 | 1-3 | 1-3 | |
| New | Early Summer | L | 1929 \pm 686 | 389 \pm 102 | 0.05 \pm 0.06 | 0.72 \pm 0.001 | 0.08 \pm 0.03 | 7.04 \pm 1.17 | 1.12 \pm 0.14 | 0.011 \pm 0.008 |
| | | P | 2390 \pm 659 | 395 \pm 94 | 16.25 \pm 15.45 | 3.31 \pm 0.74 | 0.34 \pm 0.08 | 9.31 \pm 1.18 | 3.51 \pm 0.32 | 0.019 \pm 0.007 |
| | Peak Summer | L | 2881 \pm 155 | 508 \pm 341 | 0.51 \pm 0.4 | 0.93 \pm 0.44 | 0.04 \pm 0.03 | 5.34 \pm 1.59 | 0.73 \pm 0.33 | 0.002 \pm 0.001 |
| | | P | 2101 \pm 86 | 544 \pm 384 | 0.31 | 2.13 | 0.18 \pm 0.03 | 6.73 \pm 1.11 | 2.61 \pm 0.71 | 0.021 \pm 0.007 |
| | Fall | L | 2583 \pm 278 | 35 \pm 60 | 4.91 \pm 4.24 | 1.34 \pm 0.03 | 0.1 \pm 0.05 | 2.58 \pm 0.27 | 3.5 \pm 1.7 | 0.022 \pm 0.018 |
| | | P | 2444 | 271 | < DL | 0.69 | 0.13 | 8.84 | 1.45 | 0.013 |
| Dredged | Early Summer | L | 3226 \pm 977 | 784 \pm 232 | 13.5 \pm 15.26 | 23.27 \pm 3.57 | 0.29 \pm 0.04 | 36.32 \pm 4.12 | 0.82 \pm 0.18 | 0.004 \pm 0.001 |
| | | P | – | – | < DL | 8.06 \pm 1.75 | 0.33 \pm 0.04 | 6.8 \pm 1.25 | 4.67 \pm 0.26 | 0.033 \pm 0.004 |
| | Peak Summer | L | 1596 \pm 481 | 311 \pm 83 | 1.94 \pm 0.67 | 2.03 \pm 0.27 | 0.12 \pm 0.02 | 8.15 \pm 4.92 | 1.85 \pm 1.14 | 0.007 \pm 0.001 |
| | | P | 1893 \pm 128 | 316 \pm 14 | 1.09 \pm 0.63 | 19.75 \pm 5.59 | 1.4 \pm 1.02 | 13.78 \pm 1.48 | 8.78 \pm 5.25 | 0.096 \pm 0.059 |
| | Fall | L | 2552 \pm 1318 | 16 \pm 28 | – | – | 1.97 \pm 0.57 | 26.81 \pm 4.37 | 6.83 \pm 1.73 | 0.054 \pm 0.015 |
| | | P | 1980 \pm 245 | 154 \pm 80 | < DL | 2.04 \pm 0.89 | 0.09 \pm 0.03 | 2.22 \pm 0.2 | 3.57 \pm 1 | – |
| Mature | Early Summer | L | 8333 \pm 695 | 855 \pm 194 | < DL | 9.53 \pm 6.17 | 0.86 \pm 0.64 | 31.05 \pm 6.13 | 2.5 \pm 1.35 | 0.073 \pm 0.011 |
| | | P | 4283 \pm 453 | 314 \pm 195 | 0.1 \pm 0.12 | 17.69 \pm 19.48 | 0.34 \pm 0.28 | 20.91 \pm 7.8 | 1.46 \pm 0.64 | 0.033 \pm 0.006 |
| | Peak Summer | L | 2003 \pm 893 | 781 \pm 402 | – | – | 0.66 \pm 0.09 | 29.25 \pm 14.92 | 2.54 \pm 1.04 | 0.057 \pm 0.025 |
| | | P | 4189 \pm 3113 | 532 \pm 175 | – | – | 0.72 \pm 0.19 | 12.89 \pm 5.54 | 5.73 \pm 1.9 | 0.069 \pm 0.021 |
| | Fall | L | 3941 \pm 1303 | < DL | 0.45 | 2.48 | 1.25 \pm 0.33 | 45.23 \pm 0.49 | 2.7 \pm 0.71 | 0.055 \pm 0.006 |
| | | P | 6310 \pm 1668 | < DL | 0.22 \pm 0.38 | 40.75 \pm 18.03 | 0.89 \pm 0.34 | 21.83 \pm 4.73 | 3.85 \pm 0.59 | 0.069 \pm 0.021 |

Table S5: Summary of plant biomass and carbon exudate from the littoral zone of

the mature pond for Early Summer, Peak Summer, and Fall. Data is summarized as mean \pm standard deviation.

| | Plant variables | | | |
|--------------|-------------------------|-------------------------|---|---------------------|
| | Aboveground biomass (g) | Belowground biomass (g) | Plant exudate (mg l ⁻¹ g biomass ⁻¹) | SUVA ₂₅₄ |
| Early Summer | 7.77 \pm 4.02 | 1.28 \pm 0.77 | 1.94 \pm 0.69 | 0.18 \pm 0.08 |
| Peak Summer | 22.8 \pm 6.51 | 10.8 \pm 3.96 | 0.13 \pm 0.09 | 0.71 \pm 0.03 |
| Fall | 18.03 \pm 4.87 | 4.37 \pm 1.19 | 0.1 \pm 0.03 | 0.46 \pm 0.12 |

Supplementary References

- 1 M. Horvat, N. S. Bloom and L. Liang, *Anal. Chim. Acta*, 1993, **281**, 135–152.
- 2 H. Hintelmann and R. D. Evans, *Fresenius J. Anal. Chem.*, 1997, **358**, 378–385.
- 3 A. Drott, L. Lambertsson, E. Björn and U. Skyllberg, *Environ. Sci. Technol.*, 2008, **42**, 153–158.