Electronic Supplementary Material (ESI) for Environmental Science: Processes & Impacts

Electronic Supplementary Information

Assessment of mercury bioavailability to benthic macroinvertebrates using diffusive gradients in thin films (DGT)

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Table S1. Detection limits for total Hg and MeHg analysis[a]

Analyte	Matrix	Mass or Volume[b]	Detection Limit
THg	Sediment	1 g	0.15 ng g^{-1}
	Pore water	1 mL	15 ng L^{-1}
	Tissue	0.1 g	1.5 ng g^{-1}
	DGT	10 mL	1.5 ng L^{-1}
MeHg	Sediment	2.5 g	0.01 ng g^{-1}
	Pore water	1 mL	1 ng L^{-1}
	Tissue	0.1 g	1 ng g^{-1}
	DGT	40 mL	0.025 ng L^{-1}

[a] The detection limits were 3× one standard deviation of eight blank spikes for each matrix (water, sediment and biota) and analyte (THg and MeHg).

[b] The reported masses and volumes are typical of those used in the analyses.

Analysis of the Hg species:

Calibrations were performed on a daily basis for both THg (six points) and MeHg (seven points) Standards solutions were prepared from $HgCl_2$ and MeHgCl (Sigma – Aldrich) salts. Every batch had at least one standard analyzed with it, using reference materials for THg in water (NIST 1641d, diluted 1000 ×), biota (NRCC DORM-3; 0.2 g) and sediment (MESS-3; 0.2 g), and MeHg in biota (NIST 1946; 0.05 g) and sediment (RTC SQC-1238; 0.5 g). There is no reference material for MeHg in water, and therefore, two laboratory control spikes (from the MeHgCl stock solution) were analyzed instead. At least one replicate was analyzed with each batch. In every batch, one QC set per 10 samples was performed. For THg and MeHg in water, this constituted a matrix spike (MS) and a matrix spike duplicate (MSD). The recoveries of the MS and MSD determined accuracy, and the relative percent difference (RPD) of the MS and MSD determined precision. For THg and MeHg in biota and sediment, a duplicate, MS, and MSD were performed. The RPD of the MS, MSD and the duplicate determined precision, and the

recoveries of the MS and MSD determined accuracy. In some cases, where the mass was insufficient to perform a MS/MSD, a post-preparation spike was analyzed to check for accuracy. The following table reports the ranges for the %recovery for the reference materials, the MSs and the MSDs, and the RPDs for the MSDs:

	Water	**Sediment**	**Biota**
THg; %recovery	99-118	99-108	95-122
THg; RPD	0.04-7	0.4-4	0.5-14
MeHg; %recovery	70-122	75-128	95-122
MeHg; RPD	2-19	1-26	1-26

Table S2. Coefficients of variation (CV = standard deviation/mean) for the DGTs in water and in sediments containing the organisms

DGT deployment	**THg**[a]	**MeHg**[a]
Water[b] (ppt)	0.09 (0.06-0.13)	0.07 (0.03-0.09)
Sediment (*N. virens*; ng cm^{-2})	0.24 (0.05-0.55)	0.22 (0.14-0.24)
Sediment (*M. Nasuta*; ng cm^{-2})	0.34 (0.11-0.50)	0.18 (0.05-0.24)
Sediment (*L. plumulosus*; ng cm^{-2})	0.24 (0.08-0.57)	0.52 (0.30-1.00)

[a] Reported as means with the range in parentheses.

[b] DGT deployment in water refers to a set of experiments, where DGTs were deployed in well-mixed water samples spiked with known concentrations of inorganic Hg(II) and MeHg in duplicates. Time-concentration plots for these experiments were developed (figures not shown here). These experiments were conducted partly to show the variability caused by the DGT synthesis and mercury measurement processes.

Table S3. Fitting parameters for the biota uptake model (Eq. 7)

Organism	**Metal**	k_u **(g-sediment L^{-1} d^{-1})**	k_e **(d^{-1})**
M. nasuta	THg	8.80×10^{-3}	1.04×10^{-1}
	MeHg	1.15×10^{-1}	9.28×10^{-2}
L. plumulosus	THg	5.85×10^{-2}	2.19×10^{-1}
	MeHg	1.14×10^{0}	1.89×10^{-1}
N. virens	THg	2.72×10^{-1}	2.18×10^{0}
	MeHg	9.94×10^{-2}	1.12×10^{-1}

Paddle-Type DGT Configuration and Construction

The paddle-type DGT devices were made of Delrin® plastic by the Advanced Manufacturing Center on-site at the University of Maine. The main portion of each paddle device is 8×11 cm, with an additional 1.9×3 cm tab on the top, allowing the device to easily be inserted and removed from the sediment. As shown in Figure S1, the paddle-type DGT devices are designed as one unit, with two sides that fold along the center to contain the gels and filter paper. In the schematic (Fig. S1), the lower half includes a 6×9 cm depression that holds the resin, diffusive, and membrane filter paper layers. The upper half also has a 6×9 cm depression, as well as a 5×8 cm window to expose the filter paper to the sediment. The depression in each half is 0.6 mm in depth (1.2 mm combined) to accommodate the gels and the filter paper. The total thickness of the DGT device when folded in half is 3 mm. The DGT devices are held closed with thin plastic clips that run the length of the sides, adding 2 mm to the total device thickness (Figure S2).

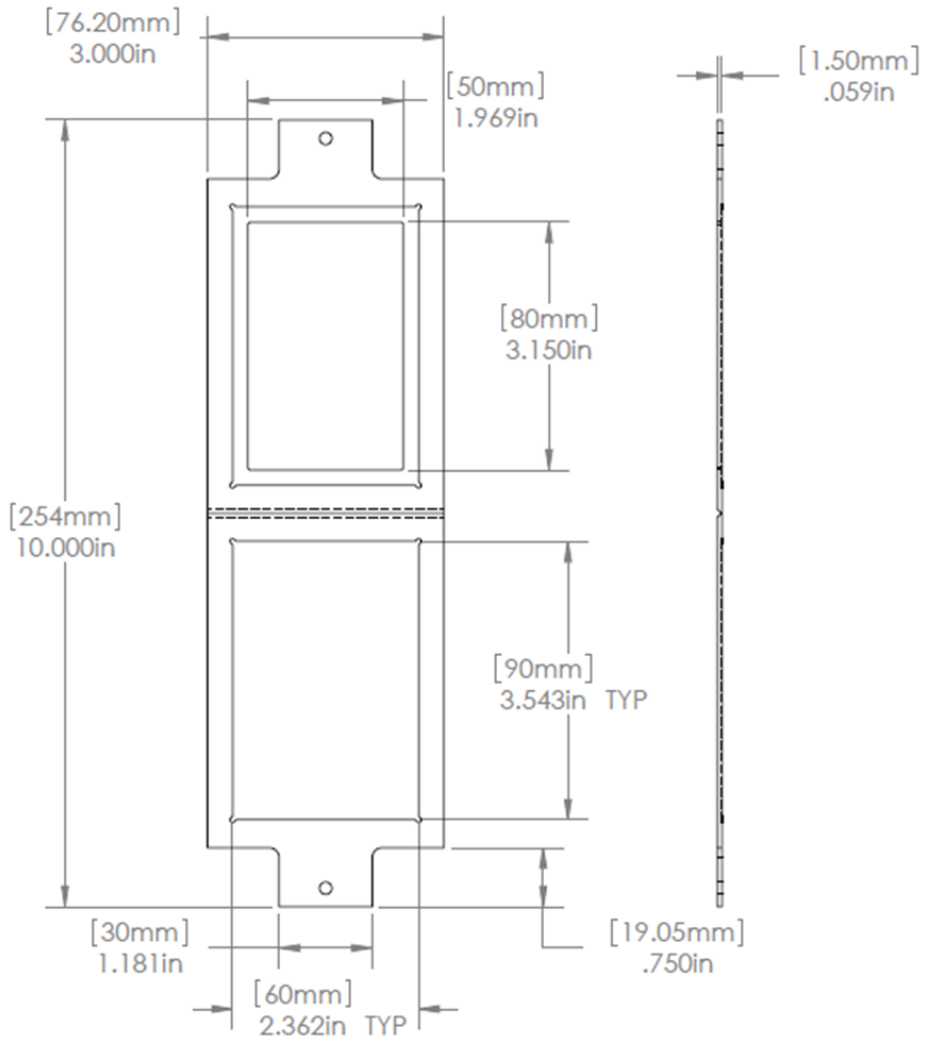

Figure S1. Schematic of paddle-type DGT device with exact dimensions. The resin, diffusive, and membrane filter layers are placed in the lower portion and the device is then folded over at the dotted line such that the area of only the 5x8 cm window is exposed.

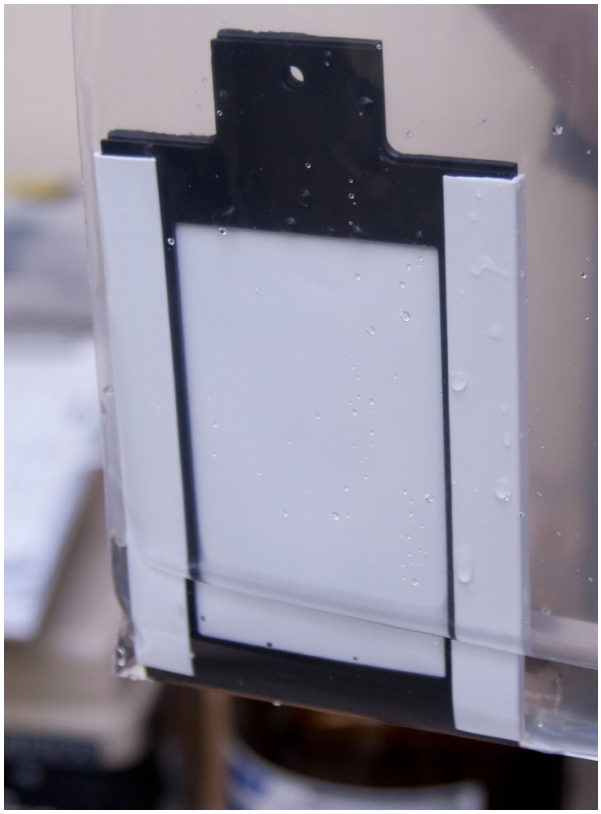

Figure S2. Assembled paddle-type DGT device.

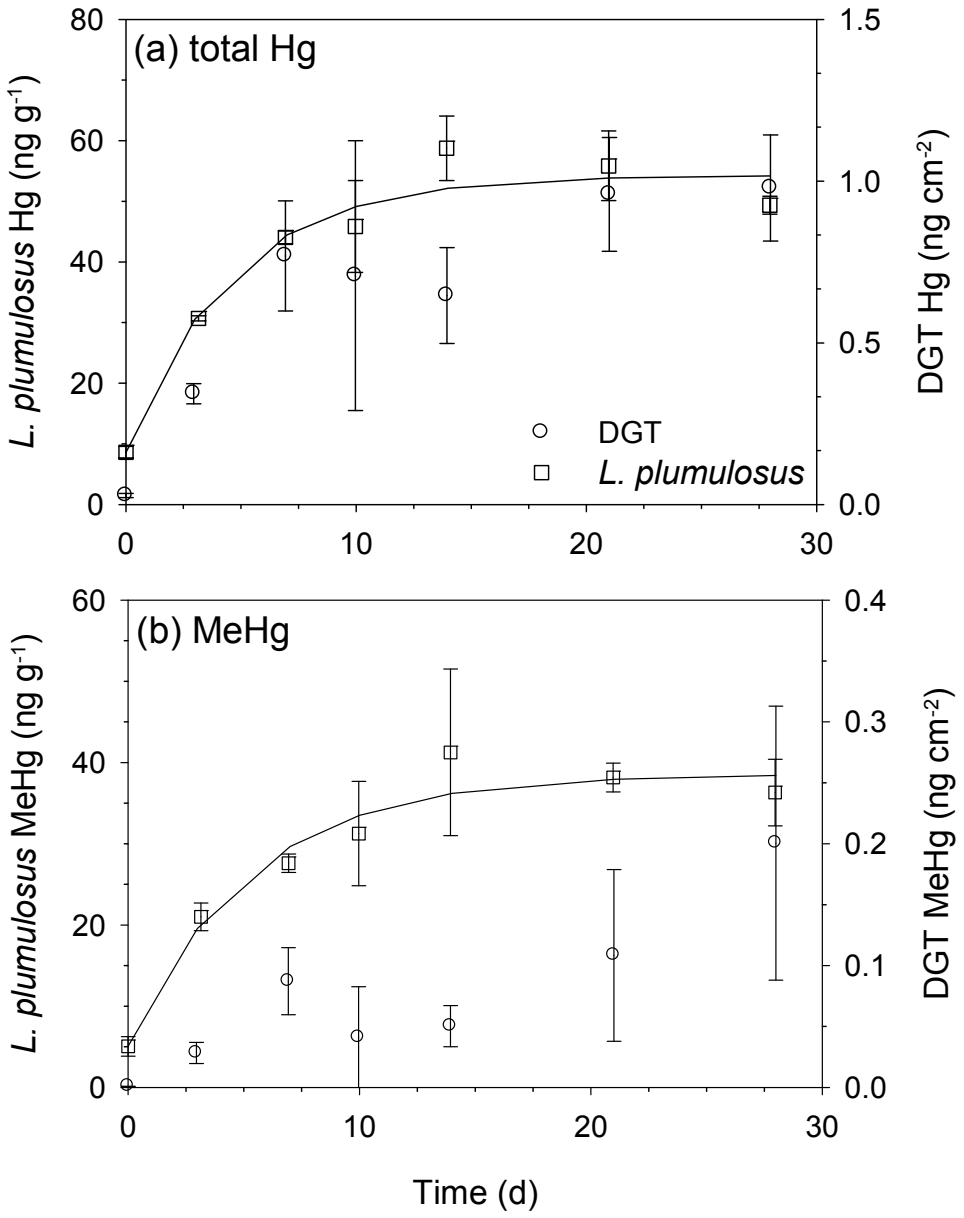

Figure S3. Time-dependent concentrations of (a) total Hg and (b) MeHg in *L. plumulosus* tissue and the piston DGT that sampled the sediment surface only. The lines are fits to the tissue concentrations from Eq. 7. Fitting parameters are given in Table S3.

Figure S4. Comparison of the protective filter membranes from two DGTs. The DGT on the left was in the presence of *N. virens*, and the DGT on the right was in the presence of *M. nasuta*. Note the buildup of Fe(III) hydroxide on the DGT filter membrane in the presence of *N. virens*. The slight yellow color on the membrane on the right was largely due to its short exposure time to air, from the time the DGT was pulled out of the sediment, to the time that it was disassembled and the photo was taken.