

Use of a Carbon Amendment to Reduce Bio-uptake of Mercury in a South River Floodplain Pond: Technical Briefing Paper

This briefing paper summarizes the objectives, study approach, and preliminary findings of the South River Pond Pilot Study. Ongoing annual monitoring has been conducted since the study pond was amended in the spring of 2011. The data reviewed and presented herein include results and findings from monitoring conducted in 2011, 2012, and 2013.

Introduction

Mercury was used between 1929 and 1950 at DuPont's Waynesboro, Virginia site, and was released and transported into surface water, sediments, soils, and biota of the South River. Remedial options are currently being evaluated for their ability to reduce the bioavailability of mercury to South River biota; one involves the use of carbon based sediment amendments. To assess the viability and efficiency of a sediment amendment remedial option, the Pond Pilot Study was implemented in 2011 in a South River floodplain pond using a two-phased approach (URS, 2011). Phase I included pond site selection, characterization of the pond, permitting, strategy development, and delineation of water/wetlands surrounding the pond. Phase II included amendment selection and deployment, engineering activities, and post-amendment annual monitoring (on-going).

References

- ✓ Hopkins, W. A. 2009. Reproduction and Development in *Bufo Americanus* from the South River, VA. 2008-2009 Annual Report. Prepared for E.I. DuPont de Nemours Company.
 - ✓ Ptacek C. and D. Blowes. 2010. *Riverbank Sediment Characterization and Preliminary Treatment Results*. University of Waterloo Powerpoint Presentation. South River Science Team Expert Panel Meeting, October 2010, Virginia.
 - ✓ Reible, D., P. Bireta, and R. Landis. 2012. Field measurement of porewater Hg using DGT. South River Science Team Expert Panel Meeting, October 2012, Virginia.
 - ✓ URS Corporation, 2011. Amendment Pilot Work Plan, South River Amendment Pilot Study, Waynesboro, Virginia. Wilmington, Delaware.
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Objectives

The purpose of the study is to test the efficacy of a sediment carbon amendment in limiting the bioavailability of mercury to biological receptors. Specific objectives are listed below:

- ❑ Assess the efficacy of the carbon amendment in reducing mercury concentrations in environmental media and bioavailability to biological receptors.
- ❑ Assess potential unintended consequences of the carbon amendment on water quality, sediment characteristics, and the benthic community.
- ❑ Demonstrate progress toward innovative remedial strategies.

Study Area Selection Process

A review of aerial imagery was performed to identify ponds within the South River floodplain for potential carbon amendment. The following descriptive information was gathered for each pond: accessibility, pre-existing data, presence of suitable monitoring organisms, and location on the floodplain. Based on review of this information, a candidate pond near relative river mile (RRM) 8.7 was chosen for the Pond Pilot Study (Figure 1).

The Pond Pilot Study site (pond) is adjacent to a smaller pond which was included in a previous study concerning mercury concentrations in the tissue of American toads (*Anaxyrus americanus*) (Hopkins, 2009). The property is not easily accessible by the public and is not located near public roads. The property is part of the Conservation Reserve Enhancement Program (CREP), and has broad areas that are planted with a variety of hardwood saplings. The property will be restored to pre-disturbance conditions at the conclusion of the pilot study, including vegetative cover.

The pond is approximately 42 feet by 103 feet, but physical features vary with groundwater elevation, river stage, and flood inundation. During the initial study period in 2011, the pond had a surface area of 3,365 ft² and volume of 2,580 ft³. The surface water level in the pond varies seasonally from approximately 2.5 to 6.0 feet in depth. The pond is an isolated, groundwater-fed floodplain feature, which also receives input from the river during flooding conditions. The direction of groundwater flow in the vicinity of the pond is toward the southeast based on groundwater elevation data. The substrate of the pond is not uniform—the margins are primarily silt, which increases in depth on the northwestern edge; the central area of the pond is primarily cobble.

Investigation Approach

In June 2011, a ‘semi-impermeable’ barrier was installed in the pond to create two discrete study areas or cells. The southern cell received the carbon amendment and is referred to as the amended cell. The northern cell remained untreated, serving as a control. The primary materials used to construct the barrier consisted of galvanized pipe, high-density polyethylene (HDPE) membrane (20-30 mm thickness), and sandbags.

In July 2011, approximately 2,000 pounds of commercially available biochar (i.e., Cowboy Charcoal®) were saturated with water and applied to the amended cell of the pond by way of a pneumatic biochar applicator. Biochar is a carbon-rich product created from biomass (e.g., hardwood) that is heated to elevated temperatures under oxygen deficient conditions. Biochar has proven effective in reducing biological uptake in metal-contaminated sediments (Ptacek, 2010).

Physical media (i.e., surface water, sediment, and pore water) and biological tissues [*Caenis* sp. (Mayfly nymph), Chironomidae (midge larvae), Planorbidae (aquatic snail), young-of-year bluegill (*Lepomis macrochirus*), green sunfish (*Lepomis cyanellus*) and wood frog tadpoles (*Rana sylvatica*)] have been monitored for inorganic mercury (IHg) and methylmercury (MeHg) as part of the Pond Pilot Study. Pore water IHg has also been monitored using diffusion gel thin film (DGT) devices (Reible et al., 2012). Additionally, the benthic macroinvertebrate community, *in situ* water quality, and sediment characteristics have been monitored to assess potential unintended

consequences of the carbon amendment. Monitoring took place prior to barrier installation (“pre-barrier”), prior to adding the carbon amendment (“baseline”), and at 1, 2, 4, 8, 12, 16, 20, 43, 50, 61, 97, and 104 weeks post-amendment. One additional monitoring event is scheduled to take place at approximately 118 weeks post-amendment.

Study Results

A summary of results thru the 2013 annual monitoring from the South River Pond Pilot Study is provided below. While the setup of the pilot study occurred in such a way to eliminate differences between the amended and control cells, not all conditions can be controlled for in a field pilot. Hence, these preliminary results should be reviewed in the context of uncertainties associated with any dynamic natural system such as the effects of surface water mixing from overtopping barrier during natural flooding events, redistribution of biochar over time, water depth, fresh particulate Hg deposition due to periodic runoff or flooding, baseline sediment physical and chemical differences between the amended and control side, biological and chemical factors.

Study results from the South River Pond Pilot Study thru the 2013 annual monitoring are as follows:

- ❑ Surface Water: Filtered inorganic mercury (FIHg) and filtered methylmercury (FMeHg) concentrations in surface water are significantly lower in the amended cell than the control cell (Figure 2).
- ❑ Aquatic Macroinvertebrates:
 - IHg concentrations in *Caenis sp.*, Chironomidae, and Planorbidae tissue are generally lower in the amended cell (Figure 3).
 - MeHg concentrations in *Caenis sp.* and Planorbidae tissue are significantly lower in the amended cell (Figure 4). Chironomidae tissue MeHg results are less consistent.
- ❑ Wood Frog Tadpoles: MeHg concentrations in wood frog tadpole tissue were significantly lower in the amended cell at post-amendment weeks 43 and 97 (Figure 5). There was no difference in IHg tissue concentrations at week 43. However, concentrations of IHg in tadpole tissue were significantly lower in the amended cell at post-amendment week 97.
- ❑ Bluegill Sunfish: MeHg concentrations in young-of-year bluegill tissue were significantly lower in the amended cell at post-amendment week 50. However, concentrations of MeHg in fish tissue were significantly lower in the control cell at week 104. (Figure 5). There was no difference in IHg tissue concentrations.
- ❑ Pore Water: IHg and MeHg concentrations in pore water are generally lower in the amended cell (Figure 6).
- ❑ Sediment: Consistent overall trends in grain-size-normalized sediment IHg and MeHg concentrations between cells are not evident (Figure 7).

- ❑ Benthic Community: Unintentional consequences of the carbon amendment on the native benthic community composition in the Pilot Study pond are not evident.

Summary of Preliminary Findings

The application of biochar appeared to remove mercury from the water column, as evidenced by the significant decline in water mercury concentrations. The amendment appeared to reduce MeHg uptake by ecological receptors that are more closely associated with surface water exposures, including snails, wood frog tadpoles, and young of the year bluegill. This is consistent with the current conceptual model for mercury exposure in low trophic level and young organisms, which may receive 50% of their mercury load via aqueous exposures.

The results of the DGT sampling, which showed a 50% decrease in pore water MeHg concentrations, strongly suggest that either methylation is suppressed in sediment or that partitioning is affected, reducing the labile MeHg (Reible et al., 2012). MeHg concentrations were lower in sediment following amendment consistent with the hypothesis that methylation was suppressed.

Preliminary findings from the South River Pond Pilot Study thru the 2013 annual monitoring are as follows:

- ❑ The carbon amendment may have had a positive effect, reducing methylmercury concentrations in surface water and biological receptors monitored during the high methylation period in Spring 2012.
- ❑ The carbon amendment may be causing a reduction in the concentrations of IHg and MeHg in environmental media, and the bioavailability of MeHg to biological receptors.
- ❑ To date, no adverse effects of the sediment carbon amendment on water quality, sediment characteristics, or the benthic community have been observed.
- ❑ Preliminary results and findings of the South River Pond Pilot Study provide input use of amendments in remedial options strategies for reducing the bioavailability of mercury to South River biota.

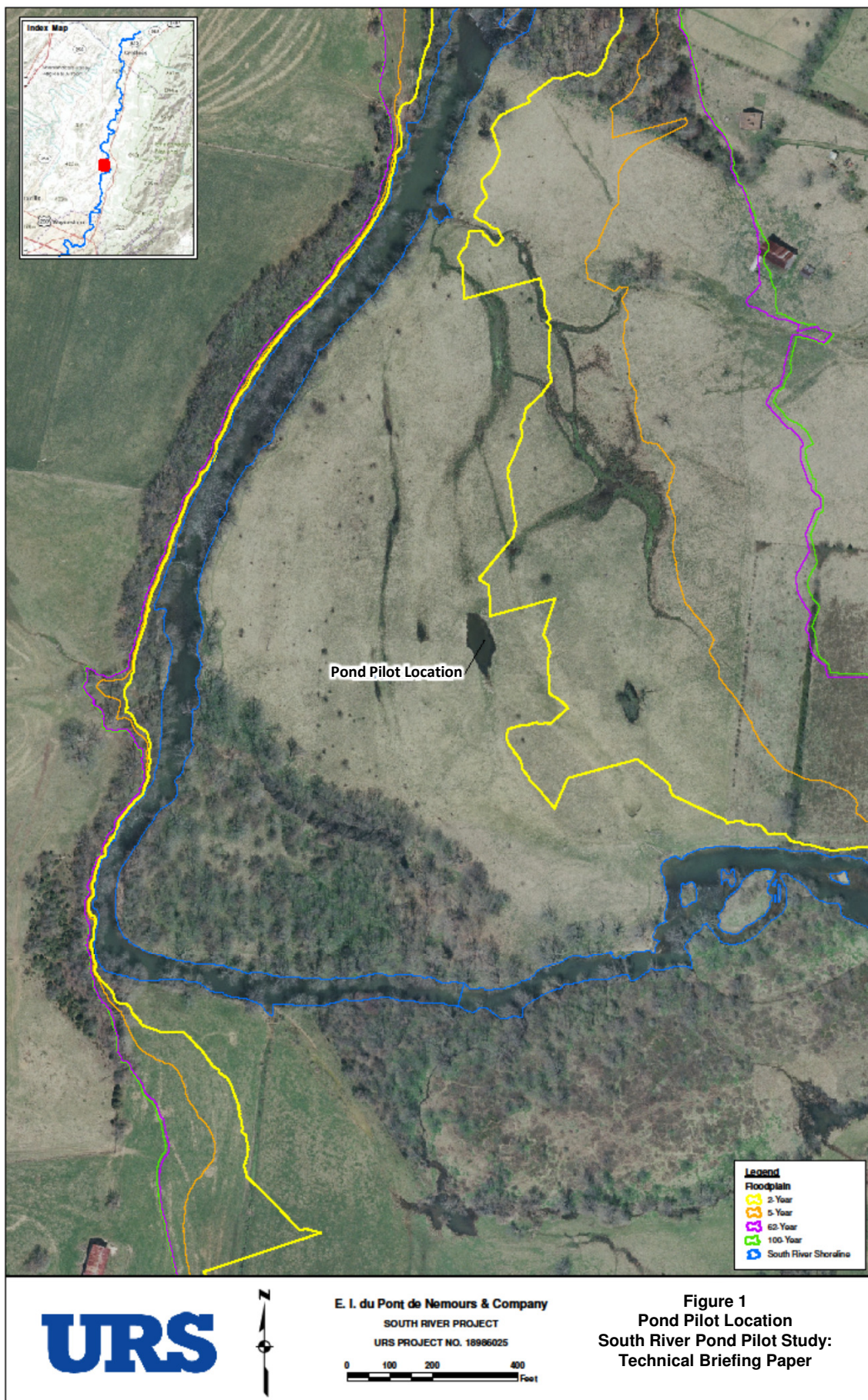
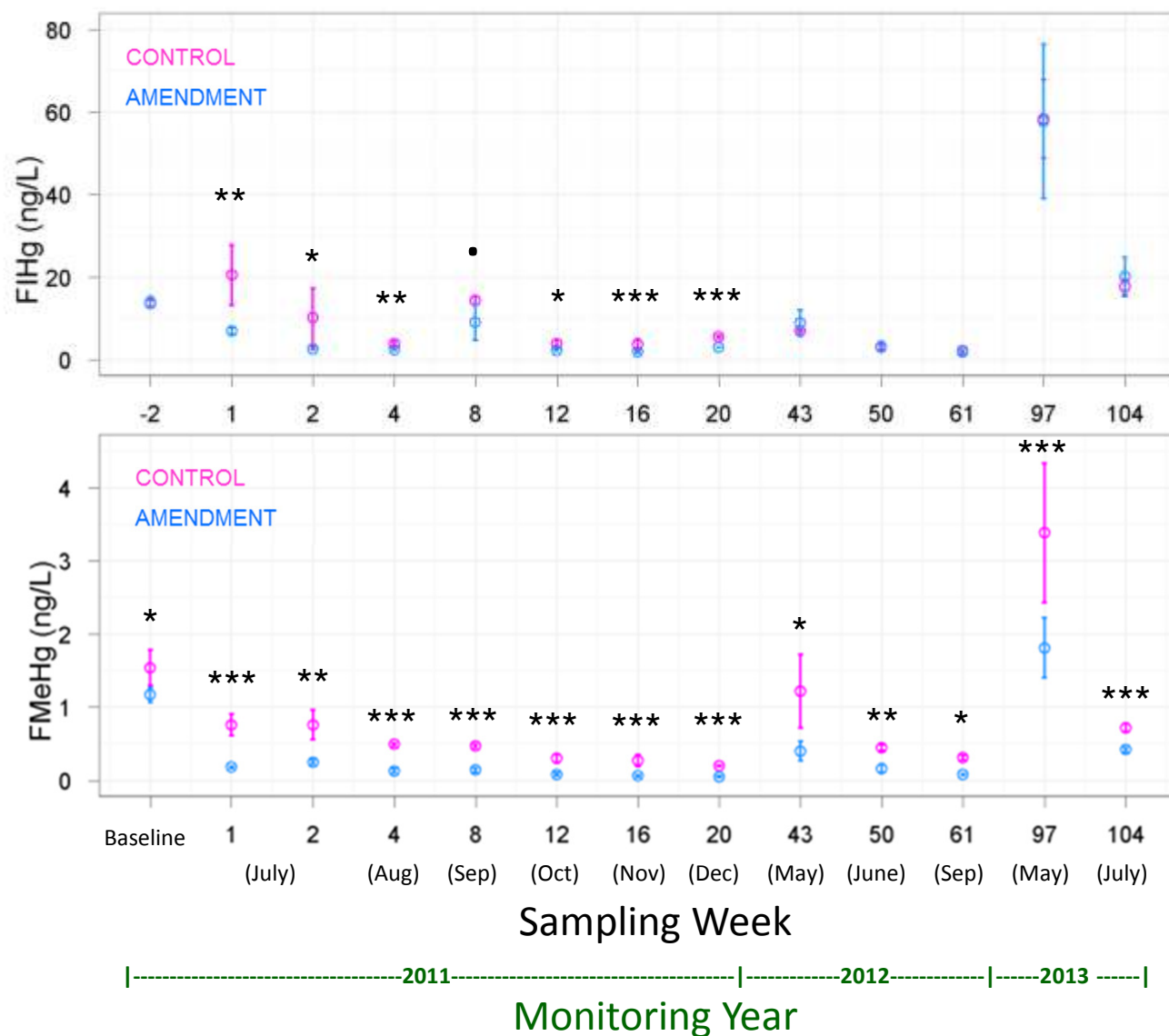


Figure 2
 Filtered Surface Water Inorganic Mercury (IHg) and Methylmercury (MeHg) Monitoring Results
 South River Pond Pilot Study:
 Technical Briefing Paper

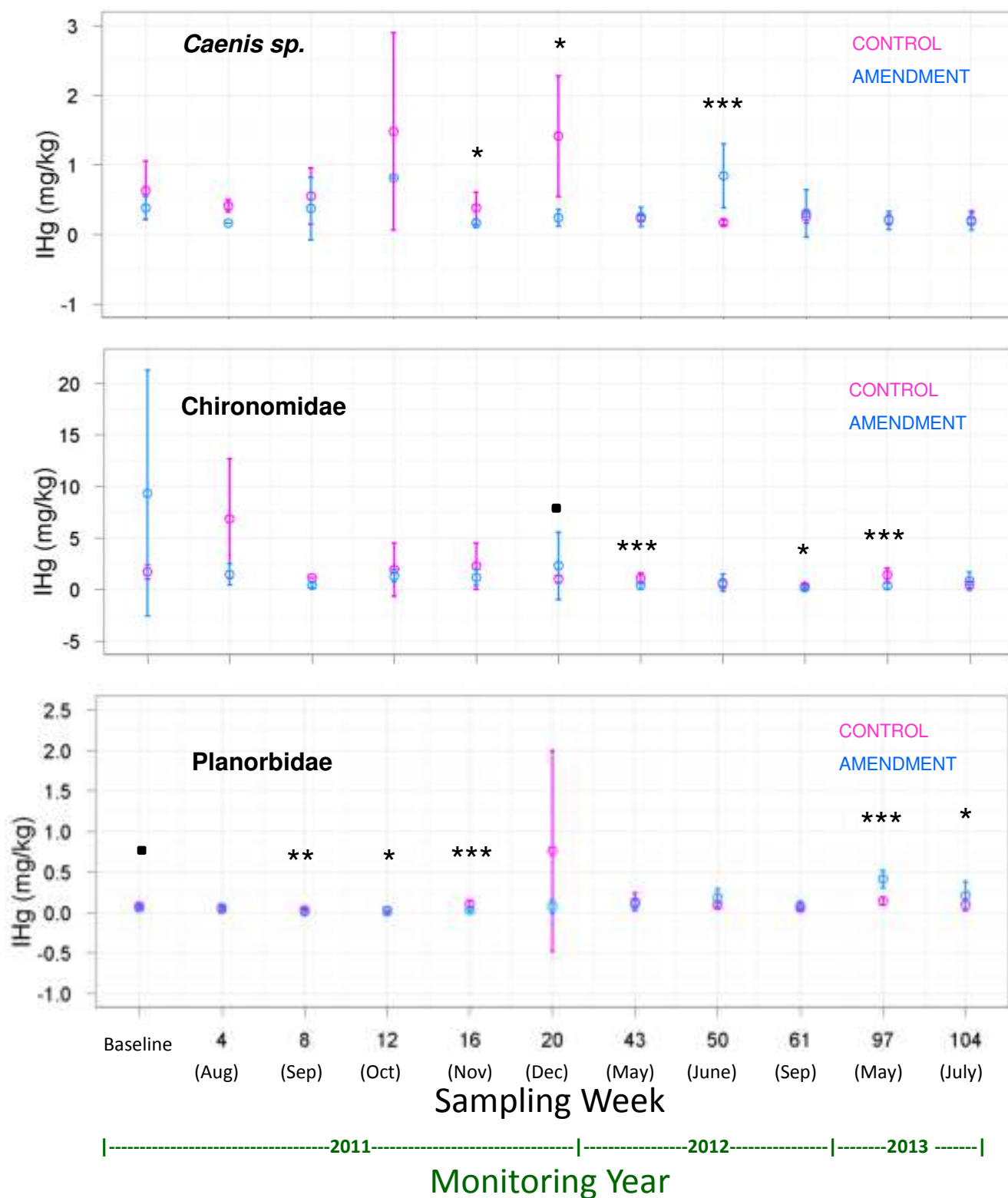


Note:

Surface water mixing occurred between cells on several occasions after slight failure of barrier beginning January, 2012. Compared log-transformed concentrations between amended and control cells (one-tailed, two-sample t-test)

	■	*	**	***
p - value	<0.1	< 0.05	< 0.01	<0.001

Figure 3
Benthic Invertebrate Tissue Inorganic Mercury (IHg) Monitoring Results
South River Pond Pilot Study:
Technical Briefing Paper



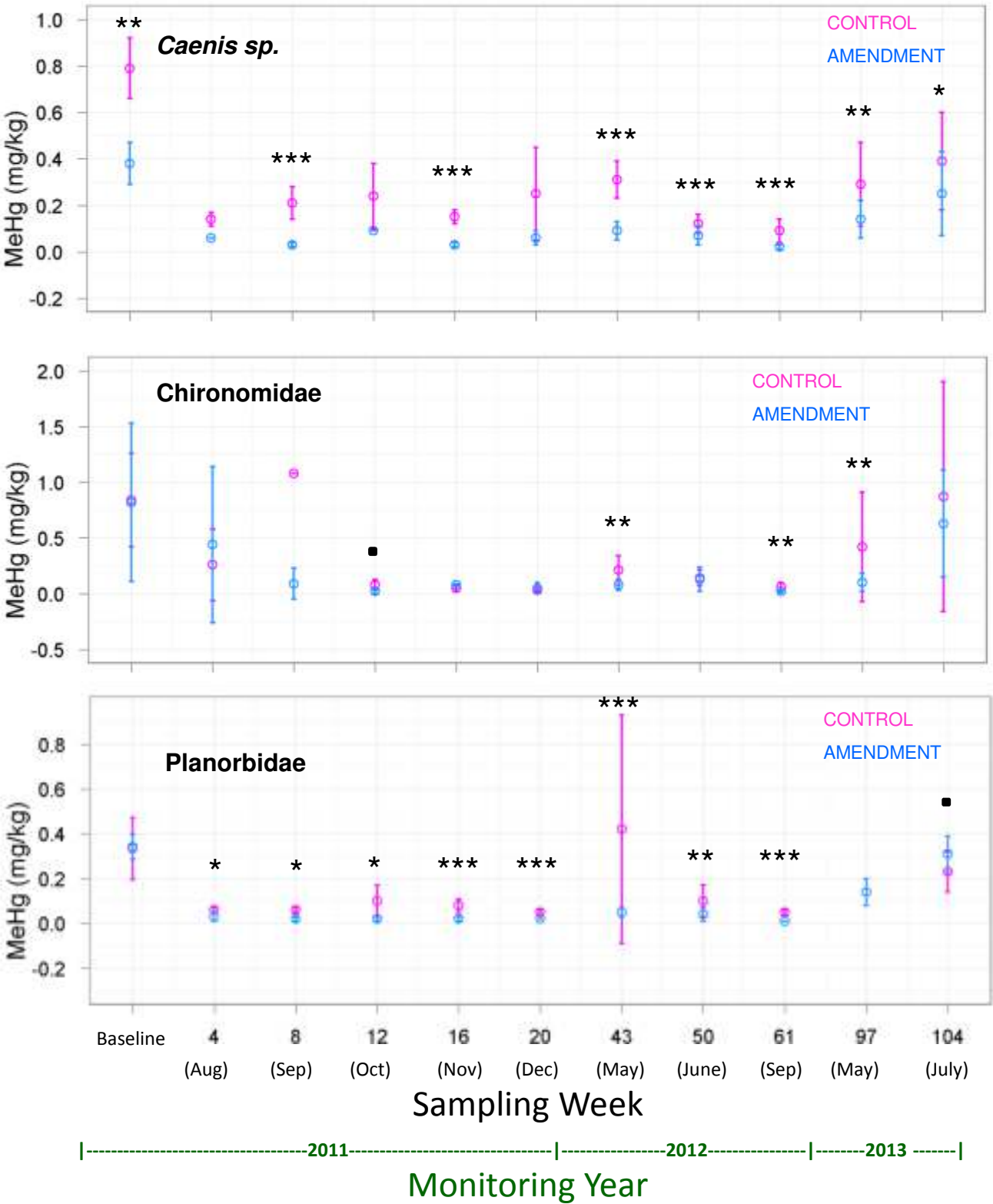
Note:

Due to lack of sample replicates, statistical tests were not conducted for *Caenis* at weeks 4 and 12, and Chironomidae at week 8.

Compared log-transformed concentrations between amended and control cells (one-tailed, two-sample t-test)

		*	**	***
<i>p</i> -value	<0.1	< 0.05	< 0.01	<0.001

Figure 4
 Benthic Invertebrate Tissue Methylmercury (MeHg) Monitoring Results
 South River Pond Pilot Study:
 Technical Briefing Paper

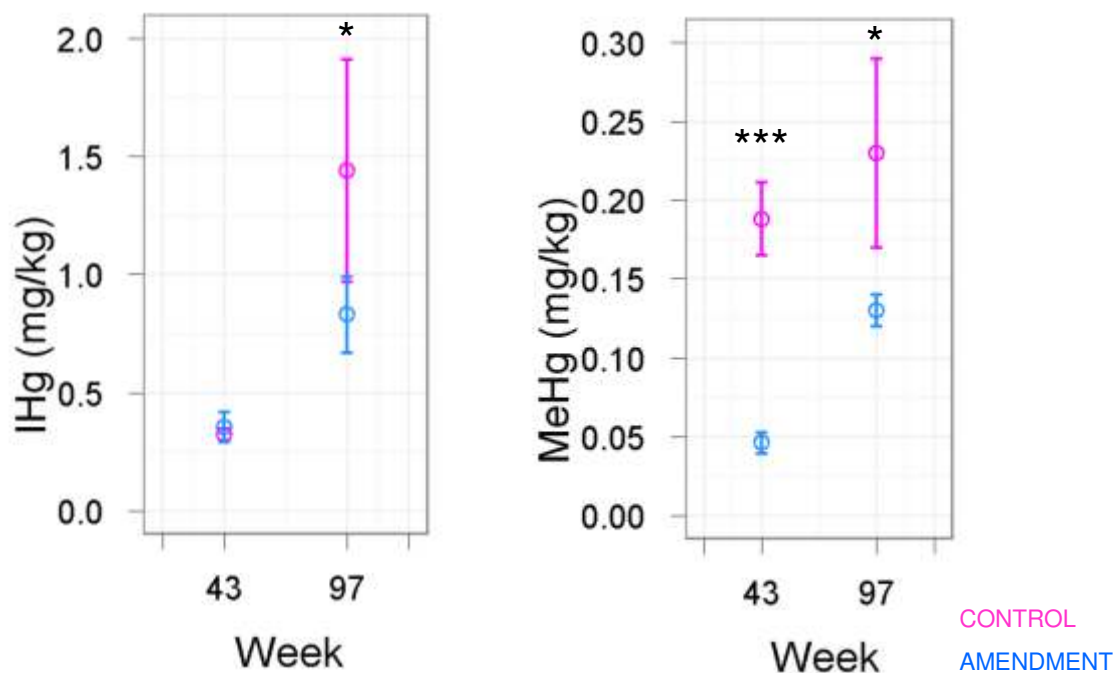


Note:
 Due to lack of sample replicates, statistical tests were not conducted for *Caenis* at weeks 4 and 12, and *Chironomidae* at week 8.
 Compared log-transformed concentrations between amended and control cells (one-tailed, two-sample t-test)

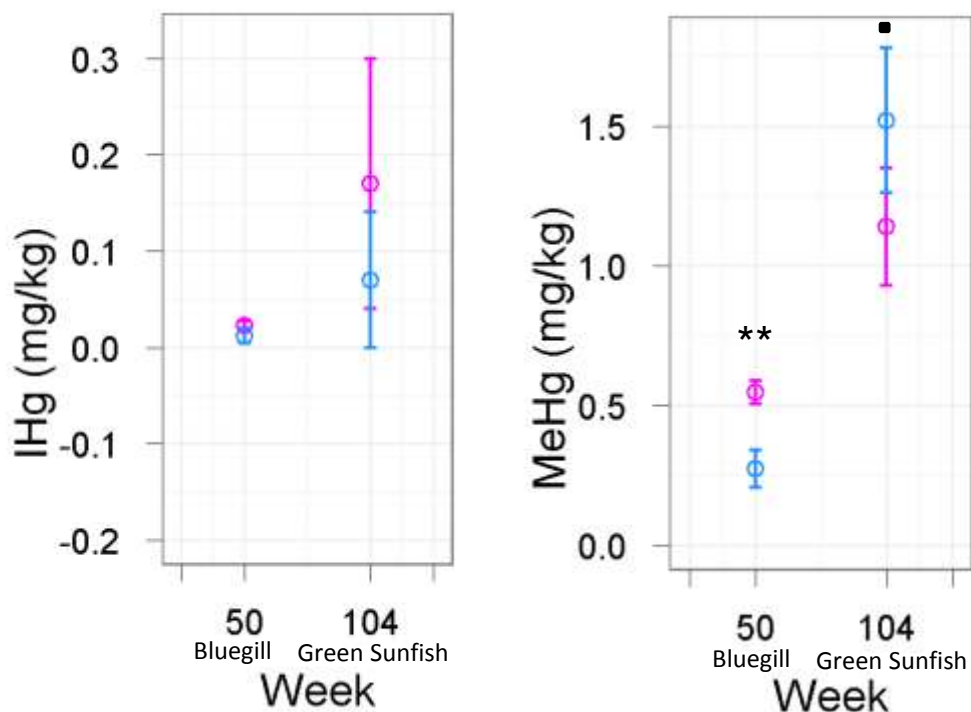
	■	*	**	***
p - value	<0.1	< 0.05	< 0.01	<0.001

Figure 5
Wood Frog Tadpole and Young-of-Year Sunfish
Inorganic Mercury (IHg) and Methylmercury (MeHg) Monitoring Results
South River Pond Pilot Study:
Technical Briefing Paper

Wood Frog Tadpole



Young-of-Year Sunfish

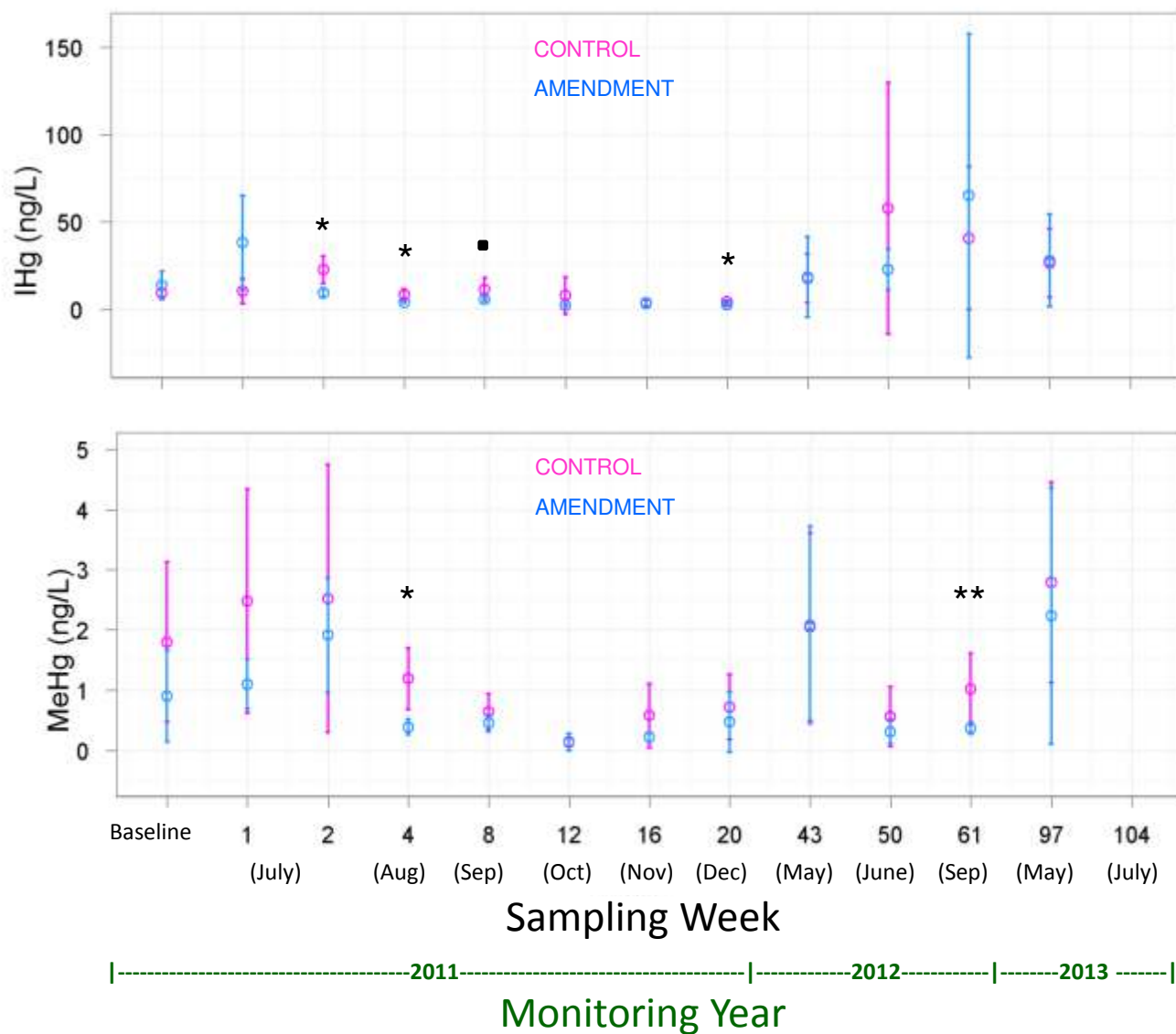


Note:

Compared log-transformed concentrations between amended and control cells (one-tailed, two-sample t-test)

	■	*	**	***
<i>p</i> - value	<0.1	< 0.05	< 0.01	<0.001

Figure 6
Pore Water Inorganic Mercury (IHg) and Methylmercury (MeHg) Monitoring Results
South River Pond Pilot Study:
Technical Briefing Paper

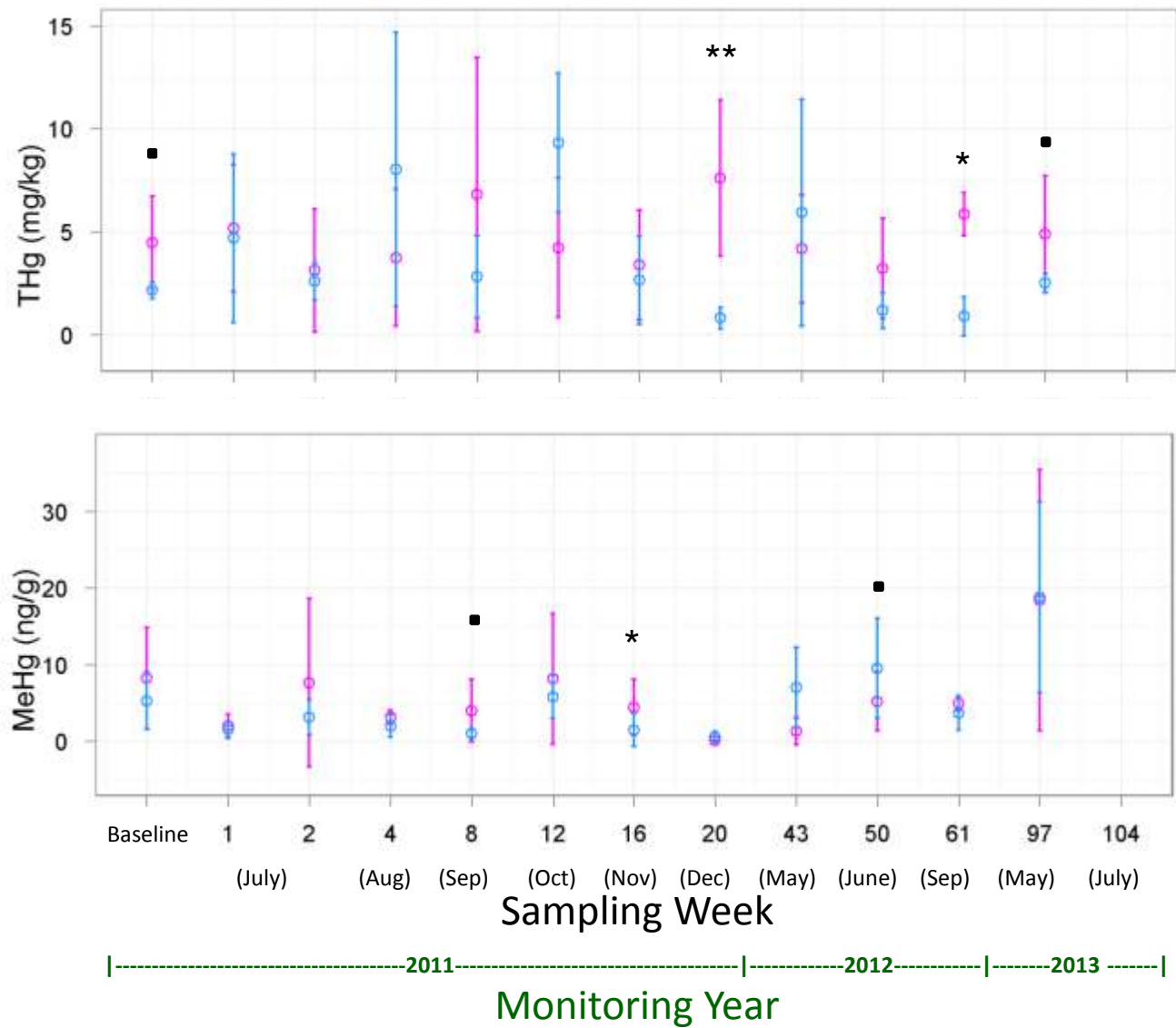


Note:

Compared log-transformed concentrations between amended and control cells (one-tailed, two-sample t-test)

	■	*	**	***
<i>p</i> -value	<0.1	< 0.05	< 0.01	<0.001

Figure 7
Sediment Inorganic Mercury (IHg) and Methylmercury (MeHg) Monitoring Results
South River Pond Pilot Study:
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Note:

Compared log-transformed concentrations between amended and control cells (one-tailed, two-sample t-test)

Sediment concentrations are grain-size normalized (<0.075mm)

	■	*	**	***
<i>p</i> - value	<0.1	< 0.05	< 0.01	<0.001