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 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 includes results and findings from monitoring conducted in 2011, 2012, 2013, and 2014.

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.
- ✓ URS. 2012. Final Report: Ecological Study of the South River and a Segment of the South Fork Shenandoah River, Virginia. September 2012.

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.

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 ft^2 and volume of 2,580 ft^3. 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 the monitoring frequency shown in Table 1.

Table 1
Monitoring Frequency
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Monitoring Frequency (Weeks Post-Amendment)	Sampling Event (Month, Year)
1	July, 2011
2	July, 2011
4	August, 2011
8	September, 2011
12	October, 2011
16	October, 2011
20	November, 2011
43	May, 2012*
50	June, 2012
61	September, 2012
97	May, 2013**
104	July, 2013
117	October, 2013
150	May, 2014
157	July, 2014

Notes:
*Prior to this sampling event, barrier breach occurred between December, 2011 and January, 2012, likely following a significant storm even on December 8, 2011.
**Flooding occurred prior to this sampling event on May 8, 2013.

Study Results

A summary of results thru the 2014 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. For example, a barrier breach and a flooding event (see Table 1) occurred that may have compromised the intended segregation of the control and the test areas. Hence, these 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 mercury 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 2014 annual monitoring are as follows:

- Surface Water: Filtered inorganic mercury (FIHg) and filtered methylmercury (FMeHg) concentrations in surface water were generally significantly lower in the amended cell than the control cell (Figure 2).
- Aquatic Macroinvertebrates:
    - IHg concentrations in *Caenis sp.*, Chironomidae, and Planorbidae tissue were generally lower in the amended cell (Figure 3).
    - MeHg concentrations in *Caenis sp.* and Planorbidae tissue were generally significantly lower in the amended cell (Figure 4). Chironomidae tissue MeHg results were 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 weeks 97 and 150.
- Sunfish: MeHg concentrations in young-of-year sunfish tissue were significantly lower in the amended cell at post-amendment weeks 50 and 157 (bluegill only). 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 were generally lower in the amended cell (Figure 6).
- Sediment: Consistent overall trends in grain-size-normalized sediment IHg and MeHg concentrations between cells were not evident (Figure 7).
- Benthic Community: Unintentional consequences of the carbon amendment on the native benthic community composition in the Pilot Study pond were not evident.

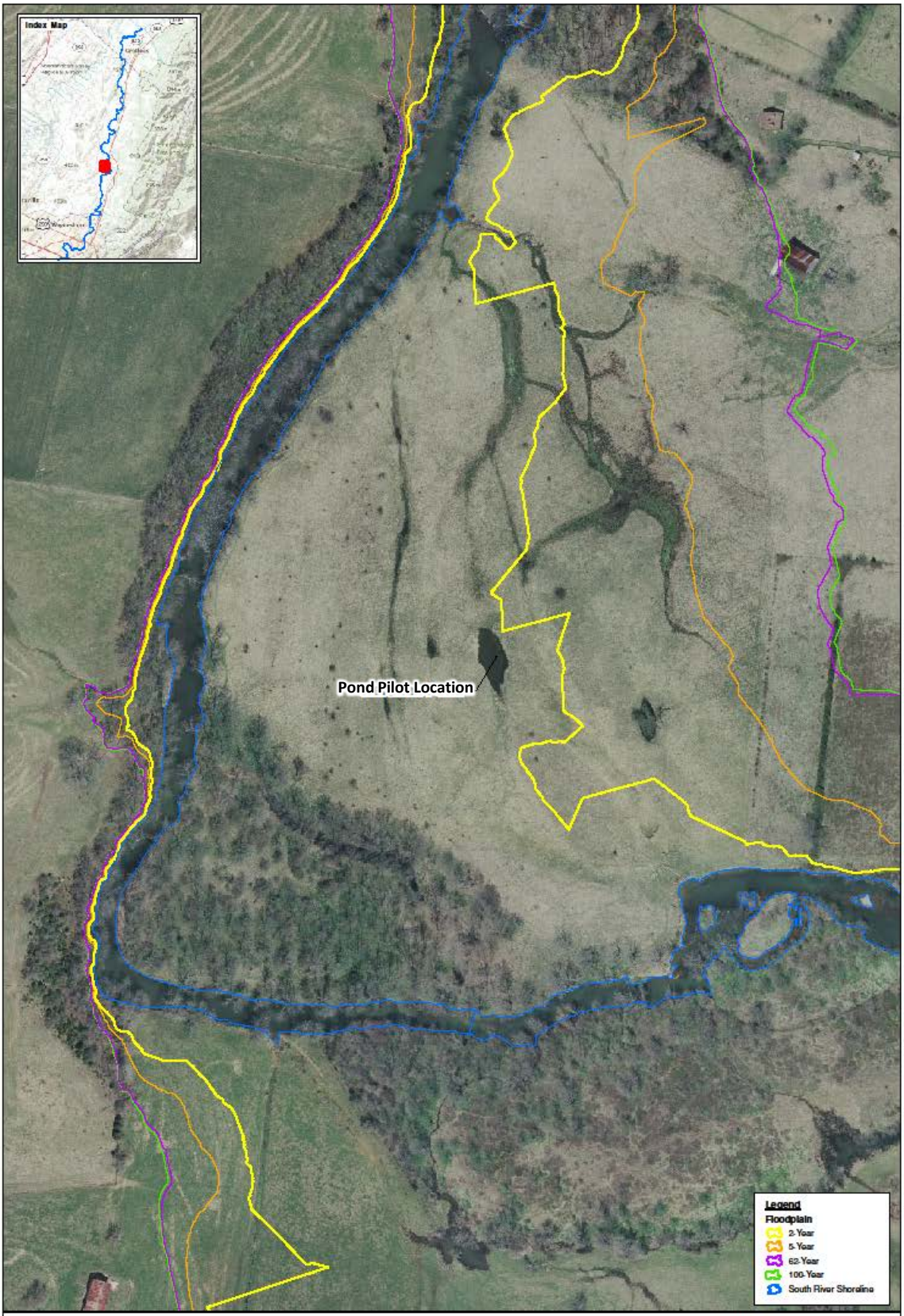
Summary of Findings

The application of biochar appeared to remove mercury from the water column, as evidenced by the significant decline in water mercury concentrations (prior to and following the barrier breach and the flooding event). 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 (URS, 2012).

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.

Findings from the South River Pond Pilot Study thru the 2014 annual monitoring are as follows:

- The carbon amendment may have had a positive effect, reducing MeHg concentrations in surface water and biological receptors monitored during the high methylation periods in Spring 2012 and 2013.
- 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.
- Increases in mercury concentrations in the water column were evident following the barrier breach and the flooding event; although the impacts of these events on the pilot study are unclear, these events likely interfered with the overall study goals (including the evaluations of biochar's efficacy in reducing mercury bioaccumulation).
- Results and findings of the South River Pond Pilot Study provide input to the potential use of amendments in remedial option strategies for reducing the bioavailability of mercury to South River biota.



URS

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E. I. du Pont de Nemours & Company

SOUTH RIVER PROJECT

URS PROJECT NO. 18986025

0 100 200 400 Feet

Figure 1
Pond Pilot Location
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Figure 2
Filtered Surface Water Inorganic Mercury (IHg) and Methylmercury (MeHg) Monitoring Results
South River Pond Pilot Study:
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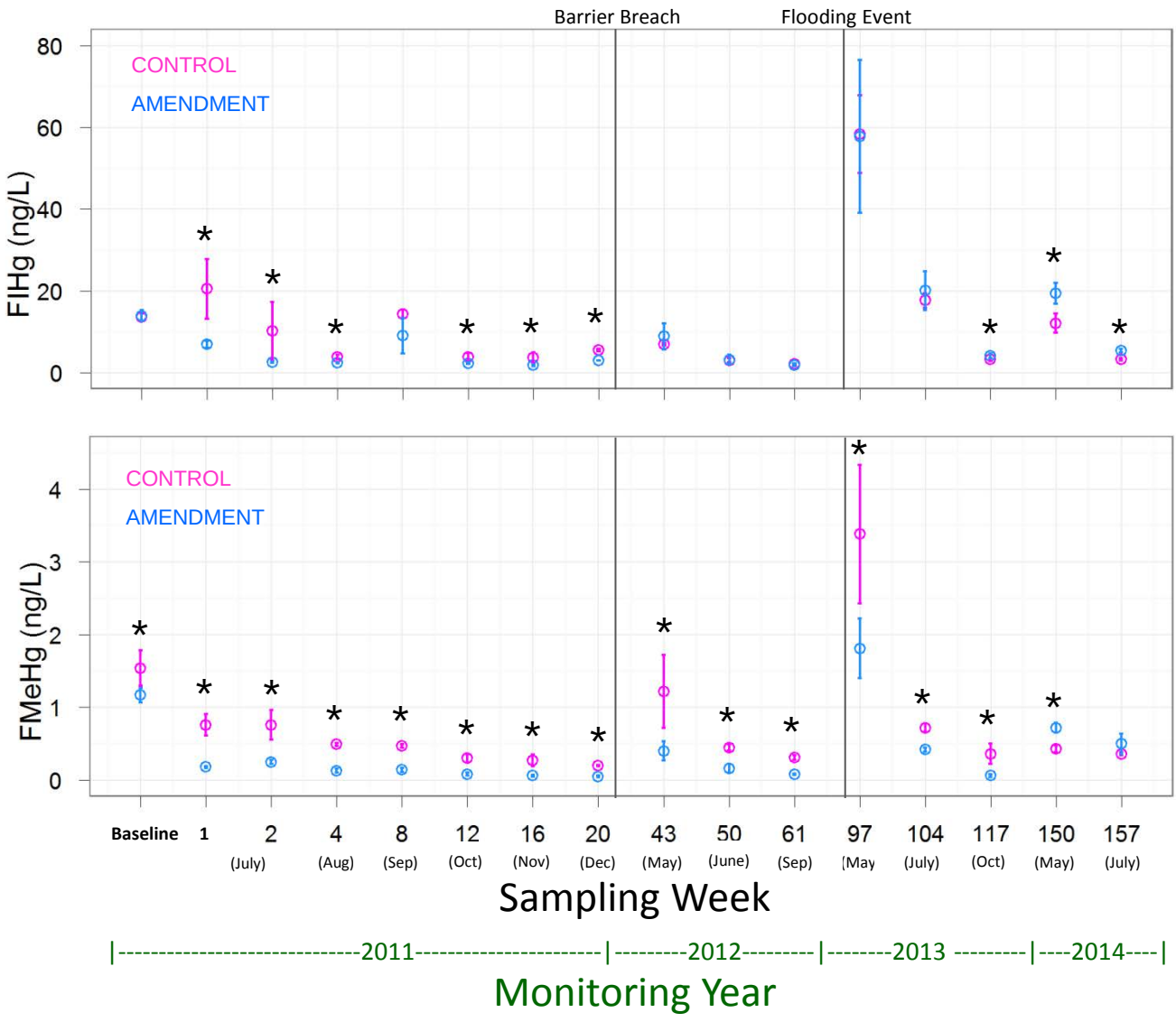

Note:
Surface water mixing occurred between cells on several occasions after slight failure of barrier beginning January, 2012.
Compared log-transformed concentrations between amended and control cells (one-tailed, two-sample t-test). Significant difference (α=0.05) indicated by an asterisk (*).

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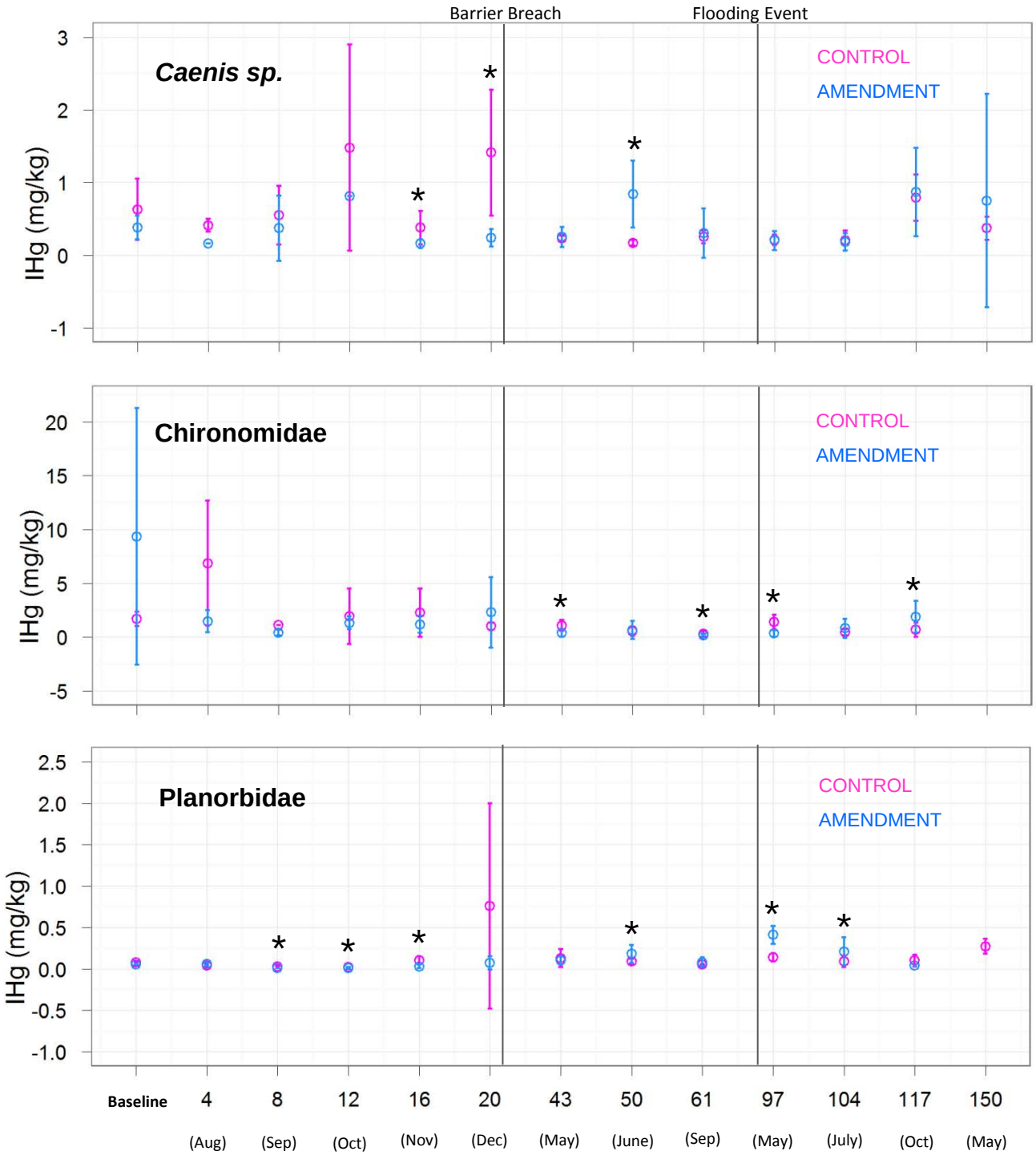

Note:
Due to lack of
117 and 150. Chironomidae was not monitored in 2014. Compared log-transformed concentrations between amended and control cells (one-tailed, two-sample t-test). Significant difference (α=0.05) indicated by an asterisk (*).

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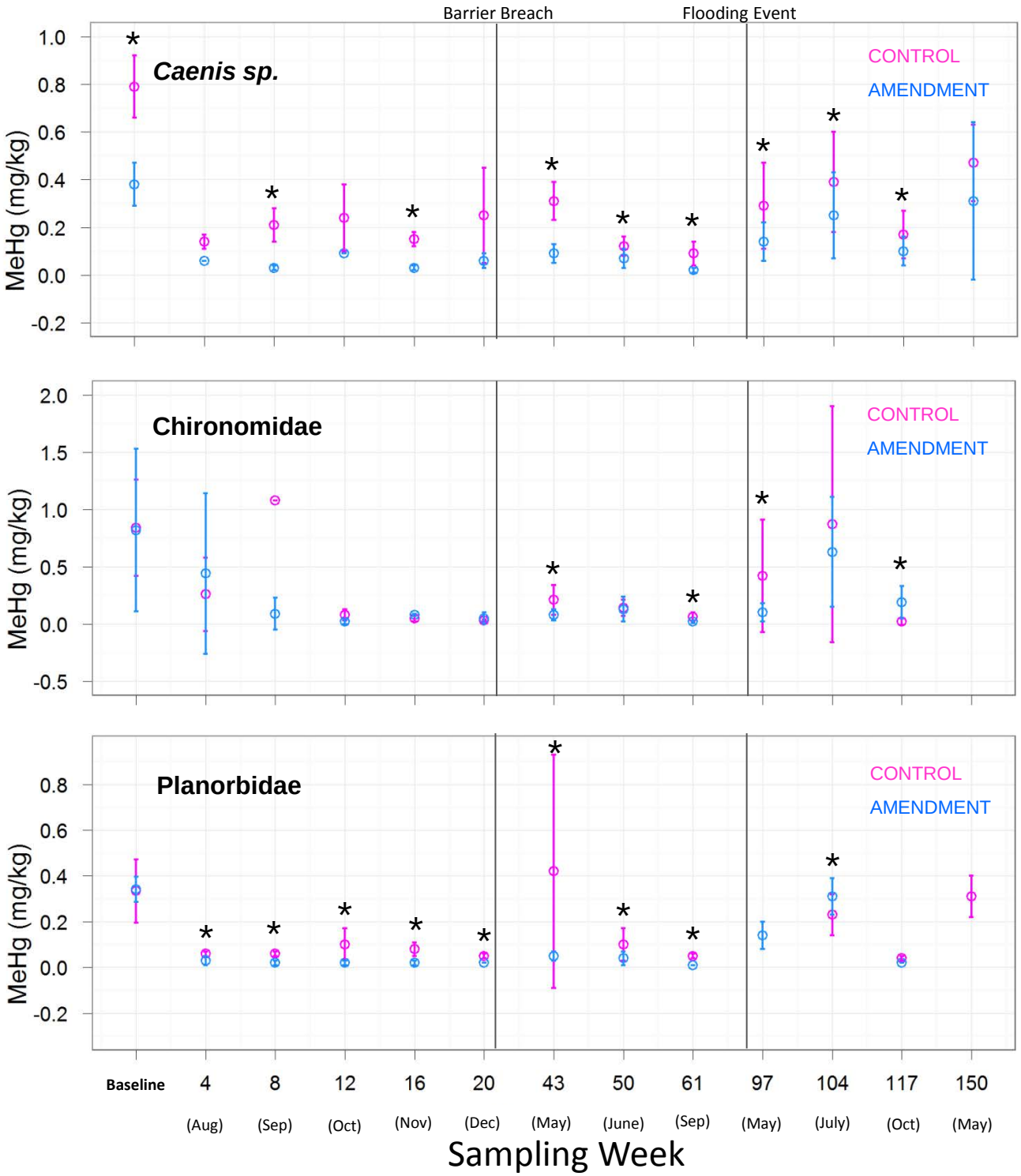

Note:
Due to lack of sample replicates, statistical tests were not conducted for *Caenis* at weeks 4 and 12, Chironomidae at week 8, and Planorbidae at weeks 117 and 150. Chironomidae was not monitored in 2014. Compared log-transformed concentrations between amended and control cells (one-tailed, two-sample t-test). Significant difference (α=0.05) indicated by an asterisk (*).

Figure 5
Wood Frog Tadpole and Young-of-Year Sunfish
Inorganic Mercury (IHg) and Methylmercury (MeHg) Monitoring Results
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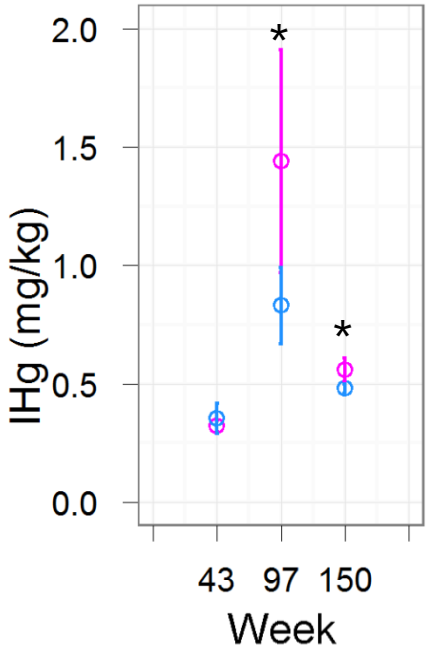
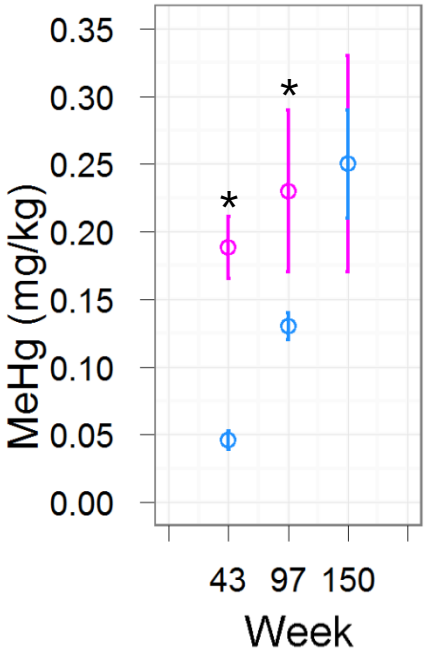
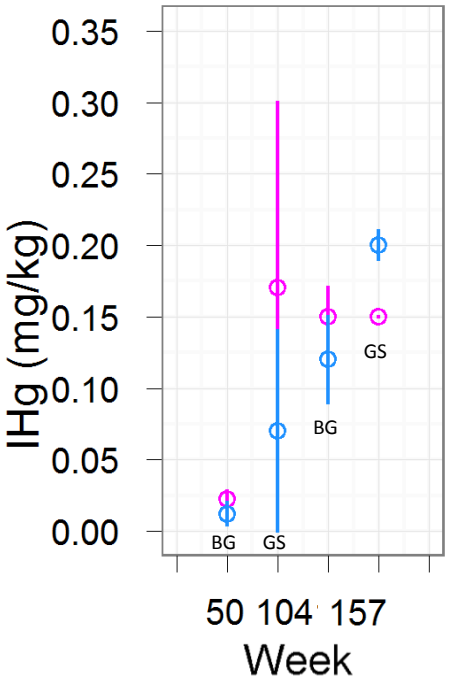
Wood Frog Tadpole

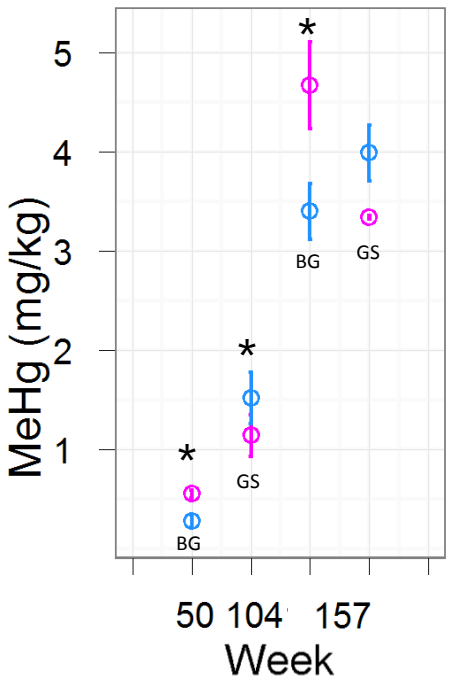




CONTROL
AMENDMENT

Young-of-Year Sunfish





Note:
BG= Bluegill; GS= Green sunfish. Compared log-transformed concentrations between amended and control cells (one-tailed, two-sample t-test). Significant difference (α=0.05) indicated by an asterisk (*).

Figure 6
Pore Water Inorganic Mercury (IHg) and Methylmercury (MeHg) Monitoring Results
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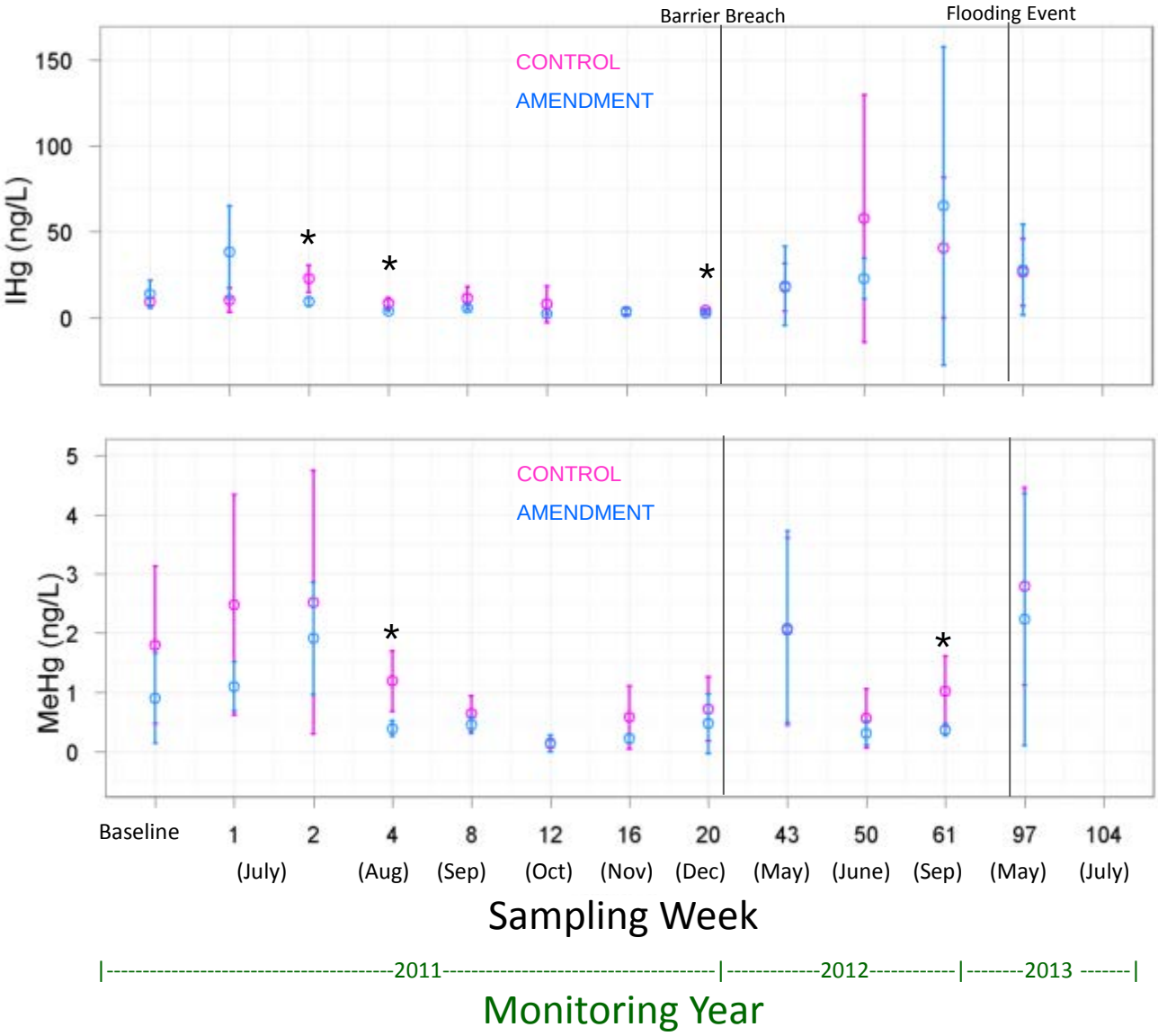

Note:
Pore water was not sampled in 2014. Compared log-transformed concentrations between amended and control cells (one-tailed, two-sample t-test). Significant difference (α=0.05) indicated by an asterisk (*).

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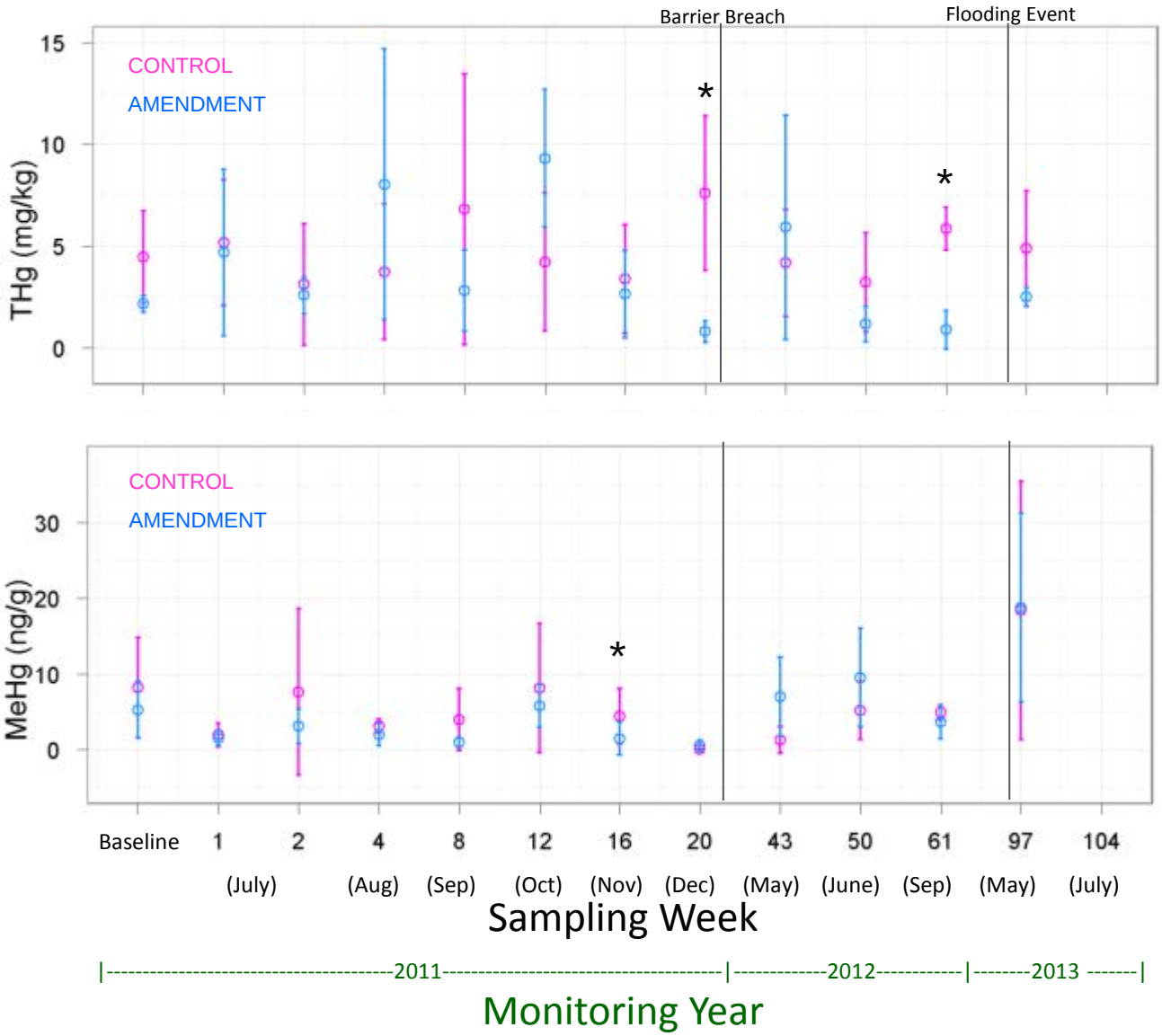

Note:
Sediment was not sampled in 2014. Compared log-transformed concentrations between amended and control cells (one-tailed, two-sample t-test). Significant difference (α=0.05) indicated by an asterisk (*).