

Supporting Information for:

Hg isotopes reveal in-stream processing and legacy inputs in East Fork Poplar Creek, Oak Ridge, TN, USA

Jason D. Demers^{a,1}, Joel D. Blum^a, Scott C. Brooks^b, Patrick M. Donovan^a, Ami L. Riscassi^{b,c},
Carrie L. Miller^{b,d}, Wang Zheng^{b,e}, and Baohua Gu^b

^aDepartment of Earth and Environmental Sciences, University of Michigan,
Ann Arbor, MI 48109, USA

^bEnvironmental Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA

^cPresent address: Department of Environmental Sciences, University of Virginia, Charlottesville,
VA 22904-4123, USA

^dPresent address: Department of Biology, Troy University, Troy, AL 36082, USA

^ePresent address: School of Earth and Space Exploration, Arizona State University, Tempe, AZ
85287, USA

¹Corresponding author: Jason D. Demers, Department of Earth and Environmental Sciences,
University of Michigan, 1100 N. University Ave., Ann Arbor, MI 48109, USA.
phone: (734) 763-9308; email: jdemers@umich.edu

Supplemental Figure Legends

Supplemental Figure S1. Hydrographs showing discharge (m^3/s) at EFK23.4 (i.e., Station 17 at the Y12 boundary) and near EFK5.0, our downstream-most sampling site. Shown is the timing of seasonal synoptic surface water sampling along the flow path, biofilm sampling, and intensive hyporheic zone and riparian wetland sampling campaigns during (A) October 2011, (B) April 2012, and (C) August 2012 on East Fork Poplar Creek, Oak Ridge, TN, USA.

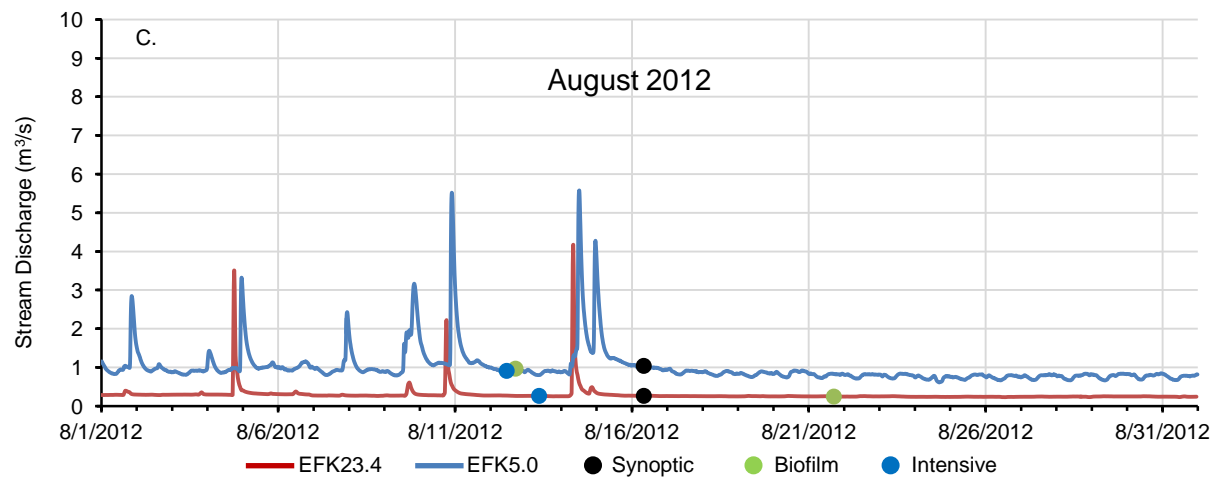
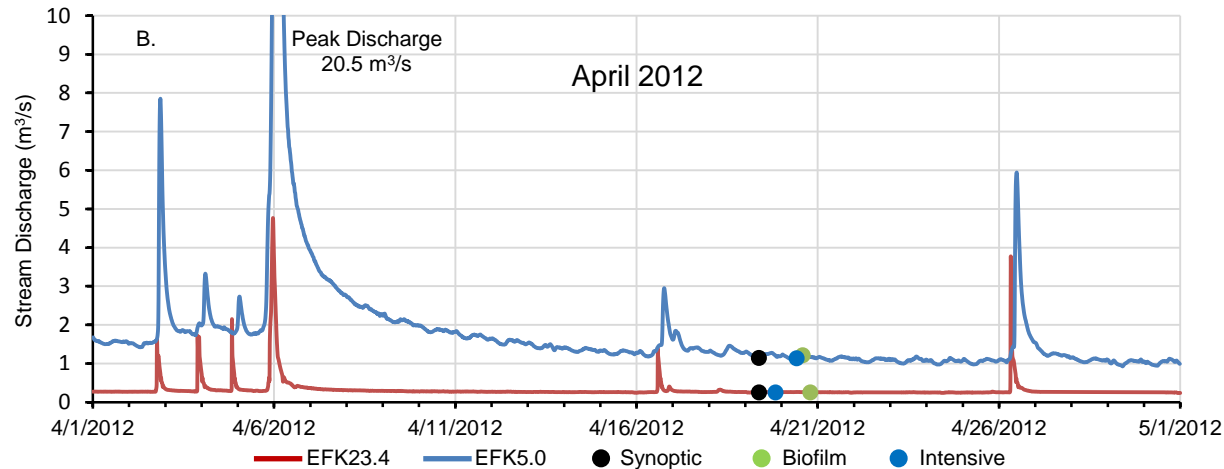
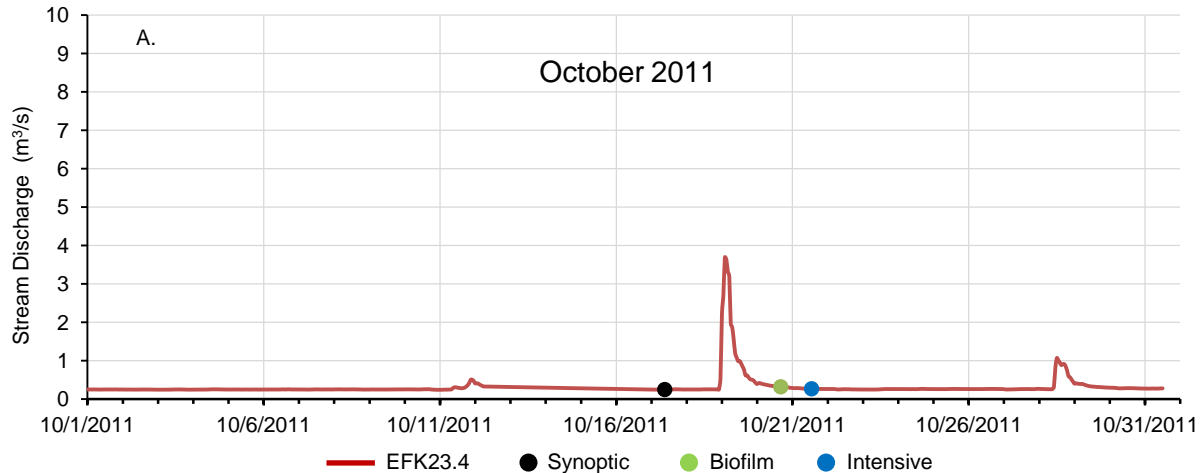
Supplemental Figure S2. Concentration of (A) total particulate-bound mercury (THg_p) associated with total suspended solids (TSS) ($n = 24$), expressed on both a volume (ng/L) and a mass ($\mu\text{g/g}$) basis; (B) total dissolved mercury (THg_d) ($n = 24$); and (C) total dissolved methyl mercury (MeHg_d) ($n = 24$) in stream water during seasonal synoptic sampling of East Fork Poplar Creek, Oak Ridge, TN, USA.

Supplemental Figure S3. Isotopic composition of (A) particulate-bound mercury (THg_p) associated with total suspended solids ($n=24$), and (B) total dissolved mercury (THg_d) in stream water ($n=23$) along the flow path of East Fork Poplar Creek, Oak Ridge, TN, USA. Analytical uncertainty is shown as 2SD of average of session averages for UM-Almaden (see *Methods*). Gray dashed lines show zero values for $\delta^{202}\text{Hg}$ and $\Delta^{199}\text{Hg}$. The upstream-most site (EFK25.4 or EFK23.4) and the downstream-most site (EFK5.0) have been identified for each seasonal synoptic campaign.

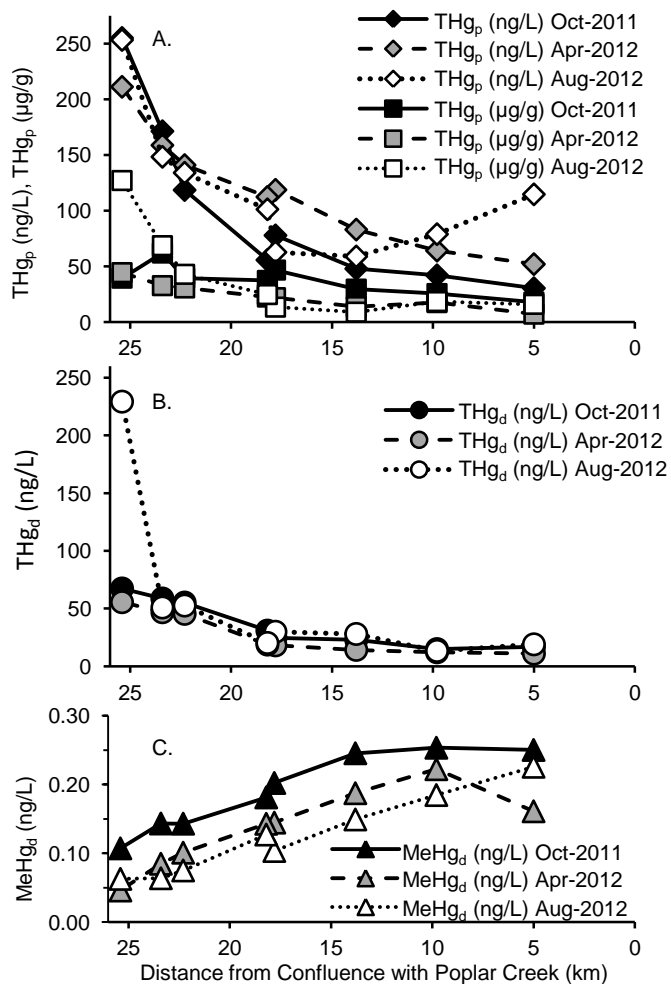
Supplemental Figure S4. Relationship between $\Delta^{201}\text{Hg}$ and $\Delta^{199}\text{Hg}$ of particulate-bound mercury (THg_p) associated with total suspended solids in stream water, and dissolved mercury (THg_d) in stream water, hyporheic pore water, and riparian pore water during three seasonal sampling campaigns in East Fork Poplar Creek, Oak Ridge, TN, USA. The mercury isotopic composition of sediment from non-Y12-impacted tributaries is also shown (Donovan et al. 2014). Analytical uncertainty is shown as 2SD of average of session averages for UM-Almaden (see *Methods*).

Supplemental Figure S5. Mercury isotopic composition ($\delta^{202}\text{Hg}$) of dissolved Hg (THg_d) in stream water, hyporheic pore water, and riparian pore water; and particulate-bound mercury (THg_p) associated with suspended solids in stream water and pore water at two intensive sampling sites (EFK5.0, EFK22.3) along East Fork Poplar Creek, Oak Ridge, TN, USA. Shown are: October 2011 samples at (A) EFK22.3 and (B) EFK 5.0; April 2012 samples at (C) EFK22.3 and (D) EFK5.0; and August 2012 samples at (E) EFK22.3 and (F) EFK5.0. Gray and blue shaded bars are equal to the values for surface water samples co-located with hyporheic and riparian pore water samples. Vertical dashed lines show small rain events that separated synoptic and intensive sampling campaigns in October and August (see hydrographs in Figure S1). Analytical uncertainty is shown as 2SD of average of session averages for UM-Almaden (see *Methods*).

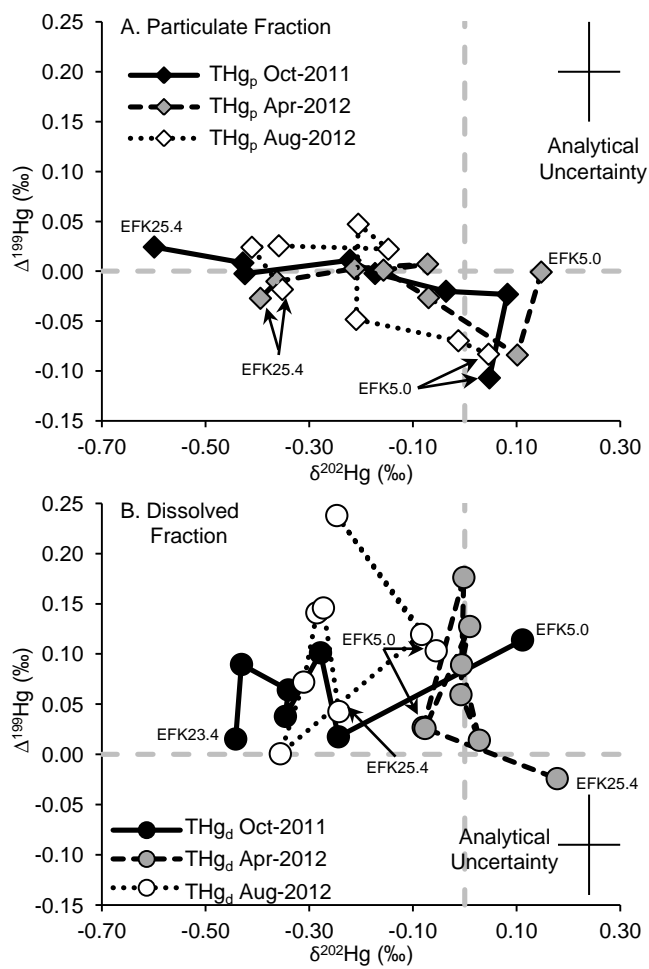
Supplemental Figure S1.



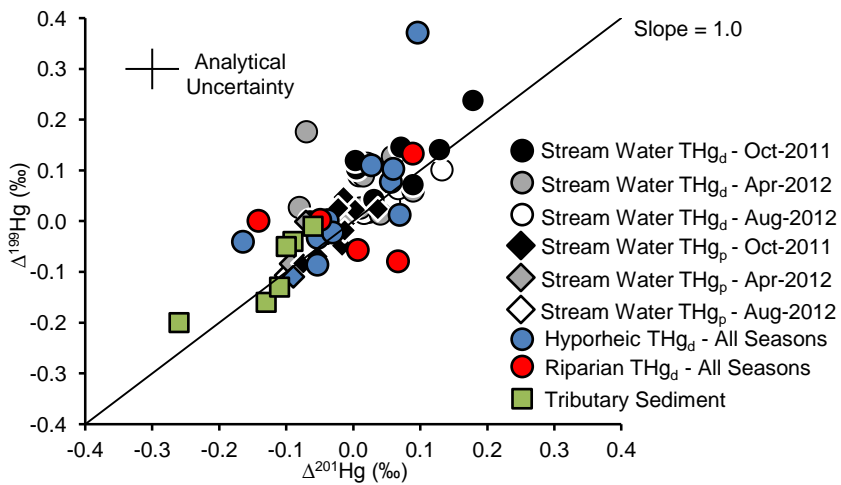
Supplemental Figure S2.



Supplemental Figure S3.



Supplemental Figure S4.



Supplemental Figure S5.

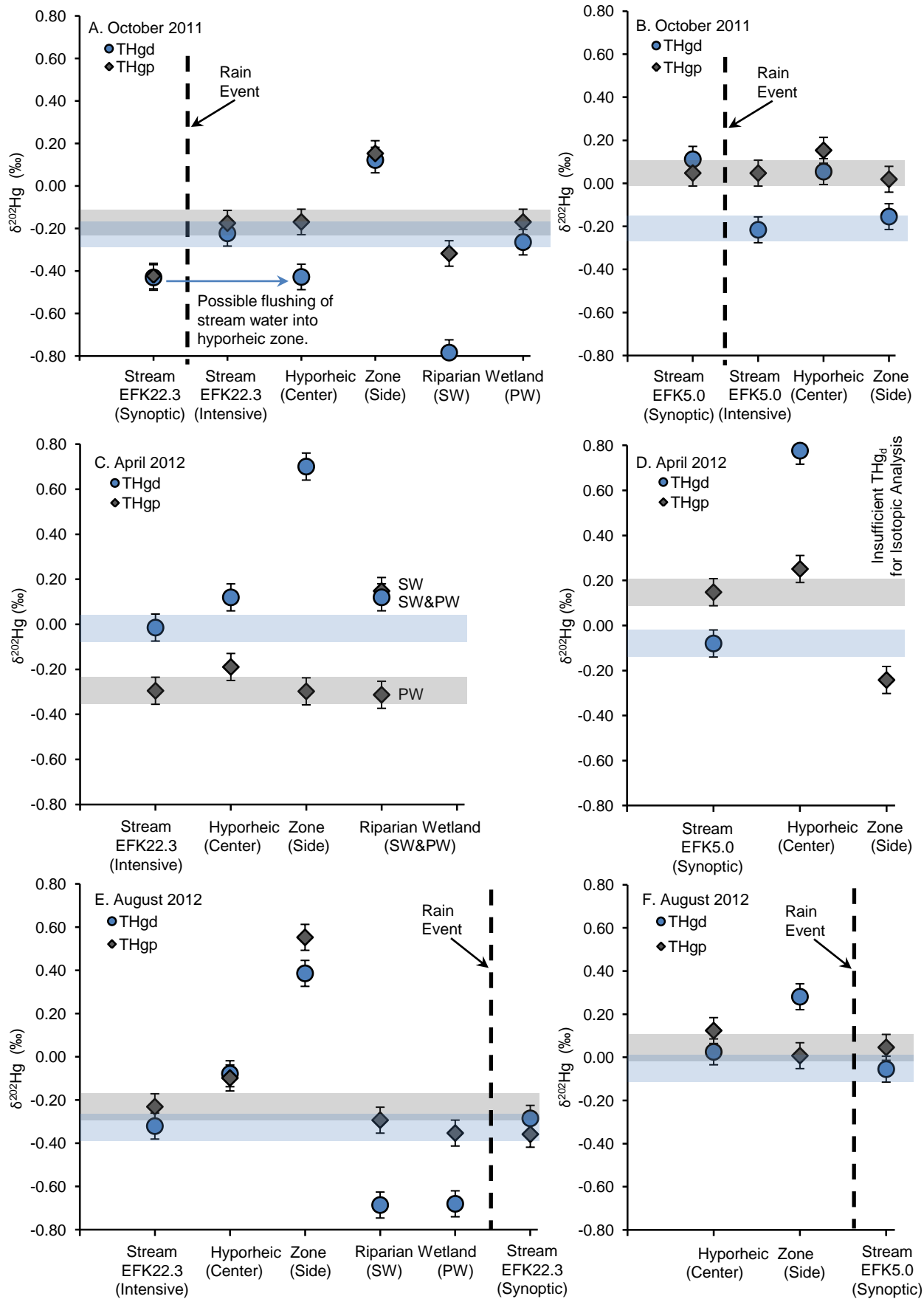


Table S1. Concentration and isotopic composition of total dissolved mercury (THg_d) in stream water during seasonal synoptic sampling of East Fork Poplar Creek, Oak Ridge, TN, USA.^a

	Sampling Site ID	THg _d				δ ²⁰⁴ Hg		δ ²⁰² Hg		δ ²⁰¹ Hg		δ ²⁰⁰ Hg		δ ¹⁹⁹ Hg		Δ ²⁰⁴ Hg		Δ ²⁰¹ Hg		Δ ²⁰⁰ Hg		Δ ¹⁹⁹ Hg		
		(ng/L)	n ₁	n ₂	n ₃	%Rec.	(‰)	2σ	(‰)	2σ	(‰)	2σ	(‰)	2σ	(‰)	2σ	(‰)	2σ	(‰)	2σ	(‰)	2σ	(‰)	2σ
October 2011	EFK5.0	17.5	1	1	1	100.3	-0.19	0.09	0.11	0.06	0.10	0.05	0.09	0.06	0.14	0.06	-0.36	0.11	0.02	0.04	0.04	0.04	0.11	0.05
	EFK9.8	15.5	1	1	1	99.6	-0.24	0.09	-0.24	0.06	-0.16	0.05	-0.17	0.06	-0.04	0.06	0.13	0.11	0.02	0.04	-0.05	0.04	0.02	0.05
	EFK13.8	23.9	1	1	1	98.8	-0.39	0.09	-0.28	0.06	-0.08	0.05	-0.11	0.06	0.03	0.06	0.02	0.11	0.13	0.04	0.03	0.04	0.10	0.05
	EFK17.8	25.7	1	1	1	98.0	-0.54	0.09	-0.35	0.06	-0.21	0.05	-0.11	0.06	-0.05	0.06	-0.02	0.11	0.05	0.04	0.07	0.04	0.04	0.05
	EFK18.2	32.3	1	1	1	100.8	-0.56	0.09	-0.34	0.06	-0.19	0.05	-0.19	0.06	-0.02	0.06	-0.05	0.11	0.07	0.04	-0.02	0.04	0.06	0.05
	EFK22.3	57.7	2	2	1	98.1	-0.61	0.09	-0.43	0.06	-0.32	0.05	-0.23	0.06	-0.02	0.06	0.03	0.11	0.01	0.04	-0.01	0.04	0.09	0.05
	EFK23.4	61.3	1	1	1	100.1	-0.54	0.09	-0.44	0.06	-0.32	0.05	-0.23	0.06	-0.10	0.06	0.12	0.11	0.02	0.04	-0.01	0.04	0.02	0.05
	EFK25.4	70.5	1	1	1	97.3	No data available. Sample destroyed during isotope analysis.																	
April 2012	EFK5.0	11.4	1	1	1	102.8	-0.01	0.09	-0.08	0.06	-0.14	0.05	-0.02	0.06	0.01	0.06	0.11	0.11	-0.08	0.04	0.02	0.04	0.03	0.05
	EFK9.8	12.4	1	1	1	99	0.03	0.09	0.00	0.06	-0.07	0.05	0.08	0.06	0.18	0.06	0.03	0.11	-0.07	0.04	0.08	0.04	0.18	0.05
	EFK13.8	14.6	1	1	1	101.7	0.13	0.09	-0.01	0.06	0.08	0.05	0.04	0.06	0.06	0.06	0.14	0.11	0.09	0.04	0.04	0.04	0.06	0.05
	EFK17.8	18.8	1	1	1	97.8	0.00	0.09	0.03	0.06	0.06	0.05	0.10	0.06	0.02	0.06	-0.05	0.11	0.04	0.04	0.09	0.04	0.01	0.05
	EFK18.2	19.5	1	1	1	98.6	-0.07	0.09	-0.01	0.06	0.01	0.05	0.01	0.06	0.09	0.06	-0.06	0.11	0.02	0.04	0.02	0.04	0.09	0.05
	EFK22.3	47.3	2	2	1	100.4	0.04	0.09	0.01	0.06	0.07	0.05	0.04	0.06	0.13	0.06	0.02	0.11	0.06	0.04	0.03	0.04	0.13	0.05
	EFK23.4	48.8	2	2	1	93.2	-0.08	0.09	-0.08	0.06	-0.05	0.05	-0.03	0.06	0.01	0.06	0.04	0.11	0.01	0.04	0.01	0.04	0.03	0.05
	EFK25.4	57.9	2	2	1	101.3	0.24	0.09	0.18	0.06	0.09	0.05	0.09	0.06	0.02	0.06	-0.03	0.11	-0.04	0.04	0.00	0.04	-0.02	0.05
August 2012	EFK5.0	19.6	2	2	2	99.8	-0.15	0.09	-0.05	0.06	-0.04	0.05	-0.02	0.06	0.09	0.06	-0.06	0.11	0.00	0.04	0.00	0.04	0.10	0.05
	EFK9.8	13.8	1	1	1	97.3	-0.31	0.09	-0.25	0.06	-0.01	0.05	-0.05	0.06	0.18	0.06	0.06	0.11	0.18	0.04	0.08	0.04	0.24	0.05
	EFK13.8	29.1	1	1	1	96.6	-0.34	0.09	-0.08	0.06	-0.06	0.05	-0.05	0.06	0.10	0.06	-0.22	0.11	0.00	0.04	-0.01	0.04	0.12	0.05
	EFK17.8	31.1	1	1	1	98.1	-0.58	0.09	-0.36	0.06	-0.33	0.05	-0.19	0.06	-0.09	0.06	-0.05	0.11	-0.06	0.04	-0.02	0.04	0.00	0.05
	EFK18.2	20.9	1	1	1	95.3	-0.50	0.09	-0.31	0.06	-0.14	0.05	-0.17	0.06	-0.01	0.06	-0.04	0.11	0.09	0.04	-0.02	0.04	0.07	0.05
	EFK22.3	53.4	2	2	1	99.2	-0.49	0.09	-0.29	0.06	-0.09	0.05	-0.12	0.06	0.07	0.06	-0.06	0.11	0.13	0.04	0.03	0.04	0.14	0.05
	EFK23.4	53.1	2	2	1	95.2	-0.34	0.09	-0.27	0.06	-0.13	0.05	-0.14	0.06	0.08	0.06	0.06	0.11	0.07	0.04	-0.01	0.04	0.15	0.05
	EFK25.4	239.8	8	4	2	97.2	-0.40	0.09	-0.24	0.06	-0.15	0.05	-0.12	0.06	-0.02	0.06	-0.03	0.11	0.03	0.04	0.00	0.04	0.04	0.05

^aDuring each seasonal synoptic sampling campaign, stream water was collected from eight locations along the flow path of East Fork Poplar Creek (EFPC) (see manuscript Figure 1). Sample ID refers to the sampling location which is identified by a three-letter stream code (EFK) followed by a number that indicates kilometers upstream of the EFPC confluence with Poplar Creek. Here, *n*₁ denotes the number of separate isotopic analyses on an individual preparation(s), *n*₂ denotes the number of individual preparations (procedural replicates, see *Methods*), and *n*₃ denotes the number of independent field replicates. The percent recovery (%Rec) shows recovery of mercury during the purge and trap procedure for preparation of stream water THg_d samples for isotopic analysis. The 2σ for all samples shows either the 2SD of average of session averages for UM-Almaden, or the 2SE of average of session averages for procedural standards, whichever uncertainty was largest (see *Methods*).

Table S2. Concentration and isotopic composition of total dissolved mercury (THg_d) in stream water and pore water during seasonal intensive site sampling of East Fork Poplar Creek, Oak Ridge, TN, USA.^a

	Sampling Site ID	Sample Type	THg _d				δ ²⁰⁴ Hg		δ ²⁰² Hg		δ ²⁰¹ Hg		δ ²⁰⁰ Hg		δ ¹⁹⁹ Hg		Δ ²⁰⁴ Hg		Δ ²⁰¹ Hg		Δ ²⁰⁰ Hg		Δ ¹⁹⁹ Hg		
			(ng/L)	n ₁	n ₂	n ₃	%Rec.	(‰)	2σ	(‰)	2σ	(‰)	2σ	(‰)	2σ	(‰)	2σ	(‰)	2σ	(‰)	2σ	(‰)	2σ	(‰)	2σ
October 2011	EFK5.0	Stream Water	12.5	1	1	1	98.8	-0.33	0.09	-0.22	0.06	-0.08	0.05	-0.14	0.06	-0.02	0.06	-0.01	0.11	0.08	0.04	-0.04	0.04	0.04	0.05
		Hyporheic Zone, Center	11.6	1	1	1	98.0	0.49	0.09	0.05	0.06	-0.12	0.05	0.07	0.06	-0.03	0.06	0.41	0.11	-0.16	0.04	0.04	0.04	-0.04	0.05
		Hyporheic Zone, Side	12.3	1	1	1	99.9	-0.44	0.09	-0.15	0.06	-0.06	0.05	-0.20	0.06	0.04	0.06	-0.21	0.11	0.06	0.04	-0.12	0.04	0.08	0.05
April 2012	EFK5.0	Stream Water	--	No stream water sample was collected during intensive site sampling. Refer to synoptic sampling results in Table S1.																					
		Hyporheic Zone, Center	60.5	1	1	1	96.9	1.18	0.09	0.78	0.06	0.49	0.05	0.47	0.06	0.09	0.06	0.02	0.11	-0.09	0.04	0.08	0.04	-0.11	0.05
		Hyporheic Zone, Side ^b	2.3	Insufficient mercury for isotopic analysis. Sample composited with August 2012 EFK5.0 Hyporheic Zone, Side.																					
August 2012	EFK5.0	Stream Water	--	No stream water sample was collected during intensive site sampling. Refer to synoptic sampling results in Table S1.																					
		Hyporheic Zone, Center	43.4	1	1	1	90.5	-0.03	0.09	0.03	0.06	-0.02	0.05	0.04	0.06	0.01	0.06	-0.07	0.11	-0.04	0.04	0.02	0.04	0.00	0.05
		Hyporheic Zone, Side ^b	6.5	1	2	2	98.0	-0.04	0.09	0.28	0.06	0.31	0.05	0.25	0.06	0.44	0.06	-0.46	0.11	0.10	0.04	0.11	0.04	0.37	0.05
October 2011	EFK22.3	Stream Water	53.8	1	1	1	99.9	-0.20	0.09	-0.22	0.06	-0.05	0.05	-0.11	0.06	0.09	0.06	0.13	0.11	0.12	0.04	0.00	0.04	0.15	0.05
		Hyporheic Zone, Center	41.8	1	1	1	99.4	-0.65	0.09	-0.43	0.06	-0.25	0.05	-0.22	0.06	-0.10	0.06	-0.01	0.11	0.07	0.04	0.00	0.04	0.01	0.05
		Hyporheic Zone, Side	15.0	1	1	1	101.8	-0.04	0.09	0.12	0.06	0.12	0.05	0.06	0.06	0.14	0.06	-0.23	0.11	0.03	0.04	-0.01	0.04	0.11	0.05
		Riparian Tributary Surface Water	16.2	1	1	1	99.9	-1.12	0.09	-0.78	0.06	-0.73	0.05	-0.46	0.06	-0.20	0.06	0.05	0.11	-0.14	0.04	-0.06	0.04	0.00	0.05
		Riparian Tributary Pore Water	53.7	2	2	1	103.6	-0.38	0.09	-0.26	0.06	-0.19	0.05	-0.13	0.06	-0.12	0.06	0.01	0.11	0.01	0.04	0.00	0.04	-0.06	0.05
April 2012	EFK22.3	Stream Water	45.8	2	2	1	102.7	-0.09	0.09	-0.01	0.06	-0.01	0.05	0.03	0.06	0.04	0.06	-0.07	0.11	0.00	0.04	0.04	0.04	0.04	0.05
		Hyporheic Zone, Center	97.4	1	1	1	97.9	0.14	0.09	0.12	0.06	0.04	0.05	0.05	0.06	0.00	0.06	-0.04	0.11	-0.05	0.04	-0.01	0.04	-0.03	0.05
		Hyporheic Zone, Side	4979	4	2	1	101.5	1.10	0.09	0.70	0.06	0.47	0.05	0.37	0.06	0.09	0.06	0.05	0.11	-0.05	0.04	0.02	0.04	-0.09	0.05
		Riparian Tributary Surface Water	5.4	1	2	2	99.6	0.14	0.09	0.12	0.06	0.18	0.05	0.21	0.06	0.16	0.06	-0.04	0.11	0.09	0.04	0.15	0.04	0.13	0.05
		Riparian Tributary Pore Water	8.3																						
August 2012	EFK22.3	Stream Water	39.9	2	2	2	100.0	-0.47	0.09	-0.32	0.06	-0.24	0.05	-0.19	0.06	-0.05	0.06	0.00	0.11	0.00	0.04	-0.03	0.04	0.03	0.05
		Hyporheic Zone, Center	6.6	1	1	1	103.2	0.06	0.09	-0.08	0.06	0.00	0.05	-0.17	0.06	0.08	0.06	0.17	0.11	0.06	0.04	-0.13	0.04	0.10	0.05
		Hyporheic Zone, Side	435	2	1	1	86.4	0.62	0.09	0.39	0.06	0.26	0.05	0.22	0.06	0.07	0.06	0.05	0.11	-0.03	0.04	0.02	0.04	-0.02	0.05
		Riparian Tributary Surface Water	12.9	1	1	1	102.2	-1.07	0.09	-0.69	0.06	-0.45	0.05	-0.29	0.06	-0.25	0.06	-0.05	0.11	0.07	0.04	0.05	0.04	-0.08	0.05
		Riparian Tributary Pore Water	16.1	1	1	1	105.4	-1.20	0.09	-0.68	0.06	-0.56	0.05	-0.38	0.06	-0.17	0.06	-0.19	0.11	-0.05	0.04	-0.04	0.04	0.00	0.05

^aNotes: During each seasonal intensive site sampling campaign, surface water and pore water samples were collected from one upstream location (EFK22.3) and one downstream location (EFK5.0) along the flow path of East Fork Poplar Creek (EFPC) (see manuscript Figure1). Sampling Site ID refers to the sampling location which is identified by a three-letter stream code (EFK) followed by a number that indicates kilometers upstream of the EFPC confluence with Poplar Creek. Here, n₁ denotes the number of separate isotopic analyses on an individual preparation(s), n₂ denotes the number of individual preparations (procedural replicates, see *Methods*), and n₃ denotes the number of independent field replicates. The percent recovery (%Rec) shows recovery of mercury during the purge and trap procedure for preparation of stream water and pore water THg_d samples for isotopic analysis. The 2σ for all samples shows either the 2SD of average of session averages for UM-Almaden, or the 2SE of average of session averages for procedural standards, whichever uncertainty was largest (see *Methods*).

^bEFK5.0 hyporheic zone side of channel sample from April and August were composited because there was insufficient Hg to independently measure the Hg isotopic composition of each alone.

Table S3. Concentration of total dissolved mercury (THg_d), total particulate-bound mercury (THg_p), total suspended solids (TSS), the distribution coefficient (log K_D) for total mercury, total dissolved methylmercury (MeHg_d), particulate-bound methylmercury (MeHg_p), dissolved gaseous mercury (DGM), dissolved organic carbon (DOC), specific UV absorbance at 254 nm (SUVA₂₅₄), anions (Cl⁻¹, NO₃⁻¹, SO₄⁻²), and pH in stream water during seasonal synoptic sampling of East Fork Poplar Creek, Oak Ridge, TN, USA.^a

	Sampling Site	THg _d (ng/L)	THg _p (ng/L)	THg _p (µg/g)	TSS (mg/L)	log K _D (L/kg)	MeHg _d (ng/L)	%MeHg _d	MeHg _p (ng/L)	MeHg _p (ng/g)	%MeHg _p	DGM (ng/L)	DOC (mg/L)	SUVA ₂₅₄ (L mg ⁻¹ m ⁻¹)	Cl ⁻¹ (ppm)	NO ₃ ⁻¹ (ppm)	SO ₄ ⁻² (ppm)	pH
October 2011	EFK5.0	17.5	30.5	18.0	1.7	6.0	0.25	2.1%	0.10	33.5	0.30%	--	2.1	2.8	--	--	--	7.7
	EFK9.8	15.5	42.1	25.7	1.6	6.2	0.25	0.8%	0.08	11.1	0.14%	--	2.3	2.5	--	--	--	7.2
	EFK13.8	23.9	48.0	29.6	1.6	6.1	0.25	0.9%	0.11	55.2	0.22%	--	1.8	2.4	--	--	--	7.9
	EFK17.8	25.7	77.9	46.8	1.7	6.3	0.20	0.8%	0.15	53.4	0.23%	--	1.7	2.3	--	--	--	7.8
	EFK18.2	32.3	55.8	37.4	1.5	6.1	0.18	0.7%	0.13	43.5	0.27%	--	1.6	2.4	--	--	--	8.0
	EFK22.3	57.7	119	39.6	3.0	5.8	0.14	0.4%	0.10	32.1	0.07%	--	1.7	2.2	--	--	--	8.4
	EFK23.4	61.3	171	62.1	2.8	6.0	0.14	0.4%	0.10	26.5	0.04%	--	1.8	2.1	--	--	--	--
EFK25.4	70.5	255	39.5	6.5	5.7	0.11	0.3%	0.09	20.3	0.05%	--	1.6	2.2	--	--	--	--	
April 2012	EFK5.0	11.4	52.1	8.0	6.5	5.8	0.16	1.4%	0.11	17.3	0.22%	0.3	1.9	2.4	12.3	13.7	20.7	7.8
	EFK9.8	12.4	64.2	21.4	3.0	6.2	0.22	1.8%	0.02	6.7	0.03%	--	1.9	2.6	12.7	12.3	20.2	7.8
	EFK13.8	14.6	83.1	15.8	5.3	6.0	0.19	1.3%	0.06	11.8	0.07%	--	1.4	2.4	7.8	4.7	23.6	7.9
	EFK17.8	18.8	119	24.9	4.8	6.1	0.14	0.8%	0.07	14.7	0.06%	--	1.2	2.6	8.3	5.5	24.7	7.8
	EFK18.2	19.5	112	26.0	4.3	6.1	0.14	0.7%	0.10	23.3	0.09%	--	1.2	3.5	8.3	5.6	25.1	8.0
	EFK22.3	47.3	141	36.1	3.9	5.9	0.10	0.2%	0.07	19.1	0.05%	4.1	1.5	2.5	9.1	6.7	25.5	8.2
	EFK23.4	48.8	159	37.4	4.2	5.9	0.08	0.2%	0.04	8.6	0.02%	--	1.5	2.3	9.3	7.1	23.7	8.3
EFK25.4	57.9	211	50.9	4.1	5.9	0.05	0.1%	0.03	8.2	0.02%	7.8	1.5	2.9	8.1	7.3	23.6	8.1	
August 2012	EFK5.0	19.6	115	18.7	6.1	6.0	0.23	1.2%	0.08	13.4	0.07%	0.2	2.4	2.7	12.9	10.7	21.3	7.9
	EFK9.8	13.8	79.0	19.0	4.2	6.1	0.18	1.3%	0.07	16.6	0.09%	--	2.0	2.4	15.9	13.9	24.9	7.9
	EFK13.8	29.1	59.0	26.6	2.2	6.0	0.15	0.5%	0.07	31.9	0.12%	--	1.4	2.1	10.4	5.8	28.9	8.0
	EFK17.8	31.1	62.8	39.9	1.6	6.1	0.10	0.3%	0.08	52.3	0.13%	--	1.2	1.9	11.2	6.5	30.5	8.0
	EFK18.2	20.9	101	32.3	3.1	6.2	0.13	0.6%	0.05	17.0	0.05%	--	1.2	1.8	11.2	6.5	30.4	8.0
	EFK22.3	53.4	134	38.4	3.5	5.9	0.08	0.1%	0.04	11.1	0.03%	2.3	1.2	1.6	10.0	7.5	31.5	8.1
	EFK23.4	53.1	148	45.1	3.3	5.9	0.06	0.1%	0.02	5.4	0.01%	--	1.3	1.6	10.2	7.9	30.5	8.1
EFK25.4	240	253	90.4	2.8	5.6	0.06	0.0%	0.01	3.8	0.00%	5.3	1.2	1.9	9.4	7.9	30.4	8.0	

^aDuring each seasonal synoptic sampling campaign, stream water was collected from eight locations along the flow path of East Fork Poplar Creek (EFPC) (see manuscript Figure 1). Sampling Site refers to the sampling location which is identified by a three-letter stream code (EFK) followed by a number that indicates kilometers upstream of the EFPC confluence with Poplar Creek. In October 2011, the MeHg_d and MeHg_p values were derived from samples filtered with a 0.2µm pore size cellulose nitrate membrane. Distribution coefficients (K_D) were calculated as the ratio of THg_p concentration (ng/kg) to THg_d concentration (ng/L).

Table S4. Concentration and isotopic composition of total suspended particulate-bound mercury (THg_p) in stream water during seasonal synoptic sampling of East Fork Poplar Creek, Oak Ridge, TN, USA.^a

	Sampling Site ID	THg _p (ng/L)	<i>n</i> ₁	<i>n</i> ₂	<i>n</i> ₃	$\delta^{204}\text{Hg}$ (‰)	2σ	$\delta^{202}\text{Hg}$ (‰)	2σ	$\delta^{201}\text{Hg}$ (‰)	2σ	$\delta^{200}\text{Hg}$ (‰)	2σ	$\delta^{199}\text{Hg}$ (‰)	2σ	$\Delta^{204}\text{Hg}$ (‰)	2σ	$\Delta^{201}\text{Hg}$ (‰)	2σ	$\Delta^{200}\text{Hg}$ (‰)	2σ	$\Delta^{199}\text{Hg}$ (‰)	2σ
October 2011	EFK5.0	30.5	1	1	1	0.01	0.09	0.05	0.06	-0.07	0.05	0.03	0.06	-0.09	0.06	-0.06	0.11	-0.10	0.04	0.01	0.04	-0.11	0.05
	EFK9.8	42.1	1	1	1	0.12	0.09	0.08	0.06	0.04	0.05	0.08	0.06	0.00	0.06	0.00	0.11	-0.03	0.04	0.04	0.04	-0.02	0.05
	EFK13.8	48.0	1	1	1	-0.12	0.09	-0.04	0.06	-0.05	0.05	-0.03	0.06	-0.03	0.06	-0.07	0.11	-0.02	0.04	-0.01	0.04	-0.02	0.05
	EFK17.8	77.9	2	1	1	-0.28	0.09	-0.17	0.06	-0.17	0.05	-0.08	0.06	-0.05	0.06	-0.02	0.11	-0.04	0.04	0.00	0.04	0.00	0.05
	EFK18.2	55.8	2	1	1	-0.33	0.09	-0.22	0.06	-0.18	0.05	-0.10	0.06	-0.04	0.06	0.00	0.11	-0.02	0.04	0.01	0.04	0.01	0.05
	EFK22.3	118.6	2	1	1	-0.59	0.09	-0.42	0.06	-0.35	0.05	-0.20	0.06	-0.11	0.06	0.05	0.11	-0.03	0.04	0.02	0.04	0.00	0.05
	EFK23.4	171.4	2	1	1	-0.63	0.09	-0.43	0.06	-0.33	0.05	-0.21	0.06	-0.10	0.06	0.01	0.11	-0.01	0.04	0.01	0.04	0.01	0.05
	EFK25.4	255.1	2	1	1	-0.90	0.09	-0.60	0.06	-0.47	0.05	-0.29	0.06	-0.13	0.06	-0.01	0.11	-0.02	0.04	0.01	0.04	0.02	0.05
April 2012	EFK5.0	52.1	2	1	1	0.22	0.09	0.15	0.06	0.04	0.05	0.07	0.06	0.04	0.06	0.00	0.11	-0.07	0.04	-0.01	0.04	0.00	0.05
	EFK9.8	64.2	2	1	1	0.14	0.09	0.10	0.06	-0.02	0.05	0.04	0.06	-0.06	0.06	-0.01	0.11	-0.09	0.04	-0.01	0.04	-0.08	0.05
	EFK13.8	83.1	2	1	1	-0.07	0.09	-0.07	0.06	-0.09	0.05	-0.02	0.06	-0.04	0.06	0.04	0.11	-0.03	0.04	0.01	0.04	-0.03	0.05
	EFK17.8	118.8	2	1	1	-0.23	0.09	-0.16	0.06	-0.15	0.05	-0.08	0.06	-0.04	0.06	0.00	0.11	-0.03	0.04	-0.01	0.04	0.00	0.05
	EFK18.2	112.4	2	1	1	-0.11	0.09	-0.07	0.06	-0.06	0.05	-0.05	0.06	-0.01	0.06	0.00	0.11	-0.01	0.04	-0.02	0.04	0.01	0.05
	EFK22.3	141.0	2	1	1	-0.28	0.09	-0.21	0.06	-0.17	0.05	-0.10	0.06	-0.05	0.06	0.03	0.11	-0.01	0.04	0.00	0.04	0.00	0.05
	EFK23.4	158.8	2	1	1	-0.50	0.09	-0.36	0.06	-0.31	0.05	-0.19	0.06	-0.10	0.06	0.04	0.11	-0.03	0.04	0.00	0.04	-0.01	0.05
	EFK25.4	211.2	2	1	1	-0.57	0.09	-0.39	0.06	-0.32	0.05	-0.21	0.06	-0.13	0.06	0.02	0.11	-0.02	0.04	-0.01	0.04	-0.03	0.05
August 2012	EFK5.0	114.8	4	2	2	0.07	0.09	0.05	0.06	-0.04	0.05	0.02	0.06	-0.07	0.06	0.00	0.11	-0.07	0.04	0.00	0.04	-0.08	0.05
	EFK9.8	79.0	2	1	1	0.06	0.09	-0.01	0.06	-0.06	0.05	-0.02	0.06	-0.07	0.06	0.08	0.11	-0.05	0.04	-0.01	0.04	-0.07	0.05
	EFK13.8	59.0	2	1	1	-0.30	0.09	-0.21	0.06	-0.17	0.05	-0.08	0.06	-0.10	0.06	0.01	0.11	-0.02	0.04	0.03	0.04	-0.05	0.05
	EFK17.8	62.8	2	1	1	-0.34	0.09	-0.21	0.06	-0.17	0.05	-0.07	0.06	0.00	0.06	-0.03	0.11	-0.01	0.04	0.03	0.04	0.05	0.05
	EFK18.2	101.3	3	1	1	-0.19	0.09	-0.15	0.06	-0.11	0.05	-0.07	0.06	-0.01	0.06	0.03	0.11	0.00	0.04	0.01	0.04	0.02	0.05
	EFK22.3	134.1	2	1	1	-0.55	0.09	-0.36	0.06	-0.29	0.05	-0.16	0.06	-0.06	0.06	-0.02	0.11	-0.02	0.04	0.02	0.04	0.03	0.05
	EFK23.4	148.4	3	1	1	-0.60	0.09	-0.41	0.06	-0.27	0.05	-0.20	0.06	-0.08	0.06	0.02	0.11	0.04	0.04	0.01	0.04	0.02	0.05
	EFK25.4	253.3	6	2	2	-0.52	0.09	-0.35	0.06	-0.28	0.05	-0.18	0.06	-0.11	0.06	0.00	0.11	-0.01	0.04	0.00	0.04	-0.02	0.05

^aDuring each seasonal synoptic sampling campaign, stream water was collected from eight locations along the flow path of East Fork Poplar Creek (EFPC) (see manuscript Figure 1). Sample ID refers to the sampling location which is identified by a three-letter stream code (EFK) followed by a number that indicates kilometers upstream of the EFPC confluence with Poplar Creek. Here, *n*₁ denotes the number of separate isotopic analyses on an individual preparation(s), *n*₂ denotes the number of individual preparations (procedural replicates, see *Methods*), and *n*₃ denotes the number of independent field replicates. The 2σ for all samples shows either the 2SD of average of session averages for UM-Almaden, or the 2SE of average of session averages for procedural standards, whichever uncertainty was largest (see *Methods*).

Table S5. Concentration and isotopic composition of total particulate-bound mercury (THg_p) in stream water or associated with pore water samples, and streambed biofilm, during seasonal intensive site sampling of East Fork Poplar Creek, Oak Ridge, TN, USA.^a

Sampling Site ID	Sample Type	THg _p (µg/g)			δ ²⁰⁴ Hg (‰)		2σ		δ ²⁰² Hg (‰)		2σ		δ ²⁰¹ Hg (‰)		2σ		δ ¹⁹⁹ Hg (‰)		2σ		Δ ²⁰⁴ Hg (‰)		2σ		Δ ²⁰¹ Hg (‰)		2σ		Δ ²⁰⁰ Hg (‰)		2σ		Δ ¹⁹⁹ Hg (‰)		2σ		
		n ₁	n ₂	n ₃	(‰)	(‰)	(‰)	(‰)	(‰)	(‰)	(‰)	(‰)	(‰)	(‰)	(‰)	(‰)	(‰)	(‰)	(‰)	(‰)	(‰)	(‰)	(‰)	(‰)	(‰)	(‰)	(‰)	(‰)	(‰)	(‰)	(‰)	(‰)	(‰)	(‰)	(‰)		
October 2011	EFK5.0	Stream Water	18.6	2	1	1	0.07	0.09	0.05	0.06	0.01	0.05	0.07	0.06	-0.02	0.06	0.00	0.11	-0.02	0.04	0.04	0.04	-0.03	0.05													
		Hyporheic Zone, Center	20.5	2	1	1	0.25	0.09	0.15	0.06	-0.02	0.05	0.07	0.06	-0.11	0.06	0.02	0.11	-0.13	0.04	0.00	0.04	-0.15	0.05													
		Hyporheic Zone, Side	8.8	2	1	1	0.00	0.09	0.02	0.06	-0.07	0.05	0.00	0.06	-0.10	0.06	-0.02	0.11	-0.08	0.04	-0.01	0.04	-0.10	0.05													
		Biofilm, Bulk	3.4	2	1	1	-0.03	0.09	-0.04	0.06	-0.07	0.05	-0.02	0.06	-0.11	0.06	0.03	0.11	-0.04	0.04	0.00	0.04	-0.10	0.05													
		Biofilm, Supernatant	--	2	1	1	-0.11	0.09	-0.05	0.06	-0.13	0.05	-0.05	0.06	-0.11	0.06	-0.03	0.11	-0.09	0.04	-0.03	0.04	-0.10	0.05													
April 2012	EFK5.0	Stream Water	--	No stream water sample was collected during intensive site sampling. Refer to synoptic sampling results in Table S4.																																	
		Hyporheic Zone, Center	22.7	2	1	1	0.38	0.09	0.25	0.06	0.10	0.05	0.13	0.06	0.01	0.06	0.01	0.11	-0.09	0.04	0.00	0.04	-0.05	0.05													
		Hyporheic Zone, Side	1.2	2	1	1	-0.37	0.09	-0.24	0.06	-0.24	0.05	-0.12	0.06	-0.15	0.06	-0.01	0.11	-0.05	0.04	0.00	0.04	-0.09	0.05													
		Biofilm, Bulk	5.5	2	1	1	0.08	0.09	0.06	0.06	-0.08	0.05	0.04	0.06	-0.06	0.06	0.00	0.11	-0.12	0.04	0.01	0.04	-0.08	0.05													
		Biofilm, Supernatant	--	1	1	1	-0.15	0.09	-0.10	0.06	-0.10	0.05	-0.02	0.06	-0.11	0.06	0.00	0.11	-0.02	0.04	0.03	0.04	-0.08	0.05													
August 2012	EFK5.0	Stream Water	--	No stream water sample was collected during intensive site sampling. Refer to synoptic sampling results in Table S4.																																	
		Hyporheic Zone, Center	18.5	3	1	1	0.18	0.09	0.12	0.06	-0.03	0.05	0.07	0.06	-0.06	0.06	0.00	0.11	-0.13	0.04	0.00	0.04	-0.09	0.05													
		Hyporheic Zone, Side	14.8	3	1	1	-0.02	0.09	0.01	0.06	-0.09	0.05	-0.02	0.06	-0.13	0.06	-0.03	0.11	-0.09	0.04	-0.02	0.04	-0.13	0.05													
		Biofilm, Bulk	5.2	2	1	1	0.40	0.09	0.19	0.06	0.06	0.05	0.04	0.06	-0.08	0.06	0.12	0.11	-0.09	0.04	-0.05	0.04	-0.13	0.05													
		Biofilm, Supernatant	--	2	1	1	0.43	0.09	0.32	0.06	0.15	0.05	0.16	0.06	-0.05	0.06	-0.05	0.11	-0.09	0.04	-0.01	0.04	-0.13	0.05													
October 2011	EFK22.3	Stream Water	22.3	2	1	1	-0.23	0.09	-0.17	0.06	-0.14	0.05	-0.05	0.06	-0.02	0.06	0.03	0.11	-0.01	0.04	0.03	0.04	0.02	0.05													
		Hyporheic Zone, Center	17.3	2	1	1	-0.27	0.09	-0.17	0.06	-0.20	0.05	-0.10	0.06	-0.11	0.06	-0.02	0.11	-0.07	0.04	-0.01	0.04	-0.06	0.05													
		Hyporheic Zone, Side	286.6	2	1	1	0.23	0.09	0.15	0.06	0.03	0.05	0.09	0.06	-0.03	0.06	0.01	0.11	-0.09	0.04	0.01	0.04	-0.07	0.05													
		Biofilm, Bulk	31.4	2	1	1	-0.40	0.09	-0.31	0.06	-0.27	0.05	-0.15	0.06	-0.11	0.06	0.07	0.11	-0.04	0.04	0.01	0.04	-0.03	0.05													
		Biofilm, Supernatant	--	2	1	1	-0.55	0.09	-0.42	0.06	-0.34	0.05	-0.18	0.06	-0.12	0.06	0.07	0.11	-0.03	0.04	0.03	0.04	-0.02	0.05													
		Riparian Tributary Surface Water	37.2	2	1	1	-0.48	0.09	-0.32	0.06	-0.29	0.05	-0.16	0.06	-0.13	0.06	0.00	0.11	-0.05	0.04	0.00	0.04	-0.05	0.05													
		Riparian Tributary Pore Water	22.2	2	1	1	-0.25	0.09	-0.17	0.06	-0.16	0.05	-0.07	0.06	-0.08	0.06	0.00	0.11	-0.03	0.04	0.02	0.04	-0.04	0.05													
April 2012	EFK22.3	Stream Water	25.7	4	2	1	-0.43	0.09	-0.30	0.06	-0.25	0.05	-0.15	0.06	-0.06	0.06	0.01	0.11	-0.03	0.04	0.00	0.04	0.02	0.05													
		Hyporheic Zone, Center	18.3	2	1	1	-0.24	0.09	-0.19	0.06	-0.19	0.05	-0.06	0.06	-0.05	0.06	0.04	0.11	-0.05	0.04	0.03	0.04	-0.01	0.05													
		Hyporheic Zone, Side	182.4	2	1	1	-0.42	0.09	-0.30	0.06	-0.25	0.05	-0.12	0.06	-0.06	0.06	0.03	0.11	-0.03	0.04	0.03	0.04	0.02	0.05													
		Biofilm, Bulk	7.6	2	1	1	-0.36	0.09	-0.23	0.06	-0.22	0.05	-0.11	0.06	-0.08	0.06	-0.02	0.11	-0.05	0.04	0.00	0.04	-0.02	0.05													
		Biofilm, Supernatant	--	2	1	1	-0.54	0.09	-0.40	0.06	-0.27	0.05	-0.17	0.06	-0.08	0.06	0.05	0.11	0.03	0.04	0.03	0.04	0.02	0.05													
		Riparian Tributary Surface Water	29.4	2	1	1	0.24	0.09	0.15	0.06	0.05	0.05	0.10	0.06	-0.07	0.06	0.02	0.11	-0.06	0.04	0.02	0.04	-0.11	0.05													
		Riparian Tributary Pore Water	19.6	2	1	1	-0.47	0.09	-0.31	0.06	-0.30	0.05	-0.14	0.06	-0.08	0.06	-0.01	0.11	-0.06	0.04	0.02	0.04	-0.01	0.05													
August 2012	EFK22.3	Stream Water	35.3	9	4	2	-0.34	0.09	-0.23	0.06	-0.20	0.05	-0.13	0.06	-0.03	0.06	0.01	0.11	-0.03	0.04	-0.02	0.04	0.03	0.05													
		Hyporheic Zone, Center	6.4	6	2	1	-0.17	0.09	-0.10	0.06	-0.14	0.05	-0.07	0.06	-0.09	0.06	-0.02	0.11	-0.06	0.04	-0.02	0.04	-0.06	0.05													
		Hyporheic Zone, Side	140.7	6	2	1	0.87	0.09	0.55	0.06	0.37	0.05	0.28	0.06	0.07	0.06	0.05	0.11	-0.05	0.04	0.01	0.04	-0.07	0.05													
		Biofilm, Bulk	3.2	2	1	1	-0.50	0.09	-0.40	0.06	-0.28	0.05	-0.15	0.06	-0.09	0.06	0.09	0.11	0.02	0.04	0.05	0.04	0.01	0.05													
		Biofilm, Supernatant	--	2	1	1	-0.85	0.09	-0.53	0.06	-0.39	0.05	-0.26	0.06	-0.14	0.06	-0.06	0.11	0.00	0.04	0.00	0.04	0.00	0.05													
		Riparian Tributary Surface Water	23.4	3	1	1	-0.47	0.09	-0.29	0.06	-0.27	0.05	-0.12	0.06	-0.10	0.06	-0.03	0.11	-0.05	0.04	0.03	0.04	-0.02	0.05													
		Riparian Tributary Pore Water	21.9	3	1	1	-0.53	0.09	-0.35	0.06	-0.33	0.05	-0.18	0.06	-0.10	0.06	0.00	0.11	-0.06	0.04	0.00	0.04	-0.01	0.05													

^aDuring each seasonal intensive site sampling campaign, surface water, pore water, and biofilm samples were collected from one upstream location (EFK22.3) and one downstream location (EFK5.0) along the flow path of East Fork Poplar Creek (EFPC) (see manuscript Figure 1). Sampling Site ID refers to the sampling location which is identified by a three-letter stream code (EFK) followed by a number that indicates kilometers upstream of the EFPC confluence with Poplar Creek. Here, *n*₁ denotes the number of separate isotopic analyses on an individual preparation(s), *n*₂ denotes the number of individual preparations (procedural replicates, see *Methods*), and *n*₃ denotes the number of independent field replicates. The 2σ for all samples shows either the 2SD of average of session averages for UM-Almaden, or the 2SE of average of session averages for procedural standards, whichever uncertainty was largest (see *Methods*).

Table S6. Concentration of total dissolved mercury (THg_d), total particulate-bound mercury (THg_p), total suspended solids (TSS), the distribution coefficient (log K_D) for total mercury, total dissolved methylmercury (MeHg_d), particulate-bound methylmercury (MeHg_p), dissolved organic carbon (DOC), specific UV absorbance at 254 nm (SUVA₂₅₄), anions (Cl⁻¹, NO₃⁻¹, SO₄⁻²), and pH in stream water and pore water during seasonal intensive site sampling along East Fork Poplar Creek, Oak Ridge, TN, USA.^a

Sampling Site ID	Sample Type	THg _d (ng/L)	THg _p (ng/L)	THg _p (μg/g)	TSS (mg/L)	log K _D (L/Kg)	MeHg _d (ng/L)	%MeHg _d	MeHg _p (ng/L)	MeHg _p (ng/g)	%MeHg _p	DOC (mg/L)	SUVA ₂₅₄ (L mg ⁻¹ m ⁻¹)	Cl ⁻¹ (ppm)	NO ₃ ⁻¹ (ppm)	SO ₄ ⁻² (ppm)	pH
October 2011	Stream Water	12.5	78.9	18.6	4.2	6.2	0.17	1.3%	0.14	29.9	0.3%	2.2	3.3	11.5	10.0	24.0	7.7
	Hyporheic Zone, Center	11.6	na	20.5	na	6.2	0.40	3.0%	na	--	--	2.3	2.9	9.8	0.9	19.6	7.7
	Hyporheic Zone, Side	12.3	na	8.8	na	5.9	0.87	7.6%	na	--	--	1.9	3.0	13.0	1.6	23.5	7.5
April 2012	Stream Water	No stream water sample was collected during intensive site sampling. Refer to synoptic sampling results in Supplemental Table S3.															
	Hyporheic Zone, Center	60.5	na	22.7	na	5.6	0.11	0.2%	na	--	--	1.1	2.6	10.3	7.3	20.1	--
	Hyporheic Zone, Side	2.3	na	1.2	na	5.7	0.07	2.9%	na	--	--	1.8	2.6	10.6	bdl	16.1	--
August 2012	Stream Water	No stream water sample was collected during intensive site sampling. Refer to synoptic sampling results in Supplemental Table S3.															
	Hyporheic Zone, Center	43.4	na	18.5	na	5.6	0.09	0.2%	na	--	--	1.4	2.8	14.8	3.3	24.6	8.1
	Hyporheic Zone, Side	6.5	na	14.8	na	6.4	0.55	8.5%	na	--	--	3.2	2.6	14.2	bdl	0.2	7.6
October 2011	Stream Water	53.8	154	22.3	6.9	5.6	0.16	0.5%	0.19	22.0	0.1%	1.7	2.4	13.6	6.9	32.7	7.9
	Hyporheic Zone, Center	41.8	na	17.3	na	5.6	0.16	0.7%	na	--	--	1.5	2.5	14.7	8.4	34.3	7.7
	Hyporheic Zone, Side	15.0	na	287	na	7.3	0.99	0.0%	na	--	--	2.0	3.9	22.2	0.8	3.8	7.2
	Riparian Tributary Surface Water	16.2	129	37.2	3.5	6.4	0.47	4.9%	0.63	57.1	0.2%	4.0	2.8	10.7	<0.2	15.6	7.0
	Riparian Tributary Pore Water	53.7	na	22.2	na	5.6	--	--	na	--	--	--	--	--	--	--	--
April 2012	Stream Water	45.8	159	25.7	6.2	5.7	0.09	0.2%	0.08	13.3	0.1%	1.4	2.6	9.0	6.4	25.3	8.2
	Hyporheic Zone, Center	97.4	na	18.3	na	5.3	0.04	0.0%	na	--	--	1.2	2.6	9.0	6.8	26.1	--
	Hyporheic Zone, Side	4979	na	182	na	4.6	0.08	0.0%	na	--	--	0.7	2.4	8.4	6.8	25.9	--
	Riparian Tributary Surface Water	5.4	291	29.4	9.9	6.7	3.33	61.9%	15.9	286	0.3%	3.0	2.6	8.5	bdl	1.5	7.0
	Riparian Tributary Pore Water	8.3	na	19.6	na	6.4	5.87	70.8%	na	--	--	3.2	2.6	8.5	bdl	0.3	--
August 2012	Stream Water	39.9	147	35.3	4.2	5.9	0.06	0.2%	0.05	11.1	0.0%	1.2	2.0	9.4	6.4	31.0	8.1
	Hyporheic Zone, Center	6.6	na	6.4	na	6.0	0.07	1.0%	na	--	--	1.0	2.1	9.5	6.9	31.6	8.0
	Hyporheic Zone, Side	435	na	141	na	5.5	0.05	0.0%	na	--	--	0.9	1.6	8.9	6.6	30.6	8.0
	Riparian Tributary Surface Water	12.9	186	23.4	7.9	6.3	1.43	11.0%	3.5	16.3	0.9%	3.2	3.2	3.4	bdl	18.0	7.9
	Riparian Tributary Pore Water	16.1	na	21.9	na	6.1	3.93	24.4%	na	--	--	3.7	3.1	3.4	bdl	14.7	7.8

^aDuring each seasonal intensive site sampling campaign, surface water and pore water samples were collected from one upstream location (EFK22.3) and one downstream location (EFK5.0) along the flow path of East Fork Poplar Creek (EFPC) (see manuscript Figure 1). Sampling Site refers to the sampling location which is identified by a three-letter stream code (EFK) followed by a number that indicates kilometers upstream of the EFPC confluence with Poplar Creek. In October 2011, the MeHg_d and MeHg_p values were derived from samples filtered with a 0.2μm pore size cellulose nitrate membrane. Distribution coefficients (K_D) were calculated as the ratio of THg_p concentration (ng/kg) to THg_d concentration (ng/L).