



# Source relationships between streambank soils and streambed sediments in a mercury-contaminated stream

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## Abstract

**Purpose** In contaminated streams, understanding the role of streambank and streambed source contributions is essential to developing robust remedial solutions. However, identifying relationships can be difficult because of the lack of identifying signatures in source and receptor pools. East Fork Poplar Creek (EFPC) in Oak Ridge, TN, USA received historical industrial releases of mercury that contaminated streambank soils and sediments. Here, we determined relationships between the contaminated streambank soils and sand-sized streambed sediments.

**Materials and methods** Field surveys revealed the spatial trends of the concentrations of inorganic total mercury (Hg) and methyl mercury (MeHg), Hg lability as inferred by sequential extraction, particle size distribution, and total organic carbon. Statistical tests were applied to determine relationships between streambank soil and streambed sediment properties.

**Results and discussion** Concentrations of Hg in streambank soils in the upper reaches averaged 206 mg kg<sup>-1</sup> (all as dry weight) ( $n = 457$ ), and 13 mg kg<sup>-1</sup> in lower reaches ( $n = 321$ ), while sand-sized streambed sediments were approximately 16 mg kg<sup>-1</sup> ( $n = 57$ ). Two areas of much higher Hg and MeHg concentrations in streambank soils were identified and related to localized higher Hg concentrations in the streambed sediments; however, most of the streambank soils have similar Hg concentrations to the streambed sediments. The molar ratio of Hg to organic carbon, correlation between MeHg and Hg, and particle size distributions suggested similarity between the streambank soils and the fine sand-sized fraction (125–250  $\mu\text{m}$ ) collected from the streambed sediments. Mercury in the fine sand-sized streambed sediments, however, was more labile than Hg in the streambank soils, suggesting an in-stream environment that altered the geochemistry of sediment-bound Hg.

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**Conclusions** This study revealed major source areas of Hg in streambank soils, identified possible depositional locations in streambed sediments, and highlighted potential differences in the stability of Hg bound to streambank soils and sediments. This work will guide future remedial decision making in EFPC and will aid other researchers in identifying source–sink linkages in contaminated fluvial systems.

**Keywords** Erosion · Fluvial · Methylmercury · Source–sink

## 1 Introduction

Known for its neurotoxicity and persistence in the environment, mercury (Hg) is a contaminant of concern with over 3000 contaminated sites identified globally (Kocman et al. 2013). The United Nations Environmental Programme has highlighted Hg as a major human health risk due to the strong potential for methylmercury to bioaccumulate in terrestrial and aquatic food chains (UNEP 2013). Mercury exists in the natural environment as inorganic metallic ( $\text{Hg}^0$ ), mercuric ( $\text{Hg}^{2+}$ ), and mercurous ( $\text{Hg}_2^{2+}$ ) ions and as organomercurial compounds (e.g., monomethylmercury: MeHg). High particle reactivity in all its chemical forms strongly promotes Hg accumulation in sediments and soils (Whyte and Kirchner 2000; Žagar et al. 2006). The primary route for human exposure to MeHg is through consumption of contaminated fish; hence, fish tissue Hg concentration is typically used in lieu of aqueous Hg concentration for exposure and risk assessment (Mergler et al. 2007).

The assessment and management of contaminated streambank soils poses remedial challenges, especially because of the methylation potential in aqueous systems. There is a critical need to identify and better understand how contaminated soils contribute to net mass fluxes of contaminants in freshwater aquatic systems; hence, this study was conducted in the East Fork Poplar Creek (EFPC), a low gradient freshwater stream in Oak Ridge, Tennessee (USA). From 1950 to 1963, an estimated  $128,000 \pm 35,000$  kg of Hg was released to the headwaters by the U.S. Department of Energy Y-12 National Security Complex (Y-12) (Brooks and Southworth 2011). Consequently, the downstream environment has elevated Hg concentrations in streambank and floodplain soils, streambed sediments, surface waters, and biota. Despite targeted remedial actions at the source in the Y-12 facility, downstream bioaccumulation of MeHg persists in the fish population (Mathews et al. 2013). EFPC is classified as an impaired water body because Hg levels in fish exceed the US EPA National Recommended Water Quality Criteria (NRWQC) and the state of Tennessee guidelines (both  $0.3 \text{ mg kg}^{-1}$  in fish tissue). A recent series of modelling studies found that the greatest flux of Hg is related to erosion of streambank soils during storm events, followed by inputs from Y-12 (Watson et al. 2016, 2017). Streambank soil erosion rates ranged from 4 to 46  $\text{cm year}^{-1}$  (Watson et al. 2016). Fluxes from bank erosion were estimated at  $38.6 \text{ kg year}^{-1}$  for Hg and

as  $5.6 \text{ g year}^{-1}$  for MeHg (Watson et al. 2017). Annual flux estimates at 5.4 km upstream from the mouth of EFPC are 98 kg of Hg and 85 g of MeHg (Riscassi et al. 2016). The studies also found that neither floodplain runoff nor infiltration contributed significantly to Hg concentrations in EFPC. To comply with water quality standards, both streambank erosion and inputs from Y-12 must be significantly reduced (Watson et al. 2017). Consequently, an improved understanding of the legacy Hg sources in streambank soils and sediments downstream of the Y-12 facility would aid in achieving these goals.

The South River near Harrisonburg, VA (USA) has a similar timeframe of Hg releases and a comparable geomorphological environment to EFPC. Highly contaminated streambank soils are now considered the major source of Hg to South River. At South River, streambed sediments exhibit peak Hg concentrations around 15 km downstream from the original point source (Rhoades et al. 2009; Flanders et al. 2010; Pizzuto 2014). At EFPC, sediments exhibit two zones of slightly higher Hg concentrations downstream from Y-12 (Brooks et al. 2017). Previous studies have identified the importance of streambank erosional processes that contribute particle-bound Hg to the stream (Southworth et al. 2010, 2013; Watson et al. 2016, 2017) but have not specifically examined how contaminant distribution in the streambank soils is related to the streambed sediments. The goal of this study is to better understand the distribution of Hg and MeHg in streambank soils and streambed sediments and to assess the potential for soils to serve as a source of contamination to streambed sediments. Our objective was achieved by examining the relationship between physiochemical properties, inferred chemical associations of Hg with solid phase materials, and MeHg and Hg partitioning between streambank soils and streambed sediments. The results of this study will help improve site assessment and management of this and other Hg-contaminated freshwater ecosystems.

## 2 Materials and methods

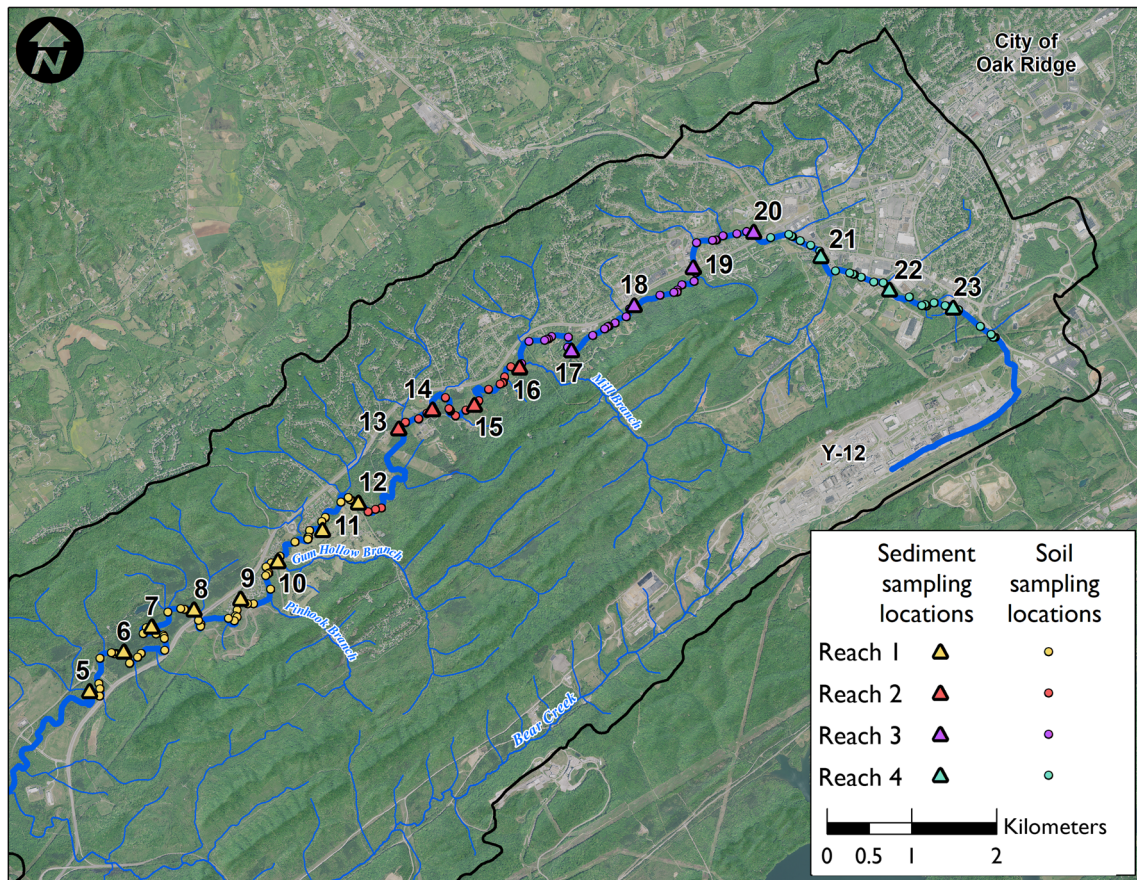
### 2.1 Site description

East Fork Poplar Creek is a 26-km, low-gradient, low-order stream in eastern Tennessee draining a  $\sim 77\text{-km}^2$  watershed above its confluence with Poplar Creek (Carmichael 1989).

Active use of Hg no longer occurs at Y-12, but smaller amounts of Hg continue to enter EFPC from residual-contaminated infrastructure and soils at Y-12. Total Hg concentration in EFPC exiting Y-12 is  $\sim 300 \text{ ng L}^{-1}$  under a baseflow of  $\sim 8200 \text{ m}^3 \text{ day}^{-1}$ , and around 60% of the Hg is in a dissolved form (Watson et al. 2017). Sites in EFPC in this study are represented with the identifier East Fork Kilometer (EFK) followed by a number which designates the creek km measured upstream from the mouth of the creek. This study focuses on EFPC immediately downstream of the Y-12 boundary beginning at EFK 23 and extending for 19 km downstream (Fig. 1). The stream is partitioned into four creek reaches according to similarity in floodplain properties and stream channel gradients (Fig. 1) (Watson et al. 2016). The dominant soils identified in the streambanks are Inceptisols from the Chenneby Series (Fluvaquentic Dystrudepts) and the Hamblen Series (Fluvaquentic Eutrudepts) (Dickson et al. 2017). The studied EFPC reach is predominately a low-gradient natural stream channel consisting of wooded lands, residential developments, riparian wetlands, and anthropogenically impacted areas where streambanks are lined with riprap and/or concrete.

### 2.2 Streambank soil sample collection

Streambank soils were sampled in September 2014 and March 2015 along the study reach using an 8/57 cyclic sampling strategy with a unit length of 17 m as outlined in Burrows et al. (2002) (Fig. S1, ESM). Core and composite bulk soil samples were collected at 143 locations from either the left or right streambank face (Fig. 1). Horizontal core samples (2.5 cm diameter and of variable length) and bulk samples (to a depth of  $\sim 7 \text{ cm}$  and only in 2014) were collected at 15%, 50%, and 85% of the bank height as measured from the ground surface to the water surface, which is usually within 0.3 to 1.2-m belowground surface. Additionally, one randomly selected location within each sampling cycle ( $n = 18$ ) was sampled at 50% bank height both 1 m upstream and 1 m downstream of the original coring location to check for consistency in Hg and MeHg concentrations over short spatial scales (Fig. S1, ESM). All of these samples are hereafter referred to as “longitudinal” samples. For all longitudinal samples, the outermost 2.5 cm of the cores was analyzed for total Hg and MeHg, while other soil chemical and physical properties were measured in bulk samples. A limited set of cores



**Fig. 1** Map of East Fork Poplar Creek and stream reaches 1–4, depicting soil sampling locations (points), and sediment sampling locations 5–23 (triangles), which correspond to kilometers above the mouth of East Fork Poplar Creek

that extended horizontally up to 20 cm into the streambanks was collected from six locations in April 2014, and Hg analyses were performed in increments of 2.5 cm throughout the length of the cores (Watson et al. 2016).

A previously identified zone of higher Hg concentration (Southworth et al. 2010, 2013) was associated with fine-grained, dark-colored layers within the upper 6 km of EFPC. These layers are herein referred to as historical release deposits (HRD). In July 2015, one to three cores of 2.5-cm diameter and of variable length and bulk soils about 7 cm deep were collected from 70 locations, approximately every 20 m where the HRD was visually apparent. A separate survey involved taking a high-resolution vertical profile of 2.5-cm-diameter core samples every 0.1 m throughout the entire height of the streambank at four locations where the HRD was exposed. For all the above samples, the outermost 2.5 cm of the cores was analyzed for total Hg and MeHg, while the other soil chemical and physical properties were measured on bulk samples.

### 2.3 Streambed sediment sample collection and analyses

Bulk streambed sediment samples (~5 kg,  $n = 19$ ) were collected at 1-km intervals with a manually operated bilge pump or by manually scooping sediments into a 4-l pitcher (Fig. 1) (Brooks et al. 2017). Samples were wet-sieved with ambient stream water in the field to three particle size fractions, fine sand (125–250  $\mu\text{m}$ ), medium sand (250  $\mu\text{m}$ –1 mm), and coarse sand (1–2 mm). A separate bulk sample was collected to determine the mass fraction each grain size contributed to bulk sediments. The material eluting from the sieve was captured for select samples and was found to account for a very small amount of the total sediment (<3%) (Brooks et al. 2017). Total Hg and MeHg concentrations for the three sediment fractions (coarse, medium, and fine sands) were multiplied by their respective sediment mass fraction and summed together to obtain total Hg and MeHg concentrations for bulk sediment samples:

$$\text{Conc}_{\text{bulk}} = \text{Wt}_{\text{coarse}}\text{Conc}_{\text{coarse}} + \text{Wt}_{\text{medium}}\text{Conc}_{\text{medium}} + \text{Wt}_{\text{fine}}\text{Conc}_{\text{fine}} \quad (1)$$

where Conc is the total concentration or content of any element of interest (e.g., Hg), Wt. refers to mass fraction, and bulk is bulk sediment sample. In this paper, we use previously published sediment data by Brooks et al. (2017) to compare with the new soils data (Sect. 2.2). Brooks et al. (2017) included three additional sediment-sampling locations upstream of the locations considered in the present study resulting in some differences in overall statistics compared with those in Brooks study.

### 2.4 Analyses

All samples were placed on dry ice in the field. Within 8 h after collection, all soil samples were stored at  $-80\text{ }^{\circ}\text{C}$  and bulk samples were stored at  $+4\text{ }^{\circ}\text{C}$ . Select samples were prepared for analysis by homogenizing and freeze-drying (Labconco 7522900 series, Kansas City, MO, USA).

The 2014 longitudinal streambank samples and some 2015 and 2016 HRD samples were analyzed by CEBAM Analytical, Inc. (Bothell, WA, USA); most other Hg analyses were conducted at ORNL by microwave direct mercury analysis (Milestone DMA-80, Shelton, CT, USA). For samples with concentrations too high for DMA or not analyzed at CEBAM, total Hg was determined by digesting samples in aqua regia ( $\text{HNO}_3\text{:HCl} = 1\text{:}3$ ,  $v/v$ ), filtered through a 0.2  $\mu\text{m}$  polyethersulfone membrane filter, followed by stannous chloride reduction and detection by cold vapor atomic absorption spectrometry (CVAAS) with  $\text{N}_2$  as the carrier gas and an Ohio Lumex RA-915+ instrument (Solon, OH, USA).

Monomethylmercury was analyzed in duplicate on the 2014 longitudinal bank soils, 2015 longitudinal samples, and the HRD soils by CEBAM Analytical, Inc. (Liang et al. 1996). MeHg was analyzed on all other soil samples at ORNL by non-aqueous phase extraction (Bloom et al. 1997). Briefly, this method consisted of a non-aqueous phase extraction of MeHg followed by a back extraction into water and ethylation/purge and trap/GC. Because of the elevated Hg levels in EFPC materials, we found it necessary to follow the back extraction step with a distillation step to further reduce the amount of ambient inorganic Hg before analysis.  $\text{Me}^{200}\text{Hg}$  was used as an internal standard for all MeHg analyses (Hintelmann and Ogrinc 2002). The isotope pattern deconvolution calculations used in this work are outlined in Meija et al. (2006).

For all total Hg and MeHg analyses, blanks (or spiked samples) and certified reference materials (NIST2709a and ERM-CC580) were used for quality control in monitoring measurement precision and accuracy. For total Hg and MeHg, the relative percent difference was <5% and their recoveries from standards ranged from 95 to 105%.

For streambank soil samples, standard chemical analyses of pH, total carbon (C), organic carbon (OC), and nitrogen (N) were performed. Soil pH was determined in one part soil to five parts equilibrated soil solutions of 0.005 M  $\text{CaCl}_2$  or distilled deionized water, using a glass electrode according to standard methods. Total carbon and N were determined by dry combustion using a NA-1200 C/N analyzer equipped with thermal conductivity detector (Carlo Erba, Milan, Italy) at the University of Georgia, Athens, GA. Prior to instrument analysis, each sample was split and half of the sample was treated with HCl (1:1) to remove inorganic carbon (TIC), and OC was obtained by subtraction from C concentrations of the untreated half of the sample. Major elements (Al, Si, Fe, Ca,

Mg, K, Na, Li, Fe, Mn, Ti, P) in select streambank soils along lower EFPC were analyzed by standard procedure using a sodium peroxide–fusion method coupled with Varian 735ES ICP-OES detection (Palo Alto, CA, USA) at Activation Laboratories, Ancaster, Ontario, Canada. Bulk soil samples were analyzed for particle size distribution according to ASTM standard test methods D422 at Analytical Resources, Inc. (Tukwila, WA, USA).

A five-step sequential extraction procedure was applied to select streambank soils to determine the relative strength of chemical associations between Hg and the solid phase (Bloom et al. 2003). The procedure involves sequential extractions of increasing strength: the F1 solution is deoxygenated double deionized water, F2 is 0.01 M HCl and 0.1 M acetic acid, F3 is 1 M KOH, F4 is 12 N HNO<sub>3</sub>, and F5 is aqua regia (HNO<sub>3</sub>:HCl = 1:3, v/v). Sample analysis was by CVAAS as described above. In general, the F1 and F2 extractions are thought to release the more “labile” fractions of Hg, while the F3, F4, and F5 solutions target Hg with stronger chemical associations with soil materials. The results are presented as the percentage of each fraction with respect to the total Hg extracted. Specific details of the application of the procedure in EFPC materials are available in Brooks et al. (2017).

## 2.5 Data and statistical analysis

The resolution of the various sampling activities was unavoidably different. Streambank soils from the longitudinal survey were collected from three places in each streambank at 143 locations (in 2014 and again in 2015), 70 locations in the HRD campaigns, 5 locations in the horizontal profile survey, 4 locations in our vertical profile survey, and 6 locations in the Southworth et al. (2010) vertical profile survey, while streambed sediments were collected from 19 different locations (Brooks et al. 2017). The longitudinal stream bank soil surveys were designed to capture variability along the entire length of the creek, while the HRD survey was intended to sample the HRD feature at high resolution. To aid in specific comparisons between soils and sediments, streambank soils were grouped into 19 bins to coincide with the 19 streambed sediment locations. The soil data mean included all soil analyses over the 1 km immediately upstream of the sediment collection location.

Statistical analyses were performed with StatPlus 5.0 (AnalystSoft Inc. 2016) using a priori significance level of  $p = 0.05$ . Spearman’s rank correlation coefficient ( $\rho$ ), a non-parametric measure of monotonic correlation, was used to test the correlation between any two variables. One-way analysis of variance (ANOVA) was used to compare the means between two groups at a family-wise confidence level of 95%. The Kruskal–Wallis ANOVA, a non-parametric method based on medians (ranks), was used to test if a sample was from the

same population. When necessary, data were log-transformed to aid in data interpretation.

## 2.6 Enrichment factor

To relate the source of contamination in EFPC sediments to the streambank soils, we calculated an enrichment factor (EF) following Wallschäger et al. (1998a) but modified to use log<sub>10</sub> concentrations:

$$EF_{\text{stream}} = \log \left( \frac{C_{\text{Hg, bank}}}{C_{\text{Hg, sediment}}} \right) \quad (2)$$

where  $C_{\text{Hg}}$  is the total Hg concentration in the bank soils or sediments. If  $EF_{\text{stream}} = 0$ , this suggests that streambank soils have concentrations similar to that of streambed sediments.

## 3 Results

All soil results are provided in an Excel™ spreadsheet in the Supplementary Information (SI Data) and are presented as sample dry weight (dw) basis.

### 3.1 Streambank soil physicochemical properties

The streambank soils throughout EFPC are classified as loam and silty loam soils (Dickson et al. 2017) consisting of  $1.0 \pm 3.8\%$  gravel (mean  $\pm$  standard deviation),  $35.2 \pm 14.2\%$  sand,  $45.2 \pm 10.5\%$  silt, and  $18.6 \pm 7.7\%$  clay. The silt content decreased with EFK distance, and no other fractions showed correlations with EFK distance (Table 1). Mean C, OC, and N contents of streambank soils were  $1.73 \pm 0.86\%$ ,  $1.41 \pm 0.71\%$ , and  $0.12 \pm 0.05\%$ , respectively, while pH was  $7.4 \pm 0.4$ . The total C content of the bank soils and the pH both decreased with EFK distance (Table 1), while OC and N were not correlated with EFK distance.

### 3.2 Streambed sediment physicochemical properties

Sediments larger than 2 mm and smaller than 125  $\mu\text{m}$  constituted less than 3% of the sediment collected, although the lowest sieve size exceeds the usual definition of sand-sized material (i.e., 63  $\mu\text{m}$ ) (Brooks et al. 2017). Of the sand-sized samples analyzed, a mean of  $33.7 \pm 8.8\%$  was classified as coarse-grained sand,  $56.0 \pm 8.6\%$  was medium-grained sand, and  $5.6 \pm 3.1\%$  was fine-grained sand (Brooks et al. 2017). Grain size was not correlated with EFK distance (Table 1). The mean content of C, OC, and N in bulk sediments was  $0.63 \pm 0.54\%$ ,  $0.31 \pm 0.16\%$ , and  $0.02 \pm 0.01\%$ , respectively (Brooks et al. 2017). The total C and OC contents of the all sediment fractions decreased with EFK distance (Table 1),

**Table 1** Correlations of physicochemical properties with EFK distance along East Fork Poplar Creek

Media	Component	Number	Spearman $\rho$	$p$ value
Soil	Sand	143	0.155	0.065
	Silt	143	-0.168	0.045*
	Clay	143	-0.159	0.058
Sediment	Coarse sand <sup>a</sup>	19	0.353	0.139
	Medium sand <sup>a</sup>	19	-0.447	0.055
	Fine sand <sup>a</sup>	19	-0.10	0.684
Soil	Total C	138	0.329	8e-5*
	TOC	138	0.147	0.086
	Total N	138	0.050	0.563
	pH	137	0.794	1e-5*
Sediment	Total C coarse	19	0.819	2e-5*
	TOC coarse	19	0.561	0.012*
	Total N coarse	19	-0.078	0.750
	Total C medium	19	0.661	0.002*
	TOC medium	19	0.504	0.028*
	Total N medium	19	0.334	0.162
	Total C fine	19	0.703	0.001*
	TOC fine	19	0.661	0.002*
	Total N fine	19	0.461	0.047*

\* $p < 0.05$  indicates statistically significant correlation

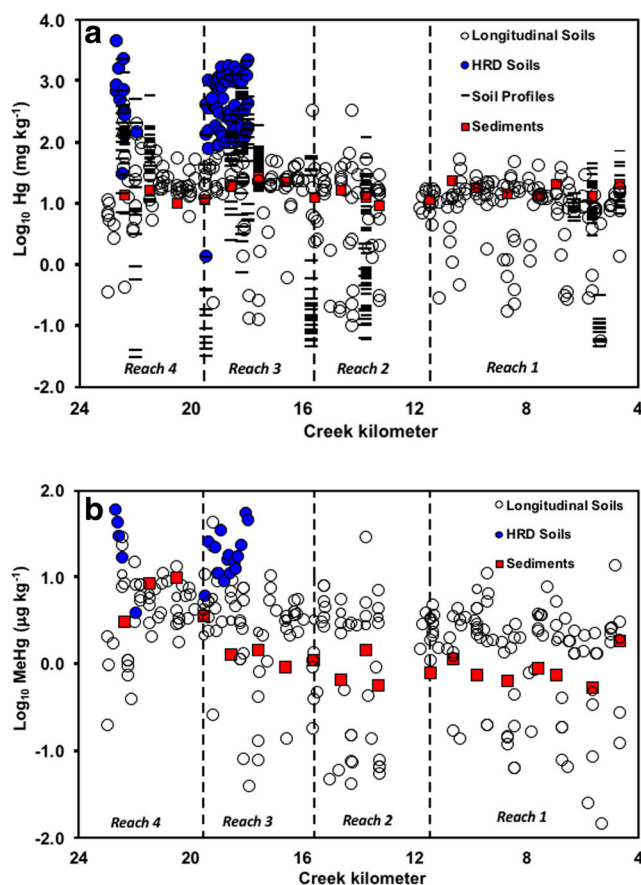
<sup>a</sup> Coarse sand (1–2 mm), medium sand (250  $\mu\text{m}$ –1 mm), fine sand (125  $\mu\text{m}$ –250  $\mu\text{m}$ )

whereas only nitrogen content in the fine sand-sized fraction decreased with EFK distance.

### 3.3 Mercury spatial trends

Longitudinal surveys in 2014 and 2015 sampled the streambank soils at the mid-point between the ground and water surfaces at 143 different locations (Fig. 2). A one-way ANOVA demonstrated that the population of Hg concentrations in the 2014 and 2015 samples were not significantly different from each other ( $p = 0.401$ ,  $n = 143$  for 2014;  $n = 138$  for 2015). The 25th and 75th percentiles of Hg concentration were 7.08 and 23.7  $\text{mg kg}^{-1}$ , respectively, with a mean and median of 26.4 and 15.3  $\text{mg kg}^{-1}$ , respectively (SI Data).

To assess within-site variability in bank soil Hg concentration as a function of lateral distance along the creek, additional samples were collected at 50% bank height 1 m upstream and 1 m downstream of 18 different initial locations ( $n = 54$ ) (Fig. S2, ESM). Mean relative standard deviation was 106.1% for total Hg and 87.9% for MeHg, indicating high spatial variability. Within-site variability in bank soil Hg concentration was assessed by analyzing the samples collected from 15 to 85% bank height for one location at every creek kilometer ( $n = 60$  samples) (Fig. S3, ESM). Samples at 50% of the streambank



**Fig. 2** Spatial distribution of **a** Hg and **b** MeHg concentrations in streambank soils and bulk streambed sediments, where all samples are oriented with respect to kilometer above the mouth of East Fork Poplar Creek. Different sampling activities are represented—longitudinal soil samplings in 2014 and 2015, historical release deposit soils (HRD) in 2015, vertical soil profiles (creek kilometers 22.4, 21.5, 17.6, 13.7, 5.6, and 4.7 are from Southworth et al. 2010), horizontal soil profiles (creek kilometers 22.0, 18.2, 15.7, 13.8, and 6.3 are from Watson et al. 2016), and streambed sediment sampling (from Brooks et al. 2017). Vertical dashed lines represent creek reaches

height were not statistically different from those at 15% and 85% of the bank height (ANOVA,  $p = 0.178$ ,  $n = 20$  locations), but high variability was noted. Additionally, 17 horizontal cores were collected from several depths at five locations beginning at the streambank face and extending up to 20 cm into the streambank face (SI Data). Of the ten cores where Hg concentrations were greater than 1  $\text{mg kg}^{-1}$  (Fig. S4, ESM), only three showed significant changes (decreases) in Hg concentrations with depth into the streambank (Table S1, ESM).

The historical release deposit (HRD) was previously identified as a discontinuous Hg-rich horizon in the soil (Southworth et al. 2010, 2013) and was suspected to exert an important influence on Hg flux to EFPC (Watson et al. 2017). During the March 2015 longitudinal survey, the absence of green vegetative cover on the streambanks and the dark color of the HRD due to inclusions of coal fines and ash

(Fig. S5, ESM) enabled better visual identification of its extent. The HRD layer was typically found between 5- and 120-cm below ground surface, which means that the longitudinal surveys had largely missed the HRD because this range usually falls below the 85% bank height and above the 50% bank height. Multiple core samples were collected within the HRD every 20-m distance along EFPC where it was visible. The thickness of the HRD ranged from 5 to 45 cm. The 25th and 75th percentiles of Hg in the HRD were 184 and 1053 mg kg<sup>-1</sup> ( $n = 83$ ), respectively, with a mean and a median of 707 and 429 mg kg<sup>-1</sup>, respectively (SI Data). The locations of HRD outcrops are readily evident because of their higher Hg concentrations (Fig. S6a, ESM). Vertical profiles of Hg concentrations along the streambank faces was collected from the ground surface to the water surface at four locations within the HRD outcrop regions ( $n = 64$ ) (Fig. S7, ESM). Overall, the location of the HRD in vertical profiles is apparent by the peak in Hg concentrations, which were consistent with two other profiles associated with the HRD (Southworth et al. 2010).

Figure 2a illustrates the sample results from the longitudinal, HRD, and profile sampling campaigns including vertical profile results reported by Southworth et al. (2010). The HRD is apparent in reaches 3 and 4, where concentrations of Hg were up to an order of magnitude higher than soils from the longitudinal survey. Overall, the concentration of Hg in the streambank soils decreased with EFK distance, for both the longitudinal dataset and the full dataset (Table 2). The mean Hg from all samples in reaches 3 and 4 is  $206 \pm 438$  mg kg<sup>-1</sup> ( $n = 457$ ) and  $13.3 \pm 15.9$  mg kg<sup>-1</sup> in reaches 1 and 2 ( $n = 321$ ). Reaches 3 and 4 are significantly different from reaches 1 and 2 (Table 2). The EFK distances of reaches 1–4 are shown in the SI Data. Mercury concentration decreased with EFK distance in reaches 3 and 4 but was unchanged with EFK distance in reaches 1 and 2. Relatively low Hg concentrations from EFK 22 to 20 are found in highly disturbed soils associated with urbanization, concrete-lined channels, and riprap-enclosed streambanks in the main commercial development zone of the town of Oak Ridge (Fig. 1).

The Hg concentrations in the bulk streambed sand-sized sediments were much less variable compared to the streambank soils (Fig. 2a). The 25th and 75th percentiles of Hg were 12.6 and 19.8 mg kg<sup>-1</sup> ( $n = 19$ ), respectively, with a mean and median of 16.1 and 14.1 mg kg<sup>-1</sup>, respectively. Only the fine-sand fraction showed a significant decrease in Hg concentration with EFK distance in EFPC, being significantly different in reaches 3 and 4 compared to reaches 1 and 2 (ANOVA,  $p = 4.1e-6$ ) (Fig. 3a).

### 3.4 Methylmercury spatial trends

The 25th and 75th percentiles of MeHg in streambank soils from the 2014 and 2015 longitudinal surveys ( $n = 163$ ) were

1.25 and 4.43  $\mu\text{g kg}^{-1}$ , respectively, with a mean of 3.76 and a median of 2.75  $\mu\text{g kg}^{-1}$ , respectively (Fig. S6b, ESM; SI Data). The 25th and 75th percentiles of MeHg from the HRD areas ( $n = 21$ ) were 11.4 and 30.1  $\mu\text{g kg}^{-1}$  with a mean of 23.5 and a median of 17.8  $\mu\text{g kg}^{-1}$ , respectively. There were significant correlations between streambank MeHg concentrations and stream distance, where concentrations decrease with EFK distance for both the longitudinal and full datasets (Table 2). In reaches 3 and 4, soil MeHg concentrations were significantly different (ANOVA,  $p = 2.64e-8$ ) and approximately three times higher ( $8.3 \pm 11$   $\mu\text{g kg}^{-1}$ ,  $n = 124$ ) than in reaches 2 and 1 ( $2.6 \pm 3.2$   $\mu\text{g kg}^{-1}$ ,  $n = 131$ ) (Fig. 2b).

The 25th and 75th percentiles of MeHg in bulk sediments were 0.76  $\mu\text{g kg}^{-1}$  and 1.66  $\mu\text{g kg}^{-1}$ , respectively, with a mean of 2.11 and a median of 1.10  $\mu\text{g kg}^{-1}$ , respectively (Brooks et al. 2017). Overall, sedimentary MeHg decreased with EFK distance (Fig. 2b). Methylmercury concentrations in coarse and fine-grained sand sediments were strongly correlated with stream distance, decreasing with EFK distance, while medium-grained sediments did not exhibit correlations with EFK distance (Fig. 3b; Table 2). Moreover, only the fine-grained sand fractions differed significantly between reaches 3 and 4 compared to reaches 1 and 2 (ANOVA,  $p = 1.3e-3$ ).

### 3.5 Chemical relationships between soils and sediments

To relate the source of contamination in sediments to the streambank soils, we calculated an enrichment factor (EF) which is a ratio of Hg concentration in the soils to that in the sediments (similar to Wallschäger et al. 1998a). To facilitate the comparison, all bank soil Hg values were binned into 1-km groups and the mean value for each 1-km bin was computed (Table S2, ESM). The EF was then calculated as the log of the mean Hg soil value divided by the corresponding bulk sediment value, for each kilometer along EFPC. The  $\text{EF}_{\text{stream}} > 0$  from EFK 23 to about EFK 15 (Fig. 4), indicating the streambank soils could be a potential source of Hg to the streambed sediments in reaches 3 and 4 (Wallschäger et al. 1998a). Indeed, streambank soils contain significantly higher Hg concentrations relative to the bulk streambed sediments only in reaches 3 and 4 ( $p = 9.4e-4$ ,  $n = 8$ ), and not in reaches 1 and 2 ( $p = 0.96$ ,  $n = 11$ ), even though there was high variability in all reaches. From EFK 15 and continuing downstream the  $\text{EF}_{\text{stream}}$  hovered  $\sim 0$  reflecting similar soil and sediment Hg concentrations.

We compared the ratio of MeHg to Hg in streambank soils to that of streambed sediments using the binned soil data means (Tables S2 and S3, ESM). The MeHg/Hg ratio was more similar between the soils and the fine sand-sized sediments ( $p = 0.016$ ) than between the streambed soils and either the coarse ( $p = 0.557$ ) or the medium sand-sized sediments ( $p = 0.606$ ) (Fig. 5). Soil Hg and MeHg were strongly and

**Table 2** Correlations of Hg and MeHg with EFK distance along East Fork Poplar Creek

Media	Component	Dataset	Number	Spearman $\rho$	$p$ value
Soil	Hg	Longitudinal	353	0.378	1e-5*
		All data	781	0.479	1e-5*
		Reaches 3 and 4 <sup>a</sup>	459	0.194	3e-5*
		Reaches 2 and 1 <sup>b</sup>	322	0.029	0.605
Soil	MeHg	Longitudinal	234	0.390	6.2e-10*
		All data	255	0.463	1e-5*
		Reaches 3 and 4 <sup>a</sup>	124	0.254	4.5e-3*
		Reaches 2 and 1 <sup>b</sup>	135	0.185	0.035*
Sediment	Hg	Coarse <sup>c</sup>	19	-0.347	0.145
		Medium <sup>c</sup>	19	0.082	0.737
		Fine <sup>c</sup>	19	0.853	3.5e-6*
Sediment	MeHg	Coarse <sup>c</sup>	19	0.665	0.002*
		Medium <sup>c</sup>	19	0.223	0.359
		Fine <sup>c</sup>	19	0.586	0.009*

\* $p < 0.05$  indicates statistically significant correlation

<sup>a</sup> Reaches 3 and 4 are from East Fork Poplar Creek kilometer 23.40 to 15.61

<sup>b</sup> Reaches 1 and 2 are from East Fork Poplar Creek kilometer 15.61 to 4.67

<sup>c</sup> Coarse sand (1–2 mm), medium sand (250  $\mu\text{m}$ –1 mm), fine sand (125  $\mu\text{m}$ –250  $\mu\text{m}$ )

positively correlated, and concentrations of both decreased with EFK distance (Fig. S8, ESM; Table 3). Similarly, the same trend was observed for Hg and MeHg in fine sand-sized sediments ( $p = 3e-5$ ). In contrast, neither medium nor coarse sand-sized sediments showed correlations between Hg and MeHg or distinct patterns with EFK distance. It is worth noting that continued methylation can alter concentrations in both soils and the stream.

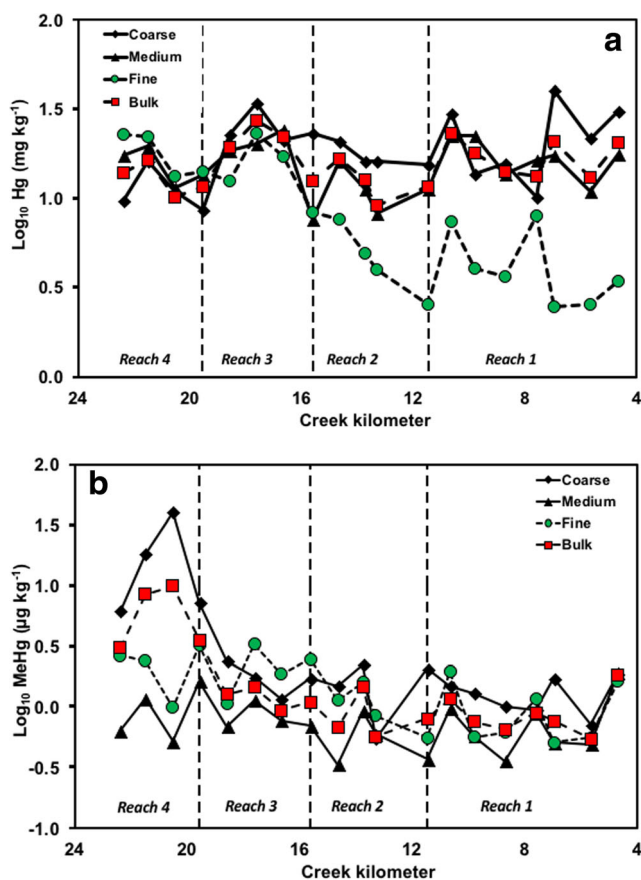
Sequential extraction of Hg was compared between streambank soils and the sand-sized fractions of the sediments (Brooks et al. 2017) to determine the strength of Hg binding to particles (Bloom et al. 2003) and to identify any differences between soils and sediments. The bulk of Hg was found in the most resistant F5 fraction (extracted with aqua regia), accounting for large proportions of Hg in the soils, coarse sand-sized sediments, and medium sand-sized sediments and to lesser proportions in the fine sand-sized sediments (Table 4; Fig. S9, ESM). For the most resistant fractions, the soils and fine sand-sized sediments differ significantly. The coarse sand-sized sediments are comparable to the soils, while the medium sand-sized sediments are similar to the fine sand-sized sediments. Soils and all sediment sand fractions had some Hg within the 12 M HNO<sub>3</sub> F4 extraction (6.7% for soils, 23% for fine-sand sediments, with medium- and coarse-sand sediments intermediate) and the 1 M KOH F3 fraction (1.5% for soils, 15% for fine sand sediments, with medium- and coarse-sand sediments intermediate). The HRD soils had a mean of 4.8% Hg within the F2 fraction, while all longitudinal soils and sediments had very low concentrations in the F2 fraction.

## 4 Discussion

Our data provides improved spatial resolution of the distribution of “hot spots” of Hg in soil layers in streambank soils, e.g., Hg concentrations in the HRD soils are an order of magnitude higher than that in the rest of the streambank soils. The highest Hg concentrations in streambank soils coincided with localized occurrences of the HRD in the upper 6-km stretch of the stream (Fig. 2a). The HRD is more extensive than previously documented (Southworth et al. 2010, 2013), particularly in reach 3 (Fig. 2a). Stream reaches 3 and 4 encompassing the HRD zones had higher Hg concentrations in comparison to reaches 1 and 2 (Table 2). Despite the large streambank soil dataset ( $n = 778$ ), high variability in observed concentrations (0.05–4590 mg kg<sup>-1</sup>) was consistent with previous reports (Gerlach et al. 1995; Southworth et al. 2013). The overall similarity of Hg concentrations in streambank soils to previous studies (Tennessee Valley Authority 1985; Southworth et al. 2010) suggests that Hg levels in the streambank soils have not declined in the past 30 years. Mercury concentrations identified in this study corroborate the assertion that large inputs of Hg from soils are available to sustain a large export rate from EFPC watershed (Southworth et al. 2013; Riscassi et al. 2016). Watson et al. (2017) attributed the majority of Hg flux to streambank soils (38.6 kg year<sup>-1</sup>), with an additional 9.8 kg year<sup>-1</sup> coming from Y-12 above EFK 23.

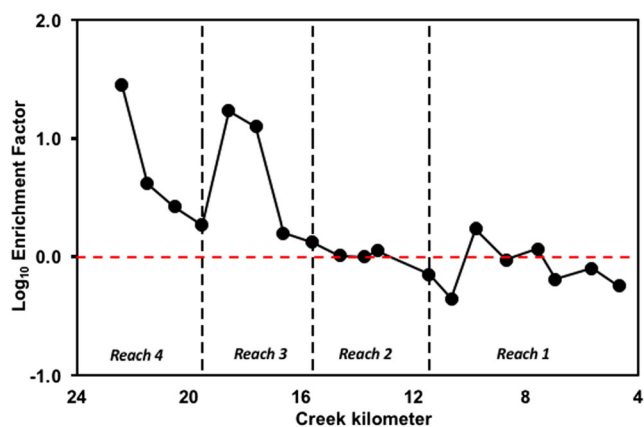
Streambed sediment Hg concentrations were significantly lower than Hg concentrations in streambank soils in reaches 3 and 4. Sediment and soil Hg concentrations in reaches 1 and 2 are similar. The Hg content of the coarse and medium sand-





**Fig. 3** Spatial distribution of **a** Hg and **b** MeHg concentrations in streambed sediments (data from Brooks et al. 2017). Vertical dashed lines represent creek reaches

sized fractions of the streambed sediments varied minimally as a function of EFK distance, while Hg concentration in the fine sand-sized sediment fraction decreased with EFK distance (Table 2). Southworth et al. (2013) observed a peak in sediment Hg concentration around EFK18, which the authors postulated could represent a pulse of contaminated sediment moving downstream from the point source at Y-12. Because Y-12 discharges Hg directly to EFKC water, it remains challenging to conclusively determine the extent to which Hg in streambed sediments originates from upstream aqueous discharges, erosion of streambank soils, or transport of



**Fig. 4** Enrichment factor (EF) and the ratio of mean total Hg in streambank soils to total Hg in bulk sediment along East Fork Poplar Creek. Streambank soils are considered a possible source of Hg to streambed sediments when  $\log_{10}(EF) > 0$ . Vertical dashed lines represent creek reaches

contaminated streambed sediments. A peak in Hg concentration is still visible in all sediment fractions near EFK18 (Fig. 3a). Our study suggests that this peak may be related to erosion and deposition from the highly contaminated HRD soils (Fig. 2a). Our findings expand the previously known extent of the HRD outcropping in streambank soils (Southworth et al. 2010, 2013). High enrichment factors are clearly evident around EFK18 (Fig. 4), consistent with peaks in sediment Hg (Fig. 3a) and soil Hg concentrations (Fig. 2a). Moreover, there is a small peak in sediment Hg concentrations near EFK 23 located near an HRD soil outcrop location. Therefore, it is highly likely that the streambank soils, particularly the HRD-containing sections, are a source of Hg to the streambed sediments. In contrast, a peak in sediment Hg near EFK11 does not appear to be associated with any distinct streambank soil source of Hg.

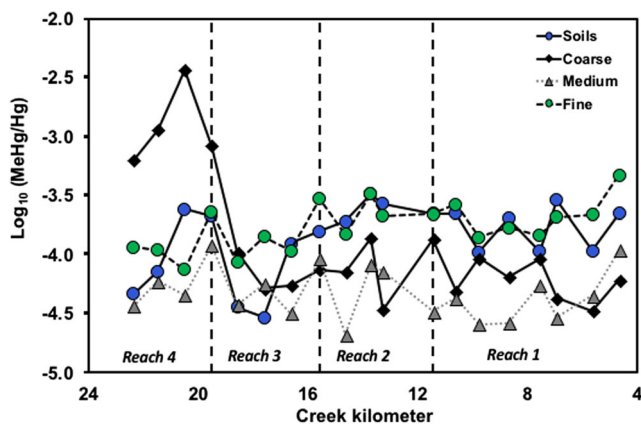
The bulk streambed sediment Hg inventory significantly decreased (~67%) compared to 1984 (Tennessee Valley Authority 1985) as reported in Brooks et al. (2017). The peak concentrations observed in streambed Hg concentrations remain relatively similar to the overall streambed sediment Hg concentrations (Fig. 2a), which is in contrast to the South River site near Harrisonburg, VA (USA), where streambed

**Table 3** Correlations between soil and sediment Hg and MeHg with EFK distance along East Fork Poplar Creek

Media	Component	Dataset	Number	Spearman $\rho$	<i>p</i> value
Soil	Hg versus MeHg	Longitudinal	234	0.771	1e-5*
	Hg versus MeHg	Longitudinal and historical release deposits	255	0.817	1e-5*
Sediment	Hg versus MeHg	Coarse <sup>a</sup>	19	-0.222	0.359
		Medium <sup>a</sup>	19	0.358	0.132
		Fine <sup>a</sup>	19	0.805	3e-5*

\* $p < 0.05$  indicates statistically significant correlation

<sup>a</sup> Coarse sand (1–2 mm), medium sand (250  $\mu\text{m}$ –1 mm), fine sand (125  $\mu\text{m}$ –250  $\mu\text{m}$ )



**Fig. 5** The  $\log_{10}$  of the ratio of MeHg to total Hg in streambank soils and sediment fractions (sediment data from Brooks et al. 2017). Vertical dashed lines represent creek reaches

sediments exhibit much stronger peak Hg concentrations at 15 km downstream from the original point source (Rhoades et al. 2009; Flanders et al. 2010; Pizzuto 2014). There are two possible explanations for the differences between South River and EFPC—first, South River is a high-gradient stream while EFPC is a low-gradient stream which may enhance sediment movement in South River, and second, the Y-12 facility continues to discharge significant amounts of Hg directly into EFPC ecosystem. Therefore, Hg concentrations in streambed sediments may be more uniformly distributed along EFPC in comparison to the South River.

The strong association of Hg with organic matter and solid mineral surfaces was used to understand more specific nuances of soil and sediment accumulation of Hg (Brooks et al. 2017). The Hg to OC mole ratio (Hg/OC) appeared mostly similar between coarse and medium sand-sized sediments (Fig. 6). The ratio increased with EFK distance due to the declining OC content of the sediment amid relatively constant Hg concentrations (Table 1). The Hg/OC ratio for fine sand-sized sediments was significantly lower than that for coarse and medium sand-sized sediments and declined with EFK distance. The Hg:OC ratio in the streambank soils was very similar to that of the fine sand-sized sediments but was different from the coarse and medium sand-sized sediments. This suggests that the streambank soils are more similar to the fine sand-sized streambed sediments compared to the coarse and medium sand-sized streambed sediments.

Similarly, the proportion of Hg present as MeHg can be used to compare soils and sediments, with the caveat that concentrations of MeHg can be altered by microbial activity. Regardless, MeHg was strongly correlated with Hg for the longitudinal streambank soils, the HRD, and the fine sand-sized streambed sediments, and the correlations reflect increasing MeHg/Hg ratios with EFK distance (Table 3; Fig. 5). In contrast, the coarse and medium sand-sized sediments do not show correlations between Hg and MeHg (Fig. S8,

ESM). Streambank soils seem more related to the fine sand-sized fraction of the streambed sediments.

The size fractions greater than 250  $\mu\text{m}$  (coarse and medium sand-sized particles) comprised approximately 90% of the sand-sized fraction of streambed sediments, while particles of this size only account for an average of 7.4% of the sand-sized fraction of the streambank soils (SI Data). This suggests the source for the coarse and medium sand-sized fractions of the streambed sediments was different from the streambank soils, e.g., through weathering of exposed bedrock materials in the stream channel and contributions from tributary channels. The fine sand-sized fractions of the streambed sediments constitute a minor fraction of the bedload, but these are the most closely related to the streambank soils. It is likely that eroded fine-grained soil material becomes entrained in EFPC waters as total suspended solid (TSS) load. Total suspended solids were sampled under baseflow conditions in EFPC using a 0.7- $\mu\text{m}$  glass microfiber filter (Riscassi et al. 2016; Brooks et al. 2018). By calculating its mass and Hg concentration with respect to a known volume of filtered water, the average Hg concentration of the TSS over a period of 13 months was 15.7  $\text{mg kg}^{-1}$  at EFK 5.4 and 14.6  $\text{mg kg}^{-1}$  when values from EFK 16.2 and 5.4 were averaged (Brooks et al. 2018). During streambed sediment sampling, only 3% of the material passed the 125  $\mu\text{m}$  sieve (Brooks et al. 2017), so we can estimate that TSS represents 3% of the streambed sediments. The average Hg concentration of the TSS is 15.7  $\text{mg kg}^{-1}$ , and it only constitutes 3% of the sediment bedload, whereas the concentration of Hg in the sampled streambed sediments averaged 16.1  $\text{mg kg}^{-1}$  which comprised 97% of the mass; therefore, the Hg concentrations of the TSS do not significantly alter our estimates of Hg concentration in the streambed sediments. This analysis offers a consistency in observed Hg concentrations of TSS, streambank soils, and streambed sediments under baseflow conditions. The streambank soils in the HRD have much higher Hg concentrations, but the outcrops are located above baseflow levels; consequently, erosion of these materials into EFPC may be confined to flooding or freeze-thaw events (Watson et al. 2017).

Despite some clear relationships between streambank soils and streambed sediments in EFPC, the sequential extraction results suggested that the lability of Hg in the soils and sediment fractions was quite different. Comparing streambank soil and streambed sediment fractions, the soils contained the highest amounts of the most resistant F5 fraction (88%), whereas fine sand-sized streambed sediments contained the least (61%) (Table 4). The fine sand-sized streambed sediments contained the highest proportion of F3 and F4 fractions, while streambank soils contained the lowest. Coarse sand-sized sediments were similar to the soils, while medium sand-sized sediments were similar to fine sand-sized sediments (Fig. S9, ESM), which is in contrast to our earlier findings that suggested a close relationship between

**Table 4** Results of sequential extractions of Hg from creek bank soils and sediments at East Fork Poplar Creek expressed as a percentage of total Hg extracted from all fractions F1–F5 (defined in text)

EFK	Number	F1	F2	F3	F4	F5
All soils	22	0.11 ± 0.06 <sup>a</sup>	3.10 ± 4.01	1.47 ± 1.48	6.74 ± 5.07	88.6 ± 5.53
HRD <sup>b</sup>	8	0.13 ± 0.06	4.84 ± 4.13	1.95 ± 1.67	3.79 ± 0.89	89.3 ± 5.60
Longitudinal soils	14	0.06 ± 0.03	0.07 ± 0.06	0.65 ± 0.41	11.9 ± 5.28	87.3 ± 5.55
Coarse sediments <sup>c</sup>	19	0.11 ± 0.09	0.17 ± 0.50	4.58 ± 8.17	8.81 ± 9.96	86.3 ± 11.2
Medium sediments <sup>c</sup>	19	0.35 ± 0.22	0.11 ± 0.40	10.5 ± 10.7	11.1 ± 7.06	78.0 ± 10.2
Fine sediments <sup>c</sup>	19	0.34 ± 0.49	0.06 ± 0.26	15.0 ± 12.2	23.2 ± 9.80	61.3 ± 16.1

<sup>a</sup> Mean ± standard deviation<sup>b</sup> Historical release deposit soils<sup>c</sup> Coarse sand (1–2 mm), medium sand (250 µm–1 mm), fine sand (125 µm–250 µm)

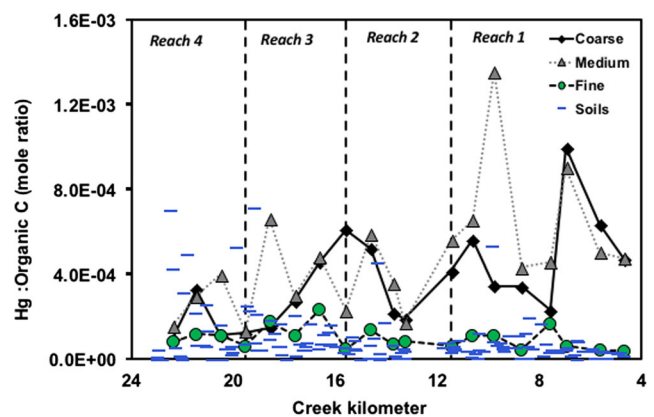
streambank soils and fine sand-sized streambed sediments. Additionally, there is a strong spatial pattern for all extractions, with smaller proportions of F5 as a function of EFK distance and greater proportions of F3 and F4. The strong spatial patterns suggest changes in sediment Hg solid phase chemistry in the most downstream EFPC waters. The streambank soils also show a decrease in F5 fraction and an increase in F4 fraction with EFK distance, but the changes are not as significant as those observed for the streambed sediments. This suggests alteration of Hg chemistry in the streambed sediments with distance from Y-12 and from the most contaminated streambank soil sources in reaches 3 and 4.

The EFPC extraction results are similar to the South River, in which F4 and F5 fractions constitute the bulk of Hg for both soils and sediments (Flanders et al. 2010). Comparisons of streambank soil and sediments are also consistent with Hg contamination from a chlor-alkali plant in the River Elbe in Germany (Wallschäger et al. 1998a, b). Similar to EFPC, much stronger immobilization was observed in soils compared to sediments in the River Elbe, as well as overall higher Hg concentrations in the soils, although the study preceded the Bloom et al. (2003) method. Wallschäger et al. (1998a, b) attributed their findings to greater abundance of organic matter and associated sulfur-containing functional groups in the soils resulting in stronger complexation between soils and Hg, which is consistent with our observations (Fig. 6; Sect. 3.2). They also reported that continuous leaching of submerged streambed sediments tended to enhance lability in the sediments compared to the soils. In our system, much of the soil Hg is associated with in situ precipitation of metacinnabar or other mercury sulfides (Barnett et al. 1995, 1997), which tends to be associated with the strongest F5 fraction (Bloom et al. 2003). However, the soils analyzed for mineralogy to date are from the HRD. Detailed mineralogical studies have not yet been performed on EPFC streambed sediments or the non-HRD streambank soils, in part because of their much lower Hg concentrations.

## 5 Conclusions

Our findings highlight the two major sources of Hg in this system—direct discharge from the upstream Y-12 facility and erosion of contaminated streambank soils. In particular, we identified two discontinuous zones of HRD outcropping in the streambanks that have Hg and MeHg concentrations an order of magnitude higher than most streambank soils and streambank sediments. Other than the HRD areas, Hg concentrations of streambank soils are similar to streambed sediments. Methylmercury concentrations in streambank soils tend to be higher than MeHg in streambed sediments, even outside of the HRD areas.

We identified linkages between Hg and MeHg in streambank soils and the potential recipient streambed sediments. The enrichment factor for lower EFPC suggested the streambank soils are a potential source of Hg inputs to the stream but only in the upper 10 km of EFPC. Relationships between OC, and Hg, and MeHg and Hg support a connection between streambank soils and fine sand-sized streambed sediments. The larger particle size of the medium and coarse



**Fig. 6** Total Hg to organic C mole ratio in streambank soils and coarse, medium, and fine sand-sized fractions of streambank sediments (sediment data from Brooks et al. 2017). Vertical dashed lines represent creek reaches

sand-sized streambed sediments may indicate sources other than streambank soils, and these materials constitute the bulk of the streambed sediment load.

Sequential extractions found that 5% of the Hg in the HRD soils was very labile, which could imply a higher potential for Hg releases from the HRD soils compared to the other streambank soils and the streambed sediments. Extractions of Hg from the fine-grained sand sediments suggested greater lability than the bulk of the streambank soils. The in-stream environment likely alters the solid-phase geochemistry of soil-bound Hg entering the creek, but the mechanism of alteration or the exact geochemistry of Hg binding to streambed sediments remains unclear.

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## Compliance with ethical standards

**Conflict of interest** The authors declare that they have no competing interests.

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