Mercury Remediation Technology Development for Lower East Fork Poplar Creek—FY 2015 Progress Report

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April 2016

OAK RIDGE NATIONAL LABORATORY

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Environmental Sciences Division

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CONTENTS

LIST OF FIGURES

LIST OF TABLES

ACRONYMS

ASTM	American Society of Testing Method
BET	Brunauer-Emmet-Teller
BGS	below ground surface
BMAP	Biological Monitoring and Abatement Program
DI	deionized
DOC	dissolved organic carbon
DOE	Department of Energy
DOM	dissolved organic matter
dw	dry weight
EFK	East Fork Poplar Creek kilometer
EFPC	East Fork Poplar Creek
EM	Environmental Management
EPA	US Environmental Protection Agency
EPT	Ephemeroptera, Plecoptera, and Trichoptera
FY	fiscal year
Hg(II)	mercury cation
HgD	dissolved mercury
Hg_R	$SnCl_2$-reducible mercury
HgS	mercuric sulfide
HgT	total mercury
HRD	historical release deposit
K_d	sorbent:water partition coefficient
LEFPC	lower East Fork Poplar Creek
MeHg	methylmercury
MeHgD	dissolved methylmercury
MeHgT	total methylmercury
NOAA	National Oceanic and Atmospheric Administration
NOM	natural organic matter
NRWQC	National Recommended Water Quality Criterion
OF200	Outfall 200
ORNL	Oak Ridge National Laboratory
OREM	Oak Ridge Office of Environmental Management
ORWTF	Oak Ridge Wastewater Treatment Facility
ppb	parts per billion
ppm	parts per million
sd	standard deviation
SR	slope ratio
SUVA	specific ultraviolet-absorbance
TD	technology development
TRL	Technology Readiness Level
TSS	total suspended solids
TVA	Tennessee Valley Authority
UEFPC	upper East Fork Poplar Creek
USDA	US Department of Agriculture
UV	ultraviolet
VOC	volatile organic compound
WEMA	West End Mercury Area
Y-12	Y-12 National Security Complex

1. INTRODUCTION

Mercury remediation is a high priority for the US Department of Energy (DOE) Oak Ridge Office of Environmental Management (OREM) because of large historical losses of mercury within buildings and to soils and surface waters at the Y-12 National Security Complex (Y-12). Because of the extent of mercury losses and the complexities of mercury transport and fate in the downstream environment, the success of conventional options for mercury remediation in lower East Fork Poplar Creek (EFPC) is uncertain. A phased, adaptive management approach to remediation[1] of surface water includes mercury treatment actions at Y-12 in the short-term and research and technology development (TD) to evaluate longer-term solutions in the downstream environment (US Department of Energy 2014b).

Over the 2014–2016 time period, there have been significant efforts to develop a mercury cleanup strategy and TD plans in Oak Ridge that will ultimately lead to decreased mercury concentrations in surface waters and in fish. Four important planning reports have been issued over this period:

1. *Strategic Plan for Mercury Remediation at the Y-12 National Security Complex, Oak Ridge, Tennessee* (2014; DOE/OR/01-2605&D2), providing the overall remediation roadmap for mercury remediation at Y-12.
2. *Mercury Technology Development Plan for Remediation of the Y-12 Plant and East Fork Poplar Creek* (2014: DOE/ORO-2489), which highlights the priorities for mercury technology development in Oak Ridge.
3. *Mercury Remediation Technology Development for Lower East Fork Poplar Creek* (2015; ORNL/SPR-2014/645), providing the overall strategy for mercury technology development activities in LEFPC.
4. *Technology Plan to Address the EM Mercury Challenge*, a DOE Headquarters 2016 report summarizing the overall approach to the DOE Environmental Management (EM) mercury challenge in Oak Ridge and at Savannah River.

The research and TD activities currently being conducted in lower EFPC (LEFPC) are a direct outgrowth of the recommendations described in these various strategic planning reports. As part of the overall strategy, mercury research and TD activities are designed to be adaptive and will likely change in the future, depending on the results of earlier studies, the financial and technical resources available, and EM task prioritization.

The broad goal of this document is to present results from characterization and experimental studies conducted in fiscal year (FY) 2015 in support of developing strategies and technologies that may lead to new options for mercury remediation in LEFPC. The TD strategy is consistent with the adaptive management paradigm and DOE's Technology Readiness Level (TRL) guidelines. That is, early evaluation should focus on literature review, site characterization, and small scale studies of a broad number of potential technologies (including ideas that may be viewed as higher risk or uncertain but with potentially high payoff). As more information is gathered, an adaptive management approach can be used to focus on technologies that may have the most promise and potential remediation benefit. High merit technologies or strategies will need to undergo more extensive and larger-scale pilot testing before remedial implementation.

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[1] As used here, "adaptive management" encompasses the concept of decision-making under uncertainty about the outcomes of specific actions, with the goal of identifying effective environmental remedies based on observing effectiveness of interim actions, as well as on results of scientific research comparing multiple causative hypotheses. Source: *Strategic Plan for Mercury Remediation at the Y-12 National Security Complex, Oak Ridge, Tennessee (DOE/OR/01-2605&D2).*

Understanding mercury transport and fate processes in the EFPC system is essential to the development of new technologies and ultimately to the development of remedial options and strategies for the creek. Thus, a major emphasis of TD studies in 2015 has been on field characterization and obtaining a watershed-scale understanding. Task 1, Soil and Groundwater Source Control, focuses on addressing downstream mercury sources to the creek (especially floodplain and bank soils) and groundwater. Task 2, Surface Water and Sediment Manipulation, centers on potential manipulation of in-stream processes, including the many water and sediment chemistry factors that affect mercury methylation. Task 3, Ecological Manipulation, investigates methods to manipulate the food chain at both lower and higher levels of organization to decrease mercury concentrations in fish. Together, the three study tasks focus on manipulating the key factors that affect mercury concentrations in fish: the amount of inorganic mercury available to an ecosystem, the conversion of inorganic mercury to methylmercury, and the bioaccumulation of methylmercury through the food web.

2. TASK 1, SOIL AND GROUNDWATER SOURCE CONTROL

2.1 STREAMBANK SOILS

2.1.1 Approach to Bank Soil Investigations

Legacy mercury contamination in streambanks, floodplain soils, and sediments has been identified as a major inventory of mercury in the EFPC watershed, accounting for the majority of the annual export of mercury to the watershed (Southworth et al. 2013a). This highlights opportunities for targeted remediation, but approximately 85% of mercury inventory is associated with floodplain soils on the 18 km reach of LEFPC downstream of Y-12, potentially rendering conventional technology (i.e., removal and disposal in a regulated facility) inadequate and cost-prohibitive. As legacy mercury is eroded from bank and floodplain soils, it contributes to concentrations in the water column and sediments and provides a source for in-stream production of methylmercury.

The LEFPC bank soils have never been characterized systematically to determine their spatial variability, and therefore there is a lack of specific understanding about their contributions to mercury and methylmercury fluxes throughout the creek. The concentrations of mercury and methylmercury as a function of creek length and bank height are at present unknown. Characteristics influencing erosional fluxes into LEFPC include soil texture and stability measures such as plastic or liquid limits, but their values and variability as a function of creek length are unknown. Mercury is in different chemical forms in soils, including elemental mercury, mercury sulfide precipitates, associations with soil and organic particles, and adsorbed complexes. Basic soil characteristics such as total carbon, organic carbon, nitrogen, sulfur, and pH may influence the form of mercury in the soils or the potential for release from the soils. However, no systematic investigations have examined chemical and physical properties of bank soils throughout the length of the creek. In fact, LEPFC soils have never been mapped at a resolution sufficient for understanding of soil-forming processes at the creek scale. Further, floodplain soils are composed of soil formed from the in situ weathering of bedrock as well as the overlying alluvial deposits. There also is limited understanding of the potential for desorption of mercury from the soils (i.e., the likelihood of release of mercury from creek bank soils). In addition, the role of interactions between groundwater and surface water may influence both mercury release and methylmercury formation, but there is limited information on the extent to which these processes influence concentrations in LEFPC. Additional information regarding soil characteristics and mercury concentrations is a great advantage when developing credible and science-based remedial strategies for bank and floodplain soils. The initial focus of Oak Ridge National Laboratory's (ORNL's) efforts is to characterize the system to allow the formation of conceptual models describing the pools, stocks, exchanges, and transfers within the system. The formulation and update of conceptual models is essential to planning remedial activities and in understanding their potential impacts.

Our objective in FY 2015 was to characterize the creek bank soils in LEFPC for basic soil, physical, and chemical characteristics and for mercury and methylmercury concentrations. The purpose of characterization is to yield a comprehensive understanding of LEFPC soils that can be used to (1) relate the spatial distribution of mercury and methylmercury to soil physical and chemical characteristics to identify the areas most likely to contribute significantly to mercury flux in the creek, (2) understand the processes influencing mercury and methylmercury concentrations in LEFPC floodplain soils, and (3) prioritize locations for future remedial activities. Activities in FY 2015 involved longitudinal surveys, including mapping creek bank soil profiles and three detailed sample collection activities. Laboratory experiments examined the desorption potential of creek bank soils. In addition, a groundwater installation was planned to determine the spatio-temporal patterns of mercury and methylmercury concentrations in groundwater in several different locations along LEFPC.

2.1.2   Results of Bank Soil Investigations

2.1.2.1   Bank soil mapping

A detailed soil map for LEFPC was not available; hence, this study was undertaken to delineate soil types within the LEFPC reach at a resolution sufficient to establish an understanding of the characteristics of vertical soil horizons exposed in the creek banks. The bank soil investigation, conducted in May and June, involved walking the entire 18 km LEFPC reach below Y-12 and above the confluence with EFPC (EFPC kilometer [EFK] 23 to EFK 4.8). Sixty-nine creek bank soil profile descriptions were completed along the creek; an example profile is shown in Fig. 1. The remaining 68 profiles are available in Dickson et al. (2015). The soils encountered at these locations were classified in accordance with the US Department of Agriculture (USDA) textural classification method and were delineated based on drainage limitations, estimated permeability, and soil taxonomy. Twenty-one soil samples were collected for bulk density determination (Dickson et al. 2015). Soil conditions described include soil permeability, depth to limiting zones encompassing zones of seasonal or perennial saturation, and identification of strata that effectively limit the movement of water, potentially resulting in seasonal saturation at shallow depths (sometimes referred to as a perched water table). The depth and degree of seasonal saturation may vary depending on the amount of precipitation from season to season and year to year. Redoximorphic features—soil colors caused by the process of reduction, translocation, and oxidation of iron and manganese oxides—that form in response to repeated and prolonged saturation in the soil generally are used to estimate limiting zones, irrespective of where the groundwater table may be observed at any given time.

The soils are classified as moderately well drained Hamblen silt loam and somewhat poorly drained Chenneby silt loam, with 0–3% slopes (USDA 2015). Hamblen and Chenneby soils are classified as Fluvaquentic Eutrudepts and Dystrudepts, respectively. These soils belong to the Inceptisol Soil Order, which is a transitional soil type with minimal or weak horizontal developments. They are generally young soils at the early stage of soil formation, found on steep mountain slopes, drainageways, and river valleys. Their locations are shown in Fig. 2. Both soil units occupy floodplains and depressions on gentle to slight slopes. Both soils are deep and somewhat poorly to moderately well drained, are formed on alluvial material weathered from sedimentary rock (limestone, sandstone, and shale), and are occasionally or frequently flooded for a brief period. More details are available in Dickson et al. (2015).

OAK RIDGE
National Laboratory

Soil Profile
Notes

Profile #: SB-10   Date of Test: 5/13/15   Soil Boring X or Test Pits X
Property Owner: DOE
Location: LEFPC   Project: Hg TD   Project #: 3380-9014
Site Evaluator: John Dickson w/Jennifer Earles   CPSS License #: 36208
Slope: 0-1%   Relief: Floodplain
Estimated Permeability (minutes/inch): (>120 mpi for design purposes)
Depth to Limiting Zone (inches below existing ground surface to redoximorphic features): n/a
Soil Series Identified: Fluvaquentic Dystrudepts-Disturbed

Horizon Master	Sub			Depth (inches)		Color Matrix	Color Mottles	Mottles Ab.	S.	Con.	Texture	Structure G	S	F/T	Consistence Moist	Wet	Cementation
—	FILL	—	—	0	8	10YR 4/ 2	— — —	—	—	—	sil	—	—	—	m	fr	— —
—	B	w	1	8	16	10YR 5/ 4	2.5Y 5/ 2	f	2	d	sil	1	m	sbk	fr	—	—
							10YR 4/ 6	f	2	d							
—	B	w	2	16	26	2.5Y 5/ 4	2.5Y 6/ 2	c	2	d	sic	2	c	sbk	fi	—	—
							10YR 4/ 6	c	1	d							
—	C	—	—	26	45	2.5Y 5/ 3	2.5Y 6/ 2	c	3	d	c	—	—	m	fi	—	—
							10YR 5/ 6	c	2	d							
—	—	—	—			— — —	— — —						—	—			
—	—	—	—			— — —	— — —						—	—			

Comments:
GPS Coordinate: N: 36.00263; W: -84.25278

SB location located within previously remediated area.
From 26-45" inclusion of few gravels.
At 48" firm, gleyed clayey horizon containing some cobbles

Depth to water surface in creek ~45" from top of bank.

Site Evaluator's Signature:_____

Fig. 1. Example of one of the 69 soil profile descriptions completed during a bank soil investigation along the entire reach of lower East Fork Poplar Creek in May and June 2015. (*Source:* Dickson, J. O., M. Mayes, T. L. Mehlhorn, K. A. Lowe, M. Peterson, and E. M. Pierce. 2015. *Soil Investigation of Lower East Fork Poplar Creek*. ORNL-TM/2015-374, Oak Ridge National Laboratory, Oak Ridge, TN.)
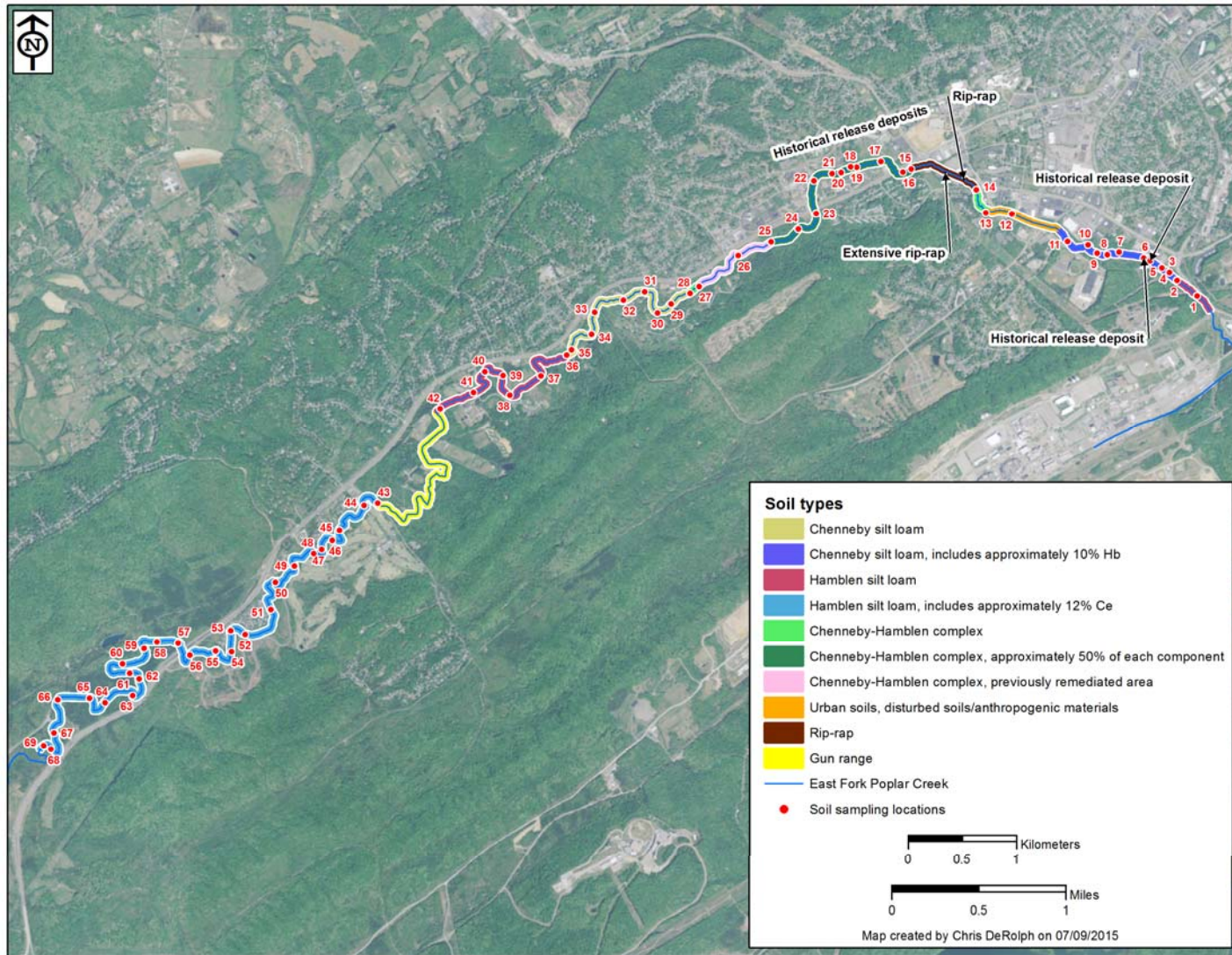
Fig. 2. Map of soil types along lower East Fork Poplar Creek.(*Source:* Dickson, J. O., M. Mayes, T. L. Mehlhorn, K. A. Lowe, M. Peterson, and E. M. Pierce. 2015. *Soil Investigation of Lower East Fork Poplar Creek.* ORNL-TM/2015-374, Oak Ridge National Laboratory, Oak Ridge, TN.)

The Chenneby series soils (Fluvaquentic Dystrudepts) in LEFPC were found at depths ranging from 6 to 18 in. below ground surface (BGS) as a surface horizon classified as a loam to silt loam texture. These soils transition to a subsurface horizon with silt loam to clay loam texture at depths ranging from 20 to 48 in. BGS. Underlying this horizon is the weathered parent or geologic material consisting of gleyed silty clay loam to clay texture at depths of 36 in. to greater than 84 in. BGS. Redoximorphic features indicative of seasonally saturated conditions were observed at depths ranging from 8 to 18 in. BGS, and free water levels observed in those parts of the creek occupied by this soil unit ranged from depths of 32 to 86 in. BGS. Based on observed soil textures, measured bulk density, and USDA saturated hydraulic conductivity classes, the permeability of these soils is moderate to moderately slow (0.20–2.00 in./h) within the surficial alluvial material but slow to very slow (<0.06 in./h) in the underlying clayey parent material.

The Hamblen series soils (Fluvaquentic Eutrudepts) in LEFPC were found at depths ranging from 5 to 12 in. BGS as a surface horizon classified as a loam to silt loam texture. These soils transition to a subsurface horizon with silt loam to silty clay loam texture to depths ranging from 28 to 58 in. BGS. This horizon is underlain by parent material consisting of silty clay loam to clay texture to depths of approximately 38 to greater than 96 in. BGS. Redoximorphic features indicative of seasonally saturated conditions were observed at depths ranging from 20 to 28 in. BGS, and free water levels observed in this soil unit ranged from depths of 38 to 96 in. BGS. Based on observed soil textures, measured bulk density, and USDA saturated hydraulic conductivity classes, the permeability of these soils is moderate to moderately slow (0.20–2.00 in./h) in the surficial alluvial material to very slow (<0.06 in./h) in the underlying clayey parent material.

Bulk density measurements were conducted in each soil map unit at select locations within LEFPC (Dickson et al. 2015). Overall, the measured bulk density ranged from 0.75 to 1.49 g/cm^3 in the Chenneby soil series and from 0.91 to 1.39 g/cm^3 in the Hamblen soil series, indicating some hydraulically restrictive layers within the underlying parent materials of both soil series.

2.1.2.2 Longitudinal sampling

Sampling of the stream banks (Fig. 3) is designed to elucidate the concentration of mercury and methylmercury throughout LEFPC. Sample analysis results will be coupled with information on erosion potential to develop prioritized locations for other sampling activities (e.g., additional erosion pins) and potential remedial testing locations.

Two longitudinal sampling activities were performed on the LEPFC bank soils: a "warm season" sampling in September 2014 and a "cool season" sampling in March 2015. The sampling strategy was based on a cyclical sampling method to enable robust geostatistical analysis of the results; e.g., Webster and Oliver (1992) and Burrows et al. (2002). Samples were taken from approximately the same locations at each site in 2014 and 2015. The sampling activity involved taking core samples and bulk soil samples in close proximity to one another from 150 locations from EFK 23 to EFK 4.8. Horizontal core samples (2.5 cm diameter and of variable length) were taken at 15%, 50%, and 85% of the distance between the water level and the stream bank height in September 2014; bulk samples were taken only at 50% bank height. Samples in March 2015 were collected from the same locations using measurements of distance from the bank height. Bulk samples were subjected to American Society of Testing Method (ASTM) F1632 to determine the moisture contents for two structural properties measured by the Atterberg limits— the plastic limit and the liquid limit. The plastic limit is the moisture content above which the soil will be transformed into a malleable plastic mass, and the liquid limit is the moisture content above which the soil will become a liquid and can flow when disturbed. Bulk samples also were characterized for moisture content, pH, carbon, organic carbon, nitrogen, and sulfur.
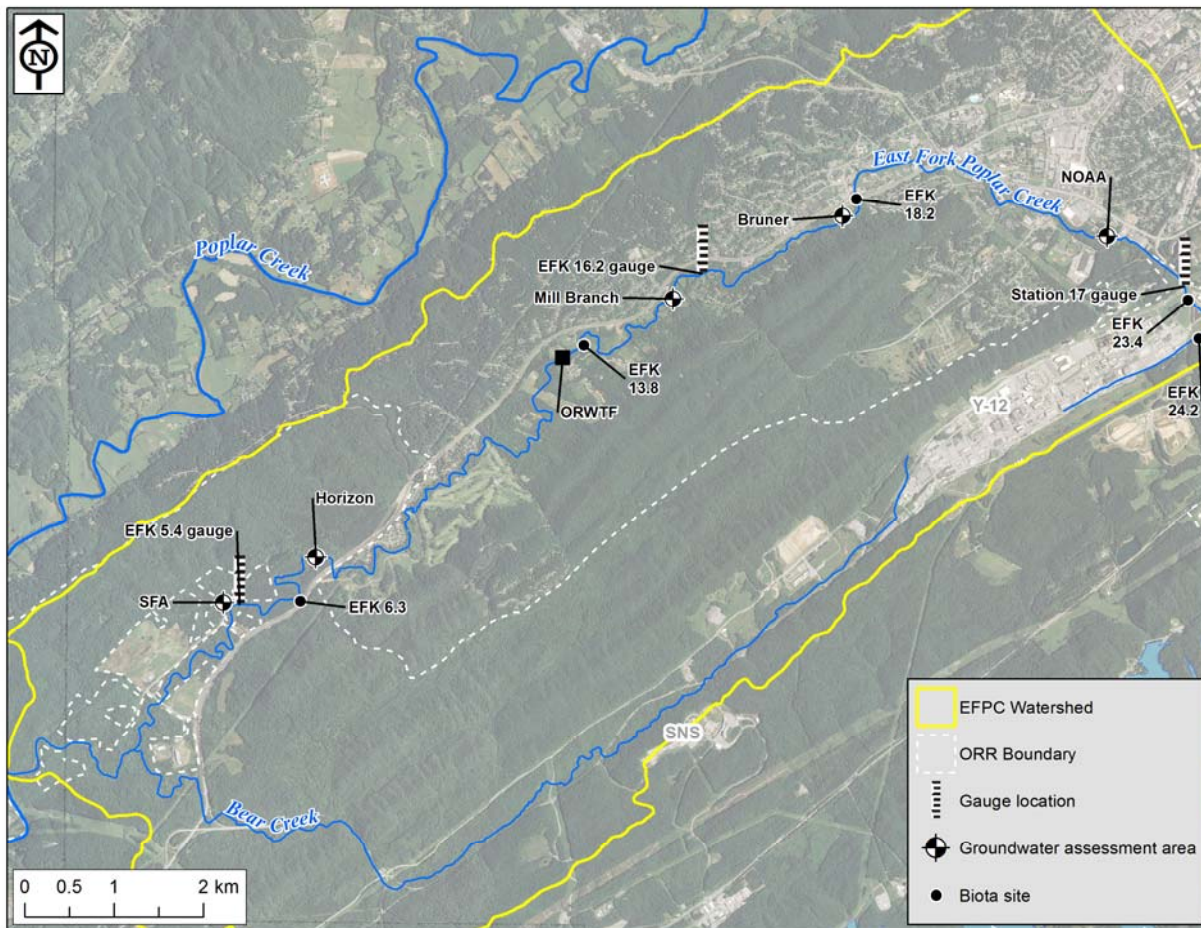
Fig. 3. Sampling locations along East Fork Poplar Creek (EFPC).(*Notes:* EFK = East Fork Poplar Creek kilometer; NOAA = National Oceanic and Atmospheric Administration; ORWTF = Oak Ridge Wastewater Treatment Facility; ORR = Oak Ridge Reservation; SFA = science focus area; SNS = Spallation Neutron Source; Y-12 = Y-12 National Security Complex.)

In FY 2015, all of the upper 2.5 cm of the 50% bank height core samples and 20 locations of the 15% and 85% bank height core samples from the 2014 sampling activity were analyzed for total mercury and methylmercury by US Environmental Protection Agency (EPA) methods 1631 and 1630, respectively. All of the upper 2.5 cm of the 50% bank height core samples from the 2015 activity were analyzed at ORNL using the Direct Mercury Analyzer, except where concentrations were too high. Select core samples from 50% bank height from the 2015 activity were analyzed for methylmercury. Figure 4 shows the 2014 and 2015 results of total mercury and methylmercury as a function of distance from the mouth of EFPC. There is general agreement between the two sampling events, with nearly all mercury concentrations being less than 100 ppm of dry weight (dw) of soil and a few concentrations from the 2014 sampling event approaching 400 ppm dw (Fig. 4, top). Nearly all methylmercury concentrations were less than 50 ng/g dw of soil (Fig. 4, bottom).
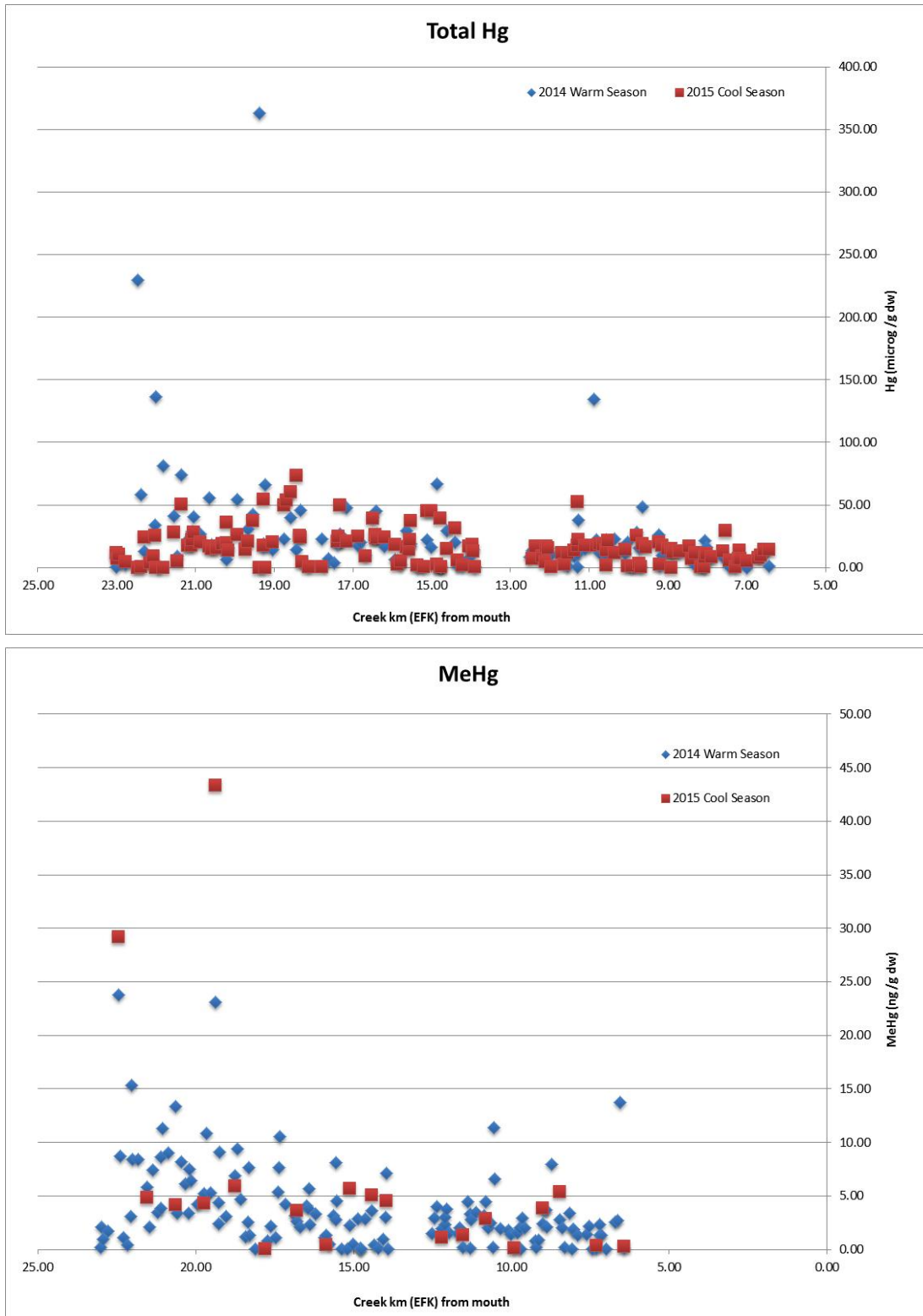
Fig. 4. 2014 and 2015 results of total mercury (Hg; top) and methylmercury (MeHg; bottom) as a function of distance from the mouth of East Fork Poplar Creek.
(*Notes:* EFK = East Fork Poplar Creek kilometer; dw = dry weight.)

9

The mercury and methylmercury concentrations were coupled with information on erosion potential from the LEFPC Mercury Source Identification Project. Coupling the information tends to highlight a few areas along EFPC with high mercury or methylmercury concentrations as well as high erosion potential (Fig. 5). These sites could be targeted as higher priority for future tests on remedial approaches.

Overall, bank samples are fairly uniform and are classified as a loam to silty loam, but a significant number of samples are classified as sandy loam or silty clay loam. These results are generally consistent with the soil mapping results (Dickson et al. 2015). The average of all samples yields 1.4% gravel (4.4% standard deviation [sd]), 36% sand (15% sd, maximum [max] 75%, minimum [min] 7%), 45% silt (11% sd, max 65%, min 19%), and 18% clay (8% sd, max 48%, min 5%). The sample moisture content averaged 22% (sd 3.5%, max 34%, min 15%). Nearly all samples exhibited medium plasticity, characteristic of a lean clay to silt. The samples exhibited plasticity at < 30% moisture and the liquid limit at < 50% moisture. Carbon ranged from 0.1 to 5.0% and averaged 1.7% (sd 0.9), total organic carbon ranged from 0.1 to 4.1% and averaged 1.4% (sd 0.9), nitrogen ranged from 0.03 to 0.4% and averaged 0.1% (sd 0.05), sulfur ranged from 0.06 to 20 mg/kg and averaged 3.4 mg/kg (sd 2.7), and pH ranged from 4.6 to 8.1 and averaged 7.5 (sd 0.5).
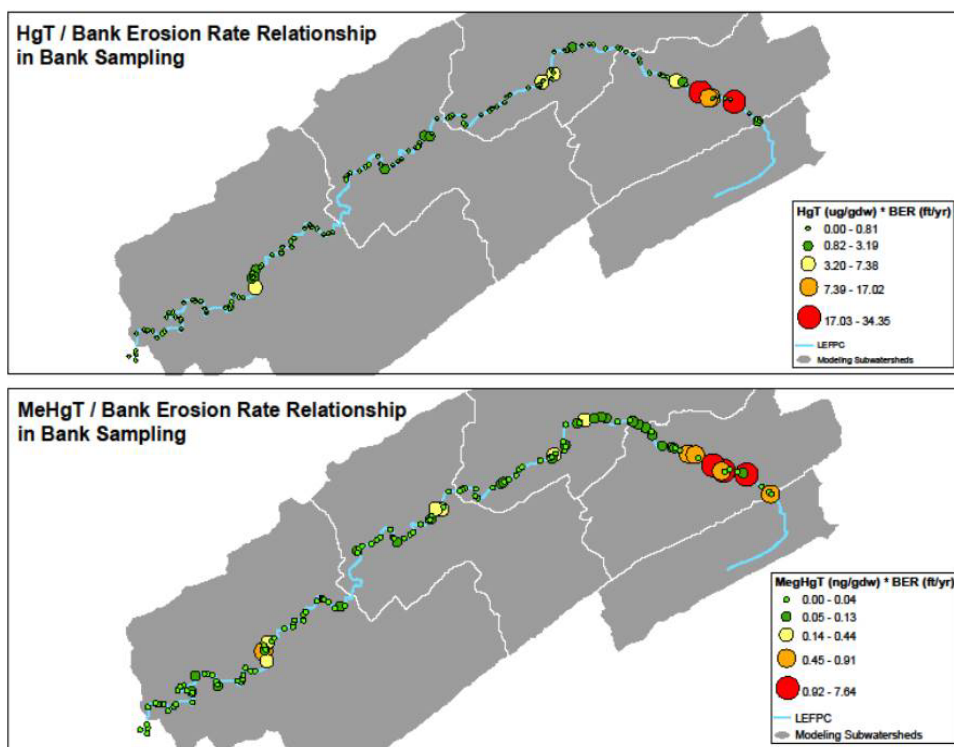
Fig. 5. Areas along lower East Fork Poplar Creek (LEFPC) with high total mercury (HgT; top) or methylmercury (MeHgT; bottom) concentrations as well as high erosion potential.(*Note:* BER = bank erosion rate.) Erosion rate data courtesy of the Lower East Fork Poplar Creek Source ID Project.

2.1.2.3 Fine-scale sampling

There are occasional higher mercury concentrations in bank soils, particularly within a 2 to 18-in. thick, dark layer or layers observed at select locations (Fig. 6). The layer(s) have mercury concentrations that can approach 2,000 ppm (Kaplan 2005). This layered deposit is a likely legacy source of mercury and is composed of soil, coal fines, fly ash, and discrete mercury-rich particles transported from Y-12 into

LEFPC. The dark coloring is believed to be related to the proportion of fly ash particles (Figs. 6 and 7) (Brooks 2015; Carmichael 1989; Southworth et al. 2010). To differentiate this layer from other soil layers, herein the layer is referred to as the historical release deposit (HRD).

The highest measured mercury concentrations in the LEFPC floodplain soils have been recorded at the National Oceanic and Atmospheric Administrative (NOAA) site (behind the NOAA building at 456 South Illinois Avenue, EFK 22.3) and the former Bruner's Market site (~750 ft west of Louisiana Avenue to ~1,000 ft west of Jefferson Avenue, EFK 17.8) (Phillips 2004). Although over 34,220 m^3 of mercury-contaminated soils were remediated at the NOAA and Bruner sites to yield less than 400 ppm in a 16-in. core sample, legacy-age mercury in the HRD is still found in some floodplain soils of the upper 5-km reach. Southworth et al. (2010) found high variability in mercury concentrations within the HRD layer in streambank soils collected from EFK 23.4 (Fig. 8). Further, they noted that the HRD is found at different depths within the streambank, even in transects taken from the same site. Follow-on studies examining the mercury profiles with depth in streambanks at EFK 18.2 have found evidence of streambank erosion, and elevated mercury concentrations were found in bank soils just below the HRD (Fig. 9). Erosion of banks including high mercury content soils could be a major source of mercury flux to EFPC, warranting an in-depth characterization of the HRD.

Fig. 6. Historical release deposit (HRD) exposed at bank location BL-35 along lower East Fork Poplar Creek.
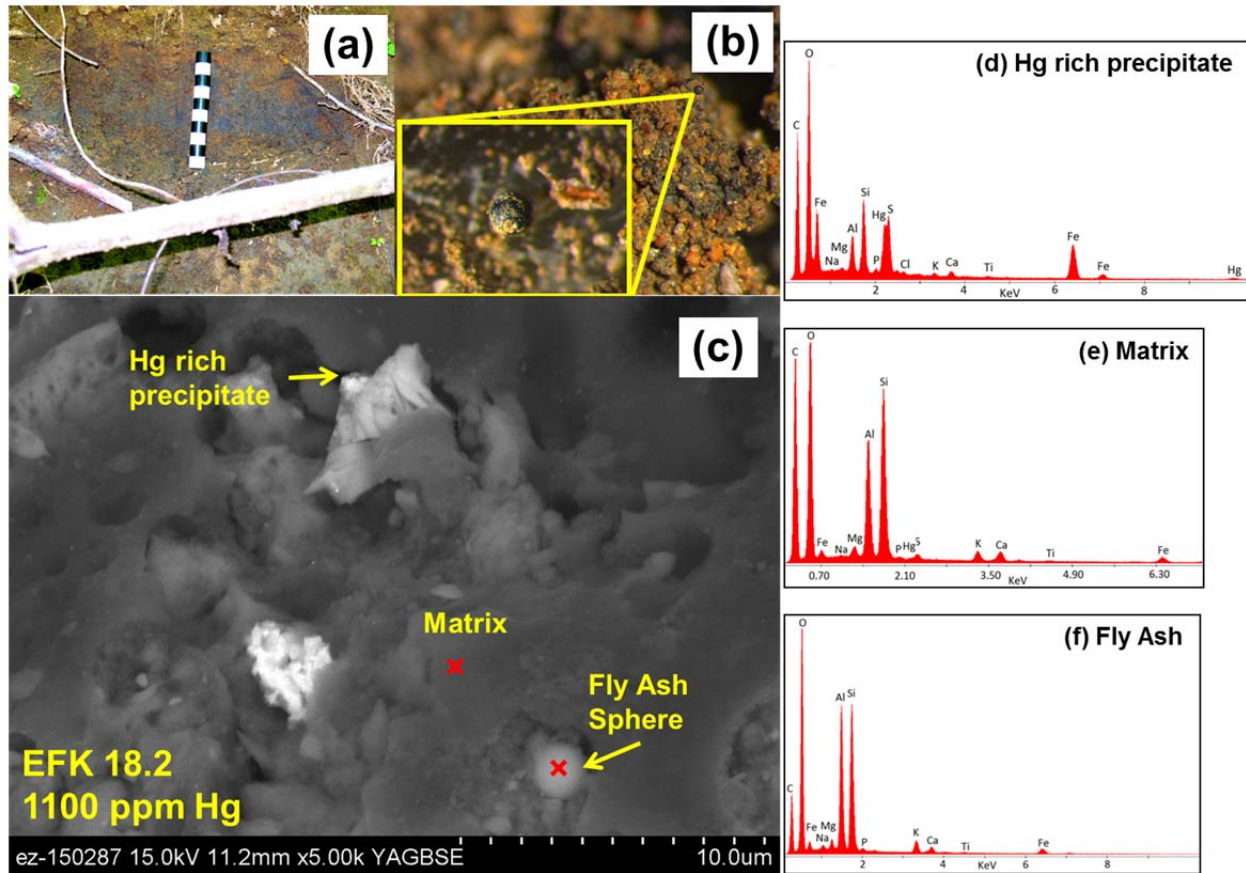
Fig. 7. (a) Photograph taken on April 23, 2014, of the historical release deposit (HRD) found at EFK 18.2. The scale in the figure is 10 cm. This figure is a contrast-enhanced version of the original digital photograph (Picasa v. 3.9.132) providing improved visibility of the HRD. (b) Photomicrograph of the HRD material under low magnification using a dissecting microscope; inset in (b) shows a spherical particle found throughout the HRD sample. (c) Electron micrograph of the HRD material showing angular mercury-rich precipitate fragments and spherical fly ash particles. Scale at bottom right of the figure is 10 μm. (d–f) Energy dispersive x-ray spectroscopy analyses of the spots marked in panel (c) (electron microscopy and energy dispersive x-ray work conducted by Dr. Debra Phillips, Queen's University Belfast). Data and figures courtesy of the Lower East Fork Poplar Creek Source ID Project.
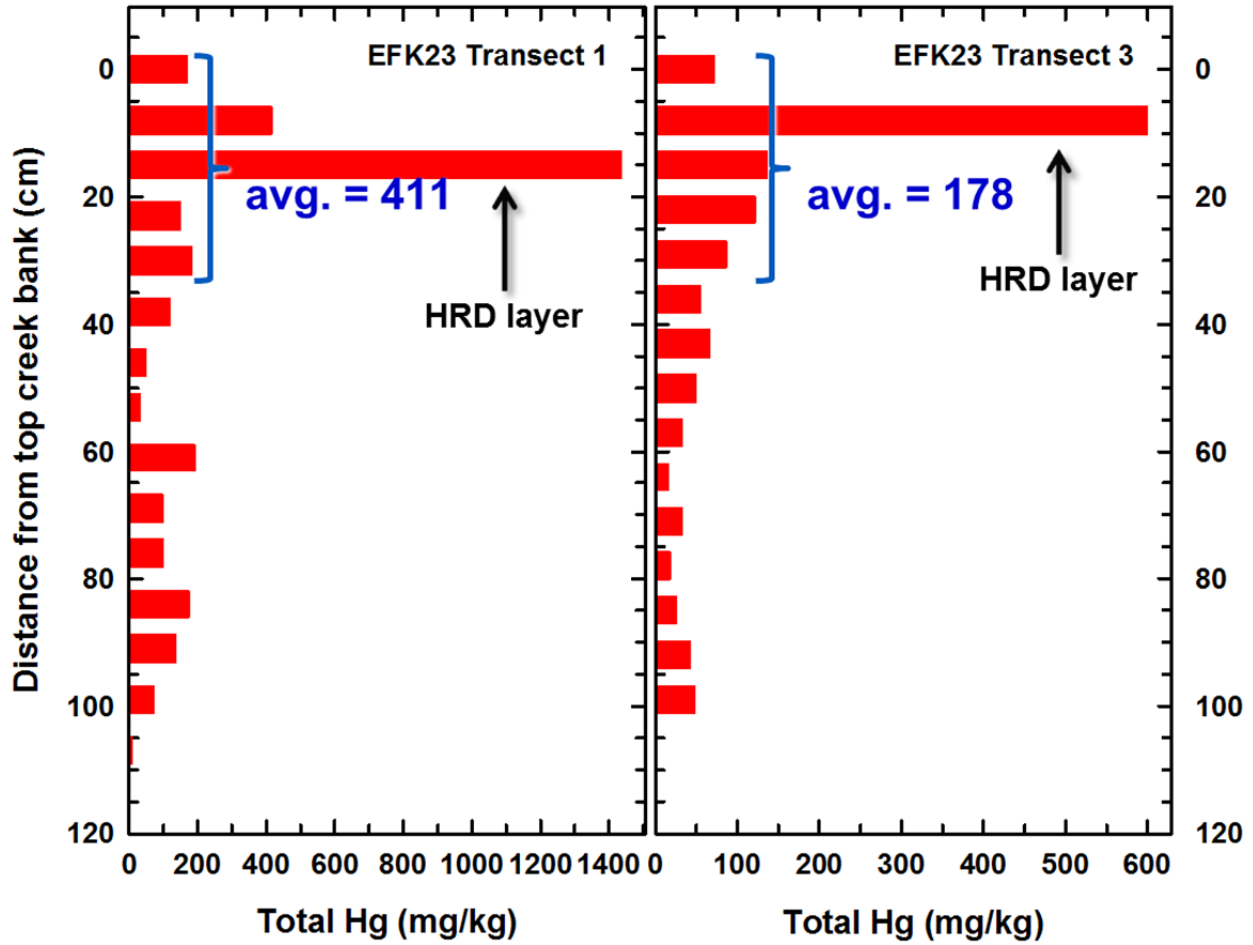
Fig. 8. Mercury concentrations with depth in bank soils sampled from two different transects at East Fork Poplar Creek kilometer (EFK) 23. Note the difference in scales on the x axes. Data and figures courtesy of the Lower East Fork Poplar Creek Source ID Project. Reproduced from: Southworth, G. R., M. S. Greeley, M. J. Peterson, K. Lowe, and R. H. Ketelle. 2010. *Sources of Mercury to East Fork Poplar Creek Downstream from the Y-12 National Security Complex: Inventories and Export Rates*. ORNL/TM-2009/231, Oak Ridge National Laboratory, Oak Ridge, TN.
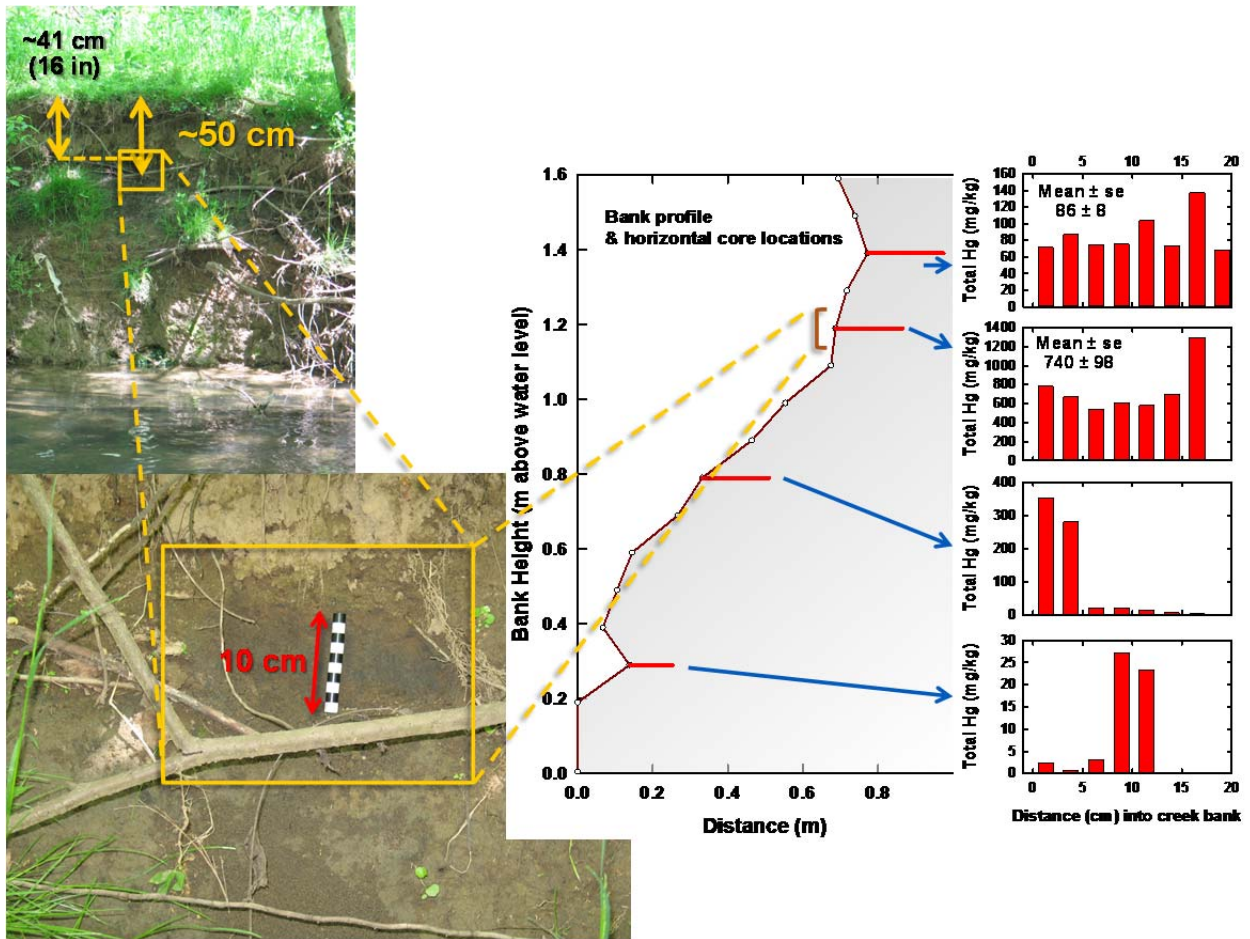
Fig. 9. Depth profile of mercury concentrations within bank soils at East Fork Poplar Creek kilometer (EFK) 18.2. Data and figures courtesy of the Lower East Fork Poplar Creek Source ID Project.

Since the HRD has not been characterized previously in terms of either spatial extent or physicochemical properties, a comprehensive characterization sampling activity within the upper 5 km of the LEFPC reach was conducted. Building upon previous investigations performed by Brooks (2015) and Southworth et al. (2010), as well as the recent LEFPC bank soil survey (Dickson et al. 2015), this current work encompassed a detailed evaluation of the linear extent, thickness, and physiochemical properties of the observed HRD along LEFPC banks (left and right banks). This new information will assist in prioritizing the highest mercury-contaminated locations within the LEFPC bank and floodplain for targeted remedial efforts.

The investigation, performed in July, involved walking an approximately 2-km LEFPC reach (Fig. 10), clearing vegetation and other debris from bank surfaces, and characterizing the exposed layer at every 20 m transect where feasible. At 67 LEFPC locations, the morphology of the encountered HRD was described in detail, and samples were collected for further chemical and microscopy characterization. The observed layer was classified according to the USDA textural classification method, and samples were collected for bulk density and moisture content. To advance scientific knowledge about these legacy mercury deposits, the sampled layers will be analyzed for total mercury, methylmercury, total carbon content, nitrogen, sulfur, iron, manganese, mineralogy, and particle size distribution in FY 2016. In addition, in collaboration with the Remediation of Mercury and Industrial Contaminants Applied Field Research Initiative Project, x-ray diffraction, total elemental analysis, scanning transmission electron microscopy, and electron energy loss spectroscopy characterization will be performed on multiple sample thin sections to elucidate elemental composition, chemical bonding, and oxidation states of mercury and other elements associated with the layers (e.g., Fig. 7) in FY 2016.

Generally, the layers are observable as dark-colored layers characterized by a relatively coarser-textured material within an exposed LEFPC bank soil profile. The evaluated HRD generally comprise very dark grayish-brown to black loamy sand to silt loam alluvial deposits with occasional inclusions of brown to dark yellowish-brown loamy to silt loam lenses. Depths to the HRD ranged from 4 to 48 in. BGS within LEFPC bank soils, and thicknesses varied from 2 to 18 in. The linear extent of the exposed layers along LEFPC banks is approximately 1,500 m, but it is not necessarily continuous. Bulk density measurements conducted on select HRD ranged from 0.46 to 0.93 g/cm^3, indicating moderate to high infiltration rates are possible within these layers. It should be noted that in most locations, the HRD is underlain by impervious silty clay to clayey deposits that could impede downward infiltration of water because their bulk densities range from 0.75 to 1.49 g/cm^3 (Dickson et al. 2015).

Fig. 10. Map of exposure of the historical release deposit (HRD) at locations along lower East Fork Poplar Creek.

2.1.2.4 Desorption potential

The desorption potential of bank soils was measured in samples from EFKs 21.4, 19.2, 14.9, and 9.6 at a ratio of 1 g soil to 30 mL solution for 6 h. Preliminary experiments determined the optimal solid to solution ratio and the length of reaction time. It was observed that desorption amounts tended to be quite variable from 0 to 12 h and decreased thereafter, likely indicating some type of longer-term readsorption. Three solutions were used—an artificial creek water solution, water from Hinds Creek (which is representative of non-contaminated stream water), and artificial creek water with 1 mg/L Sewanee River natural organic matter (NOM) (Fig. 11). Desorption extents ranged from 0.004% to 0.02% of the original mercury in the sample. The addition of NOM tended to increase desorption, and there was variability in the amount of desorption between the four sites, but the mechanism(s) remain without explanation. These experiments can be considered preliminary, will be continued in FY 2016, and will expand to include samples from the HRD.
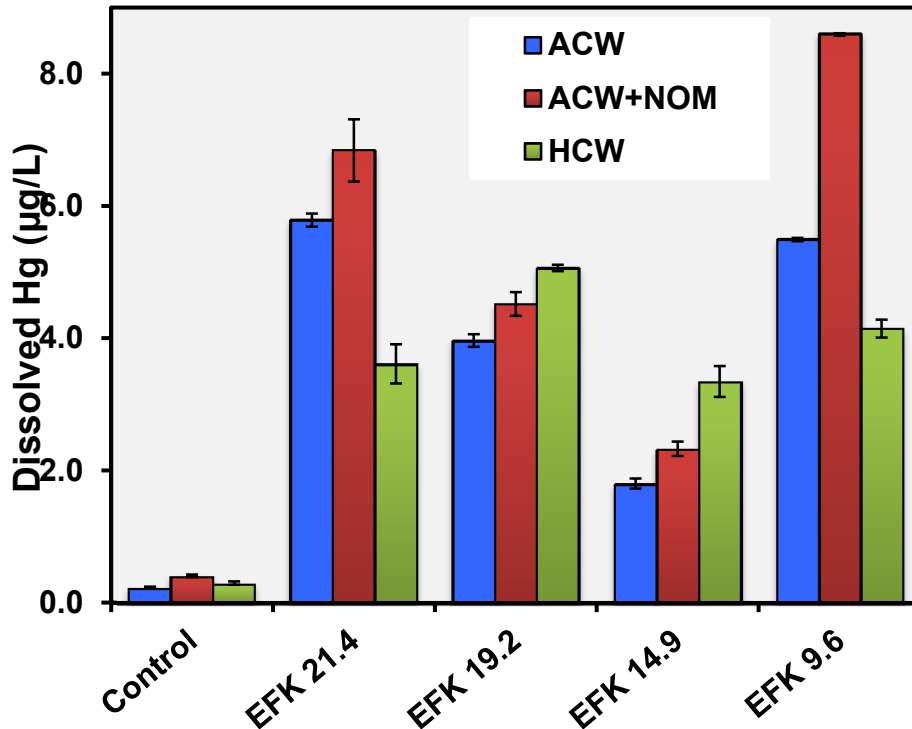
Fig. 11. Desorption extents in an artificial creek water (ACW) solution, Hinds Creek water (HCW; representative of non-contaminated stream water), and ACW with 1 mg/L Sewanee River natural organic matter (NOM).

2.2 GROUNDWATER

2.2.1 Approach to Groundwater Investigations

Groundwater is of concern because of the potential for leaching of mercury after infiltration through floodplain soils and subsequent discharge of groundwater into LEFPC. Recent modeling efforts in the Lower East Fork Poplar Creek Source ID Project have demonstrated that the groundwater contribution to LEFPC can account for only a small proportion of total mercury or methylmercury in the creek. However, there is very little data to constrain or test the model predictions. In addition, these studies neglect the potential mechanism of methylmercury production in groundwater and release into LEFPC, which can occur under reducing groundwater conditions. Reducing conditions in groundwater have been observed in the Mercury Science Focus Area Project funded through the Office of Science Biological and Environmental Research Program. Because of this issue, groundwater has been identified as an area of concern in recommendations for understanding mercury cycling in LEFPC (Looney et al. 2008; US Department of Energy 2014a). In general, the extent of groundwater–surface water exchange is largely unknown in LEFPC. In nearby Bear Creek Valley, there are springs and sections where the stream both gains and loses water with respect to groundwater, and it would be unusual if similar processes were not also occurring in LEFPC. Because of the potential importance of groundwater in transmitting mercury and potentially also generating methylmercury, a monitoring plan has been developed that is designed to elucidate interactions between groundwater and surface water.

2.2.2　Groundwater Investigations

There are currently only two locations at which groundwater and surface water are monitored—the Horizon Center and Mill Branch near Wiltshire Road. This investigation is co-funded through the Lower East Fork Poplar Creek Source ID Project and the Mercury Science Focus Area Project in the Office of Science Biological and Environmental Research Program. Horizon Center groundwater wells do not appear to exhibit significant exchange with surface water, whereas Mill Branch does. Furthermore, Mill Branch exhibits seasonal variation in terms of groundwater–surface water exchange—when base flow is higher in winter and spring, groundwater appears to be a source of water to LEFPC, but when base flow is lower in summer and fall, surface water appears to recharge groundwater. Most importantly, Mill Branch shows periods of higher methylmercury concentrations associated with low redox (i.e., reducing) conditions. The extent to which groundwater contributes to the flux of methylmercury into LEFPC, however, is unknown because of the configuration of the wells, the lack of a proximal stream water gauge, and the absence of continuous data for water level and other indicators to distinguish groundwater and surface water chemistry.

Thus, the monitoring plan is designed to elucidate interactions between ground- and surface water at three locations. The NOAA site at EFK 22.2, the former Bruner Market site at EFK 18.2, and another location near the Horizon Center at EFK 8.7 were targeted because it is possible to install small (~1.5 in. diameter), unobtrusive wells to a depth of refusal in the 100-year floodplain (which is permitted under state laws), and because these locations have landowner access agreements to facilitate access to the sites. The wells were installed in October 2015. A Geoprobe 540MT unit was used because of its small size, light weight, and portability, thereby avoiding destructive incursions with trucks and machinery into the areas. This method was preferable to other methods because it allowed for installation of the wells in only a few days, minimized the manual effort by ORNL staff, resulted in little to no risk of borehole collapse, and allowed for collection of continuous core. ORNL staff collected and characterized the lithology of the cores, and the cores are currently under storage at -80°C at ORNL. A complete investigation of the cores is likely to occur in FY 2016.

Three groundwater wells were installed at each site. Two groundwater wells were installed in relatively upstream and downstream positions near the creek bank, and one well was installed somewhat inland. The hole was bored using the Geoprobe 540MT using 4 ft intervals. Each core section was removed and characterized. When the boring reached refusal, the last core was removed, and the well was installed (Fig. 12). The installations consisted of a 1.5 in. schedule 40 PVC material, with the bottom section composed of a 5 ft prepacked sand screen, 0.01 in. slot size, and riser sections continuing above ground surface to 2 in. above the 100-year floodplain as required by the state of Tennessee (Fig. 13). Wells were sealed with bentonite above the screened interval. Wells at EFK 22.2 ranged from 5 ft, 5 in. deep; wells at EFK 18.2 ranged from 7 ft, 2 in. to 10 ft, 4.5 in. deep; and wells at EFK 8.7 ranged from 10 ft, 5 in. to 10 ft, 10. in. deep. One stilling well will be installed in FY2016 with explicit connection to the stream water.

We have purchased sensors to outfit both ground- and surface water wells. The sensors will gather continuous data on pressure head (water table elevation), temperature, and conductivity. This configuration will facilitate construction of the potentiometric surface, and the temperature and conductivity readings can be used to elucidate the signature of the groundwater versus the surface water. Continuous readings will enable understanding of how the indicators change monthly, daily, and seasonally as well as in response to storm events. Manual monitoring (FY 2016) will be used to collect data on mercury and methylmercury concentrations, nutrient concentrations, dissolved oxygen, pH, ferric and ferrous iron, and other indicators of geochemical and redox conditions. At the time of writing of this report (September 2015), installation of the groundwater wells was complete.

In FY 2016, the wells will be developed, the surface water wells will be installed, and the sensors will be placed in the wells. Then monitoring will begin.

Fig. 12. Groundwater well installation at East Fork Poplar Creek kilometer 8.7 on October 23, 2015.

	Materials Inventory
	BENTONITE SEAL: TOP: 0.00 BOTTOM: 64.5"
	FILTER PACK GRAINSIZE: 20/40
	FILTER PACK: TOP:64.5" BOTTOM:128"
	GROUT QUANTITY: 3/8" Bentonite Pellets
	GROUT: TOP: 0.00 BOTTOM:64.5"
	SCREEN TYPE: Prepacked PVC
	WELL SCREEN: In. 1.5 l.f. 5 ft
	SLOT SIZE: 0.010 in.
	WELL CASING: Inches in diameter 1.5 l.f. 10 ft
	CASING TYPE: PVC
	TOP OF CASING (AGS): 5 ft 5 in.
	BOREHOLE (in. diameter): 3.5 in.
	BOTTOM OF BOREHOLE (ft BGS): 10ft 8 in.
	TOP OF CASING ELEVATION (ft above MSL):
	TN License 991 WM Jay W Hocutt

**Fig. 13. Schematic and dimensions of groundwater well installed
near the former Bruner Market location
at East Fork Poplar Creek kilometer 18.2.**

20

2.3 SORBENT EVALUATION

2.3.1 Approach to Sorbent Evaluation

The characterization of LEFPC creek bank soils continues to provide valuable insights into the spatial distribution of the mercury and methylmercury in bank soils, the physical and chemical characteristics of soils, and processes influencing contaminant concentrations and fluxes in creek sediments and groundwater. Accurate information about the distribution, concentrations, and stability of mercury contamination in LEFPC enables the targeted development of sorbent technologies, which can effectively limit mercury fluxes to the downstream environment. The choice of any particular sorbent technology will in part depend on contaminant distribution, concentrations, and the partitioning between sorbent, soils, sediments, and pore water. Furthermore, the long-term stability of the contaminant immobilized on the sorbent and the potential leaching of solutes are important factors that should be considered.

Sorbent evaluation activities over the past year included a literature review, assessment of site-relevant conditions, studies to investigate the complexation of mercury with NOM, and lab-scale testing of potentially applicable sorbents using a standardized mercury–NOM complex. The effectiveness of sorbent technologies for the removal of mercury from a freshwater creek ecosystem such as LEFPC is governed by the partitioning of the contaminant between the water column, creek sediments, and a potential sorbent material. NOM forms strong complexes with mercury in freshwater systems with low sulfide concentrations, which changes its reactivity, redox chemistry, and bioavailability. Thus, sorption studies in the presence of competitive ligands are essential for demonstrating the effectiveness of a sorbent in limiting migration of mercury and methylmercury associated with natural organic matter and particulates. The kinetics of the association of mercury with NOM and particles have been described for upper EFPC (UEFPC) between the point source and 2.5 km downstream (Miller et al. 2009; Dong et al. 2010). The results suggest that mercury in LEFPC forms strong complexes with NOM and particles, which may have a significant impact on mercury's reactivity and interaction with sorbent materials. The association of Hg(II) with NOM has been shown to lower the reduction potential of Hg(II), resulting in the formation of mercury–NOM complexes that are not reducible by stannous chloride ($SnCl_2$). Therefore, $SnCl_2$ reduction can be used as an operationally defined measure of mercury reactivity. To assess changes in the reactivity of mercury after complexation with NOM, the fraction of $SnCl_2$-reducible mercury (Hg_R) was determined as a function of the mercury:NOM ratio and time using Suwanee River NOM. Based on the results of these experiments, a standardized mercury–NOM complex was prepared and was used for all subsequent laboratory sorption experiments.

The initial set of sorbent materials was selected (Table 1) based on a review of mercury sorption technologies described in the open literature. The most promising technologies to date are based on activated carbons and biochars (Asasian and Kaghazchi 2012; Beesley, Moreno-Jimenez, and Gomez-Eyles 2010; Ghosh et al. 2011; Gomez-Eyles et al. 2013). Activated carbons and biochars can be produced from renewable, low-cost biomass feedstocks; show low inherent toxicity (Janssen and Beckingham 2013; Jonker et al. 2009); and effectively reduce the diffusive flux of contaminants into the water column. It has been shown that reducing pore water concentrations of mercury and methylmercury results in lower bioavailability to organisms (Gilmour et al. 2013). Systems with low native sediment:water partition coefficients for mercury and methylmercury should be most effectively treated. In addition, NOM and sulfidic species may compete with sorbents with respect to binding of mercury and methylmercury, which can have a significant impact on the effectiveness of a sorbent treatment. The primary aim was to evaluate sorbents amenable for incorporation into sediments or physical barriers such as bank stabilization structures with minimal impact on the ecosystem, resulting in a sustained reduction in the concentration of methylmercury available for bioaccumulation in LEFPC.

Table 1. Overview of sorbent materials evaluated in this study

Sorbent	Description	Source	Maturity	Cost
Thiol-SAMMS®	Thiol-functionalized self-assembled monolayer on mesoporous silica support	Steward Environmental Solutions, LLC	Medium	High
Organoclay™ PM-199	Functionalized bentonite-based clay	CETCO	Medium	High
Organoclay™ MRM	Functionalized bentonite-based clay (sulfur-impregnated)	CETCO	Medium	High
SediMite™	Activated charcoal, bentonite, and sand as a weighing agent	Sediment Solutions	Medium	Medium
Biochar	Natural charcoal from Colorado pine converted by slow pyrolysis	Biochar Now	Low	Low
Lignin carbon fiber	Carbonized lignin fibers processed under various conditions	ORNL Materials Science and Technology Division	Low	Low
Lignin carbon foam	Carbonized lignin foam processed under various conditions	ORNL Materials Science and Technology Division	Low	Low
Brass wire gauze	Cu/Zn alloy, immobilizes Hg(II) by reductive amalgamation	Alfa Aesar	Low	Medium

In addition to commercially available sorbents, researchers evaluated lignin-based highly porous carbon fiber and carbon foam samples prepared by collaborators in ORNL's Materials Science and Technology Division and the Center for Renewable Carbon at the University of Tennessee, Knoxville. These materials from a low-cost lignin feedstock can be tailored toward obtaining the most desirable properties for removal of mercury in aqueous solutions. For example, the levels of sulfur in the material can be adjusted by blending various lignin feedstocks or by the use of additives. Furthermore, the carbon surface area and pore space can be controlled by physical or chemical activation during carbonization.

A standardized mercury–NOM complex at a molar Hg:C_{NOM} ratio of $2 \cdot 10^{-6}$ and at a fixed mercury concentration of 2 ppm was used to evaluate the sorbent materials in a series of batch experiments. ASTM D 4646-03, "Standard Test Method for 24-h Batch-Type Measurement of Contaminant Sorption by Soils and Sediments," was adapted to obtain sorbent:water partition coefficients (K_d) for mercury and dissolved organic carbon (DOC). The parameter K_d describes the potential for the adsorption of a mobile contaminant by a sorbent material. K_d is defined as the ratio of the contaminant concentration associated with the solid to the contaminant concentration in the surrounding aqueous solution when the system is at equilibrium. The value of K_d for a particular solid can vary substantially based on the chemical speciation of the contaminant. Therefore, K_d values should be measured as close to the site-specific conditions as possible.

Batch experiments were conducted in certified 40 mL amber glass vials with Teflon® PTFE septa using a solution volume of 30 mL. The concentrations of Hg(II) and DOC were determined after equilibration of mercury–NOM complex with the sorbents after 1, 2, 4, 12, and 24 h. An additional data point was added at 48 h to verify complete equilibration. Sorption isotherms were obtained to assess the concentration-dependence and sorption capacity for mercury and DOC. The initial concentration of Hg(II) complexed with NOM was varied from 0.3 ppb to 4.0 ppb. All samples were allowed to equilibrate for 24 h, and the final concentrations of Hg(II) and DOC in solution were measured. Ion chromatography was used to determine the equilibrium concentrations of chloride, nitrate, and sulfate released from sorbents. To evaluate the potential relationship between sorption characteristics and surface area, sorbent samples were shipped to outside contractor Quantachrome for three-point Brunauer-Emmet-Teller (BET) surface area measurements.

2.3.2   Results of Sorbent Evaluation

2.3.2.1   Mercury–NOM complexes

The kinetics of mercury–NOM complex formation as a function of $Hg:C_{NOM}$ ratio and time was investigated over several NOM concentrations in controlled laboratory experiments. Over a period of 114 h, the fraction of Hg_R decreased significantly for all tested $Hg:C_{NOM}$ ratios (Fig. 14). At low $Hg:C_{NOM}$ ratios, the formation of strong mercury–NOM complexes occurs more rapidly, resulting in a Hg_R of as low as 5.9% at a $Hg:C_{NOM}$ ratio of 0.6. The results suggest that the reactivity of mercury in freshwater systems such as LEFPC is strongly influenced by its complexation with NOM. The complexation of mercury with NOM is kinetically slow, likely involving transitions and rearrangements between various functional groups until a thermodynamically stable mercury–NOM complex is formed. Strong complexation of mercury with NOM can keep mercury in the aqueous phase (Aiken, Hsu-Kim, and Ryan 2011) and increases its bioavailability for microbial methylation (Graham et al. 2012; Zhang et al. 2012).
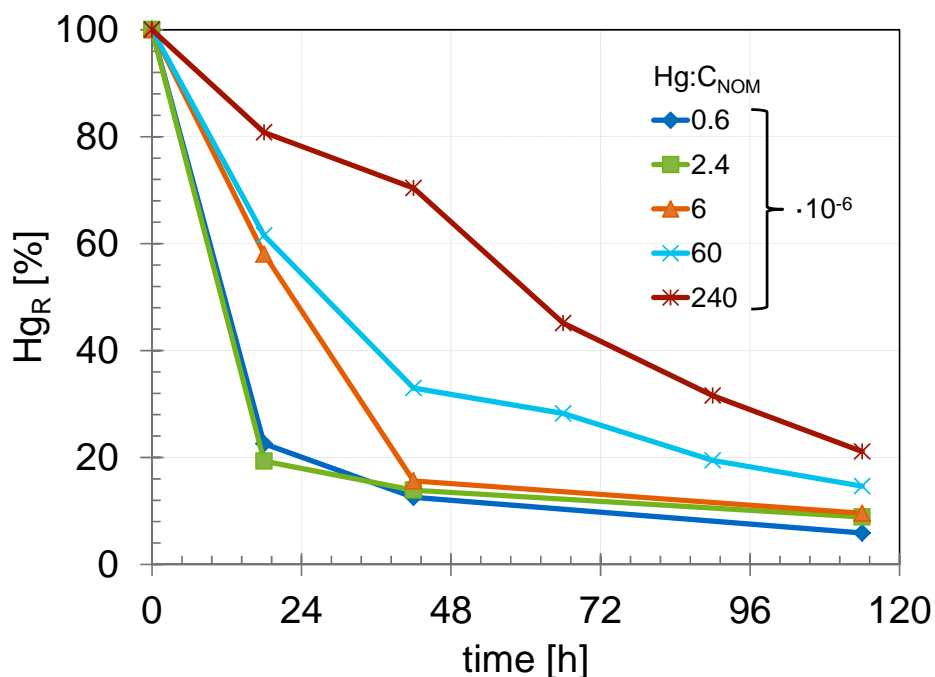
Fig. 14. Changes in the fraction of mercury present as stannous chloride–reducible mercury as a function of time at $Hg:C_{NOM}$ ratios from $6.0 \cdot 10^{-7}$ to $2.4 \cdot 10^{-4}$. The concentration of mercury was held constant at 2 ppm. Experiments were performed using an analytical $Hg(NO_3)_2$ standard solution and unfractionated Suwanee River natural organic matter (NOM), which contains approximately 50% carbon by weight.

2.3.2.2   Partition coefficients for mercury and NOM

Thiol-SAMMS®, SediMite™ (activated carbon), and biochar showed highest K_d values in batch experiments with the standardized mercury–NOM complex (Fig. 15). K_d values for the sorption of NOM (Fig. 16) are consistently lower compared with K_d values for mercury, resulting in low sorption of NOM, which suggests a ligand exchange mechanism underlying the sorption process. SediMite™ is the only sorbent that also binds significant amounts of NOM.
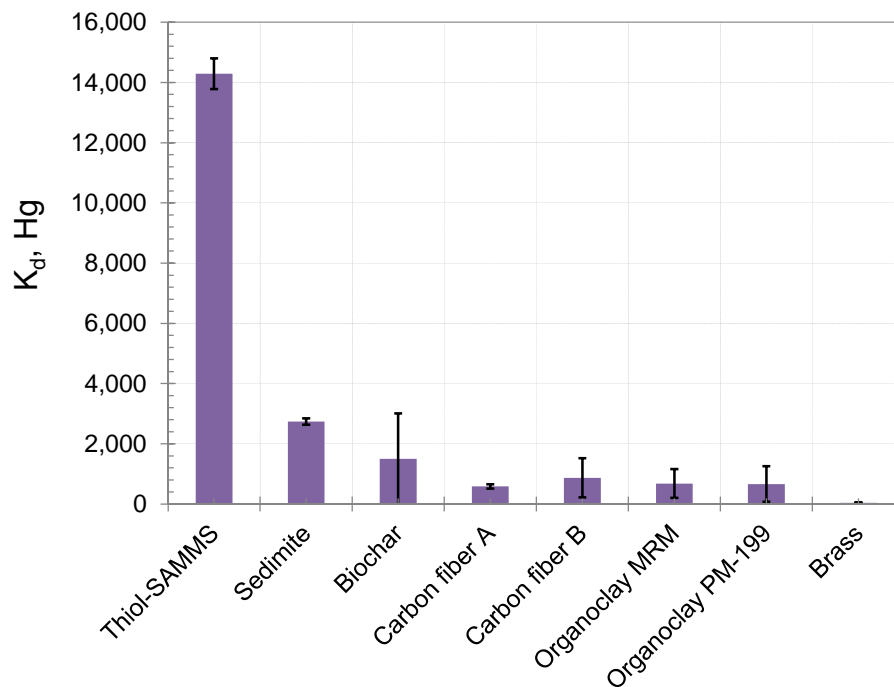
Fig. 15. Mercury K_d values for eight sorbent materials from batch experiments after 48 h of equilibration.
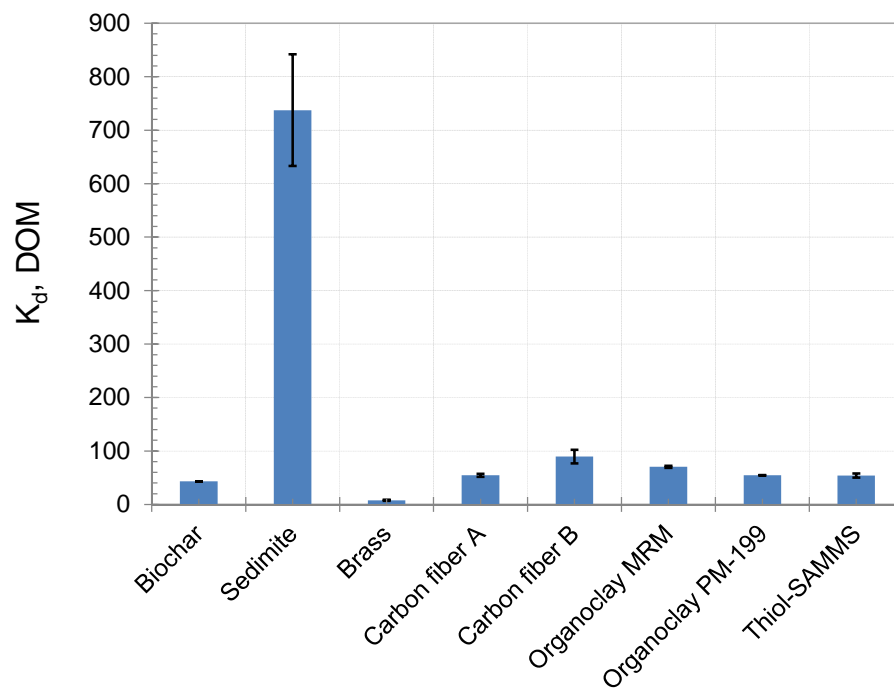
Fig. 16. Natural organic matter K_d values for eight sorbent materials after 48 h of equilibration.
Significant sorption of dissolved organic matter (DOM) was observed only for SediMite™.

2.3.2.3 Sorption isotherms

Adsorption can be described by isotherms, which correlate the solution concentration to the amount sorbed to the adsorbent. The distribution of Hg(II) between the solution phase and the sorbent phase can be described by isotherm models such as Langmuir and Freundlich. The Langmuir adsorption isotherm assumes monolayer adsorption onto a surface containing a finite number of uniform sorption sites. The surface reaches a saturation point where maximum sorption of the contaminant is achieved. The Freundlich adsorption isotherm is an empirical model, which better represents sorption processes with variable sorption sites. Preliminary evaluation of the isotherm data (Fig. 17) shows that Thiol-SAMMS®, followed by SediMite™ and Organoclay MRM®, exhibited the highest sorption capacity for Hg(II) provided as mercury–NOM complex.
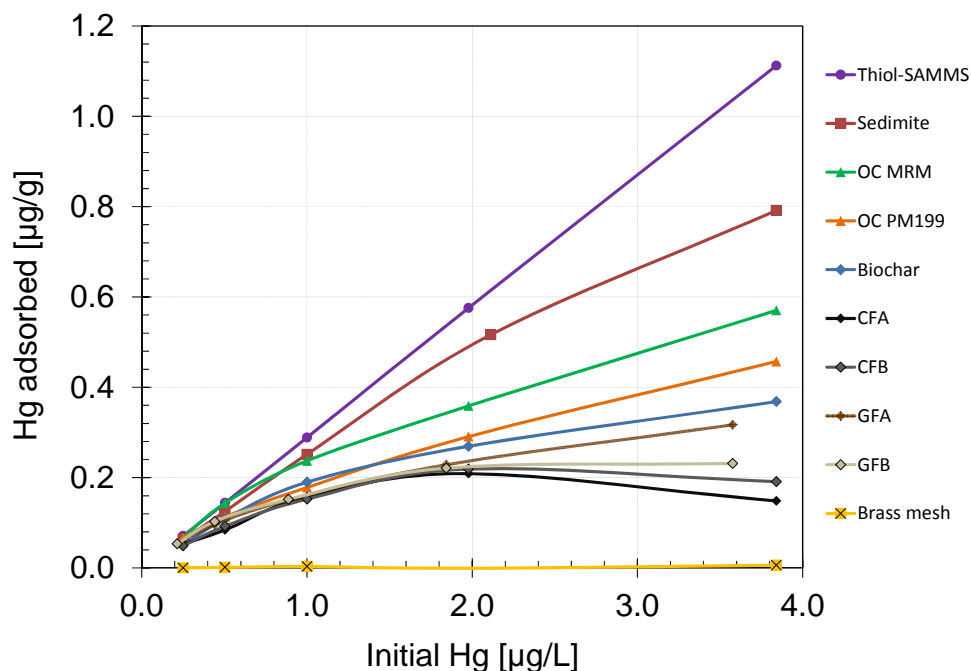
Fig. 17. Adsorption isotherms for 10 sorbent materials. Clay-based sorbents Organoclay MRM® and Organoclay PM-199® are shown as green and orange triangles, respectively. Carbon-based sorbents biochar, carbon fiber A, carbon fiber B, carbon foam A, and carbon foam B are shown in blue, black, gray, brown, and tan diamonds, respectively. Thiol-SAMMS®, SediMite™, and brass mesh are shown as violet circles, red squares, and goldenrod crosses, respectively.

The accessible surface and porosity of a sorbent are related directly to the sorbent's ability to sorb materials in solution. Liquid–solid adsorption involves accumulation of the contaminant onto the exterior and interior surfaces of a sorbent. Surface area is one of the key indicators attributed to the sorptive properties of porous materials. The BET surface areas for sorbents tested in these studies are shown in Table 2.

Table 2. Brunauer-Emmet-Teller surface areas
Surface areas for brass and carbon fiber
samples were not determined (ND)

Sorbent	Surface area [$m^2 \cdot g^{-1}$]
SediMite™	481.5
Biochar	200.2
Thiol-SAMMS®	91.3
Graphite foam A	38.1
Graphite foam B	15.7
Organoclay MRM®	2.18
Organoclay PM-199®	1.01
Brass	ND
Carbon fiber A	ND
Carbon fiber B	ND

2.3.2.4   Release of anions

In most aquatic systems, anaerobic microorganisms such as iron and sulfate reducers, as well as fermenters and methanogens, are largely responsible for MeHg production. Thus, certain terminal electron acceptors such as oxygen and nitrate must be exhausted before MeHg production is observed. The leaching of solutes from sorbent materials may result in changes to the pore water chemistry and even may enhance methylation of mercury by anaerobic microorganisms. The addition of sulfate has been found to increase the production of MeHg in sediments (Gilmour, Henry, and Mitchell 1992). Brass, biochar, and lignin-based carbon materials showed the lowest release of anions, while Organoclays resulted in relatively high concentrations of chloride and sulfate in solution (Fig. 18).
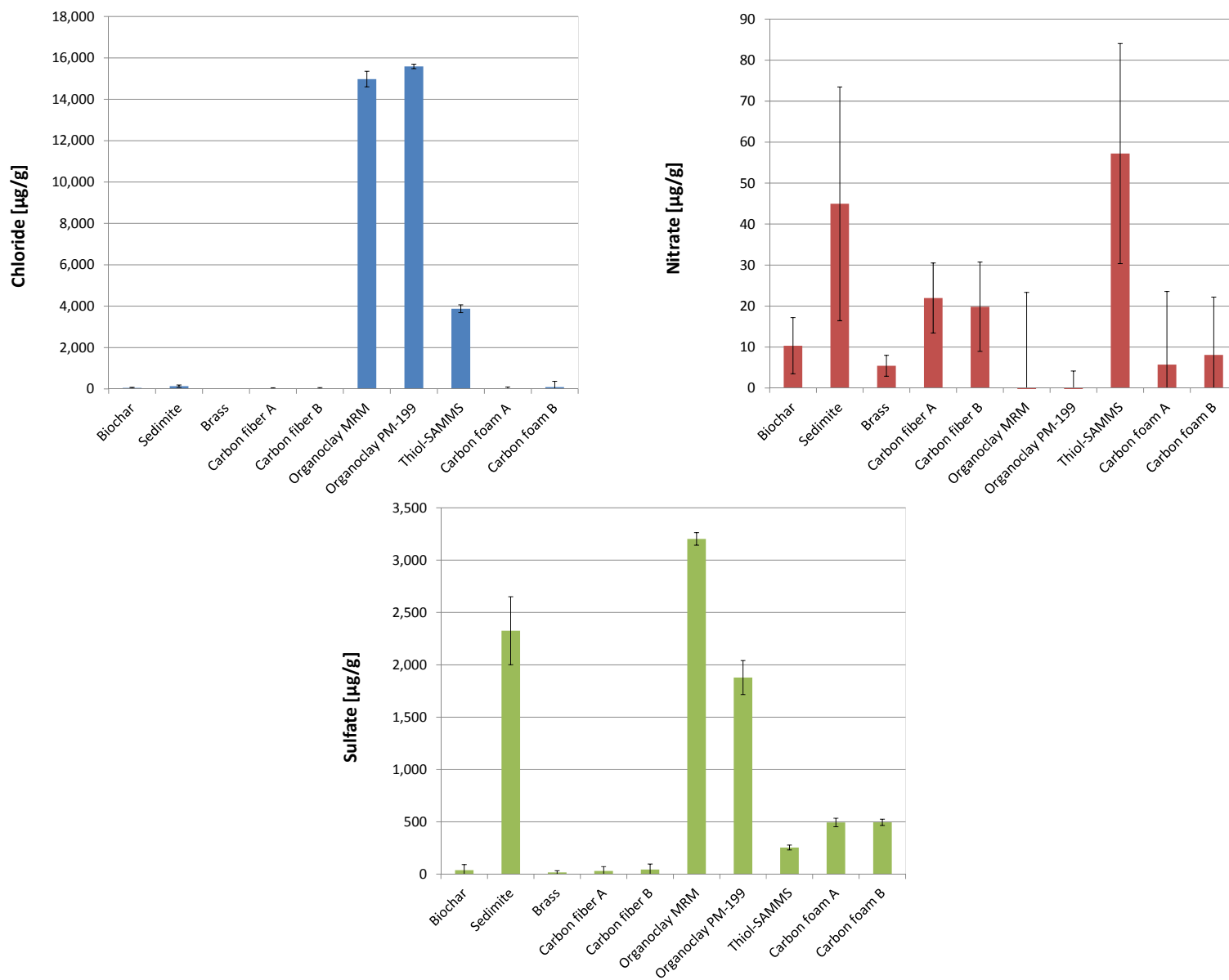
Fig. 18. Anions released from sorbents into solution after 48 h of equilibration as determined by ion chromatography.

2.4   TASK 1 FUTURE DIRECTIONS

Science-based solutions are needed to develop strategies and technologies to address LEFPC soil contamination. A key early research goal is to use field characterization data to identify high-priority locations with high mercury concentrations, high erosion potential, and/or high methylmercury production. These activities will lead to a refined site conceptual model of the LEFPC environment and to development of remedial testing approaches in FY 2016 and beyond. In addition, these efforts can help establish baseline conditions necessary for identifying the efficacy of stabilization technologies and testing remedial solutions.

Activities in FY 2015 included assessments of the site to understand the distribution of mercury and methylmercury in creek bank soils, understand the desorption potential for mercury in creek bank soils, install groundwater monitoring wells, and test potentially applicable sorbents. Watershed-scale sampling of bank soils was identified as a critical need for a more complete understanding of potential mercury sources to the creek. Initial surveys of bank soils in LEFPC have revealed substantial spatial and temporal variability in mercury and methylmercury. Understanding that variability, coupled with characterization of bank erosion potential, is essential to identifying fluxes of soils, mercury, and methylmercury into LEFPC. To that end, the determination of particle size distribution, bulk density, soil type, elemental analysis, and other soil characteristics was included with concurrent measurements of mercury concentrations. In FY 2016, completion of analyses and interpretation of the results will guide the pathway forward for prioritization of sites and testing of stabilization technologies. Groundwater monitoring in FY 2016 will enable understanding of the role of groundwater–surface water interactions and the potential role of methylmercury production in groundwater.

Ultimately, strategies in Task 1 may involve a combination of bank stabilization at locations informed by activities in Sects. 2.1 and 2.2 and techniques developed in FY 2016 and beyond. Bank stabilization may be combined with in situ amendments informed by the studies in Sect. 2.3, allowing deployment of sorbents in key locations with minimum perturbation to the existing environment and the ecosystem. The sorbent evaluation effort will identify alternate approaches that reduce mercury fluxes while working in conjunction with bank stabilization activities to avoid large-scale soil removal. Sorbent technologies are expected to limit mobilization of mercury species from stream banks and sediments and effectively reduce bioaccumulation of methylmercury in LEFPC. The results of the laboratory-based studies of sorbents provide valuable insights into how the association of mercury with resulting organic matter affects the sorption process. The major classes of sorbent materials have been evaluated and their performance determined in the presence of mercury–NOM complexes. Several of the sorbents tested were found to leach solutes, such as sulfate, which may enhance methylation by microorganisms in the environment. The scope for FY 2016 will build on these results and integrate laboratory-based studies with insights gleaned from site characterization efforts. In collaboration with other tasks, a set of bank soil and creek sediment samples will be selected with compositions and contaminant concentrations representative of EFPC. In FY 2016, the following activities are proposed:

- Continue to interpret information from the 2014 and 2015 longitudinal sampling activities and develop the results into a publishable manuscript
- Complete analysis of mercury and methylmercury concentrations and other soil properties on the HRD sampling activity
- Develop, from all of the characterization results, a list of high-priority sites based on a combination of erosion potential and mercury or methylmercury concentrations
- Install and monitor new erosion pins at prioritized locations
- Complete development of groundwater wells and installation of surface water wells
- Investigate the properties of the continuous cores collected during installation of groundwater wells

- Begin automated and monthly manual monitoring of the ground- and surface water wells
- Continue to quantify desorption potential from creek bank and HRD soils
- Identify the best potential sorbents for mercury and methylmercury in the presence of LEFPC water and soils
- Understand limitations of artificial sorbents including stability over time, release of anions with adverse effects (e.g., sulfate), and physical properties that influence deployment (e.g., sorbent size and shape)

Anticipated by the close of FY 2016, there will be enough data collected to build a preliminary site conceptual model and begin to prioritize sites for testing remedial solutions.

Consistent with the adaptive management approach, promising ideas from field and laboratory testing should move forward and up the technology readiness ladder. Monitoring baseline conditions and manipulation responses is essential to determining the outcomes of tests and identifying the most promising technologies for full-scale implementation. Whereas field characterization efforts (Sects. 2.1 and 2.2) are at TRL 1–2, sorbent evaluation efforts (Sect. 2.3) operate at TRL 2–3. Sorbent efficacy will need to be field-tested, preferably in a realistic on-site setting under semicontrolled conditions. It is likely that sorbents eventually will need to be applied in concert with other bank rehabilitation methods such as vegetation removal, bank angle reductions, bank stabilization through physical armoring, and vegetative replantings to stabilize creek banks. Sorbent evaluation studies will be coordinated with the field characterization efforts in Tasks 1 and 2 and will provide valuable information for the design of future pilot scale follow-on studies in the planned field research station. In combination with comprehensive field characterization efforts, these studies will establish a solid scientific basis for testing and future implementation of remediation activities to reduce mercury fluxes and mercury concentrations in fish.

3. TASK 2, SURFACE WATER AND SEDIMENT MANIPULATION

3.1 SURFACE WATER

3.1.1 Approach to Water Chemistry Investigations

Water chemistry can affect the speciation, transformation, and transport of mercury and methylmercury, but there remain significant knowledge gaps, particularly in freshwater stream systems. These knowledge gaps limit the ability to make informed remediation decisions for EFPC. In FY 2015, as part of earlier TD project efforts, the current understanding of factors and variables controlling mercury transformations and potential remediation alternatives was summarized (Peterson et al. 2015a) and several key questions were developed to guide research efforts, including the following:

- What changes in mercury and methylmercury flux occur along the length of EFPC? Can these changes help to prioritize shorter reaches of the creek for targeted action(s) addressing specific issues?
- Are mercury and methylmercury dynamics during high flow events indicative of any significant out-of-stream sources of these constituents to EFPC?

Fieldwork in FY 2015 has been designed largely to address the first of these two questions. The efforts in FY 2015 will provide a foundation for future work that includes addressing the second question.

East Fork Poplar Creek is operationally divided into two sections: UEFPC (the ~ 2 km portion of the creek within the Y-12 facility boundaries) and LEFPC (the ~23 km of stream that are downstream of the Y-12 facility). The water chemistry between these two portions of the stream is very different, and mercury and methylmercury behavior is thus very different. Control and mitigation strategies need to account for these differences in mercury behavior and speciation as the water chemistry changes throughout the creek. Whereas the bulk of this project deals with technology development to develop strategies to mitigate mercury contamination in LEFPC, there are reasons to consider treating UEFPC within the broader strategy. Mercury in surface water in UEFPC is accessible, is under DOE control, and is primarily dissolved Hg(II), a highly mobile, reactive, and bioavailable form of mercury. This combination of access and chemistry provides an opportunity to manipulate the water chemistry to reduce the flux of mercury and the accumulation of methylmercury in fish throughout the entire LEFPC stream system.

In FY 2015, through a combination of laboratory and field studies, we: (1) examined the role of chemicals present in UEFPC water due to ongoing plant operations on the flux and forms of mercury present and mercury methylation processes, (2) estimated mercury flux at several locations along EFPC, and (3) characterized streambed sediments along the length of EFPC. These efforts are ongoing and will provide a solid knowledge base upon which the effects of in-stream manipulations can be evaluated. Results presented in this section are given in terms of both concentration and flux or loading. Whereas biological receptors are likely responsive to concentration, flux is more important from a site management perspective. Flux estimates (i) help support site characterization and conceptual model development; (ii) help prioritize locations within a site for remedial action; (iii) are used in exposure and risk assessment; (iv) inform remediation selection and design; and (v) are used in performance, compliance, and long-term monitoring.

3.1.2 Role of UEFPC Y-12 Water Chemistry and Flux on LEFPC

The overall goal in these investigations is to assess alternatives to current chemical treatment and discharge practices and/or implement chemical manipulations in surface water that would reduce mercury

migration to LEFPC and mercury bioavailability. The DOE Office of Environmental Management plans to construct a water treatment facility at Outfall 200 (OF200) to remove mercury and, therefore, chemical manipulation alternatives would need to be compatible and complementary to those plans.

The influence of Y-12 at EFPC's headwaters on downstream water chemistry and mercury fluxes and concentrations is well known. Outfall 200 discharge from the western portion of Y-12 is a major source of base flow mercury loading to LEFPC (Peterson et al. 2011). Multiple outfalls downstream of OF200 within the eastern portion of Y-12 and the UEFPC stream channel itself also contribute important but smaller fluxes of mercury to LEFPC. Extensive historical spills of liquid mercury beads ($Hg[0]_l$) in buildings, soils, and storm drains are the sources of dissolved mercury in UEFPC surface water. The $Hg(0)_l$ found in the Y-12 storm drains are exposed to some anthropogenic chemicals on a continuous basis, whereas other chemicals are discharged only episodically (Peterson et al. 2015a). Chlorine (in potable water), dechlorination chemicals (ammonium bisulfite), and steam plant corrosion inhibitors (primarily amines) are released on a continuous basis via permitted discharges at Y-12. Treatment chemicals from cooling tower blowdown water are used and discharged only on an intermittent basis, primarily in hot weather. Many of these low-level continuous- and intermittent-use chemical discharges are known to or have the potential to affect the form and flux of mercury to LEFPC.

With a relatively low solubility, $Hg(0)$ can be oxidized to the more soluble and mobile $Hg(II)$ form by chemical oxidants. Y-12 uses City of Oak Ridge tap water in its industrial processes; this water contains residual chlorine that, when discharged to the storm drain system, can react and oxidize the dissolved ($Hg[0]_d$) and liquid $Hg(0)_l$ beads present and transform them into the more soluble and mobile $Hg(II)$ form. ORNL recently measured free chlorine concentrations as high as 3.4 ppm in the Y-12 storm drain system. This suggests that exposure of $Hg(0)_d$ and $Hg(0)_l$ in the storm drain system to residual chlorine results in the formation of soluble $Hg(II)$ species. The formation of $Hg(II)$ species could result in substantially increased total mercury fluxes to LEFPC. Ammonium bisulfite currently is used as the primary dechlorinating agent at Outfalls 200 and 21 before discharge to the creek.

Amines and other chemicals are used in the treatment of boiler system equipment. Amines have the potential to form complexes with $Hg(II)$ (Mousavi 2011). Amines also can react with chlorine to form chloramine, an oxidizing agent similar to chlorine that also probably is capable of oxidizing $Hg(0)$ to $Hg(II)$. However, it has a much longer half-life than other forms of chlorine and may release ammonia when degraded.

Chlorination byproducts like trihalomethanes and haloacetic acids form through the reaction of chlorine with other chemicals or trace amounts of organic carbon. Historical sampling data from the Oak Ridge Environmental Information System shows that chlorination byproducts are detected frequently in the West End Mercury Area (WEMA) storm drain system (e.g., Outfall 150). The chlorination byproducts also have the potential to form complexes with $Hg(II)$ (Mousavi 2011). Binding of $Hg(II)$ to organics can affect bioavailability of $Hg(II)$ in aquatic ecosystems (Haitzer, Aiken, and Ryan 2002) and limits $Hg(II)$ availability to methylating bacteria (Ravichandran 2004).

The operation of Y-12 cooling towers requires use of a variety of chemicals for corrosion control, acid cleaning, and microbiological control, as well as anti-foaming agents and surfactants (Peterson et al. 2015a). Blowdown cooling water is released to the storm drains episodically, especially during warm months. The released chemicals probably have a variety of impacts on the mercury contacted within the storm drains depending on the specific chemicals released; however, the net impact would be an increase in the flux of mercury to LEFPC because of the temporary increase in flow and chemical interactions with mercury in the storm drains.

Discharge from the Oak Ridge Wastewater Treatment Facility (ORWTF) is another source of anthropogenic chemical additions to the creek. Concentrations of nutrients and dissolved organic matter in EFPC increase because of ORWTF discharges.

The role of chemicals present in the EFPC water due to ongoing plant operations on the flux and forms of mercury present and mercury methylation processes will be evaluated in a phased approach using a combination of laboratory- and field-scale experiments. In FY 2015, the focus has been on conducting preliminary sampling and laboratory experiments to assess the potential impact of chlorination and dechlorination chemicals and other process water chemicals on the speciation and loading of mercury. The results of these experiments will be used to help determine the degree to which certain changes in Y-12 chemical usage and discharges potentially could reduce the flux of mercury to LEFPC.

3.1.2.1   EFPC sampling and analysis

Upstream and downstream sampling of the Y-12 dechlorination facility was conducted to determine the organic composition and transformation by-products of chemical additives in surface water. Upstream and downstream of the ORWTF, effluent discharge also was sampled to assess similar impacts of chemical additions potentially occurring at this facility. Analyses of the water samples were conducted at the University of Georgia's Laboratory for Environmental Analysis using gas chromatograph/mass spectrometer techniques for quantifying volatile organic compounds (VOCs) and semi-VOCs. Chlorination byproducts like trihalomethanes and haloacetic acids were targeted for detection.

Historical ORNL sampling data has shown that chlorine (up to 3.4 ppm) and chlorination by-products (e.g., chloroform, bromoform, dibromochloromethane, bromodichloromethane) are routinely detected in OF200 and the storm drain outfalls in WEMA upstream of OF200 (unpublished data). Summarized results from sampling upstream and downstream of the Y-12 dechlorination facility and ORWTF effluent discharge in December 2014 for this TD project are provided in Table 3. Chlorination by-products (e.g., including trihalomethanes and haloacetic acids) and VOCs were detected both upstream and downstream of the OF200 dechlorination facility, although concentrations were generally higher in the upstream sample. The main exception is tridecane, which was detected at 1,290 ppb downstream of the dechlorination facility but at only 311 ppb upstream. These results suggest that dechlorination with ammonium bisulfite at Y-12 has an impact on organic compound concentrations. The impact of these compounds on mercury speciation and transport is poorly understood and warrants further study.

In general, the ORWTF effluent does not appear to be a significant source of the constituents listed in Table 3. Chlorination by-products were detected upstream and downstream of the ORWTF effluent discharge location; however, the upstream location generally was slightly higher or the same as downstream locations for most of these chlorination by-product constituents, with the exception of bromoacetic acid, which was detected at a higher concentration downstream. The VOC 1,1-dichloroethene also was detected upstream of the ORWTF discharge at 6.4 ppb but was not detected downstream. Tentatively identified compounds also were detected in all samples, suggesting that there are other organic compounds present but that they could not be identified definitely.

Table 3. Select chlorination by-products and other organics detected upstream and downstream of the Outfall 200 (OF200) dechlorination system (12/17/2014) and Oak Ridge Wastewater Treatment Facility effluent discharge (12/15/2014), in parts per billion

Target compounds	Y-12 dechlorination		City of Oak Ridge wastewater discharge	
	OF200 (upstream)	OF200A (downstream)	Upstream	Downstream
Dibromochloromethane	8.8	2.1	0.03	0.01
Chloroform	2.9	2.1	0.5	0.4
Bromodichloromethane	7.0	1.4	0.03	0.02
Bromoacetic acid	36.0	6.7	33.5	80.0
Dichloroacetic acid	ND	1.7	ND	ND
Dichloropropanoic acid	6.0	3.0	16.6	ND
Trichloroacetic acid	30.0	30.0	240.0	230.0
Bromochloroacetic acid	29.9	2.1	6.9	1.2
Dibromochloroacetic acid	29.6	ND	84.0	ND
Undecane	44.0	ND	ND	ND
Dodecane	44.0	ND	ND	ND
Tridecane	310.8	1,290.0	429.2	373.7
1,1-Dichloroethene	ND	ND	6.4	ND
Tetrachloroethene	2.7	1.9	0.01	0.01

Note: ND = not detected.

3.1.2.2 Assessment of chlorine impacts

Laboratory studies were conducted to assess the impact of chlorine on the oxidation of $Hg(0)_l$ beads to the more soluble and mobile $Hg(II)$ form. The tests were conducted using tap water containing residual chlorine (typical free and total chlorine concentrations of 2.2–2.8 ppm and 2.4–3.0 ppm, respectively), a Y-12 storm drain water sample containing chlorine (~1.0 ppm total and free), distilled deionized (DI) water that was chlorine free, and tap water treated with ultraviolet (UV) light followed by carbon filtration. Mercury analysis was conducted using cold vapor atomic absorption spectroscopy (i.e., Lumex). Additional details on the experimental design are provided below.

Figure 19 shows that a 50 µl bead of $Hg(0)_l$ placed in tap water containing residual chlorine generates 85 times more total mercury (HgT) compared with a bead place in DI water with no chlorine and 44 times more HgT than a bead placed in tap water dechlorinated using UV light followed by carbon filtration. The HgT generated in the chlorinated tap water is predominately in the oxidized $Hg(II)$ form with <1% in the $Hg(0)_d$ form. Conversely, HgT in DI and dechlorinated tap water was determined to be 50% or more in the $Hg(0)_d$ form. These results indicate that beads of $Hg(0)_l$ found in the Y-12 storm drain system exposed to chlorine in process water discharged to the storm drains have the potential to greatly increase the flux of mercury in UEFPC to LEFPC through the oxidation of $Hg(0)$ and generation of soluble, more mobile $Hg(II)$.

In addition, Fig. 19 shows that the rate of HgT formation in the chlorinated tap water decreases and levels off over time. To determine if this leveling off is because of an insufficient amount of chlorine available for oxidation of $Hg(0)$, the experiment with chlorinated tap water and a bead of $Hg(0)_l$ was repeated but with a greater volume of water and, therefore, a larger mass of chlorine available for oxidation. The HgT concentration did not level off in this experiment, and the mass of $Hg(II)$ released was more than two times as much. This confirms that the amount of mercury generated with the smaller volumes of water was limited by the amount of chlorine available and was not the result of a $Hg(0)_l$ bead surface phenomenon or some other factor inhibiting the solubility.

Testing with Y-12 storm drain water, collected from invert E3125 upstream of Outfall 169, was conducted to confirm that the chlorine found in the storm drain water also would result in increased Hg(II) concentrations in the presence of a Hg(0)$_l$ bead. Results of testing (Fig. 20) show the same increase in HgT concentration over time when a Hg(0)$_l$ bead is placed in the Y-12 site water. The HgT concentrations are not as high as those observed with tap water, but this probably is because the concentration of chlorine in the storm drain sample was three times lower than the tap water concentration, and the oxidation process was limited by the smaller mass of chlorine available in the sample vials used in testing.
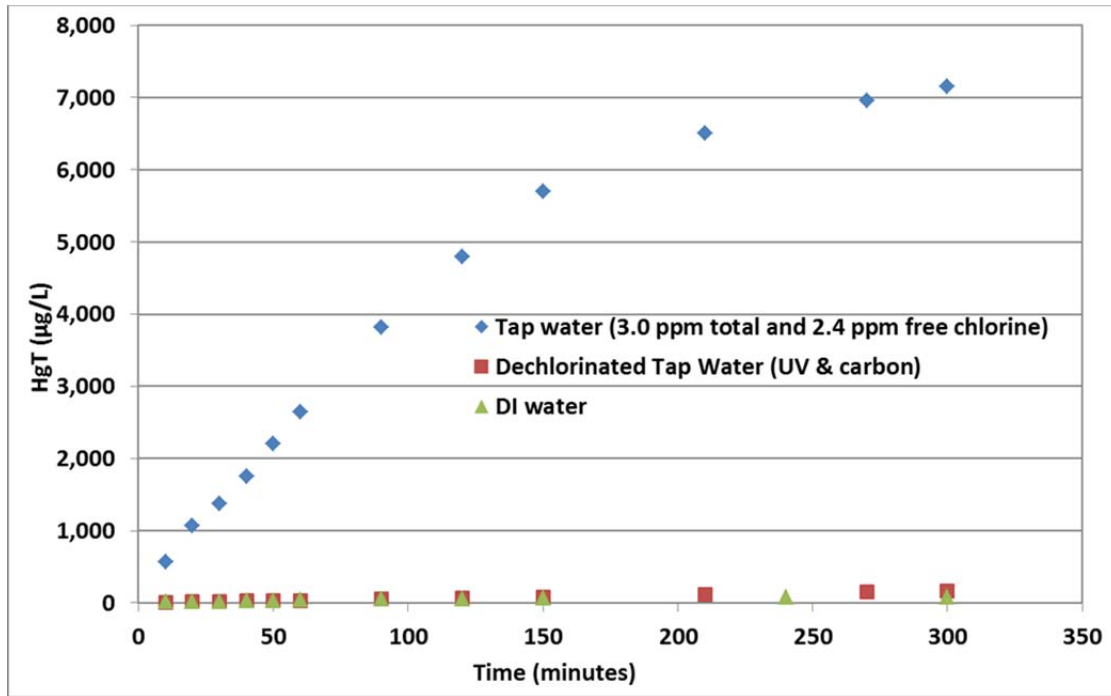
Fig. 19. Total mercury (HgT) generation over time when a 50 µl bead of Hg(0)$_l$ is placed in tap water containing ~3.0 ppm total and 2.4 ppm free chlorine, deionized (DI) water with no chlorine, and tap water that was dechlorinated using ultraviolet (UV) light followed by carbon filtration (average of two replicates shown).
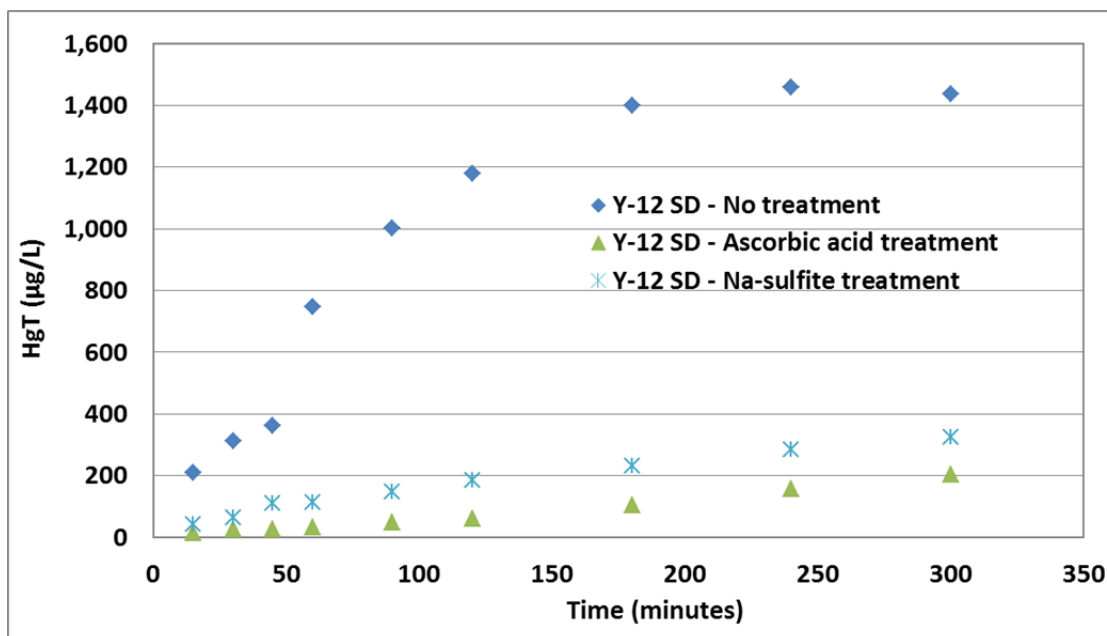
Fig. 20. Total mercury (HgT) generation over time when a 50 μl bead of Hg(0)$_l$ is placed in Y-12 storm drain (SD) water containing ~1.0 ppm total and free chlorine, Y-12 water dechlorinated with ascorbic acid, and Y-12 water dechlorinated with Na-sulfite (average of two replicates shown).

3.1.2.3   Assessment of dechlorination compounds

Laboratory studies also were conducted to assess the impact of dechlorinating the tap water with an assortment of dechlorination chemicals before conducting the Hg(0)$_l$ bead oxidation experiments. Dechlorination chemicals tested include ammonium bisulfite (currently used at Y-12), Na-bisulfite, Na-sulfite (anhydrous), ascorbic acid, Na-thiosulfate, and UV light treatment followed by carbon filtration to remove all chlorine-related compounds. The effects of dechlorination using a more limited number of dechlorination compounds also were tested on the Y-12 water to confirm that the laboratory results were applicable to site water.

For Hg(0) oxidation experiments, small beads of washed Hg(0)$_l$ (50 μl) were removed from a stock container using a gastight syringe and placed in a 40 ml glass vial. All tests were conducted in duplicate. The vial cap was fitted with an outlet port consisting of a Teflon tube (1.6 mm internal diameter) secured approximately 10 mm from the base of the vial. Aqueous samples (1 ml) were withdrawn from the vial with a plastic syringe following a 0.5 mL flush of the sample line. A subsample was analyzed immediately for dissolved Hg(0)$_d$, and the remaining aliquot was preserved with bromine monochloride for total mercury analysis. The concentrations of dissolved Hg(0)$_d$ and total mercury were measured multiple times between 10 and 300 minutes using a modification of EPA method 1631E (Miller et al. 2013). Oxidized mercury, the combination of Hg(I) and Hg(II), was determined by the difference between the HgT and Hg(0)$_d$. However, Hg(II) is used to denote all oxidized species of mercury because Hg(II) is the most likely species present.

As shown in Fig. 21, exposing beads of Hg(0)$_l$ to dechlorinated tap water results in a significant reduction in the production of HgT (i.e., Hg[II]) compared with tap water that has not been dechlorinated. Despite this, some of the dechlorination compounds tested (e.g., ammonium bisulfite, Na-bisulfite, and Na-thiosulfate) resulted in significant amounts of HgT in solution compared with the DI water and tap water dechlorinated without chemicals using UV light and carbon filtration. Ammonium bisulfite and Na-bisulfite currently are used at Y-12 and ORNL, respectively. During field testing activities for a SnCl

treatment alternative, the addition of thiosulfate was observed to temporarily increase mercury flux in a portion of the north/south pipe because of mercury complexation and desorption of mercury from the tunnel walls (Southworth et al. 2009). This temporary increase in mercury flux related to the use of thiosulfate is a concern that also may be applicable to some other sulfite compounds.

Ascorbic acid, Na-sulfite, and dechlorination using UV light followed by carbon filtration produced the least amount of HgT in solution. Na-sulfite is a dechlorinator typically used in tablet form to treat at the point of discharge.

For most of the testing, two to three times the stoichiometric amounts of the dechlorination compounds were required to remove chlorine in the tap water; this is typical of the amounts used in industrial applications. An excess amount is used because there is generally uncertainty in the peak concentrations of chlorine released; also, some of the compounds can degrade slowly over time and lose their effectiveness for removing chlorine. However, testing shows that the concentration of the dechlorination chemical used to dechlorinate can have a significant impact on the amount of HgT that ends up in solution and is available for downstream transport. In one test, decreasing the concentration of Na-bisulfite from 8.8 ppm to 4.4 ppm resulted in 6.5 times less HgT in solution (see Fig. 21). The concentrations of some dechlorinating compounds like ascorbic acid and Na-sulfite do not appear to have as dramatic an impact on HgT production, probably because they are not as prone to mercury complexation.

The Y-12 storm drain water dechlorinated with ascorbic acid or Na-sulfite before exposure to a bead of $Hg(0)_l$ produced much less HgT in solution than the storm drain water that was not dechlorinated. Ascorbic acid in general produces the least amount of HgT in solution compared with all the other dechlorinating compounds and is similar to the results using UV light and carbon filtration.

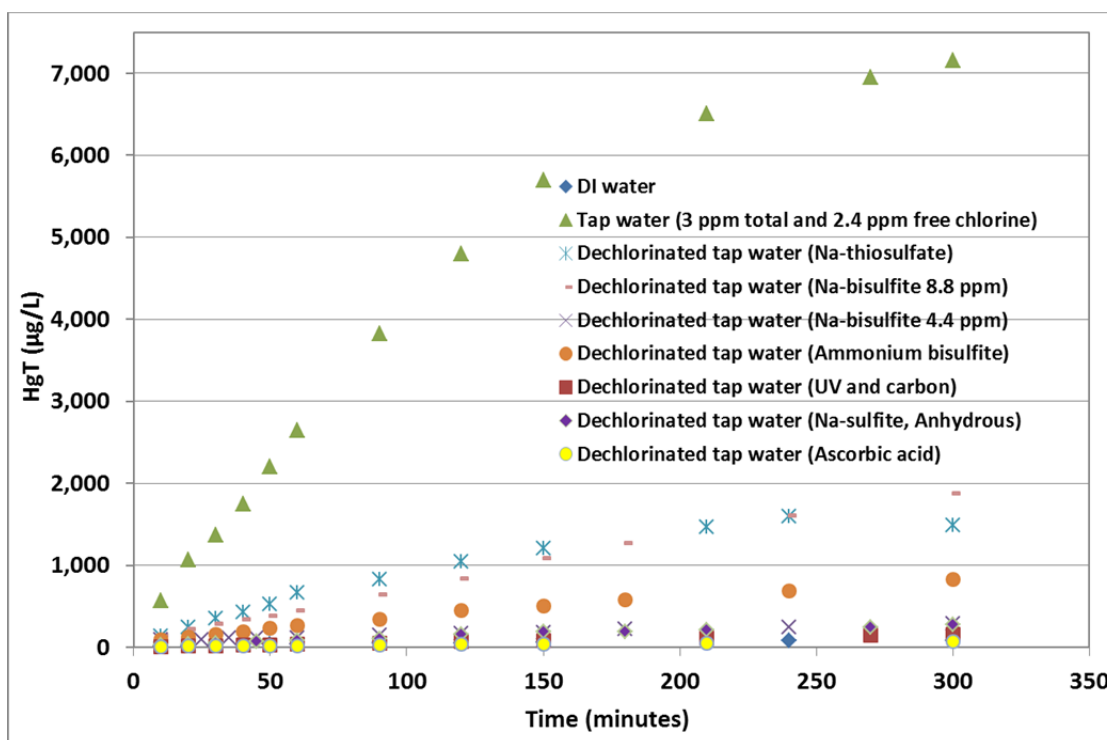**Fig. 21. Total mercury (HgT) generation over time when a 50 µl bead of $Hg(0)_l$ is placed in tap water that has been dechlorinated using an assortment of dechlorination chemicals.** Results for the untreated tap water and deionized (DI) water are also shown for comparison.

37

3.1.3 Estimates of Mercury and Methylmercury Flux along EFPC

Flux is a measure of the rate of mass flow past a boundary. It is calculated as the product of concentration (units of mass per volume or mass per mass) and volumetric flow rate (units of volume per time) and is expressed in units of mass per time. Concentrations are measured in either the field or laboratory or may be estimated from site-specific empirically derived proxy relationships (e.g., a relationship between turbidity and total suspended solids [TSS]). Determining the flow rate at a location in the stream depends on making manual discharge measurements across a range of creek water heights (stage) and developing a stage–discharge relationship or rating curve describing the relationship between creek stage and volumetric flow rate. Rating curves are site-specific because they depend on channel geometry. Continuous measurements of creek stage using dedicated sensors then can be converted to a continuous record of flow rate by means of the rating curve. Rating curves must be checked continually, principally to account for (1) changes to the stream cross sectional area due to erosion and deposition, (2) growth and decay of aquatic vegetation, and (3) debris dams upstream or downstream that exercise local control on flow.

By comparing the flux at two locations along the creek, one can estimate whether the reach of creek between those locations is a net source or sink of the measured constituent. Identifying a source reach can help with site prioritization by targeting specific reaches of the creek for action as opposed to treating the entire creek. Alternately, identifying reaches that are net sinks can provide clues to desirable system characteristics that could be applied along other reaches. Before December 2014, there were only two locations along EFPC where continuous water level data were being collected that would support flux calculations. One location was at EFK 23.4 (Station 17), and the other was located 18 km downstream at EFK 5.4. Rating curves existed or could be constructed from existing data for each of these locations. Nevertheless, the absence of other gauging stations along this 18 km reach did not permit assessment of which, if any, shorter reaches were sources or sinks of mercury or methylmercury.

3.1.3.1 Wiltshire Drive (EFK 16.2) monitoring station

To address the gap in flux data between EFK 23.4 and EFK 5.4, a new stream gauging and water quality monitoring station was established at EFK 16.2—the Wiltshire Drive overpass of EFPC. The site has been instrumented with (1) a staff gauge and pressure transducer to measure and record water depth at 15-min intervals and (2) a YSI 6920V2 multiparameter sonde to measure and record water temperature, specific conductance, pH, dissolved oxygen, and turbidity at 15-min intervals. The staff gauge was surveyed so that water depths can be converted to water surface elevations above mean sea level. A rating curve is being developed for EFK 16.2 by making physical measurements of flow using a Marsh-McBirney Flo-Mate 2000 flow meter across a range of creek stages.

For each physical flow measurement, there is a corresponding measurement of creek stage read from the staff gauge installed at the site (Fig. 22). Flow for unregulated streams in East Tennessee typically is higher in winter and spring, primarily because of lower evapotranspiration. Therefore, measurements of creek flow at higher stages are most likely to be made between December and March before vegetation leafs out.

Frequently, rating curves do not cover high flood flows because of challenging conditions. EFPC has not been an exception. Making flow measurements during very high creek stages has proven very challenging for two reasons: (1) entering the creek is not safe at those stages, so discharge measurements have to be made from the overpass, which is more difficult and time-consuming; and (2) a necessary condition for accurate flow measurements is that the creek stage remain relatively steady during the measurement. Because of the very flashy nature of EFPC during high flows, this condition generally is not met. For example, during one attempt to measure flow at a high stage in spring 2015, the water level ranged over

3 ft during the time the measurement was being made. Similarly, rating curves often do not cover or exhibit greater variability at very low flows because of difficulties inherent in measuring low flow. This greater variability in flow at low stages is evident in the EFK 16.2 rating curve (Fig. 22).
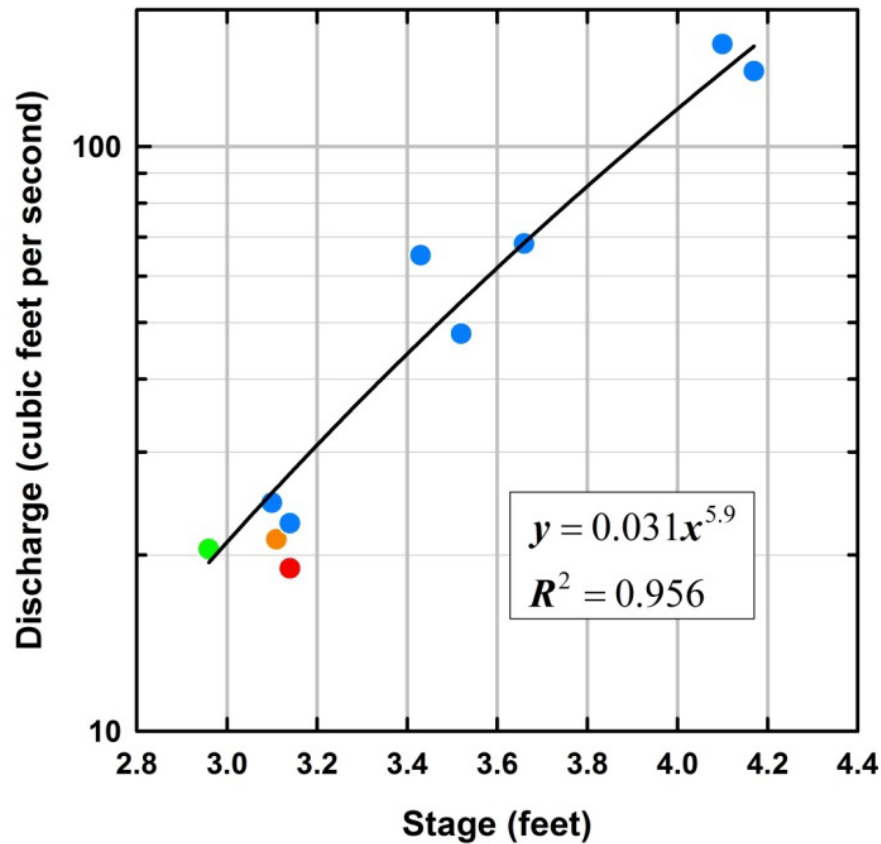
Fig. 22. Stage–discharge relationship for the newly established gauging station at East Fork Poplar Creek kilometer 16.2 (Wiltshire Drive). Points represent manual measurements of discharge and stage. Symbol color indicates the season in which measurements were made (orange = autumn; blue = winter; green = spring; red = summer). The black line represents the power equation fit to the data by adjusting the value of the equation coefficients.

Data recorded while measuring stream flow can be used to calculate the elevation of the streambed across the channel (Fig. 23a). These calculations illustrate the dynamic erosion–deposition patterns within the channel. The indicated erosion–deposition patterns correspond to changes in the channel cross sectional area (Fig. 23b) and contribute to variability in the stage–discharge relationship. From December 2014 through mid-March 2015, enough material had deposited to change the cross-sectional area by 0.85 m^2. Subsequent storm floods eroded much of that material, and by late June 2015, net deposition had altered the area by 0.27 m^2. These changes in stream geometry reflect both localized reworking of bed material and the unidirectional downstream transport of creek sediments.
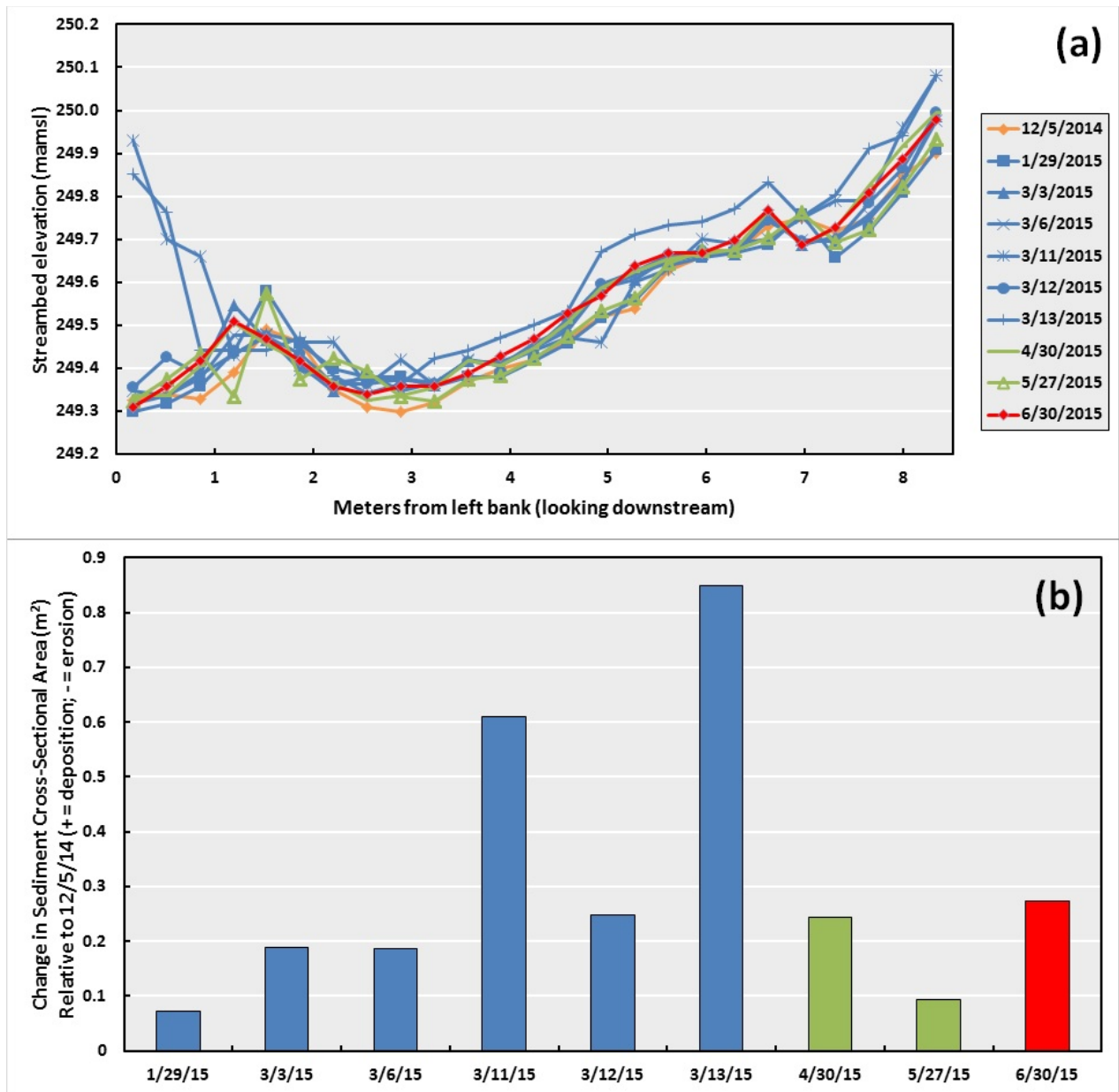
Fig. 23. Streambed elevations and changes in sediment cross-sectional areas at East Fork Poplar Creek kilometer (EFK) 16.2. (a) Streambed elevations at EFK 16.2, in meters above mean sea level (mamsl), during discharge measurements. In addition to graphically displaying the dynamic nature of the streambed over a relatively short period, the erosion-deposition patterns indicated in the data yield changes in the channel cross-sectional area and contribute to variability in the stage-discharge relationship. (b) Change in sediment cross-sectional area at EFK 16.2 over time relative to measurements made December 5, 2014. All values indicate net sediment deposition, although changes in sequential measurements show dynamic erosion–deposition patterns. In both panels, colors are coded to the season in which the measurement was made: orange = autumn; blue = winter; green = spring; red = summer.

40

3.1.3.2 Water quality results

In conjunction with establishing the EFK 16.2 gauging station, water samples are being collected at regular intervals under base flow conditions from EFKs 5.4, 16.2, and 23.4. Field parameters measured at the time of sample collection include temperature, specific conductance, creek stage, pH, and dissolved oxygen. Water samples also are returned to the lab for analysis of total and dissolved (passes through a 0.2 μm filter) mercury and methylmercury (HgT, HgD, MeHgT, MeHgD, respectively), non-purgeable DOC, TSS, anions (chloride, nitrate, sulfate), and optical proxy measures of dissolved organic matter (DOM) composition. Flux estimates are based on results of a grab sample and creek discharge measured at the time of sampling and, therefore, represent instantaneous flux estimates.

Creek Flow. Creek flow increases steadily downstream (Fig. 24). Flows are generally higher in winter and early spring before leaf out and decline through the rest of spring, summer, and into autumn. The two traces from July 2015 do not fit this pattern because of the high rainfall experienced that month. Total rainfall in July 2015 was nearly 60% greater than average July rainfall for the Oak Ridge area.
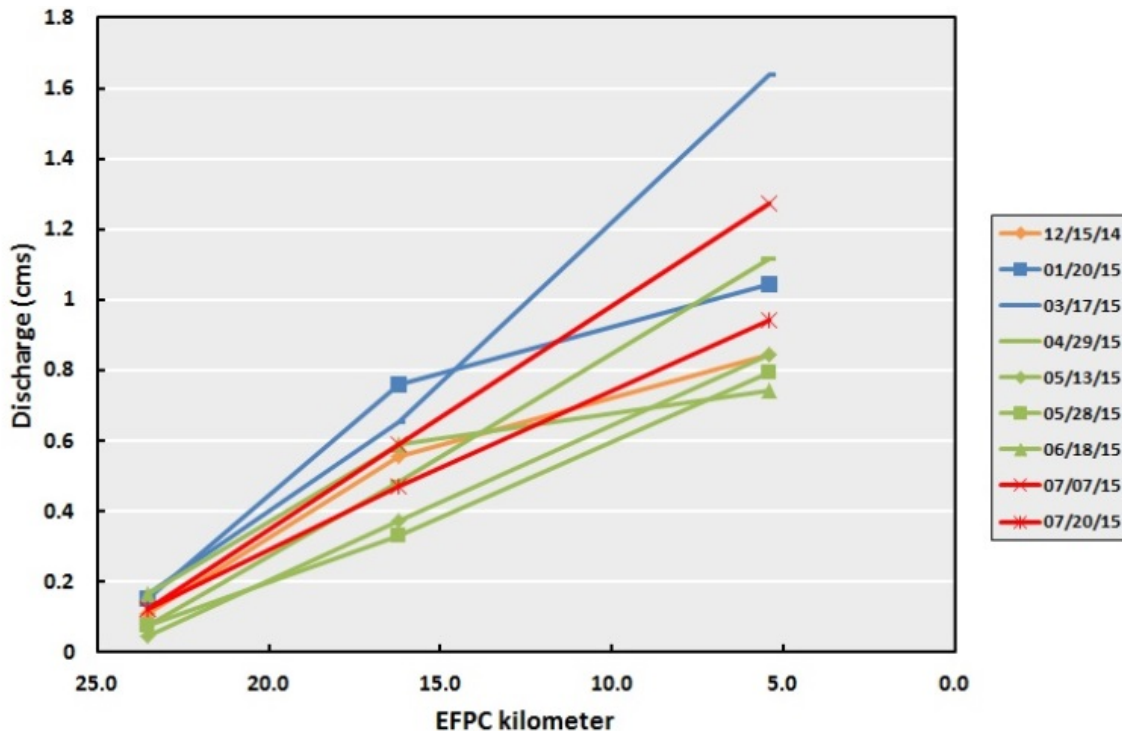
Fig. 24. Creek discharge at three locations along the length of East Fork Poplar Creek (EFPC).
Colors correspond to the season in which the measurement was made: orange = autumn;
blue = winter; green = spring; red = summer.

Total Suspended Solids. Within a given sampling event, TSS concentration (mg/L) remained constant or increased slightly with downstream distance (Fig. 25). Data from July 7, 2015, show a steady increase in TSS downstream likely because of the unusually high rainfall and stream discharge for that month, as noted above. A clear seasonal pattern emerged where TSS increases from late autumn/winter minima to spring/summer maxima. Increased TSS in spring was counterintuitive given the concurrent decrease in creek discharge. Increased TSS may be caused by increases in suspended phyto- and zooplankton; however, previous work has shown that the organic carbon content of TSS does not change with season, suggesting that increased TSS is not caused by plankton blooms. One possibility is that increased activity of creek macrobiota (benthic invertebrates and fish) in warmer months may contribute to seasonal TSS

patterns. TSS flux (kilograms per day) increased steadily downstream, and the increases were greater in spring than in autumn or winter.
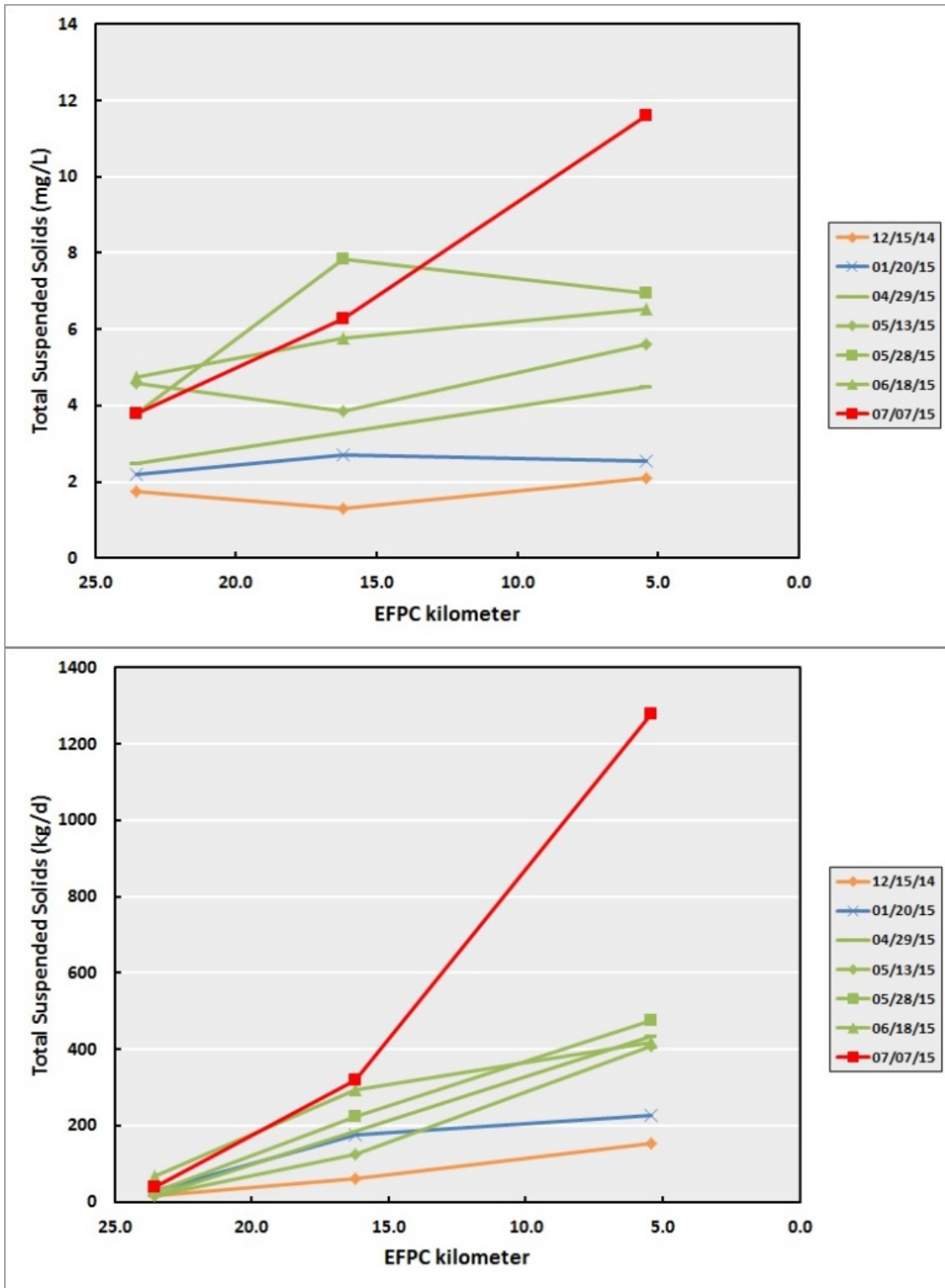

Fig. 25. Total suspended solids concentration (top) and flux (bottom) along East Fork Poplar Creek (EFPC). Colors correspond to the season in which the measurement was made: orange = autumn; blue = winter; green = spring; red = summer.

Dissolved Organic Carbon. The composition of DOM plays a prominent role in governing mercury behavior in the environment and specifically in EPFC (Miller et al. 2009; Dong et al. 2011; Dong et al. 2009). DOM's major role in mercury solid–aqueous partitioning is being addressed explicitly in the sorbent studies described in Sect. 2.3. In these studies, the specific UV-absorbance at 254 nm ($SUVA_{254}$) and slope ratio (SR) was measured—the ratio of calculated slopes of the log-transformed absorption coefficients measured between wavelengths 275–295 nm and 350–400 nm (Fig. 26) as proxies for DOM composition. $SUVA_{254}$ and SR have been positively and negatively correlated, respectively, with increases in terrestrially-derived DOM, which has higher molecular weight and percent aromaticity (Helms et al. 2008; Imai, Matsushige, and Nagai 2003; Wei et al. 2008; Weishaar et al. 2003). Total dissolved mercury has been correlated positively with $SUVA_{254}$ (Dittman et al. 2009). There is a strong correlation between mercury methylation rate constants and SR and $SUVA_{280}$, a similar proxy measure of DOM composition to $SUVA_{254}$ (Mitchell and Gilmour 2008). The cinnabar (α-HgS) dissolution rate is positively correlated with $SUVA_{280}$ and percent aromaticity of the DOM. Previous studies have identified metacinnabar (β-HgS) as a dominant form of mercury in EFPC floodplain soils (Barnett et al. 1995; Barnett et al. 1997; Revis et al. 1989), and current studies suggest much of the mercury in creek sediments is in similar HgS phases. Therefore, an understanding of DOM composition may help inform the understanding of source area contributions (allochthonous terrestrial sources versus autochthonous aquatic sources), spatial–temporal variability in mercury methylation, and the stability of incipient or engineered solid phases of mercury.
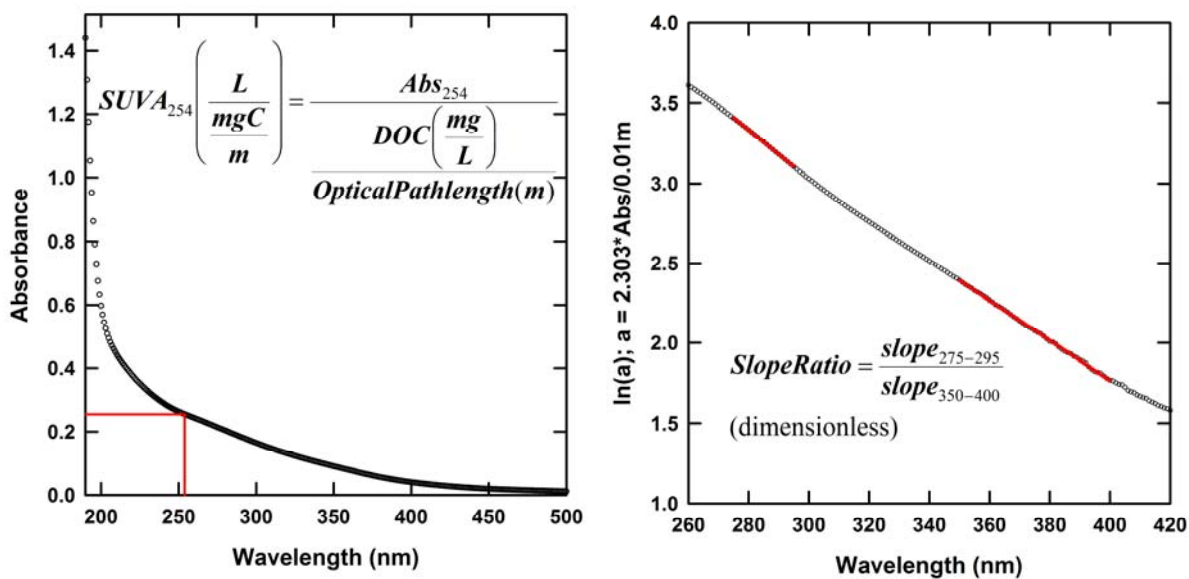
Fig. 26. Graphical depiction of how specific ultraviolet-absorbance at 254 nm ($SUVA_{254}$, left) and slope ratio (right) are determined from ultraviolet-visible spectroscopy.

In autumn and winter, there was no clear pattern in DOC concentration (mg/L) along the creek. Throughout the spring, DOC concentration was slightly higher along the upper creek reach (EFK 23.4 to EFK 16.2; Fig. 27). DOC concentration then increased ~90% along the lower reach (EFK 16.2 to EFK 5.4). In all seasons, SR (a DOC concentration-independent optical proxy for DOM composition) decreased with distance downstream, suggesting increasing amounts of terrestrially derived DOM in the creek. Patterns in DOC concentration and SR are consistent with changes in land use surrounding EFPC as it moves from industrial, through urban, suburban, and mixed open land to woodland sections of the valley. It also is important to note that ORWTF discharges treated water into EFPC at EFK 13.5. This discharge typically has a DOC concentration approximately two times that of the creek and a lower SR value (~1). However, discharge from ORWTF contributes only about 15% of the flow as measured at

EFK 5.4. In addition, this discharge point operates year-round and has no clearly discernible effect in autumn and winter, suggesting that the changes seen in the spring are due in part to sources other than ORWTF. Given that both discharge and DOC concentration increase downstream, it follows that DOC flux (kilograms per day) also increases downstream with the lower reach of the creek, contributing a greater load than the upper reach contributes in spring.

Fig. 27. Dissolved organic carbon concentration (top) and flux (bottom) along East Fork Poplar Creek (EFPC). Colors correspond to the season in which the measurement was made: orange = autumn; blue = winter; green = spring.

Total mercury. Patterns in mercury concentration and flux along the creek and through the year reflect the dynamics of creek discharge, TSS, DOC, mercury aqueous–solid partitioning, photochemical reactions, and the interactions among these variables. In autumn, winter, and mid-spring, total mercury (HgT) concentration decreases substantially at a similar rate (nanogram per liter per creek kilometer) in the upper reach of the creek (EFK 23.4 to EFK 16.2; Fig. 28). In the lower reach of the creek (EFK 16.2 to EFK 5.4), HgT concentration did not change or decreased much more slowly than in the upper reach. The HgT loss along both reaches did not change in late spring, and the HgT concentration was generally higher in spring than in autumn or winter. The fraction of mercury associated with particles increased substantially in the upper reach of the creek, then remained constant in the lower reach; this fraction was highest during the spring. However, the concentration of mercury on particles (nanograms per milligram) decreased downstream. Given that TSS concentration remains constant, this suggests the net deposition of mercury-bearing particles and suspension of "cleaner" particles diluting the concentration of particle-bound mercury. Total mercury flux increased gradually downstream in autumn and winter and increased much more rapidly (grams per day per creek kilometer) during the spring. Although HgT flux increases in both reaches of the creek, the upper reach of the creek (EFK 23.4 to EFK 16.2) contributes more than the lower reach contributes to HgT flux on a per-kilometer basis.

Dissolved mercury concentration (HgD; passes through a 0.2 µm filter) decreased rapidly in the upper reach, then remained constant in the lower reach. The HgD concentration was higher in the lower reach of the creek in late spring relative to other times of the year. It is noteworthy that in about half of the samples collected, the proportional increase in discharge substantially outpaces the proportional decrease in HgD, suggesting that whatever dilution effect may be afforded by increased discharge is being counteracted by a secondary mercury source. This appears likely because of mercury partitioning off the solid phases (TSS or creek sediments) effectively buffering dissolved mercury concentration in the creek. It appears less likely to be because of mercury being carried into the creek from the sources that account for the increased discharge. If the former is true, this could have major implications for the perceived success of remedial actions targeting the water column only. Dissolved mercury flux remained constant (autumn) or decreased (winter) downstream. In spring, HgD flux increased downstream, and the lower reach has a higher rate of increase than the upper reach in HgD flux in late spring.
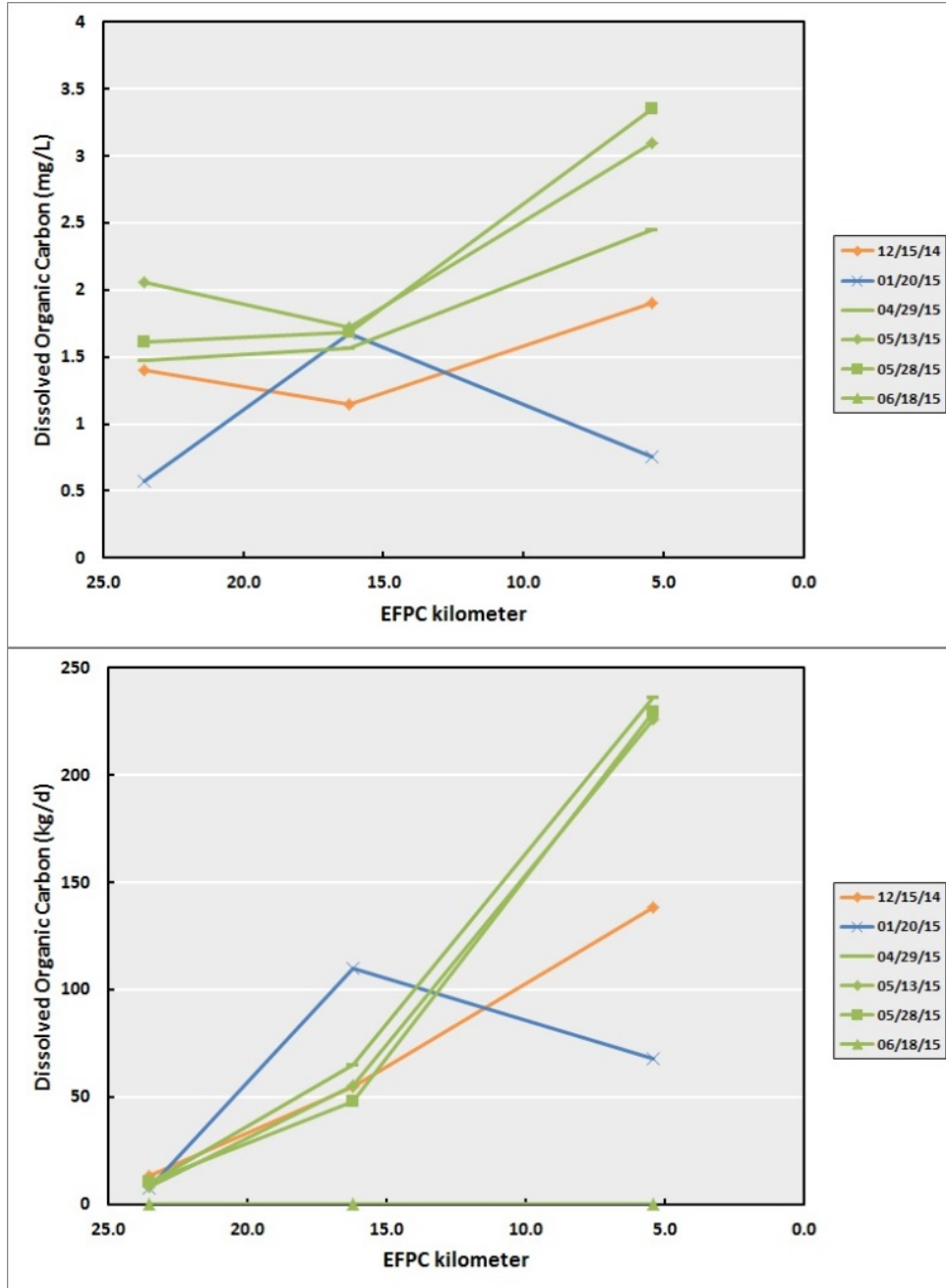
Fig. 28. Total mercury (left) and dissolved mercury (right) concentration (top) and flux (bottom) along East Fork Poplar Creek (EFPC).

Colors correspond to the season in which the measurement was made: orange = autumn; blue = winter; green = spring. Analytical results of summer sampling are pending.

Monomethylmercury (MeHg). Spatial-temporal patterns in MeHg concentration and flux depend on the same variables mentioned for total mercury plus a biotic component because MeHg is produced via bacteria operating in anaerobic environments. Total MeHg generally increases steadily downstream, and the rate of increase (nanogram per liter per creek kilometer) varies with season, being fastest in late spring (Fig. 29). Dissolved MeHg (passes through a 0.2 μm filter) also increases downstream. The rate of increase in the upper reach (EFK 23.4 to EFK 16.2) is similar for all seasons, although concentrations are higher in the spring. The rate of MeHgD increase in the lower reach rises dramatically throughout the spring relative to autumn/winter lows.

The fraction of MeHg associated with particles exhibits much more variability than total mercury. The concentration of MeHg on particles (nanograms per milligram) increases slightly throughout the creek and over seasons. The MeHg solid–aqueous partitioning coefficient decreases approximately 60% from EFK 23.4 to EFK 5.4 in the spring (log[pseudo K_d] = 5.2 versus 4.8, respectively). This decrease in MeHg particle association that coincides with an annual increase in the MeHg concentration in EFPC may have important implications for MeHg bioaccumulation.

In accordance with the patterns described above, MeHgT and MeHgD flux increase with distance downstream. In autumn and winter, the upper reach of the creek contributes more to MeHg flux than does the lower reach of the creek, whereas the opposite is true in spring.
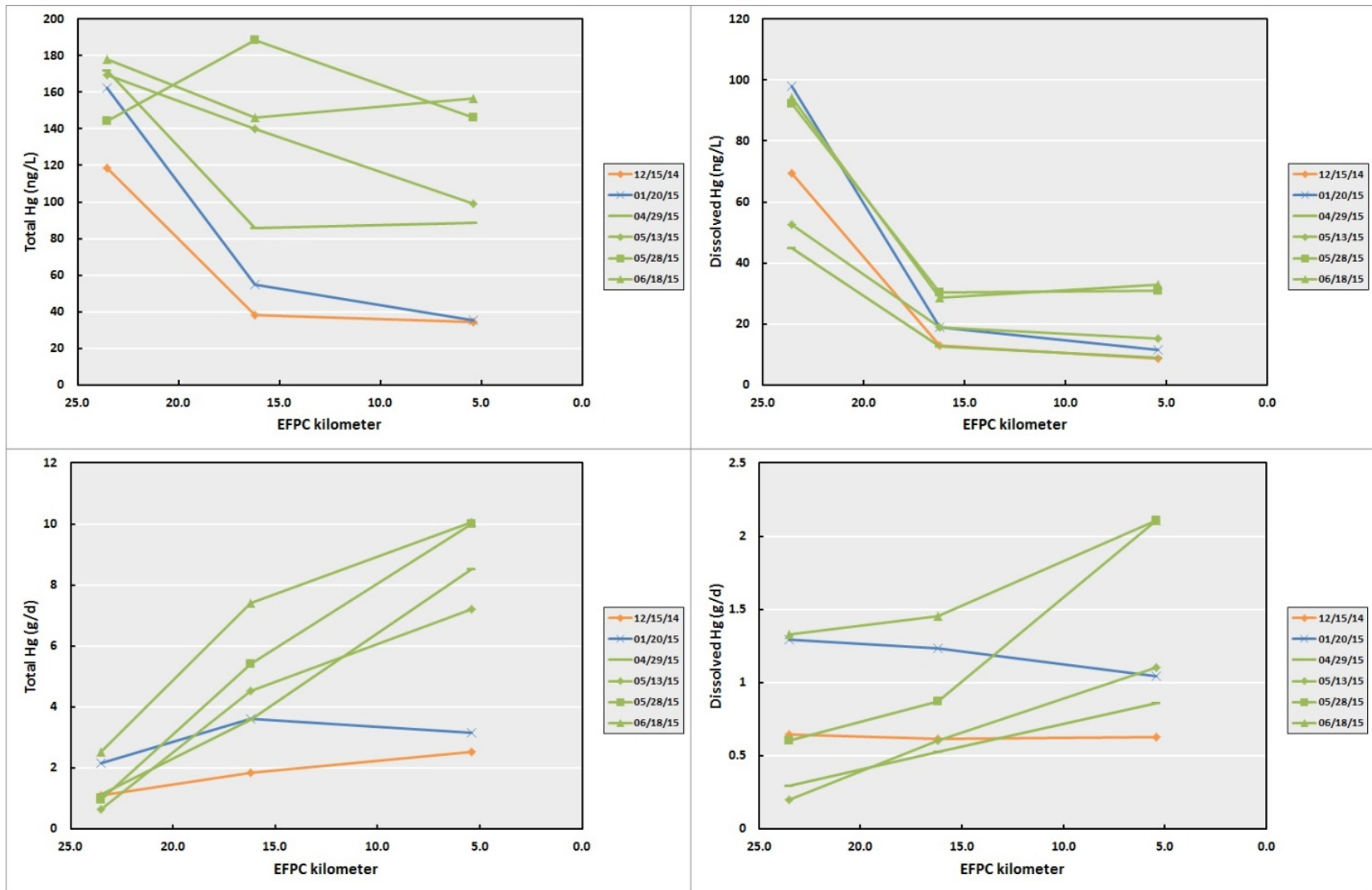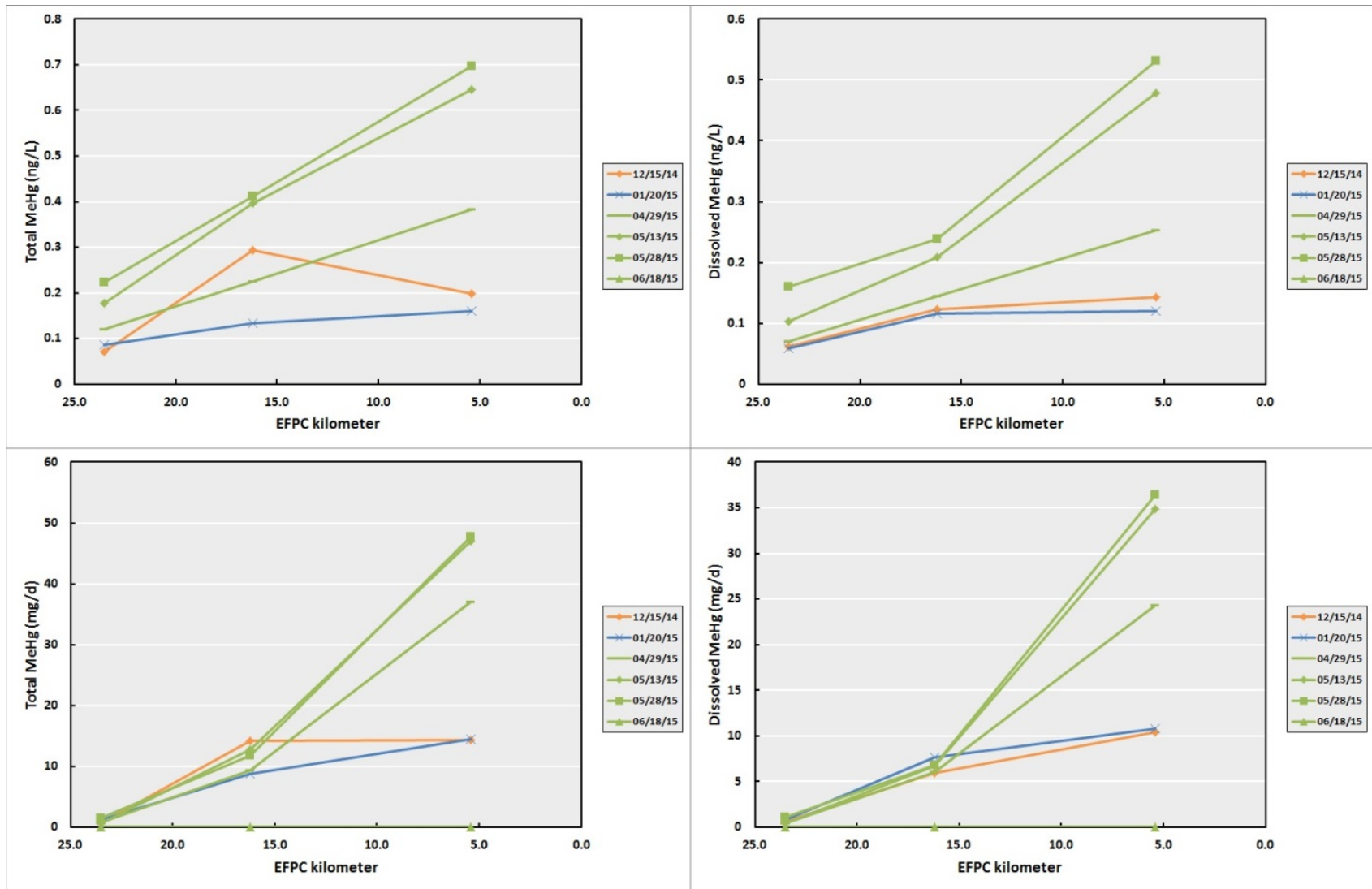
Fig. 29. Total methylmercury (MeHg, left) and dissolved MeHg (right) concentration (top) and flux (bottom) along East Fork Poplar Creek (EFPC).
Colors correspond to the season in which the measurement was made: orange = autumn; blue = winter; green = spring.

3.2 SEDIMENT

3.2.1 Approach to Sediment Investigations

Mercury has a high affinity for particle surfaces including suspended solids in the creek as well as sediments on the bed of the creek. In addition to constituting the greatest fraction of the inventory of mercury in the creek (nearly 90%) (Southworth et al. 2013a), desorption or dissolution of particle-associated mercury can be a long-term source of mercury to the water, confounding those remedial actions designed to improve creek water quality. These mercury-laden sediments move through the creek under base flow and stormflow conditions. Movement of the coarser particles is enhanced under higher flow, but the finer sediments move under both conditions and will be the first to be mobilized on the rising limb of storm hydrographs and the last to deposit as the flood recedes. Additionally, overbank flow can deposit mobilized creek sediments onto the adjacent floodplain.

Total mercury concentration in EFPC sediments and sediment mobility was studied in some detail in the early- to mid-1980s as part of the site-wide remedial investigation (Tennessee Valley Authority 1985a, c), but in the intervening 30 years, there have been few follow-on studies to address how creek sediments have responded to improvements in water quality over that time (specifically, decreasing total mercury concentration in water). Southworth and coworkers (Southworth et al. 2013a; Southworth et al. 2010) sampled creek sediments at 5 km intervals over a 17-km reach of EFPC (EFK 23 to EFK 6) and analyzed the sediments for total mercury (< 1 mm size fraction), operationally defined lability of mercury based on a sequential extraction procedure (< 1 mm), and MeHg (< 125 µm fraction only). The results show a peak in total mercury concentration at EFK 18 (close to the Rocky Top market where Jefferson Avenue meets Oak Ridge Turnpike) with a concentration almost two times that found at the other three locations (34.4 mg/kg versus 17.3 ± 1.2 mg/kg). The results also show that > 98% of the mercury at all sites is only extracted with the more chemically aggressive extractants. MeHg in the sediment fines was higher at the upstream and downstream locations (2.23 µg/kg and 2.75 µg/kg, respectively) and lower at the two intermediate locations (1.53 µg/kg and 1.23 µg/kg). MeHg associated with fine particles may be an important early step in MeHg bioaccumulation because these fine materials are ingested by filter feeders, scrapers, and grazers.

Specific objectives in this initial phase of the sediment work were the following:

- Obtain higher spatial resolution sampling of total mercury in creek sediments as a function of particle size.
- Obtain higher spatial resolution sampling of MeHg in creek sediments as a function of particle size.
- Assess the propensity for mercury to be released from sediments to aqueous phase as a function of sediment particle size.

The general methodology to the sediment investigation is as follows. Bulk creek sediment samples were collected at ~1 km intervals from EFK 5 to EFK 26 following the gradient from lower to higher total mercury in water (i.e., downstream to upstream) between April 22 and May 6, 2015. Samples were wet sieved in the field with ambient creek water. Size fractions retained were 1 mm < x < 2 mm, 250 µm < x < 1 mm, and 125 µm < x < 250 µm, which are referred to here for simplicity as coarse, medium, and fine. Sieved sediments were well mixed, then stored in Ziploc bags at −80°C until further processing and analysis. To prepare materials for analysis, samples were thawed, then freeze-dried. For determination of total mercury, samples were digested in aqua regia, with the supernatant filtered (0.2 µm) and retained for total mercury analysis. Sequential extraction analyses followed the method described by Bloom et al. (2003), which uses a sequence of increasingly aggressive chemical solutions to liberate mercury from the solid phase. The extraction solutions used, in order, are F1: deionized water;

F2: 0.01 M HCl + 0.1 M acetic acid, pH 2; F3: 1 M KOH; F4: 12 M HNO_3; and F5: aqua regia (concentrated HCl: concentrated HNO_3, 10:3). Samples of the fine fraction (125 μm < x < 250 μm) were shipped to CEBAM Analytical, Inc. (Bothell, Washington) for MeHg analysis.

3.2.2   Results of Sediment Investigations

The analysis for total mercury in the coarse and medium fractions has been completed. The fine fraction will have to be reanalyzed because of a potential analytical bias discovered for the instrument used to analyze those samples. Also completed are a few of the sequential extractions, but the majority of those samples are pending. MeHg results for the fine fraction have been received from CEBAM.

Total mercury. Total mercury concentration in sediments in the coarse and medium fractions ranged from 7.6 mg/kg dw to 64 mg/kg dw, and overall results were comparable (coarse geometric mean [mean$_{geom}$] = 18.9 [12–29.6; ± 1 standard deviation], medium mean$_{geom}$ = 17.3 [10.6–28.3]) (Fig. 30). However, mercury in the medium fraction was noticeably higher than in the coarse fraction in upper EFPC (above EFK 23.3). There is a strong longitudinal gradient in mercury concentration with the coarse and medium mercury concentration decreasing 360% and 250%, respectively, over the upper 4 creek km. There appears to be a secondary peak in mercury concentration between EFK 20 and EFK 14 centered on EFK 18–EFK 16.3 for both size fractions. This feature coincides spatially with the extensive HRD that has been found in the bank soils and may reflect local enrichment of the creek sediments with high mercury-bearing soils eroded from the creek banks.
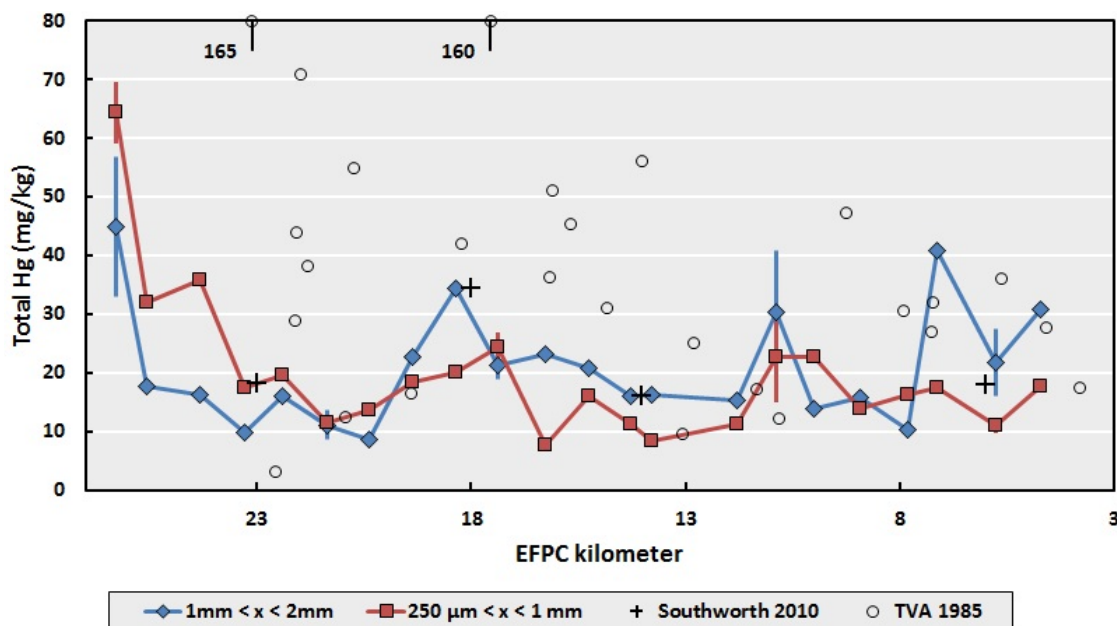
Fig. 30. Total mercury (Hg) in coarse and medium textured creek sediments along East Fork Poplar Creek (EFPC). Variability based on triplicate analyses for samples from EFPC kilometers (EFKs) 26 (near Outfall 200), 21, 17, 11, and 6 is shown by error bars representing ± 1 standard deviation. The "+" symbols indicate results reported by Southworth et al. (2010), and open circles represent results reported by the Tennessee Valley Authority (1985b); symbols at the upper margin of the graph indicate two values from the Tennessee Valley Authority (TVA) that are off the y-axis scale.

Overall, the results are consistent with those of Southworth et al. (2010) but provide more definitive evidence of a downstream "hump" in mercury concentration in the sediments. In addition, both these results and those of Southworth et al. (2010) indicate noticeable improvement in the sediment mercury burden relative to the results from the remedial investigation conducted in the early- to mid-1980s.

Sequential Extraction Results. Sequential extraction analyses are ongoing. Here the results are presented for two samples of the medium size fraction (250 μm < x < 1 mm) collected from EFK 6. For these two samples, the full extraction sequence has been completed, and these results can be compared with a nearby sampling location from Southworth et al. (2010). Early results of the sediment sequential extraction analyses show that less than 1% of the mercury contained in the sediments is easily extracted with relatively mild extractant solutions (F1: DIW or F2: HCl + acetic acid at pH 2). Stated another way, more than 99% of the mercury can be extracted only using more aggressive chemical extractants—1 M KOH, 12 M HNO_3, or aqua regia, with greater than 80% of the mercury removed by the latter two extractants. These results are similar to those of Southworth et al. (2010), although the relative amount of mercury in various fractions differs from current analyses.

The greater amount of mercury in the F3 fraction (1 M KOH) in this analysis is noteworthy. In the original description of this sequential extraction procedure, inorganic mercury extracted in the F3 fraction was most strongly correlated with methylation potential.

Monomethylmercury (MeHg). MeHg on fine creek sediments ranged from 0.5 to 6.5 μg/kg dw (mean$_{geom}$ = 1.6 [0.71–3.4]). Similar to total mercury results, MeHg decreased rapidly in the first few kilometers downstream from EFK 26, then decreased more gradually to EFK 5. These results suggest MeHg may be formed throughout upper EFPC. The pattern in MeHg sediment concentration mirrors that seen in waterborne inorganic mercury (decreases with increasing distance downstream). The pattern in MeHg sediment concentration is the opposite of the pattern in waterborne MeHg, which increases with distance downstream. Visually, there appears to be a secondary peak in MeHg that coincides with the one seen for total mercury, but the variability in the data makes it hard to assess if a real correlation exists. Overall, results are similar to those reported by Southworth et al. (2010), the notable exception being the farthest downstream sample (Figs. 31 and 32). Differences in sample site, processing, and time of sampling all may contribute to this difference.
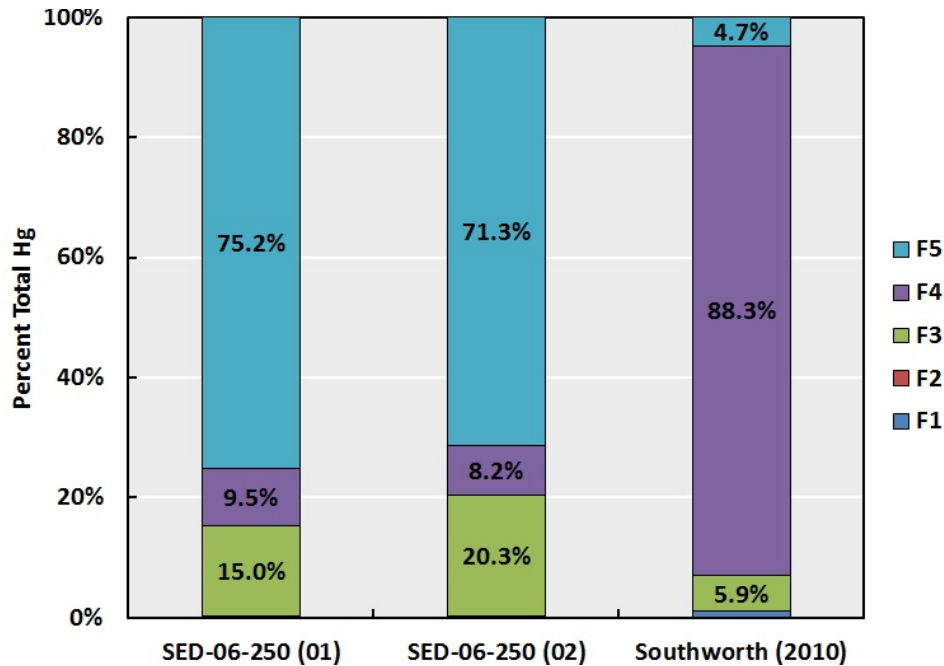
Fig. 31. Percent of total mercury (Hg) extracted from medium-textured sediments (250 μm < x < 1 mm) from ~East Fork Poplar Creek kilometer 6. Data from Southworth et al. (Southworth, G. R., et al. 2010. *Sources of Mercury to East Fork Poplar Creek Downstream from the Y-12 National Security Complex: Inventories and Export Rates*. ORNL/TM-2009/231, Oak Ridge National Laboratory, Oak Ridge, TN.). are shown in the last column for comparison. For all three samples, the vast majority of mercury is released in the last three (more chemically aggressive) extractant solutions. F1 through F5 are defined in Sect. 3.2.1 of this report.
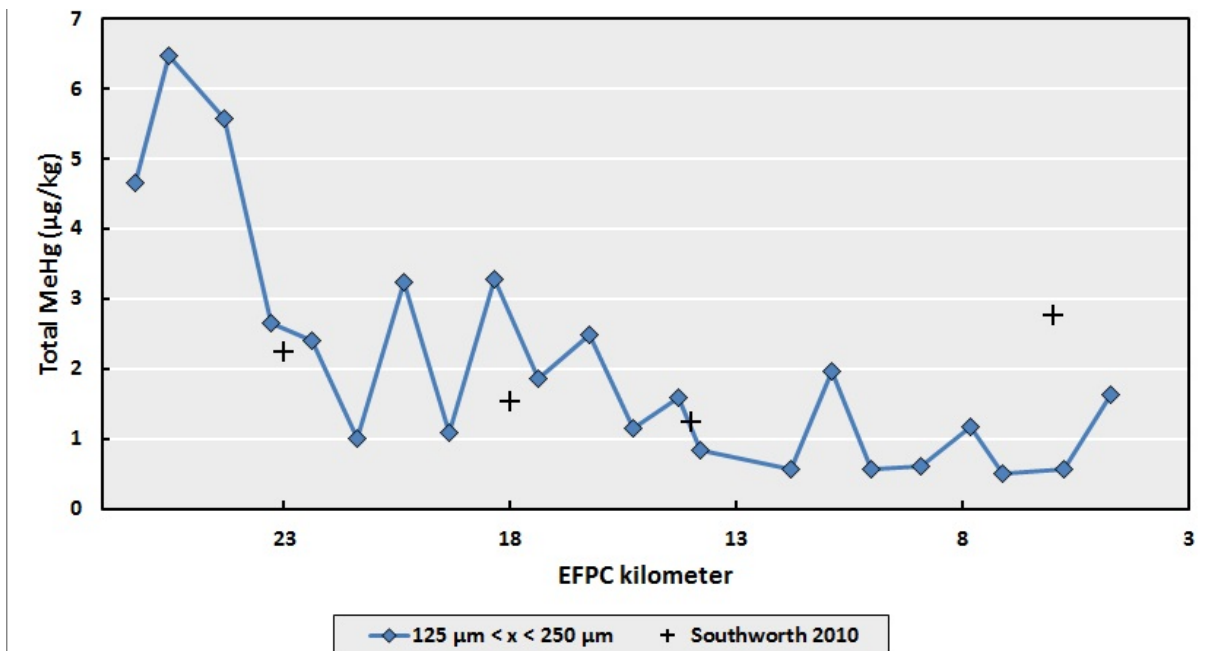
Fig. 32. Methylmercury (MeHg) in the fine sediment fraction (125 μm < x < 250 μm) along East Fork Poplar Creek (EFPC). Blue diamonds and lines are from this sampling effort; the "+" symbols represent MeHg in the < 125 μm fraction reported by Southworth et al. (Southworth, G. R., et al. 2010. *Sources of Mercury to East Fork Poplar Creek Downstream from the Y-12 National Security Complex: Inventories and Export Rates*. ORNL/TM-2009/231, Oak Ridge National Laboratory, Oak Ridge, TN.).

3.3 TASK 2 FUTURE DIRECTIONS

Within UEFPC, various alternatives (Peterson et al. 2015a) to current chemical treatment and discharge methods used in Y-12 industrial processes, in addition to controlled chemical additions and manipulations, are being considered to reduce mercury fluxes and forms that enhance migration of mercury to LEFPC. Because the impacts of some of the numerous chemicals present in UEFPC water (Table 3) on mercury forms and transport are still not that well understood, a systematic phased approach of alternatives identification and evaluation, combined with laboratory- and field-scale experiments, is needed to test and select viable alternatives for implementation. This is particularly true for the large assortment of chemicals currently used for the treatment of cooling tower blowdown water and other intermittent industrial discharges to the storm drains.

Most of the flow in the storm drain system contains residual chlorine because of the discharge of chlorinated process water (drinking water from the City of Oak Ridge water supply system) from various uses (primarily cooling water). Residual chlorine is aggressive in its oxidation and solubilization of mercury, and therefore, the mercury in water exiting Outfall 200 and other outfalls contains reactive dissolved $Hg(II)$. Results show that eliminating or reducing chlorine concentrations in the storm drain system could significantly reduce the amount of soluble $Hg(II)$ produced as chlorinated water comes in contact with liquid $Hg(0)_l$ and dissolved $Hg(0)_d$ and also could reduce the total mercury discharged to LEFPC. Reduction of chlorine concentrations in the storm drain system could be accomplished by conducting dechlorination of the process water before or just downstream of discharge points to the storm drain, especially in areas with $Hg(0)_l$ and dissolved $Hg(0)_d$, and also could reduce the total mercury discharged to LEFPC. Reduction of chlorine contamination is known to exist. Although technologically feasible, this effort would require some operational modifications at Y-12 to achieve its objectives. However, making these changes could have a substantial beneficial impact on the flux and form of mercury leaving Y-12 and is considered a high priority from a cost–benefit perspective.

Future investigations within UEFPC could include the following:

1. Complete current preliminary laboratory and field testing.
    a. Complete preliminary chlorine–$Hg(0)$ oxidation experiments. Expand to include assessment of impacts of other chemicals in the process water including chlorination byproducts, chloride, etc. In other words, determine if removal of just chlorine will have the desired effect of less $Hg(0)$ reduction to $Hg(II)$ or if other chemicals in the water also need to be removed.
    b. Complete preliminary assessment of potential impact of dechlorination chemicals.
    c. Coordinate with Y-12 to sample in one of the outfalls during cooling tower blowdown activities.
2. Continue discussions with Y-12 Utilities and other Y-12 divisions to better understand chemical usage types, quantities and timing of discharges, and institutional capability to alter current systems. Revise tables of chemical usage found in Peterson et al. (2015a) with this information.
3. Based on 1 and 2, develop a plan for additional laboratory testing and creek/storm drain sampling and analysis to assess impacts of chemical additions—especially discharges of chlorine, dechlorination compounds, amines, and intermittent discharges from the cooling towers.
4. Conduct additional sampling and analysis at OF200 and in storm drains, especially when there are releases from cooling towers.
5. Conduct additional laboratory studies to assess potential impacts of Y-12 chemical releases on the magnitude and forms of mercury transported from UEFPC to LEFPC. Confirm which dechlorination chemicals do not enhance $Hg(0)$ oxidation.
6. Conduct preliminary field tests in one of the Y-12 storm drains to assess the effect of dechlorinating at the point of process water release to the storm drain upstream of the known pools of $Hg(0)_l$ in the pipes, instead of downstream at OF200.
7. Prepare a report on phase 2 testing and sampling results.

8. Develop and rank a list of alternatives to reduce mercury fluxes from UEFPC to LEFPC that will result in forms of mercury that are less mobile and biologically available. Some alternatives might require laboratory and field testing before selection and/or implementation (e.g., addition of chemical sequestrates).

Within LEFPC, in the near term, samples will continue to be analyzed that have been collected. Additionally, ongoing efforts will continue to quantify water quality and creek discharge at existing locations. These results are critical to support the evaluation of source areas and fluxes and their considerable spatio-temporal variability. Therefore, it is highly advisable to capture as much of that variability as possible. It will be difficult at best to distinguish real system response to remedial actions from natural variability without a better idea of that variability.

Preliminary sampling conducted in March 2015 indicated intraday variability in the concentration of some constituents along EFPC. Dissolved MeHg concentration was 16% and 20% greater in the afternoon relative to the morning at EFK 23.4 and EFK 5.4, respectively. These samples were collected at a time of year when the system was in transition from winter minima to large springtime increases in concentration, so the samples likely represent conservative estimates of diel variability. A second sampling is planned later this year to quantify intraday variability during a time of year when MeHg concentrations are near their peak. Better understanding of this variability has important implications for source attribution, sampling designs, flux, and exposure calculations.

Finally, the surface water sampling to date has been conducted under base flow conditions. Whereas these data provide important insights into system behavior and a much-needed baseline against which to compare response to remedial actions, most of the flux occurs under short-lived high flow flood events. Sampling of multiple storm events is planned at all three monitoring locations to better understand these flow-driven dynamics along EFPC.

To identify potential areas for stream sediment manipulations, the analysis of total mercury in the fine fraction will be completed, as will the sequential extraction analysis for all the size fractions. Additionally an expansion of the MeHg analyses will include the other two size fractions because this may provide a clearer indication as to whether a secondary hump in MeHg along EFPC occurs and corresponds to the hump seen in total mercury. Early indications from the sequential extractions suggest that mercury is tightly bound to the sediments. Initial mercury desorption experiments will be conducted using a simulated creek water to better understand the potential role contaminated creek sediments may play in buffering aqueous mercury concentration (see "Total mercury" subsection in Sect. 3.2.2) as mercury removal actions are taken. These results will help to delineate which areas need to be targeted and to prioritize the order in which they are addressed (e.g., water only, sediment only, water and sediment simultaneously).

Creek cross sections (Fig. 22) from the Wiltshire Drive station highlight the dynamic reworking of bed sediments. Given the large amount of mercury associated with particles in bed sediments, sediment transport could account for a significant fraction of mercury loading and downstream movement. However, this term currently is poorly constrained. Several actions are proposed to address this lack of understanding in the creek conceptual model and to better quantify this term. Creek sections will be determined at several new locations selected along the creek that leverage existing or planned activities within this and other projects. These new locations will include EFK 5.4 and the three locations along the creek where groundwater wells are planned (approximately EFK 8.1, EFK 18, and EFK 22). Additionally at these locations, installation of a series of scour chains within the creek bed is proposed. Scour chains are used to quantify vertical erosion and aggradation of bed sediment over time. They are the in-stream equivalent to bank erosion pins, which have been employed in other projects (and which are planned under Task 1 of this project) to quantify streambank erosion and deposition. Finally, an evaluation and

selection of methods to quantify the particle size distribution of bedload transport using passive collectors is proposed. These measurements will help to better inform the scientific understanding of in-stream processes contributing to mercury movement and loading and align with a longer-term technology development implementation. Bedload interception can be an effective means of mitigating the downstream migration of contaminated sediment, is far less disruptive to the stream ecosystem, and is substantially less expensive than dredging.

By working cooperatively with other projects, researchers will leverage resources to install and monitor instream piezometers at several locations to measure vertical head gradients across the hyporheic interface. These measurements will indicate the propensity for water movement between surface water and subsurface areas that may be active zones of mercury methylation. Understanding the potential contributions of hyporheic/subsurface water to the surface water MeHg budget is necessary for the evaluation and design of potential sediment-capping remedial strategies.

Finally, discussions have begun with the Task 1 team regarding the results of the sorbent evaluations and ways to apply those results to evaluate sorbent effectiveness when mixed with, or used to cap, creek sediments to reduce mercury and methylmercury release from sediments to the water column. Initial testing likely will occur in the coming year.

4. TASK 3, ECOLOGICAL MANIPULATION

4.1 BIOTA

4.1.1 Approach to Ecological Investigations

In contrast to virtually all other metals, mercury (especially in its organic form, MeHg) biomagnifies, or becomes increasingly concentrated as it is transferred through aquatic food chains, leading to elevated concentrations of this toxin in fish. Because the primary exposure route for mercury in humans and other wildlife is through the consumption of contaminated fish, national guidelines for the protection of human and ecological health include a fish tissue concentration (0.3 ppm MeHg in fish fillet), which is considered to be a more consistent indicator of exposure and risk than aqueous guidelines. Because of this explicit regulatory guideline, remediation actions and research efforts have long focused on understanding and mitigating mercury bioaccumulation in EFPC fish.

The Biological Monitoring and Abatement Program (BMAP) at ORNL has tracked the progress of remediation efforts in EFPC since 1985. Over the past 30 years, bioaccumulation monitoring in EFPC has shown that remediation efforts have succeeded in significantly reducing aqueous HgT concentrations, but these reductions in water concentrations have not affected fish HgT concentrations (Mathews et al. 2013; Southworth et al. 2013b). This disconnect is likely because: (1) mercury bioaccumulation is largely driven by MeHg (not HgT) concentrations, and (2) bioaccumulation of mercury occurs predominantly through food chain (not aqueous) exposure.

Like many other bioaccumulation monitoring programs at mercury-contaminated sites, BMAP has focused on comparing HgT concentrations in fish to ambient water HgT concentrations collected at strategic locations throughout the creek. Although the fish tissue guideline is a MeHg (not HgT) concentration, MeHg is not routinely measured in water or fish in because MeHg analysis can be prohibitive in terms of cost and time, and because previous studies have shown that >90% of the HgT in fish fillets is MeHg. Total mercury concentrations are therefore assumed to be a reasonable proxy for MeHg concentrations in fish fillet in EFPC. Further, previous studies have shown that the length of the food chain leading to fish affects mercury bioaccumulation, where longer food chains offer more opportunities for mercury to biomagnify, leading to higher concentrations in fish (Cabana and Rasmussen 1994). To date, mercury transfer throughout the EFPC food chain has not been characterized, though food web dynamics are likely critical to understanding and explaining observed mercury bioaccumulation patterns in EFPC fish.

The objective of Task 3 is to mitigate mercury transfer to fish by manipulating the aquatic food web in EFPC. This could be achieved, for example, through the addition or removal of key species that can significantly disrupt mercury transfer, or through the manipulation of physical factors (e.g., nutrients, light) that may favor mercury transformation. There is precedent on the Oak Ridge Reservation for the proposed mitigation strategy; ecological manipulations have been implemented previously to mitigate contaminant bioaccumulation, obtaining positive results at a fraction of the cost of traditional remediation methods; e.g., Peterson et al. (2015b).

As with any other remediation technology, a thorough baseline characterization is needed before manipulation to discern the effectiveness of the action. The current understanding of mercury bioaccumulation in EFPC is limited to a few target fish species; however, the BMAP fish and macroinvertebrate community data sets provide valuable information on the food web structures and, therefore, on the potential opportunities for ecological manipulations. By quantifying the mercury transfer within EFPC food webs using historical data and field surveys, the key linkages for mercury transfer and manipulation strategies to decrease that transfer can be identified.

Once field characterization is completed, a detailed food web complete with mercury transfer essentially can provide a road map outlining key focus areas of efficient mercury transfer, which may be amenable to manipulation. From this road map, detailed pilot studies at the mesoscale (e.g., in streamside tanks) are needed to assess the effects of manipulations in the laboratory before field implementation. By conducting studies using DOE's TRL approach, technologies and approaches that have the most merit can move beyond laboratory and field testing to larger-scale pilot testing.

Here presented are the results of the food web characterization studies conducted in FY 2015, obtained through both the analysis of historical BMAP community structure data and targeted field sampling. Also presented are the results of investigatory studies to examine the effects of mussel additions on mercury removal from EFPC.

4.1.1.1 Site and Community Characterization

Field surveys were conducted in the summer of 2014 and the spring of 2015 to characterize mercury/methylmercury bioaccumulation and trophic transfer throughout the food chain at sites along EFPC. Invertebrates and fish were targeted in separate sampling events. Periphyton, sediment, water, and TSS samples were taken during invertebrate surveys, as well as monthly beginning in January 2015. Historical BMAP data were used to inform the selection of species from each site along EFPC.

During each field survey, as well as monthly beginning in January 2015, water, sediment, periphyton, and TSS were collected from four sites along EFPC—EFKs 23.4, 18.2, 13.8, and 6.3. A fifth site, EFK 24.5, was added in April 2015. Water grab samples were taken at each site in acid-washed, high-density polyethylene containers and transported on ice to ORNL. Filtered (0.2 μm) and unfiltered water samples were frozen until further analysis. At each site, two to four rocks were collected in plastic containers with stream water and transported to ORNL on ice. In the laboratory, each rock was scrubbed with a small brush to remove periphyton, and samples were frozen until further analysis. Estimates of the periphyton-covered surface area of each rock were calculated by wrapping the scrubbed portion of each rock in aluminum foil, tracing the outline of the scrubbed portion, and cutting out the shape. Sediment samples were collected in glass jars at each site and transported to ORNL on ice. All water, periphyton, and sediment samples were processed and analyzed for mercury and methylmercury. Samples of periphyton, sediment, and TSS (collected from water samples) were analyzed by continuous flow isotope ratio mass spectrometer at the University of California, Davis, to determine the relative abundance of stable isotopes of carbon and nitrogen ($\delta^{13}C$ and $\delta^{15}N$). Periphyton samples were measured with a fluorometer for chlorophyll content and visually for community composition.

In August 2014, the focus of the invertebrate field survey was to collect large numbers of dominant species from each EFPC and reference site to compare mercury/methylmercury bioaccumulation in the same species across sites. Sites sampled included EFKs 23.4, 18.2, 13.8, and 6.3, as well as a reference site, Hinds Creek kilometer 20.6. Clams (*Corbicula fluminea*; the invasive Asiatic clam) were collected from sandy areas of the stream bottom within each stream site, snails were picked off rocks, and other invertebrates (crayfish, flat-headed mayflies [family Heptageniidae], and net-spinning caddisflies [family Hydropsychidae]) were collected in a kicknet after agitating substrate within stream riffles. Invertebrates were sorted in the field and kept in containers with stream water on ice until arrival at ORNL. In the laboratory, invertebrates were rinsed with deionized water and frozen at −20°C. Some invertebrates were not present at all sites or not present in sufficient numbers to carry out analyses; therefore, they are not represented in the dataset.

The goal of the May 2015 invertebrate field survey was to collect species that represent the food chain at each sampling site. The same sites were sampled as above, along with one additional site—EFK 24.5. Invertebrate groups sampled in August 2014 were collected using methods described above. Additional

invertebrate species were collected using methods described above, as well as by sampling new substrate (e.g., roots along the streamside) with a kicknet. In the laboratory, efforts were made to obtain replicates of species groups with sufficient body mass as well as to split invertebrates into different size classes.

All invertebrates with adequate sample mass were analyzed for total mercury and methylmercury. Stable isotope ratios were measured at the University of California, Davis, by continuous flow isotope ratio mass spectrometer. All aquatic insect samples were freeze-dried before further analysis. Only soft tissue was analyzed for clams. Only soft tissue was analyzed from snails collected in August 2014, but whole bodies (soft tissue + shell) were analyzed from snails collected in May 2015. Crayfish were filleted—only tail muscle was analyzed for crayfish collected in August 2014, and both tail muscle and carcass were analyzed separately in crayfish collected in May 2015.

Fish were collected throughout the summer of 2014 and spring of 2015 from the sites listed above. In August 2014, largescale stonerollers (*Campostoma oligolepis*), striped shiners (*Luxilus chrysocepahalus*), redbreast sunfish (*Lepomis auritus*), and rock bass (*Ambloplites rupestris*) were collected for mercury, methylmercury, and stable isotope analyses. These species each have different feeding strategies and thus obtain mercury (and methylmercury) from different diets. The spring 2015 survey focused on collecting the most abundant/ecologically important species at each site.

In both surveys, fish were obtained by electroshocking and brought to the laboratory on ice. In the laboratory, efforts were made to obtain replicates of species groups with sufficient body mass as well as to split fish of the same species into different size/age classes. Lengths and weights of each individual fish were recorded. Fillets of larger fish (e.g., rockbass, redbreast) and whole bodies of smaller fish (e.g., shiners, stonerollers) were used for analysis. Tissue was freeze-dried and analyzed for mercury, methylmercury, and stable isotopes using methods described above.

4.1.2   Results of Ecological Investigations

4.1.2.1   Periphyton surveys

Across sites, variability in total mercury and methylmercury concentrations in periphyton was high (Table 4). In general, methylmercury concentrations at each site were highest in May, and methylmercury concentrations followed the pattern May > April > March. This pattern tracks with temperature. There was not a clear pattern with total mercury measurements in periphyton over time. Across sites, periphyton collected from EFK 13.8 generally had the highest average MeHg concentrations of any site. Upstream sites (EFKs 24.5 and 23.4) generally had the highest concentrations of total mercury. Analysis of mercury, methylmercury, and stable isotope concentrations in periphyton is ongoing.

Table 4. Total mercury (Hg) and methylmercury (MeHg) concentrations in periphyton samples collected and analyzed thus far from monthly and seasonal surveys of East Fork Poplar Creek

EFK Site	Total Hg ppm (sd)			MeHg ppb (sd)		
	March	April	May	March	April	May
24.5	N/A	N/A	22.4 (9.8)	N/A	N/A	6.3 (1.1)
23.4	16.1 (7.3)	19.6 (20.2)	11.0 (5.1)	3.4 (1.4)	3.4 (2.1)	7.5 (3.3)
18.2	6.1 (0.5)	6.9 (2.1)	24.1 (3.5)	3.6 (0.5)	9.5 (6.0)	19.2 (2.7)
13.8	7.4 (0.9)	8.8 (0.9)	14.7 (9.5)	5.6 (1.2)	14.0 (0.6)	18.2 (11.2)
6.3	6.1 (2.1)	6.7 (0.7)	N/A	3.8 (1.2)	3.3 (0.8)	16.3 (3.7)

Notes: EFK = East Fork Poplar Creek kilometer; ppm = parts per million; sd = standard deviation; ppb = parts per billion; N/A = not applicable.

4.1.2.2 Invertebrates and fish surveys

Mercury and methylmercury concentrations within the different invertebrate groups collected in August 2014 varied across taxonomic groups but also varied spatially across sites (Fig. 33). Of all invertebrate groups, crayfish (medium and large, >15 mm carapace) had the highest concentrations of MeHg across sites. Mollusks (snails and clams) had the next highest levels of MeHg, followed by aquatic insects (caddisflies and mayflies). Clams, by far, had the highest levels of total mercury across sites, likely due to their filtering feeding strategy. EFK 13.8 had the highest MeHg concentrations of all sites across invertebrate species groups. In general, the trend for MeHg concentrations followed EFK 13.8 > EFK 6.3 > EFK 18.2 > EFK 23.4. Trends in total mercury concentrations across sites were less obvious.

Methylmercury and mercury concentrations in fish species varied across groups and across sites in summer 2014 (Fig. 34). Rock bass, a predatory fish, had the highest MeHg and total mercury concentrations of any fish species tested, with the highest concentrations measured at EFK 6.3 (no rock bass were collected at EFK 13.8). Total mercury and methylmercury concentrations in redbreast sunfish were highest at EFK 13.8 (no redbreast were collected at EFK 23.4). Shiners and stonerollers showed similar patterns in mercury and methylmercury concentrations, with the highest total mercury concentrations present at EFK 23.4 and the highest MeHg concentrations present at EFK 13.8 (no shiners or stonerollers were collected at EFK 18.2).

Stable isotope ratios of carbon ($\delta^{13}C$) and nitrogen ($\delta^{15}N$) were measured for samples collected in summer 2014 (Fig. 35). Ratios of nitrogen can be used to reconstruct the food web of each site because increases in $\delta^{15}N$ signify movement up the food chain. As $\delta^{15}N$ increased at EFK 18.2, the percent of total mercury as methylmercury increased across species groups. Thus, rockbass, the top predatory species of EFPC, had the highest $\delta^{15}N$ and the highest percent of total mercury as MeHg. Because of the limited number of species sampled in 2014, as well as data gaps where certain species were not present at a site, complete food webs have not been constructed. The dataset provided by the spring 2015 sampling effort will be sufficient for this construction.
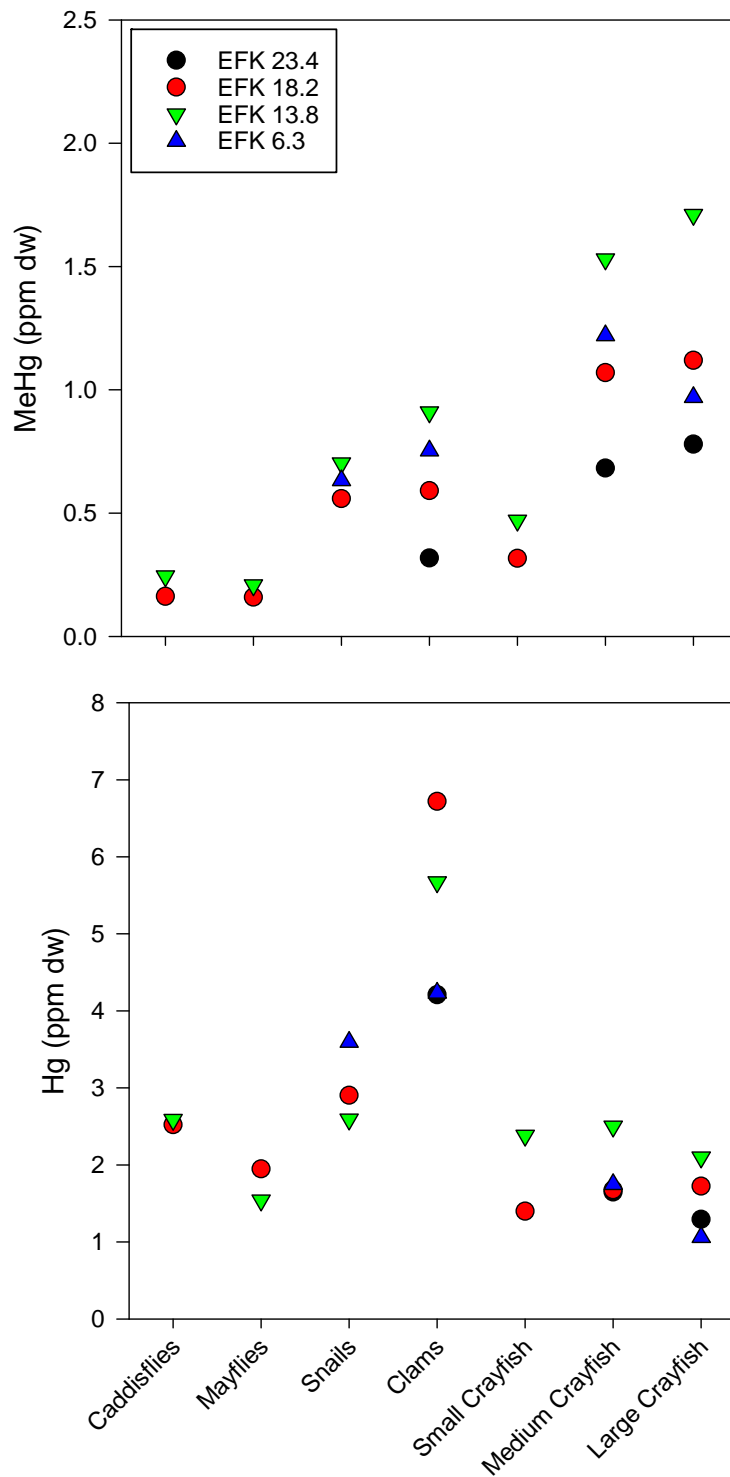
Fig. 33. Methylmercury (MeHg; top) and total mercury (Hg; bottom) concentrations in different invertebrate groups collected from various East Fork Poplar Creek kilometer (EFK) locations. All concentrations are on a dry weight (dw) basis.
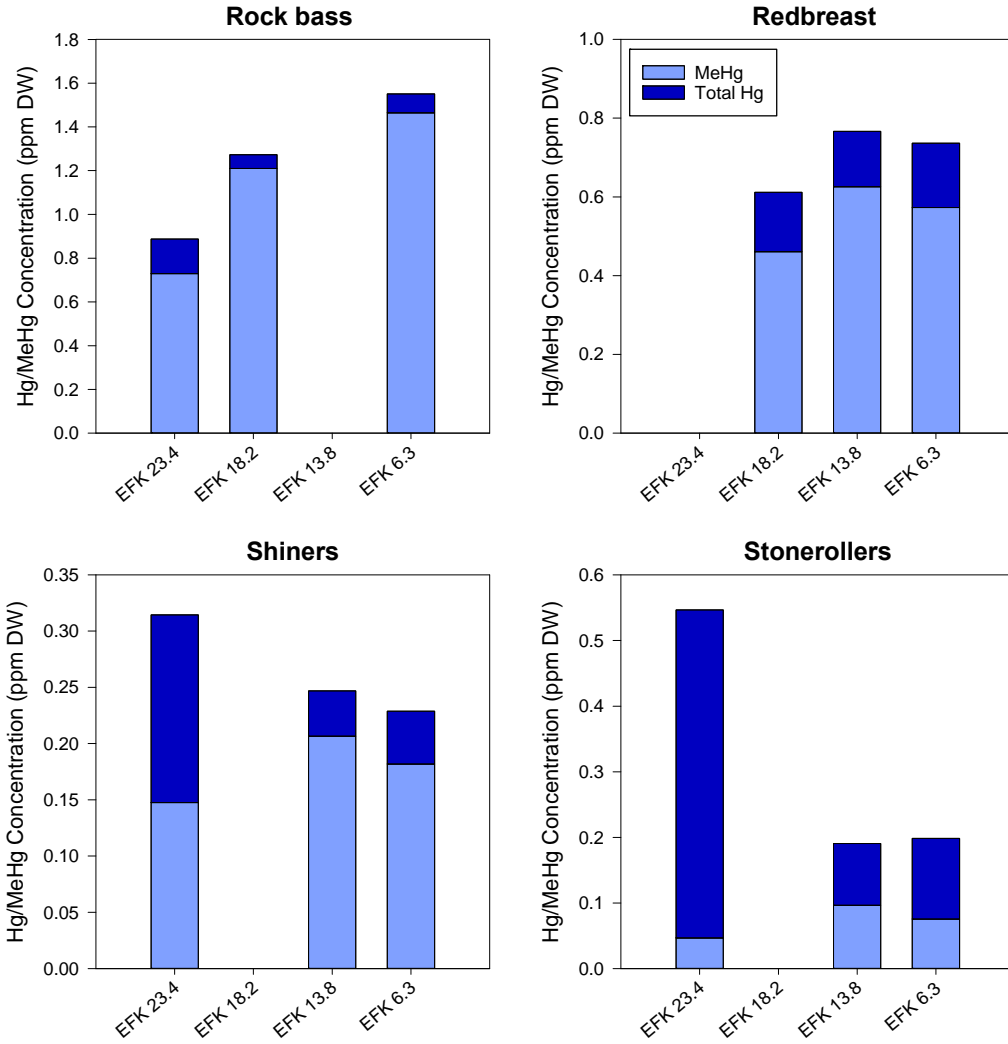
Fig. 34. Methylmercury (MeHg) and mercury (Hg) concentrations in four species of fish collected in summer 2014 from various East Fork Poplar Creek kilometer (EFK) locations. All concentrations are on a dry weight (dw) basis. Rock bass and redbreast sunfish concentrations are of fillets; shiner and stoneroller concentrations are of whole body.
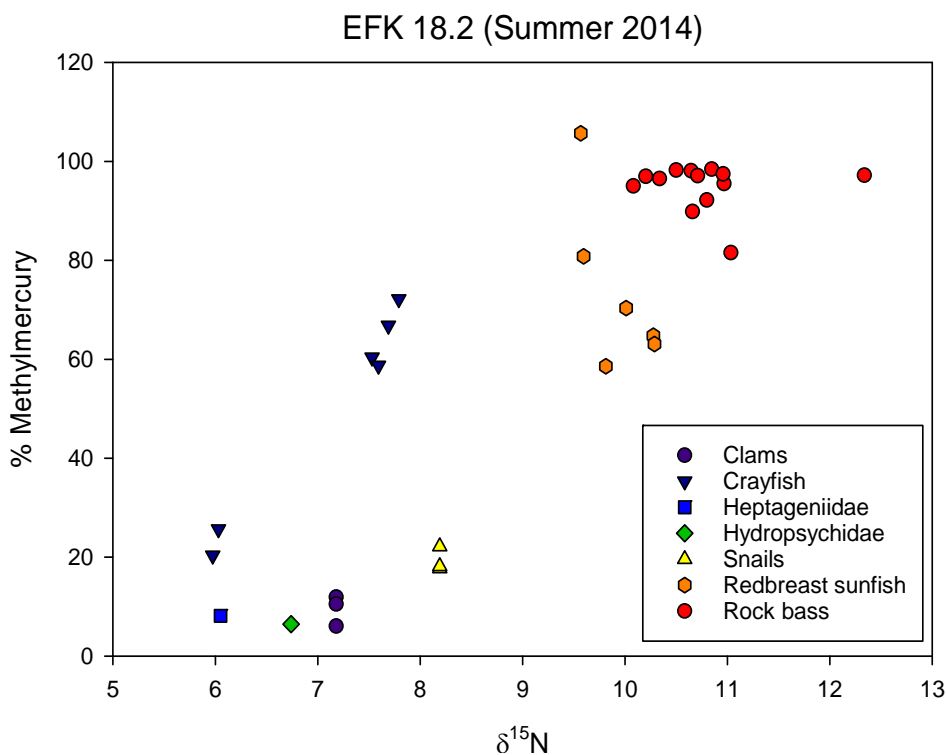
Fig. 35. The percentage of total mercury as methylmercury in species collected at East Fork Poplar Creek kilometer (EFK) 18.2 in summer 2014.

During spring 2015 field surveys, 20 species of fish and 19 invertebrate families were collected from five sites (Table 5). Mercury and methylmercury concentrations and stable isotope ratios currently are being analyzed. Because of the extensive processing time for samples and turnaround time for sample analyses, few complete datasets are available as of yet.

Table 5. Breakdown of invertebrate and fish samples collected during the spring 2015 sampling effort on East Fork Poplar Creek

Group	Diversity	Number of individuals	Number of samples	Analyses
Fish	20 species	1,017	185	Stable isotope, HgT, MeHg
Invertebrates	19 families	4,012	287	Stable isotope, HgT, MeHg

Notes: HgT = total mercury; MeHg = methylmercury.

Clams collected during the May 2015 sampling events had significantly varied total mercury and methylmercury concentrations (Fig. 36). Clams from EFK 24.5 had the highest total mercury concentrations of any site ($p < 0.0001$). Clams from EFKs 23.4 and 18.2 had significantly higher mercury concentrations than clams from EFKs 13.8 and 6.3 ($p < 0.05$). Methylmercury concentrations were highest at EFK 13.8 ($p < 0.0001$). EFK 18.2 clams had higher MeHg concentrations than clams at EFKs 24.5, 23.4, and 6.3 ($p < 0.0001$). Methylmercury concentrations in clams did not differ among EFKs 24.5, 23.4, and 6.3.
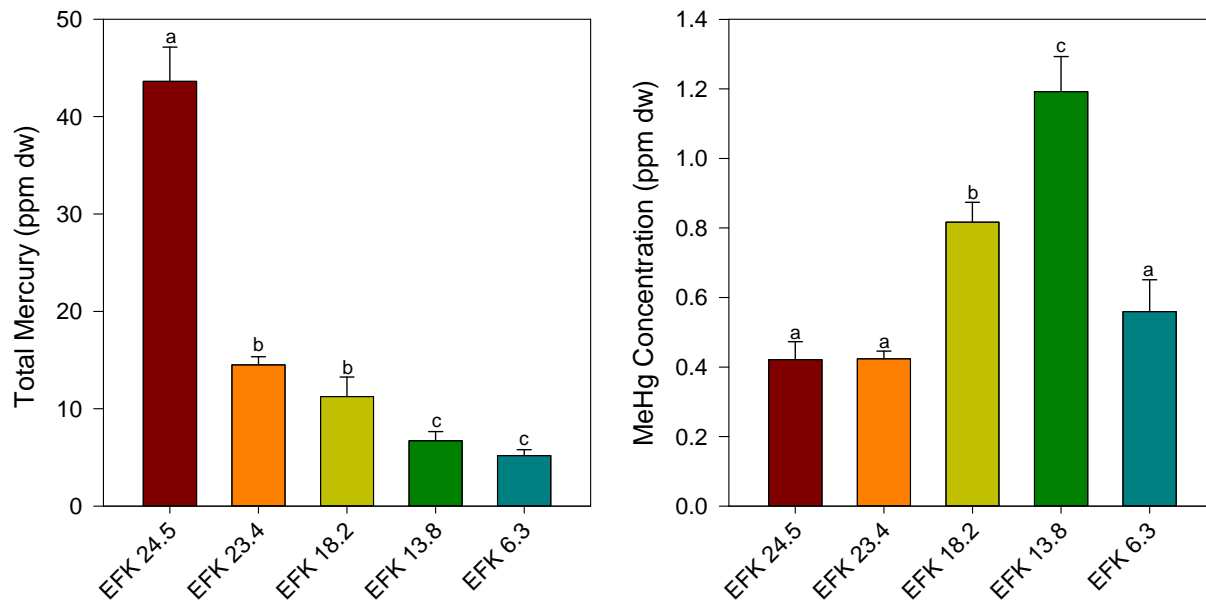
Fig. 36. Total mercury and methylmercury (MeHg) concentrations in *Corbicula fluminea* collected as a part of the May 2015 sampling event on various East Fork Poplar Creek kilometer (EFK) locations. Concentrations are on a dry weight (dw) basis. Bars are mean concentrations, whereas error bars are standard deviation. Different letters signify significant differences.

For invertebrates, six feeding groups were represented across sites. Predators sampled included dragonflies (Aeshnidae, Gomphidae), damselflies (Calopterygidae, Coenagrionidae), and alderflies (Megaloptera). Omnivores are organisms that eat other living organisms as well as scavenge, and those sampled included only small crayfish (< 50 mg, whole body analyzed) and larger crayfish (tail muscle analyzed). Collector–filterers filter organic matter from the water column, and those sampled included clams (*Corbicula fluminea*) and caddisflies (Hydropsychidae). Collector–gatherers scavenge organic matter from the streambed and sediment; those collected included blood worms (Chironomidae) and worms (Oligochaeta). Scrapers eat periphyton off rock surfaces, and those collected include snails, mayflies (Heptageniidae), and water pennies (Psephnidae). Shredders eat terrestrial leaves, and those collected included small crustaceans (Amphipoda) and crane flies (Tipulidae).

Total mercury concentrations in invertebrates were very different across sites, species, and feeding groups (Fig. 37). Overall, total mercury concentrations decreased from upstream to downstream sites. Chironomids and oligochaetes, both sediment-dwelling collector–gatherers, and *Corbicula fluminea*, collector–filterer clams, had the highest total mercury concentrations of all invertebrates at each site. Methylmercury concentrations in invertebrates varied across site and across species group (Fig. 38). In general, methylmercury concentrations increased with farther distance downstream. Scrapers, the invertebrates that eat periphyton off rocks, generally had the lowest MeHg concentrations. The MeHg concentrations of predators were generally higher than other non-predatory invertebrates. Crayfish had the highest MeHg concentrations of any invertebrate, though these concentrations are in tail muscle only and not in whole body samples. Future analyses will determine whole body methylmercury and mercury concentrations in crayfish.

Fig. 37. Total mercury (Hg) concentrations in collected macroinvertebrate species at four selected East Fork Poplar Creek kilometer (EFK) sites. Each symbol represents a separate sample from a given site. All concentrations are in dry weight (dw). Two-letter abbreviations in the legend are feeding strategies: PR = predator; CF = collector–filterer; CG = collector–gatherer; SC = scraper; OM = omnivore; SH = shredder.
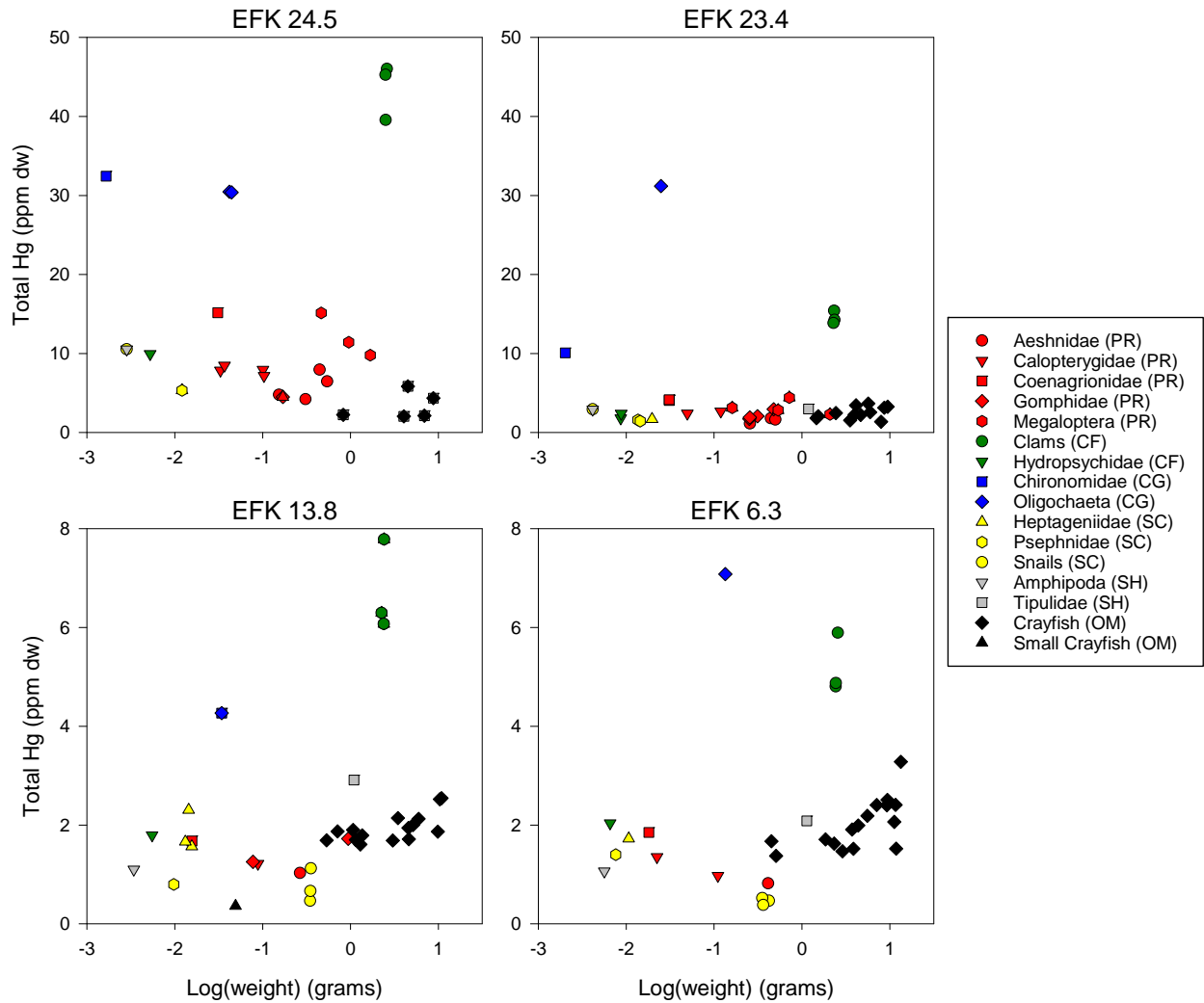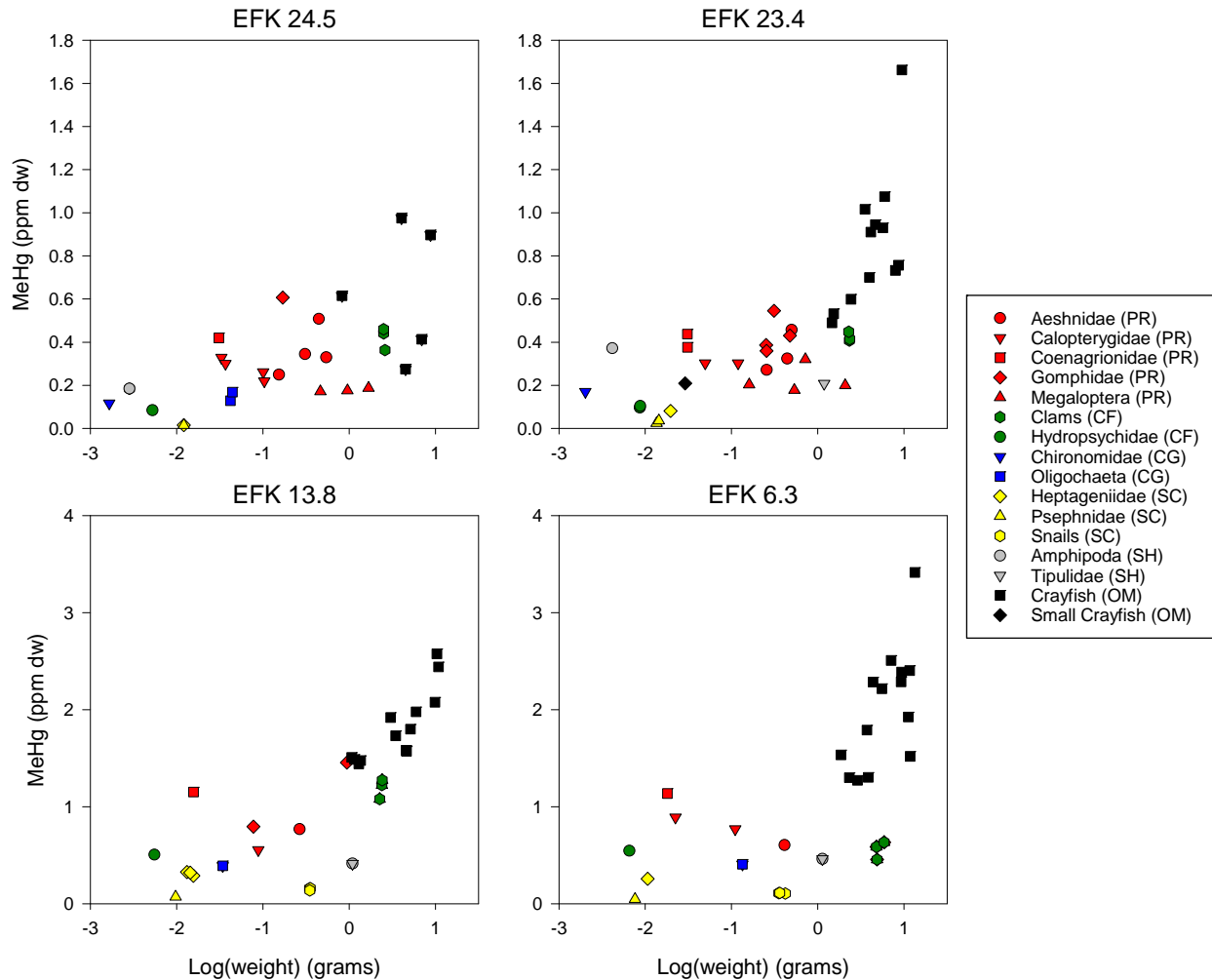
Fig. 38. Methylmercury (MeHg) concentrations in collected macroinvertebrate species at four selected East Fork Poplar Creek kilometer (EFK) sites. Each symbol represents a separate sample from a given site. All concentrations are in dry weight (dw). Two-letter abbreviations in the legend are feeding strategies: PR = predator; CF = collector–filterer; CG = collector–gatherer; SC = scraper; OM = omnivore; SH = shredder.

Feeding groups exhibited differing patterns in the percentage of total mercury in their bodies as methylmercury (Table 6). Crayfish (omnivores) had the highest percent of MeHg of any group across all sites. Collector–gatherers generally had the lowest percent of MeHg of the invertebrates. The percent of MeHg generally increased in invertebrates with increasing distance downstream. However, across six feeding groups, EFK 13.8 had the highest percent of MeHg in three groups, EFK 6.3 had the highest percent of MeHg in two groups, and EFK 18.2 had the highest percent of MeHg in one group.

Table 6. Average percent of total mercury as methylmercury (MeHg) in different feeding guilds of invertebrates across various East Fork Poplar Creek kilometer (EFK) sites

Site	Average percent of MeHg					
	Scraper	Collector–filterer	Collector–gatherer	Shredder	Omnivore	Predator
EFK 24.5	0.29	0.94	0.45	1.75	23.90	4.59
EFK 23.4	2.95	3.67	1.69	9.79	34.09	14.90
EFK 18.2	16.58	7.73	N/A	N/A	99.27	43.42
EFK 13.8	18.69	20.47	9.17	14.21	88.16	67.39
EFK 6.3	18.41	14.80	5.75	22.16	94.26	70.09

Fish species analyzed thus far have shown patterns in mercury and methylmercury bioaccumulation similar to those seen in the previous sampling event. As fish are sampled farther and farther downstream (EFK 24.5 to EFK 6.3), the percentage of total mercury that is methylmercury increases (Fig. 39). With a complete data set, species comparisons—as well as comparisons across different feeding strategies and age classes—will be possible.
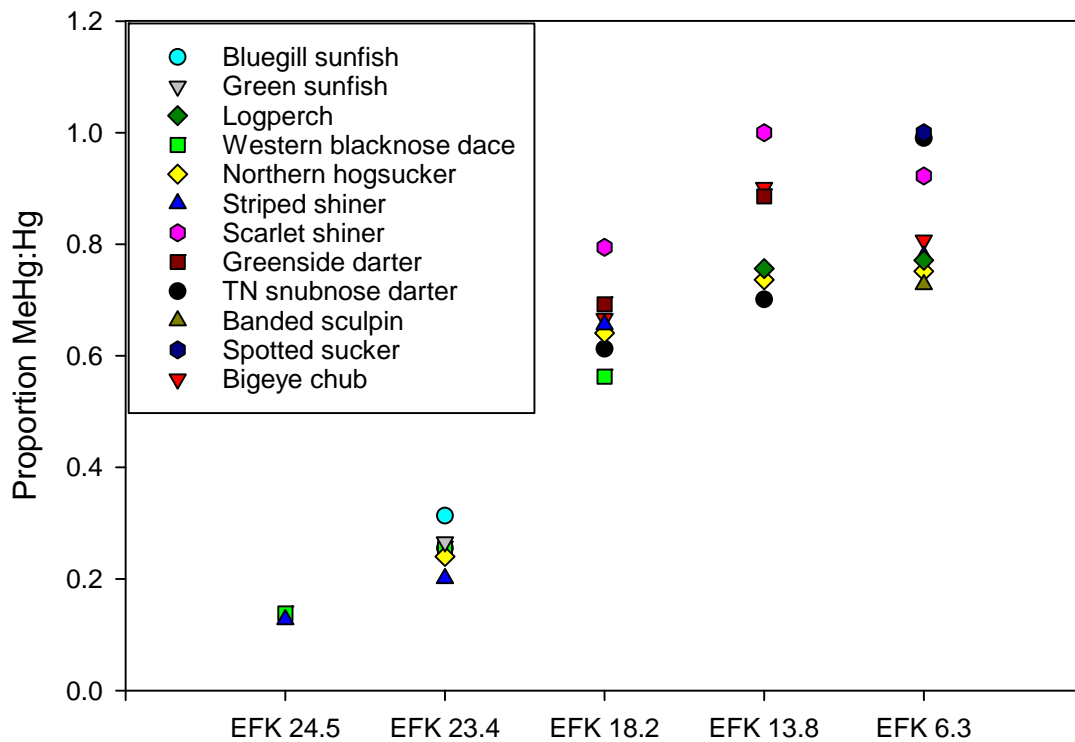

Fig. 39. Ratio of methylmercury:mercury (MeHg:Hg) in fish collected at each East Fork Poplar Creek kilometer (EFK) site during spring 2015. Each symbol represents the mean MeHg:Hg proportion at a given site for a different fish species. This represents fish results obtained thus far; some species have not been analyzed yet.

4.1.2.3   Historical Community Analyses

All available BMAP invertebrate and fish community data were obtained to examine spatial and temporal trends in community structure in EFPC. For invertebrate community analysis, included data were from spring (April) and fall (October) surveys from 1986 to 2013. Surveys performed outside of the 2 months examined were not included in analyses. For spatial comparisons, two sites were examined along EFPC—EFKs 23.4 and 13.8. For temporal comparisons, 3-year composites (1988–1990, 1999–2001, 2010–2013) were formed to account for year-to-year variability. Invertebrates were divided into species groups (e.g., order or family), and feeding guilds—scrapers (grazers), collector–filterers, collector–gatherers, predators, and shredders. Feeding guilds were determined for insects using the literature (Poff et al. 2006; Zhang et al. 2008) and personal observations. All analyses for fall and spring were kept separate because of the short life spans of many of the invertebrates in the communities. Because of year-to-year variability, when making comparisons between the two sites, means of three generally consecutive years were used as replicates. The three periods analyzed include 1988–1990, 1999–2001, and 2010/2012/2013. For fish community analysis, species were divided into taxonomic groups, feeding guilds (e.g., primary, secondary, tertiary consumers), size classes, and trophic levels using the literature and personal observations. Temporal and spatial analyses of fish community trends are ongoing.

From 1985 to 2013, total genera richness increased at both the upstream (EFK 23.4) and downstream (EFK 13.8) sites in both spring and fall seasons (Fig. 40). In the spring, average genera richness at EFK 23.4 increased from 5.2 to 27.0 genera, and average genera richness increased from 12.6 to 34.0 genera in EFK 13.8. Average genera richness in the fall increased from 6.8 to 26.8 genera at EFK 23.4 and from 14.2 to 29.0 genera at EFK 13.8. Thus, whereas both sites experienced increases in genera richness, EFK 13.8 typically had more genera than EFK 23.4. Likewise, Ephemeroptera, Plecoptera, and Trichoptera (EPT) genera richness also increased at each site over time in both spring and fall. In the spring, average EPT genera richness increased from 0.2 to 8.5 genera at EFK 23.4 and from 2.4 to 10.5 genera at EFK 13.8. In the fall, average EPT genera richness increased from 0.6 to 8.3 genera at EFK 23.4 and from 4 to 10.3 genera at EFK 13.8.
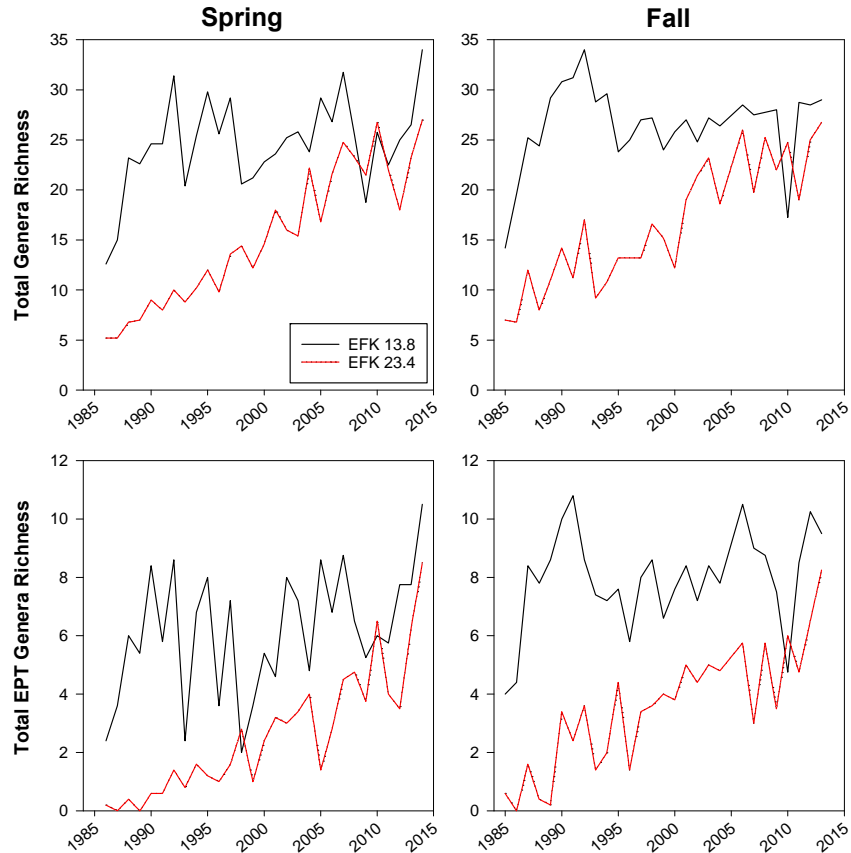
Fig. 40. Total genera richness and total Ephemeroptera, Plecoptera, and Trichoptera (EPT) genera richness over time at upstream (East Fork Poplar Creek kilometer [EFK] 23.4) and downstream (EFK 13.8) sites. Spring (left) and fall (right) seasons were analyzed separately.

The feeding guild compositions of invertebrate communities have changed spatially and temporally (Fig. 41). Spring communities at both EFK 13.8 and EFK 23.4 were dominated by collector–gatherers during each period examined (1988–1990, 1999–2001, and 2010–2013). At EFK 23.4 over the examined periods, collector–gatherers accounted for 95%, 91%, and 92% of the insects within the site, respectively, and chironomids accounted for the majority of species analyzed ($\geq$ 82%). At EFK 13.8, collector–gatherers accounted for 87%, 87%, and 85% of the individuals over the analyzed periods, respectively. Spatially, collector–gatherers accounted for a higher percentage of the spring communities at EFK 23.4 than at EFK 13.8 during each period. The percentage of scrapers in EFK 23.4 invertebrate spring communities hasn't changed substantially over time (3.2, 2.3, and 3.6% community makeup across time periods); however, the predominant scraper species group present shifted from snail to water beetle. At EFK 13.8, the percentage of scrapers in spring communities has increased from 4.6 to 8.0%, and the makeup has shifted from predominately water beetles to a higher percentage of mayflies. Collector–filterers made up less than 6% of each period examined at each site.
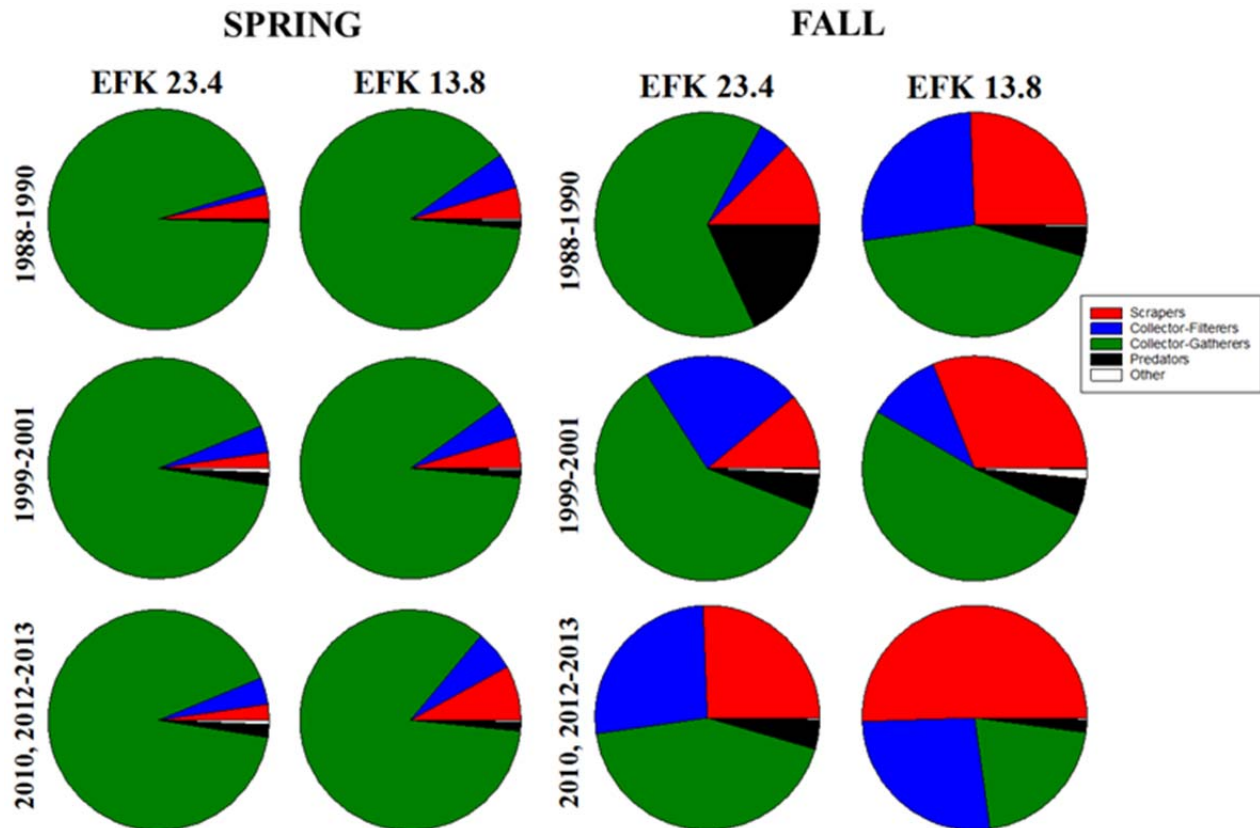
Fig. 41. Analysis of feeding guilds present in the invertebrate communities of upstream (East Fork Poplar Creek kilometer [EFK] 23.4) and downstream (EFK 13.8) sites of East Fork Poplar Creek. Analyses for each season (spring and fall) were separate. Three-year composites were used to calculate percentages of each feeding strategy present.

Fall communities were much more diverse in feeding guilds than spring communities were. Dominance of collector–gatherers in EFK 23.4 decreased from 64% to 43% across the periods examined. During these same periods at EFK 23.4, the mean percentage of scrapers more than doubled (from 12% to 26%), and the mean percentage of collector–filterers increased by a factor of 6.5 (from 4% to 26%). In recent years, the species groups that dominate EFK 23.4 riffles are collector–filterer caddisflies (24%), collector–gatherer chironomids (26%), and scraper beetles (20%). At EFK 13.8, the presence of collector–gatherers trended downward over time (from 41% to 19%). During the same period, the percentage of scrapers increased from 29% to 51%, and the mean percentage of collector–filterers slightly increased from 23% to 27%. In recent years, the species groups that dominate EFK 13.8 riffles are scraper mayflies (37%) and collector–filterer caddisflies (25%).

Figure 42, created with BMAP data, shows that the species richness of both fish and benthic macroinvertebrates is greater at downstream locations than it is at upstream locations, suggesting a more complex food web in LEFPC than in UEFPC. More steps within a food web allow for greater mercury biomagnification from primary producers to the top predatory species. This, along with the spatial trends in aqueous MeHg concentrations in EFPC, could explain the trends in fish mercury concentrations throughout the creek. Whereas controlling MeHg production may not be a realistic goal with the current understanding of mercury methylation dynamics, manipulating the food web structure to encourage the colonization of lower trophic level fish may be more achievable on timescales relevant to remediation

decisions. This would provide an opportunity for decreased mercury bioaccumulation and potentially decreased ecological and human health exposure and risk.
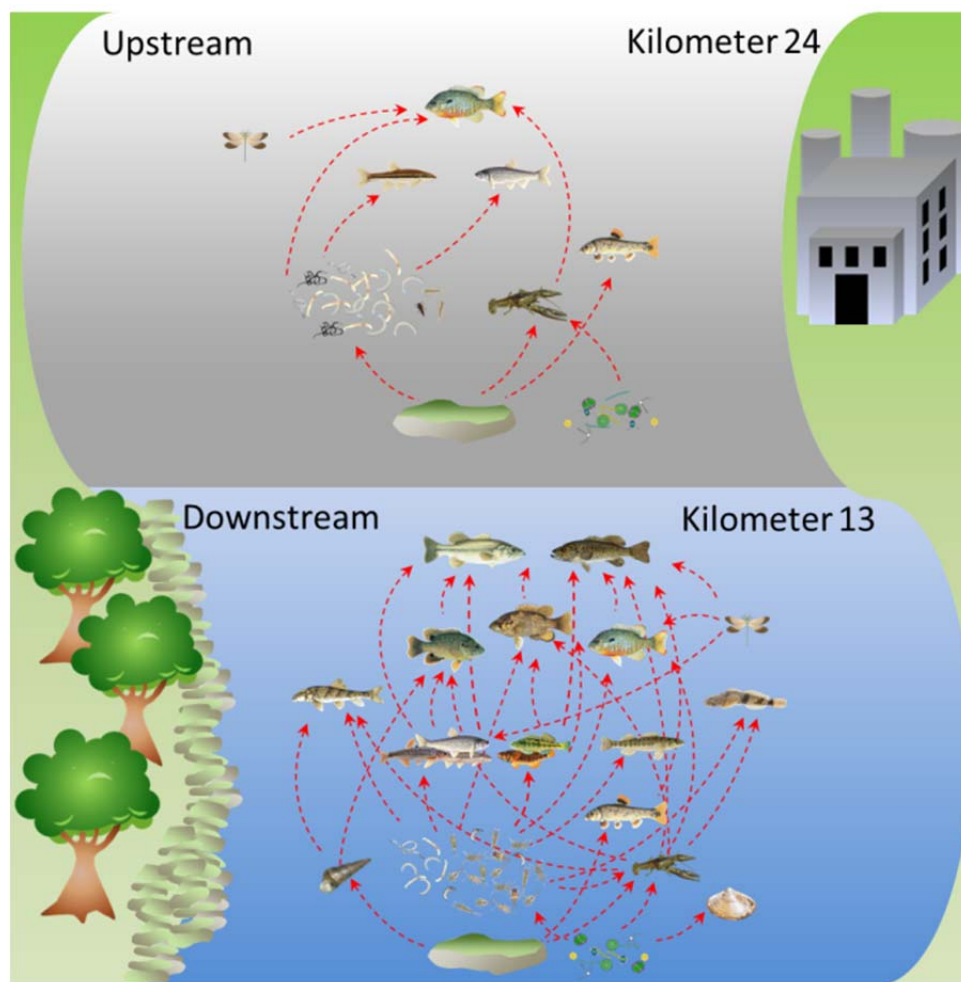

Fig. 42. Schematic representation of food webs at upstream (East Fork Poplar Creek [EFPC] kilometer [EFK] 24) and downstream (EFK 13) sites of EFPC. More complex food webs mean more opportunity for mercury biomagnification within the food web. (*Source:* Peterson, M. J., S. C. Brooks, T. J. Mathews, M. Mayes, A. Johs, D. B. Watson, M. D. Poteat, and E. Pierce. 2015. *Mercury Remediation Technology Development for Lower East Fork Poplar Creek*. ORNL/SPR-2014/645, Oak Ridge National Laboratory, Oak Ridge, TN.)

4.1.2.4 *Corbicula fluminea* Deployments in EFPC

Two separate clam deployments occurred in 2015—one in January and one in May. *Corbicula fluminea* used in each deployment study were collected from Sewee Creek, a reference site in Meigs County, Tennessee. Clams were dug from riffles using nets and collected in large buckets with stream water for transport to ORNL. Upon arrival, clams were transferred to laboratory water. Clams were housed in large flow-through tanks until deployment. Ten clams were weighed individually and placed in each deployment basket. All baskets for a given site were zip-tied together, and lids were securely fastened with zip ties. Reference clams were kept for mercury and methylmercury analysis.

In January 2015, six baskets containing 10 clams each were deployed at each of four sites—EFKs 23.4, 18.2, 13.8, and 6.3. In May 2015, three baskets containing 10 clams each were deployed at each of four

70

sites—EFKs 24.5, 23.4, 18.2, and 6.3. Deployed baskets were tied to existing stable structures (e.g., tree roots), and locations were noted for later retrieval. Clams were deployed for 26 days in January and 27–28 days in May. Upon retrieval, clams were weighed individually and frozen until further analysis. Before analyses, shells were removed. Clam tissue was freeze-dried and analyzed for mercury and methylmercury using methods described above.

After 26 days of exposure at each site in January, clams from EFK 23.4 had significantly higher total mercury concentrations than levels found in clams at any other site ($p < 0.001$) (Fig. 43). Clams from EFK 13.8 had significantly higher mercury concentrations than clams from either EFK 18.2 ($p = 0.04$) or EFK 6.3 ($p = 0.001$) had. Clams from EFK 13.8 and EFK 6.3 had significantly higher MeHg concentrations than concentrations in clams from either EFK 23.4 or EFK 18.2 ($p < 0.05$).
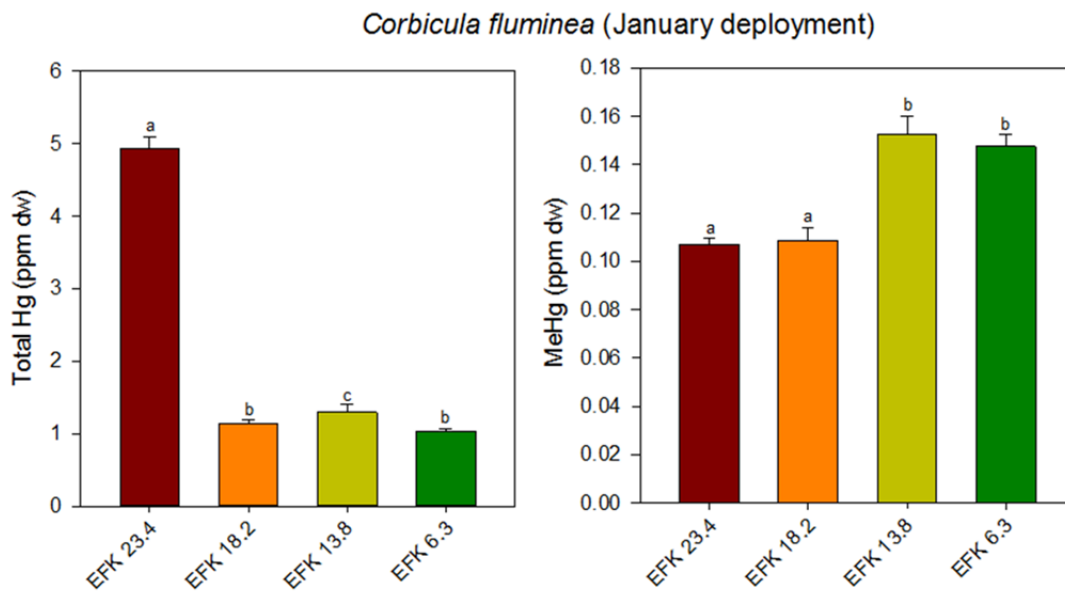

Fig. 43. Total mercury (Hg) and methylmercury (MeHg) concentrations in clams (*Corbicula fluminea*) deployed for 26 days at each of four East Fork Poplar Creek kilometer (EFK) sites.Bars are mean concentrations (dry weight [dw]); error bars are standard deviation. Different letters represent significant differences.

4.1.2.5 Mussel Filtration

Preliminary experiments to examine the effects of introducing mussel species into EFPC on mercury removal rates were conducted in FY 2015. These experiments began with the invasive Asian clam, *Corbicula fluminea*, collected from Sewee Creek (Meigs County, Tennessee), and continued with two native species obtained from the North Carolina Wildlife Resources Commission: the rainbow mussel, *Villosa iris*, and the slipper shell mussel, *Alasmidonta viridis*. All bivalves were acclimated to laboratory conditions for at least one week before experiments. During acclimation period, clams were fed phytoplankton from strains maintained in the laboratory. Preliminary experiments determined appropriate experimental setups and design.

Filtration rates of clams were determined for light and dark conditions and to examine the effects of population density on filtration rates. Ten replicates were used for each experiment; each replicate consisted of a clam in a separate container. Clams were placed in small plastic cups with 100 mL of First Creek water and aeration. Parafilm was used to reduce evaporation. After at least one hour, and when all

clams exhibited filtering behavior (siphon visible), algae (*Chlamydomonas reinhardtii)* were added to each container. After algae were sufficiently mixed with existing water (~1 min), water samples were taken to determine algae concentrations at the start of the experiment. After 30 and 60 min, water samples were taken from each replicate. Control containers consisting of water, algae, parafilm, and aeration (no clam) were monitored to determine growth rates of algae over the duration of the experiment. After the experiment, algae cells from each sample were counted using a hemocytometer, and filtration rates were calculated.

Corbicula fluminea filtration rates did not differ significantly between day (143 ± 78 mL/individual per hour) and night (182.3 ± 144 mL/individual per hour) treatments ($p > 0.05$) (Fig. 44). Large variations in the data may warrant further studies. Filtration rates measured here are comparable to other measured rates in the literature (Viergutz, Linn, and Weitere 2012).
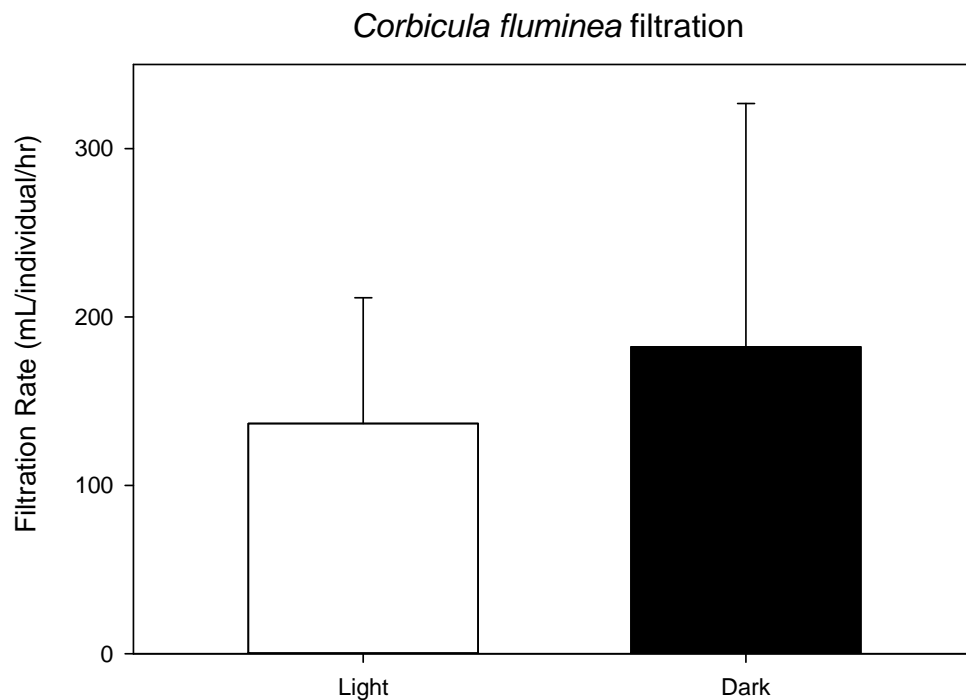

Fig. 44. Average filtration rates of clams (*Corbicula fluminea*) in light and dark conditions.
Bars are mean filtration rates for each treatment; error bars are standard deviation.

4.2   TASK 3 FUTURE DIRECTIONS

Important research and technology development needs are to quantify the trophic transfer efficiency of mercury through the EFPC food chain and to identify the critical linkages for mercury transfer to fish. By understanding these critical linkages, design strategies can be developed to sustainably alter, or manipulate, the aquatic food chain to mitigate mercury transfer to fish. Currently, work is underway to characterize the fish community structure at EFPC sites using historical BMAP data (as was done with the invertebrate communities). Analyses also are ongoing on the field-collected samples from spring 2015. When all data are obtained, work will begin to characterize the trophic structure of each EFPC site as well as to quantify the transfer of mercury/methylmercury up the food chain.

In the coming year, small-scale laboratory experiments will be used to better understand mercury methylation and subsequent transfer through the food web in EFPC. Experiments using radiotracer

Me^{203}Hg will allow for the tracking of MeHg from exposure to live target organism (e.g., MeHg from water to periphyton, or MeHg from algae to clams) over time. Experiments in the immediate future will measure the filtration rates of three native mussel species, allowing for (1) comparisons of these filtration rates to those of *Corbicula fluminea*, and (2) estimates of how many mussels would be needed in EFPC to affect mercury/methylmercury concentrations. Laboratory experiments planned for the next year will inform future mesocosm-scale experiments slated to take place in the field research station in FY 2017. Experimental plans include the following:

- Experiments to examine the effects that riparian shading may have on MeHg production and bioaccumulation
- Determination of effects that the addition of native mussel species may have on dissolved and particle-associated mercury and methylmercury within the creek
- Determination of the effects of mussel filtration on nutrient uptake and secondary effects of MeHg production by periphyton
- Experiments to examine the effect of fish population density on mercury and methylmercury bioaccumulation
- Experiments to examine the effects of stocking mussels and lower trophic level fish on mercury bioaccumulation throughout the food chain

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