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Sources of Mercury to East Fork Poplar Creek Downstream from the Y-12 National Security Complex: Inventories and Export Rates

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LIST OF ACRONYMS

BJC	Bechtel Jacobs Co. LLC
BMAP	Biological Monitoring and Abatement Program
CVAA	Cold Vapor Atomic Absorption
DOE	Department of Energy
EFK	East Fork kilometer
EFPC	East Fork Poplar Creek
EPA	Environmental Protection Agency
ESD	Environmental Sciences Division
ETTP	East Tennessee Technology Park
FGS	Frontier Geosciences, Inc.
GPS	Global Positioning System
Hg	mercury
LEFPC	Lower East Fork Poplar Creek
MeHg	methylmercury
NOAA	National Oceanographic and Atmospheric Administration
ORNL	Oak Ridge National Laboratory
ORR	Oak Ridge Reservation
TSS	total suspended solids
TVA	Tennessee Valley Authority
UEFPC	Upper East Fork Poplar Creek
USGS	United States Geological Survey
WRRP	Water Resources Restoration Program
Y-12 NSC	Y-12 National Security Complex

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1. INTRODUCTION

East Fork Poplar Creek (EFPC) in Oak Ridge, Tennessee, has been heavily contaminated with mercury (also referred to as Hg) since the 1950s as a result of historical activities at the U.S. Department of Energy (DOE) Y-12 National Security Complex (formerly the Oak Ridge Y-12 Plant and hereinafter referred to as Y-12). During the period from 1950 to 1963, spills and leaks of elemental mercury (Hg^0) contaminated soil, building foundations, and subsurface drainage pathways at the site, while intentional discharges of mercury-laden wastewater added 100 metric tons of mercury directly to the creek (Turner and Southworth 1999). The inventory of mercury estimated to be lost to soil and rock within the facility was 194 metric tons, with another estimated 70 metric tons deposited in floodplain soils along the 25 km length of EFPC (Turner and Southworth 1999). Remedial actions within the facility reduced mercury concentrations in EFPC water at the Y-12 boundary from > 2500 ng/L to about 600 ng/L by 1999 (Southworth et al. 2000). Further actions have reduced average total mercury concentration at that site to ~300 ng/L (2009 RER). Additional source control measures planned for future implementation within the facility include sediment/soil removal, storm drain relining, and restriction of rainfall infiltration within mercury-contaminated areas. Recent plans to demolish contaminated buildings within the former mercury-use areas provide an opportunity to reconstruct the storm drain system to prevent the entry of mercury-contaminated water into the flow of EFPC. Such actions have the potential to reduce mercury inputs from the industrial complex by perhaps as much as another 80%.

The transformation and bioaccumulation of mercury in the EFPC ecosystem has been a perplexing subject since intensive investigation of the issue began in the mid 1980s. Although EFPC was highly contaminated with mercury (waterborne mercury exceeded background levels by 1000-fold, mercury in sediments by more than 2000-fold) in the 1980s, mercury concentrations in EFPC fish exceeded those in fish from regional reference sites by only a little more than 10-fold. This apparent low bioavailability of mercury in EFPC, coupled with a downstream pattern of mercury in fish in which mercury decreased in proportion to dilution of the upstream source, lead to the assumption that mercury in fish would respond to decreased inputs of dissolved mercury to the stream's headwaters. However, during the past two decades when mercury inputs were decreasing, mercury concentrations in fish in Lower EFPC (LEFPC) downstream of Y-12 increased while those in Upper EFPC (UEFPC) decreased. The key assumption of the ongoing cleanup efforts, and concentration goal for waterborne mercury were both called into question by the long-term monitoring data.

The large inventory of mercury within the watershed downstream presents a concern that the successful treatment of sources in the headwaters may not be sufficient to reduce mercury bioaccumulation within the system to desired levels. The relative importance of headwater versus floodplain mercury sources in contributing to mercury bioaccumulation in EFPC is unknown. A mercury transport study conducted by the Tennessee Valley Authority (TVA) in 1984 estimated that floodplain sources contributed about 80% of the total annual mercury export from the EFPC system (ORTF 1985). Most of the floodplain inputs were associated with wet weather, high flow events, while much of the headwater flux occurred under baseflow conditions. Thus, day-to-day exposure of biota to waterborne mercury was assumed to be primarily determined by the Y-12 source. The objective of this study was to evaluate the results of recent studies and monitoring within the EFPC drainage with a focus on discerning the magnitude of floodplain mercury sources and how long these sources might continue to contaminate the system after headwater sources are eliminated or greatly reduced.

Several of the key information needs identified in a conceptual model for mercury bioaccumulation in EFPC under development by Bechtel Jacobs Company LLC (BJC) and the Environmental Sciences Division (ESD) of Oak Ridge National Laboratory (ORNL) are related to the role of mercury deposited in the watershed of LEFPC as a continuing source of contamination to surface water. Although the inventory of mercury in the contaminated soils of the EFPC floodplain has been well documented, there is little information on how much mercury remains within the streambed itself, and how rapidly streambed mercury is removed or replaced. Similarly, there is little information on the linkage between floodplain contamination and the surface water in EFPC. Focused studies were originated in the second half of FY2008 to address these questions.

2. METHODS

2.1 STREAMBANK SOIL, STREAMBED GRAVEL AND BIOFILM MERCURY SURVEYS

2.1.1 Site Description

Measurements of mercury and methylmercury (also referred to as MeHg) in eroding streambanks, streambed gravel and the streambed biofilm were made at four locations in LEFPC downstream from the headwater mercury source within Y-12. Those locations were selected to coincide with locations where mercury bioaccumulation in fish has been routinely monitored by ORNL/ESD since 1985 for the Y-12 Biological Monitoring and Abatement Program (BMAP). Waterborne total mercury and methylmercury are also monitored twice yearly at these locations by the DOE Oak Ridge Reservation (ORR) Water Resources Restoration Program (WRRP) managed by BJC. The sites (Fig. 1) are spaced at roughly 5 km intervals between Y-12 and the lowermost portion of the creek that is impounded by Watts Bar Reservoir on the Tennessee River. Locations are designated by the notation EFK (East Fork kilometer) and an integer representing the approximate distance in kilometers from the site to the junction of EFPC with Poplar Creek.

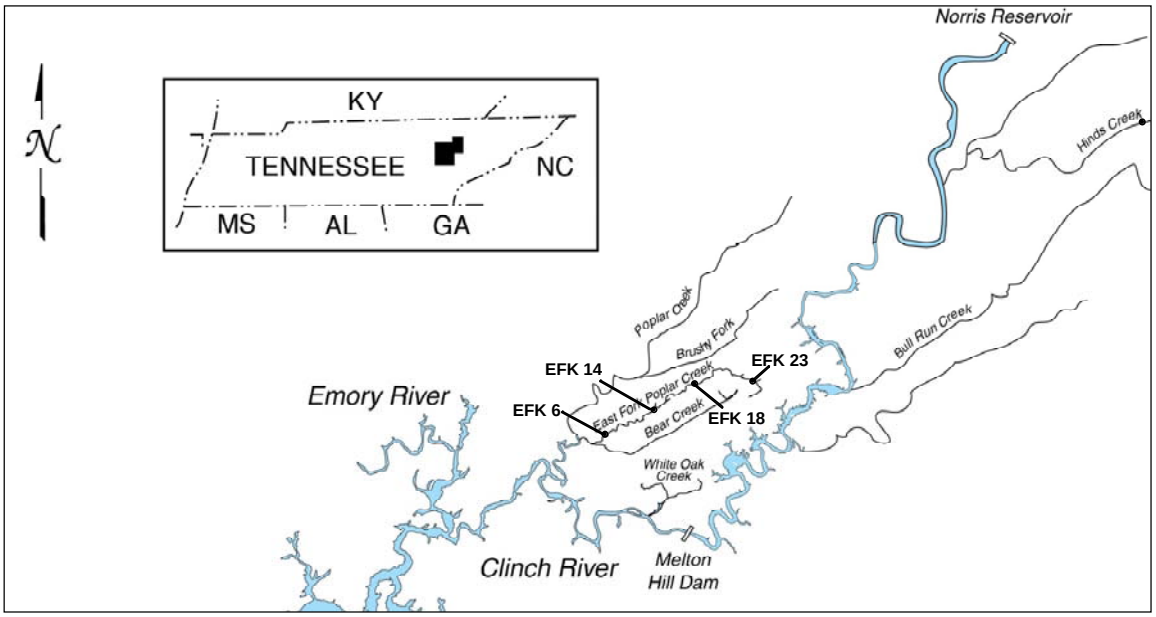

Fig. 1. Sampling locations in East Fork Poplar Creek, Oak Ridge, Tennessee.

At each location, three separate gravel riffles were selected for transects for the measurement of mercury within the streambed. Three core samples representing the center of each third of the stream cross section along the transect were collected. Surface biofilm samples were collected near each transect sample. Although it was often necessary to move a distance of roughly 20 m upstream and downstream from each transect streambed site to obtain an adequate number of surface samples, each surface sample maintained the alignment (left third, center, right third) of the nearby transect. Three separate eroding streambank sites were selected at each location for sampling. Details of sampling procedures follow. Photographic depiction of the specific sampling sites is presented in Figs. 2–5.

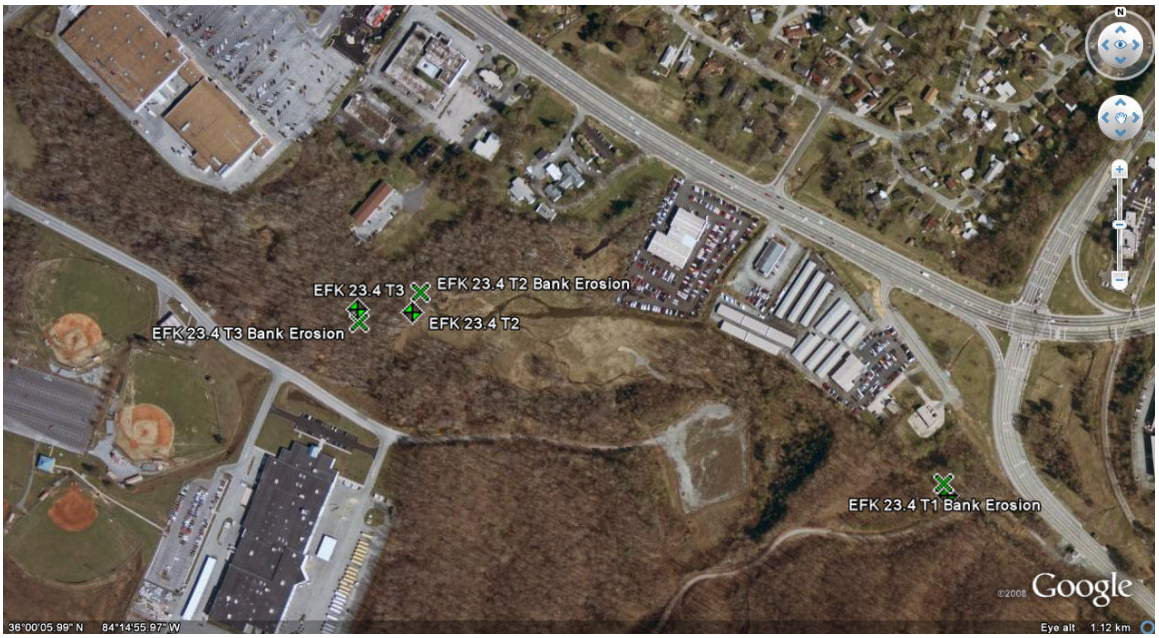

Fig. 2. Streambed and bank sampling sites at EFK 23. Photo from Google Earth.

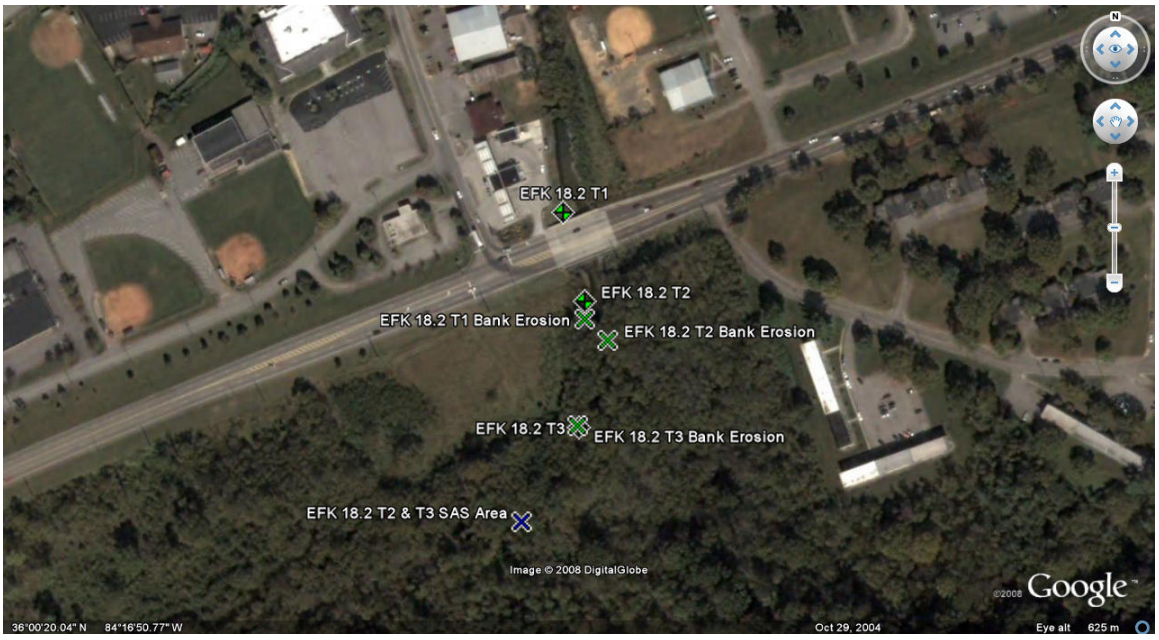

Fig. 3. Streambed and bank sampling sites at EFK 18. Photo from Google Earth.

Fig. 4. Streambed and bank sampling sites at EFK 14. Photo from Google Earth.

Fig. 5. Streambed and bank sampling sites at EFK 6. Photo from Google Earth.

2.1.2 Streambank Soils

Historical mercury deposition in the EFPC watershed left highly contaminated soil on the surface of the floodplain along the entire length of the stream. That material can re-enter the aquatic system by surface erosion of the 200 ha of contaminated floodplain soil (Turner and Southworth 1999) and by erosion and collapse of streambanks where the contaminated soil is directly exposed to flow of the stream under stormflow conditions. The role of bank erosion as a source of mercury can be estimated from the erosion rate of streambanks and mercury content of the eroding soil. In order to refine our estimate of the magnitude of this source, profiles of mercury concentration in soil versus depth below the soil surface (or height above the water surface) were measured at twelve locations in LEFPC. Three visibly eroding streambank sites were selected within each of four experimental reaches that corresponded to sites where fish are regularly collected for mercury analysis by the Y-12 BMAP program (EFK 23, EFK 18, EFK 14, and EFK 6). Fifteen samples of the outer 1-cm surface of each of three bank transects were collected at each of the four study reaches using disposable spatulas. Those samples were dried at 40°C overnight and homogenized using a mortar and pestle. Very little unpulverized material was found in the soil deposits and that was removed. Samples were digested in aqua regia and analyzed for total mercury by CVAA analysis. Total mercury concentrations in those samples are tabulated in Table A-1 and depicted graphically in Figs. 9–12. A composite sample was generated from one bank transect in each experimental reach by combining equal amounts of each of the fifteen samples comprising a transect. The composite samples were then analyzed by Frontier Geosciences, Inc. (FGS) using the speciation protocol developed by Bloom et al. 1993. This procedure separates the mercury content of the sample into six fractions: methylmercury, water soluble mercury, weak acid soluble mercury, organic-complexed mercury, strongly complexed mercury, and nominal mercury sulfide (hereinafter referred to as HgS). A semi-quantitative procedure was employed by FGS to detect the presence of elemental mercury (hereinafter referred to as Hg^0) in the samples.

2.1.3 Streambed Biofilm

Biofilm mercury was sampled by brushing the fine material from the surface of rocks in gravel beds at the four study reaches described previously. Three composite samples (left side, middle, right side) from 6 to 12 rocks were collected for each of three transects in each reach. Surface area of each rock was measured by covering the surface with aluminum foil, trimming off excess foil, and weighing the foil sheets and multiplying by the weight of foil per unit area. An aliquot of the resulting suspension was then filtered through a tared 1.2 μm glass fiber filter, and the net weight used to calculate the solids content of the biofilm sample. The suspension was then settled and centrifuged to separate the solids content, which was sent to FGS for analysis of total mercury and methylmercury by EPA methods 1630 and 1631.

2.1.4 Streambed Gravel

Streambed sediment samples were collected from three transects (three samples per transect) in each of the four study reaches. Samples were collected by using a split spoon coring device. Each sample was sieved in the field to separate stones and debris from the sand/silt/clay fraction (<1 mm). The mass of fines in each sample was computed from the density of the resulting suspension of that material in creek water present in the sample, while the mass of stones was determined directly by weighing. A small portion of the fines was wet sieved to <125 μm, dried at 40°C and analyzed for total mercury by CVAA spectrometry following aqua regia digestion. Samples of the <1mm fraction were de-watered by centrifugation and shipped to FGS for analysis of total mercury and methylmercury.

2.2 FLOODPLAIN WET-WEATHER CATCHMENTS STUDY

2.2.1 Study Sites

Contaminated floodplain soils are a potential source of mercury to EFPC via surface runoff under wet weather conditions. The relative contribution of mercury to EFPC from floodplain soils during rain events is currently unknown. In order to address this data gap, two study sites located entirely within contaminated sections of the EFPC floodplain were selected, each containing a small ephemeral wet weather conveyance where flow could be collected and measured during rain events. Study sites were located adjacent to BMAP aquatic survey reaches at EFK 23 in the vicinity of the National Oceanographic and Atmospheric Administration (NOAA) facility in Oak Ridge (Fig. 6) and at EFK 6 within the Horizon Center industrial park (Fig. 7) to facilitate integration of results with existing baseline data on mercury in fish and water of EFPC. The perimeter of each study catchment area was determined by visual inspection during and following rain events and surface areas were approximated by both physical and Global Positioning System (GPS) measurements (Table 1). The NOAA study site consists of a lower and an upper area separated by a berm through which flow was determined to seep into the lower drainage channel during rain events. The upper area is located entirely within the NOAA zone of floodplain that was remediated in the 1990s during the LEFPC Remedial Action; the adjacent lower area was not remediated. In total, the NOAA catchment study site is approximately 0.136 hectares in area. The Horizon Center study site is a relatively small catchment of only 0.022 hectares located between a patrol road and EFPC. Both sites contain several small depressions along the primary flow-path where drainage collects and, in lesser rain events (particularly when the soil is relatively dry), percolates into the floodplain and thus fails to reach EFPC as surface runoff.

2.2.2 Assessment of Mercury in Floodplain Soils

Transects for sampling mercury in floodplain soils were established at both wet-weather catchment study sites. At the NOAA site, sampling transects were marked at approximate 6 m intervals perpendicular to the preferential drainage flow path with sampling points spaced 2 m apart, for a total of six transects in the lower NOAA site and three transects in the upper site. At the Horizon Center site, five transects were established at approximate 6 m intervals along the preferential flow path; each transect had six evenly-spaced sampling points. At both sites, a few additional individual sampling points were also established to ensure sampling of all available soil types or micro-habitats within the catchments.

Samples of the uppermost 1-cm layer of surface soil were collected along transects at each of the study sites using disposable spatulas. Soil samples were dried at 40°C overnight and homogenized using a mortar and pestle. Rocks and solid plant material were removed and the soil digested in aqua regia and analyzed for total mercury by CVAA analysis. Three composite soil samples were also obtained from each catchment by combining equal amounts of soil from three samples per composite. The composite samples were then prepared and analyzed by FGS for mercury speciation as described in Section 2.1.2 of this report.

2.2.3 Wet-Weather Catchment Study Design

Experimental weirs were constructed along the preferred flow paths for surface runoff at the NOAA and Horizon Center study sites (Fig. 8). Runoff from the floodplain was sampled from each weir with an ISCO sampler cooled with ice and triggered to begin sampling when flow was detected at the weir notch. Rainfall was measured at Station 17 at Y-12 as an indicator of rainfall at the nearby NOAA site and at Outfall 170 at the East Tennessee Technology Park (ETTP) as a surrogate for rainfall at the

Fig. 6. Wet-weather catchment study site at the NOAA complex in Oak Ridge, TN, on the EFPC floodplain adjacent to EFK 23. Photo from Google Earth.

Fig. 7. Wet-weather catchment study site at the Horizon Center in Oak Ridge, TN, on the EFPC floodplain adjacent to EFK 6. Photo from Google Earth.

Table 1. Area and estimated percentages of total mercury-contaminated East Fork Poplar Creek floodplain included in wet-weather catchments mercury study

Site	Area (sq ft)	Area (hectares)	Percentage of floodplain[1]
NOAA			
Upper area	8300	0.077	0.0385
Lower area	6300	0.059	0.0295
Total NOAA	14600	0.136	0.068
Horizon Center	2400	0.022	0.011

[1]Based on estimated 200 mercury-contaminated hectares of East Fork Poplar Creek floodplain published in Turner and Southworth 1999.

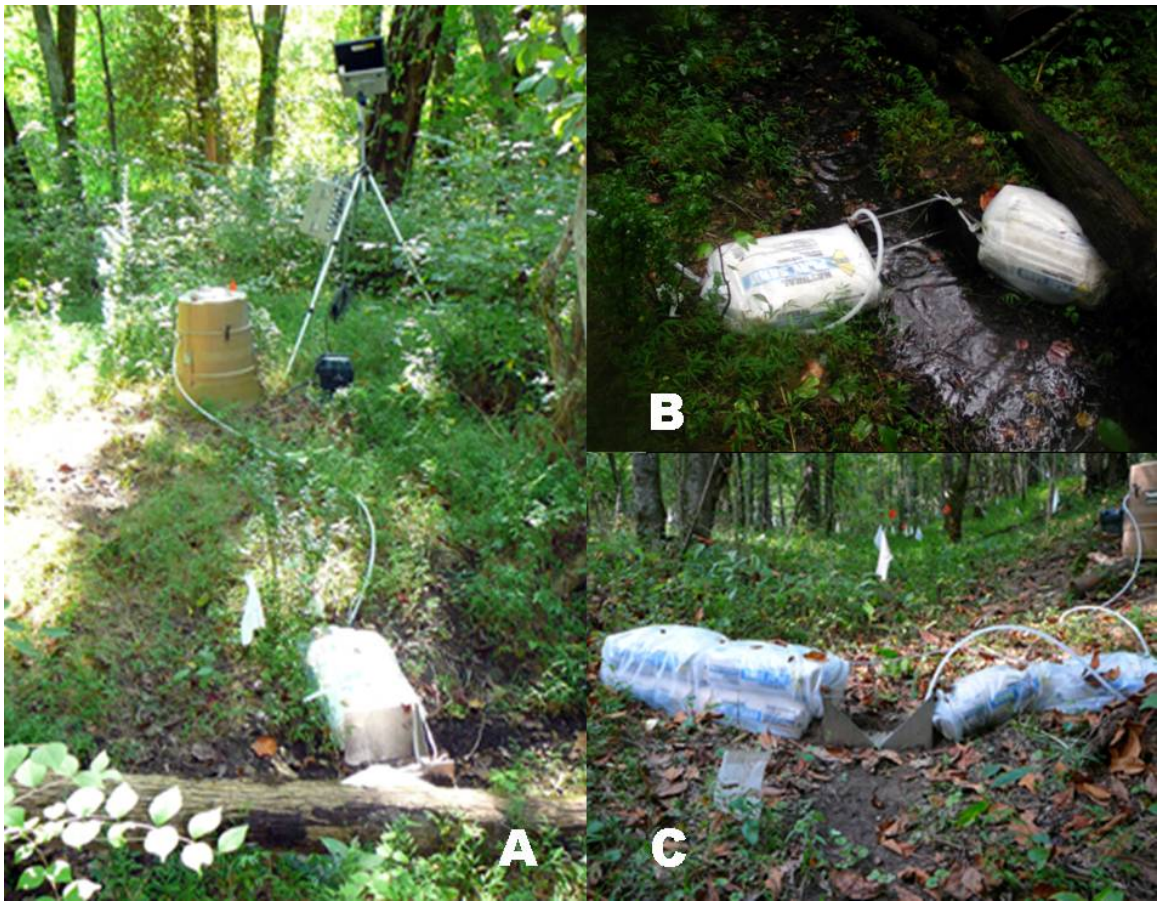

Fig. 8. Floodplain runoff sampling design for the wet-weather catchment study: (A) weir, ISCO sampler, and flow meter at the NOAA site; (B) close-up of weir at the NOAA site during a rain event; (C) view through weir at the Horizon Center site showing floodplain wet-weather catchment.

Horizon Center site. Runoff was sampled at 10-minute intervals during a rain event in August 2008 and again at 1-hr intervals during a rain event in May 2009. Water samples were split, with one portion preserved with BrCl for analysis of total mercury, another portion filtered before preservation to be analyzed for dissolved mercury, and a third portion analyzed for total suspended solids (TSS).

2.3 WET AND DRY WEATHER EXPORT OF MERCURY FROM THE WATERSHED

Total mercury and methylmercury are monitored twice yearly at sites in EFPC (EFK 23, EFK18, EFK 14 and EFK 6) as part of the WRRP. These data were used to evaluate dry weather export of mercury from the watershed, along with results of a synoptic survey of downstream concentrations of dissolved and total mercury conducted under baseflow conditions in December 1997 by the Y-12 BMAP. The Y-12 BMAP also monitored total mercury concentrations in surface sediment (<125 μm) in 1997 and 2009. Analytical methods used in BMAP and WRRP are described in Sections 2.1 and 2.2.

In May 2009, a study was conducted in conjunction with the wet-weather catchment study to separately estimate the stormflow export of mercury from the Y-12 facility and the contaminated watershed downstream. Water samples were collected over a 24-hour period during which 1.75 cm of rain fell in two intense thunderstorms. Samples were collected hourly at EFK 23, where streamflow is gauged and recorded continuously, and every two hours at EFK 6. Streamflow at EFK 6 was roughly estimated by linear extrapolation of low-flow measurements of discharge versus staff height, with staff height readings taken manually over the 24-hour period. Although only a rough measure, the comparison of the volumetric discharge estimated at EFK 6 with that measured accurately at EFK 23 (740,000 m^3 vs 64,350 m^3) corresponded well with the difference in watershed areas between the sites (19.5 square miles vs 1.69 square miles). Cumulative rainfall, if evenly distributed over the watershed, was 880,425 m^3 and 76,303 m^3 for the watershed above EFK 6 and EFK 23, respectively. It would appear that most rainfall from this event rapidly ran off the already water-saturated soils.

3. RESULTS AND DISCUSSION

3.1 BANK EROSION

Contaminated streambanks along the length of EFPC undoubtedly contribute additional mercury to the system when freeze/thaw cycles, rainfall, and elevated stream stage act to erode those banks. The banks of EFPC contain numerous sections where depositional floodplain soils are exposed and can contribute mercury to the stream. Such sites comprise approximately two-thirds of the total length of EFPC downstream of Station 17. Mercury profiles of streambank sites are presented in Figs. 9–12 and Table A-1. The EFK 23 T1 profile contained the most highly contaminated soil, a layer rich in coal fines that was deposited during the period of active use of mercury at Y-12 when mercury discharges to the creek were very high. That so called 'black layer' contained nearly 1500 ppm mercury (Fig. 9). Mercury concentrations in streambank soils farther downstream were much lower, and generally contained concentrations similar to fine particle sediments in nearby reaches of EFPC (Tables 2–4). Mean mercury concentrations in profiles at EFK 23 were heavily influenced by the single profile that contained a 'black layer' sample. Mercury maxima were clear in most profiles, usually in the upper 30 cm. In some cases, particularly EFK 18 where bridge and sewer construction appeared to disturb soil profiles, the maximum was deeper or the profile more uniform.

In Table 2, the mean concentration of mercury in the streambank samples within each of the four study sites was used in conjunction with estimates of % erodable streambank to compute an inventory of mercury in the aggregate of all such streambank sections in LEFPC. This analysis estimated that a 1 cm thick surface of erodable bank over the 20 km reach of EFPC would contain 23 kg of mercury, with most of that occurring in the upper half of the watershed. Streambank erosion rates of 1–2 cm/year would be required to contribute an amount of mercury comparable to that estimated to be exported annually from sources in LEFPC (Section 4.2). An erosion rate of 1 cm/y would correspond to a loss of soil equivalent to 29 kg/m/y in EFPC. Bank erosion rates in the South River, a mercury-contaminated stream similar in geology and gradient to EFPC, averaged approximately 5 cm/y over a 68-year period (Rhoades et al. 2008). Erosion rates in that stream doubled following the removal of mill dams in the 1950s (Pizzuto and O'Neal 2009). Thus, a 1–2 cm/y rate would perhaps more likely typify conditions similar to EFPC, which did not undergo such a change from depositional to erosional conditions.

The results of speciation analysis of inorganic mercury in streambank samples (Fig. 13, Table 5) and in-stream media support the view that streambank erosion contributes significantly to the total mercury transport in EFPC. Among the streambank samples, only that from EFK 23 has a substantial fraction in the HgS extract of the sequential extraction procedure. The streambed biofilm samples, however, have a HgS pattern that suggests a source near or above EFK 23 and downstream dilution consistent with no major additions of HgS. The pattern in streambed gravel shows a peak concentration at EFK 18 and downstream decreases below that. While intriguing, we must caution that these are single samples and thus may not be closely representative of the sites from which they were obtained. The EFK 23 sample, in particular, contained 'black layer' material very high in inorganic mercury. This layer is restricted to a relatively localized reach of EFPC that may not be large enough to add enough mercury to generate the pattern observed in Fig. 13. Although the proportions of various strongly bound complexes vary among sites and matrices, in general, virtually all mercury in all samples was present in the three highly sequestered forms (i.e., organic-complexed, strongly complexed, and HgS) (Fig. 14). Recent data collected by the ORNL Mercury Science Focus Area research team indicates that mercury-rich streambed particulates near the source of EFPC within Y-12 contain a similarly high percentage of mercury within the HgS fraction of the sequential extraction protocol.

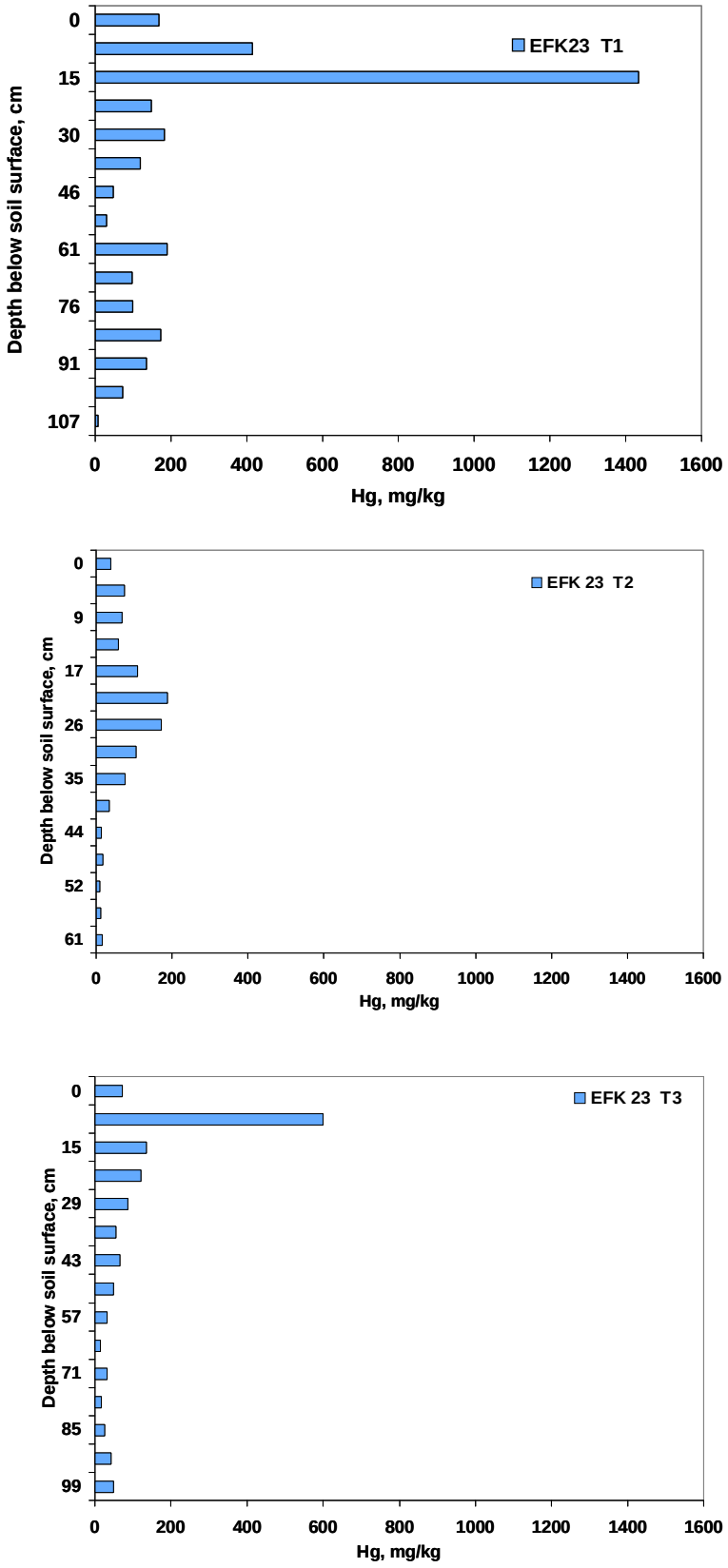

Fig. 9. Profile of total mercury concentrations in eroding streambanks, EFK 23.

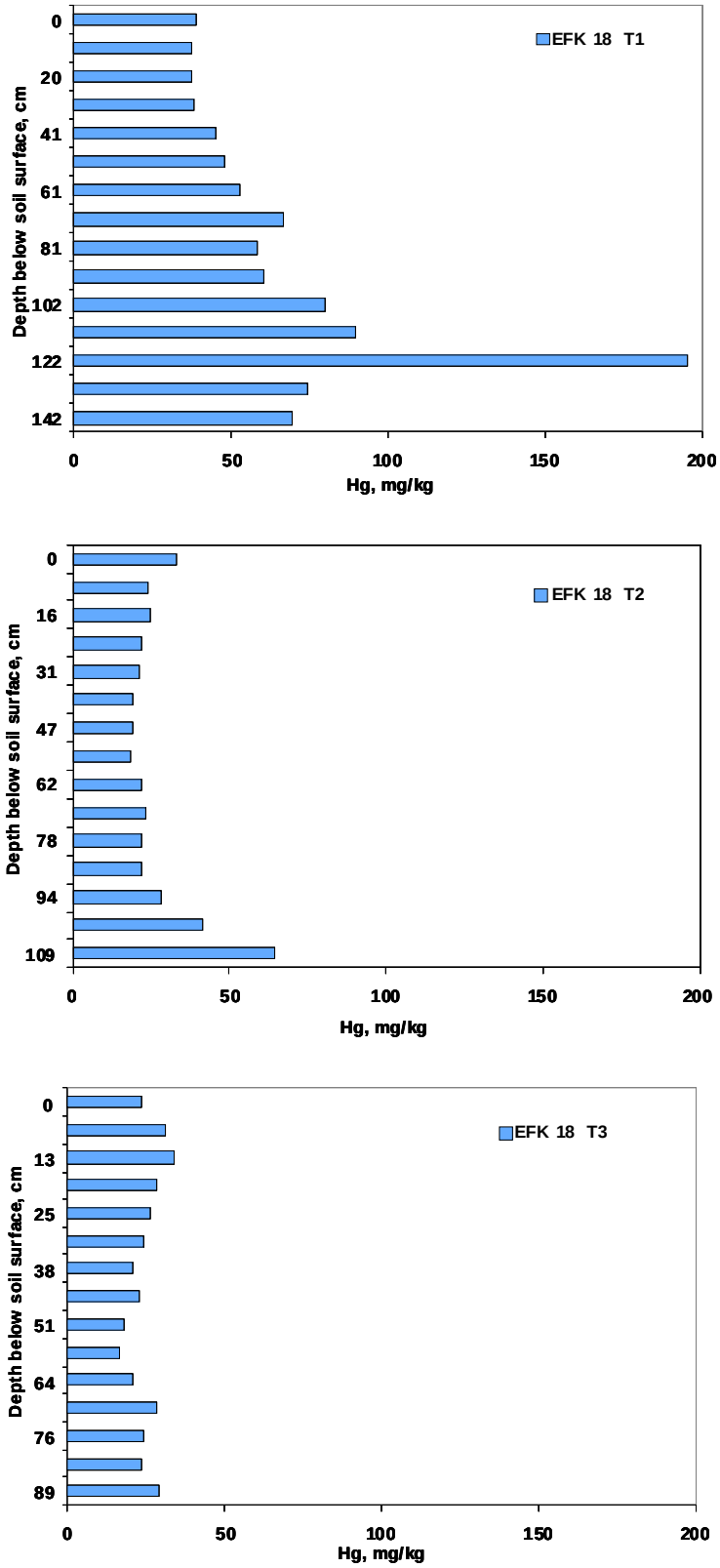

Fig. 10. Profile of total mercury concentrations in eroding streambanks, EFK 18.

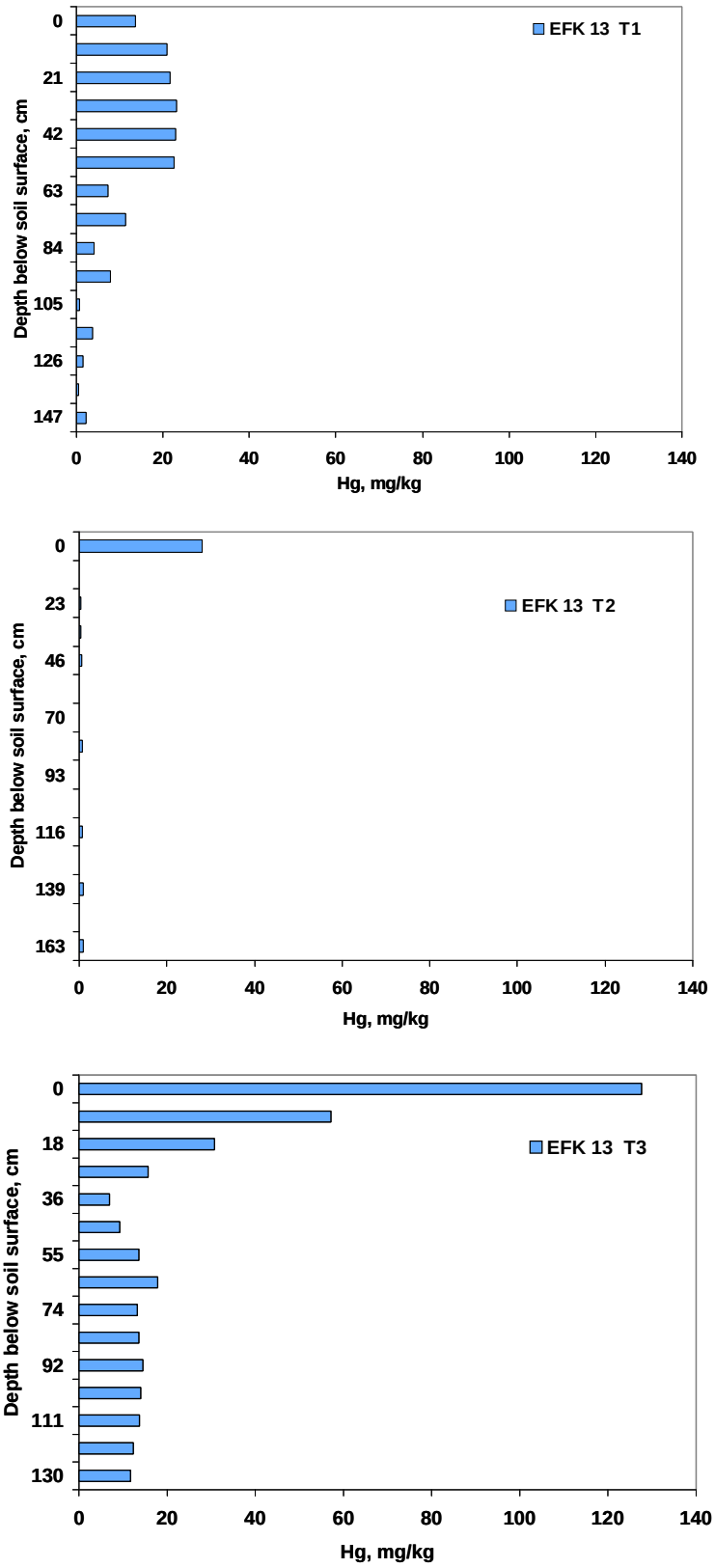

Fig. 11. Profile of total mercury concentrations in eroding streambanks, EFK 14.

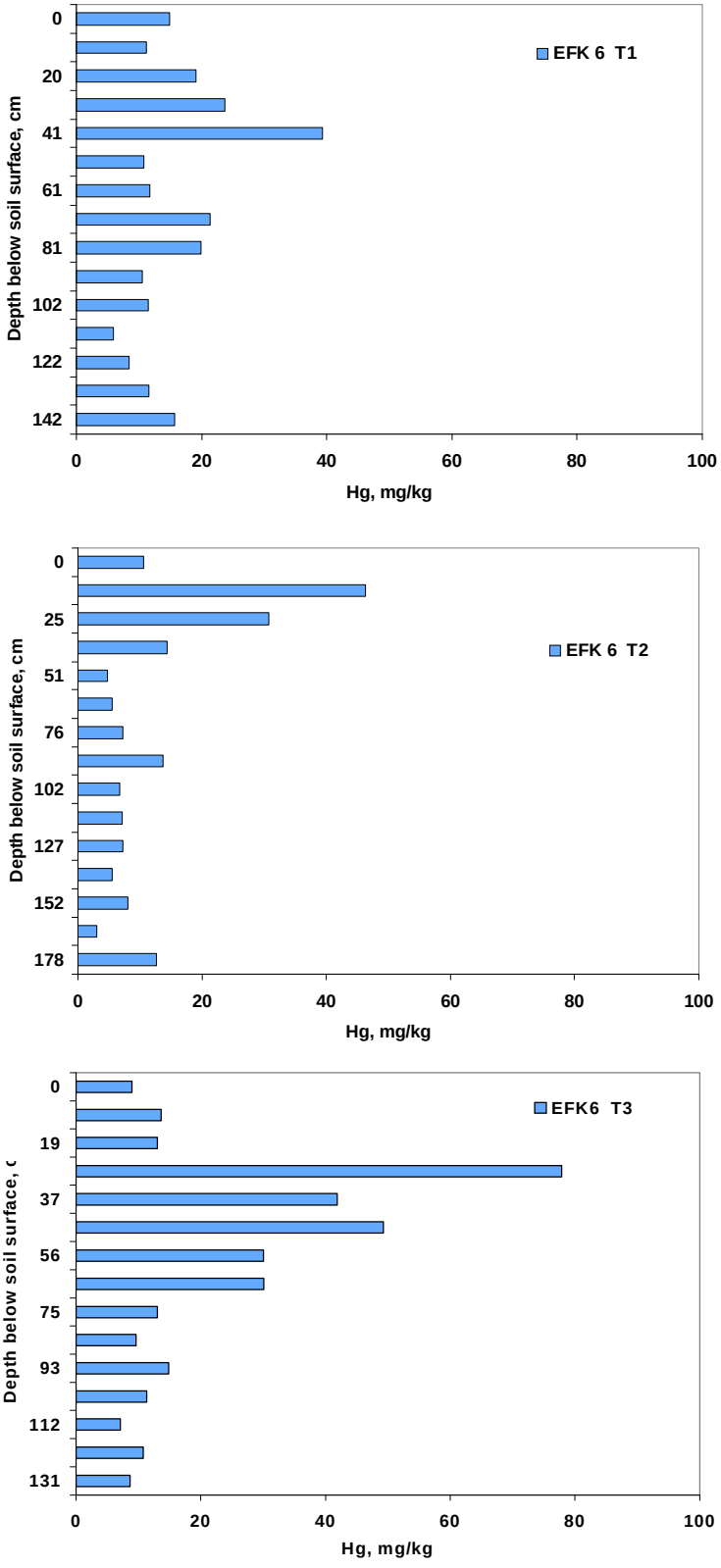

Fig. 12. Profile of total mercury concentrations in eroding streambanks, EFK 6.

Table 2. Inventory of mercury (Hg) in 1-cm layer of lower EFPC streambank

Reach	Length m	Bank height (m)	Bank depth m	Soil Hg mg/kg	% erodable bank	Hg inventory kg
EFK 23	5000	0.89	0.01	127 ± 48	53	10.8
EFK 18	5000	1.13	0.01	39 ± 13	90	7.1
EFK 14	5000	1.47	0.01	13 ± 6.6	51	1.8
EFK 6	5000	1.50	0.01	18 ± 3.8	63	2.9
Total						23

Table 3. Estimated inventory of mercury (Hg) and methylmercury (MeHg) in solids in the surface biofilm of EFPC

Reach	Biofilm mass kg/m^2	Hg mg/kg	MeHg µg/kg	Width m	Length m	Hg inventory g	MeHg inventory mg
EFK 23	0.12 ± 0.03	20 ± 3.2	7.1 ± 0.8	5.5	5000	66	23
EFK 18	0.20 ± 0.04	18.2 ± 4.0	18.0 ± 4.0	6.5	5000	118	117
EFK 14	0.12 ± 0.02	14.7 ± 3.1	18.7 ± 2.6	7.5	5000	66	84
EFK 6	0.13 ± 0.05	12.0 ± 4.3	16.1 ± 4.0	8.5	5000	66	89
Total						317	313

Table 4. Estimated inventory of mercury (Hg) and methylmercury (MeHg) in streambed gravel of EFPC, assuming 50% of EFPC is gravel riffles

Reach	Fines kg/m^2	Hg mg/kg	MeHg µg/kg	Width m	Length m	Hg inventory kg	MeHg Inventory g
EFK 23	76 ± 31	7.8 ± 1.3	1.4 ± 0.24	5.5	5000	8.2	1.5
EFK 18	165 ± 31	43.5 ± 10.9	4.8 ± 0.49	6.5	5000	117	13
EFK 14	91 ± 26	8.3 ± 2.3	1.9 ± 0.73	7.5	5000	14	3.3
EFK 6	98 ± 23	15.8 ± 4.9	5.5 ± 2.6	8.5	5000	33	12
Total						172	29

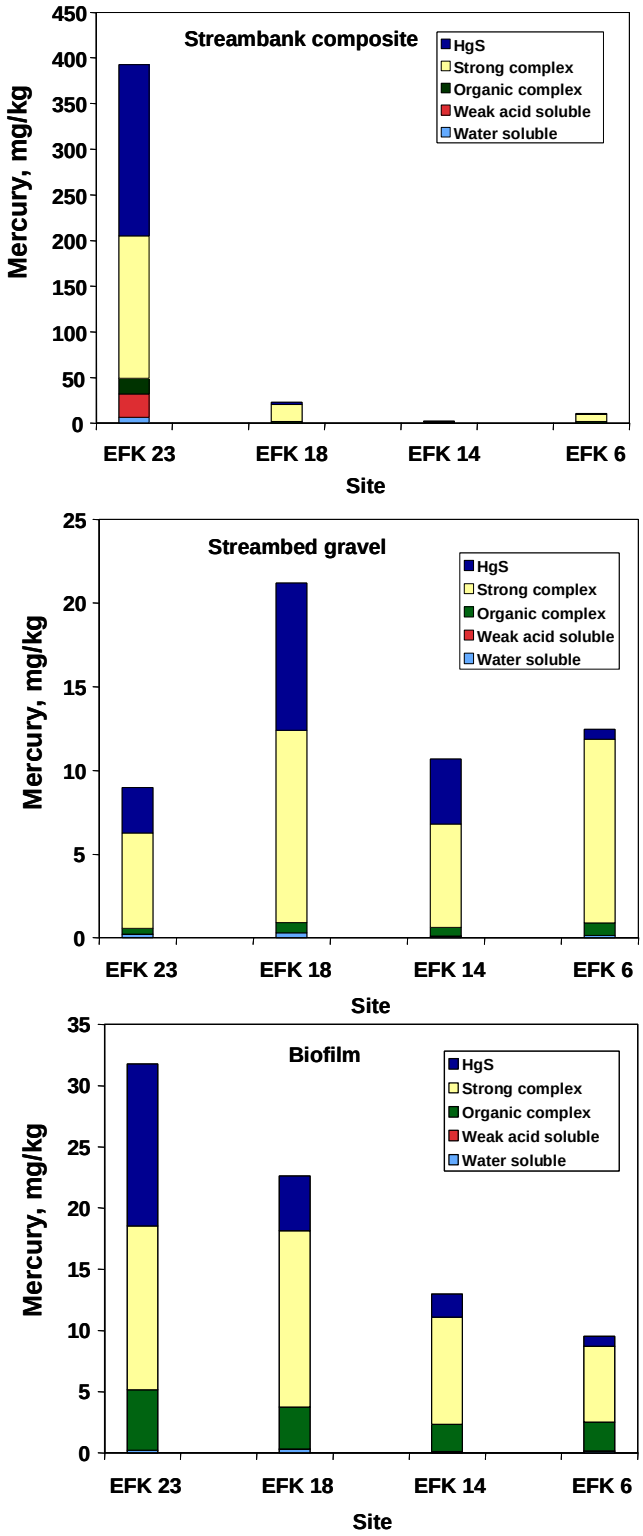

Fig. 13. Speciation of inorganic mercury in samples of streambank, gravel, and the surface biofilm of EFPC at sites along a downstream gradient. Numerical values for all fractions are presented in Table 5.

Table 5. Speciation of mercury in composite samples of eroding streambank and individual samples of streambed biofilm and streambed gravel fines (<1 mm) at sites in EFPC

Sample type	Site		MeHg ng/g	% MeHg	Water soluble µg/g	Weak acid soluble µg/g	Organic complex µg/g	Strongly complexed µg/g	HgS µg/g	HgT µg/g	Sum of fractions µg/g
Streambank	EFK 23 T1	Composite	24.4	0.0046	6.5	25.7	17	156	187	531	393
	EFK 18 T3	Composite	5.8	0.0225	0.09	0.004	1.88	18.5	2.5	25.6	23
	EFK 14 T2	Composite	0.37	0.0137	0.0088	0.012	1.14	0.13	0.83	2.7	2.1
	EFK 6 T1	Composite	12.3	0.0925	0.136	0.0054	1.63	7.92	0.93	13.3	10.6
Streambed biofilm	EFK 23 T1	SAS1	11.5	0.0321	0.111	0.0064	4.94	13.4	13.2	35.8	31.7
	EFK 18 T2	SAS2	14.4	0.0603	0.188	0.007	3.44	14.4	4.47	23.9	22.5
	EFK 14 T3	SAS1	25.4	0.1801	0.081	0.0045	2.23	8.77	1.86	14.1	12.9
	EFK 6 T1	SAS3	2.58	0.0146	0.052	0.0046	2.35	6.23	0.79	17.7	9.4
Streambed gravel	EFK 23 T3	SB1	2.23	0.0123	0.21	0.014	0.333	5.7	2.71	18.2	8.97
	EFK 18 T1	SB3	1.53	0.0044	0.3	0.0067	0.6	11.5	8.8	34.4	21.2
	EFK 14 T3	SB3	1.23	0.0077	0.088	0.0034	0.537	6.17	3.89	15.9	10.7
	EFK 6 T2	SB3	2.75	0.0154	0.137	ND	0.736	11.0	0.591	17.8	12.5

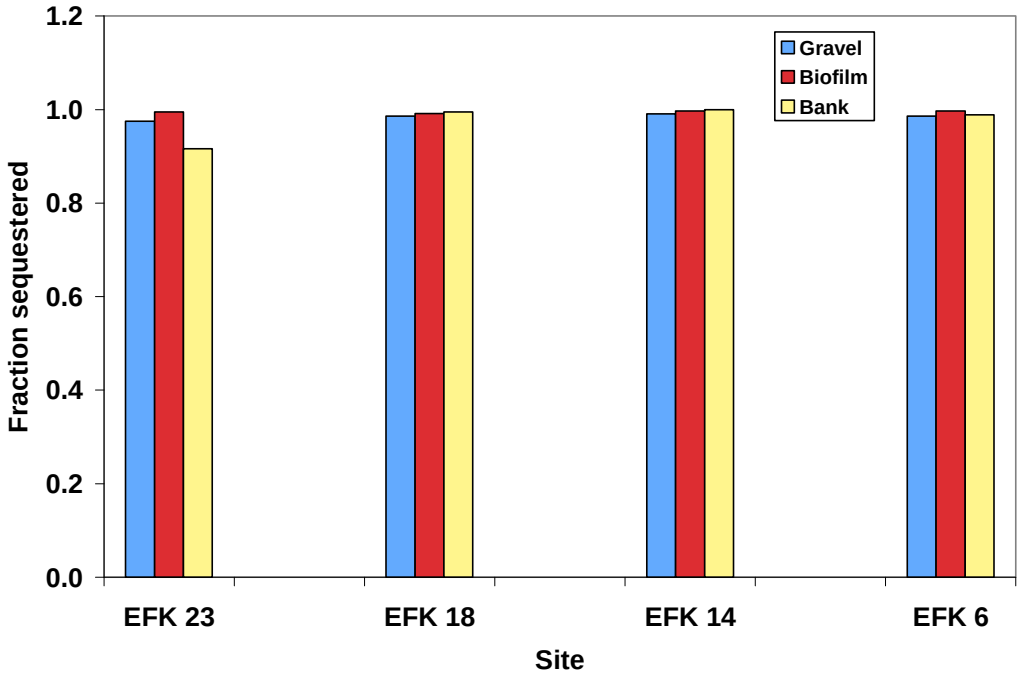

Fig. 14. Fraction of total mercury that is 'sequestered' (organic complex, strong complex, and HgS fractions in sequential extraction speciation analysis).

3.2 MOBILIZATION OF STREAMBED MERCURY

3.2.1 Streambed Biofilm

Fine particulate material retained in the biofilm coating contains mercury contamination that reflects the waterborne inorganic mercury concentration and the high affinity of mercury for solids (K_d approximately 10^6). This material is readily disturbed and returned to the water column, and thus represents an important contribution to stormflow mercury export. The size of the inventory of mercury stored in such deposits represents a potential limit on how much this source can contribute.

The estimate of mercury content of the streambed biofilm is presented in Table 3 and Table A-2. This computation assumes that the surface area of the irregular stream bottom is equivalent to that of a smooth surface (thus is an underestimate) and also assumes that the entire streambed biofilm is similar to that found in gravel riffles (probably also an underestimate). Nevertheless, the inventory of mercury retained in this compartment, 317 g in Table 3, was relatively small. If the annual daily mean mercury input at Station 17 at Y-12 is 10 g/d, the streambed biofilm throughout the rest of the creek contains an amount equivalent to only a 30-day export from the Y-12 site.

3.2.2 Bedded Sediment

Results of total mercury analyses of the sand/silt/clay fraction (< 1 mm) were used to estimate the streambed inventory (Table 4, A-3). The inventory was computed using estimates of the mean width of each experimental reach and assumed that 50% of streambed was composed of gravel riffles (the

visual survey estimated each reach to be approximately 50% riffles). The mass of mercury stored within the EFPC streambed can thus be seen to be substantial, in excess of 170 kg. Although large, this would only constitute the equivalent of about three years of mercury export from the EFPC system at the 53 kg/y rate estimated in Section 4.2, and thus suggests that streambed mercury requires continual replenishment to sustain current rates of mercury export.

Total mercury concentrations in samples from the EFK 18 reach can be seen to exceed those from the other three reaches, and the depth of the gravel beds sampled in that reach exceeded the depth of the other reaches by nearly a factor of two (Table 5, Fig. 15). Consequently, the bulk of the estimated streambed mercury inventory in lower EFPC appears to occur in that reach. The EFK 18 reach marks the head of a section of the EFPC floodplain where heavy deposition of contaminated soils occurred, and was one of two sites within the EFPC floodplain where mercury-contaminated soil was excavated and replaced with clean soil in a CERCLA action. The high mercury content of streambed gravel in this reach may reflect historic contamination that is resistant to removal by erosion. Alternatively, it may represent the present location of a peak in mercury concentration that is gradually moving downstream in response to successful cleanup actions in the headwater source areas. Total mercury concentrations in streambed biofilm and the silt/clay fraction of the gravel are similar at other sites in EFPC, but higher in the gravel than in the surface biofilm at EFK 18 (Fig. 15).This suggests that much of the mercury in the streambed in that reach may be relatively unsusceptible to erosion.

3.3 EROSION OF SURFACE SOILS FROM THE EFPC FLOODPLAIN

3.3.1 Mercury in Floodplain Soils

Total mercury concentrations in the top 1 cm of surface soil at the NOAA and Horizon Center wet-weather catchments are shown in Figs. 16 and 17, respectively. Mean surface soil concentrations at the wet-weather catchments ranged from a low of 15.0 ± 6.5 at the Horizon Center site to 23.8 ± 18.8 mg/kg at the upper NOAA area and 43.6 ± 19.7 mg/kg at the NOAA lower area (33.7 ± 21.5 at the combined NOAA site). Lesser soil mercury concentrations at the upper NOAA area as compared to the lower NOAA area can be attributed to the former lying within the zone of the LEFPC Remedial Actions in the 1990s. The patterns of soil mercury in this upper NOAA area (markedly higher in low-lying depressions behind the berm separating the upper and lower portions of the NOAA site) indicate this is primarily floodplain deposition since the remediation.

Mercury at both the NOAA and Horizon Center catchments exists predominantly in highly sequestered forms such as organic-complexed mercury and HgS (Fig. 18). The most highly sequestered forms such as HgS comprise a much higher percentage of the mercury at the NOAA site in comparison with the Horizon Center site, similar to the results of speciation analysis with streambank soils (Section 3.1). Furthermore, although still only a relatively low percentage of the total mercury at the site, there is a greater percentage of mercury in more water-soluble forms at the Horizon Center site in comparison with the NOAA site.

3.3.2 Mercury in Floodplain Runoff

Floodplain runoff from the NOAA and Horizon Center sites was sampled and analyzed for total mercury, dissolved mercury and TSS during rainfall events in August 2008 and May 2009. Associated measurements were made of runoff flow through constructed weirs at each site. Rainfall was recorded concurrently by gauges located nearby on the Oak Ridge Reservation.

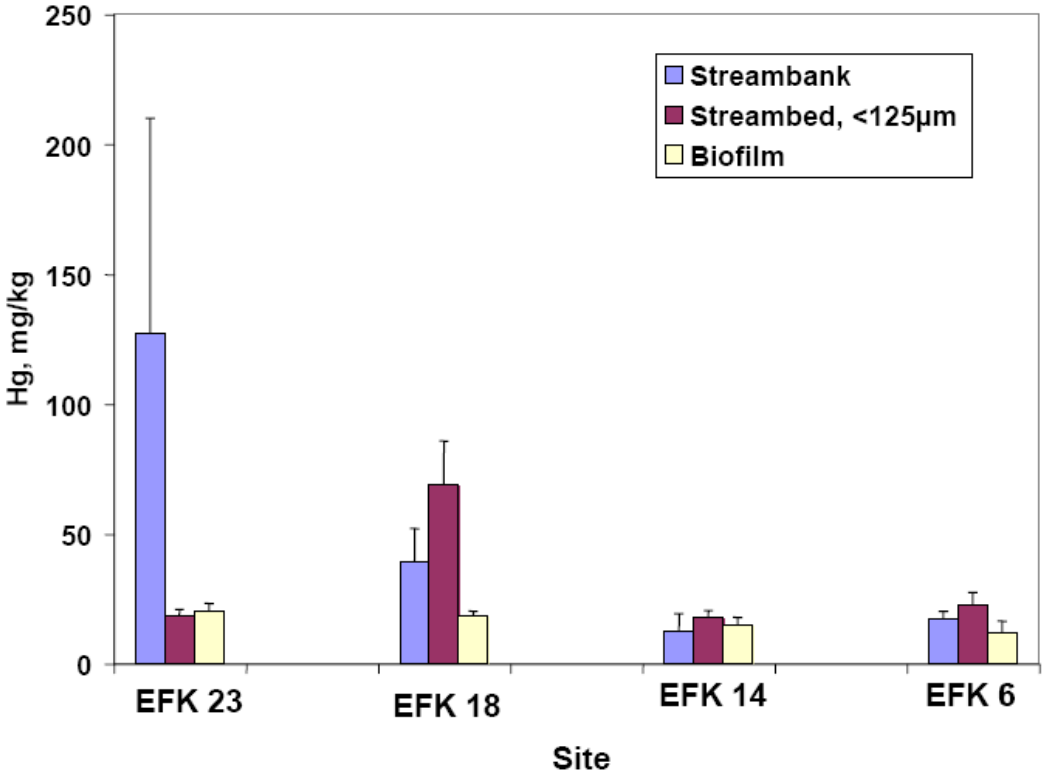

Fig. 15. Mean total mercury concentrations (means ± SEM) in EFPC bank, biofilm, and sediments.

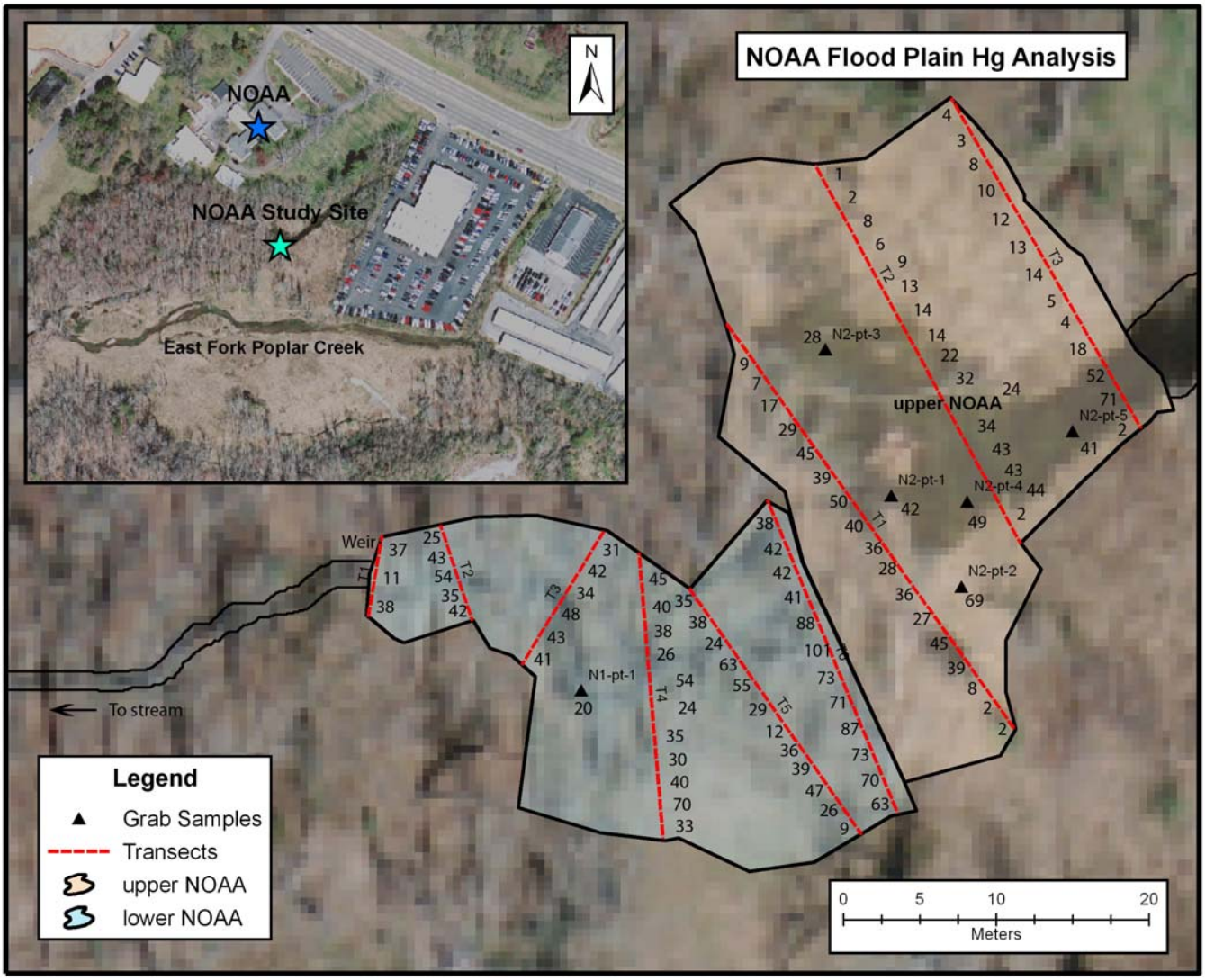

Fig. 16. Wet-weather catchment on the EFPC floodplain at the NOAA study site showing soil sampling transects, additional individual sampling points, and total mercury concentrations (mg/kg) in the top 1 cm of soil. Water flow is from right-to-left in the image; the upper and lower NOAA areas are separated by a berm which pools water in the upper area, although water eventually seeps at the midpoint of the berm into the lower area along the preferred flow path. Map from Google Earth.

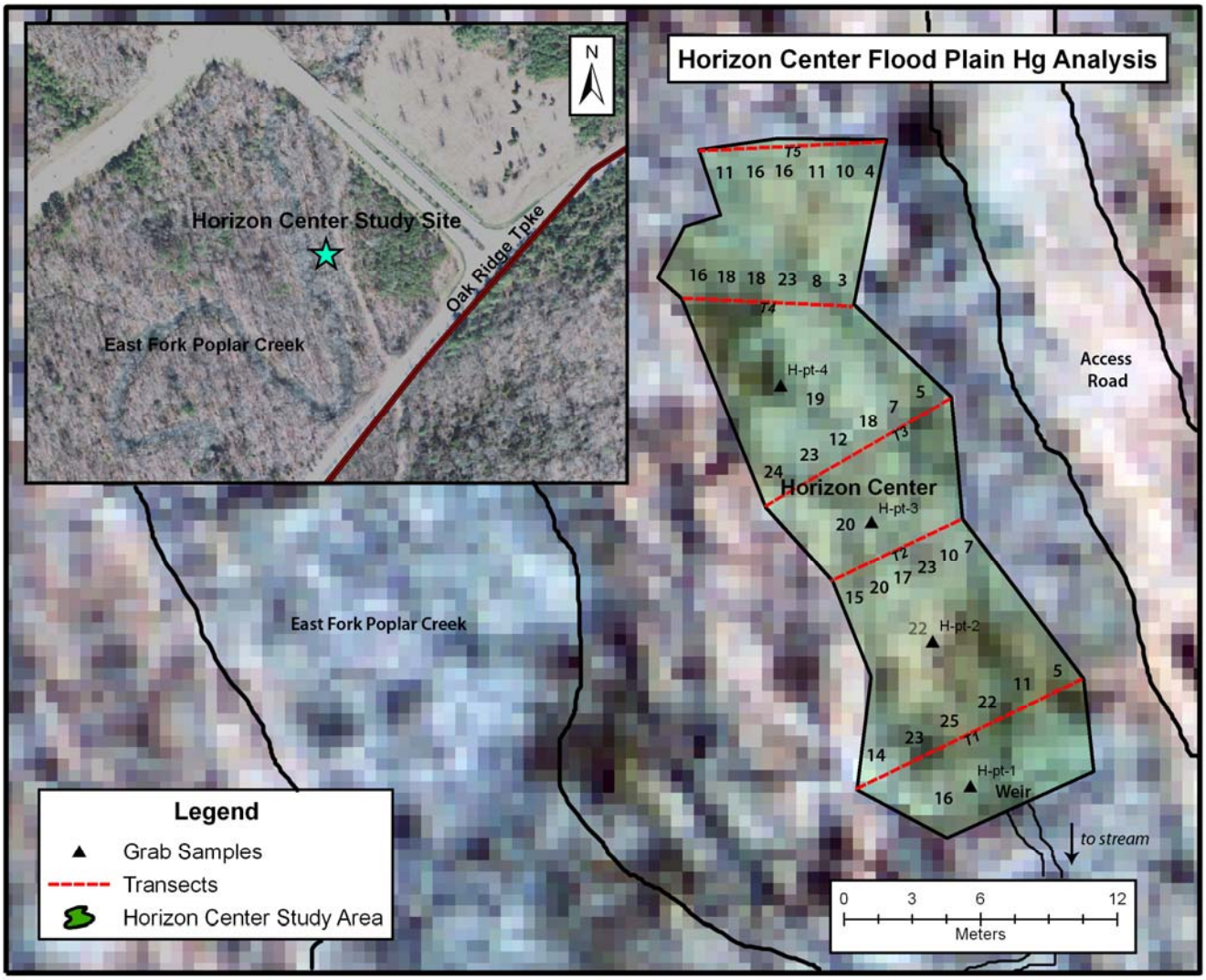

Fig. 17. Wet-weather catchment on the EFPC floodplain at the Horizon Center study site showing soil sampling transects, additional individual sampling points, and total mercury concentrations (mg/kg) in the top 1 cm of soil. The preferred water flow path is from the top to the bottom of the figure. Map from Google Earth.

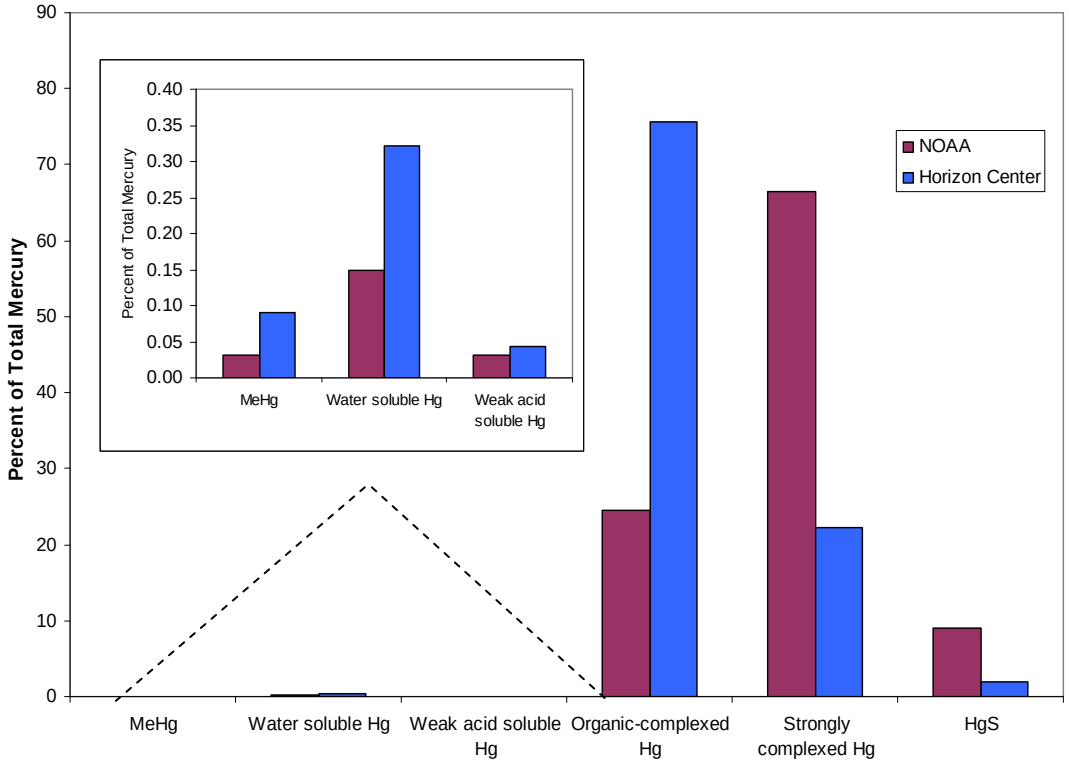

Fig. 18. Speciation of mercury in EFPC floodplain soils at the NOAA and Horizon Center floodplain study sites. Sequestered mercury (organic-complexed, strongly complexed, and HgS fractions in the sequential extraction speciation analysis) are to the right of the figure, while more accessible Hg species and methylmercury are shown in the inset to the left of the figure.

August 2008 rain event – For the initial sampling event in August 2008, ISCO samplers were set to collect water samples every 10 minutes in anticipation of sampling transitory surface flow from scattered summer thunderstorms. However, rainfall that developed in summer 2008 after the sampling equipment was installed in the experimental catchments generally failed to result in surface runoff due to the extreme dryness of the floodplain soils from an extended dry spell. A sustained rainfall event in late August 2008, with rainfall totals from 2.32–2.93 inches over a period of days, was eventually sufficient to re-hydrate the floodplain soil and cause surface runoff at the study sites (Fig. 19). Even with such a steady soaking, rainfall durations of nearly a day at the Horizon Center site and more than a day in the case of the NOAA site were required before surface runoff was first detected at the experimental weirs. The ISCO sampler at the lower NOAA location captured the first flush of the surface runoff and continued collecting water samples until the surface flow reached an initial steady-state; however, a second peak of much greater flow that occurred after the over-topping of the berm separating the lower NOAA area from the upper NOAA was not captured by this sampling design. The sampler at the Horizon Center missed the first flush from this catchment due to an equipment malfunction, but then sampled through two transitory surges of surface flow prior to sampler shut-down. This sampler was emptied and started again, catching the tail-end of the initial flow event and also another small mini-peak of surface flow that occurred following additional rain a few hours later. As in the case of the NOAA site, the period of maximum surface flow through the Horizon Center catchment was not sampled due to the relatively short sampling intervals chosen for this preliminary study. All sample bottles had already filled prior to the maximum surface flow.

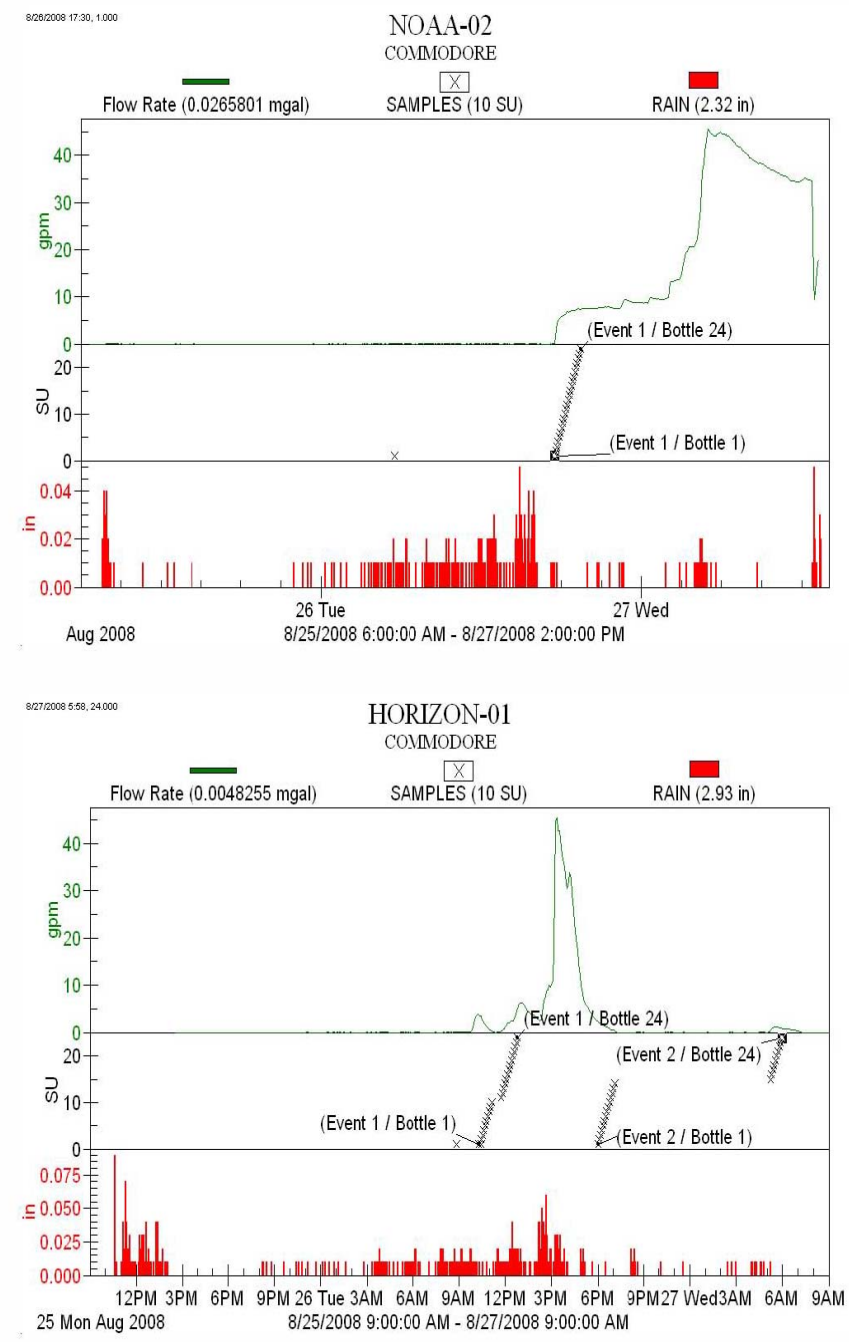

Fig. 19. Rainfall and water flow in wet-weather catchments at the NOAA and Horizon Center floodplain study sites during an August 2008 rain event. Graphs supplied by Tim Herrell, Commodore Applied Technologies.

The concentration of total mercury in the unfiltered first flush off the NOAA catchment during the August rain event was nearly 5000 ng/L (Fig. 20), but subsequent unfiltered samples rapidly decreased in concentration to a mean of 139 ng/L for the duration of the sampling run. At the Horizon Center site, the first flush was missed due to the afore-mentioned equipment failure, but subsequent unfiltered runoff samples had much higher concentrations of total mercury than at the NOAA site (other than the NOAA first flush sample), ranging from 713–2377 ng/L. Mercury concentrations of filtered samples ranged from a mean of 32 ng/L at the NOAA site to 180 ng/L at the Horizon Center site. TSS averaged 21mg/L at the NOAA site and 15 mg/L at the Horizon Center site.

Since peak runoff flows were not sampled for mercury at either site, total mercury flux estimates for this rain event (Table 6) are based on both measured mercury samples and estimated mercury concentrations during the non-sampled portions of flow. In the case of the NOAA site, flux was estimated for the period of time during which flow continued to be measured through the weir. Mercury concentrations were assumed to remain at the level of the last measured sample. For the Horizon Center site, mercury concentrations between sampling events 1 and 2 were assumed to remain at the mean of the concentration of the last sample collected in the first ISCO sampling run and the first sample collected in the second ISCO run. Based on these assumptions, total mercury flux during this rain event site was estimated to be approximately 12 mg from the NOAA site and 32 mg from the Horizon Center site. With the additional assumption that runoff from the entire mercury-contaminated portion of the floodplain was similar to these two catchments, it was then further estimated that approximately 56 grams of total mercury was exported from the floodplain to EFPC via surface runoff during this August 2008 rain event.

In preliminary surveys of the floodplain to determine suitable wet-weather catchments for these studies, it was observed that such discrete drainages were relatively uncommon within the mercury-contaminated portions of the floodplain. Much of the wet-weather drainage from these areas of the floodplain was confined by a slightly elevated strip or berm of land adjacent to the streambank so that rainfall appeared to generally percolate into the soil rather than drain directly via surface runoff to EFPC. Thus, the extrapolation of erosional inputs from these experimental catchments to the entire mercury- contaminated floodplain represents a likely overestimate of the potential contribution of this source to mercury flux in the watershed.

May 2009 rain event – Experience gained during the August 2008 rain event sampling was applied to a subsequent floodplain runoff study conducted during a rain event in May 2009. For this investigation, ISCO samplers were set to collect water samples at hourly intervals to avoid potentially missing peak flow during an extended rain event as occurred during the 2008 study. Furthermore, in order to better compare mercury flux from the floodplain soils via surface runoff during this rain event to the accompanying flux of mercury in EFPC, EFPC samples upstream of the NOAA floodplain site (Station 17 at the Y-12 National Security Complex) and adjacent to the Horizon Center floodplain site were collected along with the floodplain runoff samples.

During the May 2009 study, floodplain soils were saturated due to previous rainfall; surface flow occurred rapidly in response to a significant rainfall event (Fig. 21). The concentrations of total mercury in unfiltered samples from the NOAA site ranged from 67 ng/L to 5020 ng/L in the first flush, with a mean concentration of 635 ng/L. At the Horizon Center site, concentrations of total mercury in unfiltered samples ranged from 42 ng/L to 11,387 ng/L, with a mean of 906 ng/L. Mercury was much lower in filtered samples from both sites, with average concentrations of 28 ng/L at NOAA and 58 ng/L at the Horizon Center.

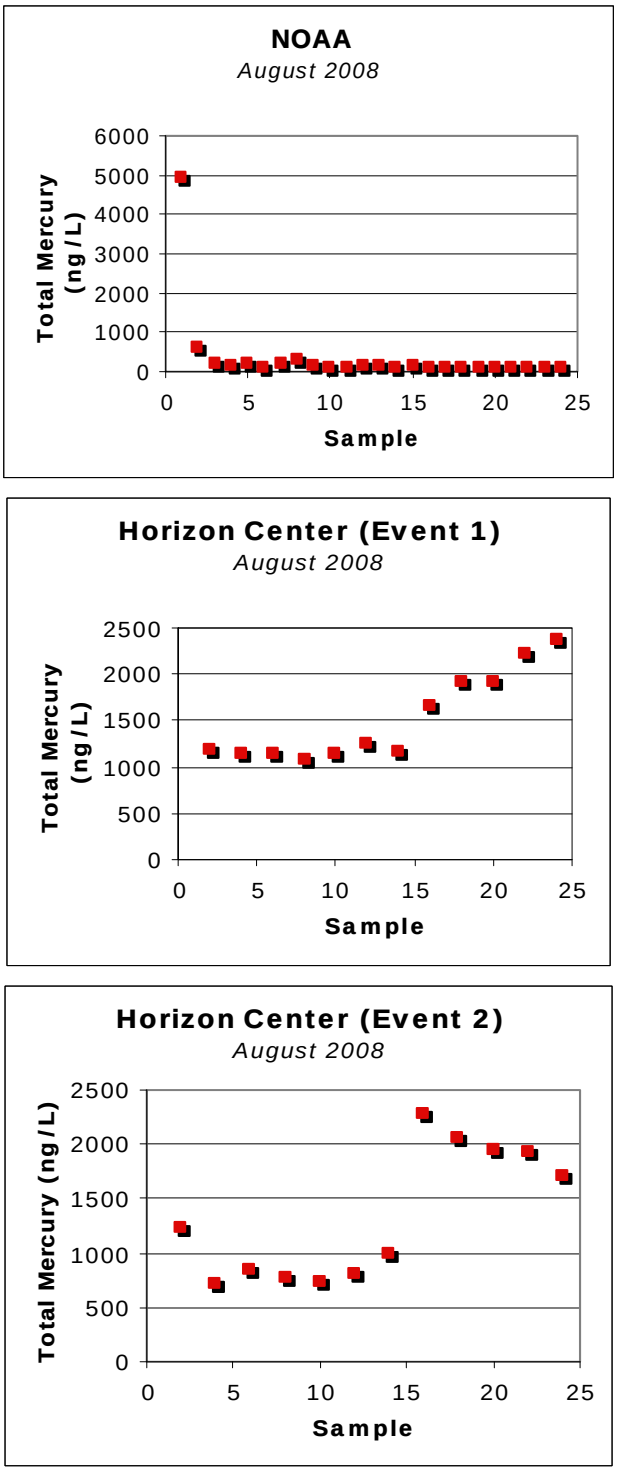

Fig. 20. Total mercury concentrations in surface runoff from wet-weather catchment runoff from floodplain soils at the NOAA and Horizon Center study sites during an August 2008 rain event. Samples were obtained at 10-minute intervals following the beginning of flow across constructed experimental weirs. Rainfall and water flow during the rain event are shown in Fig. 19.

Table 6. Estimates of total mercury flux via surface runoff from wet-weather catchments at the NOAA and Horizon Center floodplain study sites during an August 2008 rain event

Site	Duration of flow (hr)	Discharge during event (L)	Estimated total Hg flux during event (g)
NOAA (EFK 23)	20+	101,000+	0.012
Horizon Center (EFK 6)	12	18,300	0.032
Total Hg flux from catchments	–	–	0.044
Estimated Hg flux from entire floodplain[1]	–	–	56

[1]Based on estimated East Fork Poplar Creek floodplain area of 200 mercury-contaminated hectares published in Turner and Southworth 1999.

The hour-by-hour flux of total mercury from the NOAA and Horizon Center sites during this rainfall event is shown in Fig. 22. It is evident from this figure that mercury flux into EFPC via floodplain runoff can be highly episodic during rainfall events, especially in this example at the Horizon Center study site. Estimates of total mercury exported via surface runoff from the floodplain to EFPC during the entire 24-hr period of this study are provided in Table 7. A total of 33 mg of mercury was exported from the floodplain catchment at NOAA to EFPC via surface runoff during 24 hrs of this May 2009 rain event, while 73 mg was exported from the floodplain catchment at Horizon Center. Assuming once again that runoff from the entire mercury-contaminated portion of the floodplain was similar to these two catchments, it is then estimated that 134 g of total mercury was exported from the floodplain to EFPC via surface runoff during a 24-hr period of this rain event.

The accompanying mercury flux in EFPC during the May rain event is shown in Fig. 23. The Y-12 NSC was calculated to contribute 104 g of total mercury to EFPC during this 24-hr period, a figure somewhat less than the 134 g estimated to be exported from the floodplain via surface runoff during the same period. However, with the mercury flux through lower EFPC at EFK 6 estimated to be 1307 g, it is obvious that over 80% of the mercury flux from EFPC during this rain event must have been due to other potential mercury sources such as streambank erosion or streambed sources.

3.4 MERCURY EXPORT DURING BASEFLOW

Semi-annual grab samples have been collected and analyzed for filtered (dissolved) and unfiltered (total) mercury from FY 2000 through FY 2008 at Station 17, EFK 18.2, EFK 13.8, and EFK 6.3. Sampling has occurred under baseflow conditions during winter and summer to provide seasonal comparisons of dissolved and total mercury concentrations.

A USGS streamflow gauging station was operated at EFK 6 on EFPC from 1960 to 1986. Water usage by Y-12 and subsequent wastewater discharges to EFPC declined greatly in the 1990s. In 1998, initiation of a system to stabilize minimum flow at Station 17 at 7 to 8 mgd essentially restored flow in the stream headwaters to pre-1986 conditions. Because of this, historical records of the USGS station from 1960 to 1986 provide a reasonable basis for inferring present day baseflow conditions. Under that assumption, the dilution of the Station 17 flow between that site (EFK 23) and EFK 6 in lower EFPC was approximately 4- to 5-fold under winter (wet season) flow conditions, and about 2.5-fold under summer (dry season) conditions. During winter the dissolved mercury measured at Station 17 exhibits dilution downstream by a factor of about 4 to 5 as predicted by the flow proportionality

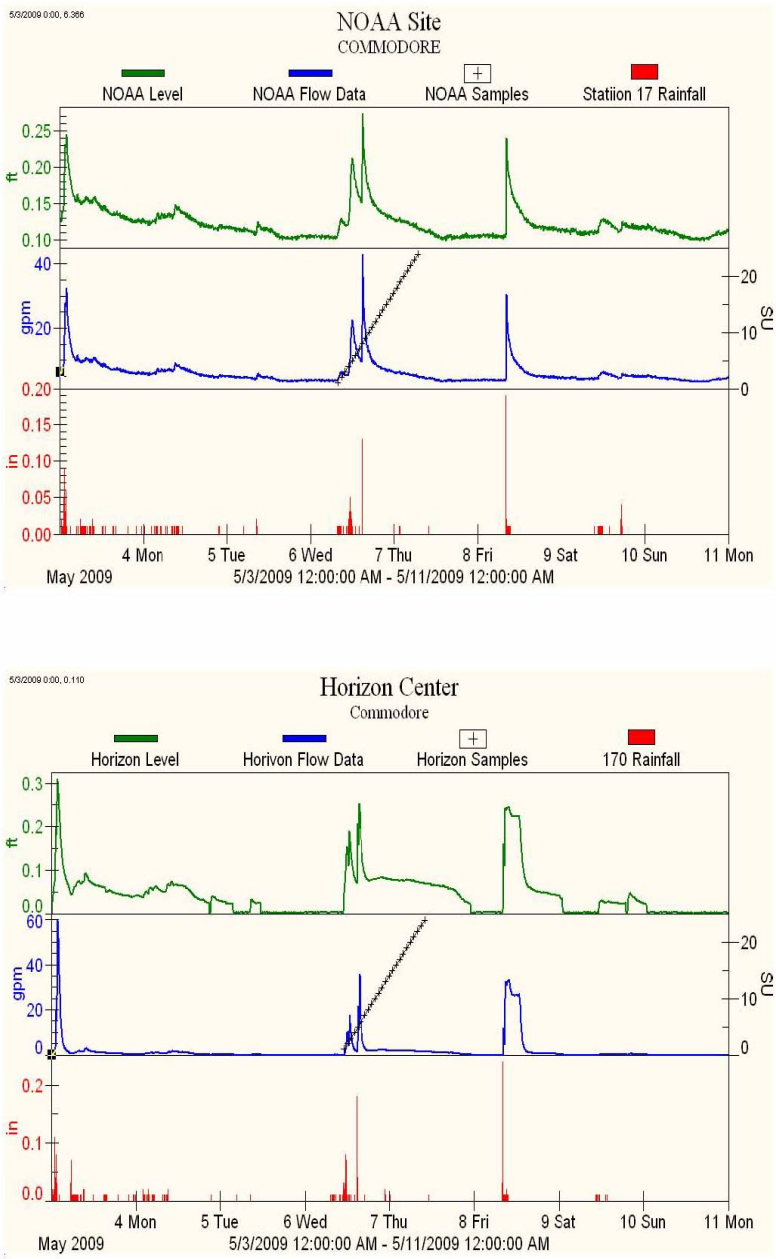

Fig. 21. Rainfall, stage and water flow in wet-weather catchments at the NOAA and Horizon Center floodplain study sites during a May 2009 rain event. Water samples for mercury analysis were obtained at 1 hr intervals after initiation of flow across constructed experimental weirs. Graphs supplied by Tim Herrell, Commodore Applied Technologies.

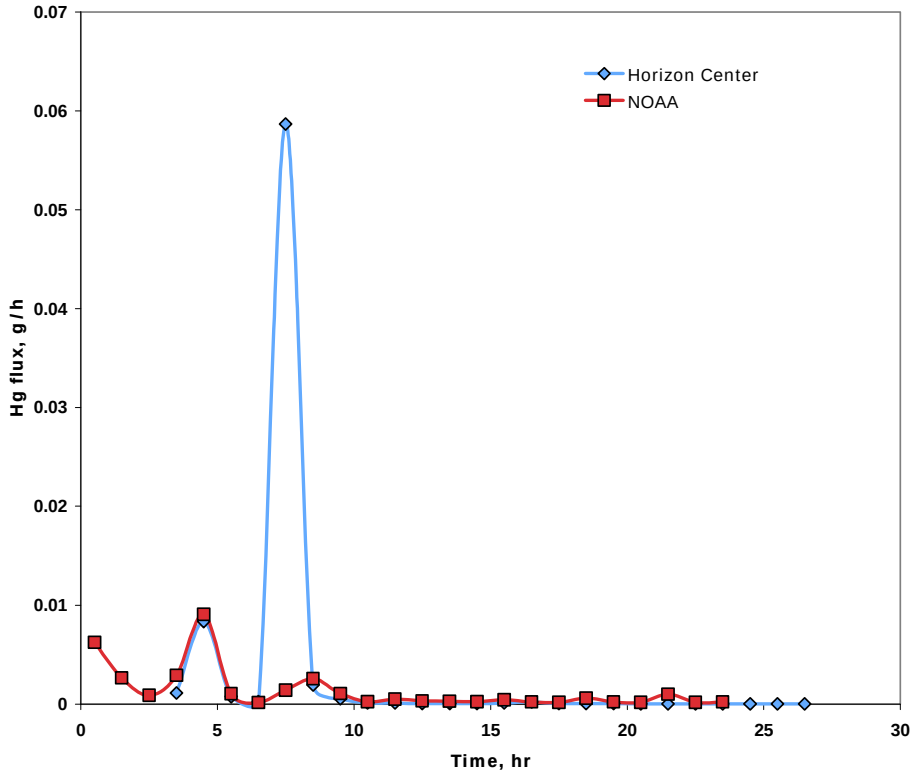

Fig. 22. Mercury flux from wet-weather catchments at the NOAA and Horizon Center floodplain study sites during a 24-h period of a May 2009 rain event. Individual data are in Table A-4.

Table 7. Estimates of total mercury flux via surface runoff from wet-weather catchments at the NOAA and Horizon Center floodplain study sites during a 24-h period of a May 2009 rain event

Site	Duration of flow during study (hr)	Discharge during 24-h study period (L)	Estimated total Hg flux during rain event (g)
NOAA (EFK 23)	24	468,288	0.033
Horizon Center (EFK 6)	24	1,185,811	0.073
Total Hg flux from catchments	–	–	0.106
Estimated Hg flux from entire floodplain[1]	–	–	134

[1]Based on estimated East Fork Poplar Creek floodplain area of 200 hectares published in Turner and Southworth 1999.

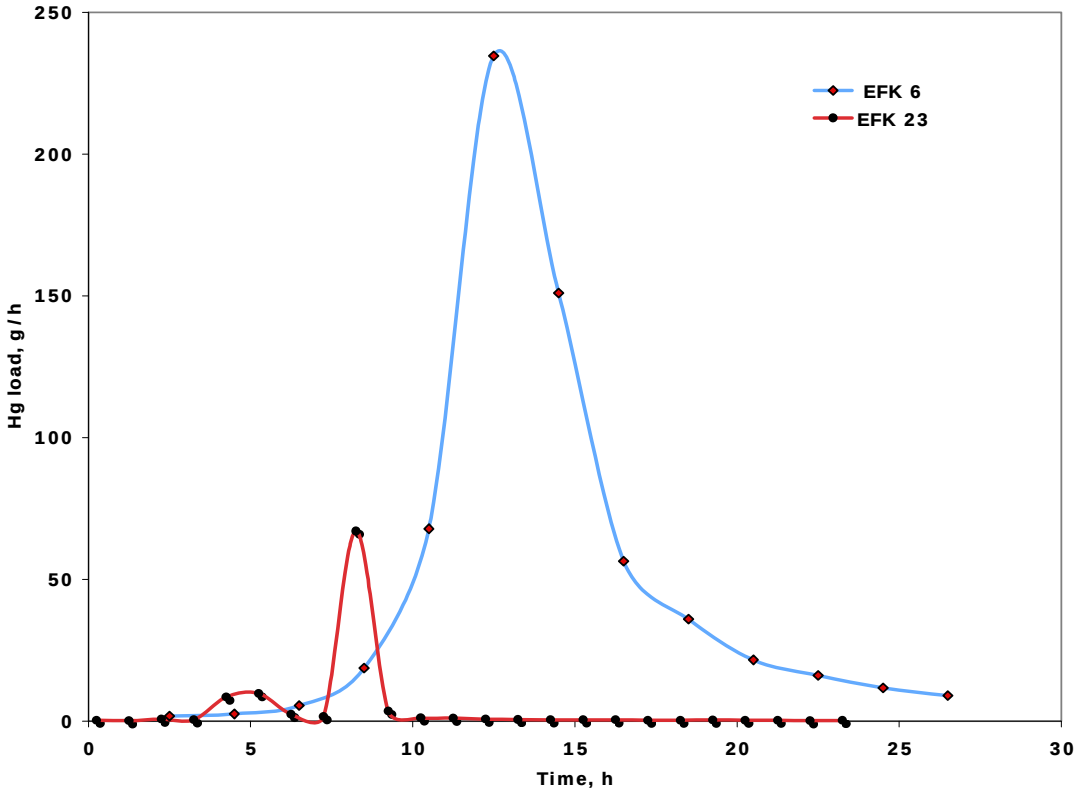

Fig. 23. Mercury export from EFPC headwaters (Station 17 at Y-12, EFK 23) and the rest of the watershed (EFK 6) during a 24-h period of a May 2009 rain event. Individual data are in Table A-5.

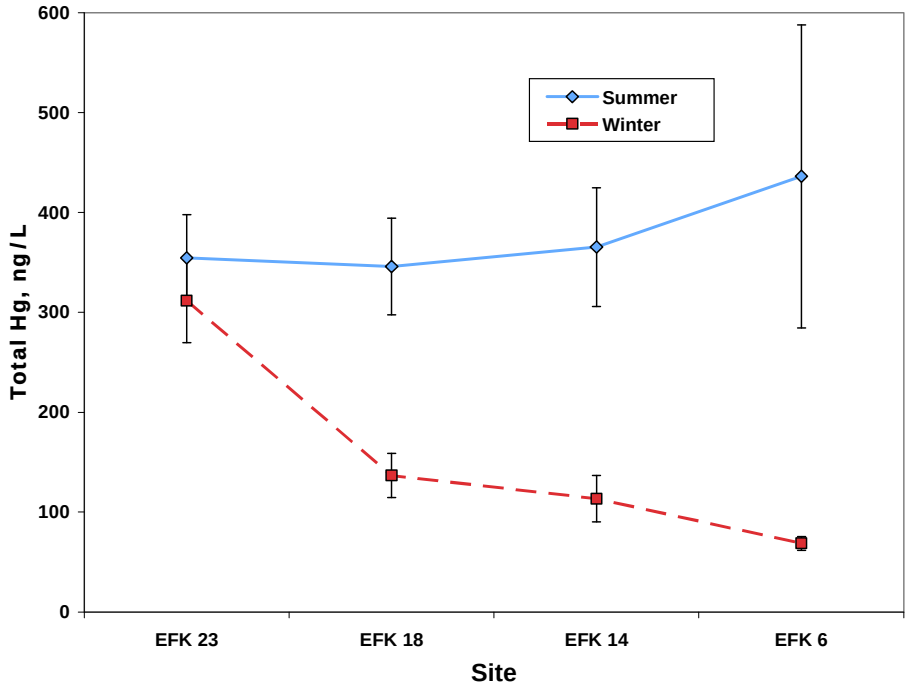

Fig. 24. Downstream profile of total mercury concentrations (means ± SEM) in twice yearly sampling of EFPC water, 1998–2008. Data from routine monitoring by BJC WRRP (OREIS 2008).

between Station 17 (~9 mgd) and the USGS winter average discharge at EFK 6 (~43 mgd). The behavior of total mercury mass balance is complicated by the high variability of suspended solids content and the overwhelming effect that TSS has on the total mercury load. The wet season total mercury dilution factor observed between Station 17 and EFK 6.3 between 2000 and 2008 ranges from about 2.5 to 5 with a mean of about 4.3. During summer the observed dilution factor ranges from about 0.2 to 2.1 with a mean of ~1.1. The low summertime total mercury dilution factor is observed at all 3 sampling locations in LEFPC downstream from Station 17. The reason for relatively little dilution of total mercury levels compared to the observed dissolved mercury dilution factor is that the suspended solids content increases downstream during summer. The average summer season baseflow suspended solids values measured at Station 17 were about 6.1 mg/L (with 7 of 12 results less than the 5 mg/L detection level) while the average at EFK 6.3 was about 18 mg/L (with no values less than the 5 mg/L detection level). The increase in suspended solids during summer months is thought to be caused by bioturbation of streambed sediment which can cause suspension of the finer fraction of streambed sediment. The winter baseflow sample average suspended solids at Station 17 averaged about 5.4 mg/L (with 3 in 10 results greater than the 5 mg/L detection level) and at EFK 6.3 the average was about 5.2 mg/L with 3 of 11 results greater than the detection level.

3.5 MERCURY EXPORT DURING STORMFLOW

In 1984, as part of its role in the Oak Ridge Task Force investigating mercury pollution in EFPC, TVA estimated annual mercury export from the EFPC watershed. That study found that the contaminated floodplain contributed most of the annual flux of mercury to downstream waters (Watts Bar Reservoir). No estimate has been made of changes in this source since that time. Therefore an effort was made to evaluate how much mercury export from the EFPC watershed has changed as a result of decreased headwater inputs, remedial actions in the EFPC floodplain, and increased urbanization of the watershed.

Much of the export of mercury from EFPC arises from the resuspension of fine particulates retained in the surface biofilm of the streambed, particularly in response to small increases in flow. Large increases in flow actively erode streambank deposits of contaminated soil and fine particulates within the streambed gravel. Changes in mercury content of the silt/clay fraction of the streambed biofilm would therefore be expected to translate into similar changes in mercury export during low to median/mean flow conditions. As can be seen in Fig. 25, successful reductions in headwater and floodplain inputs of mercury have been reflected in reduced concentrations of inorganic mercury in the streambed biofilm. The change is most pronounced in the upper reaches of the stream, where the present day mercury is roughly one-third what it was in 1989.

In an effort to quantify changes in mercury export from the EFPC that have taken place since the 1980s, total suspended solids concentrations and mercury concentrations on suspended particulates were measured during stormflow conditions and compared with measurements made by TVA in 1984. By assuming that watershed sediment yield has not changed between 1984 and 2008, we could use the sediment transport model developed in 1984 by TVA for EFPC to estimate annual mercury export from the watershed. Figure 26 plots mercury on suspended solids versus TSS concentration for 1984 and 2007. It is clear that mercury concentrations on suspended solids have decreased strikingly over the two decades. Annual mercury export from the watershed is estimated to have decreased from 227 kg/y to 63 kg/y, with similar changes from both headwater (Y-12 at Station 17, 34 to 9 kg/y) and floodplain (193 to 54 kg/y) sources. Although this analysis makes it appear that the contaminated floodplain of EFPC is the primary source of mercury to the stream, it is important to note that stormflow mercury inputs occur primarily as episodic events and that most of the mercury transport occurs within these stormflow events. In Fig. 27, the output of the TVA transport model is depicted

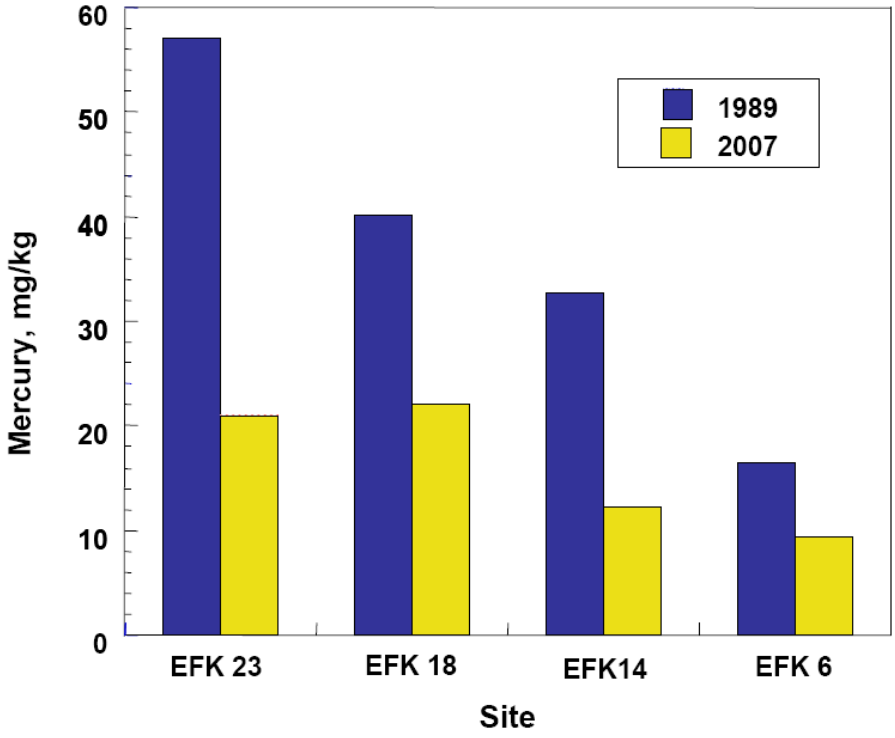

Fig. 25. Mercury concentration on fine particulate matter (<125 µm) retained by streambed biofilm versus distance downstream from Y-12, 1998 versus 2007.

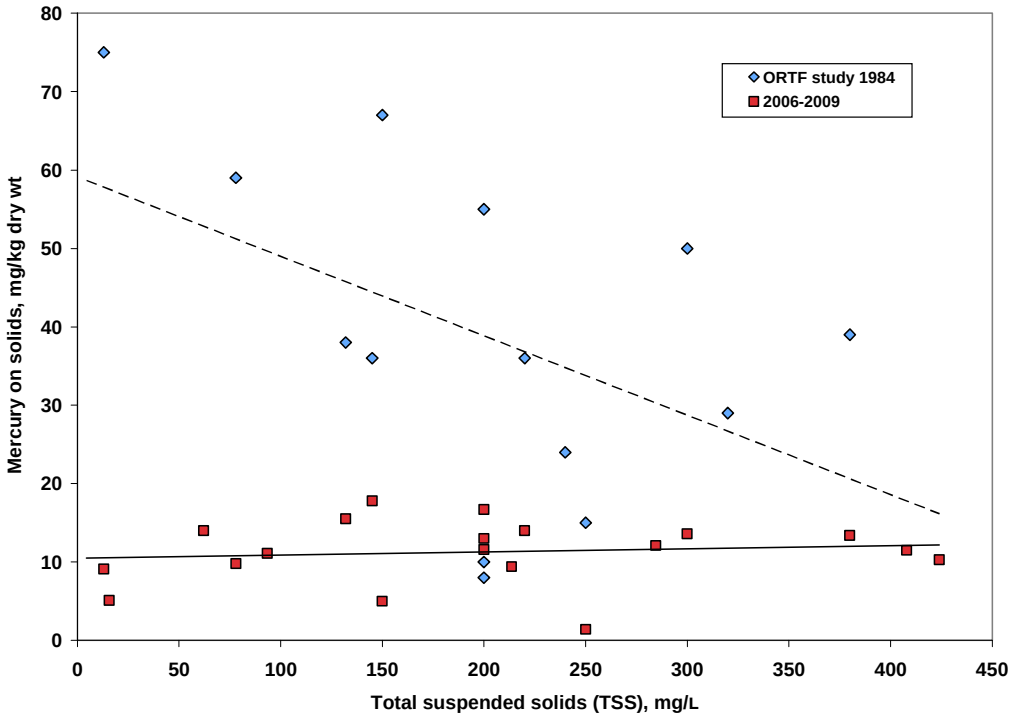

Fig. 26. Mercury concentration on suspended solids versus concentration of suspended solids in lower EFPC (EFK 6), 1984-1985 and 2006-2009.

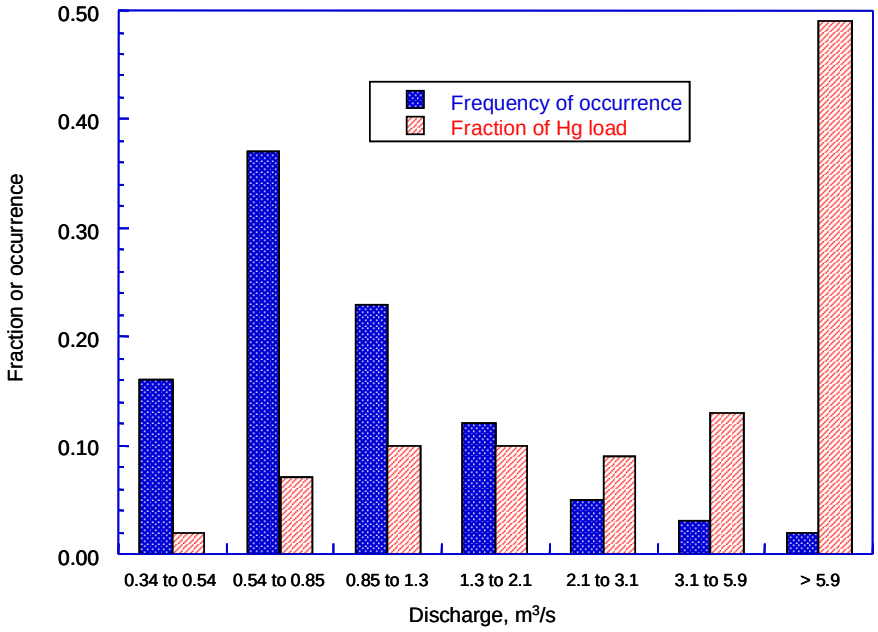

Fig. 27. Relationship between flow and mercury export in TVA (1985) sediment transport model for EFPC.

under varied flow conditions. Less than 10% of total mercury export occurs when flows are at or below the median (50% of the time), and nearly 50% of the mercury export occurs in flows that happen only 2% of the time.

Results of the May 2009 wet weather measurement of mercury flux from the EFPC watershed were consistent with the output of the modeling exercise described above. Estimates of mercury loading versus time are presented in Fig. 23. Mercury exported from both the contaminated source area (Y-12) and watershed downstream increased greatly with increased flow; the mass of mercury mobilized from the downstream watershed (1300 g) far exceeded that exported from the headwater site (130 g). Mercury export at EFK 6 also exceeded the estimate of the inventory in the surface biofilm of 20 km of stream (317 g) by four-fold, indicating that bank erosion, surface erosion, and resuspension of particulates embedded in streambed gravels were likely sources of mercury exported during the storm. Very conservative (likely to overestimate) calculations of the role of surface soil erosion (Section 3.3.2) indicate this source to be at most a minor contributor to the stormflow flux.

Total mercury concentrations within the water column increase greatly during high flow, with maximum concentrations of 4000 and 8250 ng/L observed at EFK 6 and EFK 23 during the May 2009 stormflow study. Dissolved (filter-passing) mercury changed relatively little, exhibiting maximum concentrations of 71 and 23 ng/L at the same sites. Data collected at EFK 6 from multiple storm events between 2005 and 2008 clearly demonstrate the extent to which 'dissolved' mercury is buffered by the strong association between mercury and particulates (Fig. 28). Although total mercury ranged as high as 6000 ng/L in that data set, dissolved mercury remained within a relatively narrow range and showed no relationship with the amount of mercury present in association with waterborne particulates.

The relative importance of the inventory of mercury in streambed gravel versus floodplain sources (bank erosion and surface erosion of floodplain soil) was explored through the use of a simple mass balance model to track mercury in the streambed over time. A simple spreadsheet model with one-year increments was used to describe the streambed inventory over time, with:

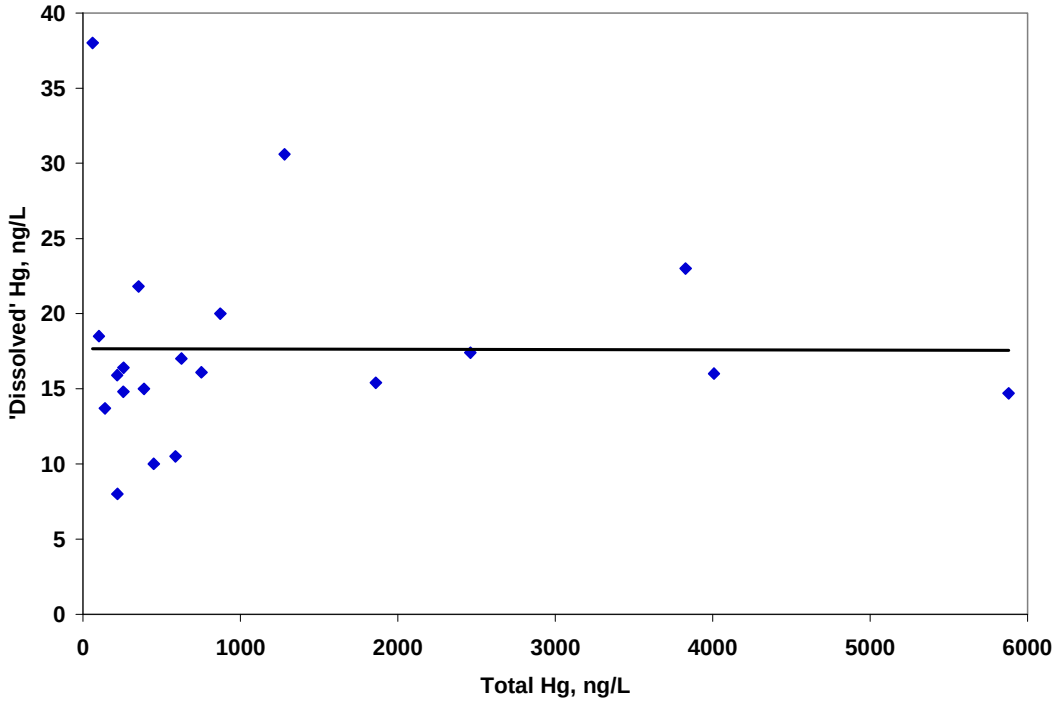

Fig. 28. Relationship between nominal dissolved (<0.45 µm filtered) and total mercury at EFK 6 in baseflow and stormflow samples collected 2005–2008.

$$\text{Hg inventory}_{(t=x+1)} = \text{Hg inventory}_{(t=x)} + \text{Annual Hg input, EFK 23}_{(t=x)} + \text{Annual Hg input, floodplain sources}_{(t=x)} - \text{Annual Hg export, EFK 6}_{(t=x)}.$$

The ratio of the estimated annual export rate at EFK 6 (54 kg/y) to the inventory of mercury in the streambed (343 kg) was used to calculate the first order rate constant for erosion of mercury from the streambed (0.157 y-1, roughly 16% per year). Mercury input from EFK 23 (Station 17) was obtained from published sources (RER 2009, BJC/OR-422, Turner et al. (1985). The initial inventory of mercury in the streambed between EFK 23 and EFK 6 was estimated by assuming the inventory in 1985 was approximately 3 times greater then than now (from the ratio of mercury concentrations on fine particulates at EFK 23 in Fig. 25. The inventory of mercury in the streambed was thus estimated at 1000 kg as an initial value (1985), and modeled to change based on the annual export loss (~ 16%/y) and inputs from the EFK 23 discharge and floodplain sources. The value of the floodplain input was varied until model output matched the 2008 estimates for mercury inventory and annual export (Fig. 29). An input rate of 45 kg/y from floodplain sources was required to obtain the fit to the observed values. The modeled results (Fig. 29) suggest that the streambed inventory of mercury in EFPC is no longer being diminished but rather is maintained by fresh inputs from floodplain soils.

Results of the catchment flux measurements indicate that annual export from surface erosion and runoff from the contaminated floodplain contributes only a small fraction of wet weather mercury export from the watershed (Section 3.3.2). Consequently, it appears that bank erosion is responsible for most of the annual mercury export from the watershed.

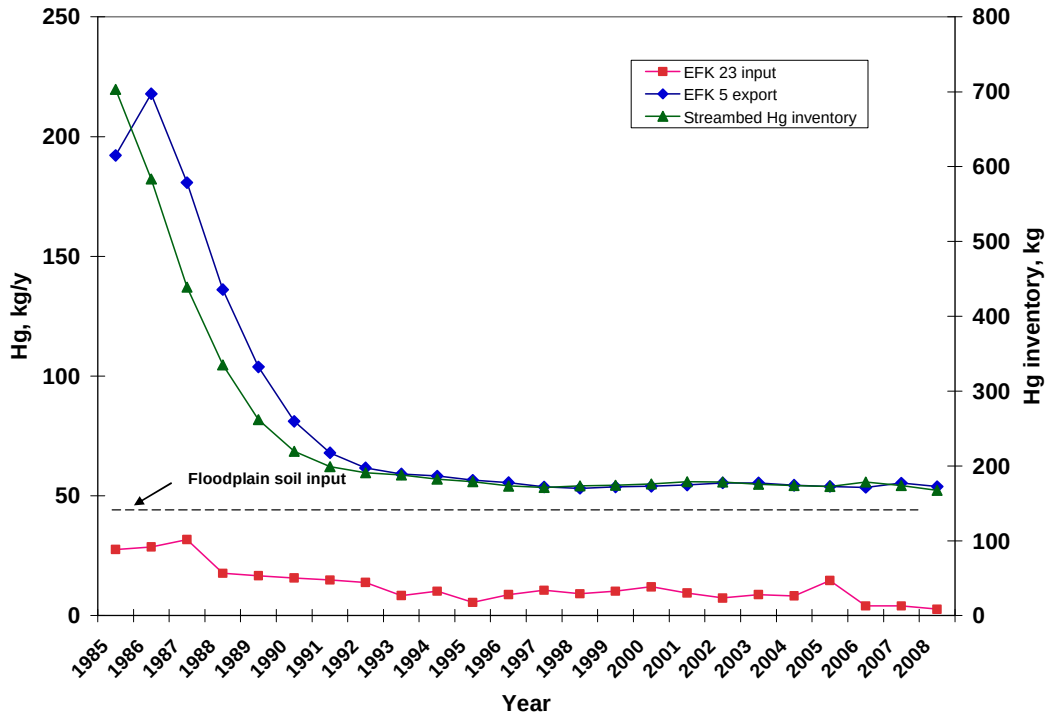

Fig. 29. Modeled mercury export and change in streambed inventory using annual measurements of mercury export from Y-12 (EFK 23), annual mercury export at EFK 5 of 193 kg/y in 1985 and 54 kg/y in 2008, and floodplain input of 45 kg/y.

3.6 METHYLMERCURY EXPORT

3.6.1 Sites of Methylmercury Production

One of the key questions yet to be answered in the EFPC system is where the methylmercury in the water column is produced. Mercury methylation is generally known to be most significant in zones of redox transition. Within a shallow, moderately fast flowing stream such as EFPC, deep anaerobic sediments are uncommon. Redox transition zones are likely to occur within gravel beds and on a micro-scale within the streambed biofilm.

The estimated inventories of methylmercury in the biofilm and streambed gravels of EFPC are shown in Tables 3 and 4. Because of its much smaller mass the surface biofilm contains a very small fraction of the methylmercury within the creek, despite having much higher concentrations at all sites than the streambed particulates (Fig. 30). Under an assumed mean flow of 125,000 m^3/d at EFK 6 and a mean waterborne total methylmercury concentration of 1.0 ng/L, the warm weather export of methylmercury from the creek is estimated to be approximately 125 mg methylmercury per day. The amount of methylmercury estimated to be in the streambed biofilm, 313 mg, thus would represent approximately the amount of methylmercury exported in three days.

The estimated inventory of methylmercury in the streambed gravel, i.e., 58 grams, is more than 100-fold that in the biofilm. That inventory could sustain the estimated mean flow export of methylmercury for approximately 1.3 years. It is likely, however, that the turnover time of methylmercury in sediments is determined by the rate of demethylation, and the inventory of methylmercury must be maintained by continued production of methylmercury within the streambed.

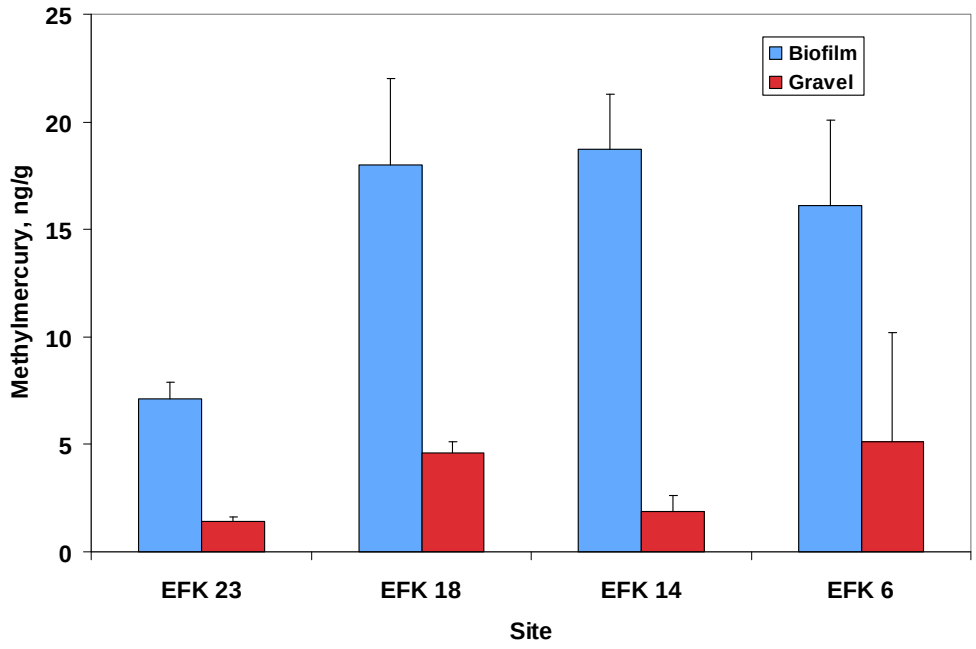

Fig. 30. Methylmercury concentrations (means ± SEM) in streambed particulates in EFPC.

Total mercury concentrations on biofilm solids and the silt/clay fraction of the gravel samples were similar at two of four locations and higher in gravel samples at two (Fig. 15). This implies that porewater-dissolved mercury concentrations within the gravel are similar or higher than is typical of the biofilm. However, the ratio of methylmercury to total mercury is considerably higher in the biofilm samples than in the gravel samples (Fig. 31). The observation that precursor inorganic concentrations are similar but percent methylmercury is much higher at the stream surface suggests that either the biofilm is a very active site of net methylmercury production or that net production within the streambed is concentrated near the surface. The percent methylmercury observed in suspended solids in EFPC (the average of twice yearly sampling conducted by the BJC WRRP over the past three years) corresponds well with the values measured in the streambed biofilm. Together, the small inventory of methylmercury in the streambed biofilm relative to the rate of export of methylmercury via surface flow suggests that net methylation must be extremely rapid within the biofilm or methylmercury production within the streambed gravel contributes substantially to the surface water methylmercury.

3.6.2 Bank and Soil Erosion as a Source of Methylmercury

Mercury-contaminated riparian soil was found to contain methylmercury (~0.04%). Therefore erosion provides a mechanism for introducing that methylmercury to the stream. If EFPC streambanks and floodplain soils are assumed to contribute 45 kg of mercury per year to EFPC, the daily average methylmercury load arising from this source, if it was uniformly distributed, would be 45 kg*.0004, or 0.018 kg/y, corresponding to a daily export rate of 48 mg/d methylmercury. Of course, streambank erosion would be skewed toward high flow events, and thus most of the methylmercury export from streambank soils would not occur under baseflow conditions. If 20% of streambank-derived methylmercury was exported under baseflow conditions, streambank methylmercury would constitute 10% or less of the daily methylmercury exported during baseflow conditions in the creek. Nevertheless, methylmercury inputs from floodplain soils and streambanks cannot be considered trivial, and in some uncontaminated streams, riparian soil may be an important source of methylmercury to aquatic life.

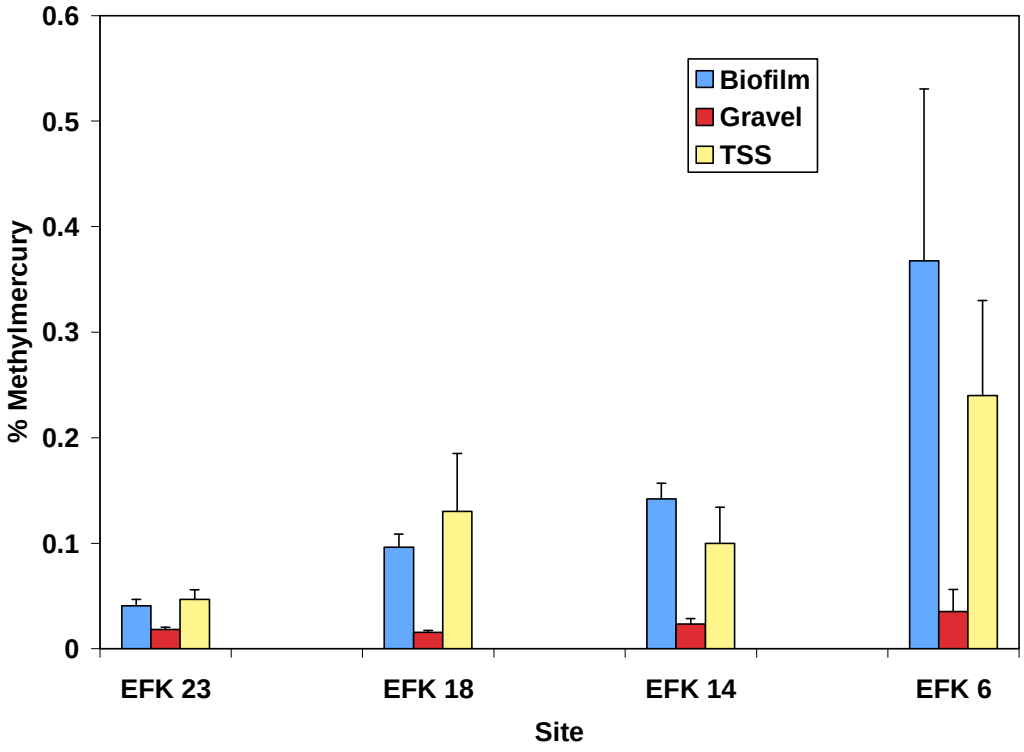

Fig. 31. Percent methylmercury (means ± SEM) in streambed particulates and TSS in EFPC.

4. CONCLUSIONS

This is the first attempt to estimate and compare the magnitude of various sources to the export of mercury from the East Fork Poplar Creek watershed. As such, the objective was to generate estimates that would enable us to determine which pathways and compartments were most important in determining the day-to-day and annual export of mercury and methylmercury from the system. More sophisticated and expansive sampling and analysis could then be applied to refine the accuracy and precision of those measurements of apparent greatest importance. Estimates made in this study should therefore be viewed as reasonable approximations, with substantial uncertainty and imprecision. Nevertheless, they lead to some relatively clear conclusions that should act as a guide for further investigation.

Most mercury (>90%) exported from the EFPC watershed under wet weather flow arises from the watershed downstream from Y-12, not within the headwater industrial complex. Inputs from surface erosion of floodplain soils were a relatively small fraction (~10%) of total mercury export from the LEFPC under wet weather conditions, indicating that mobilization of mercury from streambed and streambanks was the source of most high flow mercury export.

The inventory of inorganic mercury in the EFPC streambed is not large enough for it to sustain the existing rates of mercury export from the watershed for more than a few years. Large inputs (~45 kg/y) from the erosion of streambank soils are required to maintain the observed export rate. A large fraction of the length of EFPC contains unvegetated, steep, mercury-contaminated streambanks susceptible to erosional processes that would deposit mercury-contaminated soil into EFPC. Such inputs undoubtedly occur during high flow conditions, but frost-heave sloughing and similar dry weather erosional processes may also contribute to a gradual accumulation of streambank-derived material in the streambed.

The biologically active coating on the surface of the EFPC streambed (biofilm) is readily resuspended as streamflow increases, but the inventory of mercury in it is too small to represent more than short-term storage of mercury being transported downstream. Although it may provide a large fraction of the mercury exported during a single storm event, rapid replenishment of the mercury content of the biofilm from another source would be required to sustain the annual export rate.

Inputs of particle-associated mercury to EFPC during wet weather events have little impact on the concentration of 'dissolved' inorganic mercury in the stream. The strong association of inorganic mercury with solids ($K_d \geq 10^6$) causes the stream to be at a near steady-state condition vis a vis desorption of mercury from particulates under baseflow conditions. Re-suspension of particulates from the streambed to the water column does not change the steady-state concentration of dissolved mercury.

The inventory of methylmercury in the surface biofilm of EFPC is too small to sustain the baseflow export rate without rapid generation of new methylmercury within the biofilm or rapid delivery of dissolved methylmercury from deeper sediments to the surface. The difference in the ratio of methylmercury to total mercury in the surface biofilm to that in underlying sediments suggests that methylmercury is produced primarily within the biofilm or sediments near the stream surface. Riparian soils may contribute some methylmercury to EFPC, but the rate of delivery is not high enough to account for baseflow export rates.

Floodplain sources (soils and streambanks) of mercury have the potential to continue contaminating EFPC for decades or more even if headwater sources are completely eliminated. Although the limited bioavailability of mercury in those sources may constrain waterborne inorganic mercury concentrations and the bioaccumulation of methylmercury in EFPC, it is also possible that mercury from floodplain sources could sustain the current levels of contamination in aquatic life. However, it is also critically important to differentiate between the temporal nature of the two sources. Although stream channel and bank Hg sources appear to be the most significant contributor to annual export of Hg from the watershed, the relatively constant input of dissolved Hg to the stream's headwaters from Y-12 appears to be much more important in sustaining baseflow Hg concentrations and thus the day-to-day exposure of aquatic life to inorganic Hg. Much remains to be learned before we can differentiate with confidence the respective roles of inputs of dissolved Hg from the headwaters and particle-associated Hg from the watershed downstream in determining the bioaccumulation of methylmercury in aquatic life in East Fork Poplar Creek.

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APPENDIX A

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Table A-1. Total mercury in samples from profiles of eroding streambanks

Site	Transect	Sample	Depth (below surface) cm	Hg mg/kg	Mean ± SE mg/kg
EFK23	T1	B1	107	7	
EFK23	T1	B2	99	72	
EFK23	T1	B3	91	135	
EFK23	T1	B4	84	173	
EFK23	T1	B5	76	99	
EFK23	T1	B6	69	97	
EFK23	T1	B7	61	190	221 ± 90
EFK23	T1	B8	53	30	
EFK23	T1	B9	46	47	
EFK23	T1	B10	38	119	
EFK23	T1	B11	30	182	
EFK23	T1	B12	23	148	
EFK23	T1	B13	15	1434	
EFK23	T1	B14	8	415	
EFK23	T1	B15	0	168	
EFK23	T2	B1	61	15	
EFK23	T2	B2	57	12	
EFK23	T2	B3	52	11	
EFK23	T2	B4	48	17	
EFK23	T2	B5	44	14	
EFK23	T2	B6	39	34	
EFK23	T2	B7	35	76	66 ± 15
EFK23	T2	B8	30	105	
EFK23	T2	B9	26	172	
EFK23	T2	B10	22	188	
EFK23	T2	B11	17	108	
EFK23	T2	B12	13	59	
EFK23	T2	B13	9	68	
EFK23	T2	B14	4	75	
EFK23	T2	B15	0	37	
EFK23	T3	B1	99	48	
EFK23	T3	B2	92	42	
EFK23	T3	B3	85	25	
EFK23	T3	B4	78	18	
EFK23	T3	B5	71	32	
EFK23	T3	B6	64	15	
EFK23	T3	B7	57	32	93 ± 37
EFK23	T3	B8	50	49	
EFK23	T3	B9	43	66	
EFK23	T3	B10	36	55	
EFK23	T3	B11	29	86	
EFK23	T3	B12	22	121	

Table A-1. (cont'd)

Site	Transect	Sample	Depth (below surface) cm	Hg mg/kg	Mean ± SE mg/kg
EFK23	T3	B13	15	136	
EFK23	T3	B14	8	599	
EFK23	T3	B15	0	72	
EFK18	T1	B1	89	28.8	
EFK18	T1	B2	83	23.6	
EFK18	T1	B3	76	23.9	
EFK18	T1	B4	70	27.9	
EFK18	T1	B5	64	20.4	
EFK18	T1	B6	57	16.8	
EFK18	T1	B7	51	17.8	25 ± 1.2
EFK18	T1	B8	44	22.5	
EFK18	T1	B9	38	20.8	
EFK18	T1	B10	32	24.2	
EFK18	T1	B11	25	26.5	
EFK18	T1	B12	19	28.2	
EFK18	T1	B13	13	33.8	
EFK18	T1	B14	6	31.3	
EFK18	T1	B15	0	23.5	
EFK18	T2	B1	142	69.6	
EFK18	T2	B2	132	74.6	
EFK18	T2	B3	122	195	
EFK18	T2	B4	112	89.1	
EFK18	T2	B5	102	79.6	
EFK18	T2	B6	91	60.2	
EFK18	T2	B7	81	58.6	66 ± 10
EFK18	T2	B8	71	66.5	
EFK18	T2	B9	61	52.9	
EFK18	T2	B10	51	47.9	
EFK18	T2	B11	41	44.9	
EFK18	T2	B12	30	38	
EFK18	T2	B13	20	37	
EFK18	T2	B14	10	37.2	
EFK18	T2	B15	0	38.3	
EFK18	T3	B1	109	64.2	
EFK18	T3	B2	101	41.4	
EFK18	T3	B3	94	28.1	
EFK18	T3	B4	86	22.3	
EFK18	T3	B5	78	22.2	
EFK18	T3	B6	70	22.9	
EFK18	T3	B7	62	21.6	27 ± 3.0

Table A-1. (cont'd)

Site	Transect	Sample	Depth (below surface) cm	Hg mg/kg	Mean ± SE mg/kg
EFK18	T3	B8	55	18.2	
EFK18	T3	B9	47	19.2	
EFK18	T3	B10	39	19.1	
EFK18	T3	B11	31	21.3	
EFK18	T3	B12	23	22.2	
EFK18	T3	B13	16	24.6	
EFK18	T3	B14	8	23.7	
EFK18	T3	B15	0	32.8	
EFK14	T1	B1	147	2.22	
EFK14	T1	B2	137	0.62	
EFK14	T1	B3	126	1.55	
EFK14	T1	B4	116	3.78	
EFK14	T1	B5	105	0.68	
EFK14	T1	B6	95	7.91	
EFK14	T1	B7	84	4.14	11 ± 2.3
EFK14	T1	B8	74	11.4	
EFK14	T1	B9	63	7.26	
EFK14	T1	B10	53	22.5	
EFK14	T1	B11	42	22.9	
EFK14	T1	B12	32	23.1	
EFK14	T1	B13	21	21.6	
EFK14	T1	B14	11	20.9	
EFK14	T1	B15	0	13.6	
EFK14	T2	B1	163	0.9	
EFK14	T2	B2	151	0.19	
EFK14	T2	B3	139	0.93	
EFK14	T2	B4	128	0.22	
EFK14	T2	B5	116	0.8	
EFK14	T2	B6	105	0.2	
EFK14	T2	B7	93	0.15	
EFK14	T2	B8	81	0.73	2.2 ± 1.9
EFK14	T2	B9	70	0.06	
EFK14	T2	B10	58	0.06	
EFK14	T2	B11	46	0.52	
EFK14	T2	B12	35	0.41	
EFK14	T2	B13	23	0.34	
EFK14	T2	B14	12	0.11	
EFK14	T2	B15	0	28	
EFK14	T3	B1	130	11.7	
EFK14	T3	B2	120	12.3	
EFK14	T3	B3	111	13.7	

Table A-1. (cont'd)

Site	Transect	Sample	Depth (below surface) cm	Hg mg/kg	Mean ± SE mg/kg
EFK14	T3	B4	102	14	
EFK14	T3	B5	92	14.5	
EFK14	T3	B6	83	13.6	
EFK14	T3	B7	74	13.2	25 ± 8.0
EFK14	T3	B8	64	17.8	
EFK14	T3	B9	55	13.6	
EFK14	T3	B10	46	9.2	
EFK14	T3	B11	36	6.9	
EFK14	T3	B12	27	15.7	
EFK14	T3	B13	18	30.7	
EFK14	T3	B14	8	57.1	
EFK14	T3	B15	0	127.6	
EFK6	T1	B1	142	15.7	
EFK6	T1	B2	132	11.7	
EFK6	T1	B3	122	8.4	
EFK6	T1	B4	112	6.0	
EFK6	T1	B5	102	11.4	
EFK6	T1	B6	91	10.6	
EFK6	T1	B7	81	19.9	16 ± 2.1
EFK6	T1	B8	71	21.4	
EFK6	T1	B9	61	11.7	
EFK6	T1	B10	51	10.8	
EFK6	T1	B11	41	39.3	
EFK6	T1	B12	30	23.8	
EFK6	T1	B13	20	19.1	
EFK6	T1	B14	10	11.2	
EFK6	T1	B15	0	14.9	
EFK6	T2	B1	178	12.6	
EFK6	T2	B2	165	3.1	
EFK6	T2	B3	152	8.0	
EFK6	T2	B4	140	5.6	
EFK6	T2	B5	127	7.2	
EFK6	T2	B6	114	7.2	
EFK6	T2	B7	102	6.8	12 ± 3.0
EFK6	T2	B8	89	13.8	
EFK6	T2	B9	76	7.3	
EFK6	T2	B10	64	5.5	
EFK6	T2	B11	51	4.8	
EFK6	T2	B12	38	14.3	
EFK6	T2	B13	25	30.8	
EFK6	T2	B14	13	46.3	
EFK6	T2	B15	0	10.5	

Table A-1. (cont'd)

Site	Transect	Sample	Depth (below surface) cm	Hg mg/kg	Mean ± SE mg/kg
EFK6	T3	B1	131	8.7	
EFK6	T3	B2	121	10.8	
EFK6	T3	B3	112	7.1	
EFK6	T3	B4	103	11.3	
EFK6	T3	B5	93	14.8	
EFK6	T3	B6	84	9.6	
EFK6	T3	B7	75	13.0	23 ± 5.2
EFK6	T3	B8	65	30.1	
EFK6	T3	B9	56	30.1	
EFK6	T3	B10	47	49.3	
EFK6	T3	B11	37	41.9	
EFK6	T3	B12	28	77.9	
EFK6	T3	B13	19	13.0	
EFK6	T3	B14	9	13.7	
EFK6	T3	B15	0	9.0	

Table A-2. Surface sediment biofilm samples collected in East Fork Poplar Creek in August 2008

Site	Transect	Sample	Surface area cm^2	Sample mass g	sed/m^2 g/m^2	MeHg ng/g	HgT mg/kg	%MeHg	HgT/m^2 mg/m^2	MeHg/m^2 $\mu g/m^2$
EFK23	T1	SAS1	1008	14.4	143.3	11.5	37.1	0.031	5.32	1.65
EFK23	T1	SAS2	1311	7.3	55.4	4.04	14.9	0.027	0.83	0.22
EFK23	T1	SAS3	1187	5.7	48.4	5.04	14.5	0.035	0.70	0.24
EFK23	T2	SAS1	790	13.9	176.1	7.71	20.6	0.037	3.63	1.36
EFK23	T2	SAS2	2792	6.5	23.3	6.65	10.7	0.062	0.25	0.16
EFK23	T2	SAS3	1107	28.0	252.5	8.49	31	0.027	7.83	2.14
EFK23	T3	SAS1	1958	11.7	59.6	9.54	13.1	0.073	0.78	0.57
EFK23	T3	SAS2	1298	18.2	139.9	5.62	10.7	0.053	1.50	0.79
EFK23	T3	SAS3	481	9.6	199.3	5.46	27	0.020	5.38	1.09
EFK 18	T1	SAS1	missing	3.0		9.33	12.2	0.076		
EFK 18	T1	SAS2	845	4.4	52.4	8.11	9.05	0.090	0.47	0.43
EFK 18	T1	SAS3	545	11.6	212.8	47.5	28.3	0.168	6.02	10.11
EFK 18	T2	SAS1	641	17.4	271.8	17.6	19.9	0.088	5.41	4.78
EFK 18	T2	SAS2	624	24.5	392.0	14.4	13.5	0.107	5.29	5.64
EFK 18	T2	SAS3	674	22.8	338.3	18.7	19.9	0.094	6.73	6.33
EFK 18	T3	SAS1	1056	11.4	108.2	8.55	23.5	0.036	2.54	0.93
EFK 18	T3	SAS2	1292	19.7	152.8	18.1	15.7	0.115	2.40	2.77
EFK 18	T3	SAS3	1279	11.1	87.1	19.8	21.6	0.092	1.88	1.72
EFK 14	T1	SAS1	132	1.5	113.2	19.7	11.9	0.166	1.35	2.23
EFK 14	T1	SAS2	206	1.0	48.6	19.8	9.84	0.201	0.48	0.96
EFK 14	T1	SAS3	151	1.8	121.2	18.6	18.2	0.102	2.21	2.25

Table A-2. (cont'd)

Site	Transect	Sample	Surface area cm^2	Sample mass g	sed/m^2 g/m^2	MeHg ng/g	HgT mg/kg	%MeHg	HgT/m^2 mg/m^2	MeHg/m^2 $\mu g/m^2$
EFK 14	T2	SAS1	837	14.7	175.5	13.9	8.79	0.158	1.54	2.44
EFK 14	T2	SAS2	1244	11.2	90.4	9.08	6.61	0.137	0.60	0.82
EFK 14	T2	SAS3	1043	6.5	62.4	9.2	7	0.131	0.44	0.57
EFK 14	T3	SAS1	689	17.6	254.8	25.4	36.5	0.070	9.30	6.47
EFK 14	T3	SAS2	591	4.8	80.5	18.8	17	0.111	1.37	1.51
EFK 14	T3	SAS3	691	7.0	101.7	34	16.8	0.202	1.71	3.46
EFK 6	T1	SAS1	317	4.6	145.0	12.9	11.1	0.116	1.61	1.87
EFK 6	T1	SAS2	208	1.1	54.6	6.3	3.98	0.158	0.22	0.34
EFK 6	T1	SAS3	515	28.4	551.6	2.58	15.2	0.017	8.38	1.42
EFK 6	T2	SAS1	502	4.8	95.6	12.3	1.28	0.961	0.12	1.18
EFK 6	T2	SAS2	233	1.4	60.3	13.4	0.937	1.430	0.06	0.81
EFK 6	T2	SAS3	176	2.0	114.3	4.04	3.51	0.115	0.40	0.46
EFK 6	T3	SAS1	145	1.3	92.7	26.3	42.1	0.062	3.90	2.44
EFK 6	T3	SAS2	292	1.2	42.6	31.4	13.3	0.236	0.57	1.34
EFK 6	T3	SAS3	426	1.1	26.0	35.3	16.6	0.213	0.43	0.92

Table A-3. Results of streambed core sampling conducted in East Fork Poplar Creek, August 2008. Three samples were collected for each transect representing the stream center and halfway between the center and each bank. Three transect were taken from separate gravel riffles within a 200—400 m reach at each site.

Site	Transect	Sample	Depth cm	Rocks g	Fines (<1 mm) g	MeHg ng/g	HgT mg/kg	<125 µm Hg mg/kg	%MeHg	Fines/m^2 kg/m^2	%fines	HgT/m^2 g/m^2	MeHg/m^2 mg/m^2
EFK23	T1	SB1	23	624	270	0.96	5.63	19.9	0.017	85.2	30.2	0.48	0.082
EFK23	T1	SB2	17	484	73	1.82	10.6	8.2	0.017	23.0	13.1	0.24	0.042
EFK23	T1	SB3	15	503	23	2.33	12.9	17.8	0.018	7.3	4.4	0.09	0.017
EFK23	T2	SB1	21	330	117	1.25	7.98	20.5	0.016	36.9	26.2	0.29	0.046
EFK23	T2	SB2	30	823	145	0.66	6.15	20.5	0.011	45.7	15.0	0.28	0.030
EFK23	T2	SB3	26	484	50	0.83	2.39	19.3	0.035	15.8	9.4	0.04	0.013
EFK23	T3	SB1	32	647	352	2.23	10	29.4	0.022	111.0	35.2	1.11	0.248
EFK23	T3	SB2	32	861	172	1.75	11.8	25.4	0.015	54.3	16.7	0.64	0.095
EFK23	T3	SB3	39	282	967	0.35	2.32	2.56	0.015	305.0	77.4	0.71	0.107
EFK 18	T1	SB1	48	655	260	4.18	112	71.5	0.004	82.0	28.4	9.19	0.343
EFK 18	T1	SB2	60	666	398	5.13	21.5	41.3	0.024	125.6	37.4	2.70	0.644
EFK 18	T1	SB3	39	820	582	1.53	26.1	38.7	0.006	183.6	41.5	4.79	0.281
EFK 18	T2	SB1	71	441	937	4.58	12	15.8	0.038	295.6	68.0	3.55	1.354
EFK 18	T2	SB2	59	880	610	4.51	42.1	72.9	0.011	192.4	40.9	8.10	0.868
EFK 18	T2	SB3	53	773	398	6.6	26.7	171.2	0.025	125.6	34.0	3.35	0.829
EFK 18	T3	SB1	67	379	1010	6.39	83.5	117.9	0.008	318.6	72.7	26.60	2.036
EFK 18	T3	SB2	86	774	355	4	36.6	46.4	0.011	112.0	31.4	4.10	0.448
EFK 18	T3	SB3	57	missing	148	4.27	31.2	44.3	0.014	46.7		1.46	0.199
EFK 14	T1	SB1	45	684	1277	1.16	7.45	20.3	0.016	248.0	65.1	1.85	0.288
EFK 14	T1	SB2	28	1015	548	0.45	2.09	3.7	0.022	106.4	35.1	0.22	0.048
EFK 14	T1	SB3	32	649	553	0.85	4.7	18	0.018	107.4	46.0	0.50	0.091

Table A-3. (cont'd)

Site	Transect	Sample	Depth cm	Rocks g	Fines (<1 mm) g	MeHg ng/g	HgT mg/kg	<125 µm Hg mg/kg	%MeHg	Fines/m2 kg/m2	%fines	HgT/m2 g/m2	MeHg/m2 mg/m2
EFK 14	T2	SB1	37	721	869	1.09	3.62	8.8	0.030	168.7	54.7	0.61	0.184
EFK 14	T2	SB2	28	966	363	0.86	4.35	15.4	0.020	70.5	27.3	0.31	0.061
EFK 14	T2	SB3	22	673	135	1.93	23.9	28.4	0.008	26.2	16.7	0.63	0.051
EFK 14	T3	SB1	8	342	50	7.62	14.2	16.2	0.054	15.8	12.8	0.22	0.120
EFK 14	T3	SB2	11	332	125	1.66	5.07	20.9	0.033	39.4	27.4	0.20	0.065
EFK 14	T3	SB3	39	625	125	1.23	9.29	27.3	0.013	39.4	16.7	0.37	0.049
EFK 6	T1	SB1	22	573	158	2.27	6.91	15.6	0.033	30.7	21.6	0.21	0.070
EFK 6	T1	SB2	17	261	17	11.1	33.9	32.2	0.033	3.3	6.1	0.11	0.037
EFK 6	T1	SB3	9	191	14	23	42	11.6	0.055	2.7	6.8	0.11	0.063
EFK 6	T2	SB1	89	1158	323	1.25	15.7	32	0.008	62.7	21.8	0.98	0.078
EFK 6	T2	SB2	73	1199	787	3.08	4.23	10.4	0.073	152.8	39.6	0.65	0.471
EFK 6	T2	SB3	45	738	685	2.75	4.34	26.4	0.063	133.0	48.1	0.58	0.366
EFK 6	T3	SB1	43	1154	563	1.15	15.3	51	0.008	109.3	32.8	1.67	0.126
EFK 6	T3	SB2	40	1146	720	0.79	2.2	13.6	0.036	139.8	38.6	0.31	0.110
EFK 6	T3	SB3	51	738	935	0.77	8.91	12.7	0.009	181.6	55.9	1.62	0.140

Table A-4. Mercury flux in East Fork Poplar Creek at Y-12 NSC (EFK 23) and lower EFPC (Horizon Center, EFK 6) during May 2009 storm

Sample	Day	Time	Running time hr	Total Hg ng/L	Filtered Hg ng/L	TSS mg/L	Discharge m^3/s	Hg load g/h
EFK 23 #1	6-May	7:45	0.25	347	29	32.7	0.299	0.4
EFK 23 #2	6-May	8:45	1.25	141		8.2	0.379	0.2
EFK 23 #3	6-May	9:45	2.25	483		9.3	0.447	0.8
EFK 23 #4	6-May	10:45	3.25	328	49	122	0.421	0.5
EFK 23 #5	6-May	11:45	4.25	948		3.8	2.52	8.6
EFK 23 #6	6-May	12:14	5.25	1803	23	80.8	1.51	9.8
EFK 23 #7	6-May	13:45	6.25	838		26.8	0.821	2.5
EFK 23 #8	6-May	14:45	7.25	437		14.3	1.04	1.6
EFK 23 #9	6-May	15:45	8.25	8247	64	277	2.26	67.1
EFK 23 #10	6-May	16:45	9.25	997	62	76.6	1.003	3.6
EFK 23 #11	6-May	17:45	10.25	485		22.6	0.702	1.2
EFK 23 #12	6-May	18:45	11.25	514		13	0.606	1.1
EFK 23 #13	6-May	19:45	12.25	372		9.3	0.553	0.7
EFK 23 #14	6-May	20:45	13.25	334	71	7.6	0.516	0.6
EFK 23 #15	6-May	21:45	14.25	309		6.7	0.489	0.5
EFK 23 #16	6-May	22:45	15.25	311		4.6	0.47	0.5
EFK 23 #17	6-May	23:45	16.25	304		5.2	0.453	0.5
EFK 23 #18	7-May	0:45	17.25	262		6.8	0.441	0.4
EFK 23 #19	7-May	1:45	18.25	247		3	0.442	0.4
EFK 23 #20	7-May	2:45	19.25	270		0.4	0.446	0.4
EFK 23 #21	7-May	3:45	20.25	241		0.4	0.431	0.4
EFK 23 #22	7-May	4:45	21.25	274		2.4	0.418	0.4
EFK 23 #23	7-May	5:45	22.25	181		2.9	0.408	0.3
EFK 23 #24	7-May	6:45	23.25	211	44	2.1	0.400	0.3
EFK 6 #1	6-May	10:00	2.5	219	8	15.7	2.3	1.8
EFK 6 #2	6-May	12:00	4.5	258		19.5	2.8	2.6
EFK 6 #3	6-May	14:00	6.5	459		31.4	3.4	5.6
EFK 6 #4	6-May	16:00	8.5	1306		126.0	4	18.8
EFK 6 #5	6-May	18:00	10.5	4008	16	284.5	4.7	67.9
EFK 6 #6	6-May	20:00	12.5	3828	23	213.6	17.0	234.7
EFK 6 #7	6-May	22:00	14.5	2764		290.9	15.2	151.1
EFK 6 #8	7-May	0:00	16.5	1176		144.2	13.3	56.4
EFK 6 #9	7-May	2:00	18.5	872	20	93.4	11.5	36.0
EFK 6 #10	7-May	4:00	20.5	625	17	62.1	9.6	21.7
EFK 6 #11	7-May	6:00	22.5	577		50.2	7.8	16.2
EFK 6 #12	7-May	8:00	24.5	551		50.4	5.9	11.8
EFK 6 #13	7-May	10:00	26.5	465		39.7	5.4	9.0
EFK 6 #14	7-May	12:00	28.5	434		43.9	5.2	8.1
EFK 6 #15	7-May	14:00	30.5	449	10	31.5	4.9	7.9
EFK 6 #16	7-May	16:00	32.5	356		27.3	4.7	6.0

Table A-5. Mercury flux from floodplain catchments on the East Fork Poplar Creek floodplain near Y-12, EFK 23 (NOAA study site) and 18 km downstream (Horizon Center study site, near EFK 6) during a May 2009 storm

Site	Day	Time	Running time hr	Total Hg ng/L	Filtered Hg ng/L	TSS mg/L	Discharge L/min	Hg load mg/h
Horizon Center #1	6-May	11:00	3.5	1456	101	905	12.7	1.11
Horizon Center #2	6-May	12:00	4.5	3463	60	142	40.2	8.35
Horizon Center #3	6-May	13:00	5.5	603		21.4	20.4	0.74
Horizon Center #4	6-May	14:00	6.5	468		12.5	8	0.22
Horizon Center #5	6-May	15:00	7.5	11387	130	70	85.9	58.69
Horizon Center #6	6-May	16:00	8.5	1210	134	465	26.5	1.92
Horizon Center #7	6-May	17:00	9.5	1036			8.94	0.56
Horizon Center #8	6-May	18:00	10.5	261		21.5	7.66	0.12
Horizon Center #9	6-May	19:00	11.5	249			7.66	0.11
Horizon Center #10	6-May	20:00	12.5	110	12	15.1	7.66	0.05
Horizon Center #11	6-May	21:00	13.5	91			7.66	0.04
Horizon Center #12	6-May	22:00	14.5	77		18.6	7.66	0.04
Horizon Center #13	6-May	23:00	15.5	213			7.66	0.10
Horizon Center #14	7-May	0:00	16.5	461	10	60	7.66	0.21
Horizon Center #15	7-May	1:00	17.5	74			7.66	0.03
Horizon Center #16	7-May	2:00	18.5	128		11.6	7.66	0.06
Horizon Center #17	7-May	3:00	19.5	86			7.66	0.04
Horizon Center #18	7-May	4:00	20.5	48	7	8.3	7.66	0.02
Horizon Center #19	7-May	5:00	21.5	47			7.66	0.02
Horizon Center #20	7-May	6:00	22.5	42		16.5	7.66	0.02
Horizon Center #21	7-May	7:00	23.5	52			7.66	0.02
Horizon Center #22	7-May	8:00	24.5	66		7.4	6.7	0.03
Horizon Center #23	7-May	9:00	25.5	57			4.79	0.02
Horizon Center #24	7-May	10:00	26.5	56	6	8.1	3.83	0.01
NOAA #1	6-May	8:00	0.5	5020	26	231	20.7	6.24
NOAA #2	6-May	9:00	1.5	1933	23	77.8	22.7	2.63
NOAA #3	6-May	10:00	2.5	744		20.7	19.8	0.88
NOAA #4	6-May	11:00	3.5	970		40.5	49.8	2.90
NOAA #5	6-May	12:00	4.5	2115	25	57.6	71.5	9.07
NOAA #6	6-May	13:00	5.5	358		8.4	48.2	1.04
NOAA #7	6-May	14:00	6.5	67			39.6	0.16
NOAA #8	6-May	15:00	7.5	235	27	18.2	100.2	1.41
NOAA #9	6-May	16:00	8.5	424			58.4	1.49
NOAA #10	6-May	17:00	9.5	305		6.6	42.4	0.78
NOAA #11	6-May	18:00	10.5	96	30		36.1	0.21
NOAA #12	6-May	19:00	11.5	231		10.2	31.6	0.44
NOAA #13	6-May	20:00	12.5	165			29.7	0.29
NOAA #14	6-May	21:00	13.5	158		0.7	27.1	0.26
NOAA #15	6-May	22:00	14.5	144			26.5	0.23
NOAA #16	6-May	23:00	15.5	265	31	0.4	24.9	0.40
NOAA #17	7-May	0:00	16.5	145			23.3	0.20
NOAA #18	7-May	1:00	17.5	116		0.3	23.3	0.16
NOAA #19	7-May	2:00	18.5	423			23	0.58
NOAA #20	7-May	3:00	19.5	150		1.1	22.98	0.21
NOAA #21	7-May	4:00	20.5	122	33		22.3	0.16
NOAA #22	7-May	5:00	21.5	745		19	20.4	0.91
NOAA #23	7-May	6:00	22.5	137			19.8	0.16
NOAA #24	7-May	7:00	23.5	173	32	1.3	19.2	0.20