

# Potential Strategies and Technologies for Mitigating Stream Mercury Contamination

**Mark Peterson**

Environmental Sciences Division  
OAK RIDGE NATIONAL LABORATORY

**Research and Technology Development supported by:**  
UCOR, an AECOM-led partnership with Jacobs; DOE Oak Ridge Office of Environment Management (OREM)

## **ORNL Team:**

Mark Peterson, Scott Brooks, Terry Mathews, Melanie Mayes, Ryan McManamay, Alex Johs, Katie Muller, Leroy Goñez Rodriguez, Shovon Mandal, Sujith Nair, Chris Derolph, Eric Pierce, David Watson, plus technical staff and students.

ORNL is managed by UT-Battelle  
for the US Department of Energy



**Oak Ridge Site-Specific Advisory  
Board (ORSSAB) Meeting  
Oak Ridge, Tennessee  
March 13, 2019**

# Key Collaborations and Partnerships

- UCOR/RSI Water Resources Restoration Program
- Y-12 CNS Compliance Organization
- Y-12 Biological Monitoring and Abatement Program
- DOE Office of Science
  - Science Focus Area at ORNL
  - Joint project with U. Michigan
- Mercury Applied Field Research Initiative (AFRI)
- UT/ORNL Carbon Fiber Tech Facility
- South River Science Team
- DuPont
- USGS
- Queens University
- James Madison University
- MSIPP – New Mexico State University
- Smithsonian Environmental Research Center
- U. Minnesota
- RT GeoSciences, Canada
- Flinders University, Australia



Smithsonian Environmental  
Research Center



# Outline

- **The Mercury Challenge**
  - A complex contaminant in the environment
  - East Fork Poplar Creek (EFPC)
- **Approach to remediation technology development**
- **Recent project findings**
  - Soil and groundwater source control
  - Water and sediment manipulation
  - Ecological manipulation
- **Future directions**



*East Fork Poplar Creek*

# Chemical Forms of Mercury

## Elemental (Hg<sub>0</sub>)

- As metallic vapour, “liquid”, or bound in mercury containing minerals



1.2 lb



## As ions [Hg(I) and Hg(II)]

- In solution or bound in ionic compounds or complexes [e.g., mercuric sulfide (HgS), mercuric chloride (HgCl<sub>2</sub>)]



61 lbs



113 lbs



## Organic mercury (e.g., CH<sub>3</sub>Hg, methyl mercury)

- Gaseous or dissolved organic compounds
- Primarily formed by microorganisms
- Highly bioaccumulative
- Neurological and reproductive effects
- Primary risks to humans and wildlife through eating fish



*Cinnabar*



*Parks et al. 2013. The genetic basis for bacterial mercury methylation. Science. 339 (6125), 1332-1335.*

# Global Mercury Challenges

- Transported globally primarily from coal combustion, mining, waste incineration sources
- Complex chemistry and chemical/biological processes; acts differently depending on system
- Bioaccumulative and biomagnifies
- Even “pristine” sites affected
- Concern for human and ecological risks
- More rigorous regulatory limits over time
- Strategies and solutions difficult, but needed

*-Measured in Arctic snow  
3700 ng/L (East Fork Poplar  
Creek 300-400 ng/L)*



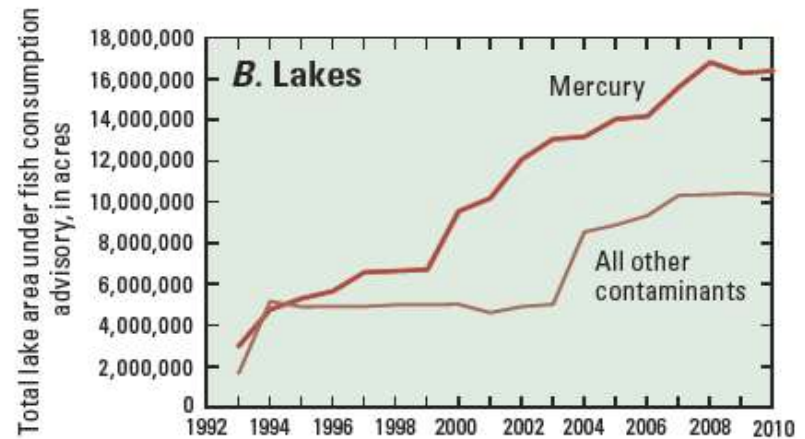
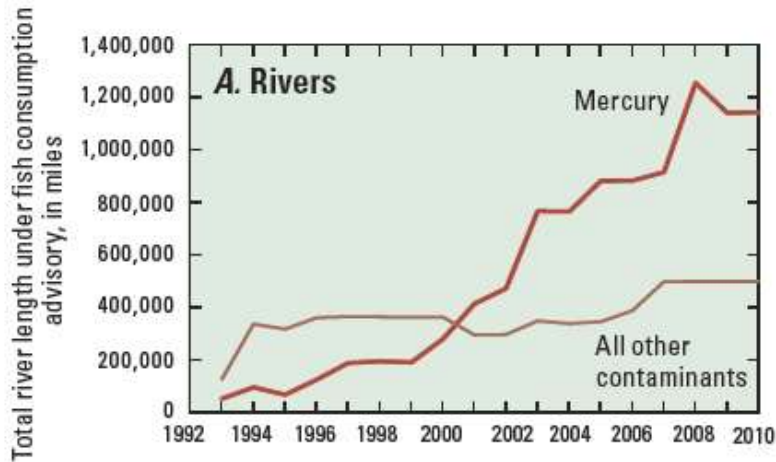
*-Northern lakes: Hg  
low in water, high  
in fish*



*United Nations  
Environmental Program*

# Mercury contamination is widespread in US

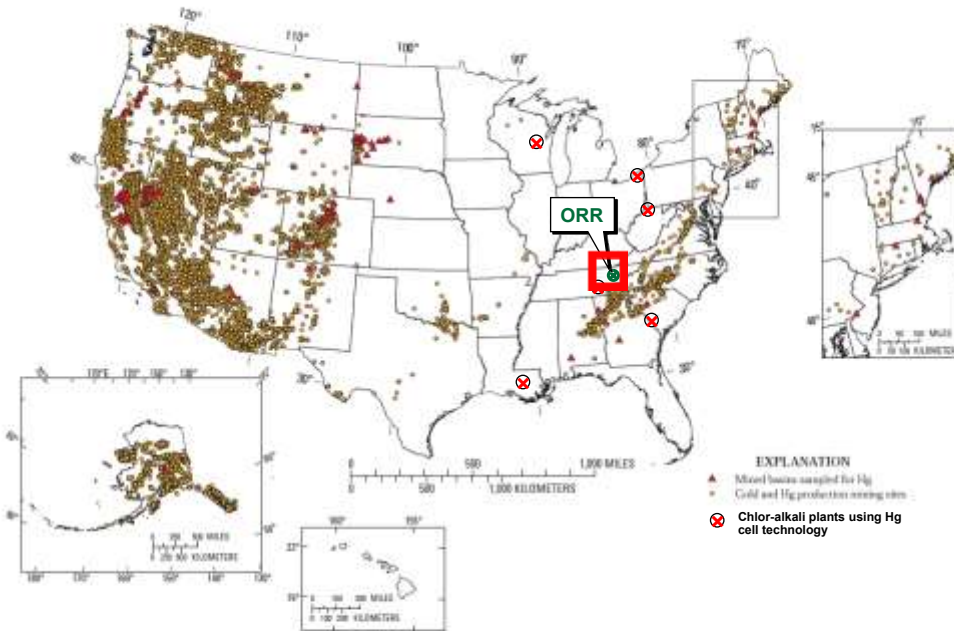
Primary risks to humans are from eating fish



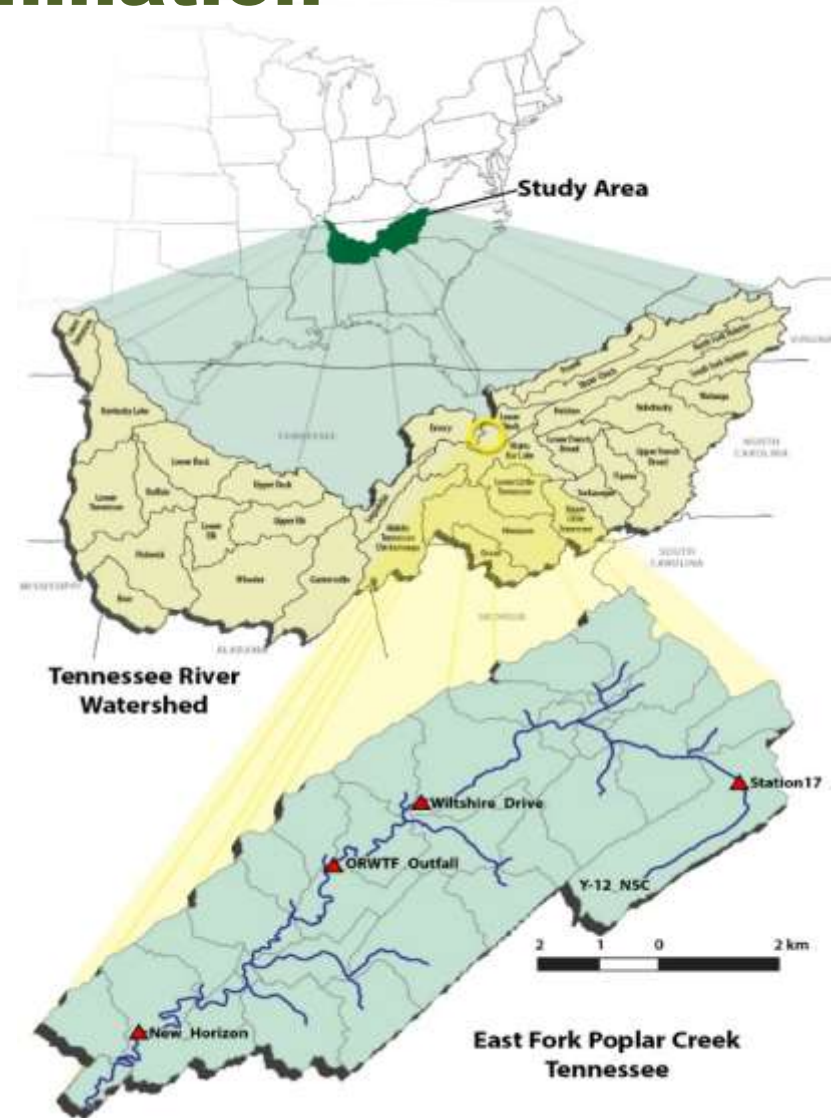
Waters that have no local industrial inputs can be affected because of **atmospheric deposition**

# Large-scale mercury use can result in severe localized contamination

## Gold and Hg mining sites, chlor-alkali plants



Adapted from Scudder et al. (2009)



Lithium isotope separation for weapons production

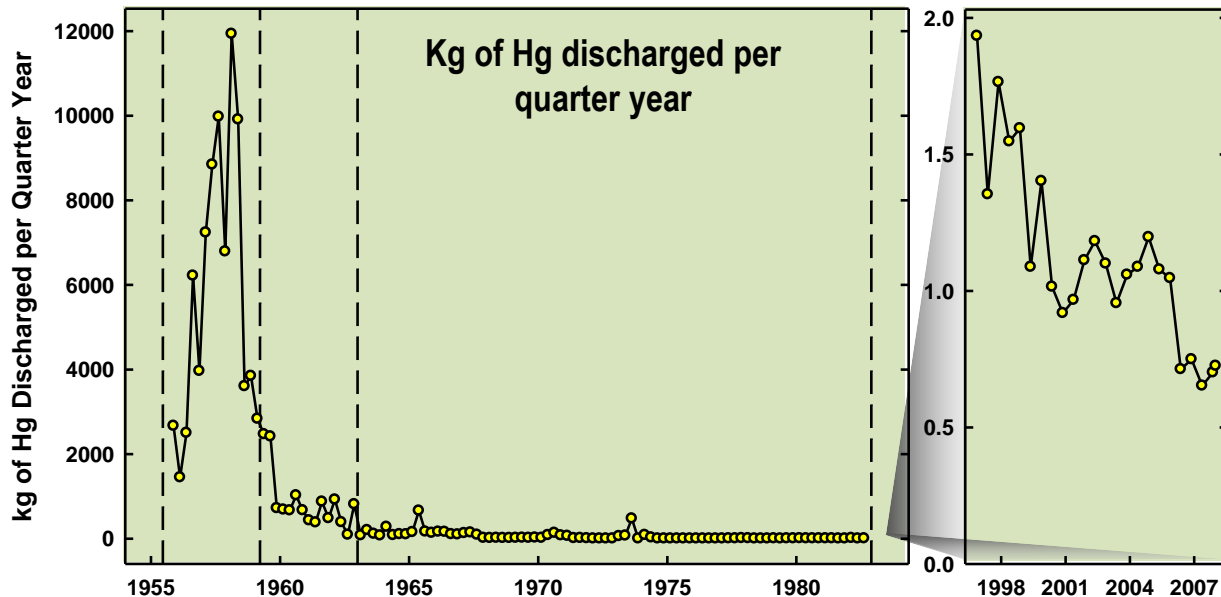
# Historical Mercury Releases at Y-12

- From 1950s – 1963 over 700,000 pounds of Hg suspected to have been released to the surrounding soils and stream
- ~15 miles of EFPC and 5 miles of Poplar Creek exceed water quality criteria. No fishing.
- Significantly less mercury releases over time



Hg flasks arriving at Y-12 (1955)

26 m<sup>3</sup> of mercury lost by volume



15-foot U-Haul

+



5X8 cargo trailer



# Y-12 Remedial and Abatement Actions, 1984-2018

Sanitary and storm sewers relined (Phase I) (Y-12/ State)

Untreated discharges consolidated and eliminated

NPDES Permit/ BMAP Initiated

New Hope Pond Closed (RCRA)

Cooling water discharges dechlorinated

1984	1985	1986	1987	1988	1989	1990	1991	1992	1993	1994	1995
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Central Pollution Control Facility



Lake Reality opened



Big Spring Water Treatment System

Old Salvage Yard scrap removal

Sanitary and storm sewers relined (Phase II)

Intermittent bypass of Lake Reality

Intermittent flow management

Permanent bypass Lake Reality

1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011
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Flow management becomes permanent

Contaminated bank stabilization project completed

Central and East End Mercury Treatment Systems (NPDES)

Lower EFPC floodplain remediation



Secant Pile Walls

OF 200 MTF construction began

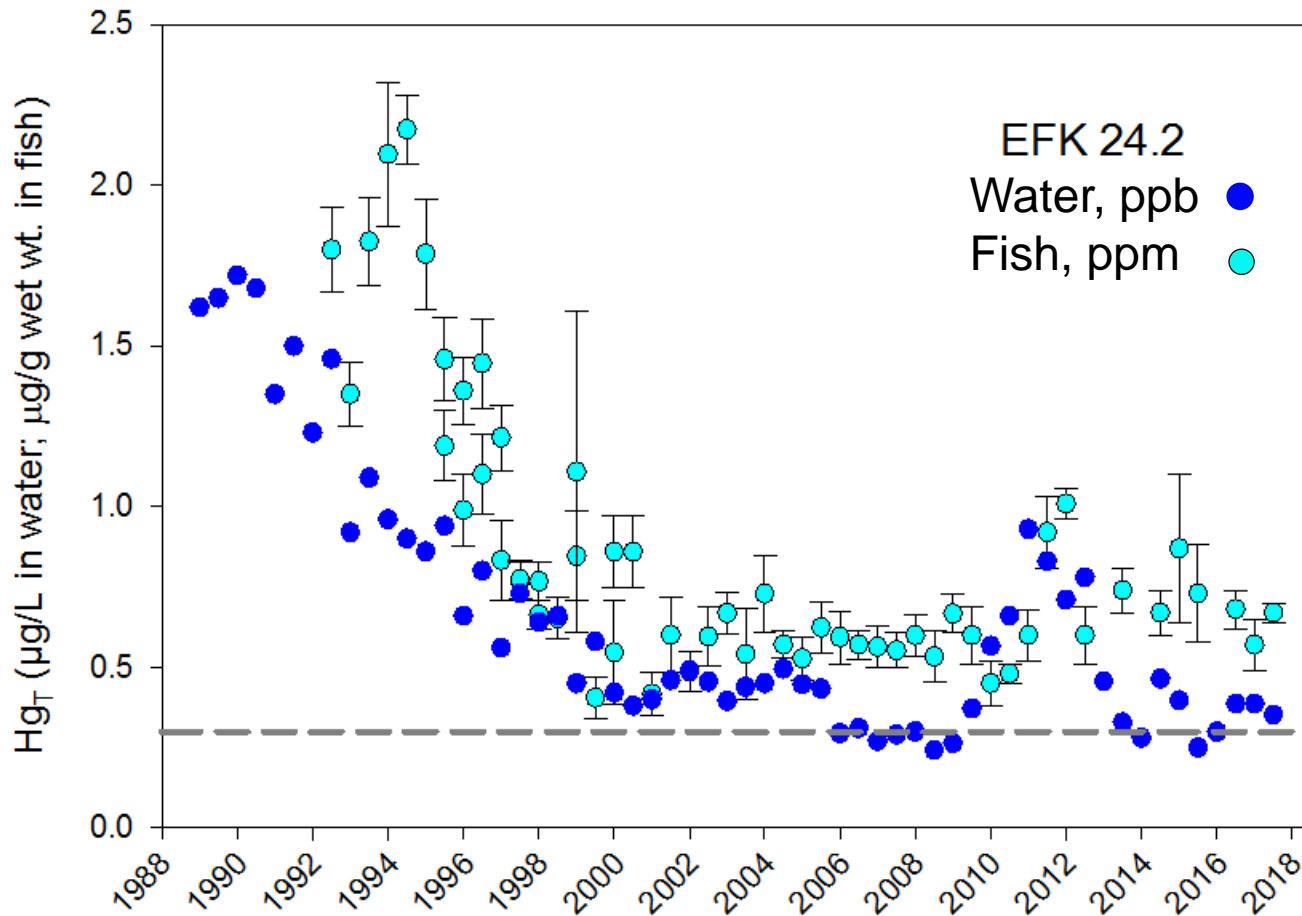
WEMA storm drain cleanout and relining

2012	2013	2014	2015	2016	2017	2018
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Flow management ends

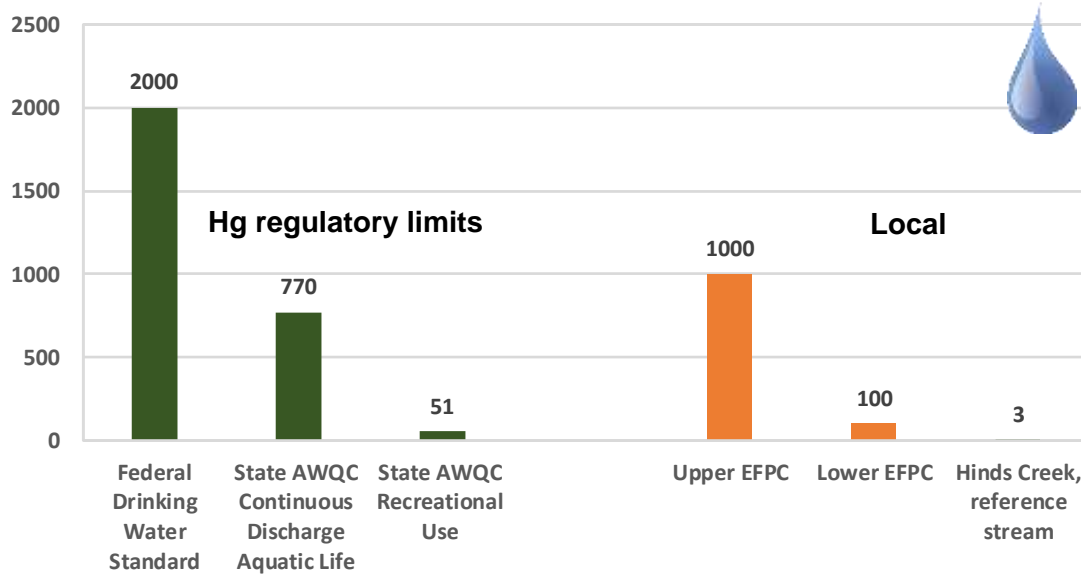
Adapted from: Loar, JM, AJ Stewart, and JG Smith. 2011. Twenty-Five Years of Ecological Recovery of East Fork Poplar Creek: Review of Environmental Problems and Remedial Actions. Environmental Management 47:6:1010-1020.

- **Significant decreases in water Hg concentrations 1989-2010**
- **Fish initially respond commensurate with water mercury concentrations, then unresponsive**



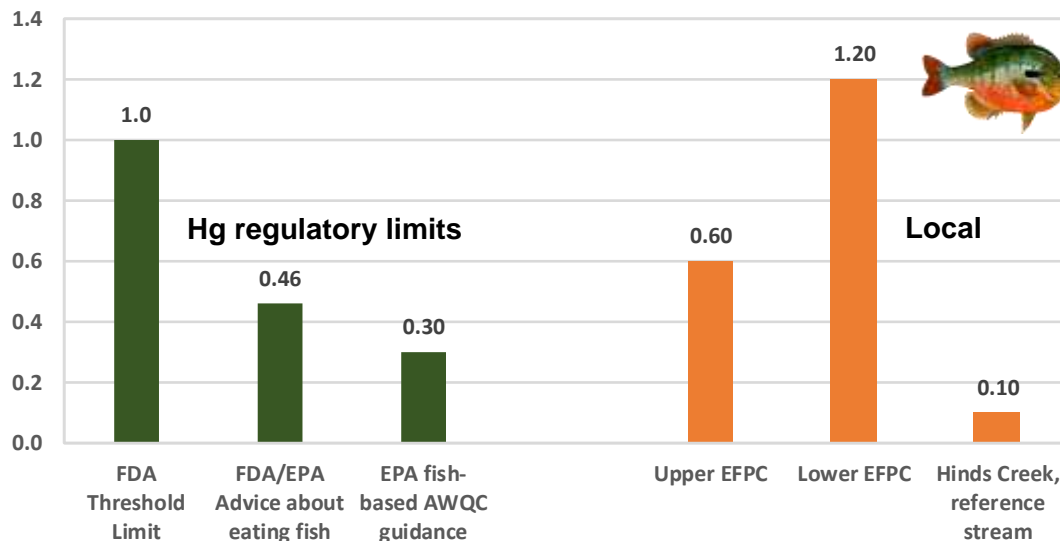
# Total Hg in water not a predictor of fish concentrations

Average mercury concentrations in water (ng/L, ppt)



East Fork Poplar Creek (EFPC) surface waters

Average mercury concentrations in fish (mg/kg, ppm)



East Fork Poplar Creek (EFPC) redbreast sunfish

# Environmental factors affect mercury methylation and bioaccumulation



*Mercury flux is only one factor controlling fish mercury concentrations*

**Near Source**

*In-stream conditions*

## Water chemistry

Hg speciation, pH, DOC, chlorine, sulfate, flow/flux

## Subsurface interactions

Chemistry, speciation, flow paths, transport

## Stream sediments/particles

Types, movement, size of zones, binding

## Soil/land/riparian inputs

Seepage and overland flow, land use, % wetlands, catchments, floodplain and stream bank erosion

## Microbial interactions

Methylation, demethylation, species and community factors

## Sediment-associated biological

Periphyton, micro-fauna, biofilm, micro-habitat

## Aquatic Food Chain

Prey availability, mercury form by species, trophic level

*biological  
chemical*

**Regulatory Endpoint**

*The regulatory measure of remediation success is attaining fish mercury limits*

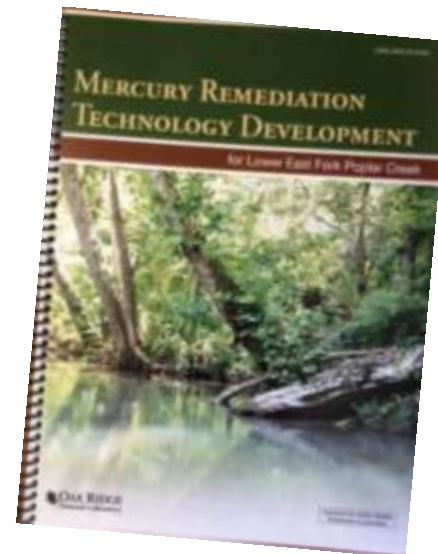


# Current mercury remediation approach to East Fork Poplar Creek

- A phased adaptive management approach
- Mercury treatment actions in the near-term at the headwaters of EFPC: the **Mercury Treatment Facility (MTF)**
  - It will reduce mercury releases into creek and provide a control mechanism for mercury disturbed during demolition
- Technology Development to evaluate potential interim actions for Lower East Fork Poplar Creek in the mid-2020s

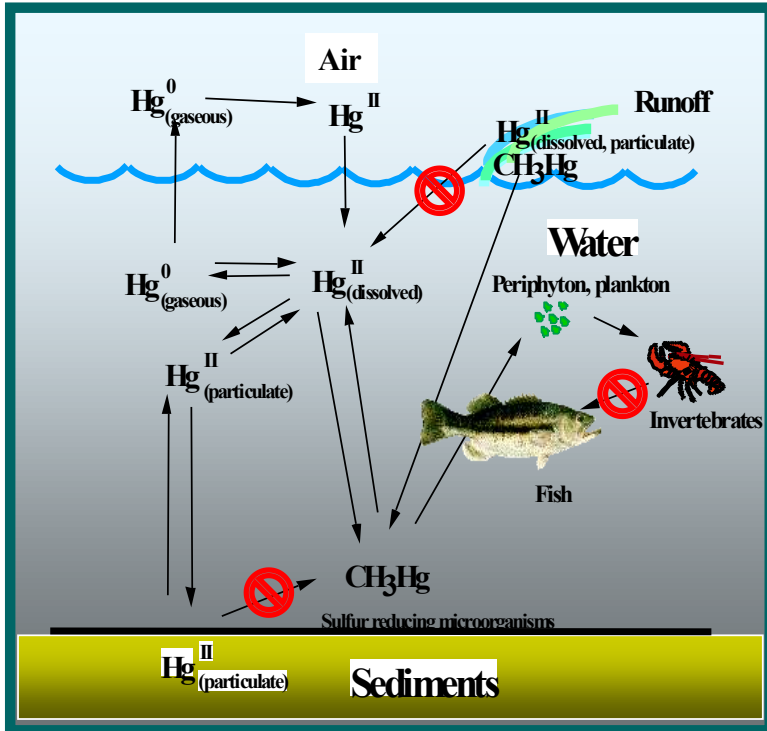


Artist rendering of Mercury Treatment Facility



Strategy document  
March 2015

# The EFPC TD strategy focuses on the major factors controlling mercury in fish



## 3 Main Tasks:

Soil and  
Groundwater  
Source Control

Water Chemistry  
and Sediment  
Manipulation

Ecological  
Manipulation

## Goals:

Decrease mercury  
source inputs, **flux**

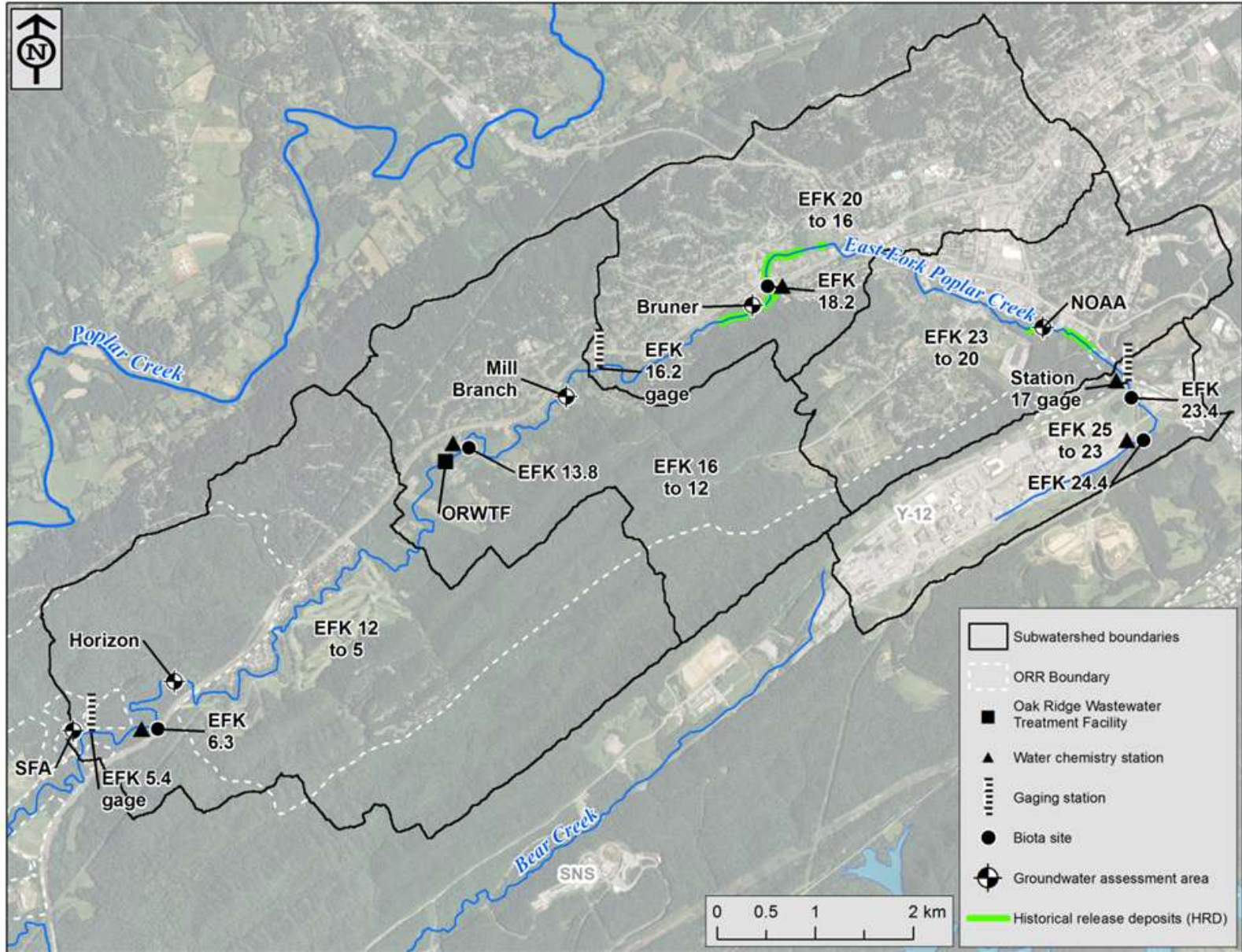
Decrease mercury  
**concentration and  
methylation**

Decrease mercury  
**bioaccumulation**

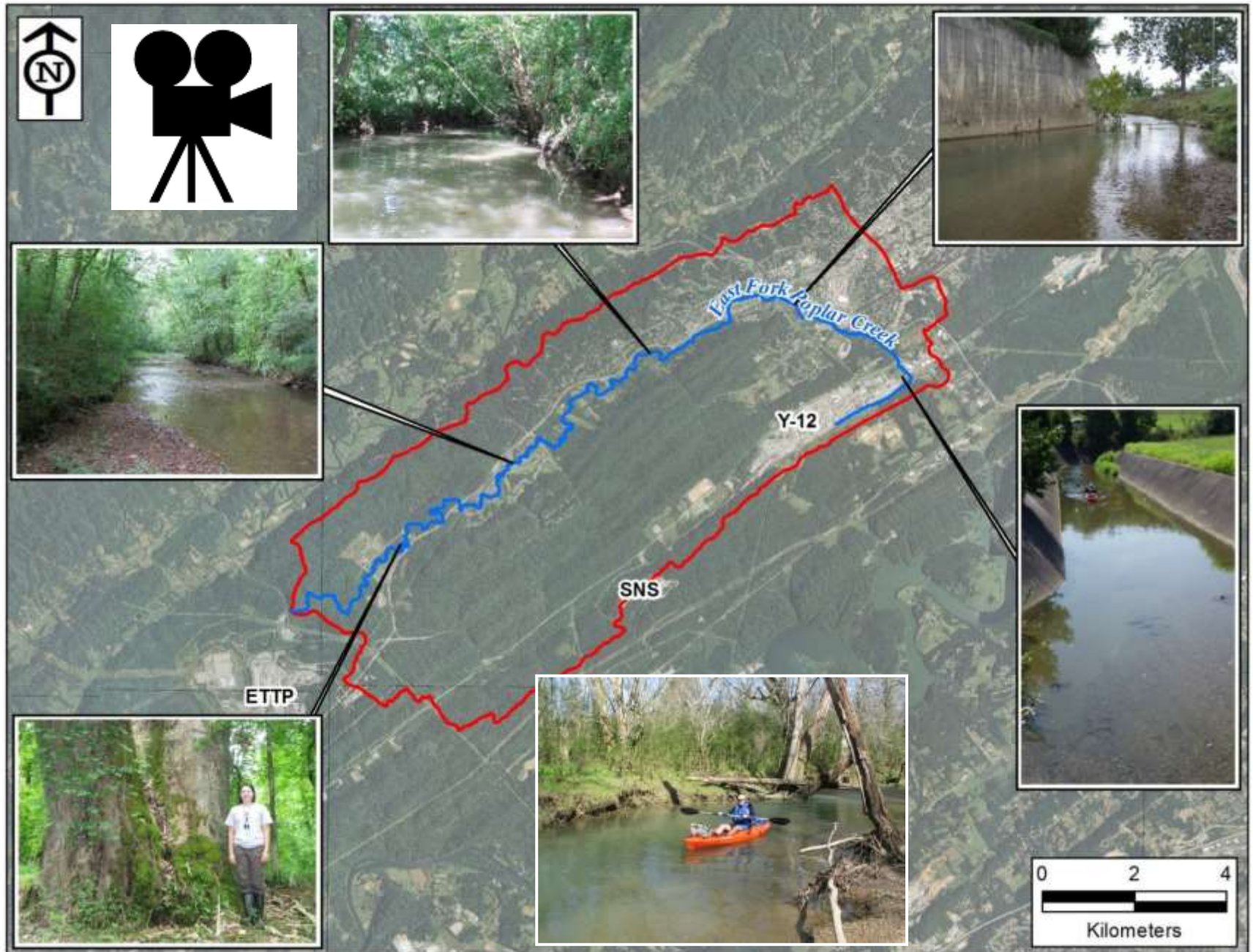
Three key factors determine the level of mercury contamination in fish—the amount of inorganic mercury available to an ecosystem, the conversion of inorganic mercury to methylmercury, and the bioaccumulation of methylmercury through the food web.

-USGS Circular 1395 (2014)

# Primary Study Locations, EFPC



# East Fork Poplar Creek Bank Soil and Sediment Survey





# East Fork Poplar Creek Bank Soil and Sediment Survey

**[https://  
youtu.be/6jm8jUbbi08](https://youtu.be/6jm8jUbbi08)**

# Task 1 Soil and groundwater source control

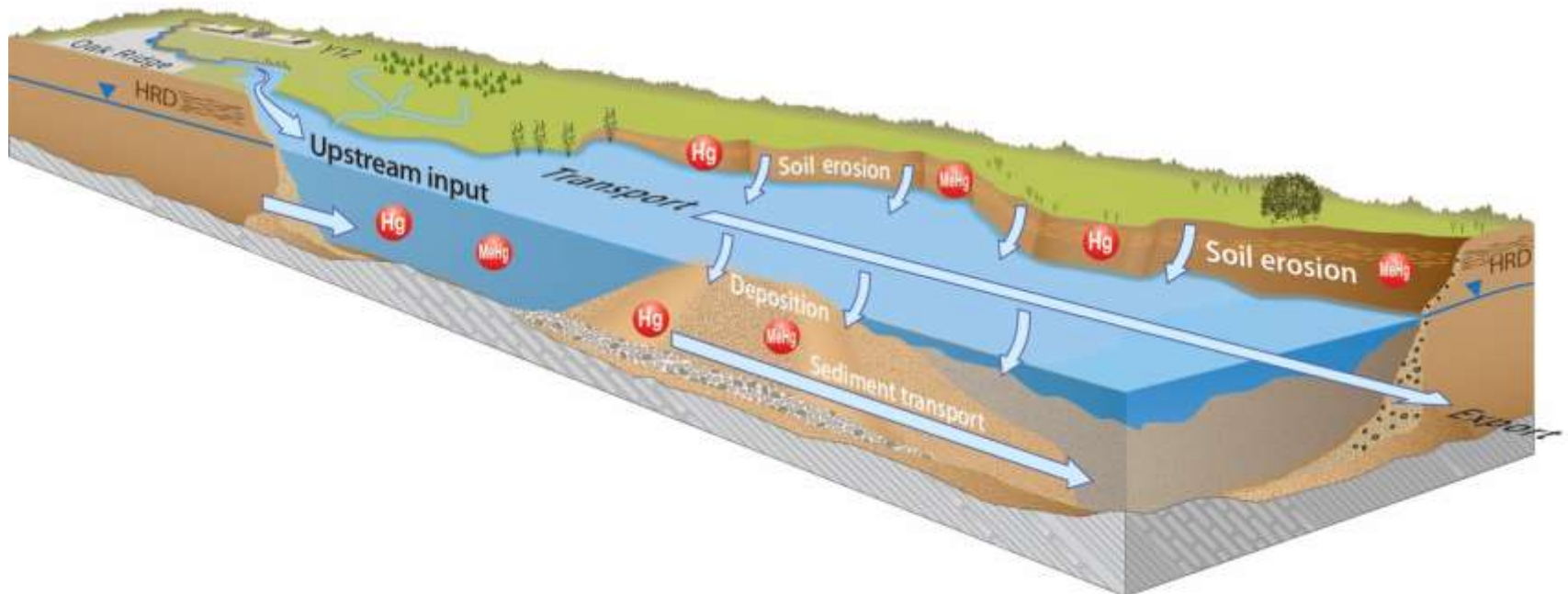
**GOAL:** Decrease mercury flux from stream banks including through erosion and leaching

- **System studies**

- Erosion studies
- Mercury concentration and flux
- Groundwater studies
- Predictive modeling

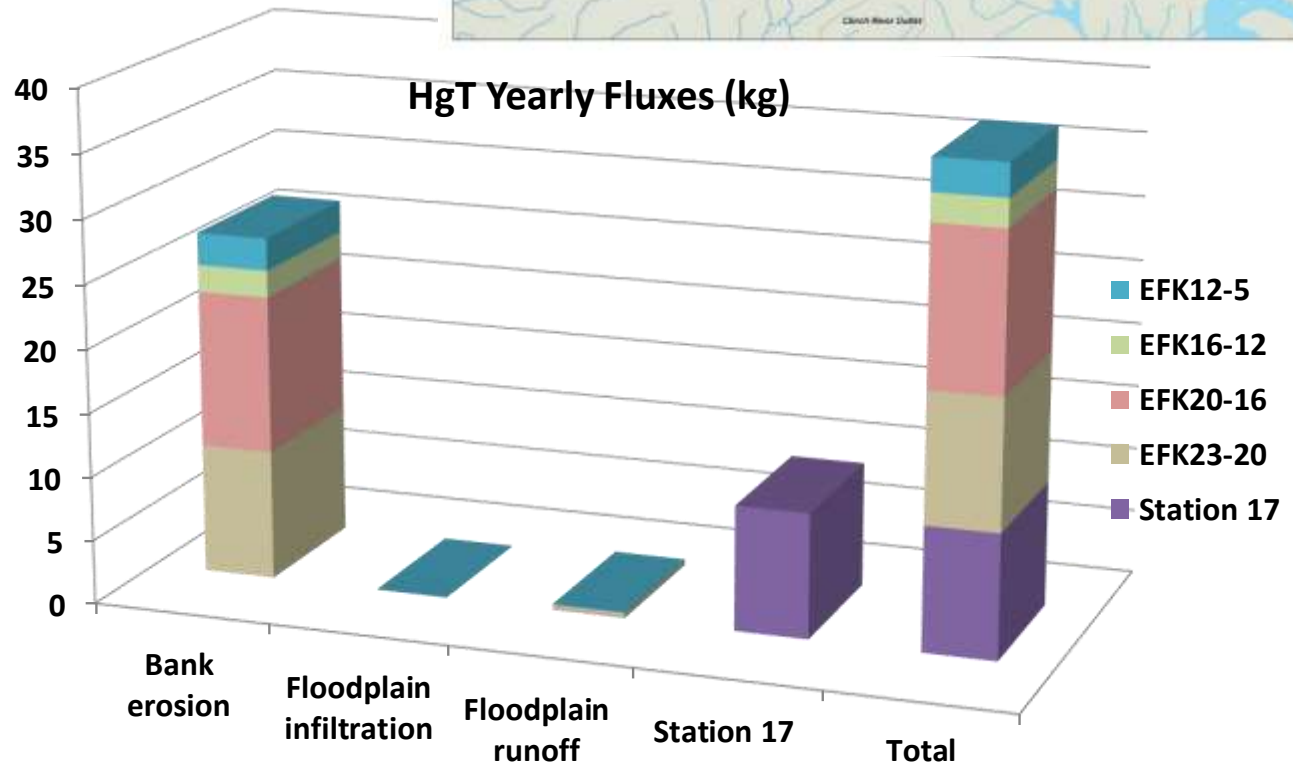
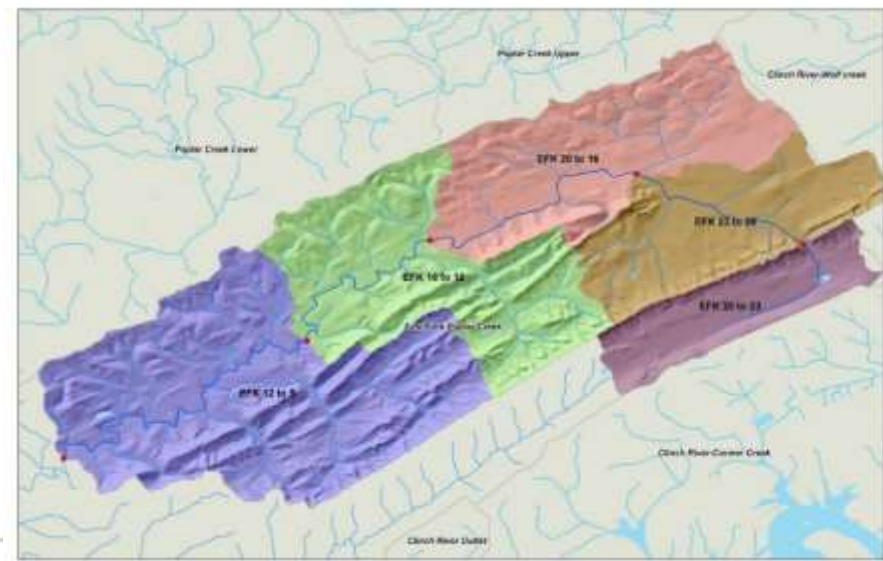
- **Technology Development laboratory studies**

- Characterization of the historical release deposits (HRD)
- Sorbent studies, lab and field



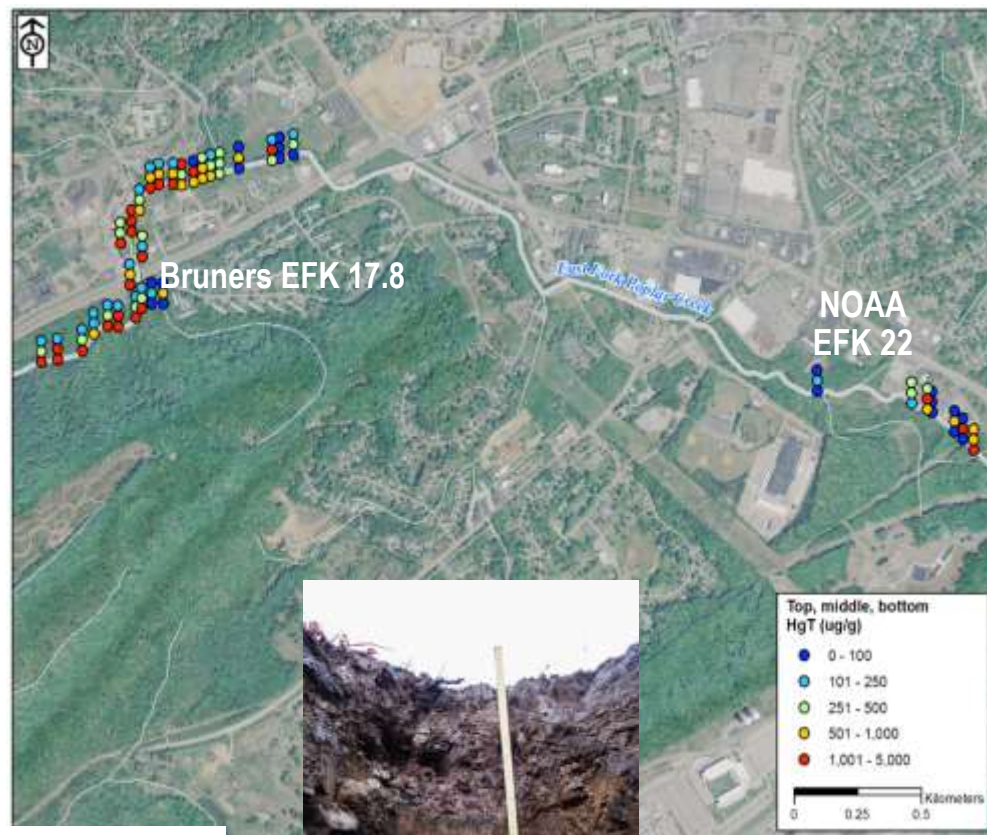
# Key Finding: Importance of bank soil erosion to mercury flux

- Primary sources of HgT to EFPC
  - Station 17
  - Bank erosion in upper two reaches of LEFPC
- Low flux from shallow groundwater and floodplain runoff
- Refining estimates



# Historical Release Deposits (HRD) in EFPC streambank soils

- The HRD is found in an ~ 5km reach in upper EFPC
- High Hg concentration coupled with high erosion in some areas
- Outside the high Hg zones, Hg concentrations are similar in bank soils and sediments
- Thus, the case is made for the prioritization of the HRD areas for technology development



Journal of Soils and Sediments  
<https://doi.org/10.1007/s11368-018-2183-0>

SEDIMENTS, SEC 1 • SEDIMENT QUALITY AND IMPACT ASSESSMENT • RESEARCH ARTICLE



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

Johnbull O. Dickson<sup>1,2</sup> · Melanie A. Mayes<sup>1</sup> · Scott C. Brooks<sup>1</sup> · Tonia L. Mehlhorn<sup>1</sup> · Kenneth A. Lowe<sup>1</sup> · Jennifer K. Earles<sup>1,3</sup> · Leroy Goñez-Rodriguez<sup>4</sup> · David B. Watson<sup>1</sup> · Mark J. Peterson<sup>1</sup>

Received: 5 June 2018 / Accepted: 28 October 2018  
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for the U.S. Department of Energy

# Sorbent Studies

- Laboratory batch and column experiments on a variety of sorbents
- Effectiveness, role of DOM, role on MeHg, and cost major factors
- Sorbent coupons are being deployed in EFPC creek banks
- Currently evaluating activated carbon fiber mats as a new remediation technology
  - Integrate Hg removal with creek bank stabilization
  - Carbon fiber precursors include polyethylene (PE) or polyacrylonitrile (PAN)
  - Initial results suggest excellent Hg removal efficiency



Samples provided by Amit Naskar (ORNL, Chemical Sciences Division)



Bank stabilization,  
South River, Virginia

# Task 2. Water chemistry and sediment manipulation

**GOAL:** Decrease mercury concentration and methylation, by disrupting: Hg transport and loading, aqueous partitioning, methylation, and exposure/ bioaccumulation

- **System studies**

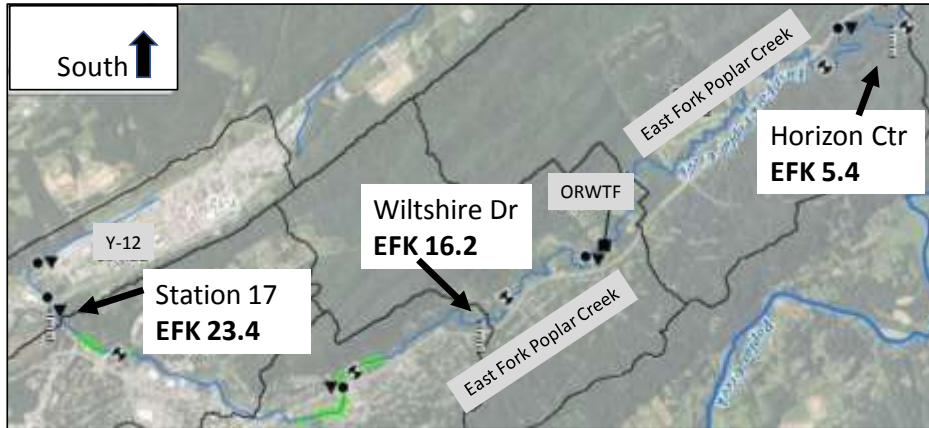
- New gauging stations established
- Better spatial and temporal resolution of concentration and flux
- Sediment source investigation

- **Technology Development**

- Ascorbic acid addition
- Sorbent studies

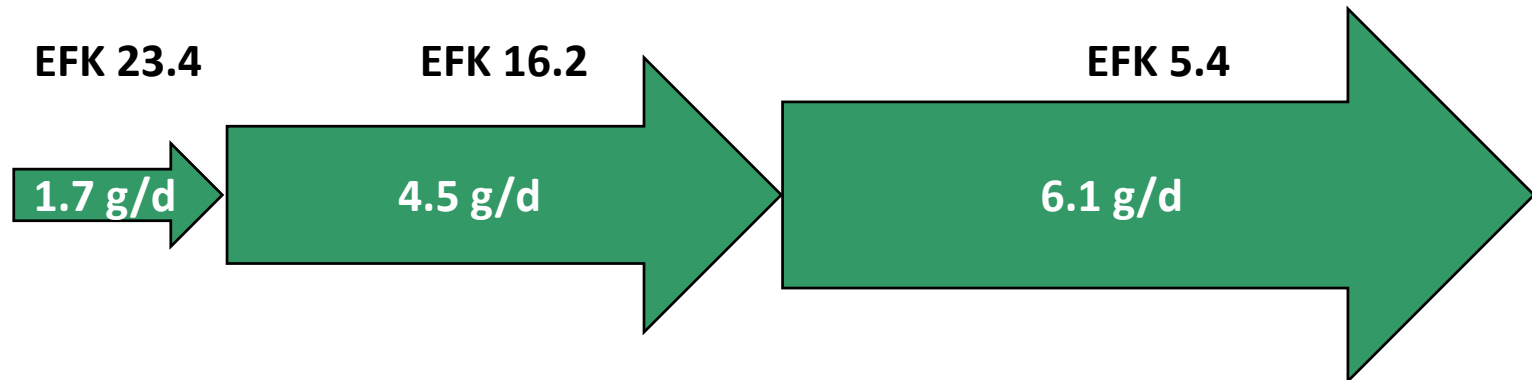


# Base flow Hg flux

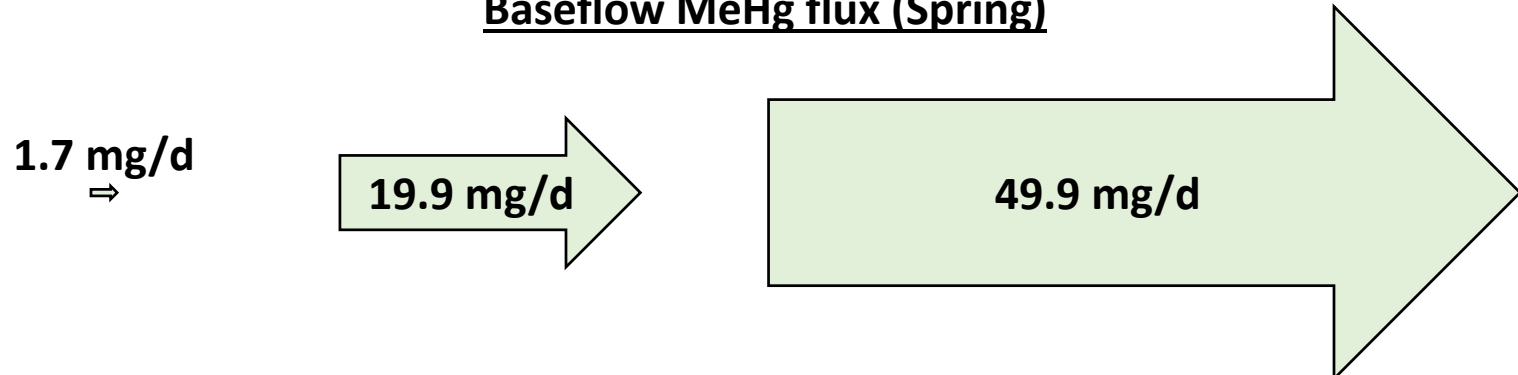


- ~75% of HgT from upper 7 km of stream
- ~60% of MeHgT from lower 11 km
- Y-12 only 28% of HgT; 3% of MeHgT

## Baseflow total Hg flux



## Baseflow MeHg flux (Spring)



# Additional Findings

- **Sediment study and report**
  - Sediment Hg decreased 67% since 1984
- **Higher particulate Hg and MeHg at night (bioturbation?)**
- **Effect of sorbents on methylation study**
- **Alternative dechlorination chemicals lab tests and 2 field trials**
- **20-25% decrease in Hg during ascorbic acid test of Y-12 storm drains**

ORNL/TM-2016/578

Mercury Content of Sediments in East Fork Poplar Creek: Current Assessment and Past Trends

ORNL/TM-2018/812

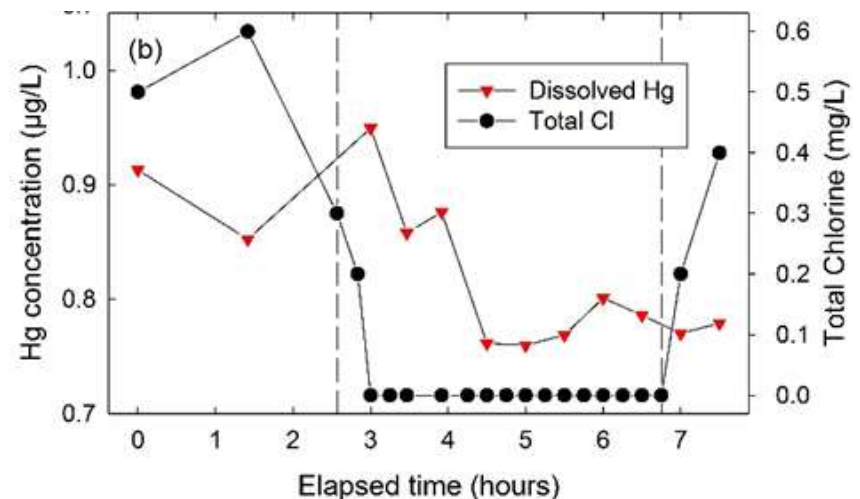
Intraday Water Quality Patterns in East Fork Poplar Creek with an Emphasis on Mercury and Monomethylmercury

Environmental Engineering Science, Ahead of Print |

## Effectiveness of Sorbents to Reduce Mercury Methylation

Katherine A. Muller and Scott C. Brooks

Published Online: 8 Dec 2018 | <https://doi.org/10.1089/ees.2018.0375>



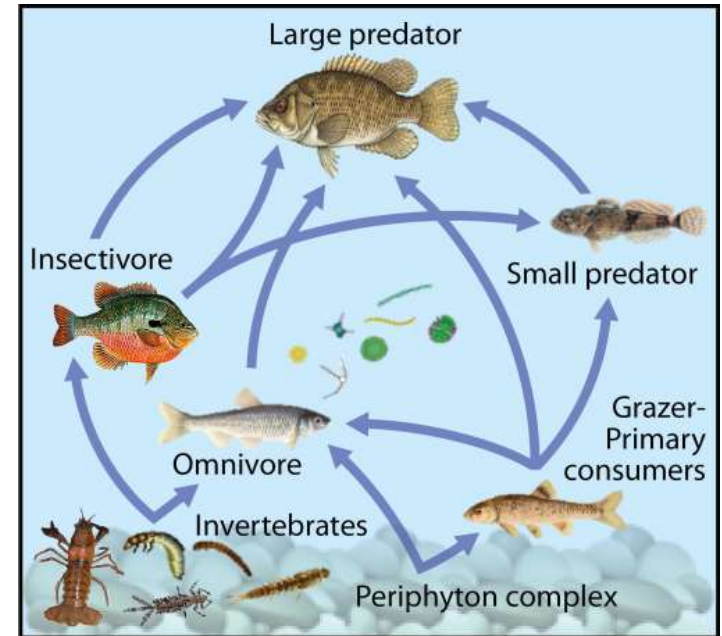


# Task 3. Ecological Manipulation

**GOAL:** Reduce methylmercury concentrations in fish

- **System studies**

- Evaluate Hg and MeHg inventories in food web
- Understand role of population/community dynamics on mercury bioaccumulation
- Understanding role of periphyton dynamics on mercury bioaccumulation in fish

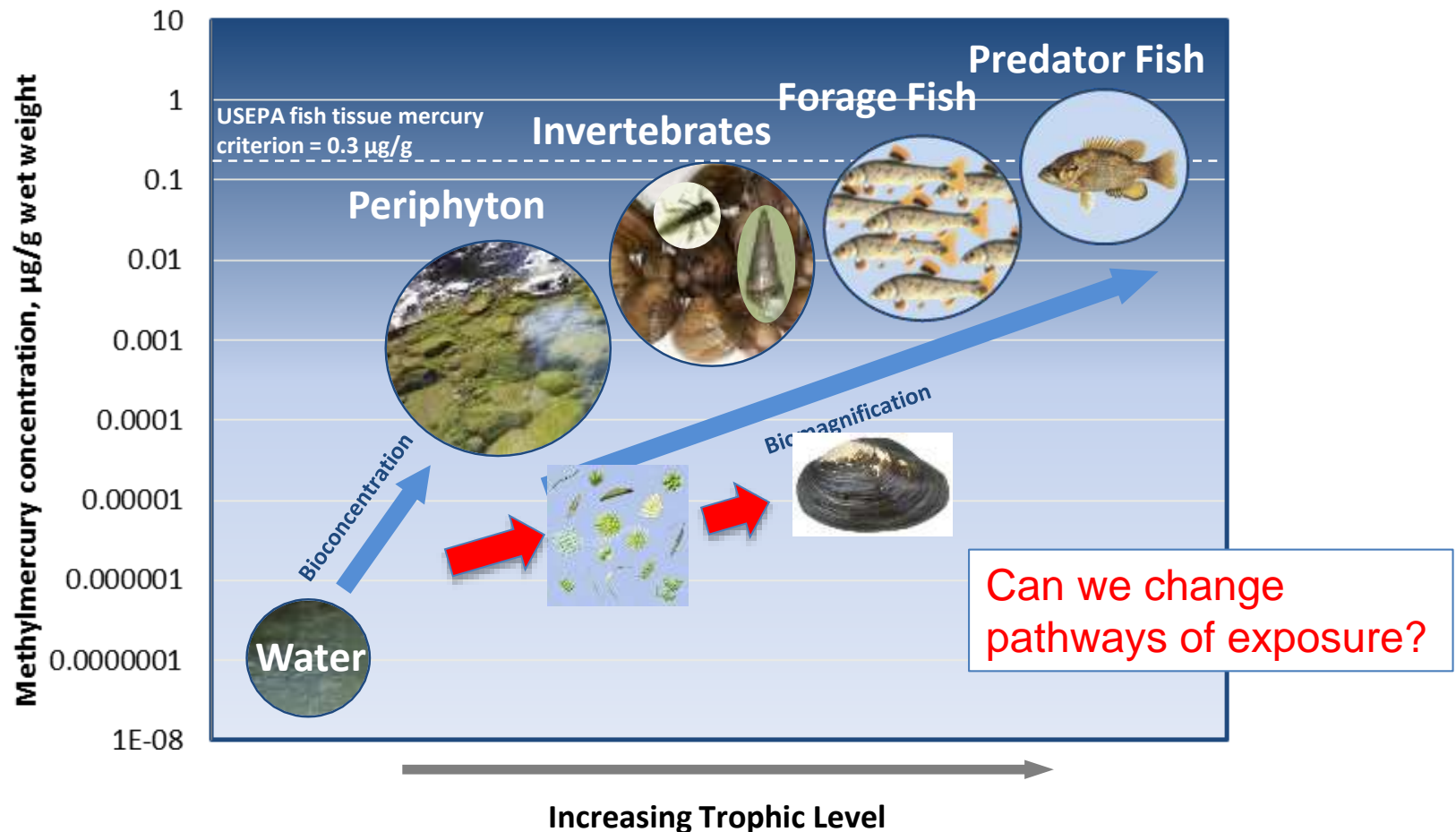


- **Technology Development**

- Evaluate effect of mussel filtration on Hg

# Food Chains Make a Difference on Hg Bioaccumulation

- Longer food chains can > Hg
- Each organism has different bioaccumulation potential
- Greatest biomagnification step low in the food chain



# First time EFPC food chain systematically surveyed for mercury bioaccumulation



Field collections



Lab processing-Taxa



Lab processing-Size

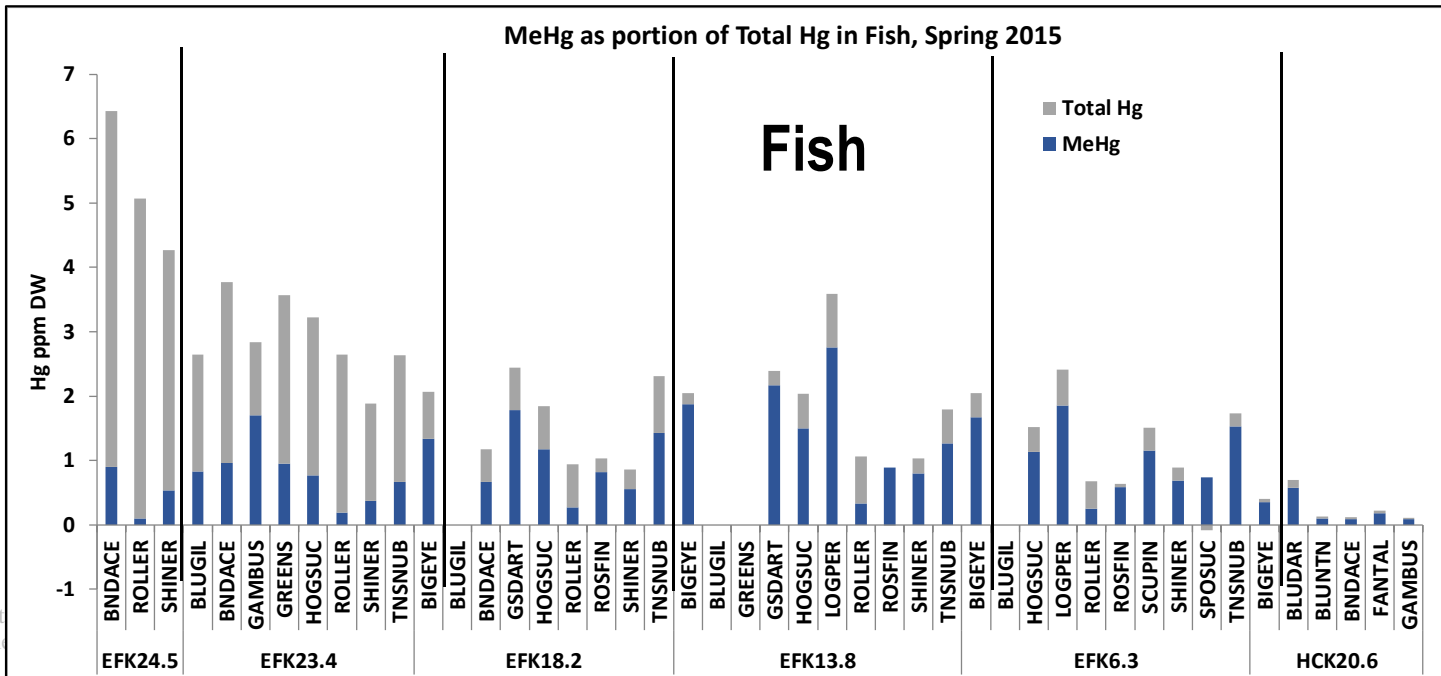
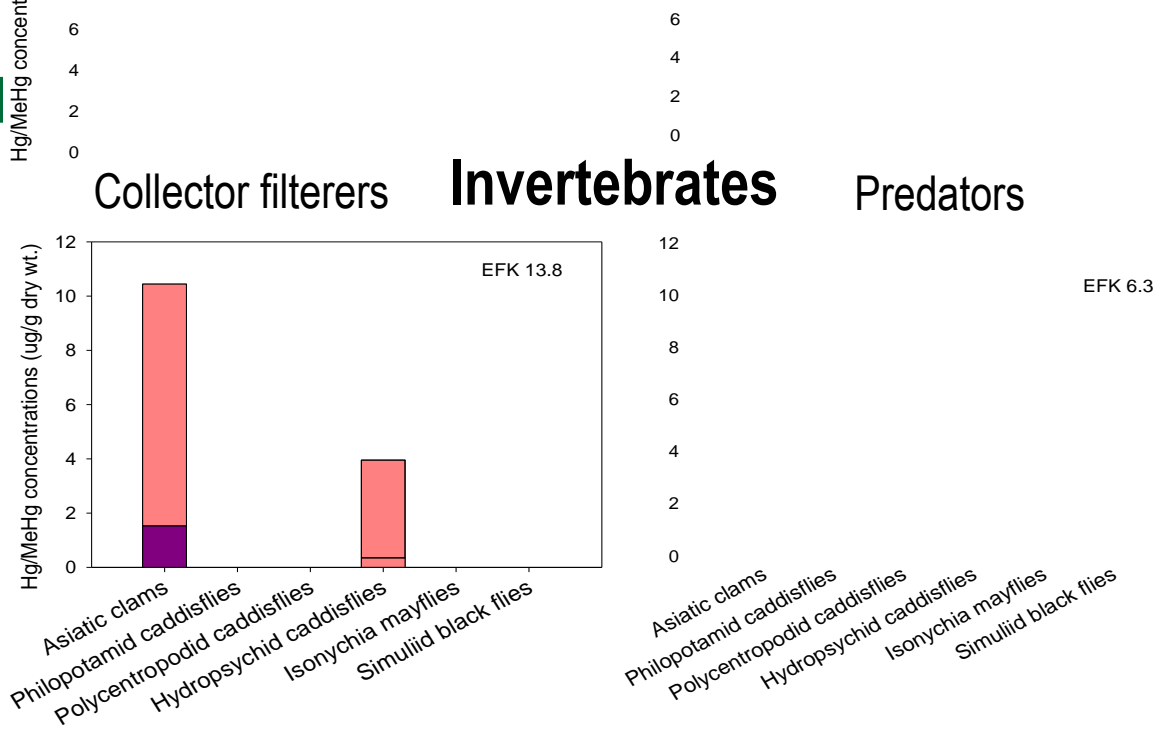


## Analysis

- Mercury
- **Methylmercury**
- Del N15

# Investigating MeHg

- Major taxa differences in MeHg uptake
- Collector filterers have a negative effect
- Higher % MeHg with distance downstream



# Bivalve Testing

- Mussels highly effective in removing particles from water
- Mussels low in HgT, low in MeHg
- Collaborating with TWRA's Cumberland Water Research Center to culture native mussels for testing



*Paper Pondshell*  
*Utterbackia*  
*imbecillis*



Aquatic Ecology Laboratory



# Fast motion mussel filtering

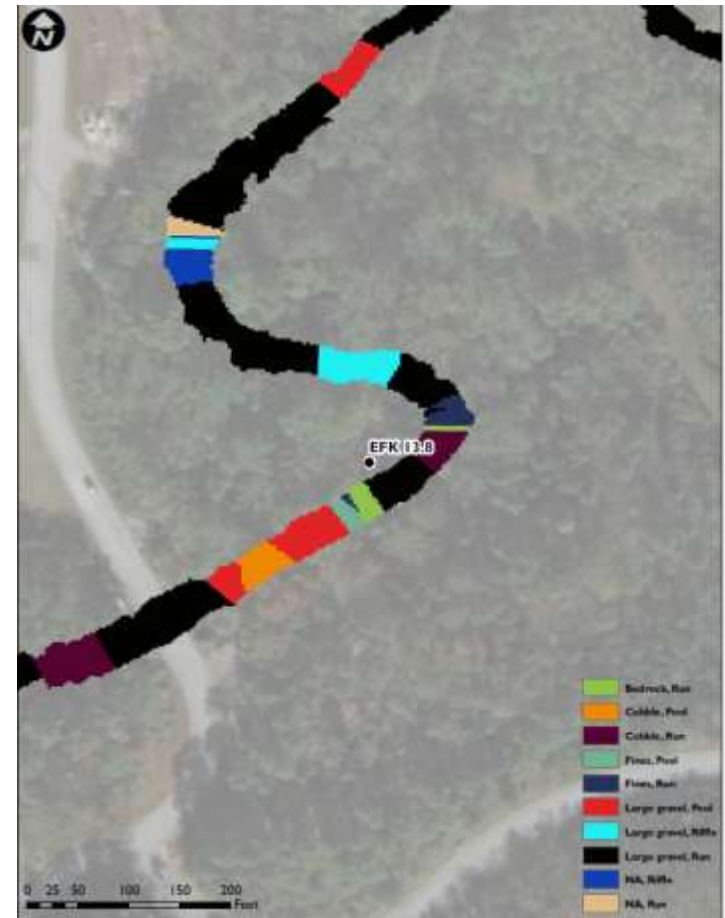
[https://  
youtu.be/ZEwg3la6t-E](https://youtu.be/ZEwg3la6t-E)



# Quantifying potential for Hg filtration by bivalves in EFPC

- Evaluating species filtration rates under different environmental conditions to examine the effects of light, temperature, and particulate load
  - Higher temperature, higher filtration
- Examination of substrate obtained from kayak surveys of EFPC
- Estimation of carrying capacity of EFPC for mussels
- Controlled stream mesocosm studies to evaluate Hg removal efficiency planned

EFPC sediment characteristics





# Potential future strategies for mitigating Hg in EFPC?

## Decrease Hg sources

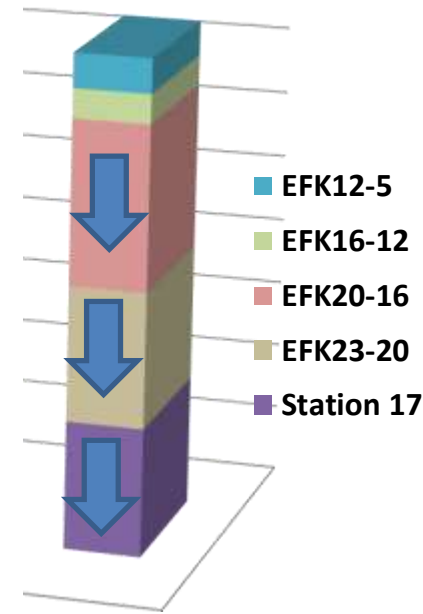
- MTF will decrease Hg flux and downstream erosion
- Develop bank stabilization and sorbent solutions for high Hg streambanks

## Develop watershed scale recommendations that can impact surface water variables

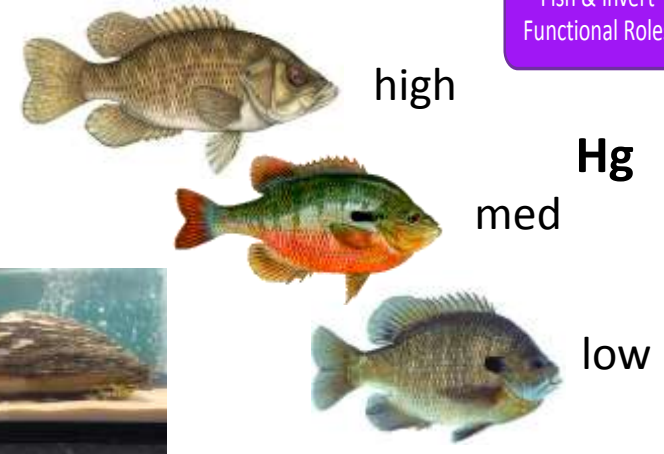
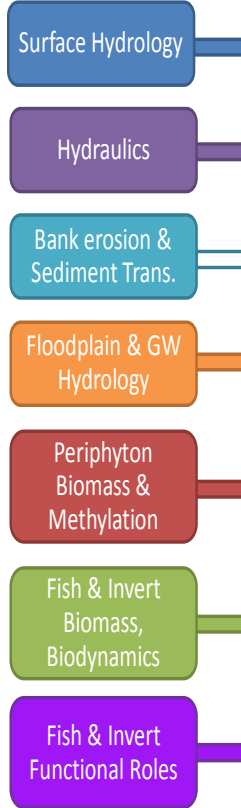
- What “knobs” need to be turned to decrease Hg methylation?
- Decrease flashy flows, modify nutrients, algae, light, habitat?

## Modify the food chain to decrease Hg risks while improving natural quality

- Reintroduce native mussels to decrease particle-associated Hg
- Fish management actions



## EFPC Ecosys



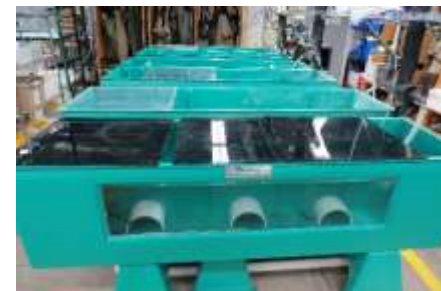
# Future technology development

## Aquatic Ecology Laboratory

- Flow-through testing of EFPC water planned



- Projected start: FY2020
- Need to advance the scale of testing beyond field studies and bench scale
- Unique facility to develop mercury remediation technologies



**SSAB: Look forward to your visit!**