Mercury contamination in East Fork Poplar Creek, Oak Ridge, Tennessee

G.R. Southworth

Environmental Sciences Division

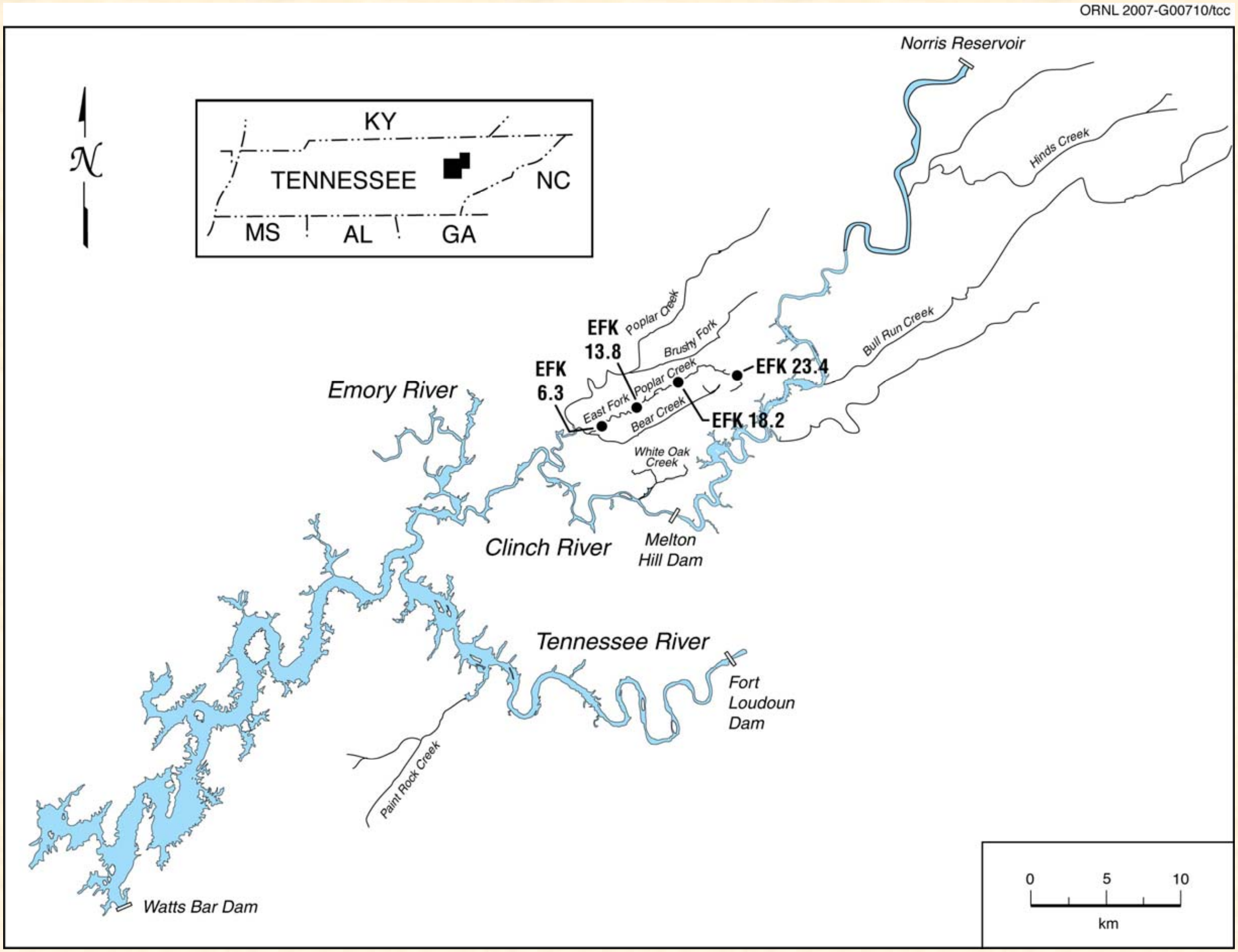
Oak Ridge National Laboratory

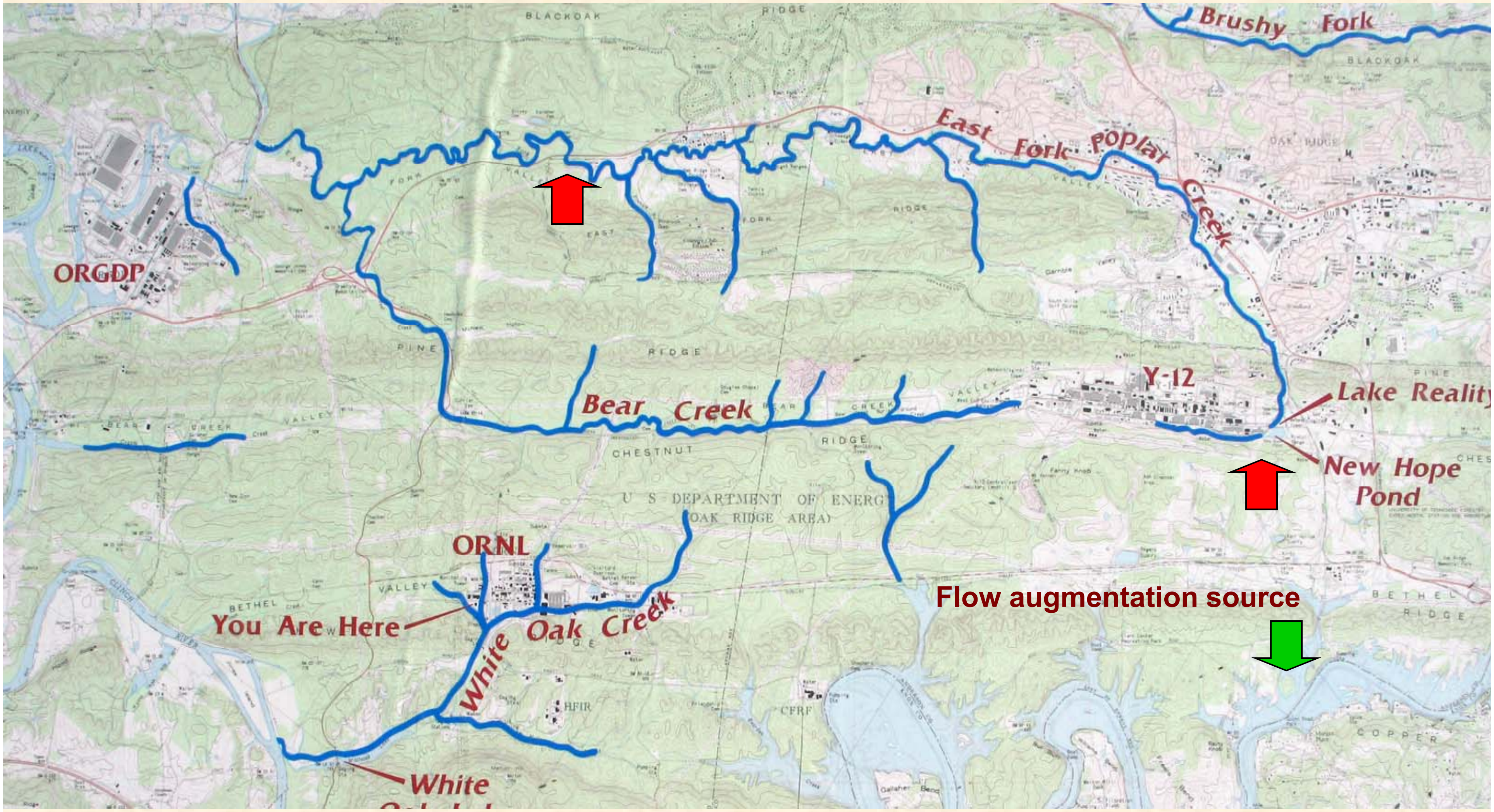
Mercury issues in Oak Ridge

Industrial use of metallic mercury in 1950's and 1960's contaminated soil, buildings, storm drain network, ground and surface water.

1.1 million kilograms of mercury were lost at the site, with about 10% of that going to East Fork Poplar Creek.

Processes using mercury were discontinued in 1963.


ORNL 2007-G00710/tcc
N
KY
TENNESSEE
NC
MS
AL
GA
Norris Reservoir
Hinds Creek
Poplar Creek
EFK
13.8
Brushy Fork
EFK
6.3
EFK 23.4
Poplar Creek
East Fork
Bear Creek
EFK 18.2
Bull Run Creek
Emory River
White Oak
Creek
Clinch River
Melton
Hill Dam
Tennessee River
Fort
Loudoun
Dam
Paint Rock Creek
Watts Bar Dam
0
5
10
km

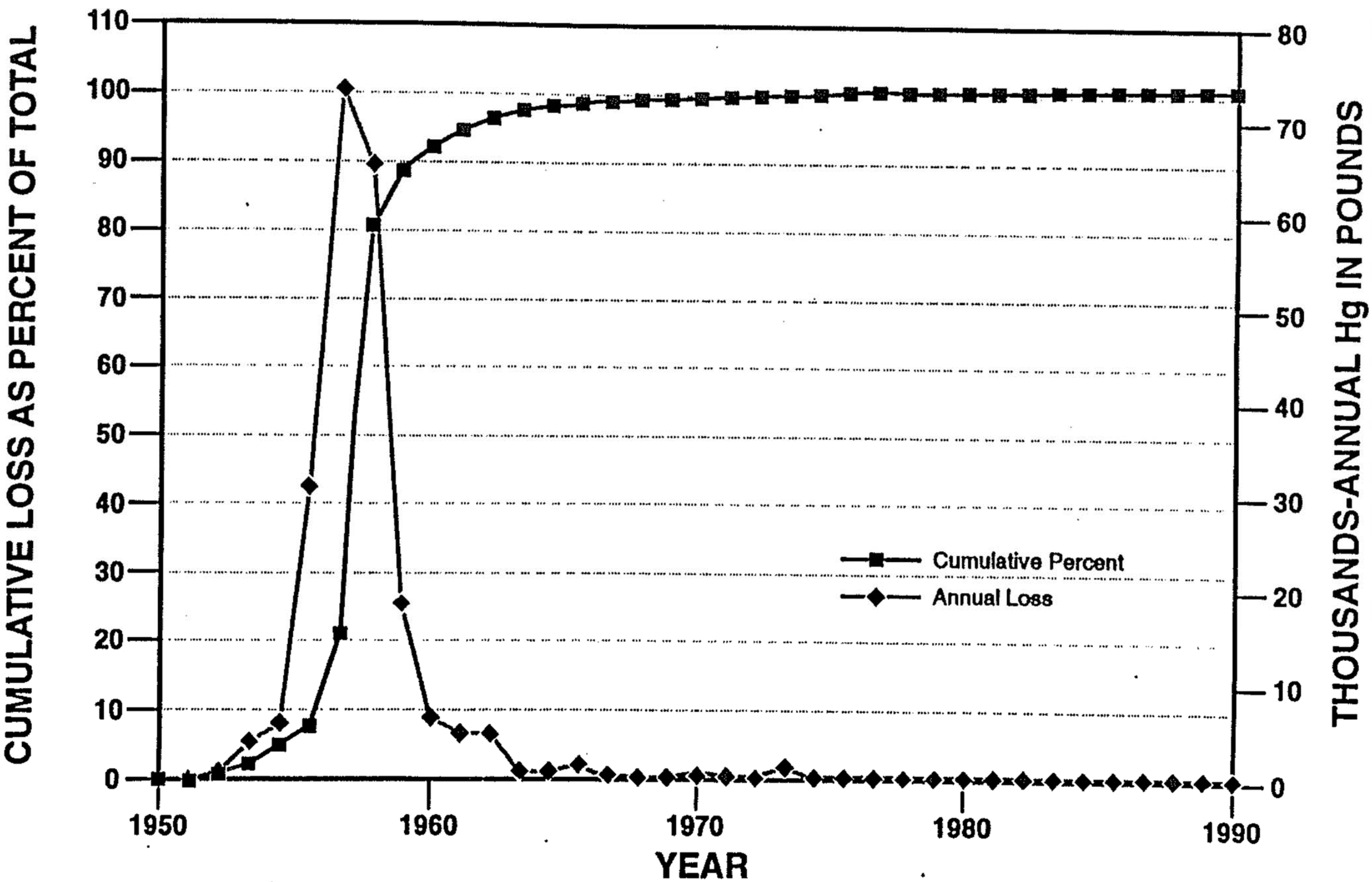

Brushy Fork
East Fork Poplar Creek
ORGDP
Bear Creek
Y-12
Lake Reality
New Hope Pond
ORNL
You Are Here
White Oak Creek
White
Flow augmentation source

History of mercury actions in EFPC

- 1950s-1960s: Industrial use of metallic mercury at Y-12 resulted in contaminated soil, buildings, storm drain network, ground and surface waters.
  - Approximately 2.4 million pounds of mercury were lost at the site, with about 10% of that going to East Fork Poplar Creek.

- 1963: Processes using mercury at Y-12 were discontinued.
- 1988 New Hope Pond replaced
- 1990's RMPE – EEMTS & CMTS construction, storm drain cleanout / lining
- 1992 Dechlorination of discharge water
- 1996 Flow Management established base flow
- 1998 Lake Reality bypassed
- 2001 Bank stabilization in UEFPC to limit Hg soil erosion
- 2005 Big Spring Water Treatment System

Mercury Losses to EFPC



East Fork Poplar Creek setting progresses from industrial to urban to agricultural to woodland

Remedial actions have focused on controlling methylmercury bioaccumulation by reducing the concentration of waterborne inorganic mercury

Success of that approach depends upon MeHg bioaccumulation being limited by the concentration of inorganic Hg

Sources of mercury to EFPC

- Mercury use area, storm drain network
- Metallic mercury in streambed sediments
- Metallic mercury in solution cavity network (karst system)
- Erosion of Hg-contaminated streambank soils and streambed sediments
- Erosion of Hg-contaminated soils (floodplain, scrapyard, etc)
- Background mercury (rain, uncontaminated soils)

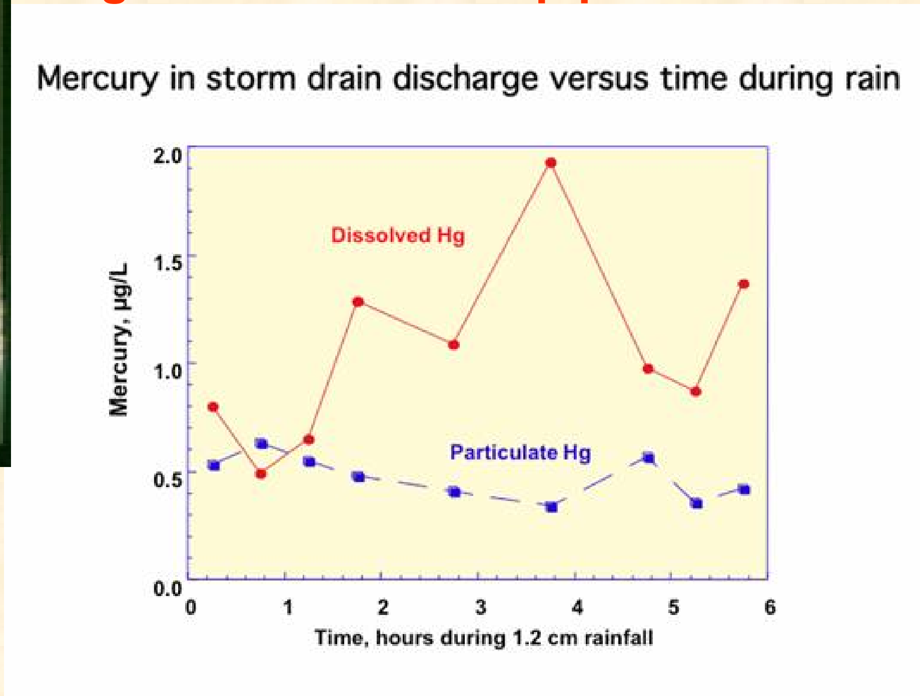
Source: Storm drain network above N/S pipe, historic Hg-use area

~ 3 – 10 g/d loading

Unique chemistry, Hg solubilized by HOCl

Metallic mercury in gravel-filled pipe

Response to rain suggests dissolved Hg sources close to pipes



Source: Metallic mercury in streambed sediments

Blobs of Hg metal on clay hardpan under armored soft sediments
Generates >30 µg/L Hg
Input to surface flow enhanced by Flow Management

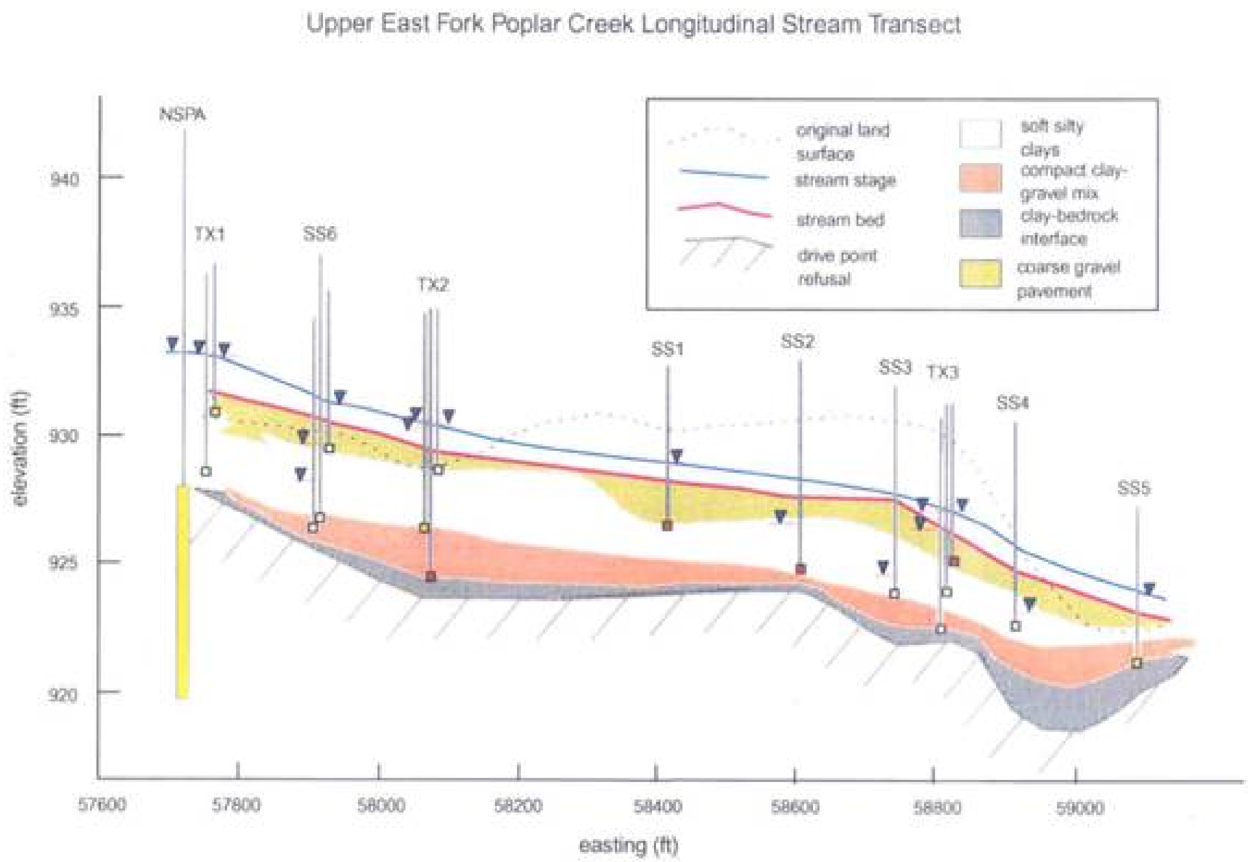


Figure 4. Longitudinal cross section through the study reach showing water levels, subsurface geomaterials, and Hg distribution.

UT-BATTELLE

Effect of Flow Management on mercury flux and concentration

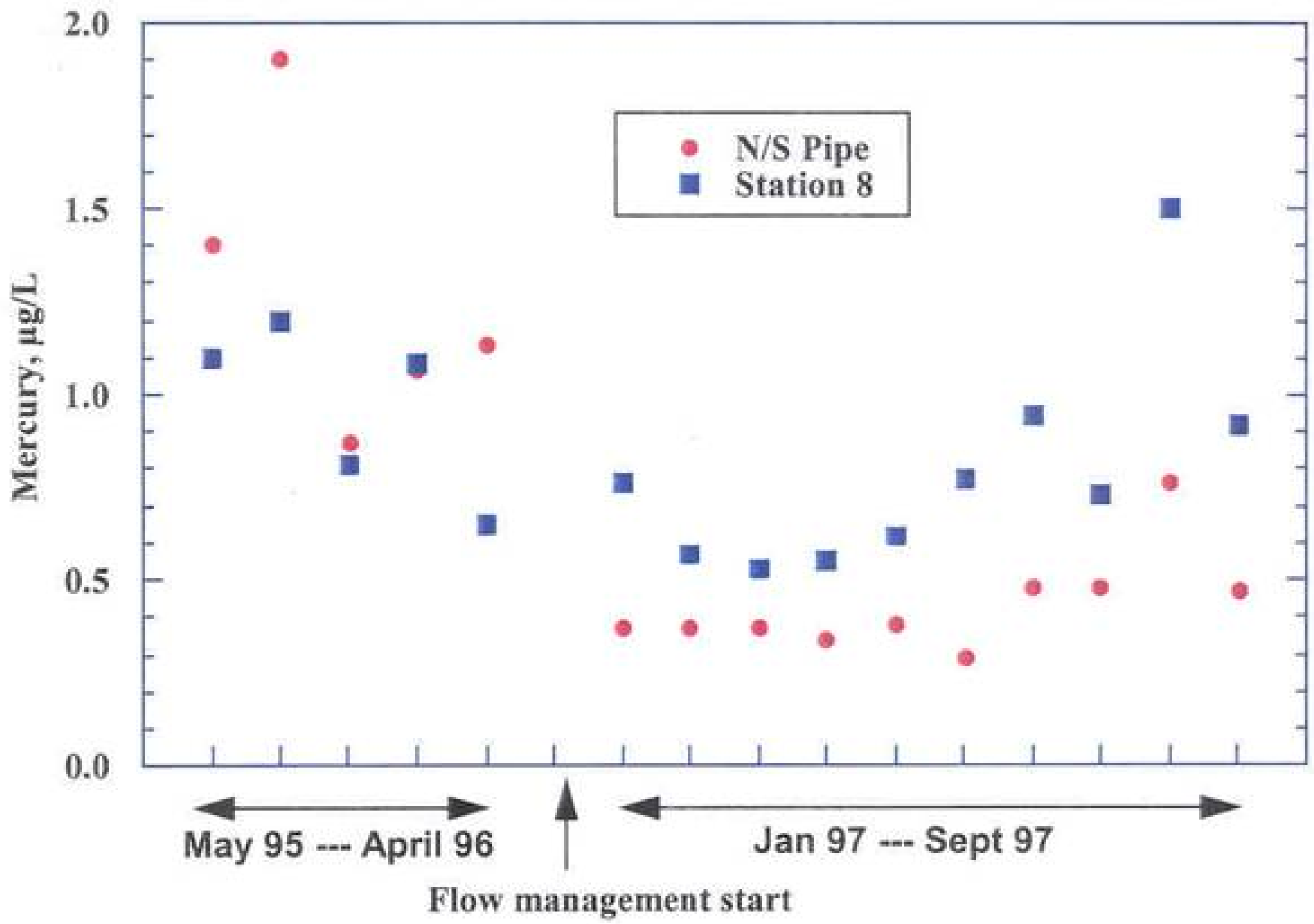
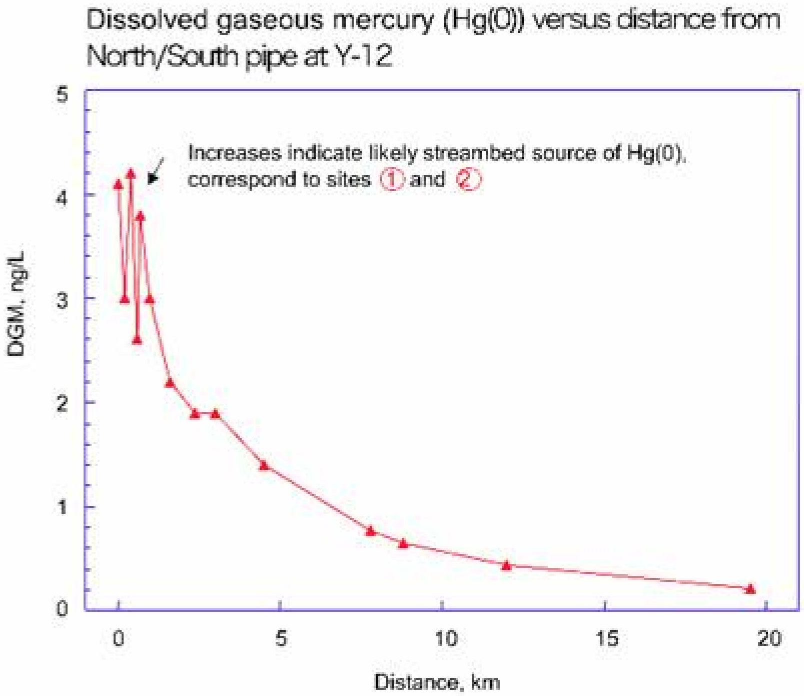
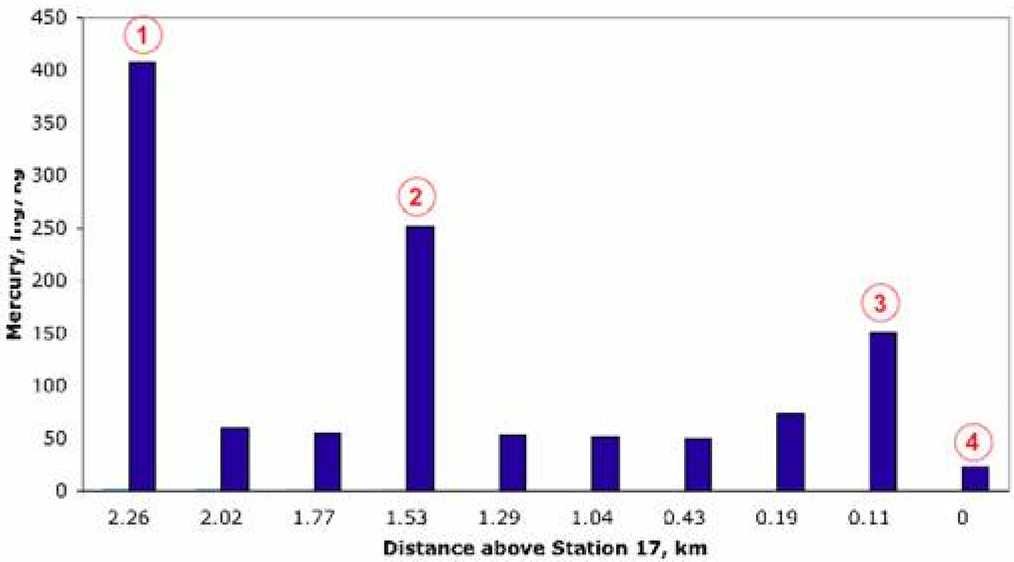


Fig. 1. Total mercury concentrations in UEFPC below the N/S Pipe and at Station 8, before and after Flow Management. Post-Flow Management samples were taken after mixing with raw water.

Indications of streambed mercury



Mercury in fine sediment suggests metallic Hg in streambed at sites 1 and 2



OAK RIDGE NATIONAL LABORATORY
U. S. DEPARTMENT OF ENERGY

Outfall 51, a Hg-contaminated spring, contributed about 3 - 4 g Hg/day to EFPC, most of which was highly reactive dissolved Hg(II) and Hg(0)

Activated charcoal treatment removes > 99% of Hg

Tracer dye added to karst system 800 m upstream emerges from spring

Source: Mercury eroded from streambank and streambed

Primary source of wet weather loading
Dissolved Hg doesn't increase during wet weather loading
Flow Management raised water level to contact highly contaminated 'black layer'

Eroding 'black layer' contained average 300 ppm Hg, highest at waterline (max 2213 ppm)

Fig. A.1. UEFPC Bank Stabilization site before construction.

Before bank stabilization

After

Fig. A.6. UEFPC Bank Stabilization final site with riprap and geotextile tubes filled with sand.

Wet weather loading

Response to rainfall event indicates that the short (1,000 m) reach of open stream from N/S pipe to Station 8 is a much greater source of Hg loading during rain than the entire watershed above the N/S pipe.

That pattern continued in next 1,000 m.

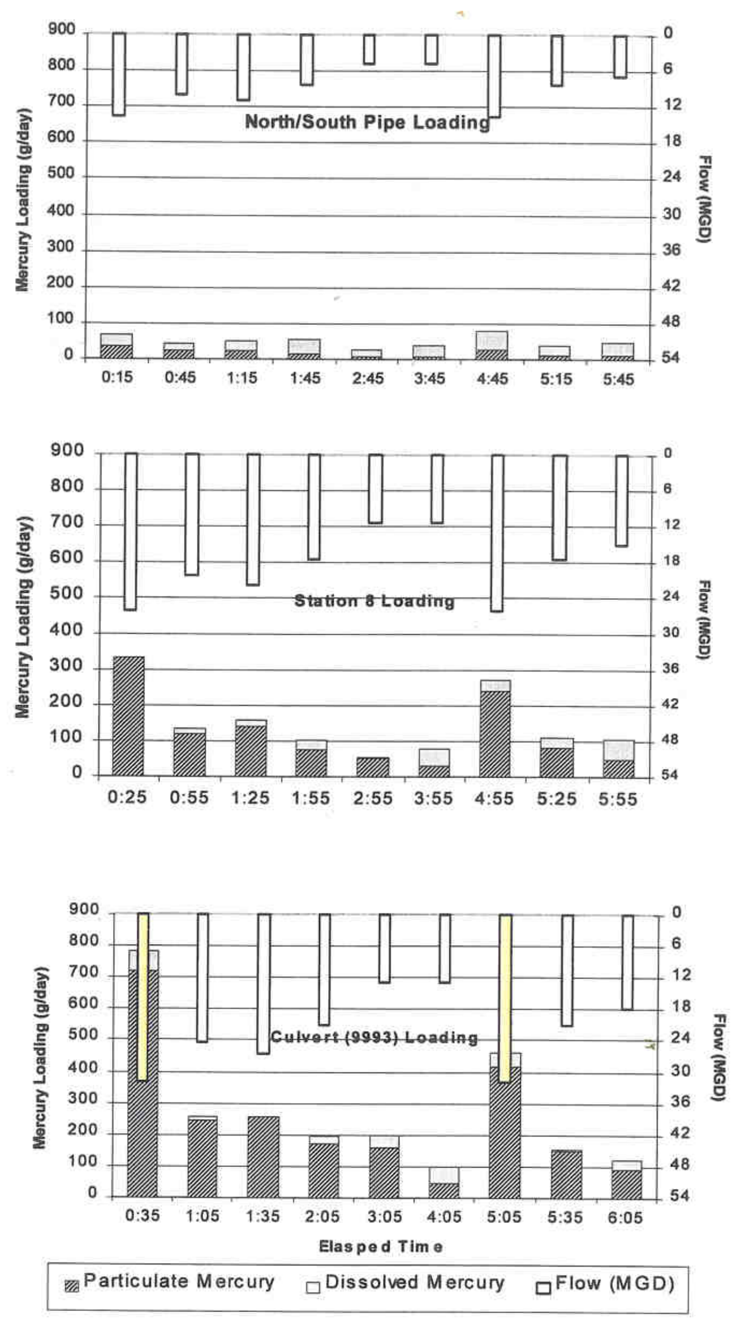


Fig. 3.15. Dissolved and particulate mercury loading in UEFPC during a storm on January 7, 1998.

Source: Erosion of mercury-contaminated soils

Lower EFPC floodplain

Soils > 400 ppm Hg removed under CERCLA

Estimated loading to EFPC in 1984 ~ 500 g/d, but almost all associated with wet weather transport

Effects on baseflow Hg transport hard to discern

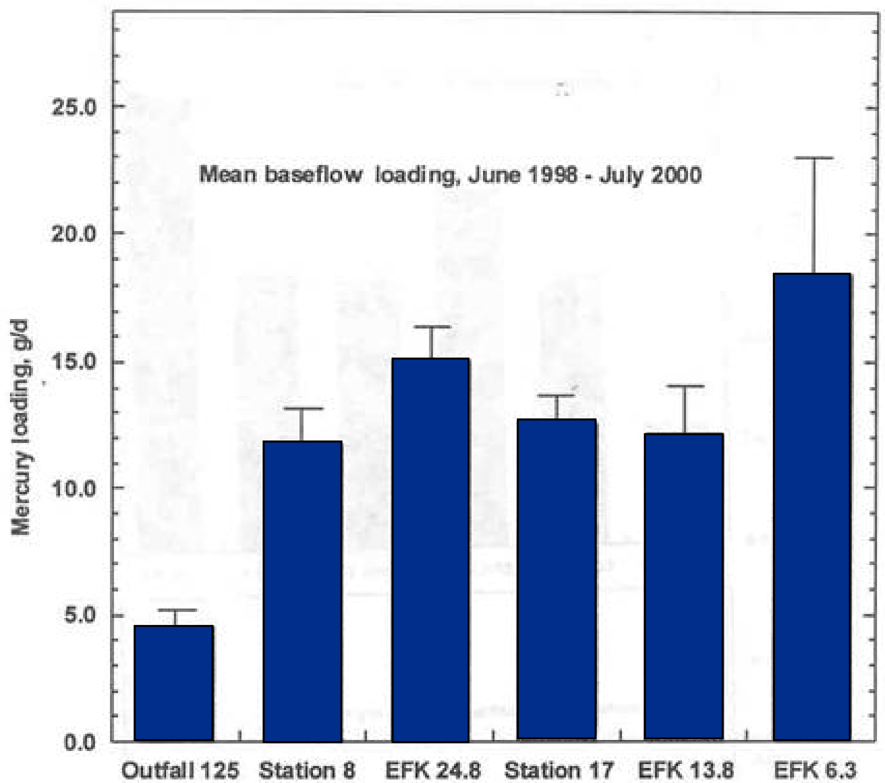
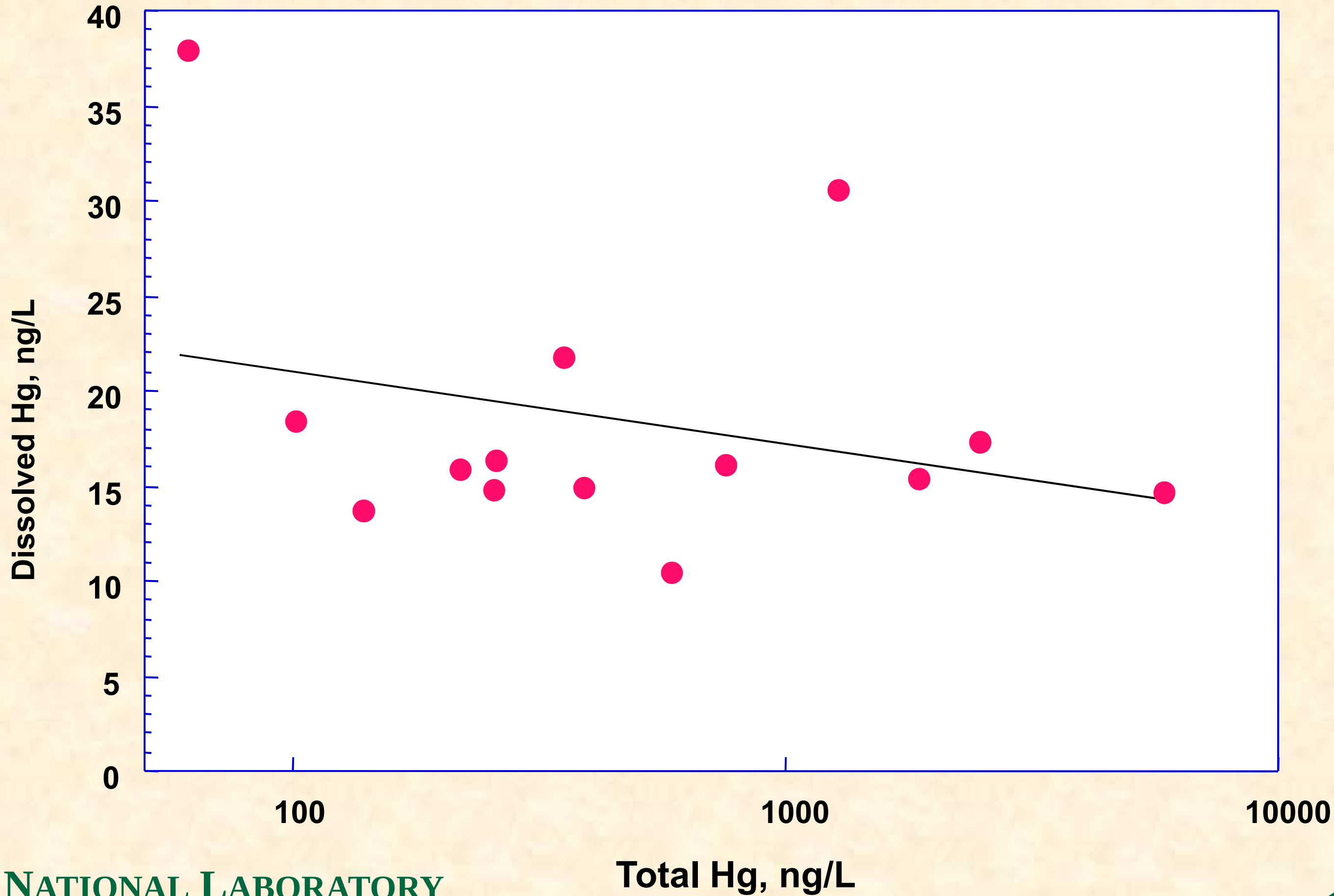


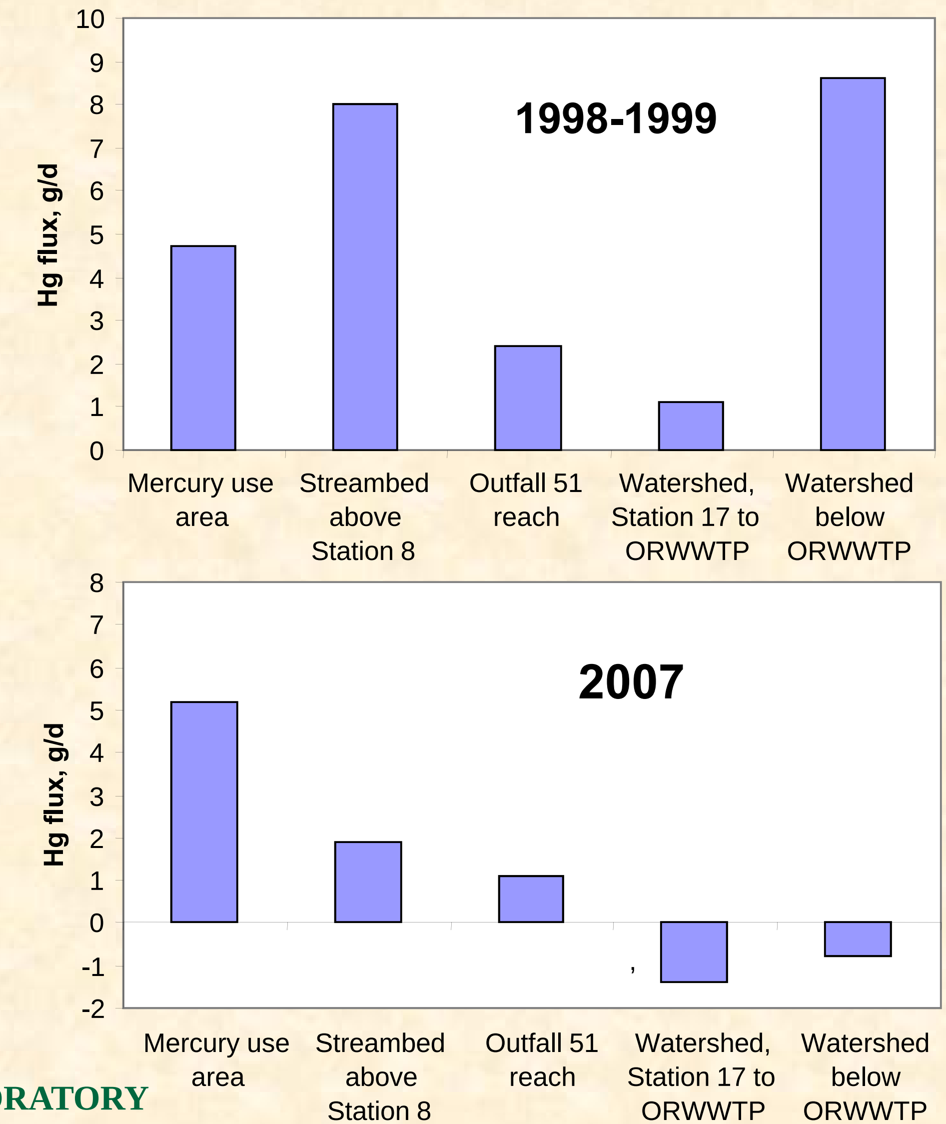
Fig. 4.4. Downstream changes in mercury loading in EFPC. Values are mean ± SE; N=8.

UT-BATTELLE

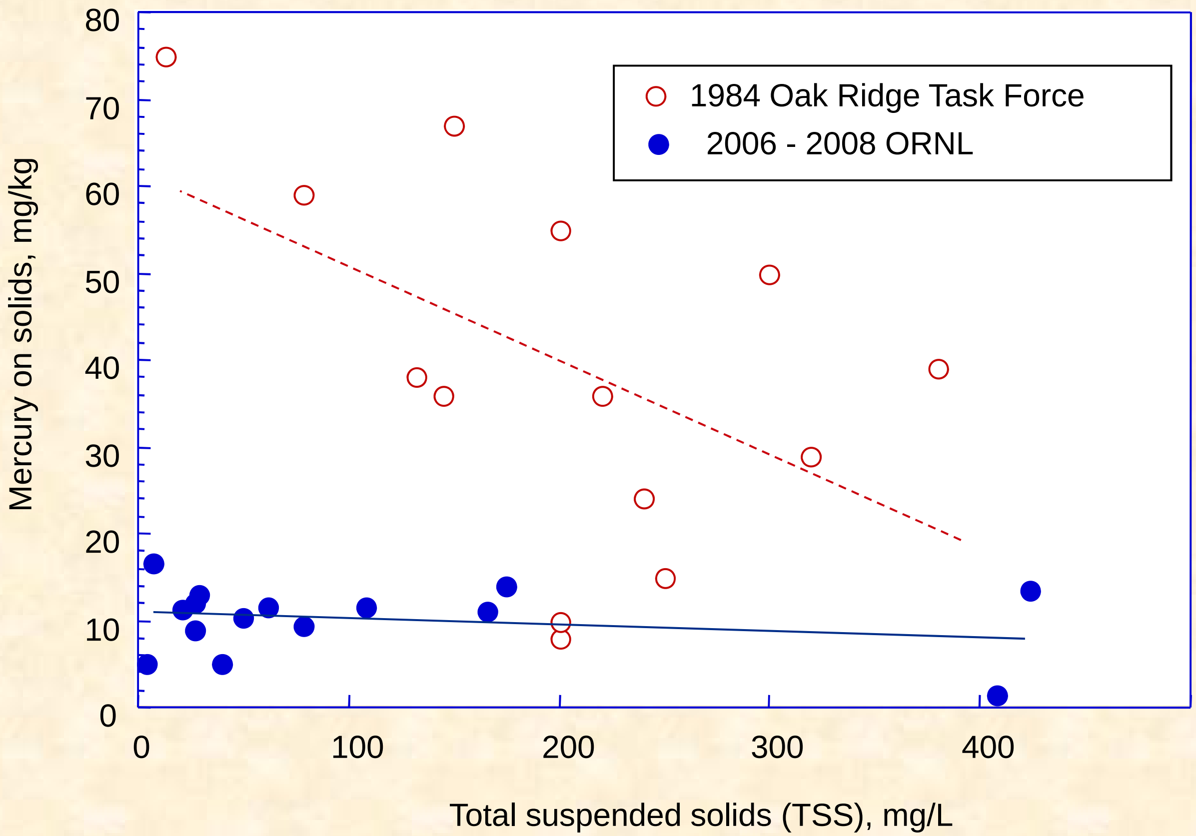
Dissolved Hg concentrations decrease during high flow when total Hg concentrations and Hg loading are highest



Baseflow mercury loading by source (N=5), 1998-1999 and 2007 (N=1)

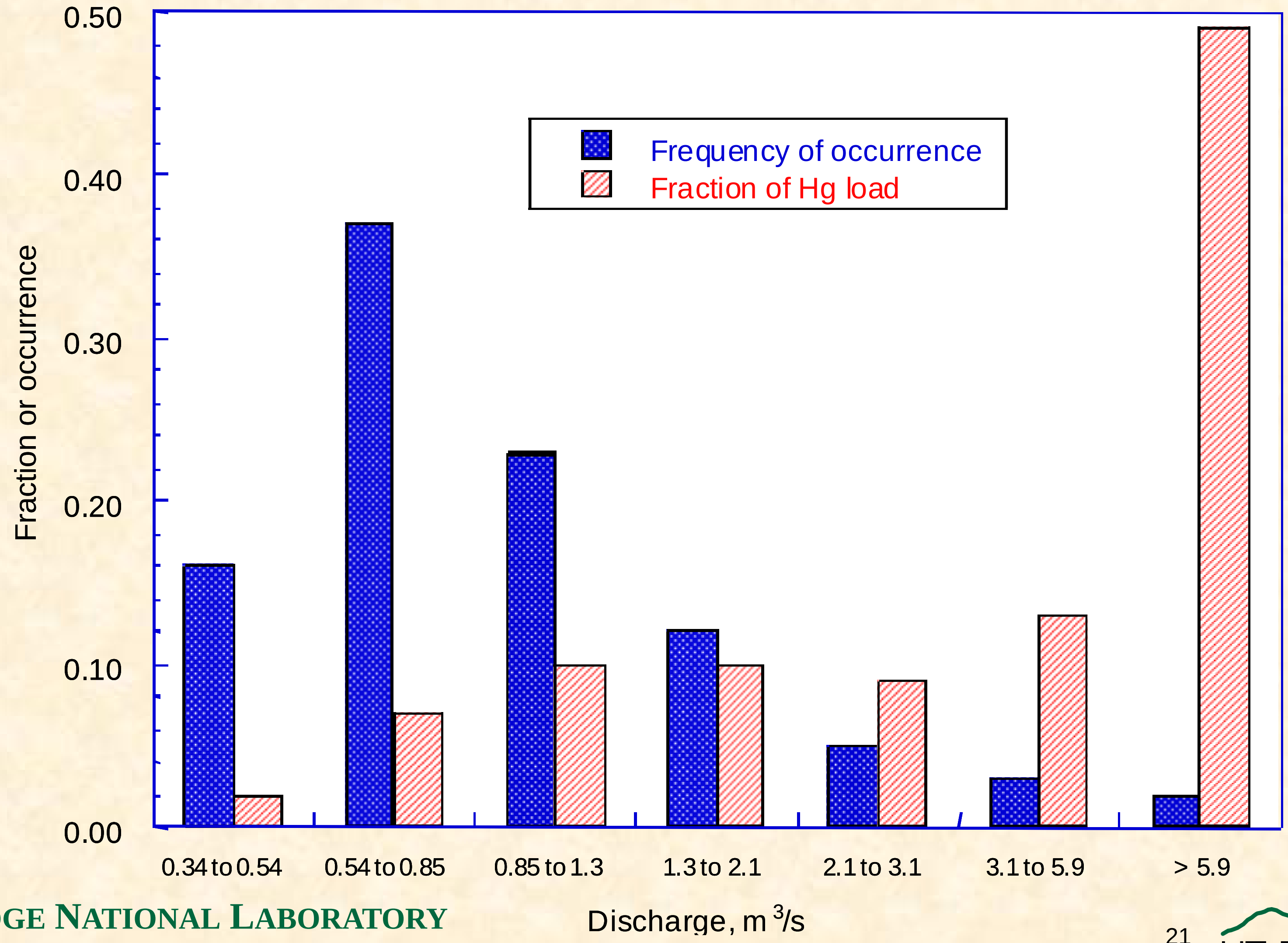


Wet weather flux 1984 versus 2007-2008

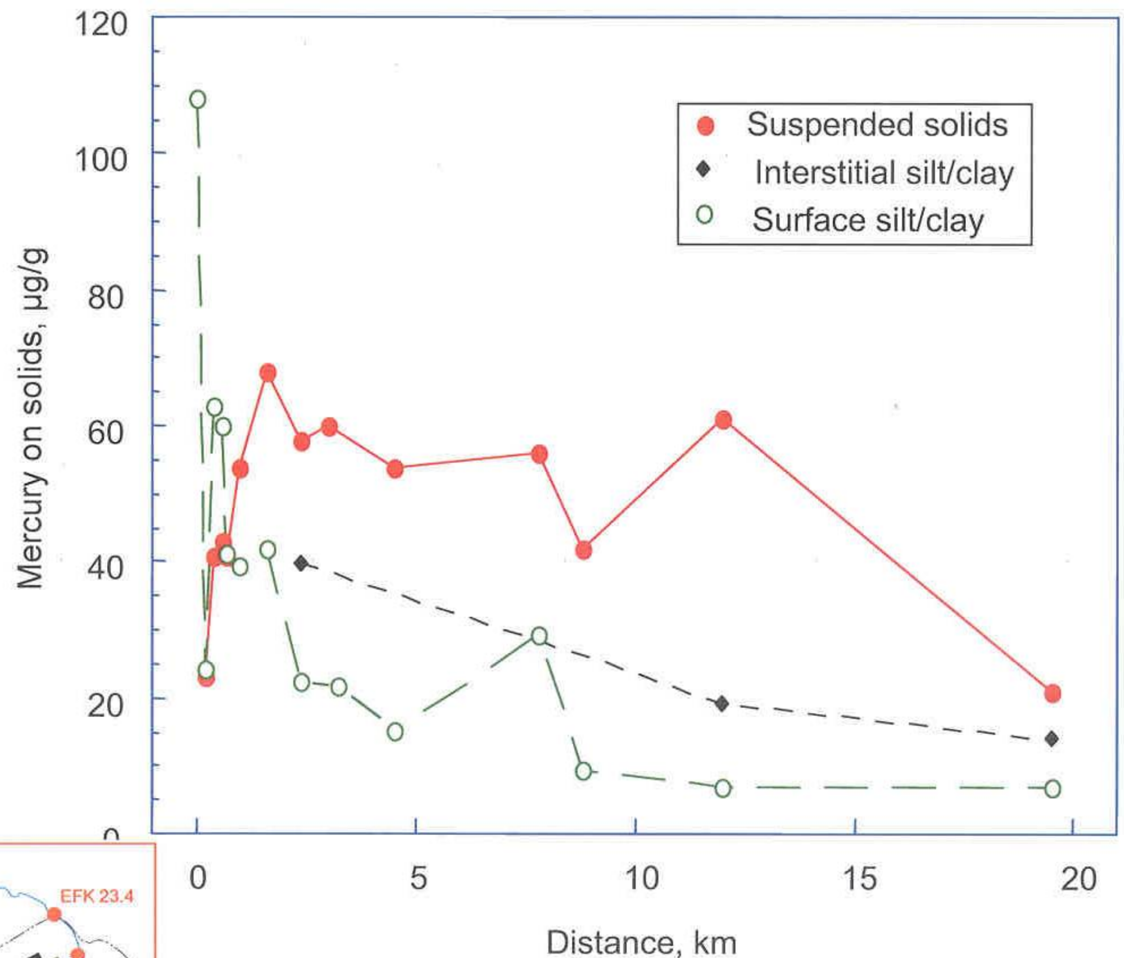


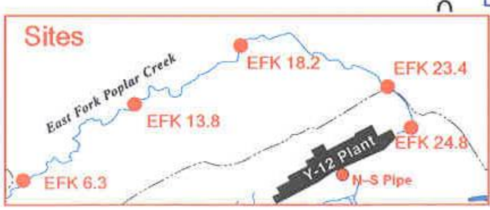
ORTF 1984 flux from watershed below Y-12 - 193 kg/y
2007/2008 estimated flux % reduction - 73% (52 kg/y)

Most Hg transport was predicted to occur in infrequent events

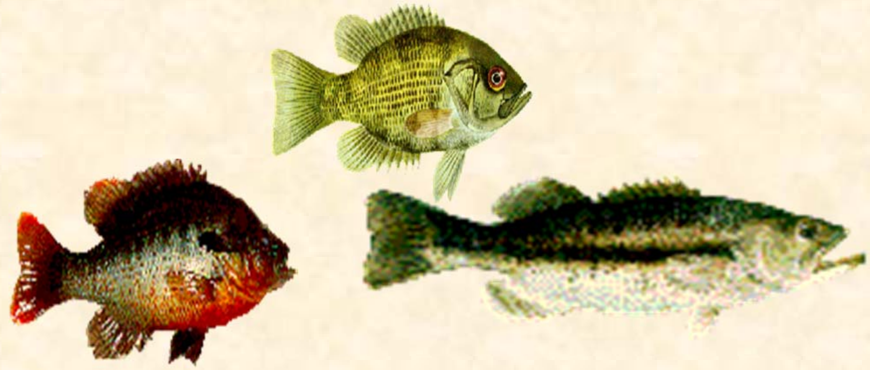


Concentrations of Hg on particulates (surface sediment, interstitial silt, and suspended solids versus distance from the N/S pipe at Y-12



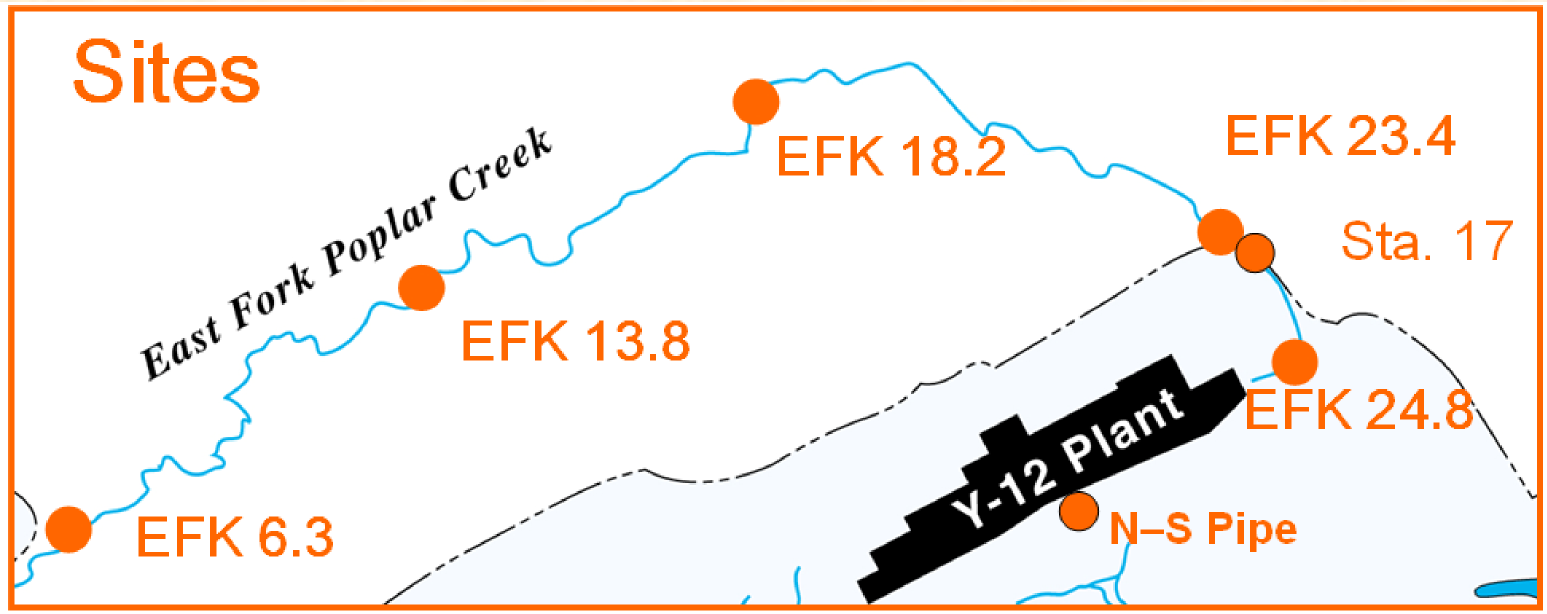


Bioaccumulation monitoring approach in EFPC



- **Monitoring of resident sunfish primarily (redbreast, rockbass)**
- **Five sites throughout length of 25 km stream**
- **Twice yearly sampling**
- **6-8 individual fish fillets/site**
- **Edible sized fish targeted, similar sizes between sites and years**

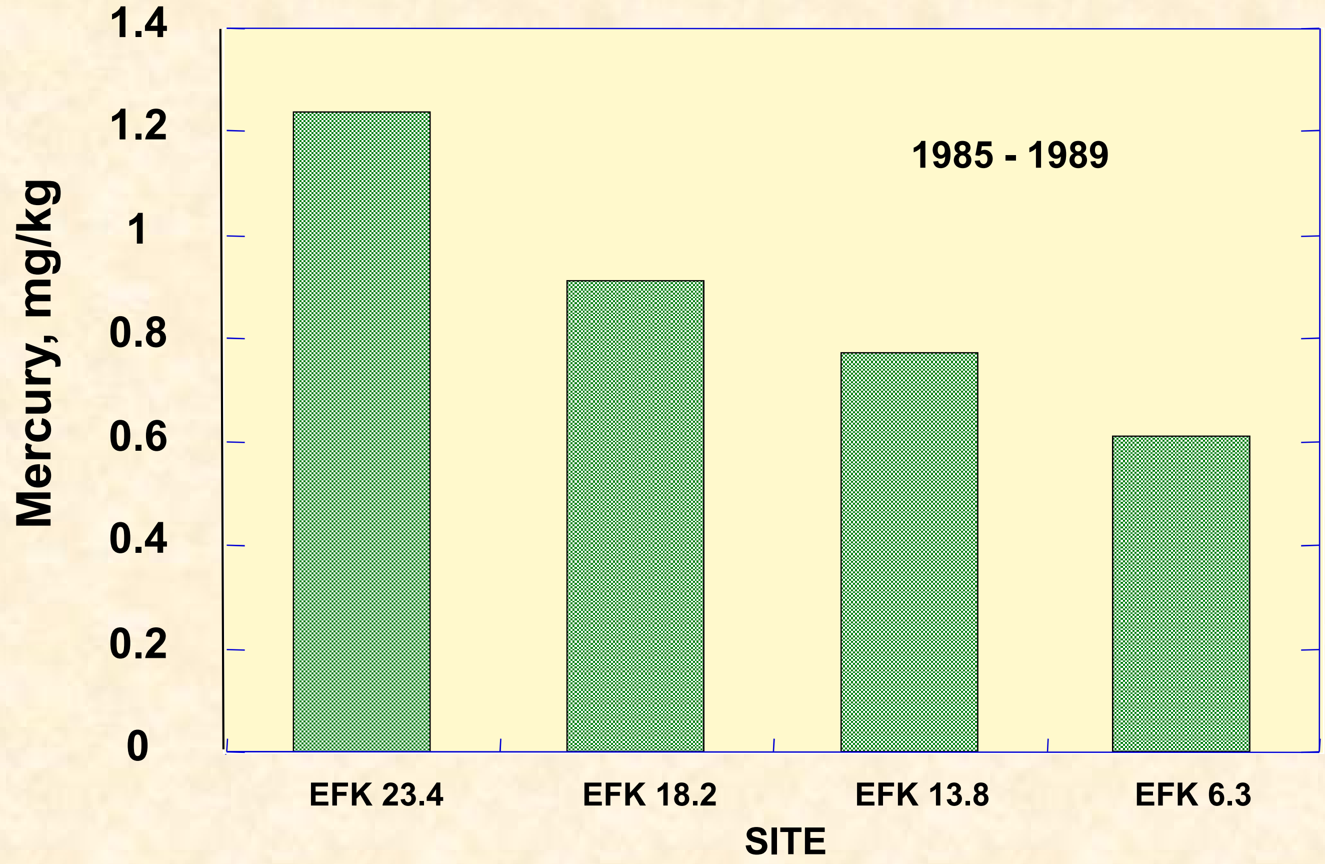
Hg in Fish Tissue : Spatial and Temporal Trends



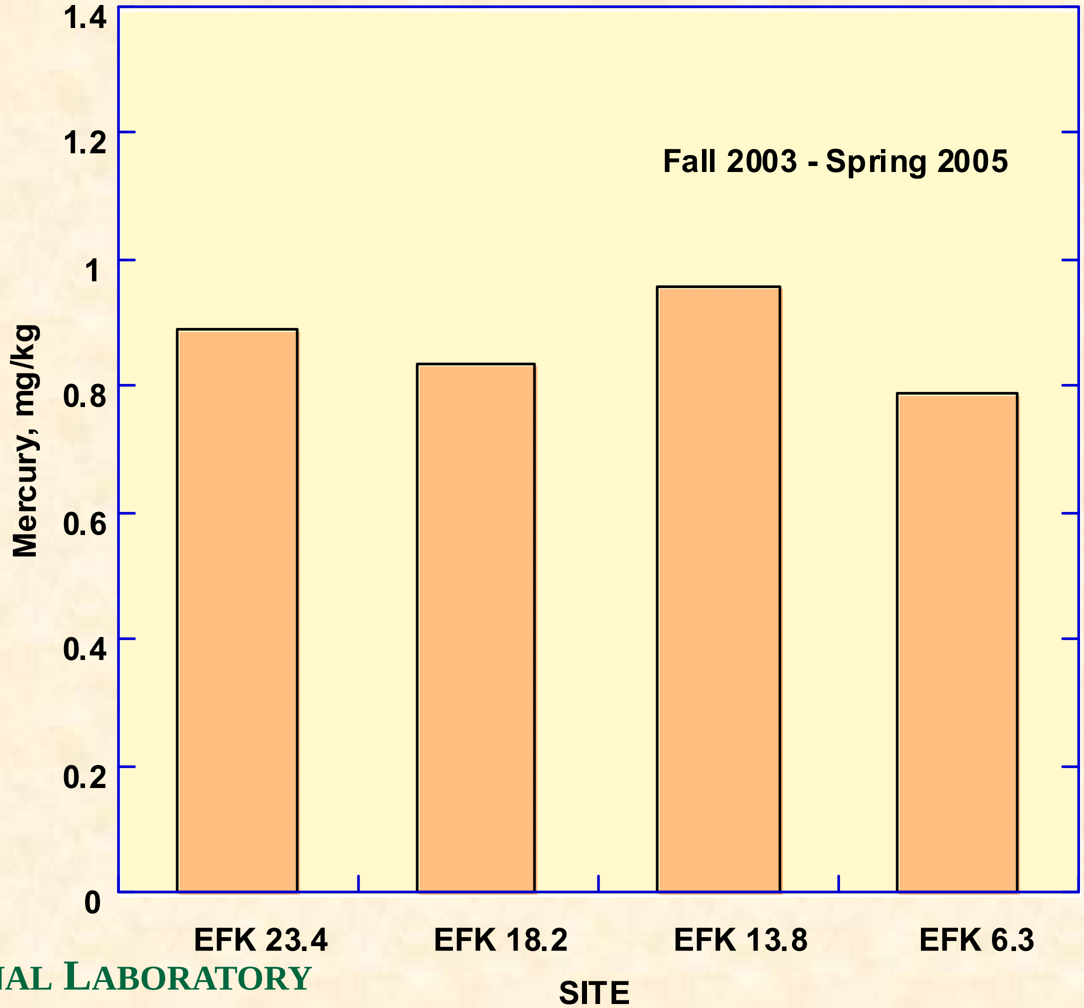
Facility Abatement Actions, 1984-present

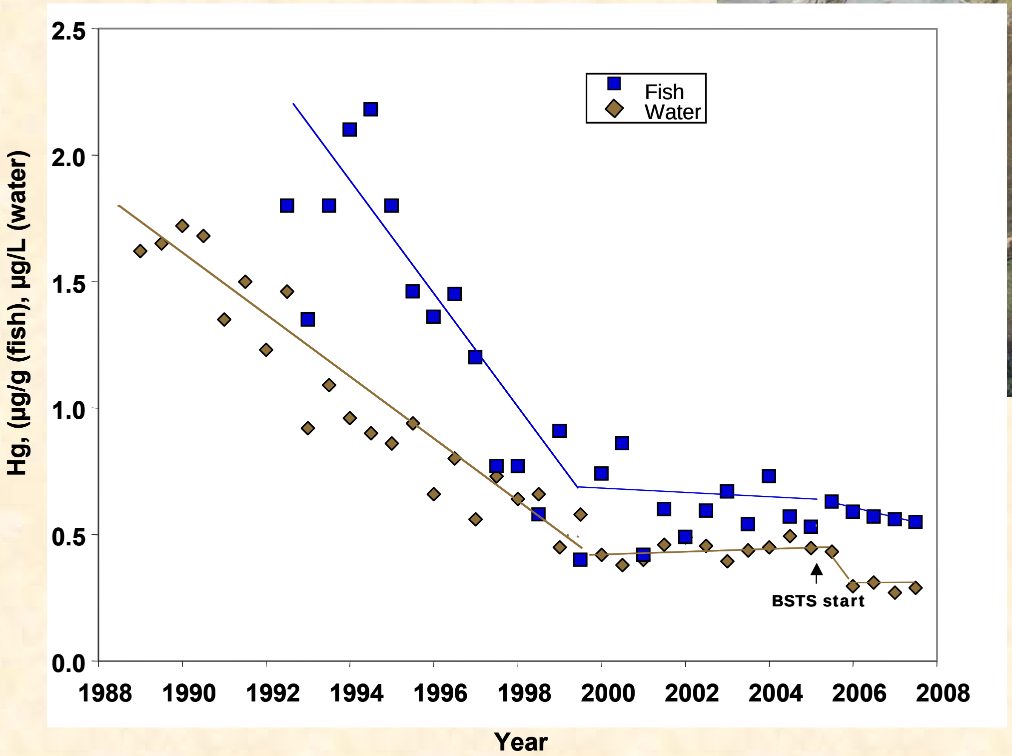
YEAR:	1984	1985	1986	1987	1988	1989	1990	1991	1992	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003
EVENT:					Pond replaced ↔				Dechlorination ↔				Flow management ↔		Pond bypassed ↔			Bank stabilized ↔		

The downstream profile of Hg in fish in EFPC in 1980's was consistent with downstream dilution of a headwater point source. Headwater Hg loading > 100 g/d Total residual chlorine ~ 0.5 ppm in upper 2 km.

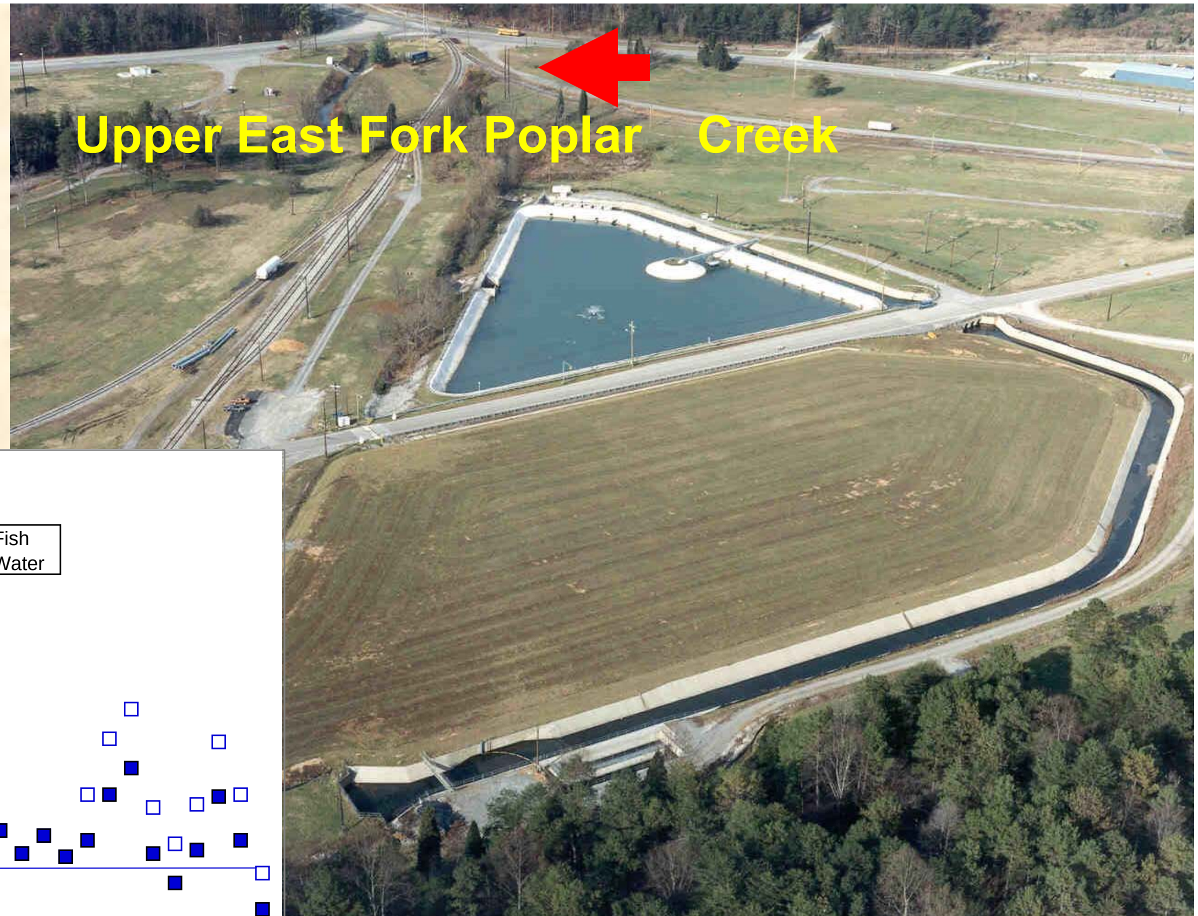


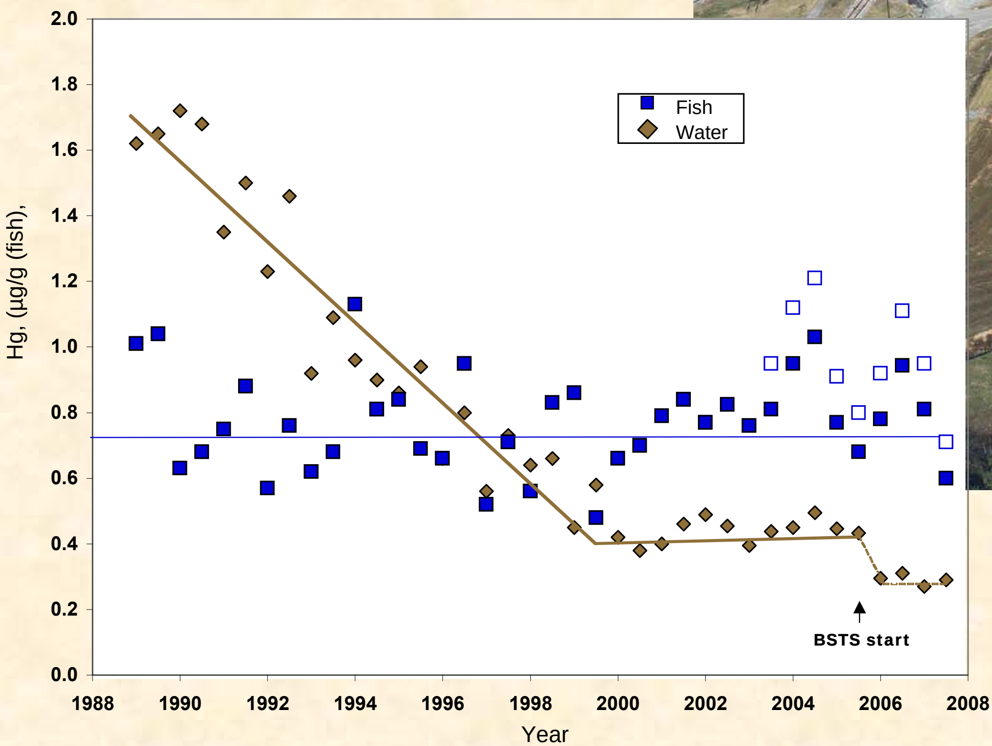
Since the early 1990’s, the downstream profile of mercury in fish has been uniform throughout the creek
Change coincides with dechlorination of all process water discharges





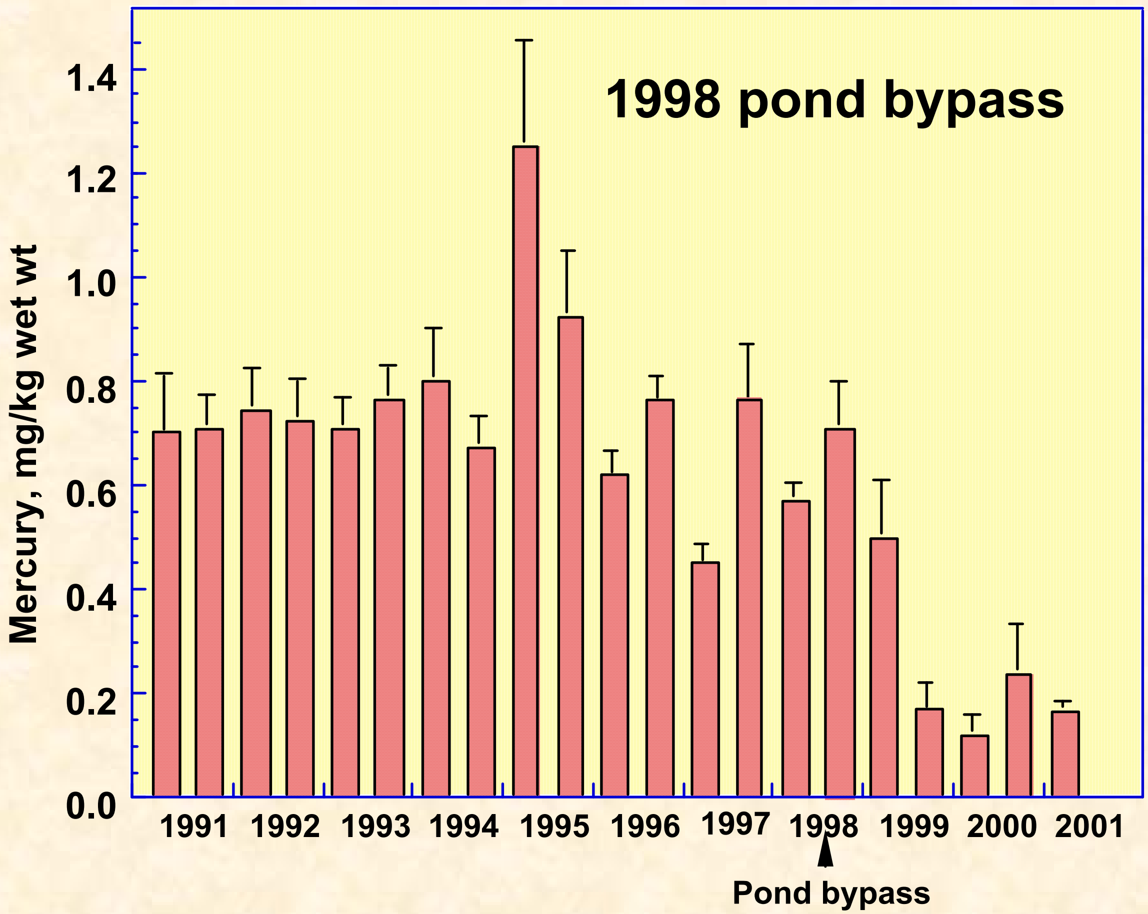
Hg in fish and water have changed commensurately in upper EFPC (above the pond in the photo)





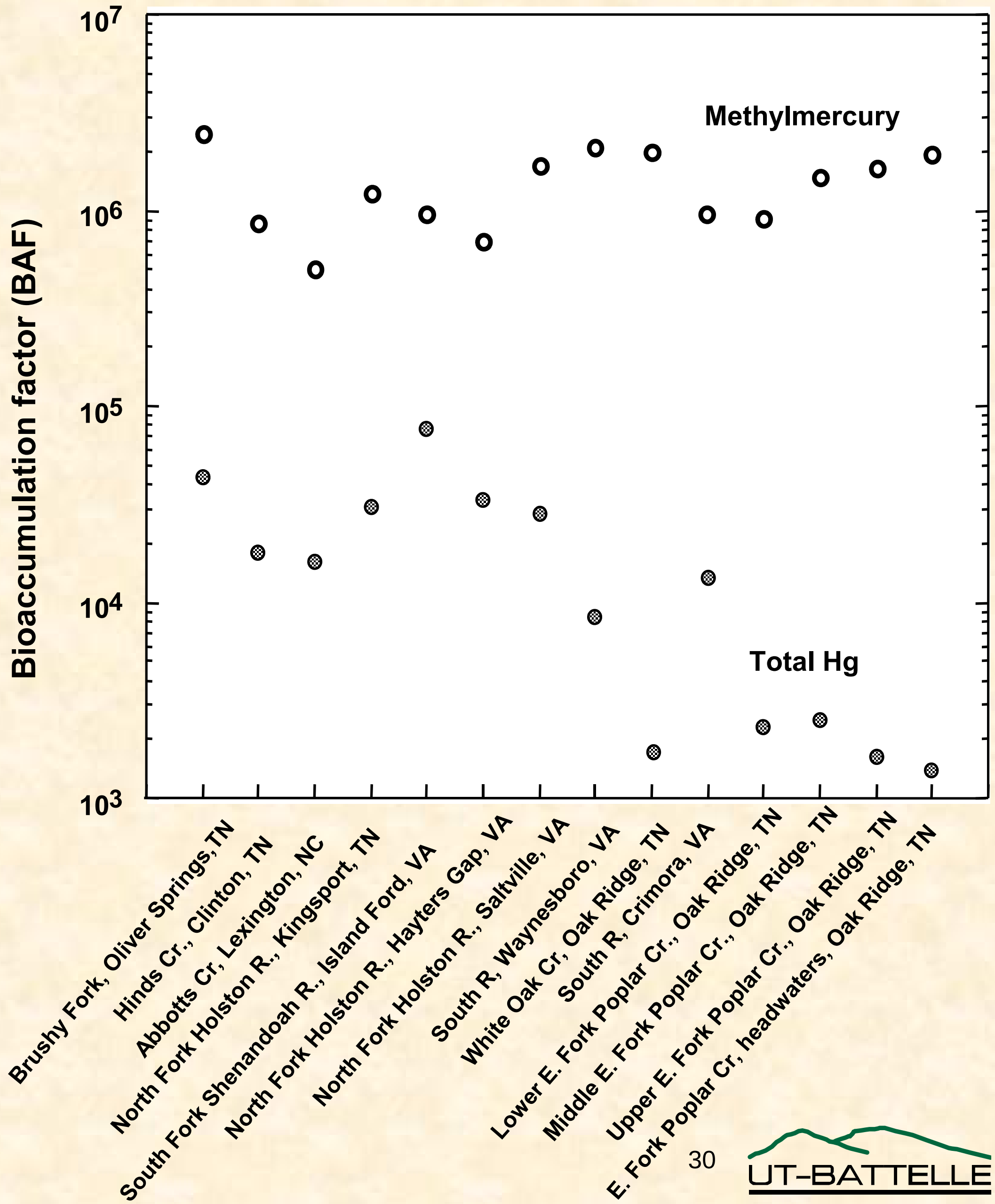
Hg in fish has not responded to upstream decrease in Hg in water at site below the pond

Eliminating waterborne Hg (but not 50 - 100 ppm Hg in sediments) produced a striking decrease in Hg bioaccumulation in bluegill in the pond

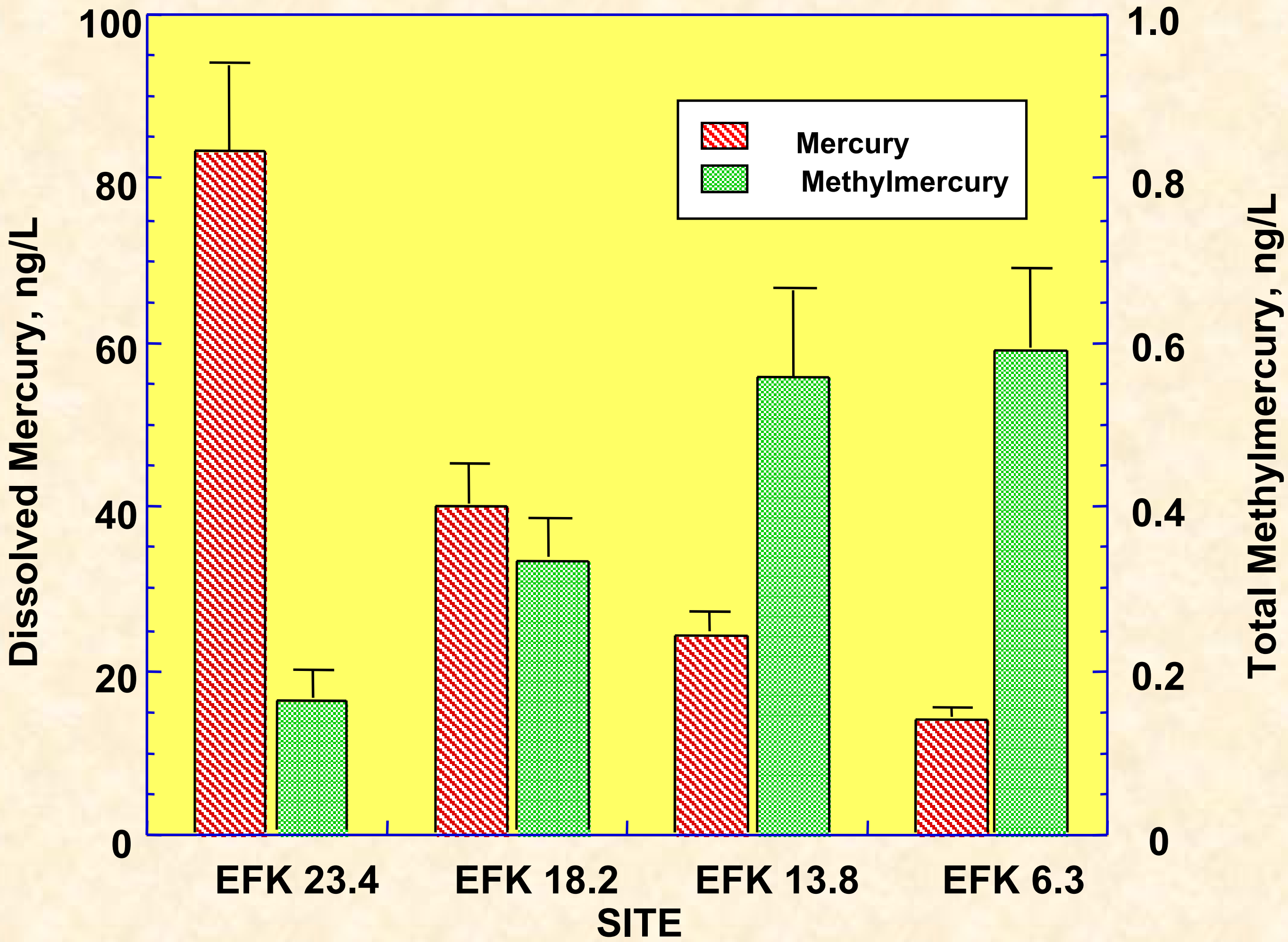


Bioavailability

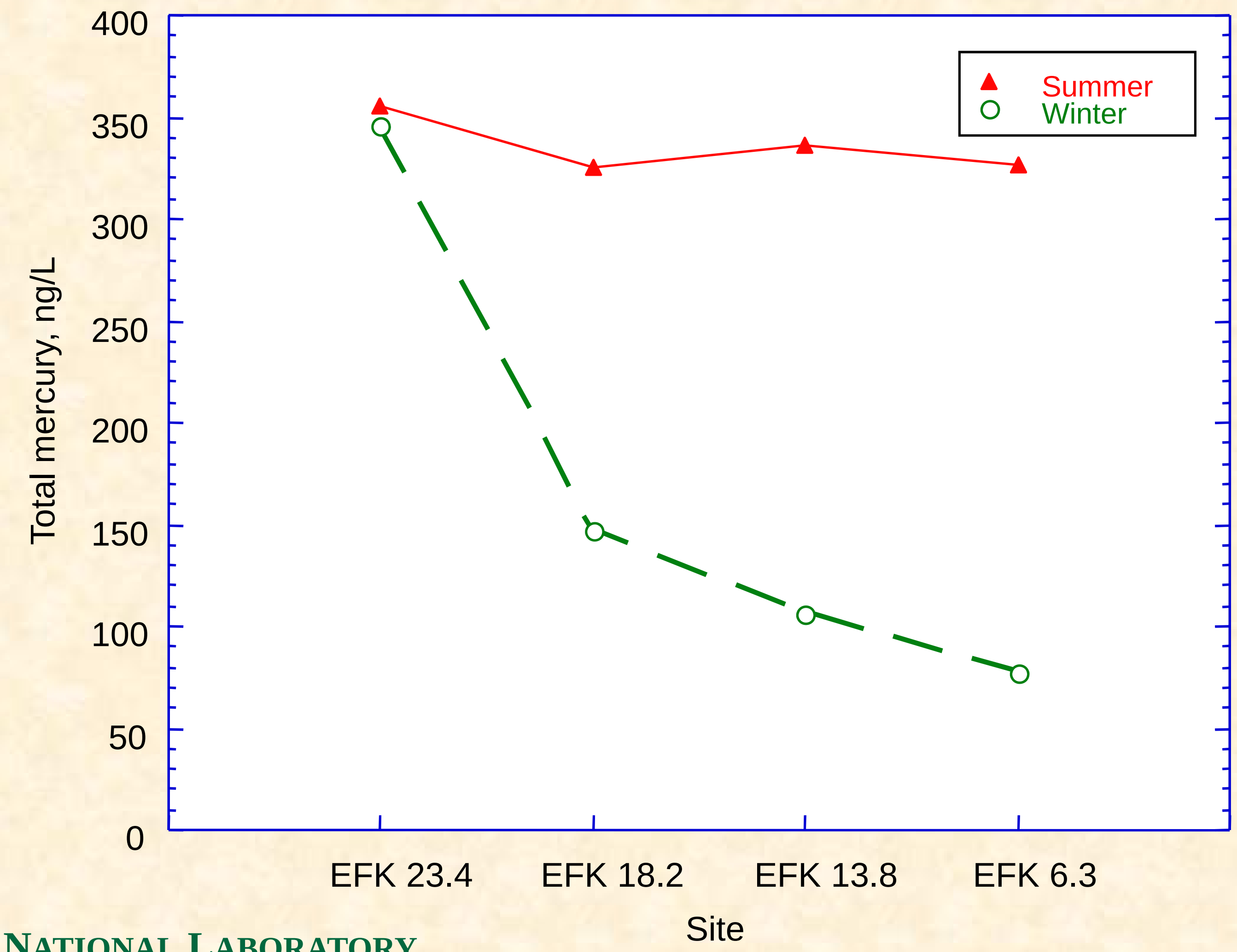
- Bioavailability of Me-Hg in EFPC appears similar to uptake factors in other streams
- Bioavailability of Hg-Total in EFPC is lower than other sites (contaminated and uncontaminated)



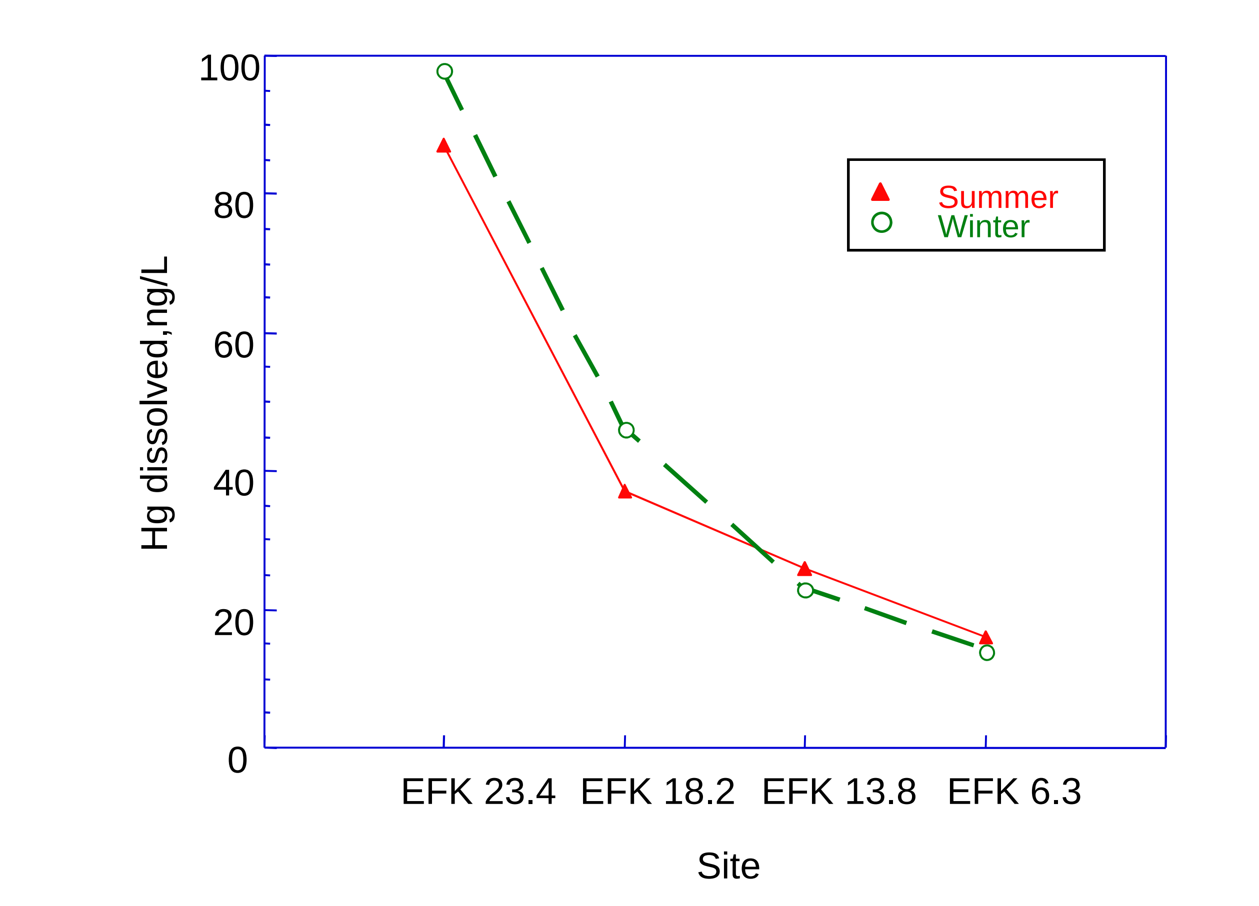
Dissolved Hg does not appear to be directly related to methylmercury production



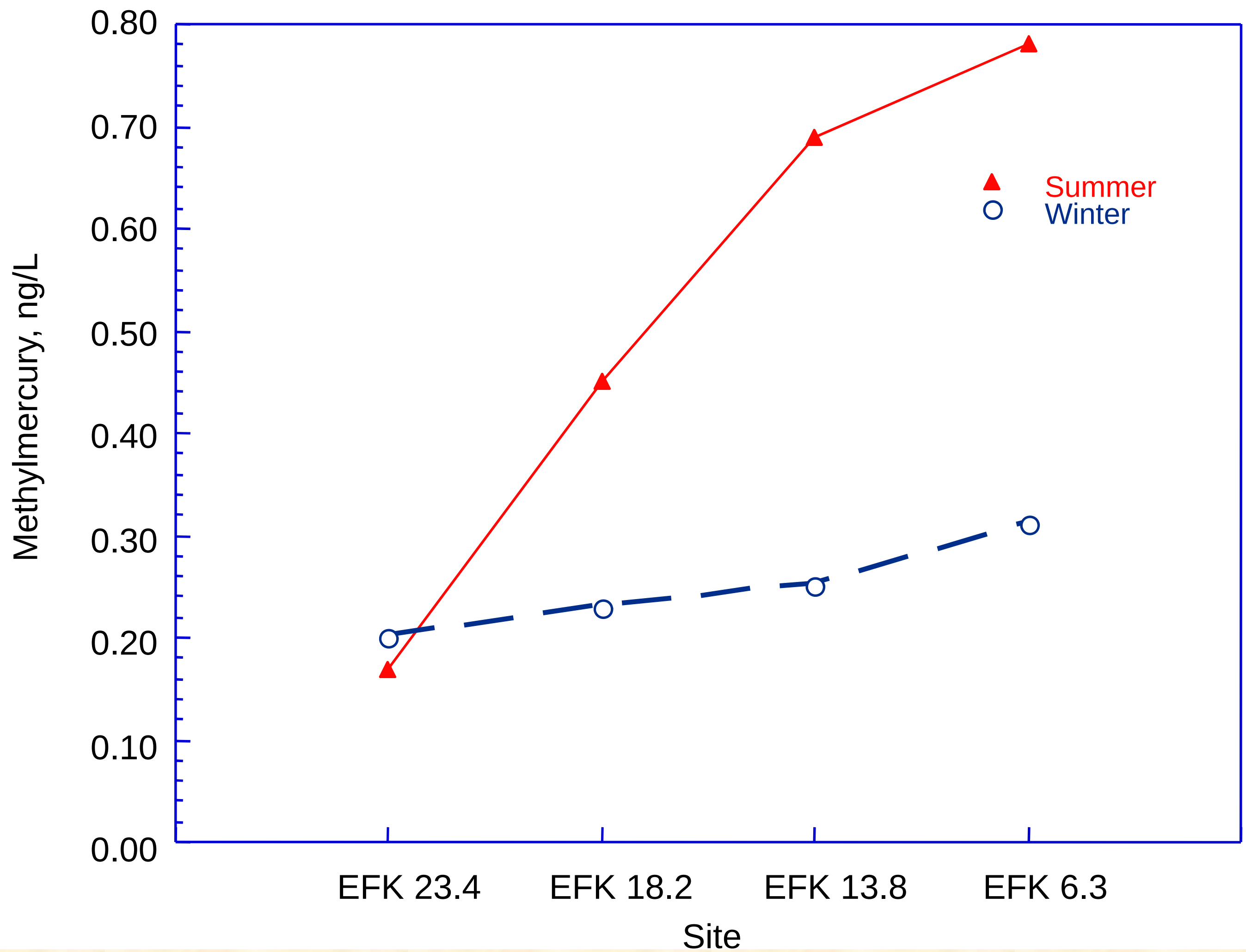
Downstream profiles of total mercury concentration in EFPC, 2000 - 2006, winter versus summer

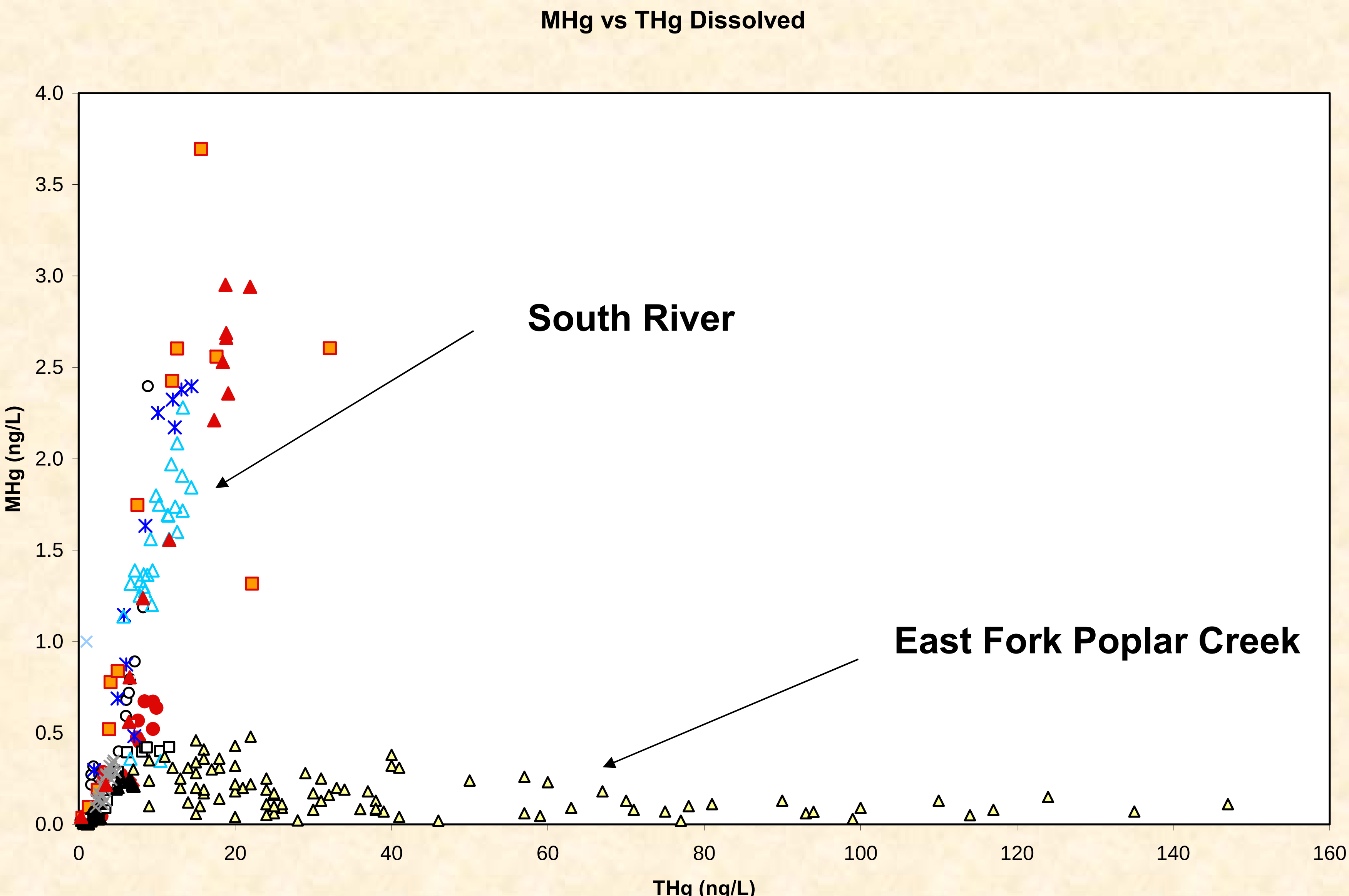


Downstream profiles of dissolved total mercury concentrations (filtered) in EFPC, 2000 - 2006, winter versus summer



Downstream profiles of methylmercury concentrations (unfiltered) in EFPC, 2000 - 2006, winter versus summer




MHg vs THg Dissolved
South River
East Fork Poplar Creek
MHg (ng/L)
THg (ng/L)
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
0
20
40
60
80
100
120
140
160

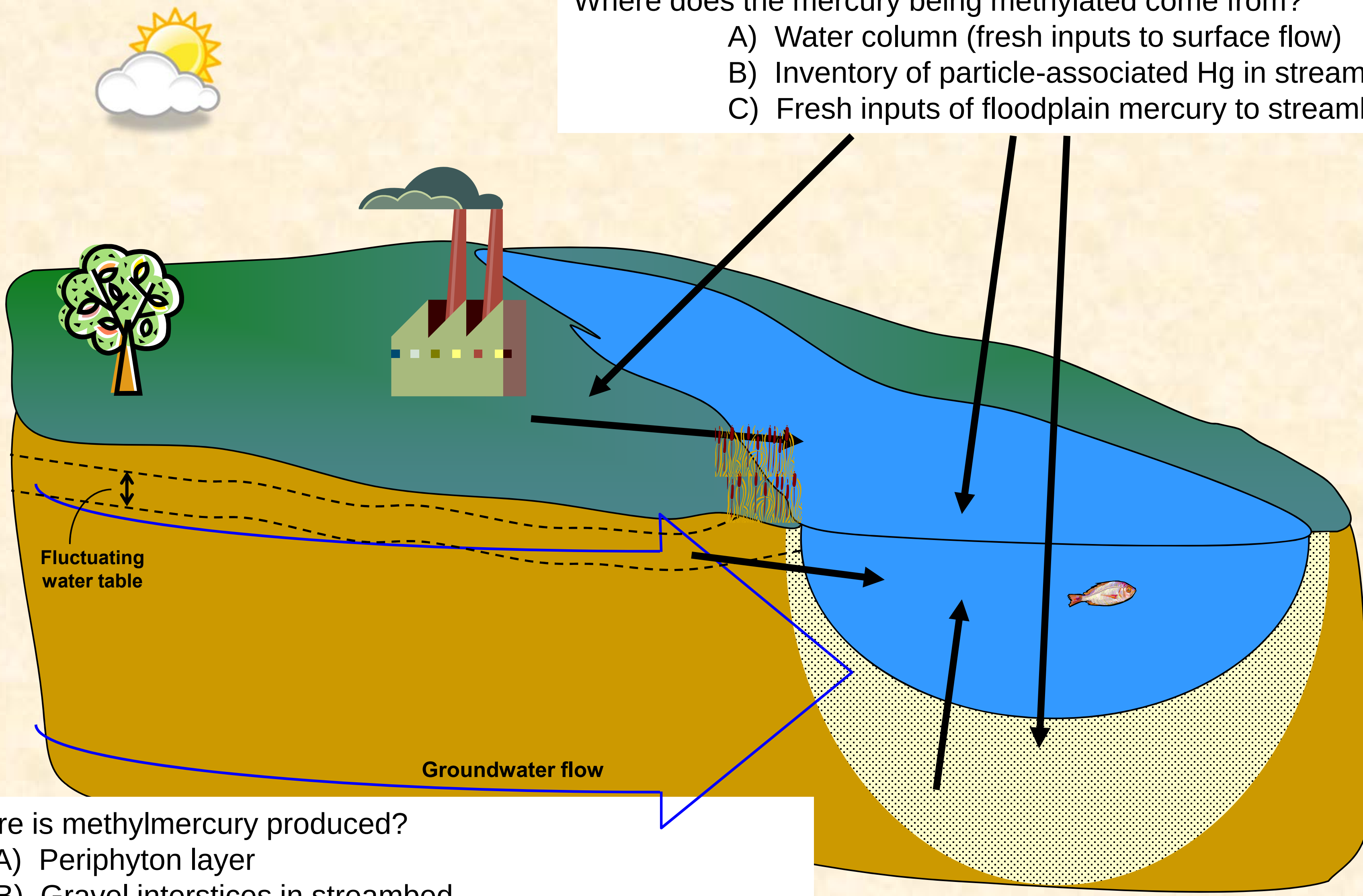
Important issues regarding bioavailability

- Mercury concentrations in fish throughout EFPC are low relative to the total concentration of Hg in water and sediment. (Low bioavailability)
- Success of Hg remediation efforts requires that bioavailability of Hg in EFPC remain low
- Does increase in Hg bioaccumulation in lower EFPC portend a system-wide change in Hg bioavailability?

Questions: Primary and Secondary Sources

Where does the mercury being methylated come from?

A) Water column (fresh inputs to surface flow)
B) Inventory of particle-associated Hg in streambed
C) Fresh inputs of floodplain mercury to streambed



Where is methylmercury produced?

A) Periphyton layer
B) Gravel interstices in streambed
C) Compact, localized streambed sites where anaerobic conditions exist
D) Other?

UT-BATTELLE

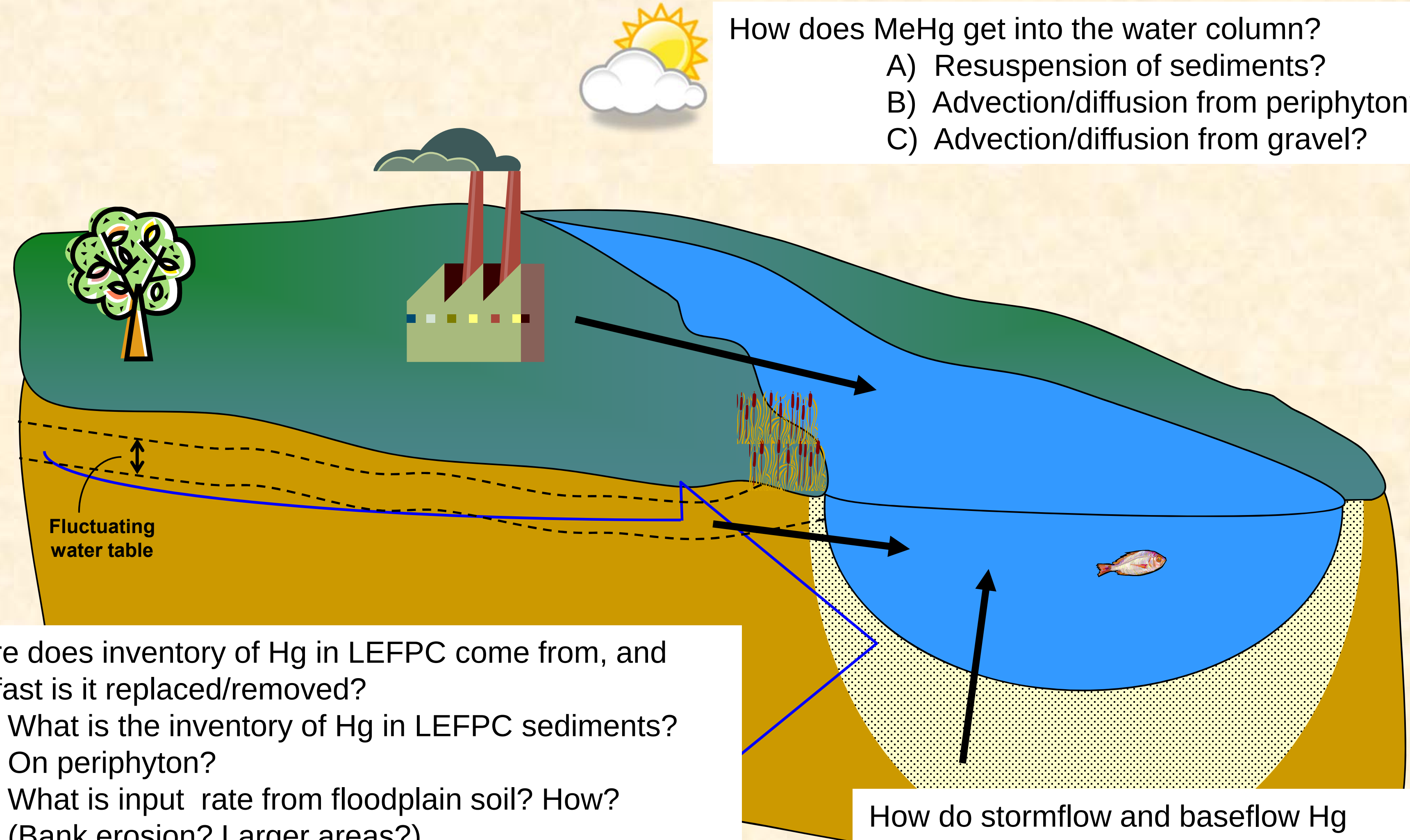
Questions: Release Mechanisms

How does MeHg get into the water column?

A) Resuspension of sediments?

B) Advection/diffusion from periphyton?

C) Advection/diffusion from gravel?



Where does inventory of Hg in LEFPC come from, and how fast is it replaced/removed?

A) What is the inventory of Hg in LEFPC sediments? On periphyton?

B) What is input rate from floodplain soil? How? (Bank erosion? Larger areas?)

C) What is annual flux of Hg from EFPC to Poplar Creek? From Y-12 to LEFPC?

D) Are there depositional hotspots where Hg(0) in streambed inputs?

How do stormflow and baseflow Hg transport interact?

A) delayed transit of particle - associated Hg through lowermost EFPC?

Questions: Mercury chemical/biological processes; Other factors

What mercury is being methylated?

- A) Dissolved mercury from the N/S Pipe input that never becomes particle- associated?
- B) Dissolved hg in equilibrium with particle-associated hg in water column.
- C) Dissolved mercury desorbed from particulates within the streambed.
- D) Direct methylation of mercury on particles
- E) Hg(0) produced by reduction of Hg(II) in water column or streambed
- F) Reactive mercury produced by oxidation of elemental mercury
- G) Other? (emphemeral Hg(I) species?)

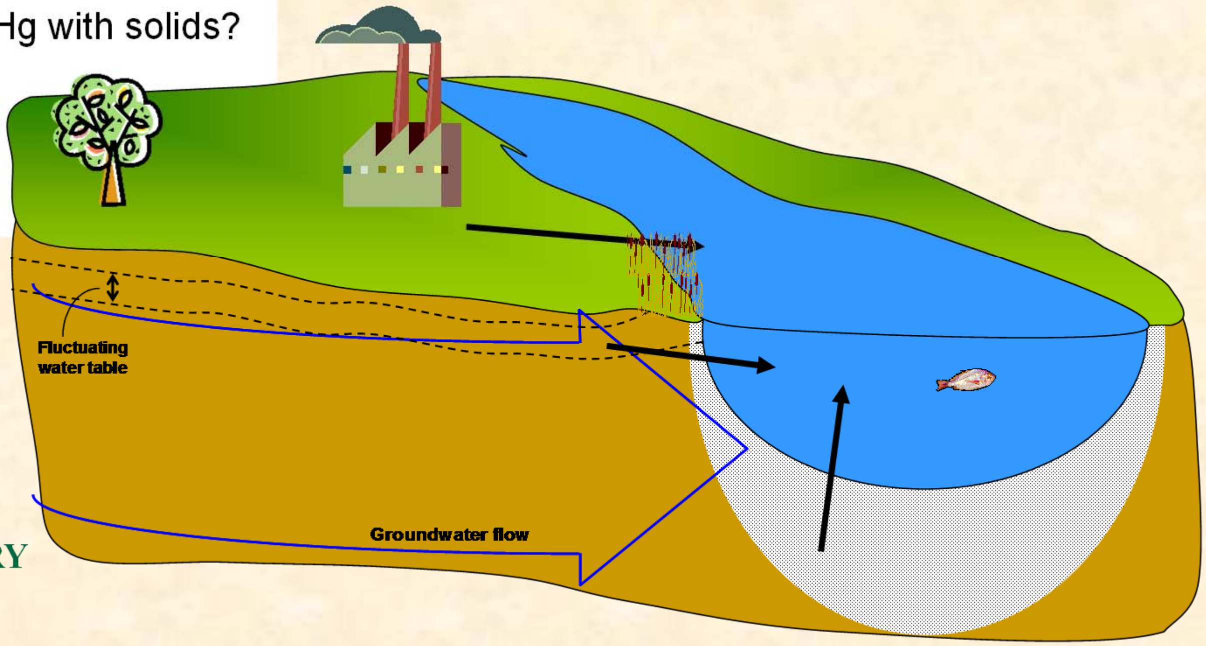
What is rate of MeHg production?

What determines/affects net MeHg production?

- A) Factors that affect methylation
- B) Factors that affect demethylation

What is the nature of the association of Hg with solids?

- Exchangeable (described by Kd)?
- Biologically incorporated?
- Precipitate (HgS)?
- Different in stream than soil?



Comparison of South R., Oak Ridge Similarities

- **Fish species**
- **Major ion water chemistry**
- **Watershed land use**
- **Degree of Hg-particle association, suspended sediments**
- **MeHg in fish**

Comparison of South R., Oak Ridge Differences

- **Source location - headwater point source EFPC**
  - non-point watershed source SR
- **Hg source chemistry - dissolved EFPC**
  terrestrial soils SR
- **Lability of Hg in floodplain soil – SR >> EFPC**
- **MeHg vs HgT - positive relationship, SR**
  - inverse relationship,EFPC
- **Concentration HgT - higher in EFPC**
- **Trace substances - Cd, Ni, Cu, Ag, U, PCBs, Zn, Mo**
  elevated in EFPC
- **Nutrients - NO_3, PO_4 high in EFPC**

Shutting off Flow Management temporarily produced a decrease in Hg flux, but an increase in Hg concentration

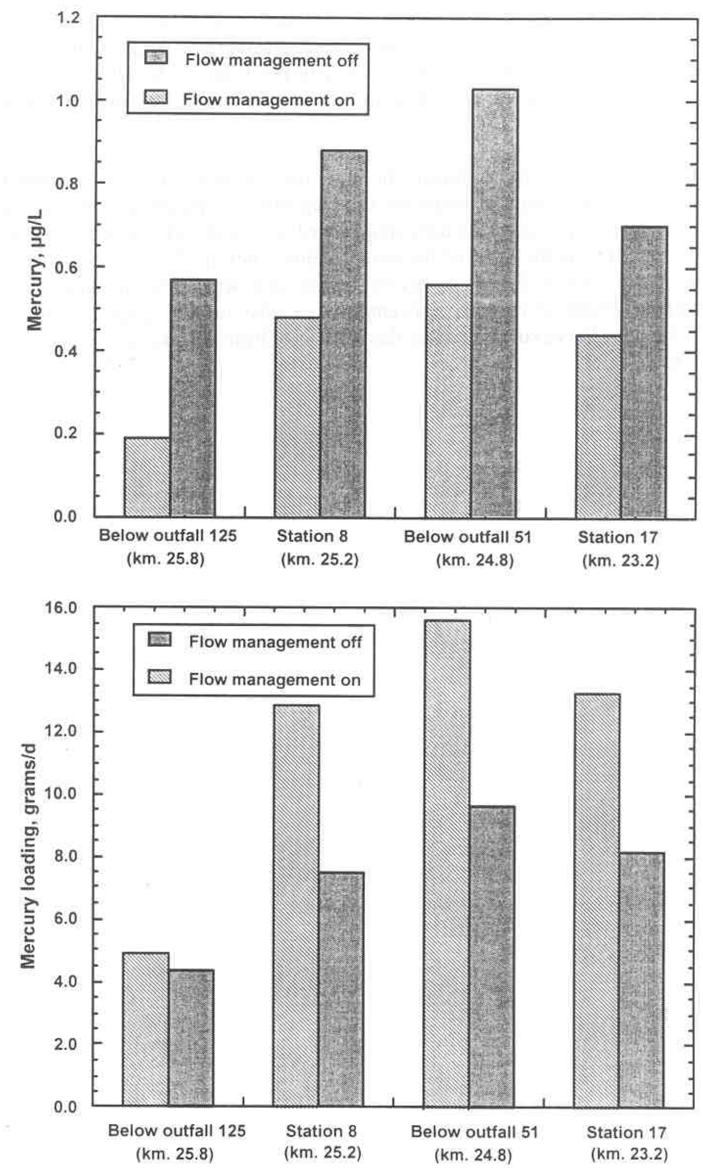


Fig. 3.17. Effects of raw water shutoff on total mercury concentrations and fluxes at sites in EFPC.

Mass flux of mercury and suspended solids at various sites in EFPC, Dec 19, 2008