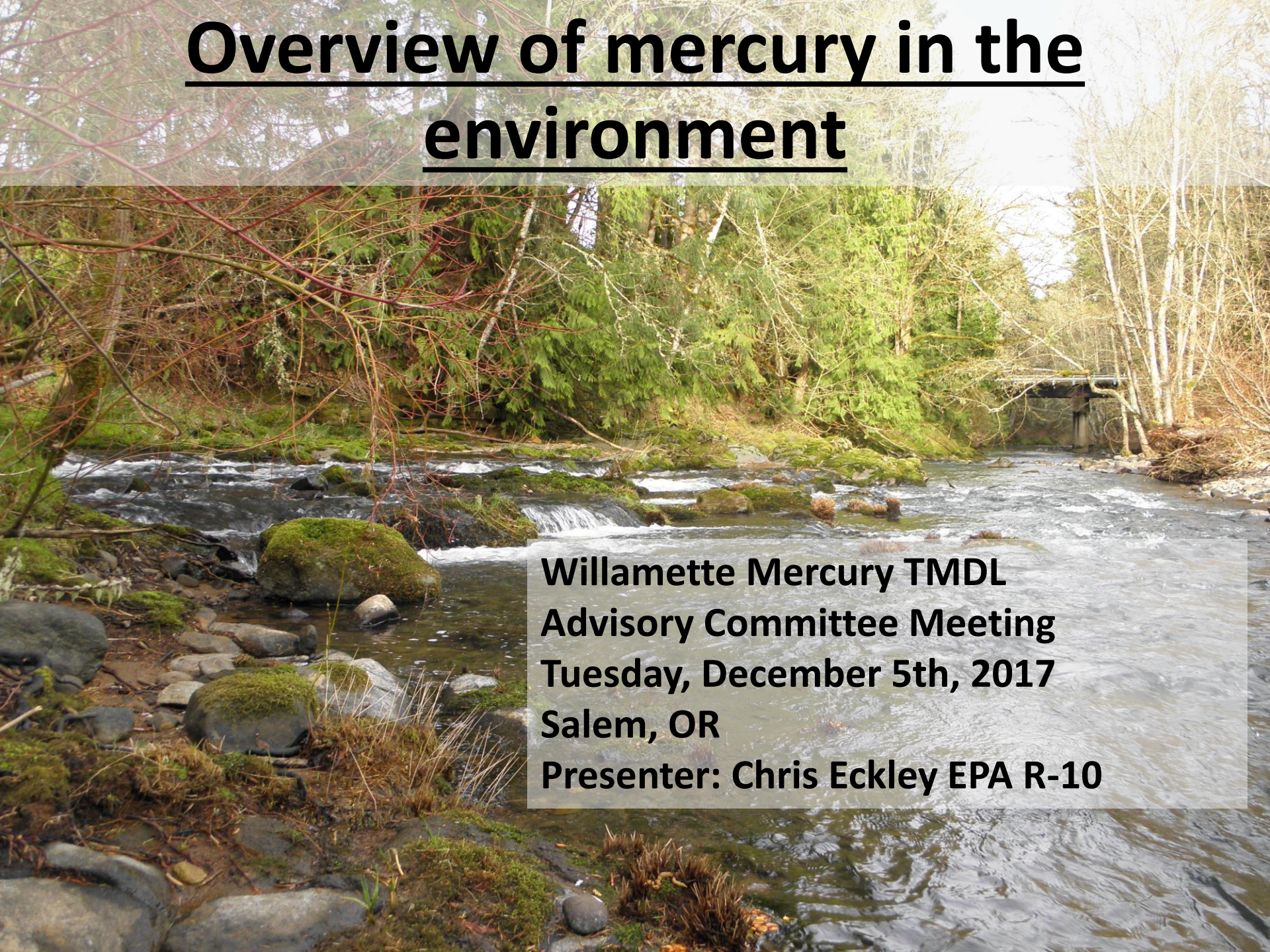
Overview of mercury in the environment



Willamette Mercury TMDL
Advisory Committee Meeting
Tuesday, December 5th, 2017
Salem, OR
Presenter: Chris Eckley EPA R-10

What is Mercury?

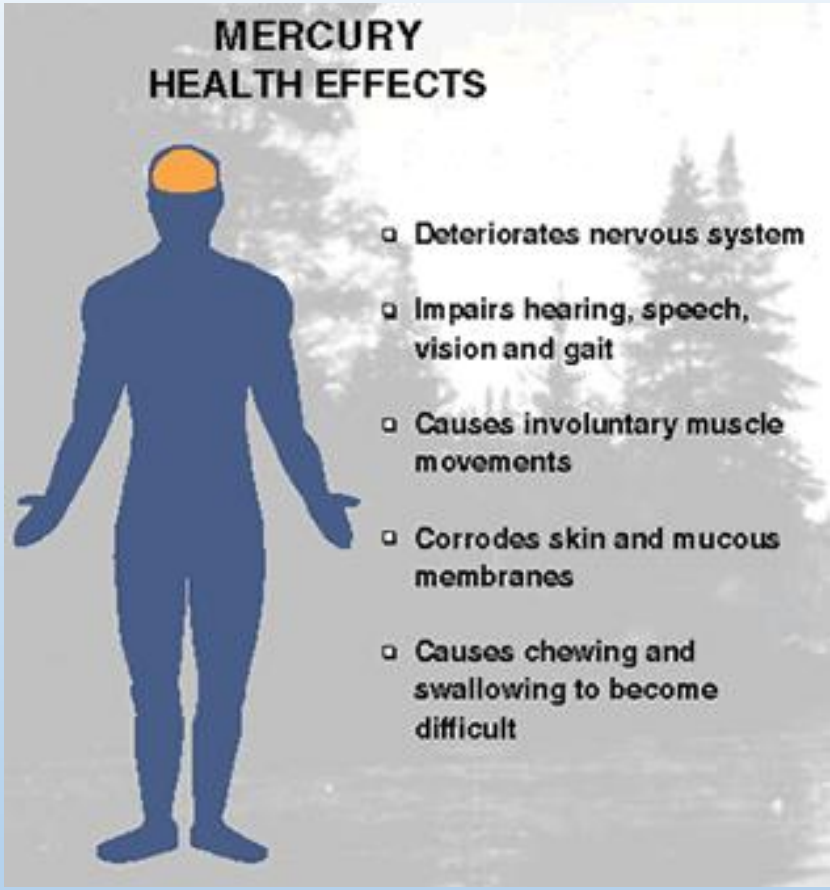
- Mercury (Hg) is a naturally-occurring element found in rock in the earth's crust, including coal deposits

- Unique among heavy metals:
  - liquid at room temperature
  - exists in pure gas phase (Hg^0)

- Historical & some ongoing uses of Hg:
  - Batteries
  - Fluorescent lights
  - Thermometers
  - Dental Fillings
  - Fungicide
  - Automotive switches

Mercury Health Effects

- Mercury is primarily a neurotoxin
- Effects related to form of Hg
- Organic Hg has higher toxicity than inorganic Hg
- Organic Hg-cysteine complex can cross blood-brain barrier and increases toxicological impact
- Developing brains of fetus/children are particularly sensitive to Hg exposure



Source: USGS Factsheet, 1995

Forms of Mercury

Hg exists in several forms:

- Inorganic Hg;
  - elemental Hg (Hg^0); oxidized Hg (Hg^{2+})
- Organic Hg;
  - methylmercury (MeHg)

Air: Mostly inorganic Hg; dominated by gas-phase Hg^0

- Smaller fractions of gaseous Hg^{2+} & particulate bound Hg

Water: Mostly inorganic Hg; dominated by oxidized forms often bound to particles or dissolve organic matter.

- Smaller fractions as MeHg

Fish: Mostly MeHg, but percentage affected by trophic position

Mercury Measurements

- Mercury is typically measured as Total-Hg (THg) and/or MeHg
- THg includes both inorganic and organic forms of Hg
- Water measurements can be whole water, dissolved, and/or particulate-bound.
- Whole water measurements include both dissolved and particulate phases.

<u>Examples of typical water measurements</u>:

Whole water THg; Dissolved water THg
Whole water MeHg; Dissolved water MeHg

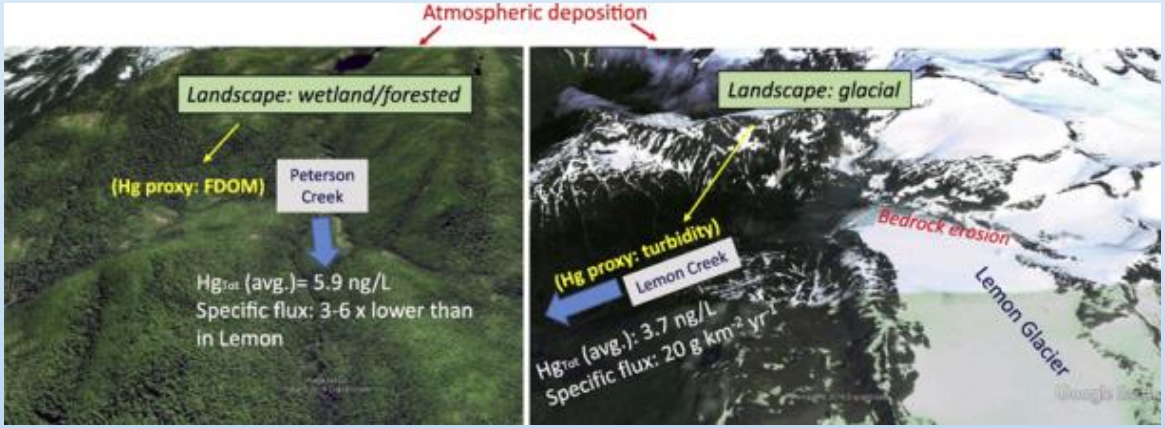
<u>Examples of typical fish measurements</u>:

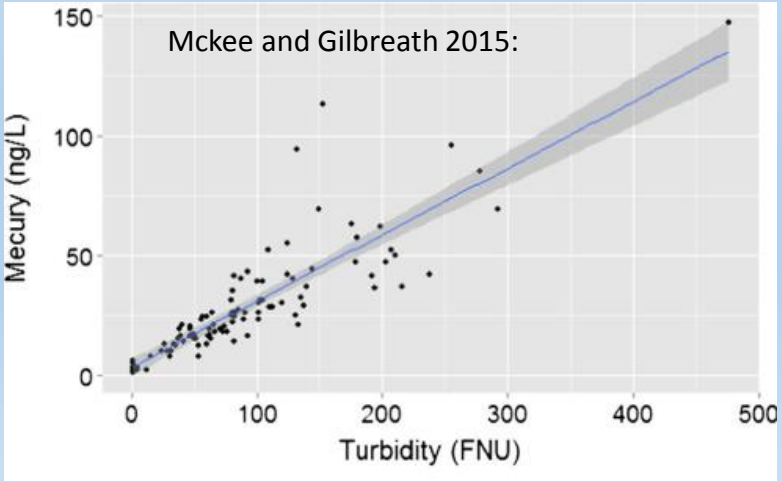
Fish (fillet) THg and/or MeHg
Fish (whole body) THg and/or MeHg

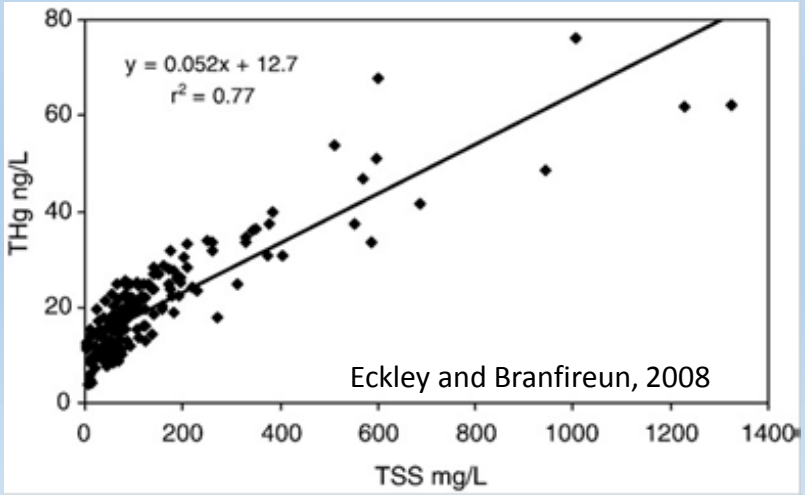
Potential Surrogate Measures of Hg

- TSS, Turbidity & FDOM: can be correlated with Hg concentrations in some streams/rivers
- Correlation strength depends on the watershed characteristics

Vermilyea et al, 2017





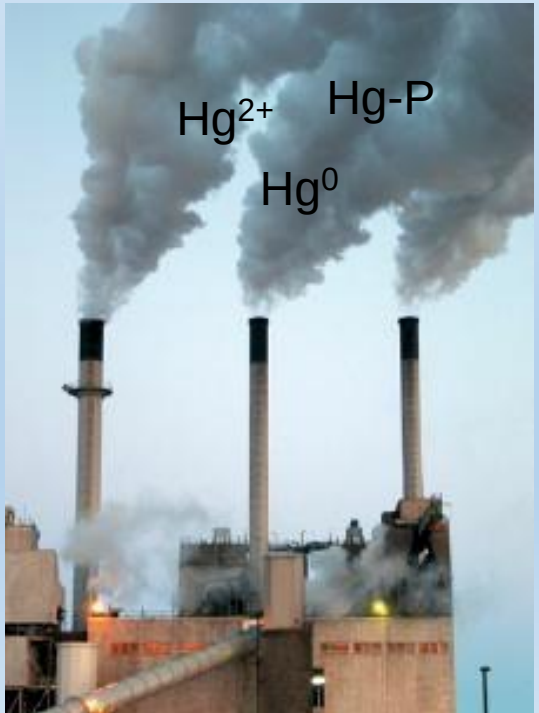


The Mercury Cycle

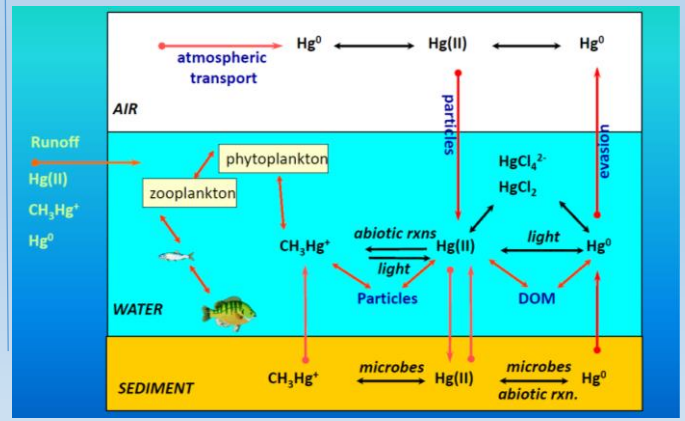
Mercury Releases

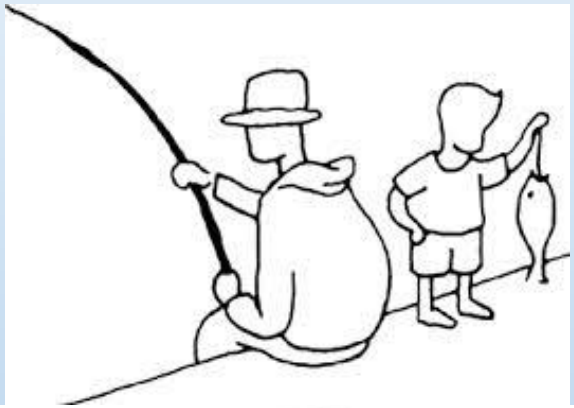
Mercury in the Environment

Mercury Exposure



Transport, Transformation, Bioaccumulation

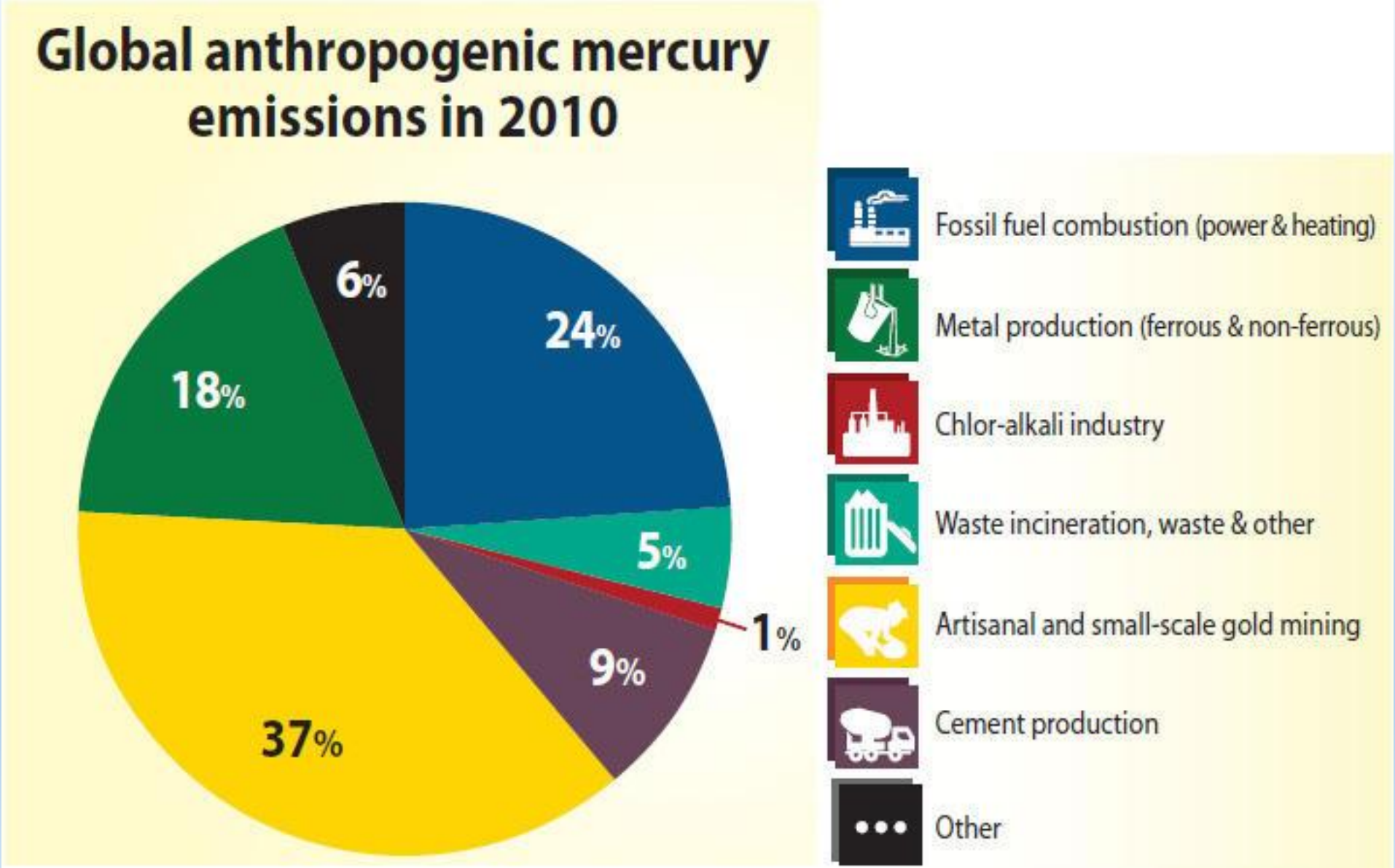




Atmospheric Hg

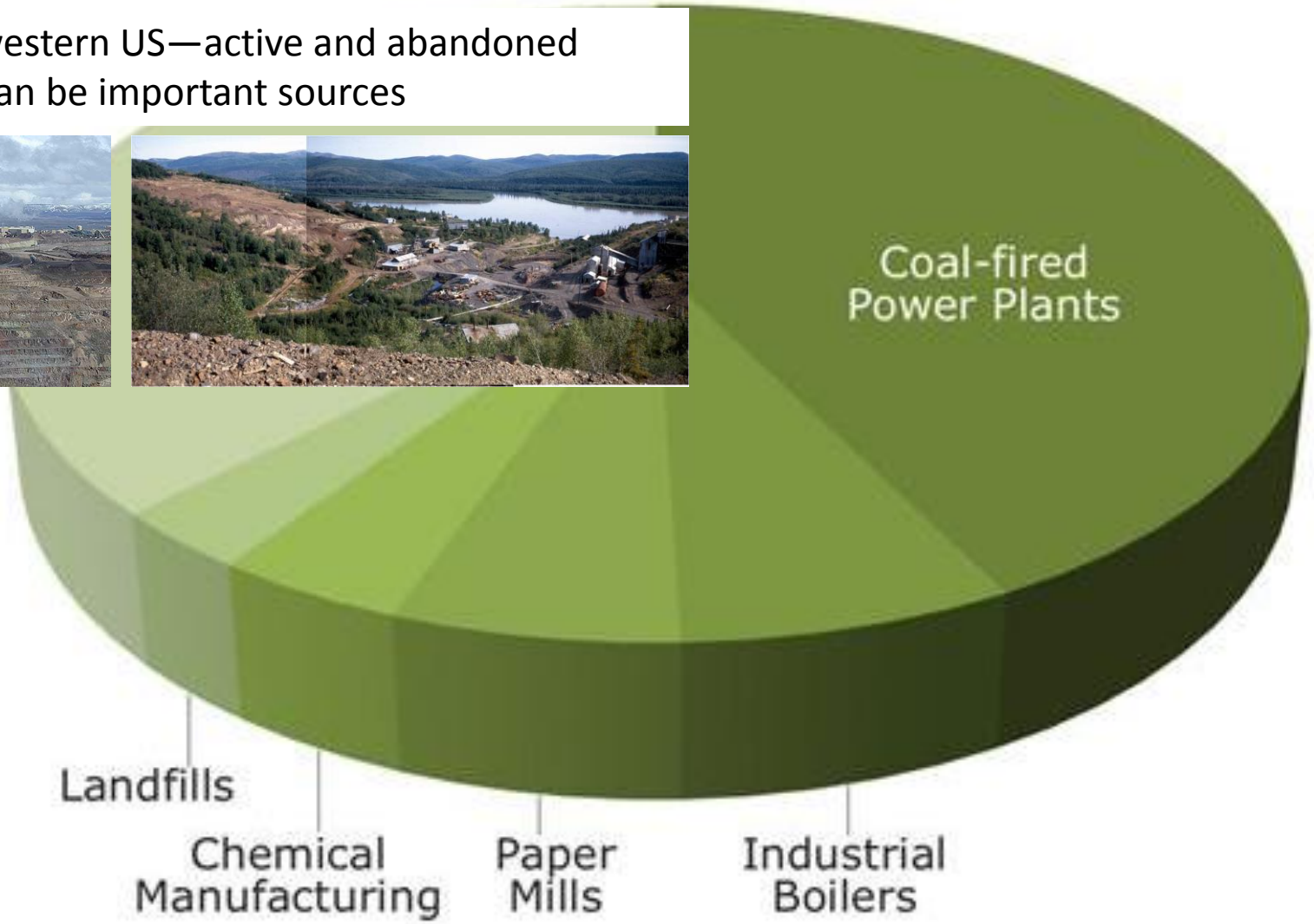
- Mercury (as Hg^0) can have a long atmospheric lifetimes (0.5-2 years) resulting in widespread global dispersion before deposition
  (summarized in Schroeder, W.H., Munthe, J., 1998)
- However, there are regional variations in atmospheric Hg sources
  (Tate et al, 2017, ICMGP, Providence, RI)

Global Hg Emissions



USA Hg Emissions

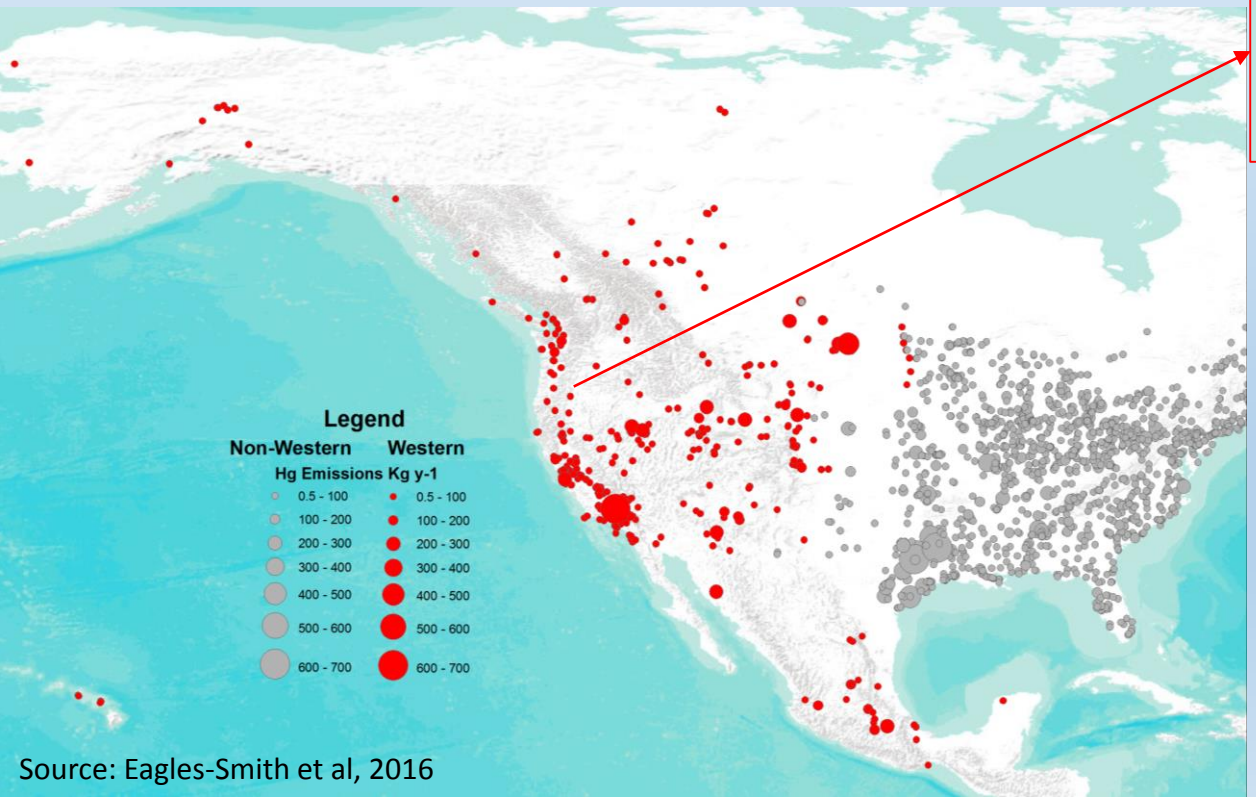
In the western US—active and abandoned mines can be important sources

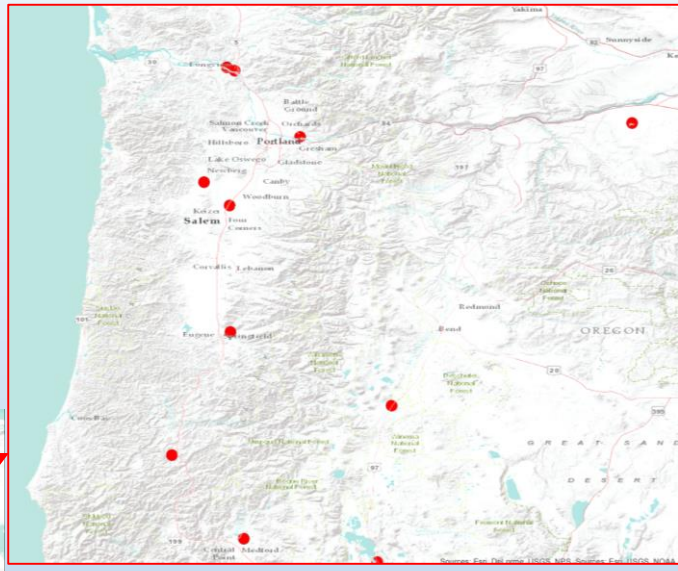


Source: U.S. EPA, National Emissions Inventory, 2007[2]

Western US Hg Emissions

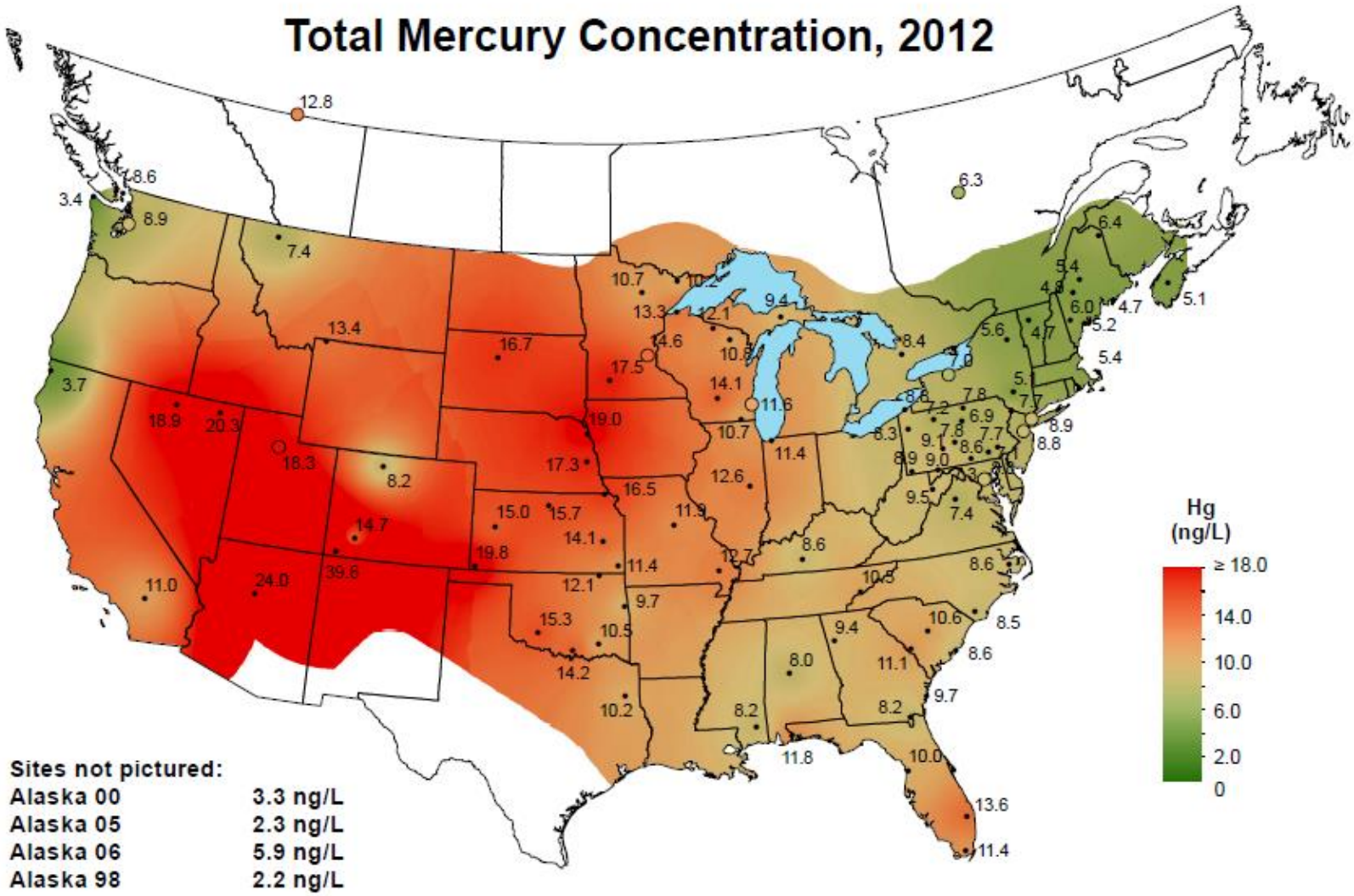
In general, fewer Hg emission sources in the Western US than the Eastern US.





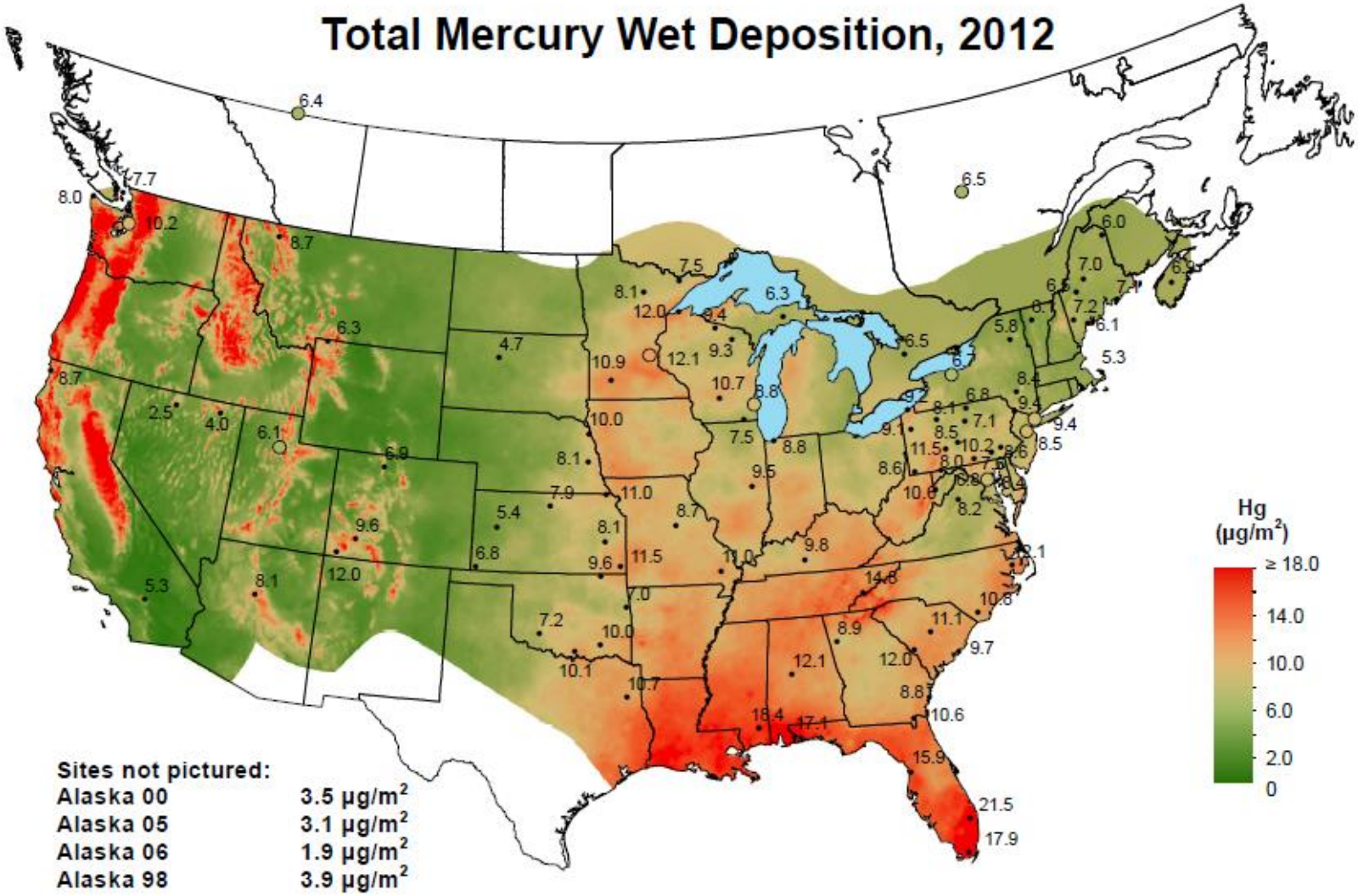
Source: Eagles-Smith et al, 2016

Mercury Deposition



National Atmospheric Deposition Program/Mercury Deposition Network
http://nadp.isws.illinois.edu

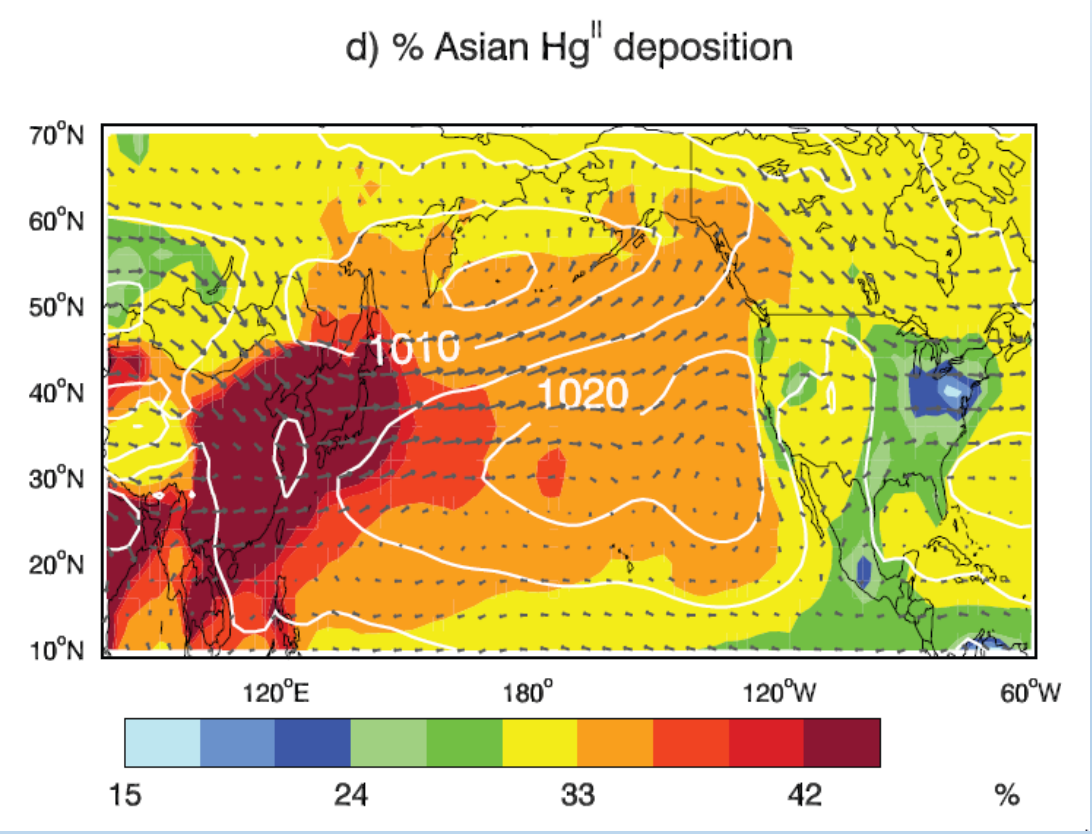
Mercury Deposition



National Atmospheric Deposition Program/Mercury Deposition Network
http://nadp.isws.illinois.edu

Trans-boundary transport

- Hg deposition can originate from both local & global sources

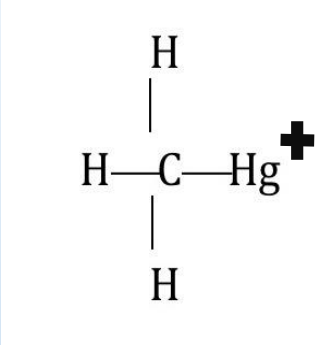


Source: Strode et al. 2008 JGR-Atmospheres

Methylmercury—Introduction

- **What is MeHg?**

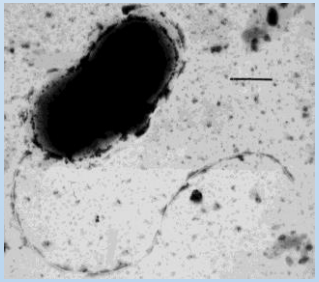
$HgCH_3^+$



(AKA: organic Hg; mono-methylmercury)

- **Where does it come from?**

Anaerobic bacteria



- **Why is it a concern?**

1) **Bioaccumulates**
2) **Increased toxicity**

Sources of Methylmercury

Methylation mostly occurs under anoxic conditions

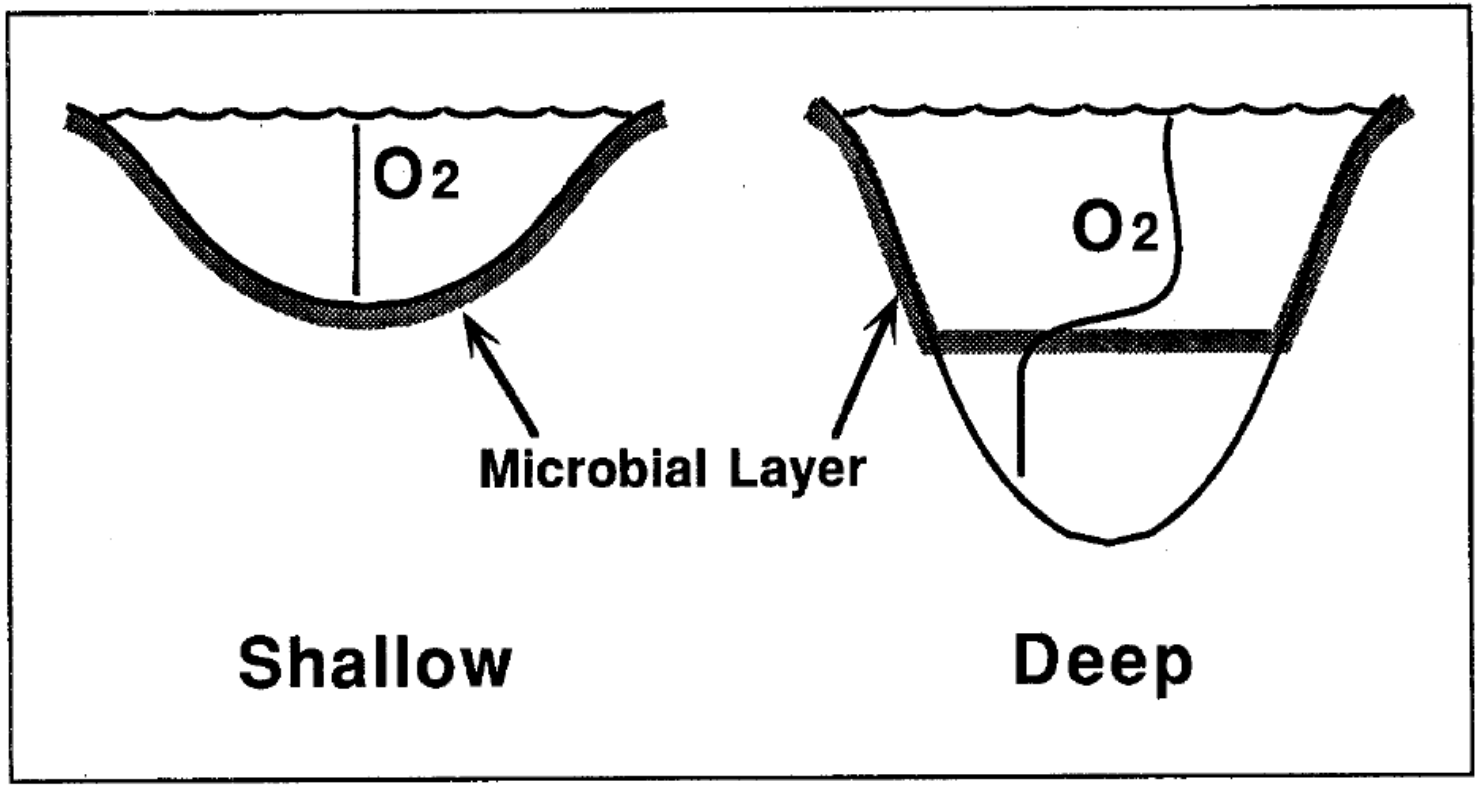
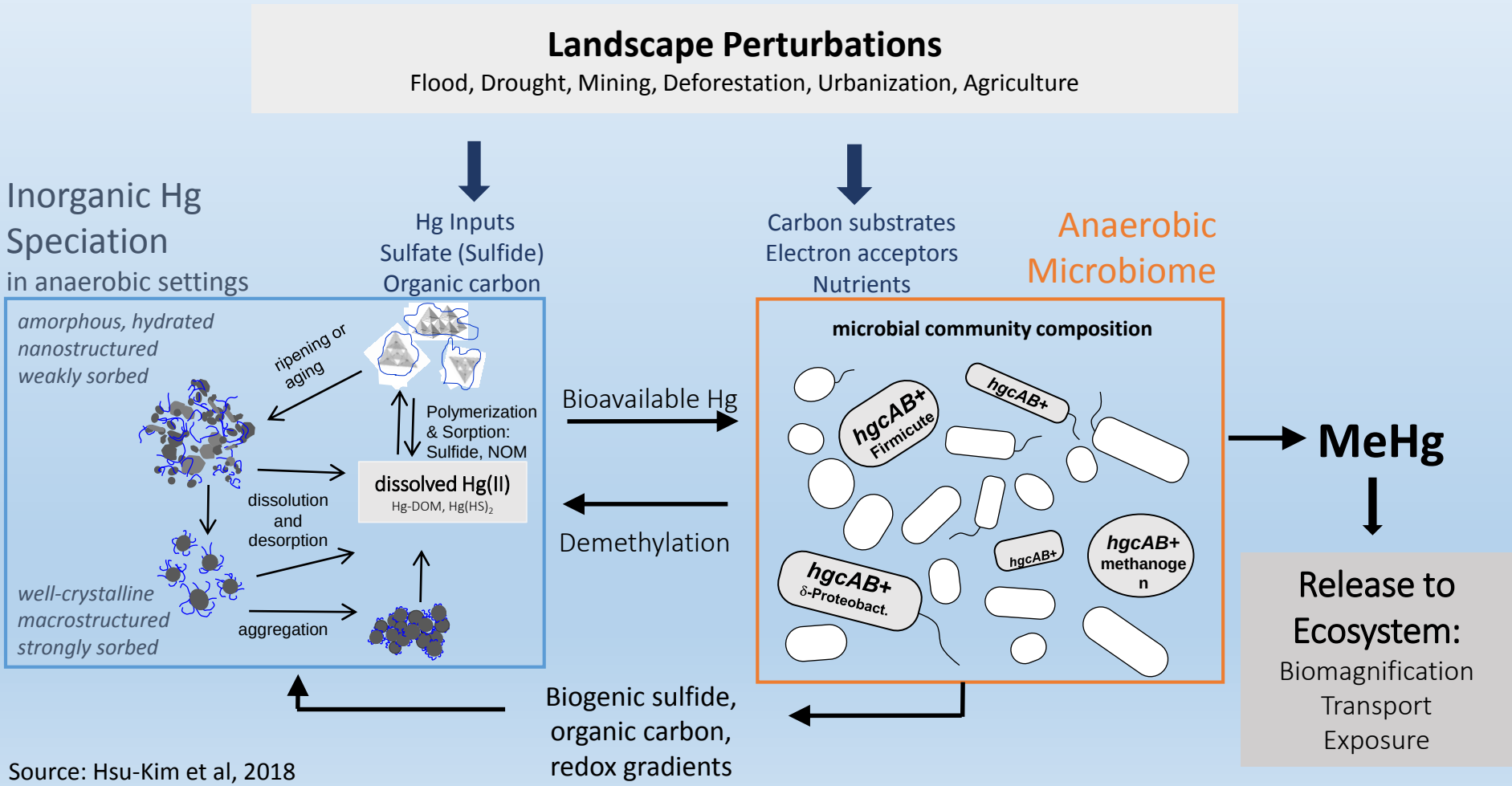


Fig. 4. Location of biogeochemically active microbial layer in shallow, well-mixed and deep, stratified lakes.

Source: Watras et al, 1995

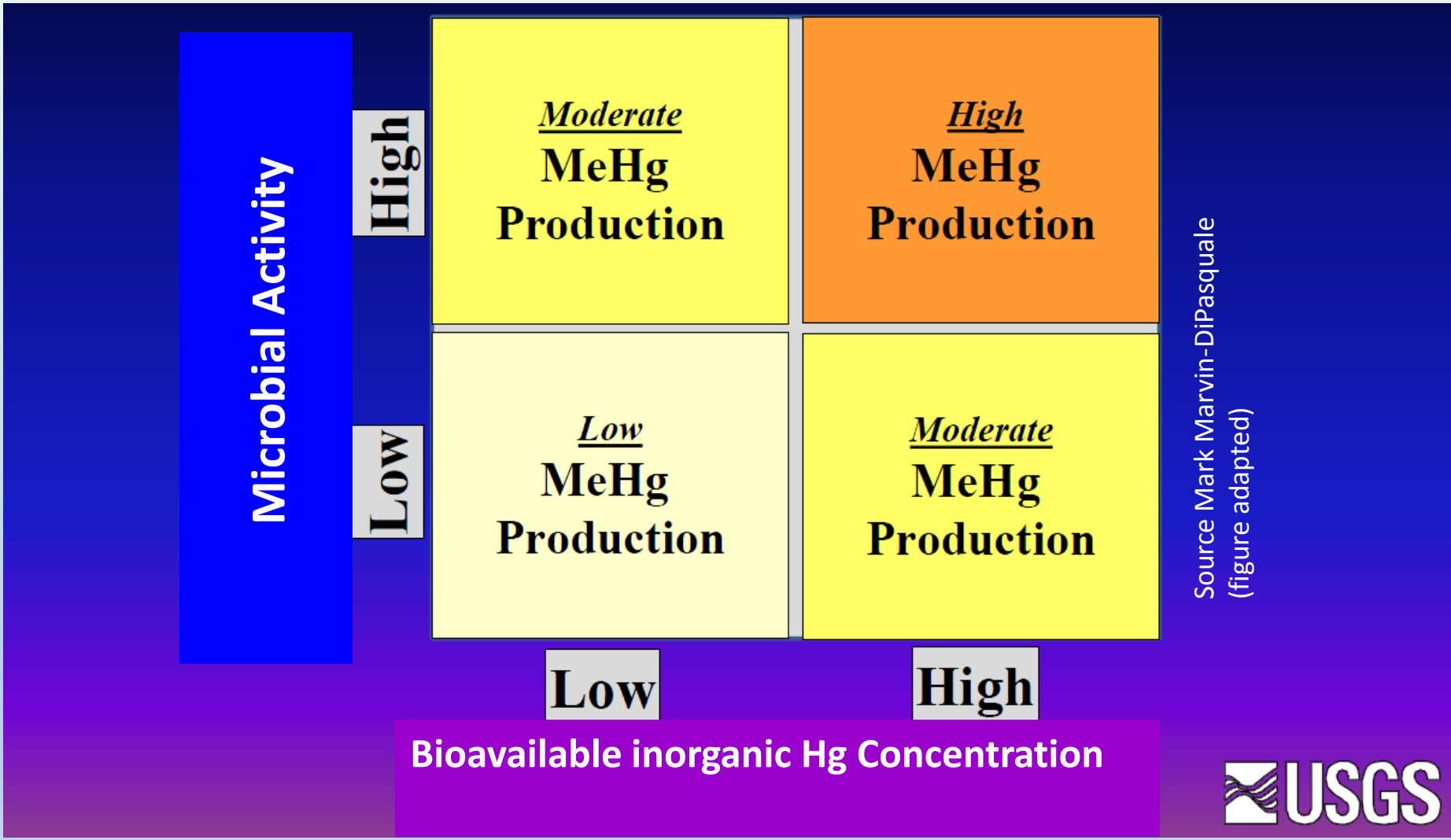
Hg Methylation: Influential Variables

- MeHg is created from inorganic Hg
- How much inorganic Hg is converted to MeHg depends on multiple factors



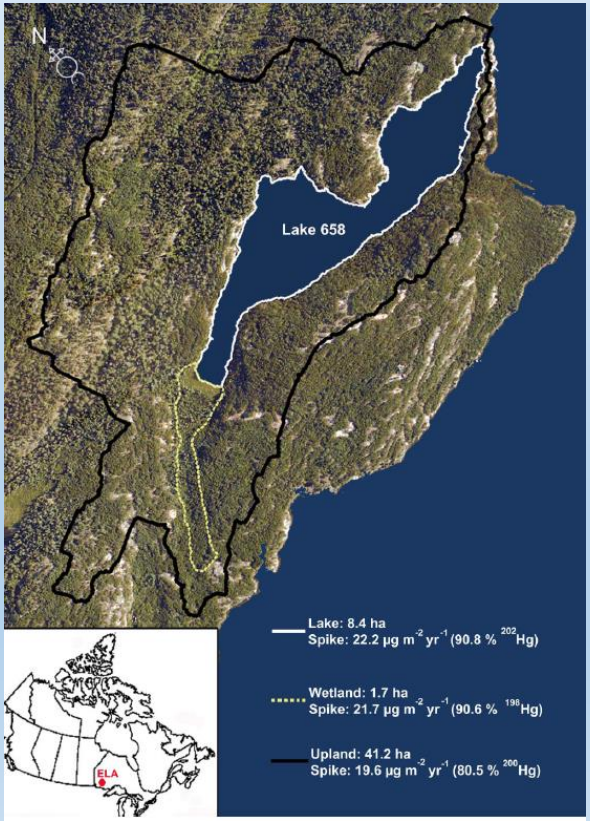
Source: Hsu-Kim et al, 2018

Methylmercury: Influential Variables



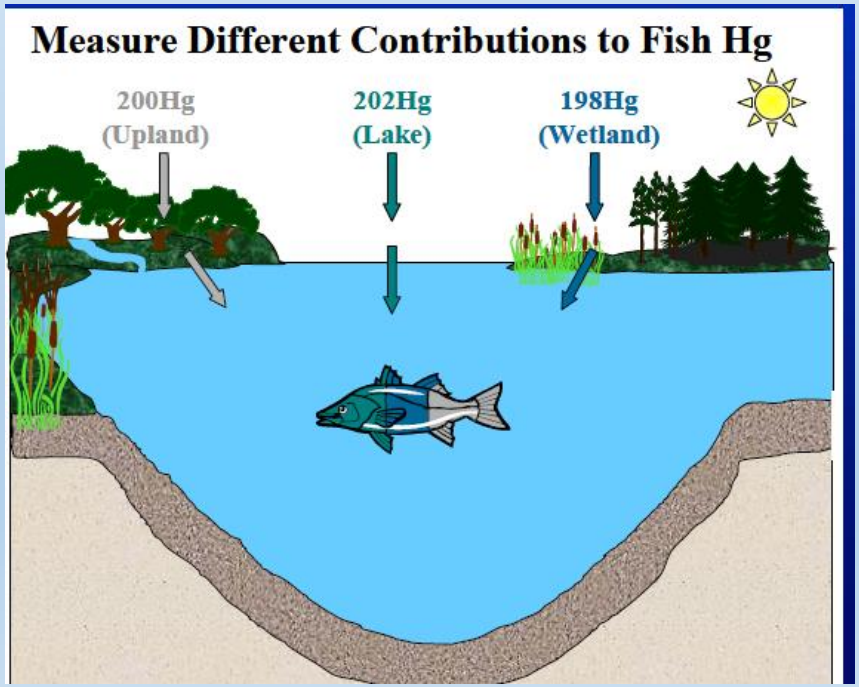
Methylmercury: Watershed Variables

- Experiment where Hg isotopes added to a lake & its watershed



METAALICUS

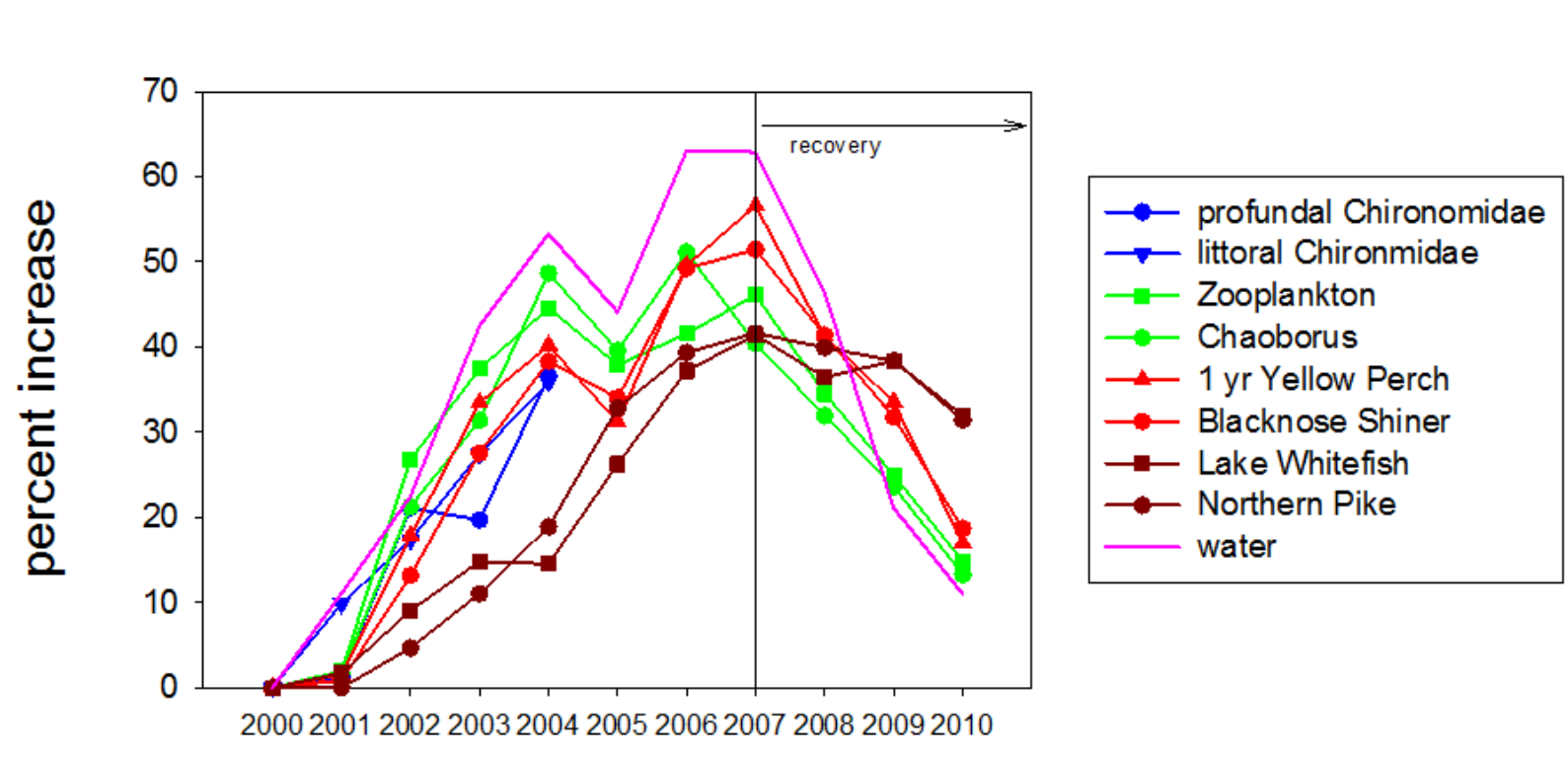
Mercury Experiment to Assess Atmospheric Loadings In Canada and the United States



Source: Harris et al, 2007

Methylmercury: Influential Variables

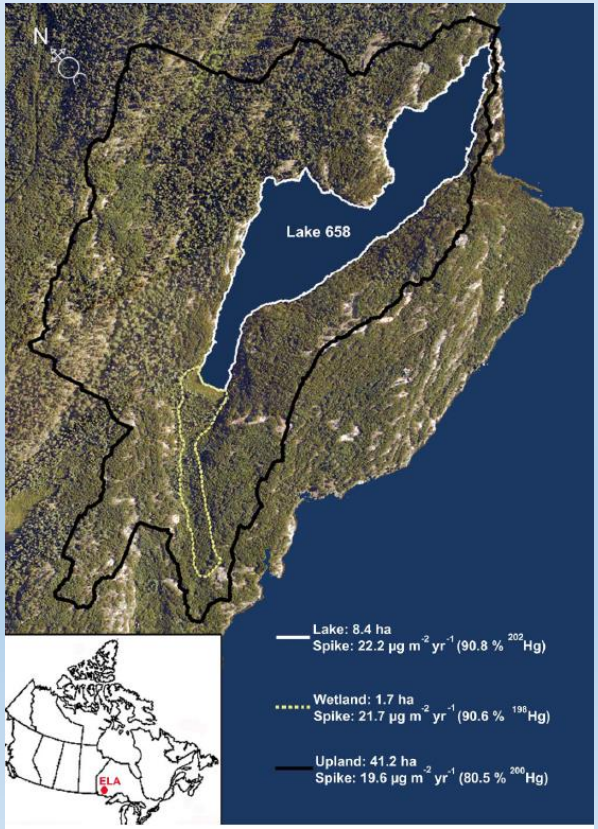
- Results showed a rapid biotic response to changes in Hg deposition to the water surface

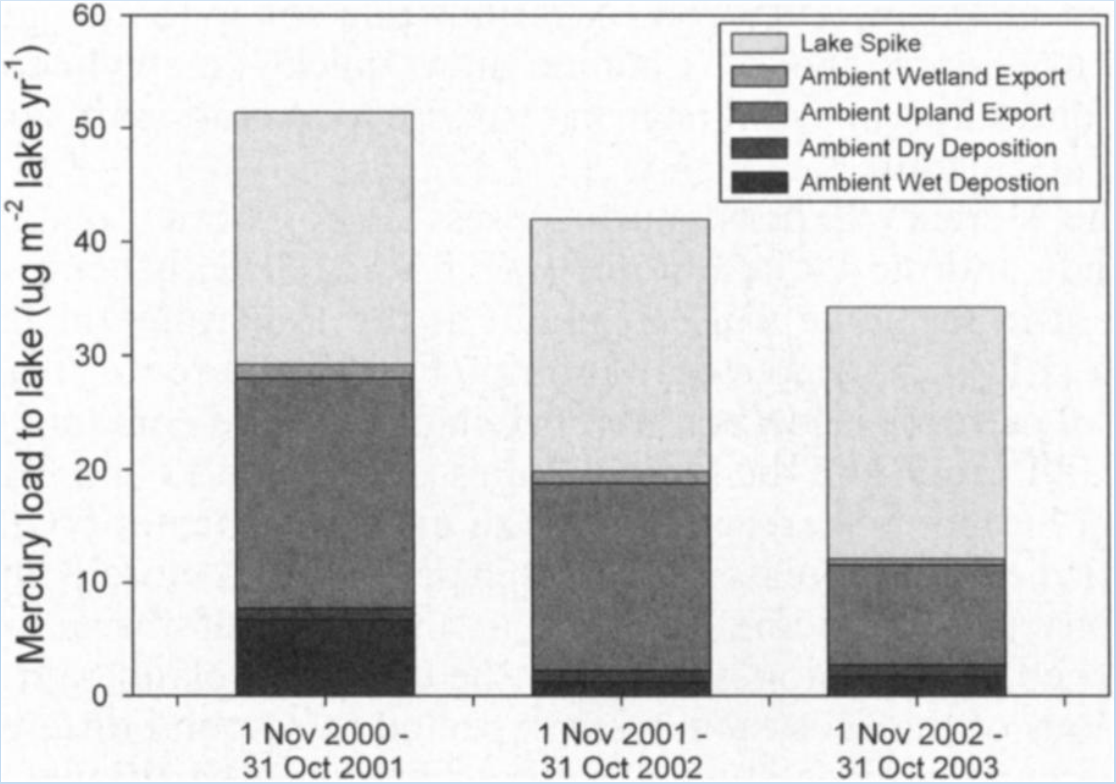


Data: Paul Blanchfield, Michael Paterson, Fisheries and Oceans Canada

Methylmercury: Influential Variables

- Results showed that the watershed was an important source of Hg to the lake
- However, there was lag period before newly deposited Hg to the watershed was mobilized from the catchment

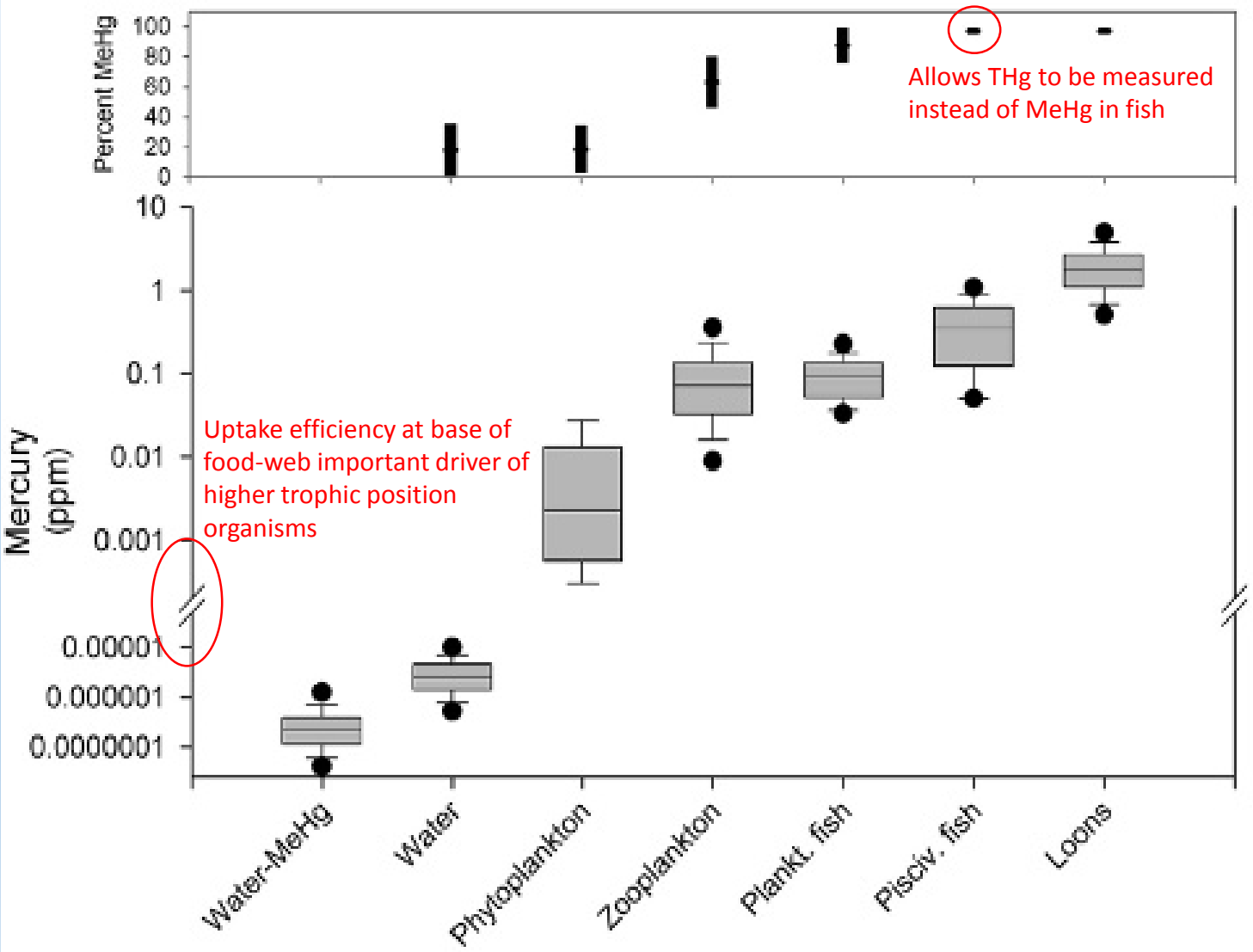




Source: Harris et al, 2007

Mercury Bioaccumulation in Fish

Methylmercury bioaccumulates/biomagnifies in biota

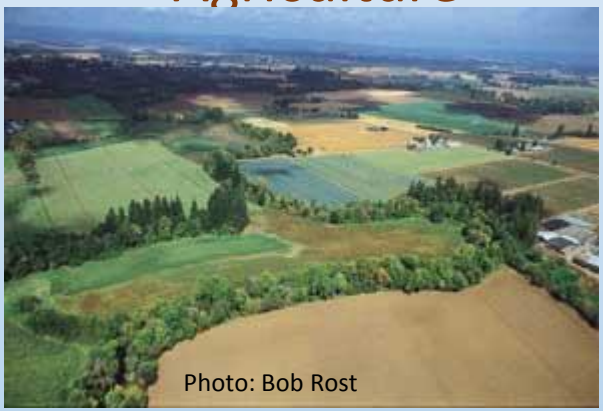


Source—Driscoll et al, 2007 Box and whisker plots of mercury (Hg) concentrations in water and aquatic biota in eastern North America. Also shown are the ranges for the percentage of total Hg occurring as methylmercury (MeHg). All values were obtained from NERC (Northeastern Ecosystem Research Cooperative) data and represent wet weight, except those for phytoplankton, which were obtained from Watras and colleagues .

Landscape Alterations: impacts of Hg cycling

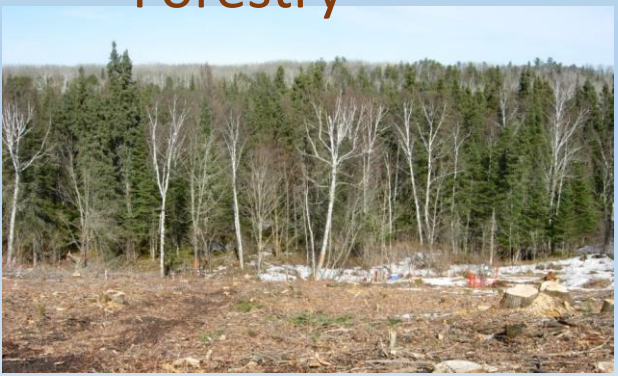
- Deposited Hg can bind to geologic material & organic matter resulting in strong retention in soil. (Grigal, 2002)
- Disruption of the soil profile via land use change can influence Hg mobility (Balogh et al., 1998; Mason and Sullivan, 1998)

Agriculture



Reservoirs

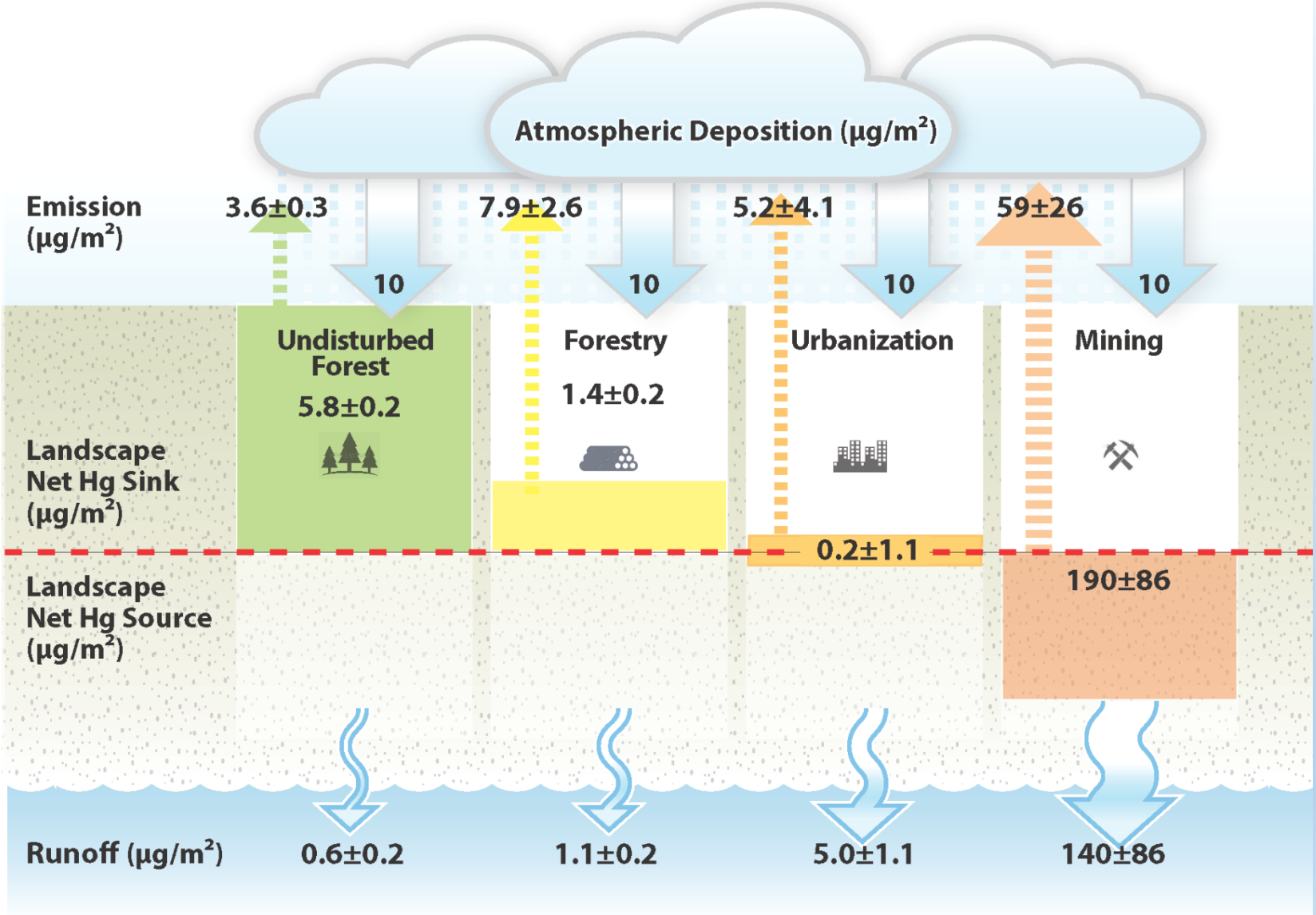
Forestry



Urbanization

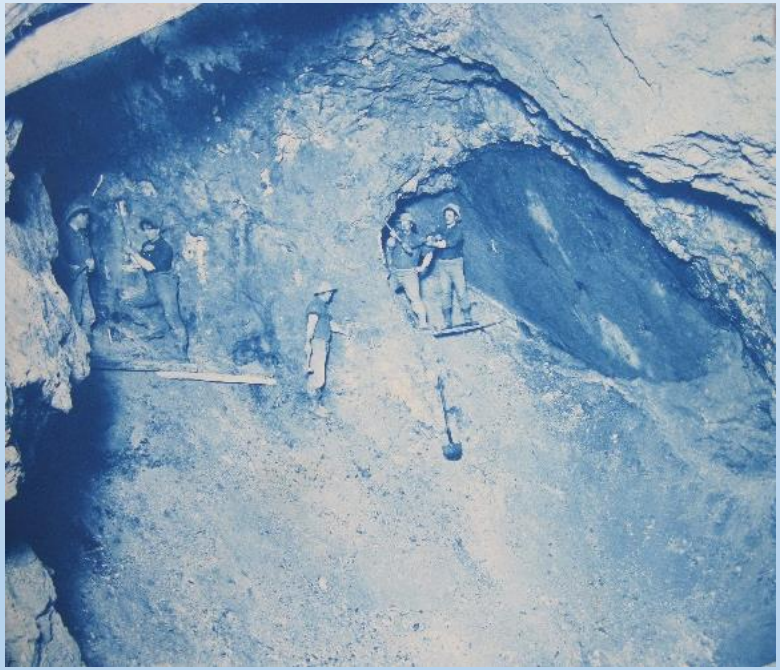
Mines

Landscape Alterations: impacts of Hg cycling



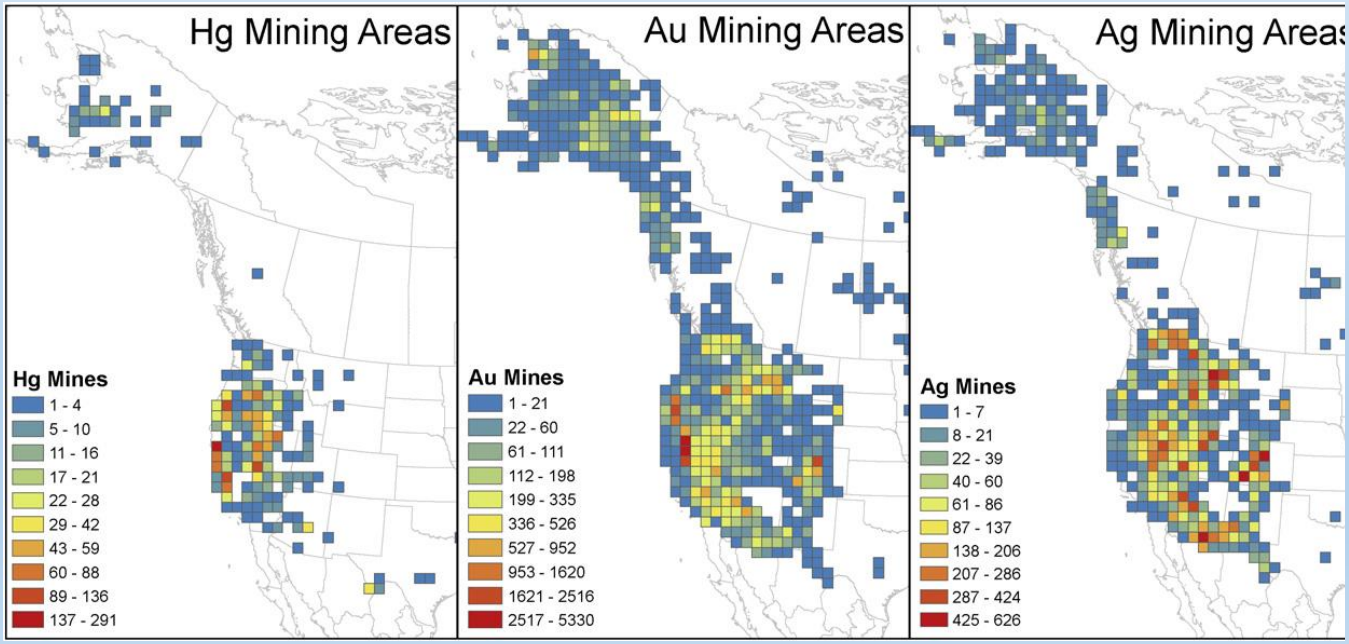
Source: Hsu-Kim et al, 2018

Landscape Alterations: Mining



Landscape Alterations: Mining

- Areas of geologic enrichment of Hg often occur as Hg-sulfide (Cinnabar)
- The western US contains thousands of abandoned mines

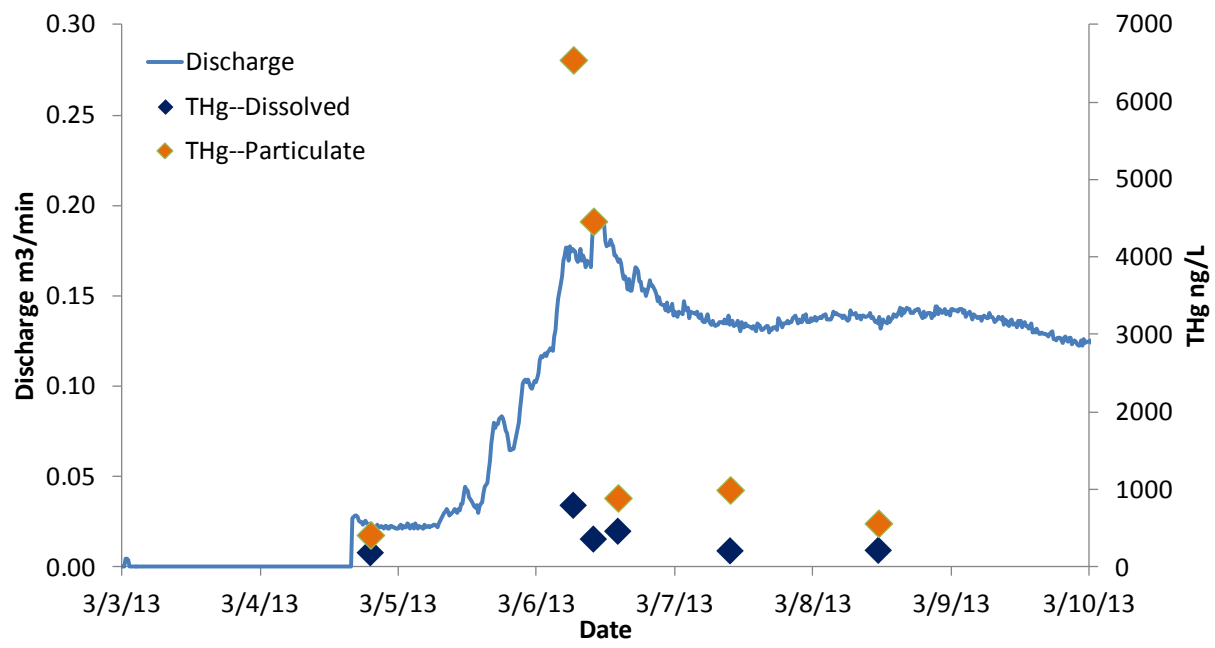


Source: Eagles-Smith et al, 2016

Landscape Alterations: Mining

- Abandoned Hg mines can be a significant source of Hg to streams —especially during periods of storm flow

- Source of Hg to streams is from erosion of high Hg content tailings



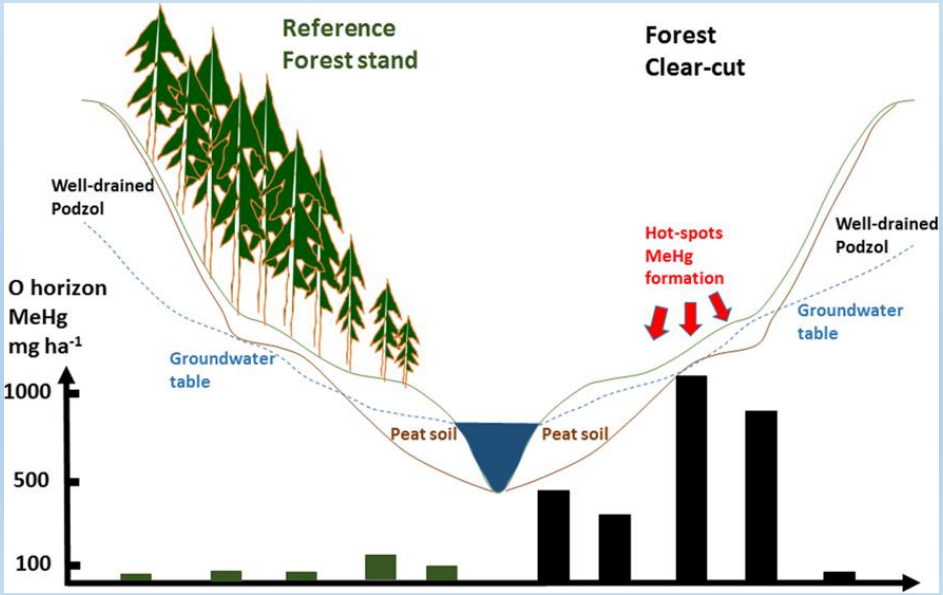
Landscape Alterations: Forestry

Photo Credit: Kelly James

Landscape Alterations: Forestry

Impacts of Forestry on Hg cycling:

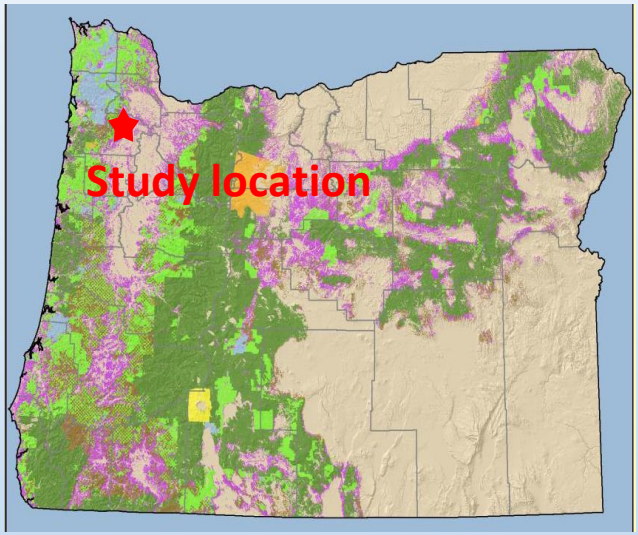
- Increased Hg mobility (& carbon, nutrients) (deWit et al (2014); Porvari et al, 2003)
- Increased runoff/Hg loads
- Increased MeHg production
- Increased surface emissions
  (Mazur et al. 2015)

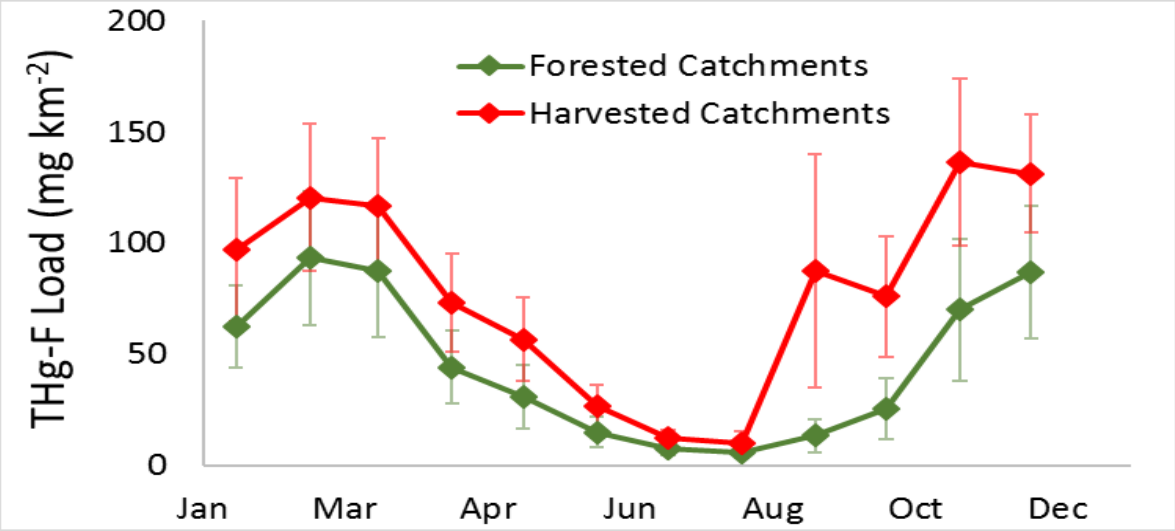


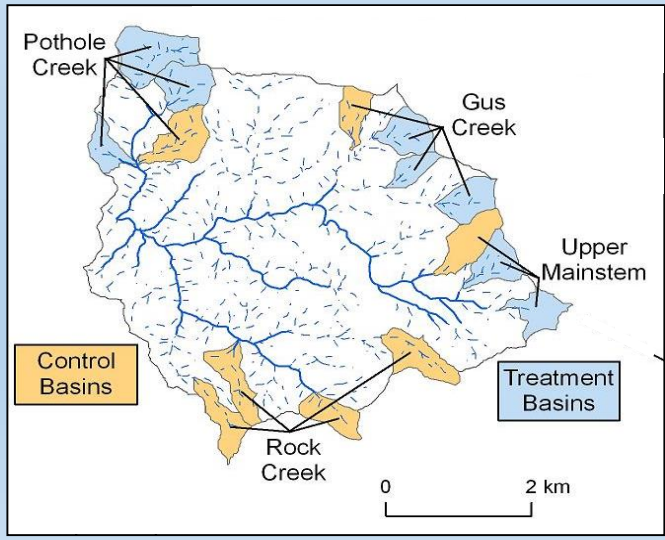
Kronberg et al (2016)

Landscape Alterations: Forestry

- Recent study conducted in the Trask Watershed, OR
- Study Results: annual dissolved THg loads were 74% higher in the harvested catchments compared to the forested catchments





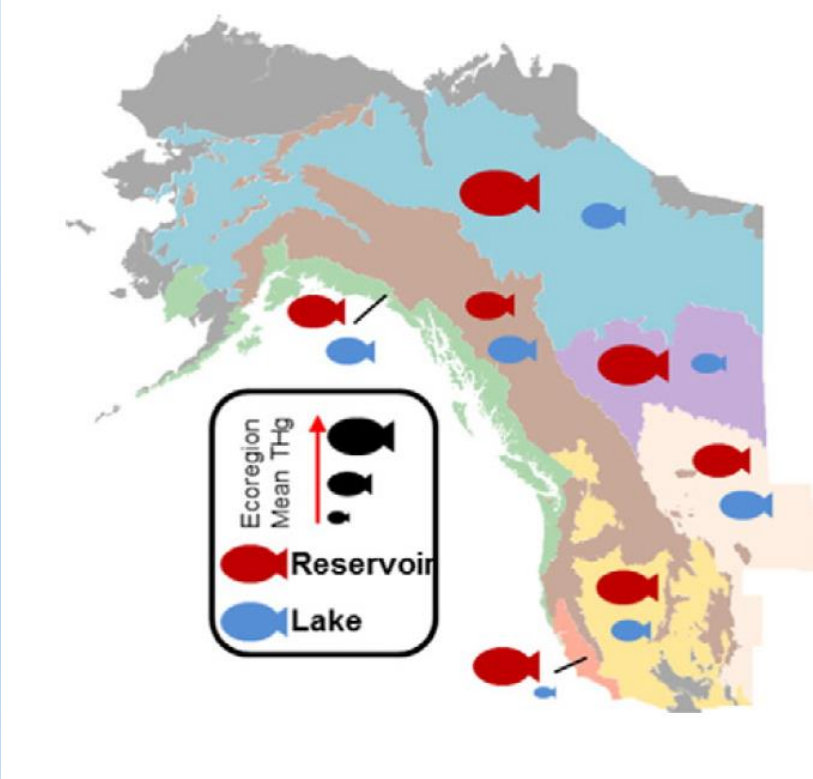


Eckley et al, 2018

Landscape Alterations: Reservoirs

Landscape Alterations: Reservoirs

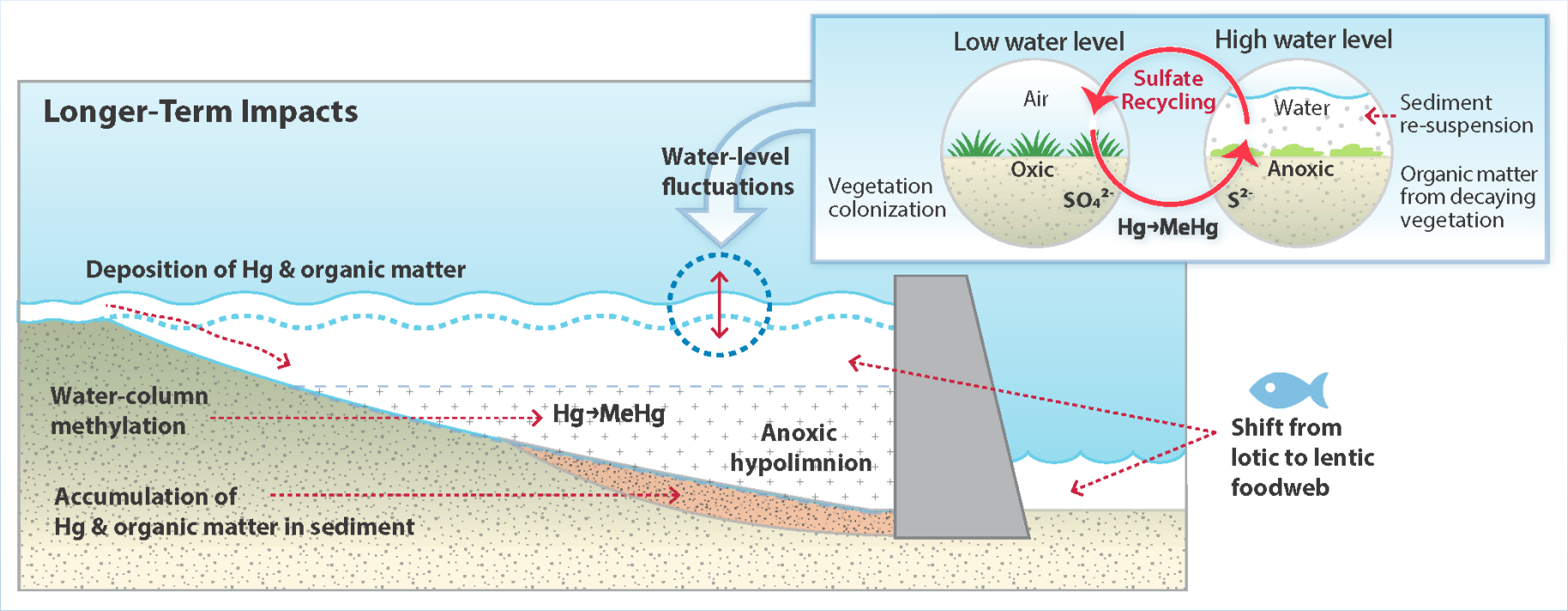
- Reservoirs have been shown to have elevated MeHg concentrations in water and fish compared to natural lakes (Brigham et al., 2002; Kamman et al., 2005; Larson et al., 2014; Montgomery et al.,2000; Selch et al., 2007; Sorensen et al., 2005; Willacker et al, 2016)



Willacker et al, 2016

Landscape Alterations: Reservoirs

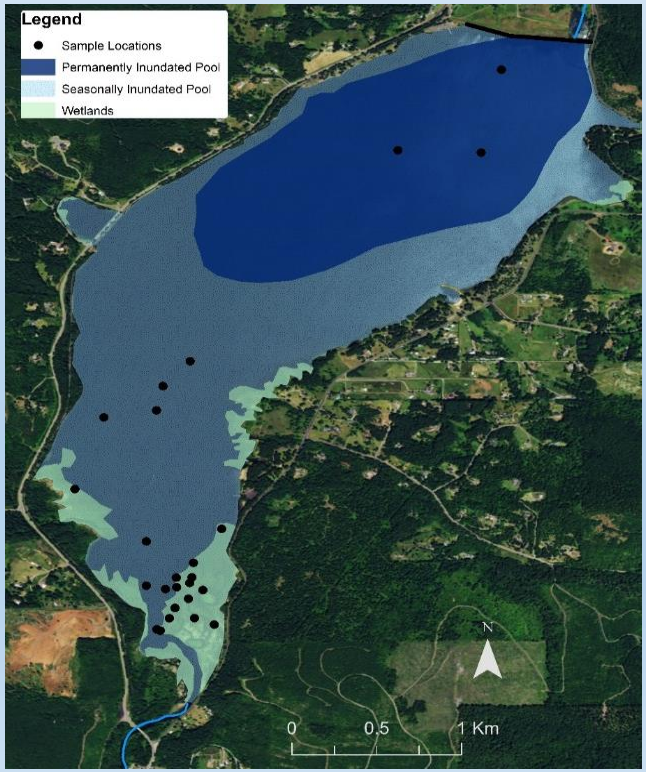
Impacts of reservoir management on Hg cylcing

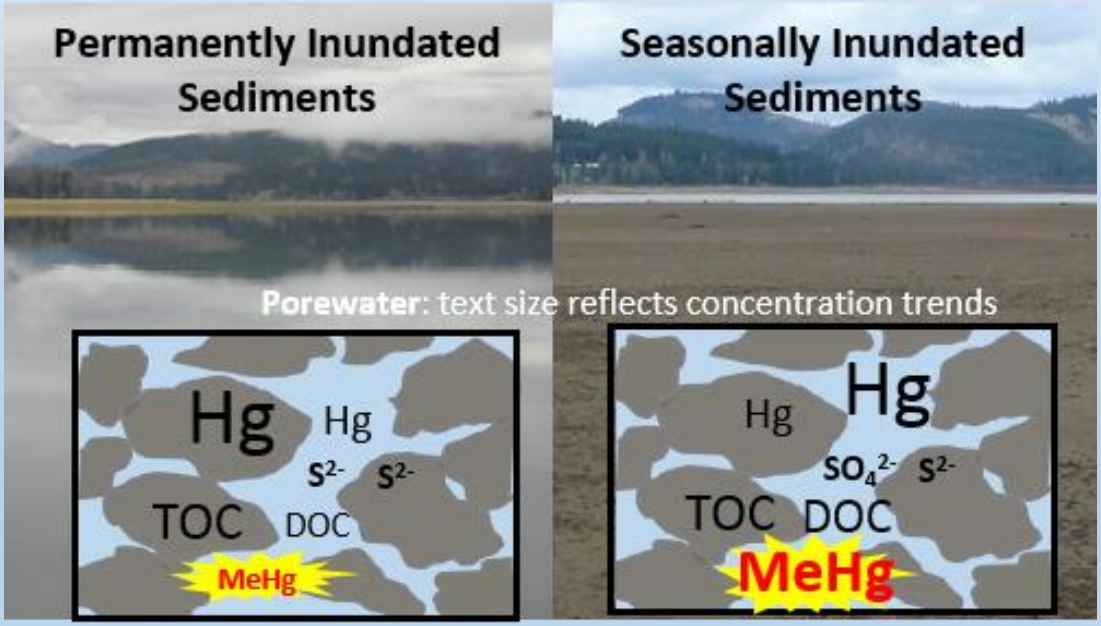


- Lotic to lentic foodweb
- Anoxic hypolimnion: water column methylation
- Accumulation of Hg and organic matter
- Water level fluctuations: fresh organic matter; sulfate recycling

Landscape Alterations: Reservoirs

- Recent Study: Cottage Grove Reservoir on the Coast Fork Willamette River
- Results showed that water-level fluctuations increase MeHg production in sediments





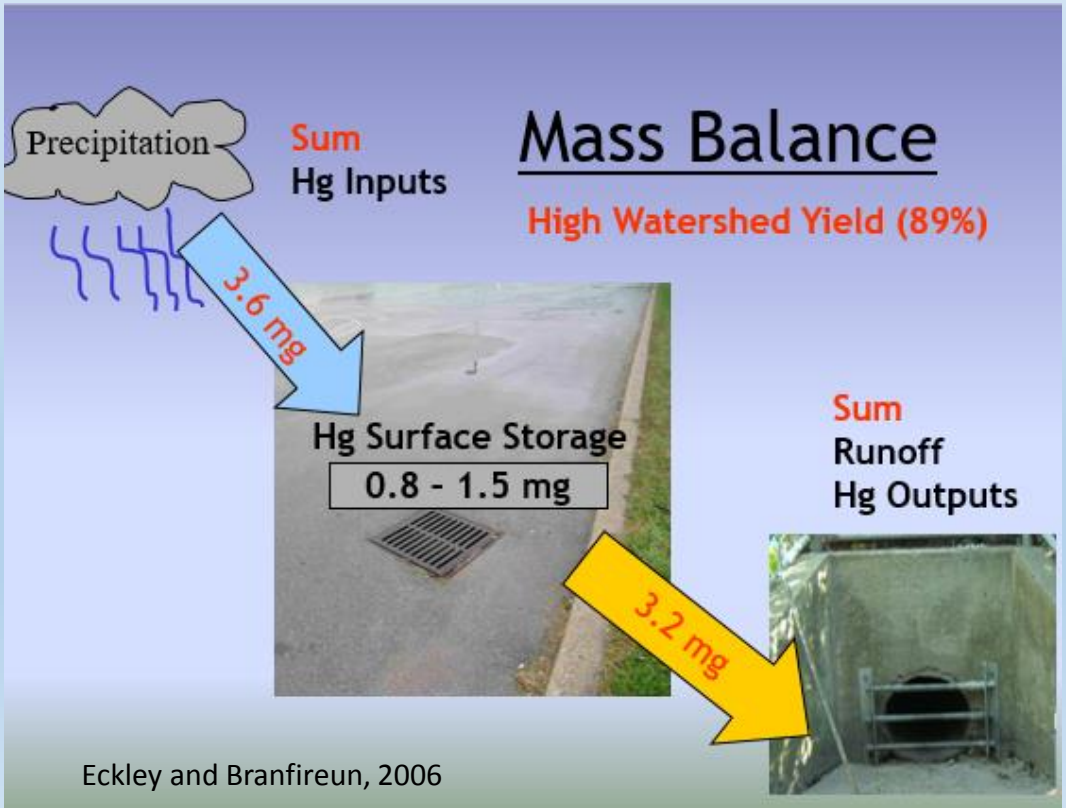
Eckley et al, 2017

Landscape Alterations: Urbanization

Landscape Alterations: Urbanization

Urbanization:

- Decreases catchment Hg retention & increases export yields
- Elevated particulate-bound Hg concentrations
- Degree of impact affected by % impervious surface

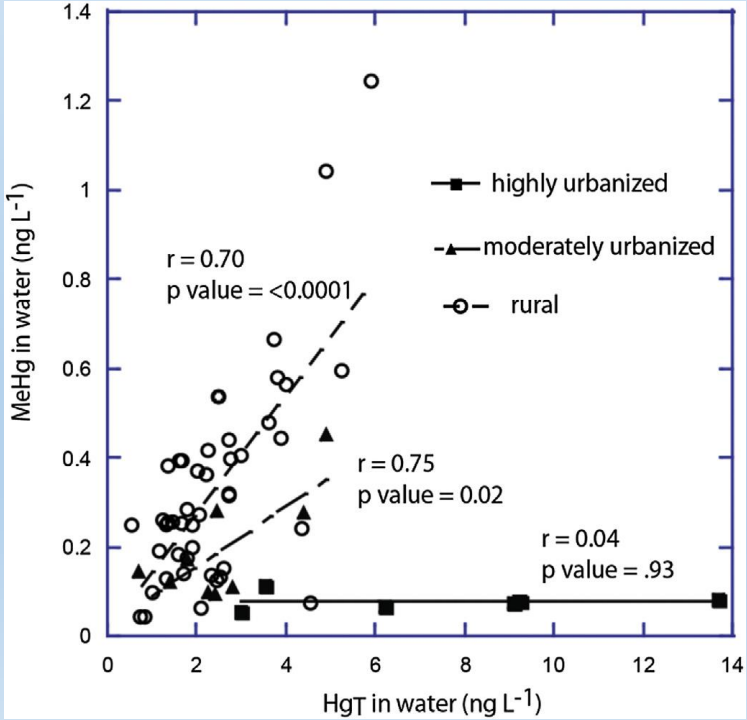


Eckley and Branfireun, 2006

Landscape Alterations: Urbanization

Urban MeHg concentrations generally low:

- Impervious surfaces (exposed to air)
- Rapid conveyance of water/lack of ponding
- Lower DOC
- Higher fraction of THg bound to particles
- Elevated nitrogen



Chalmers et al, 2014; NE US

Landscape Alterations: Urbanization

Waste Water Treatment Plants

Impact depends on facility design:

- Large decrease in THg
- Moderate decrease in MeHg (some potential for methylation)
- Even with decreases, effluent MeHg concentrations ~1-10 ng/L
- Typically, load is relatively small input to receiving water body

Landscape Alterations: Agriculture

Photo: Bob Rost

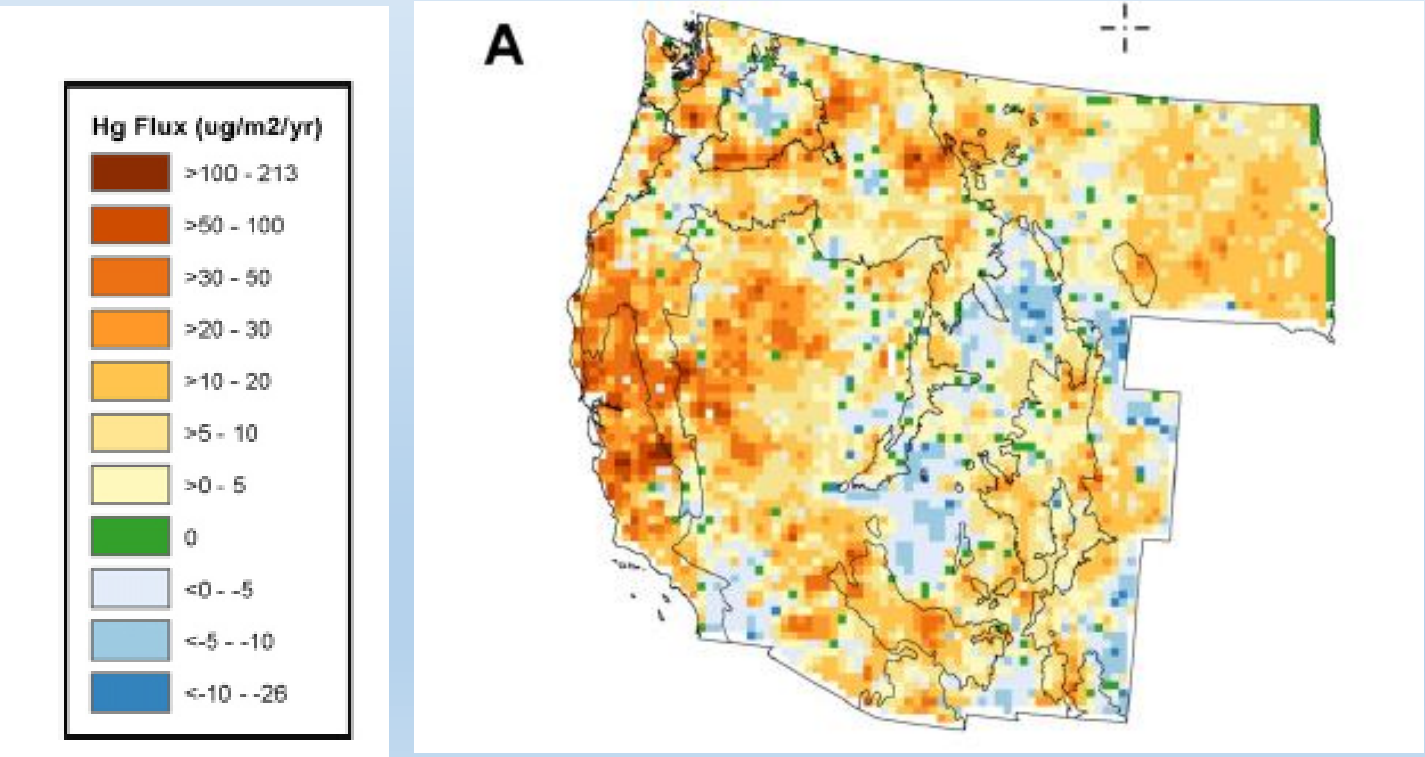
Landscape Alterations: Agriculture

- Agricultural activities have been shown to increase Hg concentrations in rivers due to soil erosion (Hurley et al(1998); Warner et al. (2005))
- Most Hg loads from agricultural lands is associated with particulate-bound Hg
- Increased loadings of carbon & other nutrients can affect MeHg production (Hsu-Kim et al, 2018)
- Increased runoff volume can also increase loads

Photo source: USGS

Landscape Alterations: Agriculture

- Surface emission can be higher from agricultural lands due to less shading and higher soil moisture



Eckley et al, 2016

Questions/Comments?