ASSESSMENT AND REMEDIATION OF MERCURY CONTAMINATED SITES

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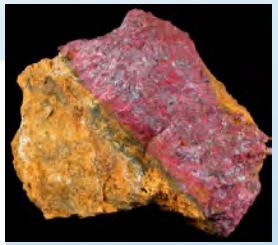
Primary Source Sites for SF Bay Region Waterbodies

Gold Mining

Mercury Mining

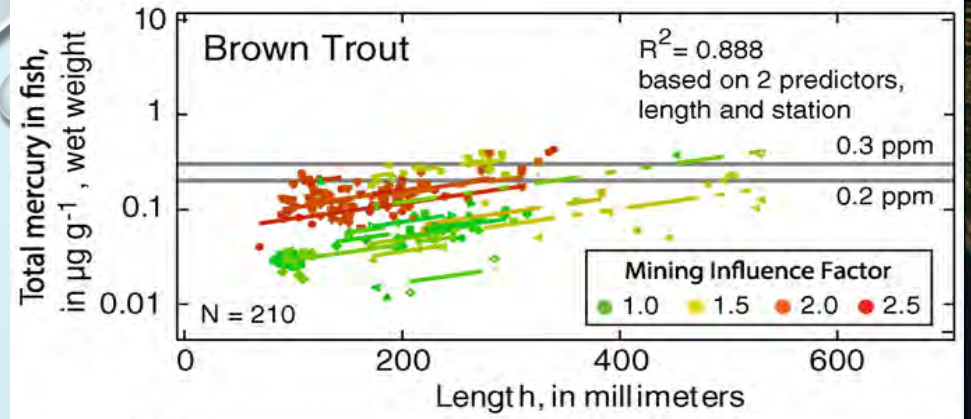


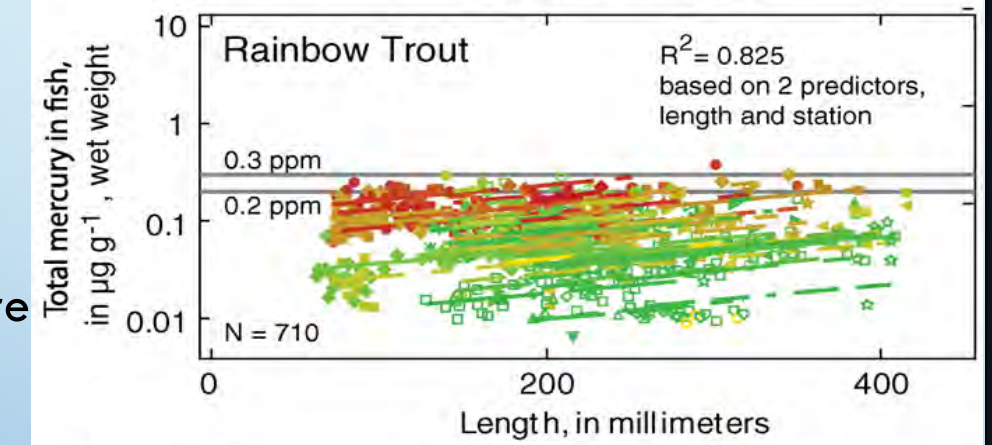
Chlor alkali

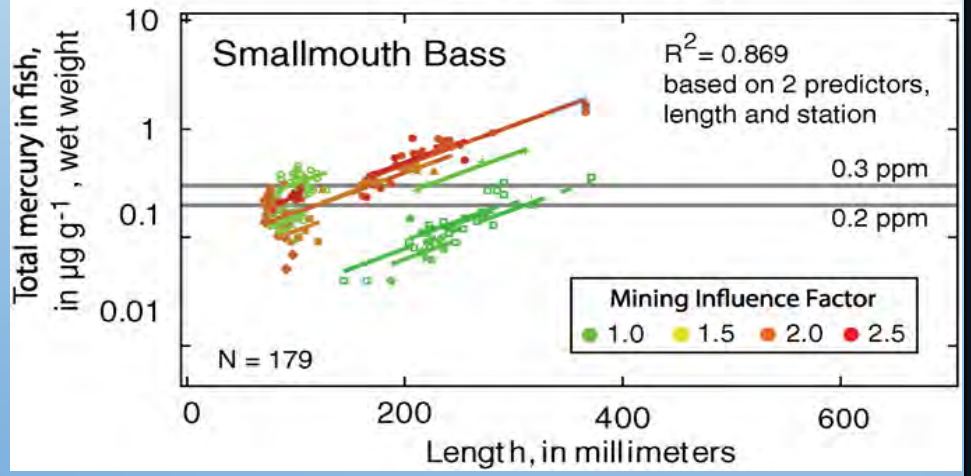
Images Library of Congress, Sierra Fund, UC Davis, Lumicrest

FISH Hg LINKED TO MINING

- Higher fish [Hg] associated w/watersheds more historical mining
- Only waterbodies downstream of Hg associated mines NOT impaired remediated or not actually connected







Alpers et al, 2016

Site Assessment: Source attribution using stable isotopes

What are stable isotopes?

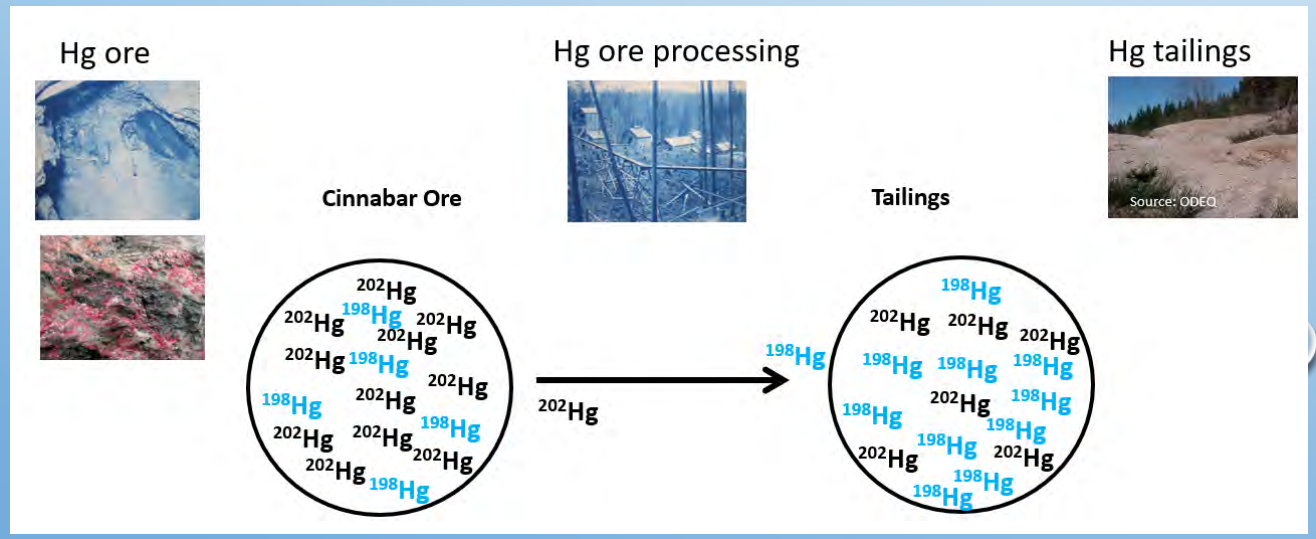
Forms of the same element that contain equal numbers of protons but different numbers of neutrons and as a result have different atomic masses

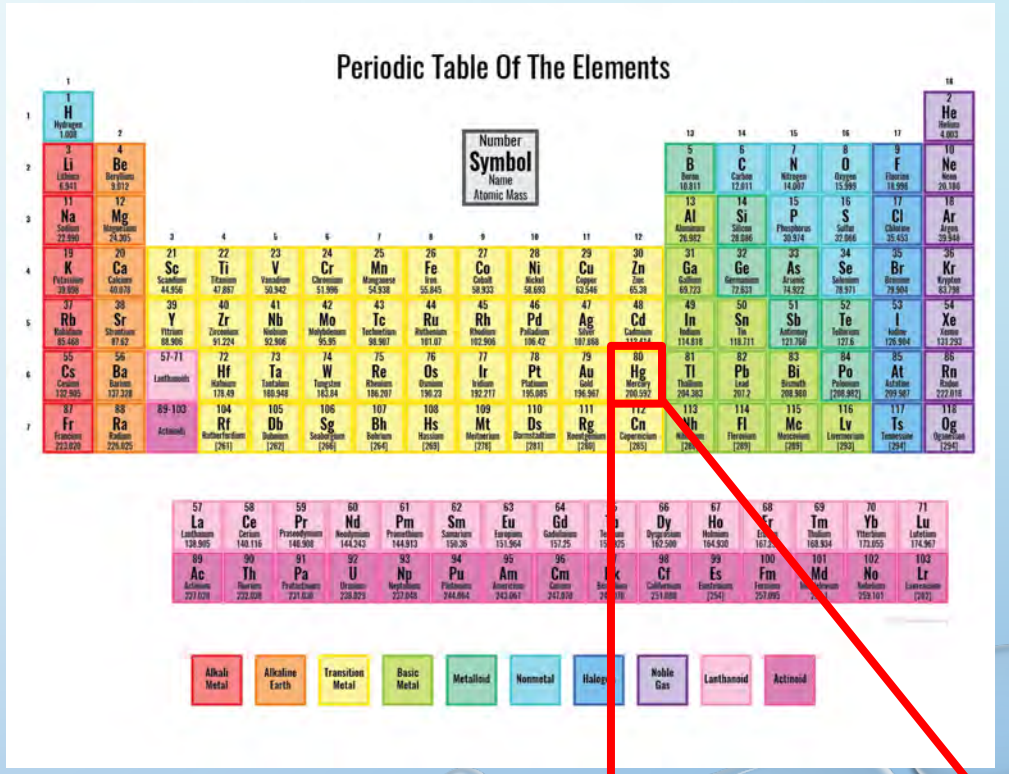
Mercury Isotopes:

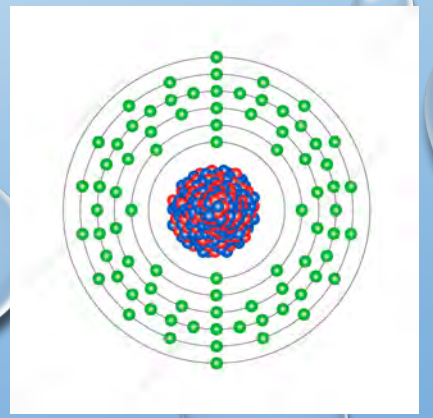
7 stable isotopes with range in mass from 196 to 204 amu

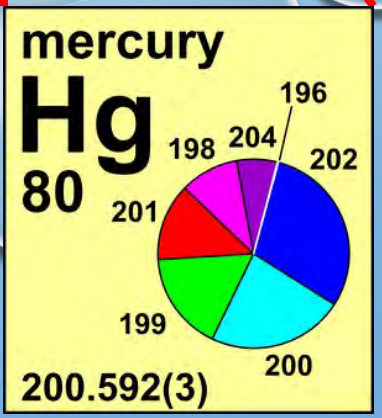
Mass dependent fractionation:

Lighter isotopes react faster and become enriched in the products



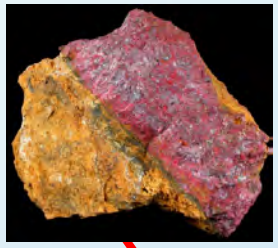




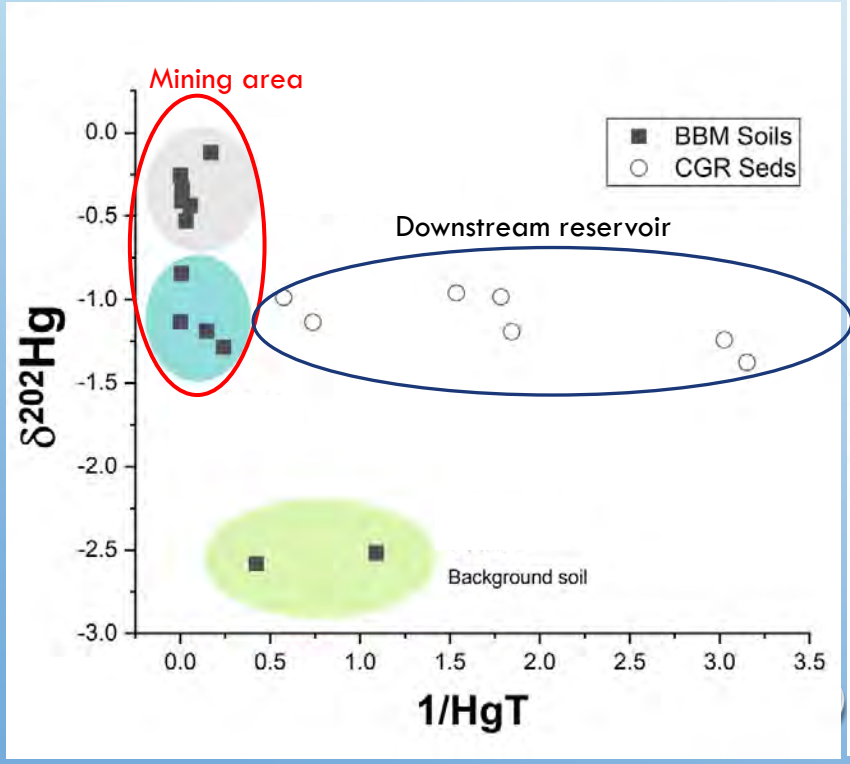


Site Assessment: Source attribution using stable isotopes

- Hg stable isotope analysis has provided insights into different sources of Hg—requires [illegible] end-members (and minimal post-source transformation)
- Mines significant source downstream

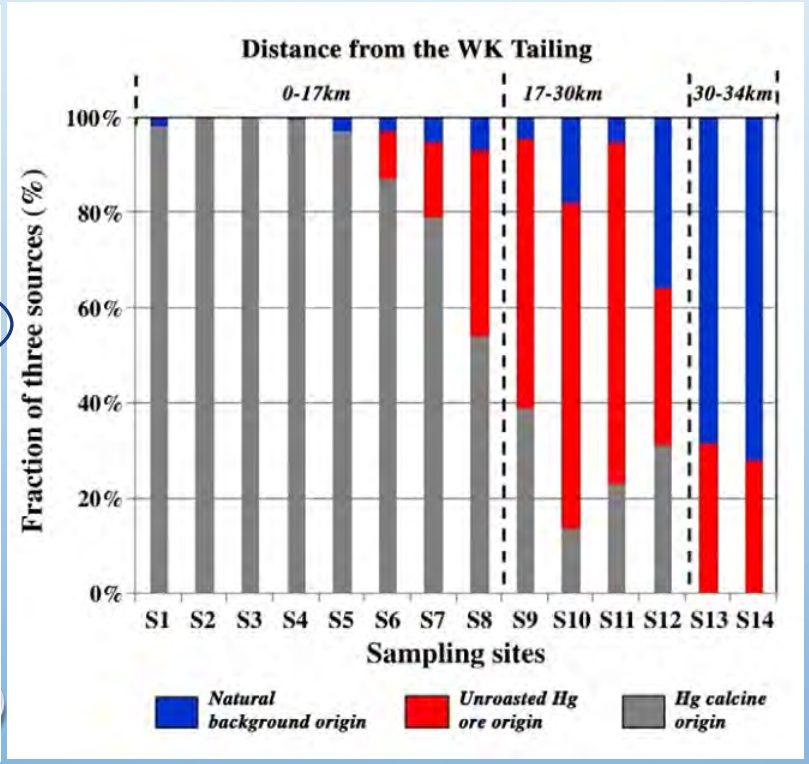


Black Butte Hg Mine, OR



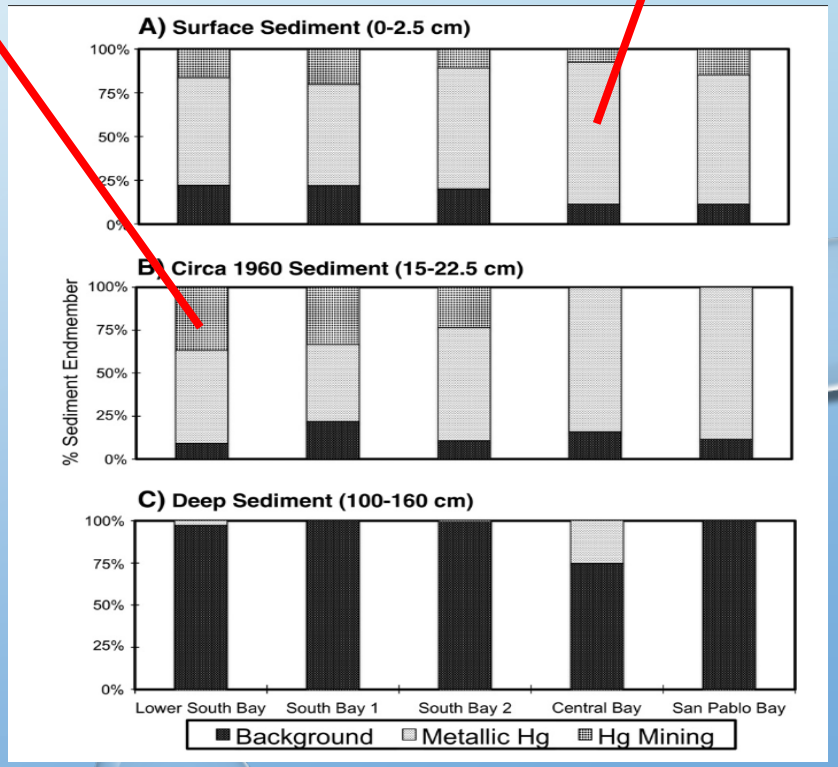
Jannsen

Wanshan Hg Mine, China



Yin et al, 2013

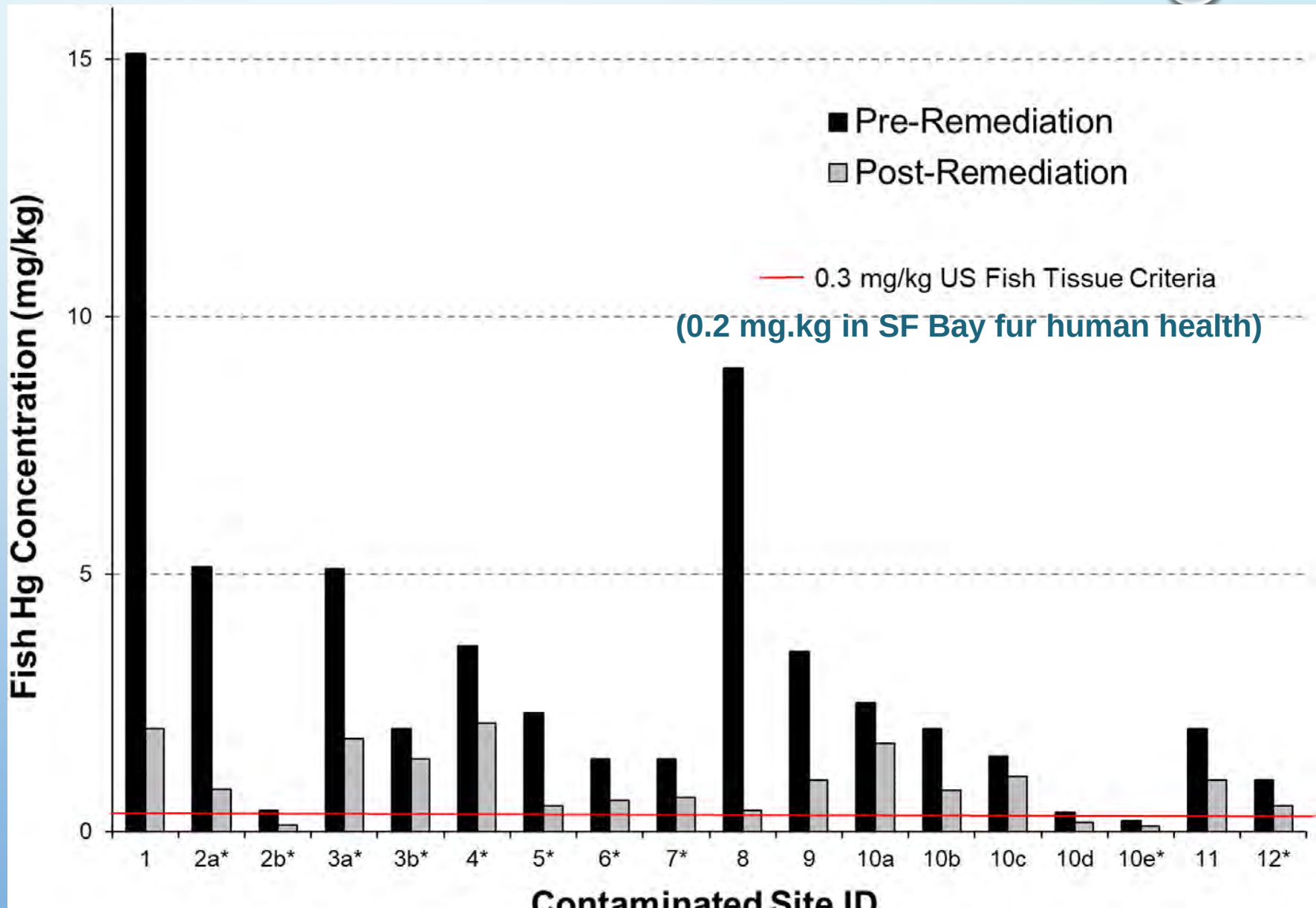
San Francisco Bay, CA



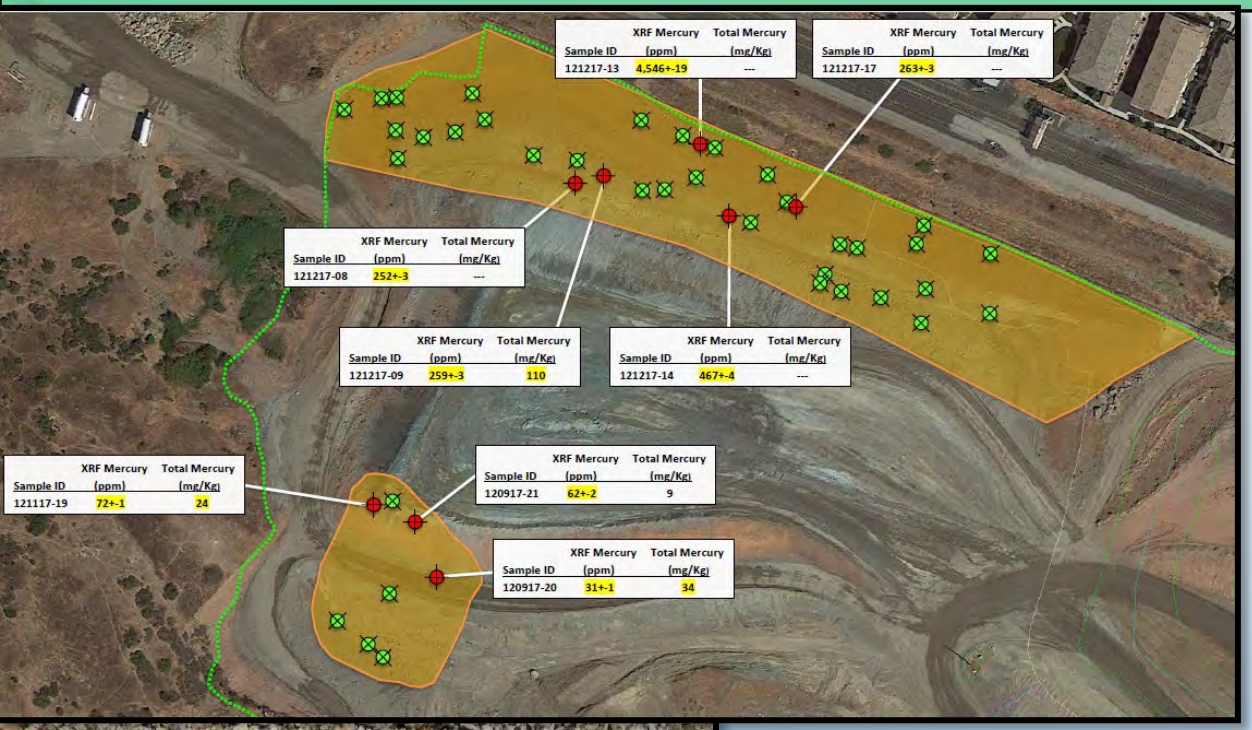
Donovan et al, 2013

Source control has been effective, but enough?

- Uncertainties may be significant, different:
  - Types of sites (3 mines)
  - Remediation strategies
  - Fish sampled
  - Temporal scales
- Downstream mitigation needed
- Improved source control needed



Site Assessment: Source/Site characterization

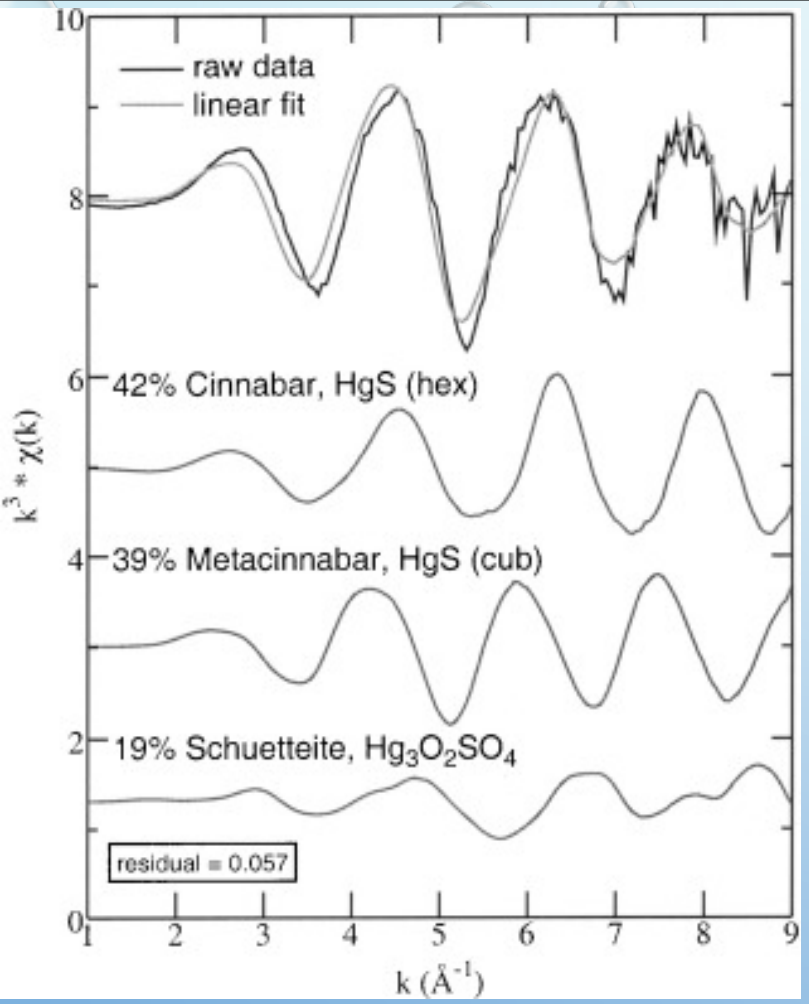


X-Ray Fluorescence Spectrometer

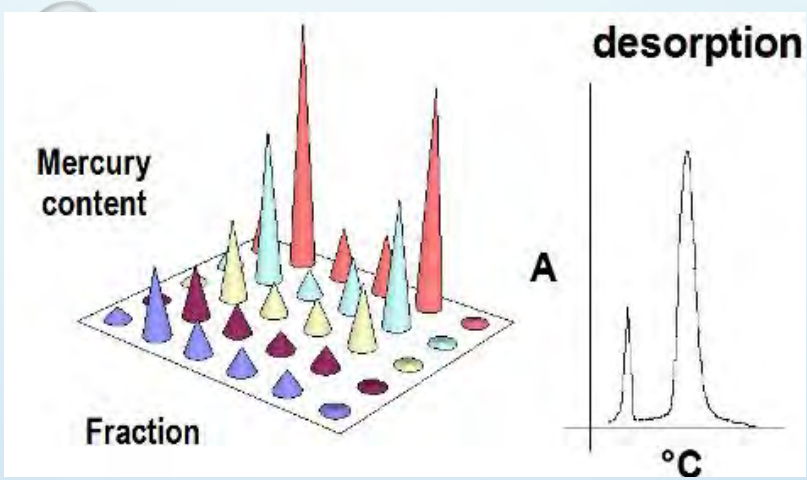
- Delineate extent of contamination
- High measurement density resolves soil heterogeneity, limited sampling $
- Reduce cost/effort
- Recommendations for quality data:
  - Site/Source-specific reference materials, analysis times
  - Aggregate measurements (ISM)
  - Reliable limit 2xmdl (~15mg/kg)
  - Lab comparison with HF digestion near action levels (or minimal false negatives)

Images: Golder Associates & Eckley et al, 2020

Site Assessment: Risk Assessment



X-Ray Absorption Fine Structure



Selective Sequential Extraction

& Thermal Desorption

- Speciation/Chemical Extractions
- Reduce cost/effort of cleanup
- Identify environmentally available Hg (EA-Hg potentially harmful/methylatable)
- Support risk assessment
- Target "harmful" Hg rather than "locked" Hg
- SSE recommendation after Bloom, F0-F3 (~F4)

Target EA-Hg Target Remedial Method

Enhanced Containment
Vapor Mitigation

F0 Hg^0 (elemental, volatile)

F1 water soluble (~DI WET)

F2 weak acid soluble (~TCLP)

F3 organically complexed

F4 strongly complexed

F5 mineral phase

Cleanup Goal

96%

SSE Fraction	Common Mine Source	Primary Exposure Routes	Transformation Exposure Routes
F-0	• Equipment, waste, & spills from ore processing • Overburden (typically low percentage)	• Vapor inhalation	• Oxidation to reactive, potentially methylatable form (F-1 through F-3)
F-1 through F-3	• Calcines (tailings) • Ore (typically low percentage) • Overburden (typically low percentage) • Equipment, waste, & spills from ore processing • Native soil contaminated by atmospheric fallout	• Dust inhalation • Dust ingestion	• Methylated or can be (mobilization to aquatic environment, bioaccumulation, fish consumption)
F-4 & F-5	• Ore • Overburden • Surrounding geology (deposit halo)	• Not considered bio- or environmentally available	• Recalcitrant

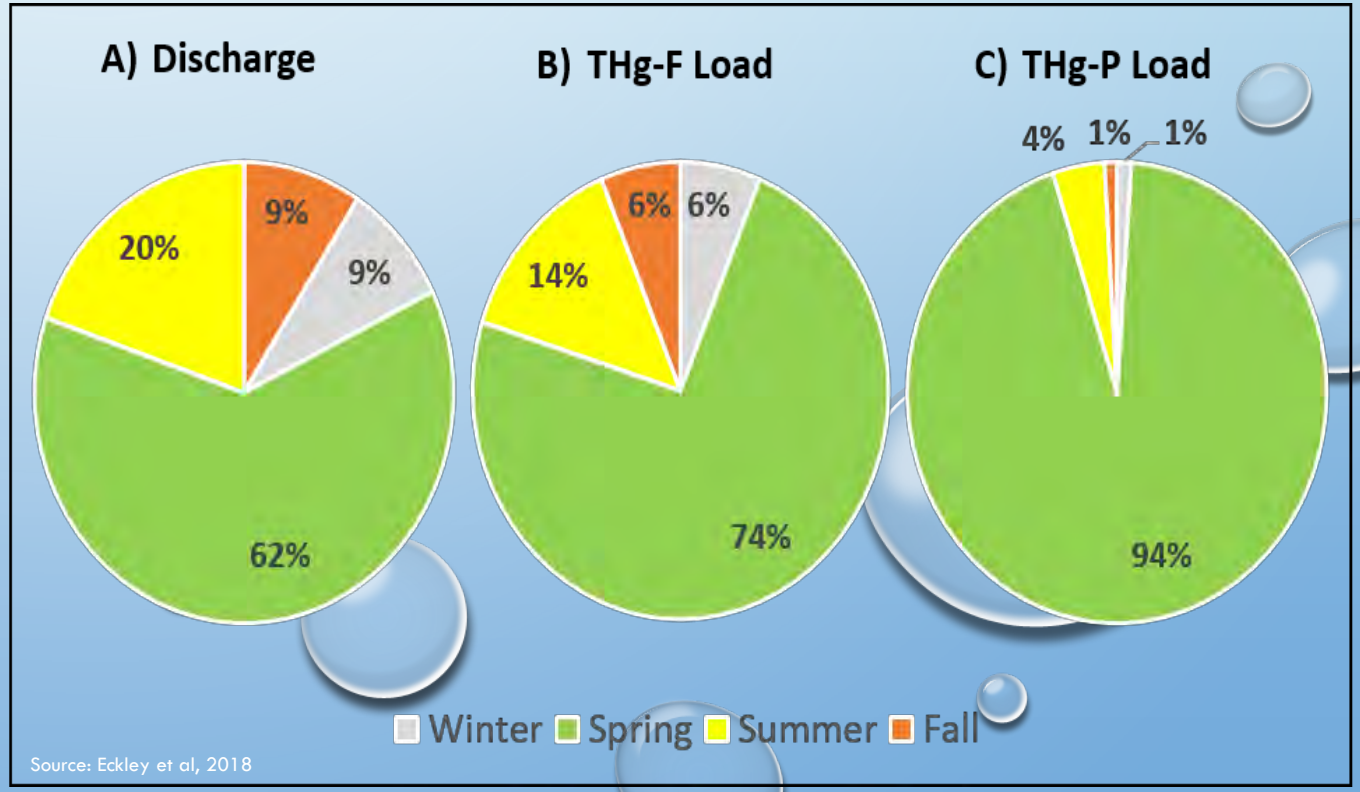
Site Assessment: Pathways of release—flux to water

Releases are a concern due to the potential for downstream methylation & bioaccumulation

- Stormflow flux >>> baseflow flux
- Annual loads dominated by a few large events
- Mobilization from erosion of particles/sediment entrainment

Example: Cinnabar Mine, ID

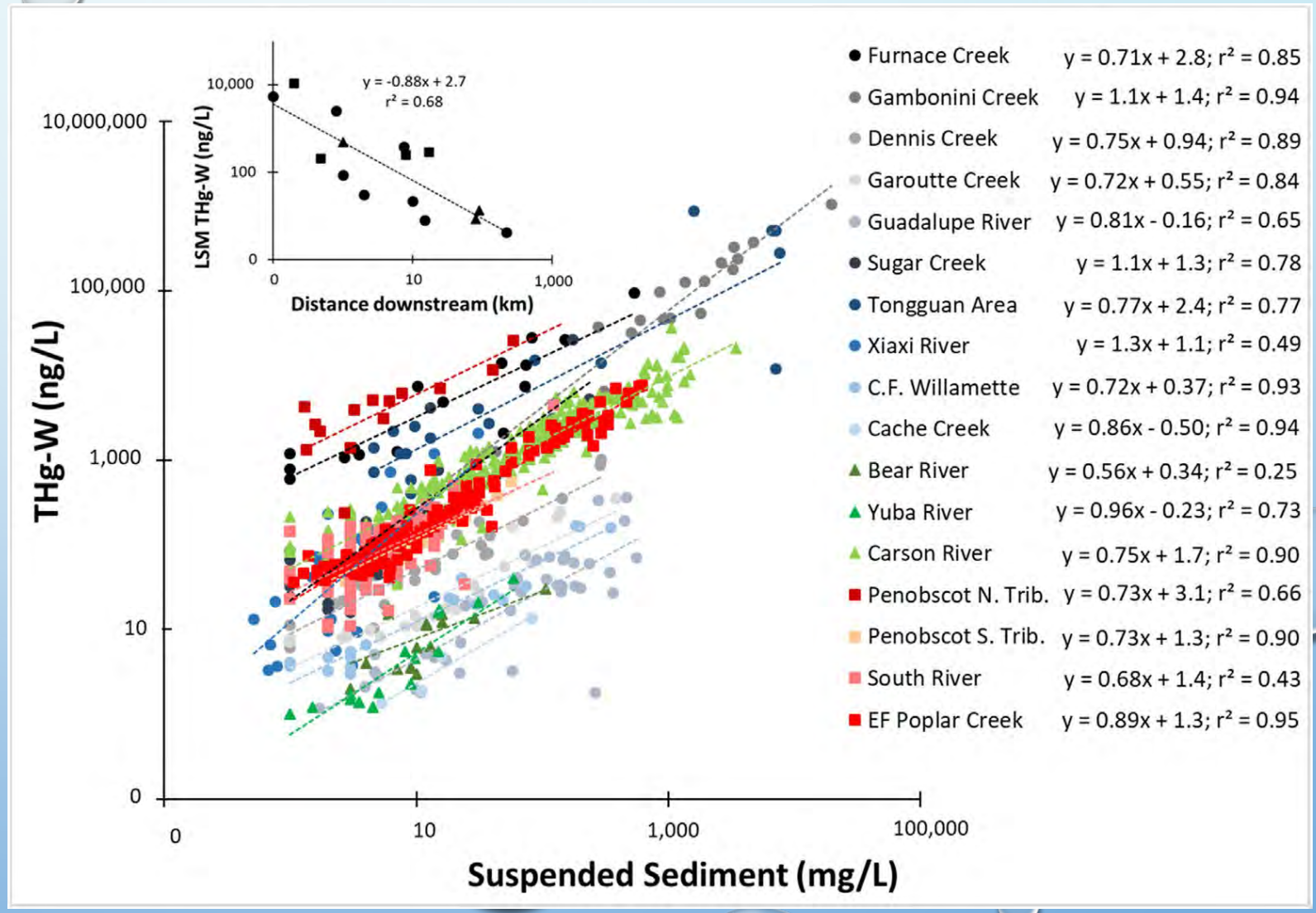
Photo: Eckley



Source: Eckley et al, 2018

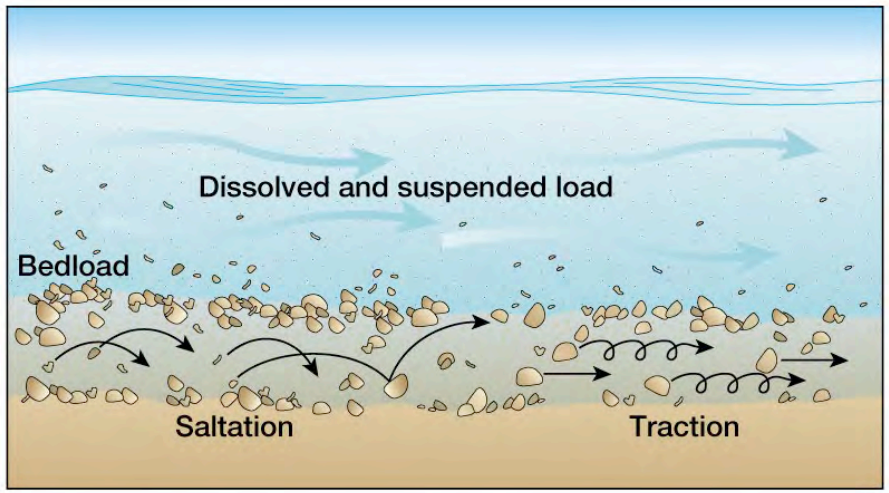
Site Assessment: Pathways of release—flux to water

- Positive relationship between THg and total suspended solids (TSS).
- Most regression slopes not significantly different.
- Most intercepts were significantly different and were correlated with the distance downstream from the contaminated source area.



Source: Eckley et al, 2020

To sieve or not to sieve?



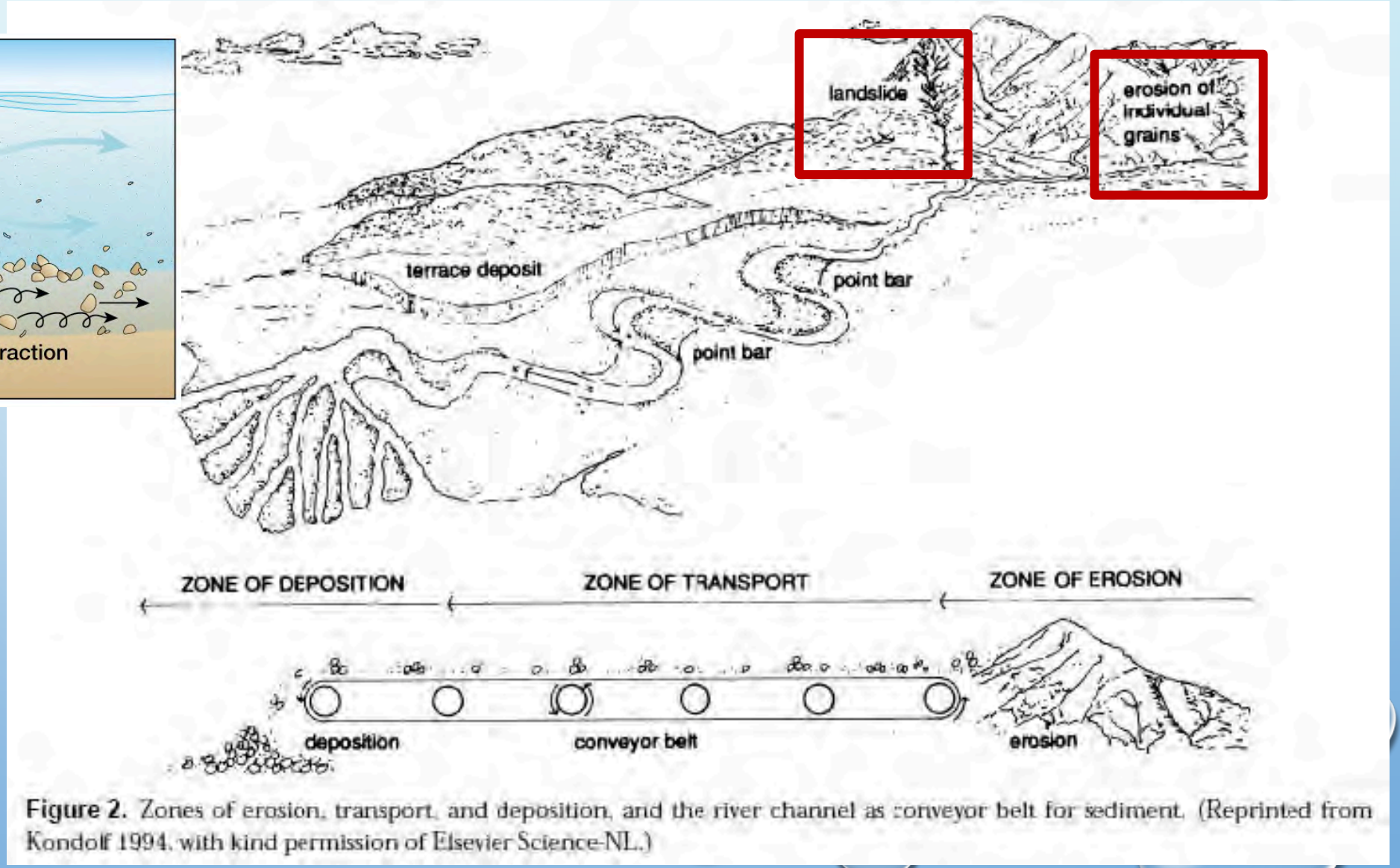


Figure 2. Zones of erosion, transport, and deposition, and the river channel as conveyor belt for sediment. (Reprinted from Kondolf 1994, with kind permission of Elsevier Science-NL.)

$[Hg]_{aq}$ necessary to exceed SF Bay Basin Plan Fish Criteria

WILDLIFE PROTECTION FISH CRITERIA

0.00006 to 0.015ug/L

- Small fish criteria= 0.03 mg/kg

Assumptions:

- MeHg/HgT 1% to 50%
- Herbivorous fish, trophic level 2
- Biomagnification range 2 to 10

HUMAN HEALTH FISH CRITERIA

0.000004 to 0.0005ug/L

- Large fish criteria= 0.2 mg/kg

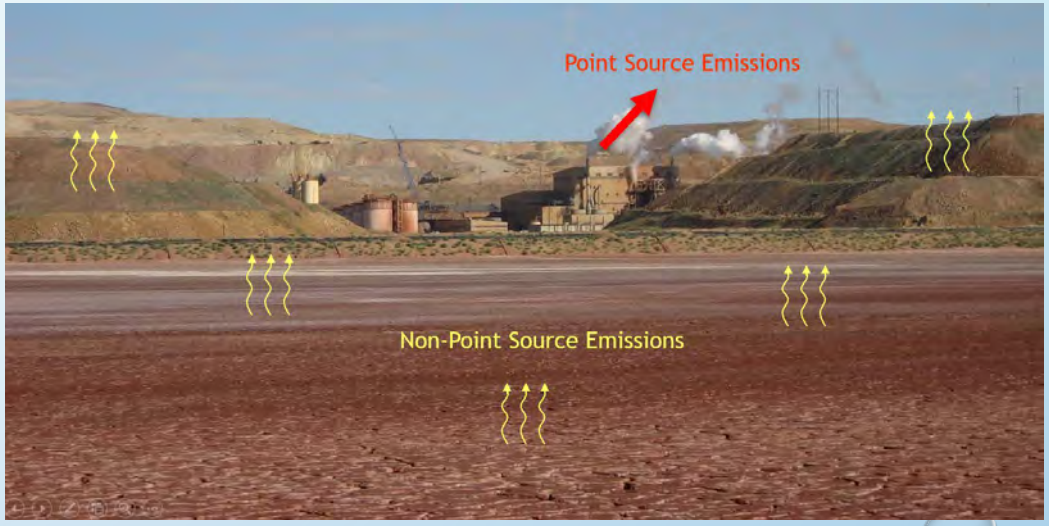
Assumptions:

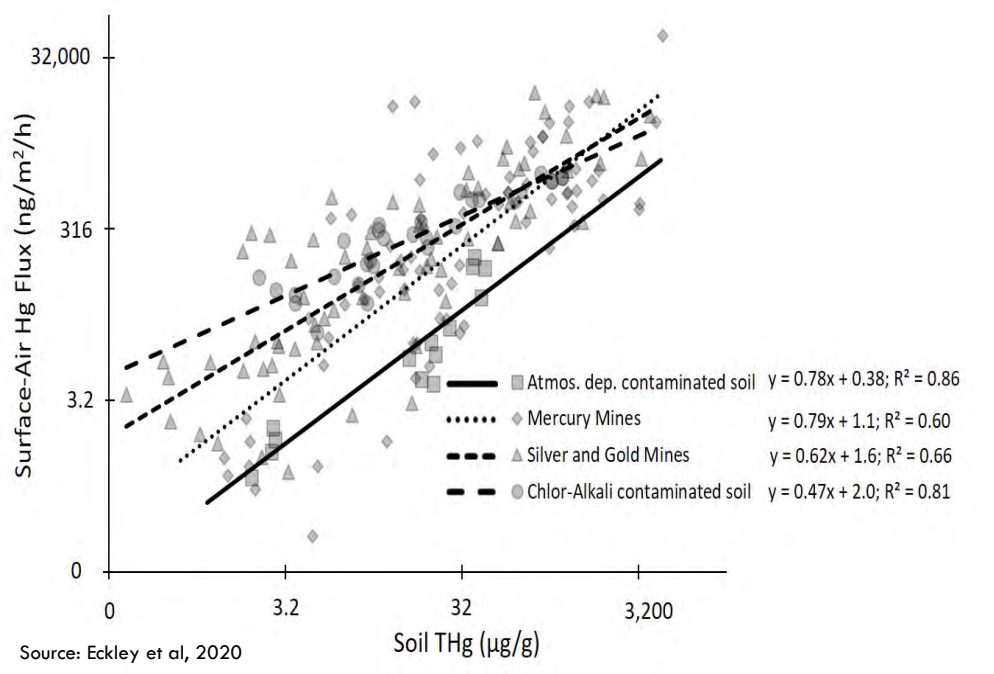
- MeHg/HgT 1% to 50%
- Herbivorous fish, trophic level 3 to 4
- Biomagnification range 2 to 10

MeHg/HgT range: Coastal = Black et al; ES&T 2009; SF Bay Delta = Choe et. al. Limnol. Oceanogr. 2004; Tidal Marsh= Zhang et. al. ES&T 2014

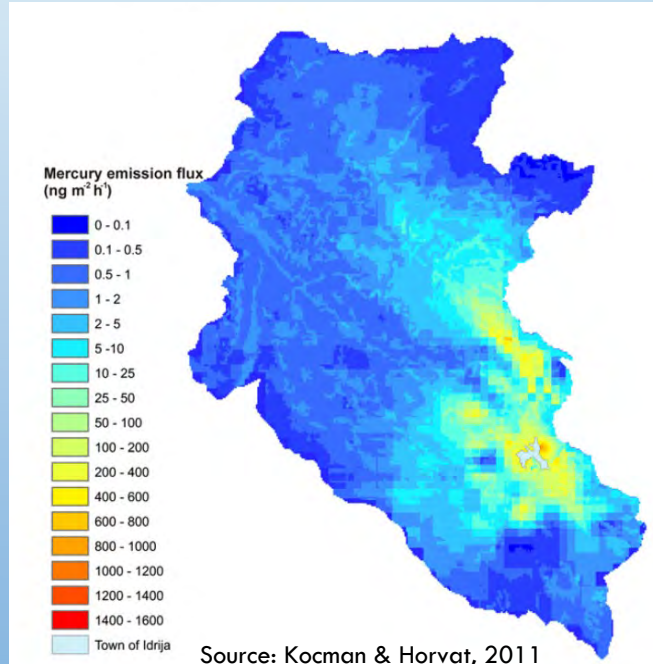
Site Assessment: Pathways of release—flux to air

- Relative magnitude of surface-air versus water flux depends on hydrological/meteorological conditions.
- Annual fluxes to the air can be 50-100 kg/year from some contaminated sites.
- Soil Hg speciation (along with several environmental parameters) affect surface-air fluxes.

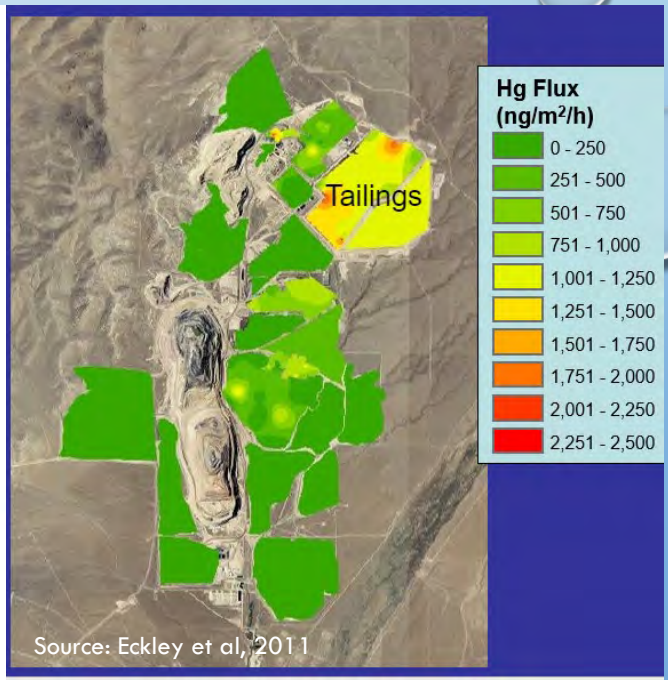




Source: Eckley et al, 2020



Source: Kocman & Horvat, 2011



Source: Eckley et al, 2011

Site Remediation: Improve Containment

Vapor Barrier

Enhanced
Erosion Control

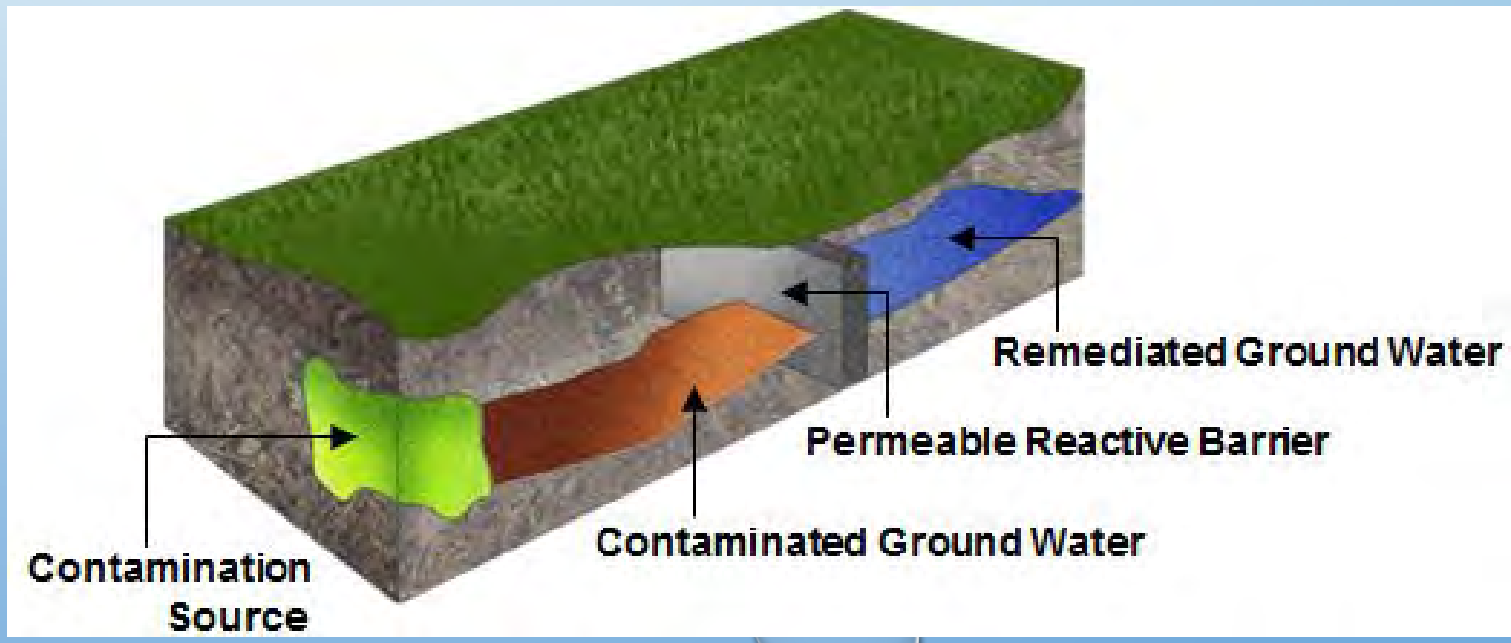
Site Remediation: Sequester environmentally available Hg

Soil Amendments

Other options:

- Soil-washing
- Solidification/stabilization
- Thermal treatment
- Electrochemical/kinetic recovery
- Bioremediation/biotreatment
- Phytoremediation/stabilization
- Chelating agents

Permeable Reactive Barrier



Conclusions:

We need to and can optimize Hg source control by:

- Using stable isotope fractionation to identify sources of contamination
- Improving site assessment:
  - Resolve spatial heterogeneity with increased sample density, XRF
  - Identify EA-Hg forms/speciation that are mobile, labile, &/or toxic with speciation/SSE
- Improving site remediation:
  - Prioritize/Target environmentally available-Hg
  - Implement enhanced remedial methods

Next Steps:

- Novel approaches to addressing contaminated sites have been identified at the laboratory and test plot scale;
- However, more examples of large-scale applications are needed to encourage broader adoption of these methods – SF Bay Water Board is implementing several currently

THANK YOU!

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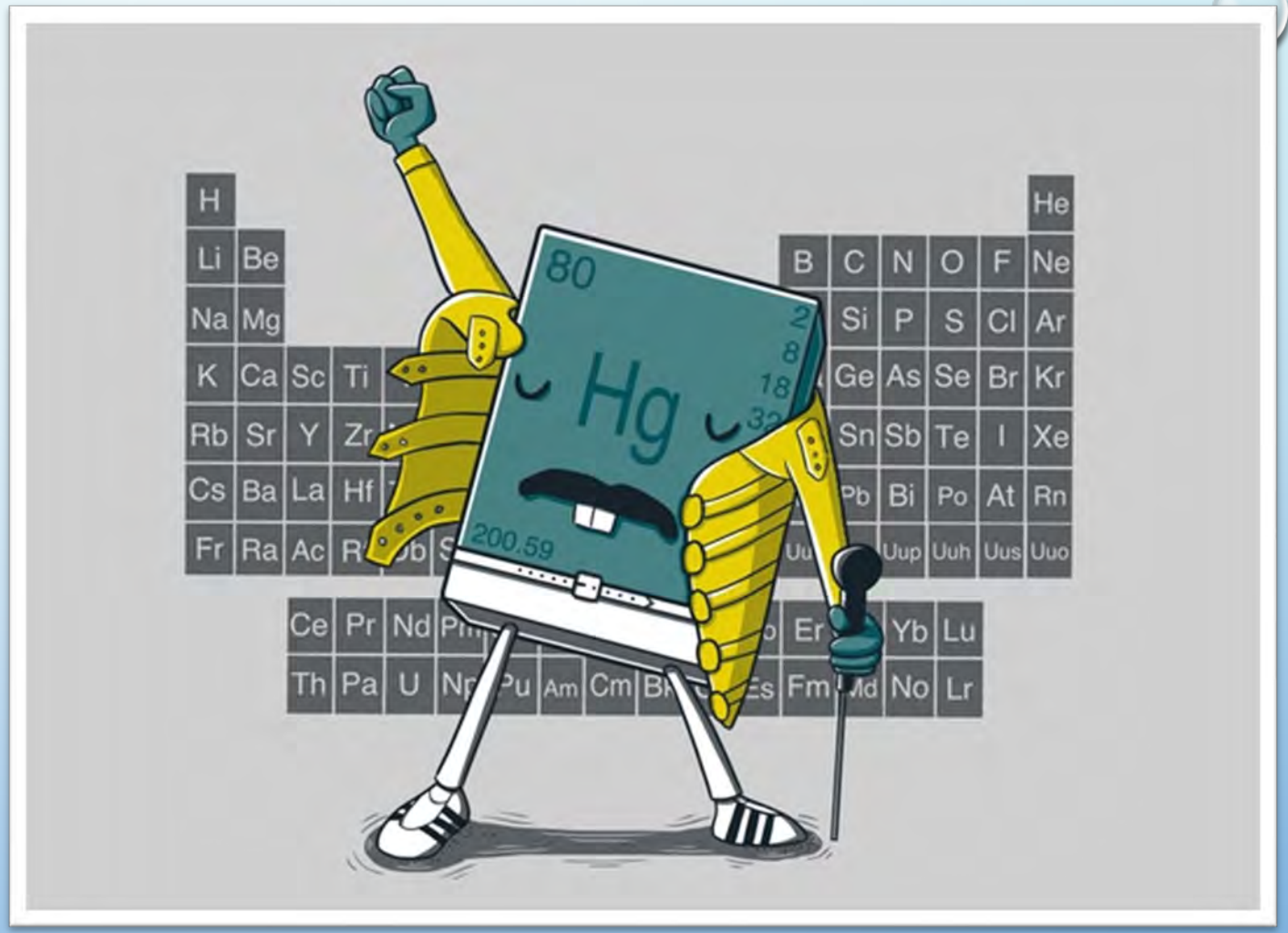

"Freddie Mercury" by Pablo Bustos