Aquatic Toxicology of Metals

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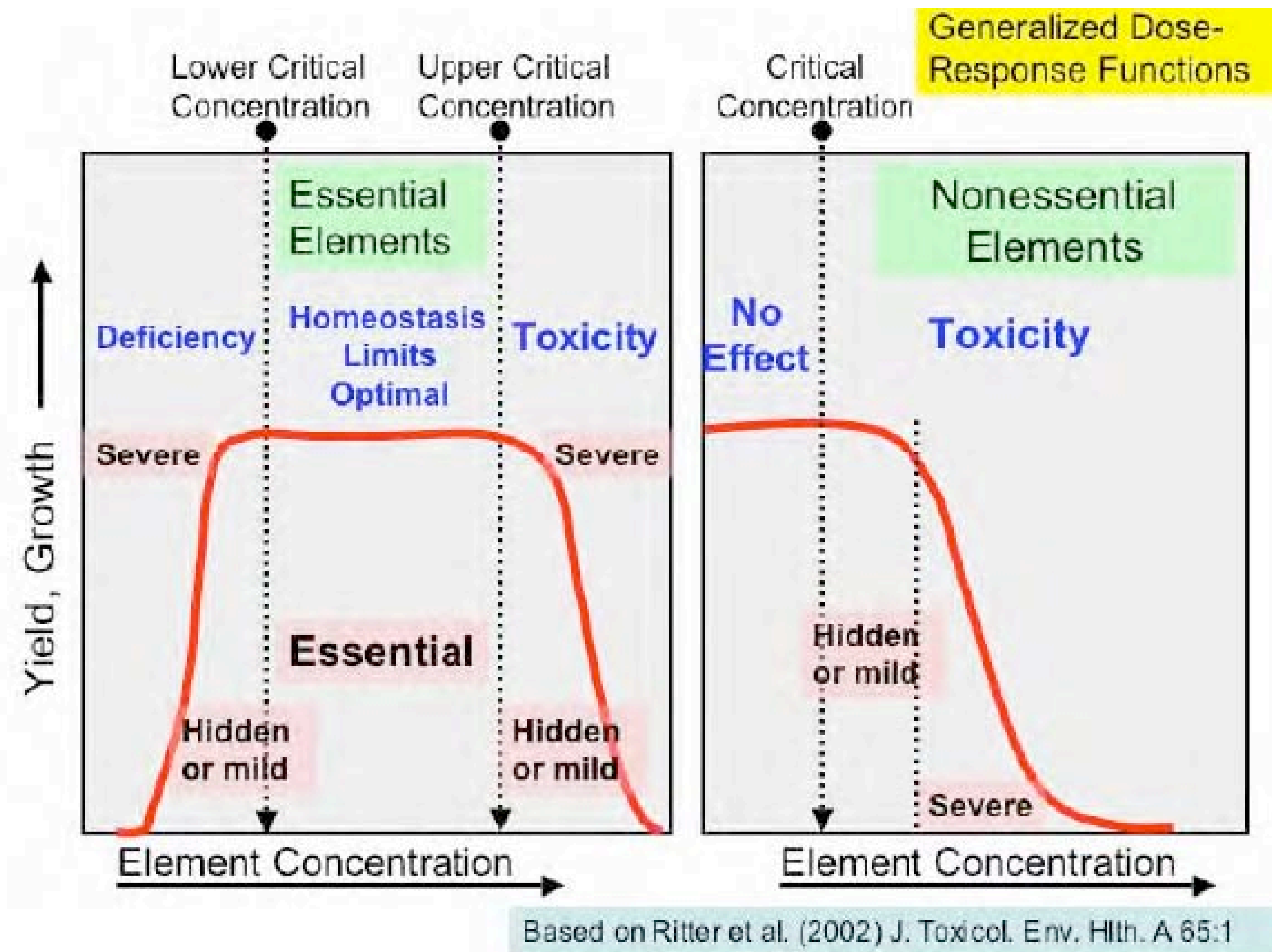
Why are metals different than organic chemicals?

- Some are essential micronutrients
- Natural parts of the earth’s crust
- Don’t “go away” (metal cycles)
- Toxicity can be dramatically affected by water chemistry

Essential vs. Non-essential metals

- Essential metals are required for health
  - Selenium
  - Copper
  - Iron
  - Manganese
  - Zinc
- No amount of non-essential metals are required
  - Cadmium
  - Silver
  - mercury

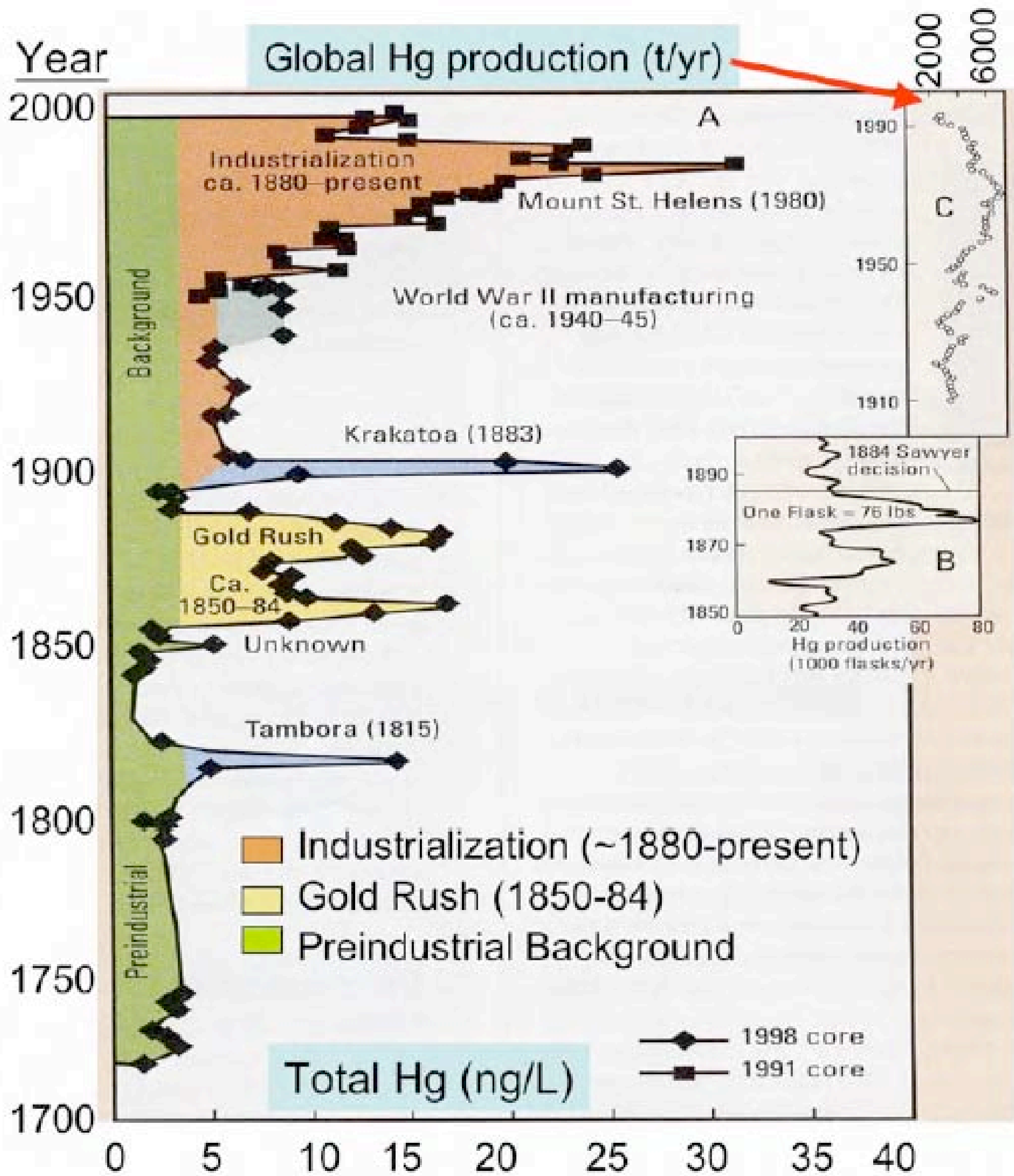

Generalized Dose-Response Functions
Lower Critical Concentration
Upper Critical Concentration
Critical Concentration
Essential Elements
Nonessential Elements
Deficiency
Homeostasis Limits Optimal
Toxicity
No Effect
Toxicity
Severe
Severe
Essential
Hidden or mild
Hidden or mild
Hidden or mild
Severe
Yield, Growth
Element Concentration
Element Concentration
Based on Ritter et al. (2002) J. Toxicol. Env. Hlth. A 65:1

Metals are natural parts of earth's crust

Element (Symbol)	Average Content in Crustal Rocks	Typical Content in Basalt Rocks	Common Range for Soils
		Essential	
Chromium (Cr)	100	16.3	1 - 1,000
Cobalt (Co)	25		1 - 40
Copper (Cu)	55	22.4	2 - 100
Iron (Fe)	60,000		7,000 - 550,000
Manganese (Mn)	950		20 - 3,000
Molybdenum (Mo)	2.3		0.2 - 5
Nickel (Ni)	75	15.0	5 - 500
Selenium (Se)	0.09		0.1 -2
Tin (Sn)	2		2 - 200
Vanadium (V)	135		20 -500
Zinc (Zn)	70	132	10 - 300
		Nonessential	
Aluminum (Al)	81,000		10,000 - 300,000
Arsenic	**5**		**1 - 50**
Beryllium (Be)	2.8		0.1 - 40
Cadmium (Cd)	**0.2**	**0.07**	**0.01 - 0.70**
Lead (Pb)	**13**	**18.0**	**2 - 200**
Mercury (Hg)	0.1	0.01	0.01 - 0.3
Titanium (Ti)	6,000		1,000 - 10,000

Releases of metals

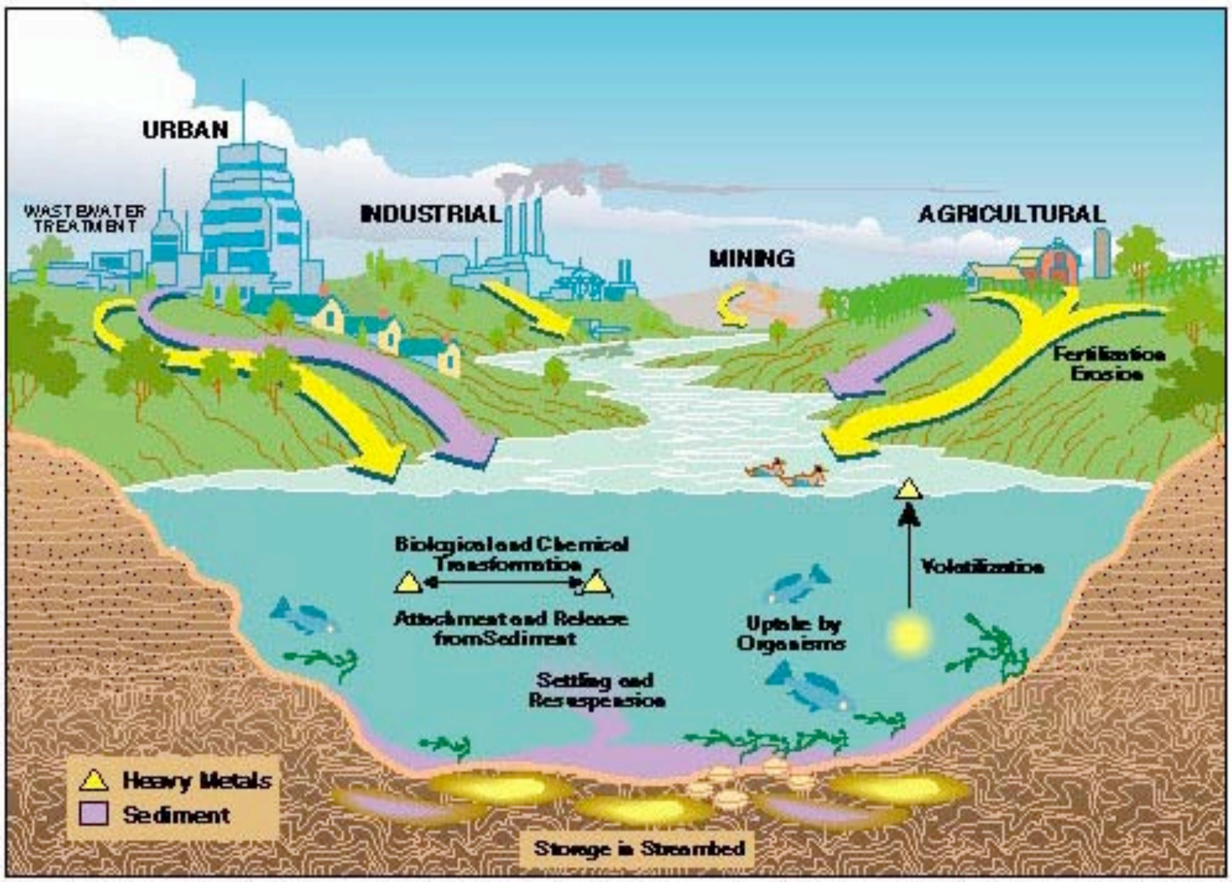
- Natural
  - Weathering of rock
  - Volcanoes
  - Forest fires
- Anthropogenic
  - Mining and smelting
  - Fossil fuel combustion
  - Industrial and municipal effluent



Year
Global Hg production (t/yr)
2000
6000
Industrialization ca. 1880–present
Mount St. Helens (1980)
World War II manufacturing (ca. 1940–45)
Background
Krakatoa (1883)
Gold Rush
Ca. 1850–84
Unknown
Tambora (1815)
Preindustrial
Industrialization (~1880-present)
Gold Rush (1850-84)
Preindustrial Background
1998 core
1991 core
Total Hg (ng/L)
A
B
C
1884 Sawyer decision
One Flask = 76 lbs
Hg production (1000 flasks/yr)

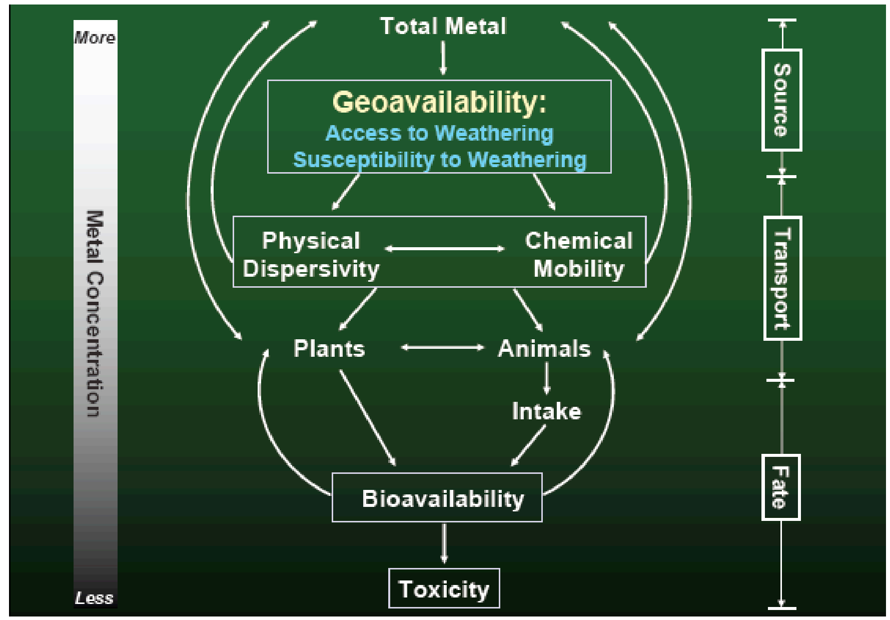
Metals are continually cycling in the Environment

Figure 21--*Sources and Sinks of Heavy Metals*

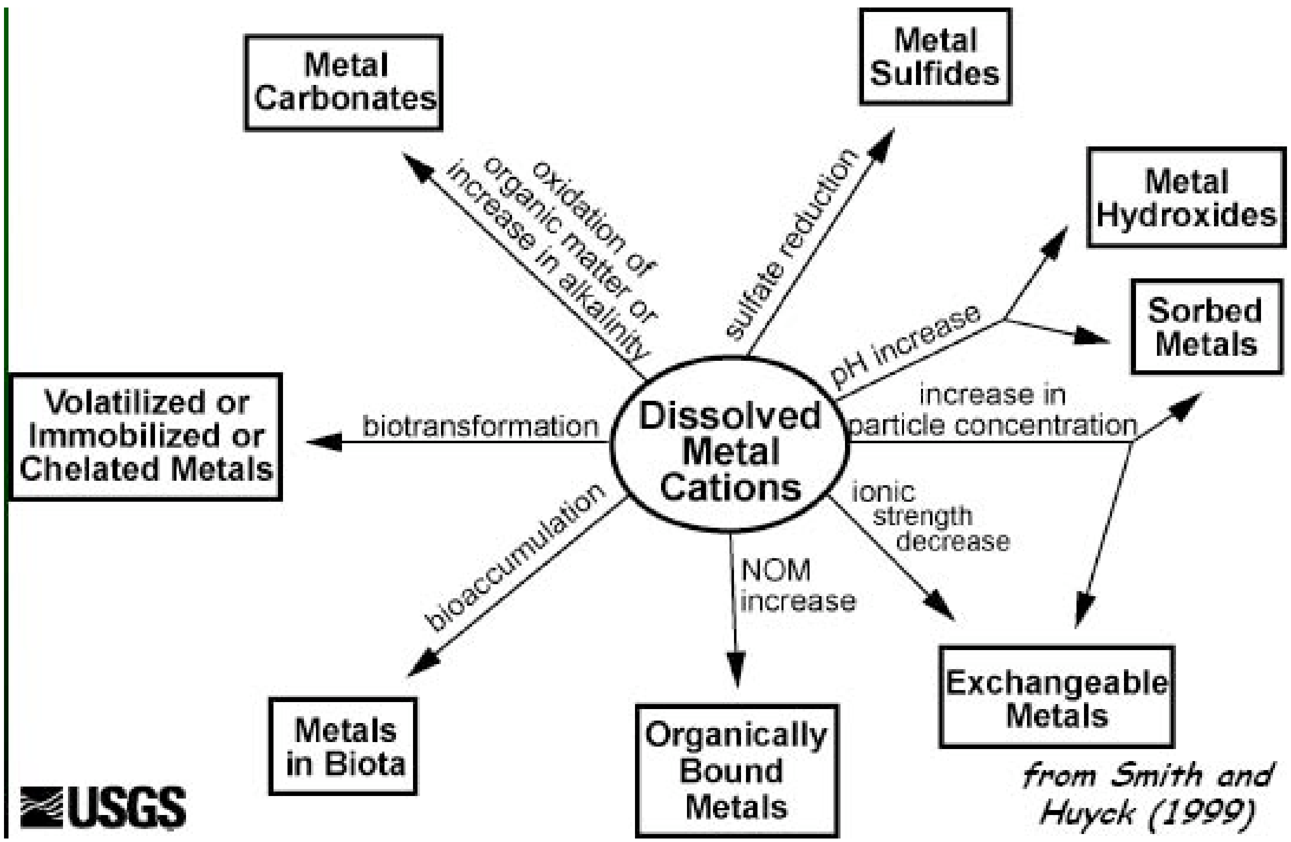


Metal Speciation and Toxicity

- In order for metals to cause toxicity, they must be bioavailable and in a specific form, usually the free ion
- Metals in the environment are present in many forms or species
  - Oxidation state
  - Complexes with ligands
  - Physical form (adsorption on particulate matter)
- Metal speciation is affected by water chemistry
  - pH
  - Inorganic ligands (carbonate, chloride, sulfate, sulfide)
  - Organic matter (DOC, NOM)
  - Reduction potential



Metal Speciation



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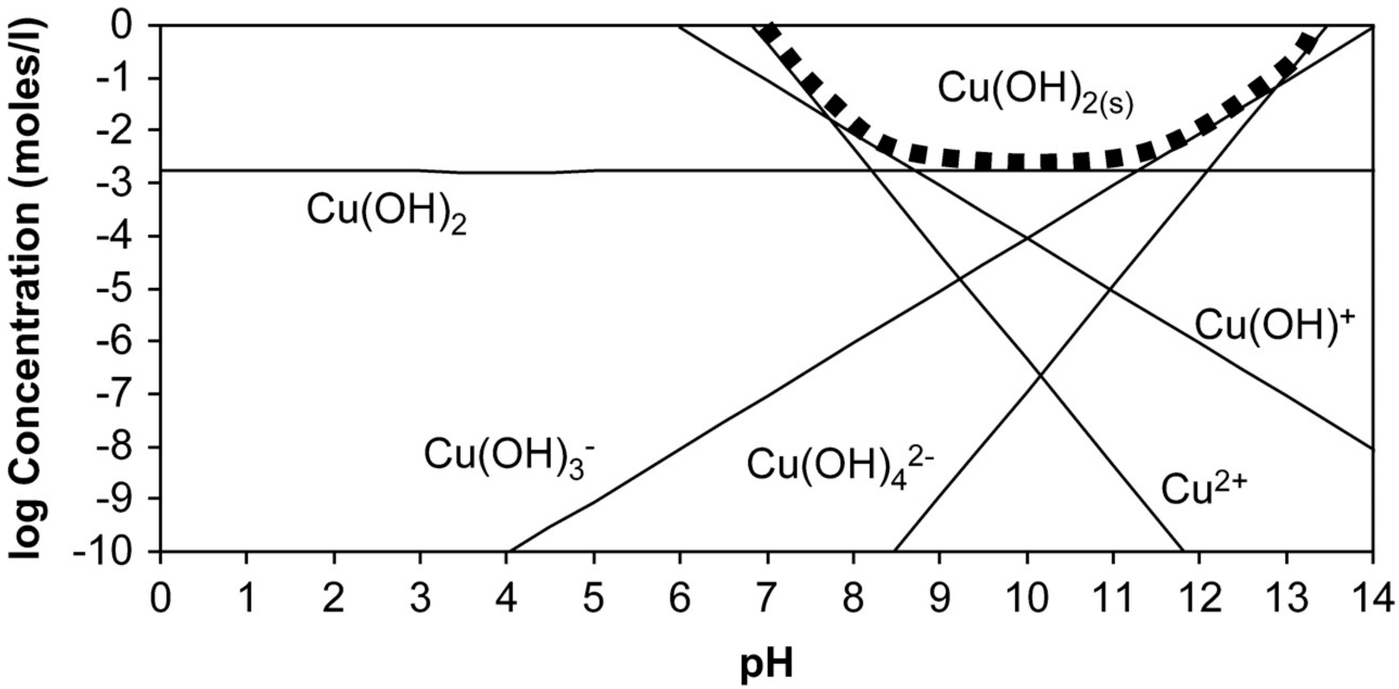
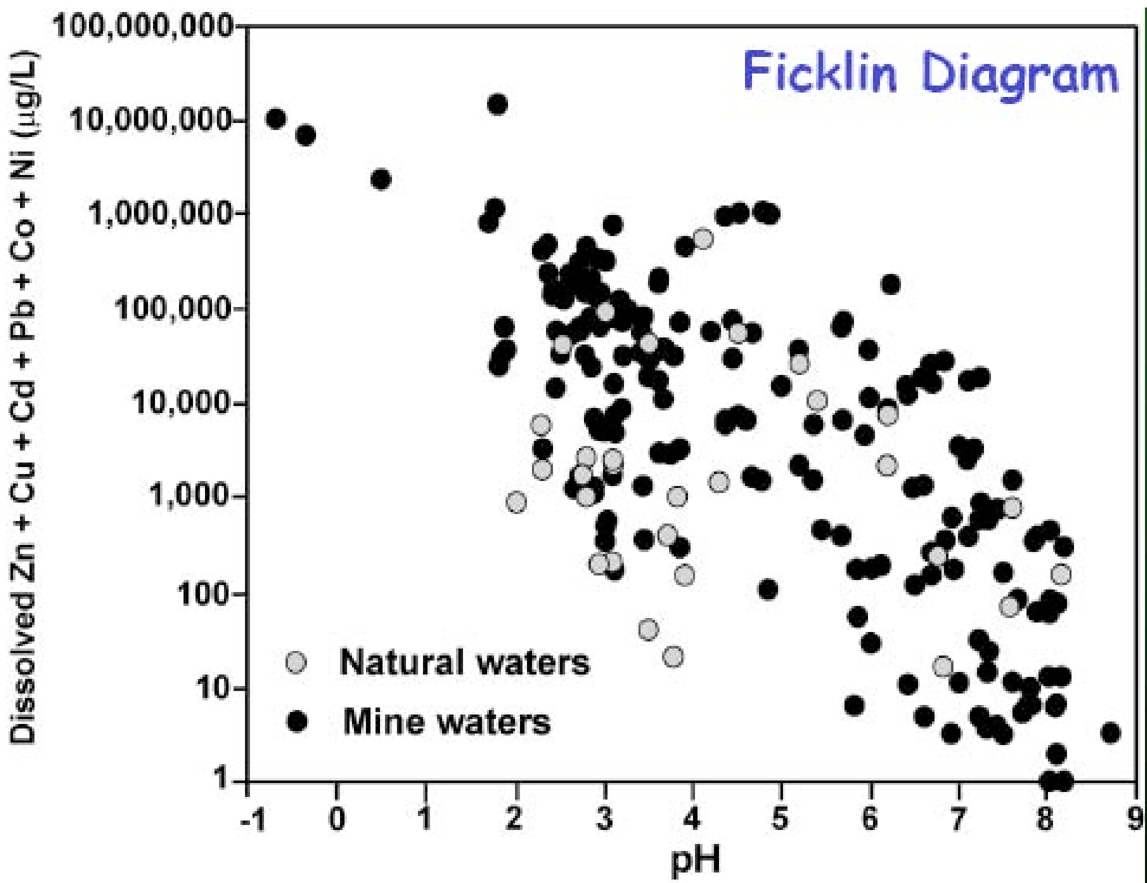


Cuppett, J. D. et al. Chem. Senses 2006 31:689-697; doi:10.1093/chemse/bjl010

pH

- Most metals are more soluble at low pH (acidic) conditions
- Low pH is also a stressor itself and can exacerbate metal toxicity
- Acid rain, acid mine drainage



From Plumlee et al. (1999)

Different Metals Precipitate at Different pH Values

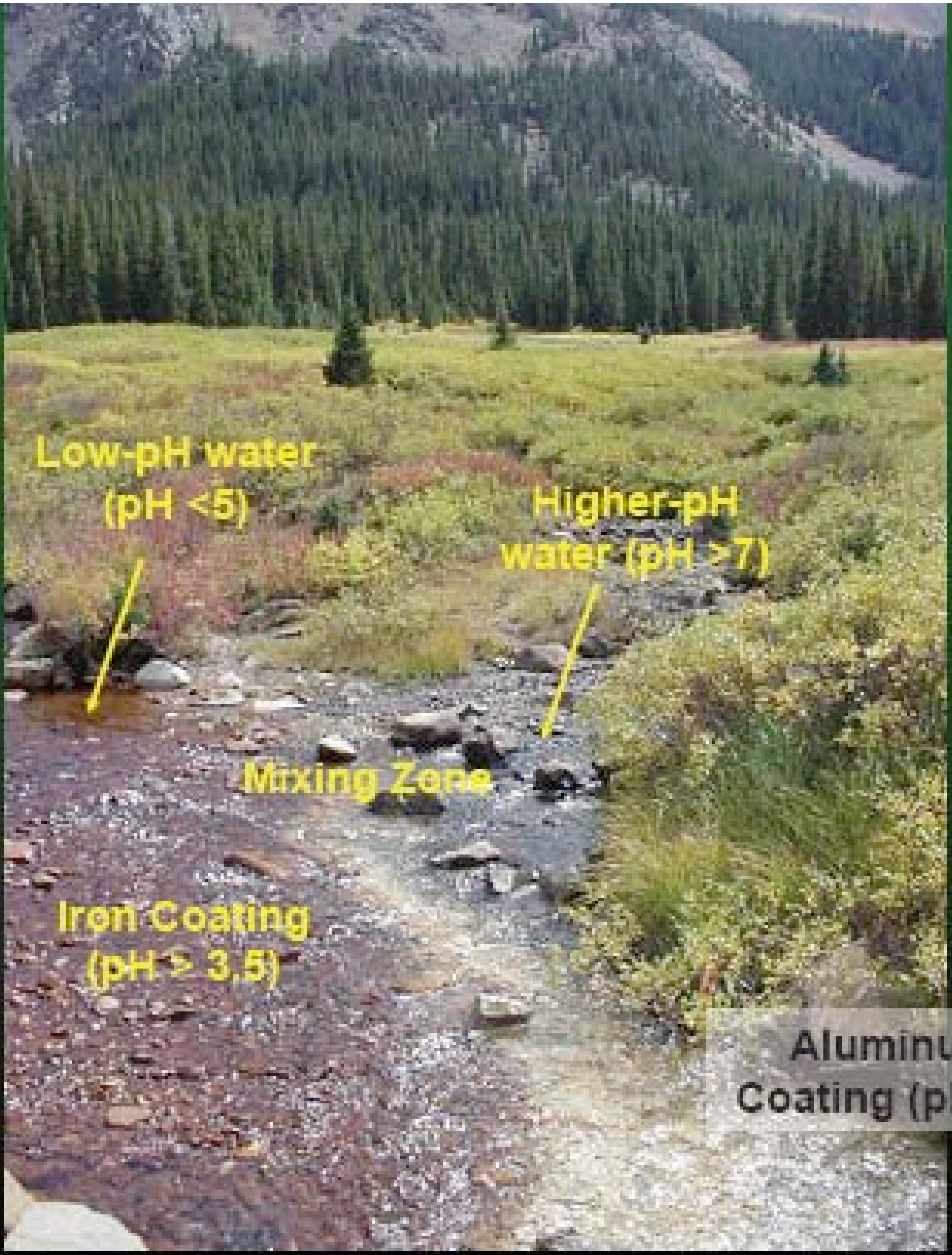
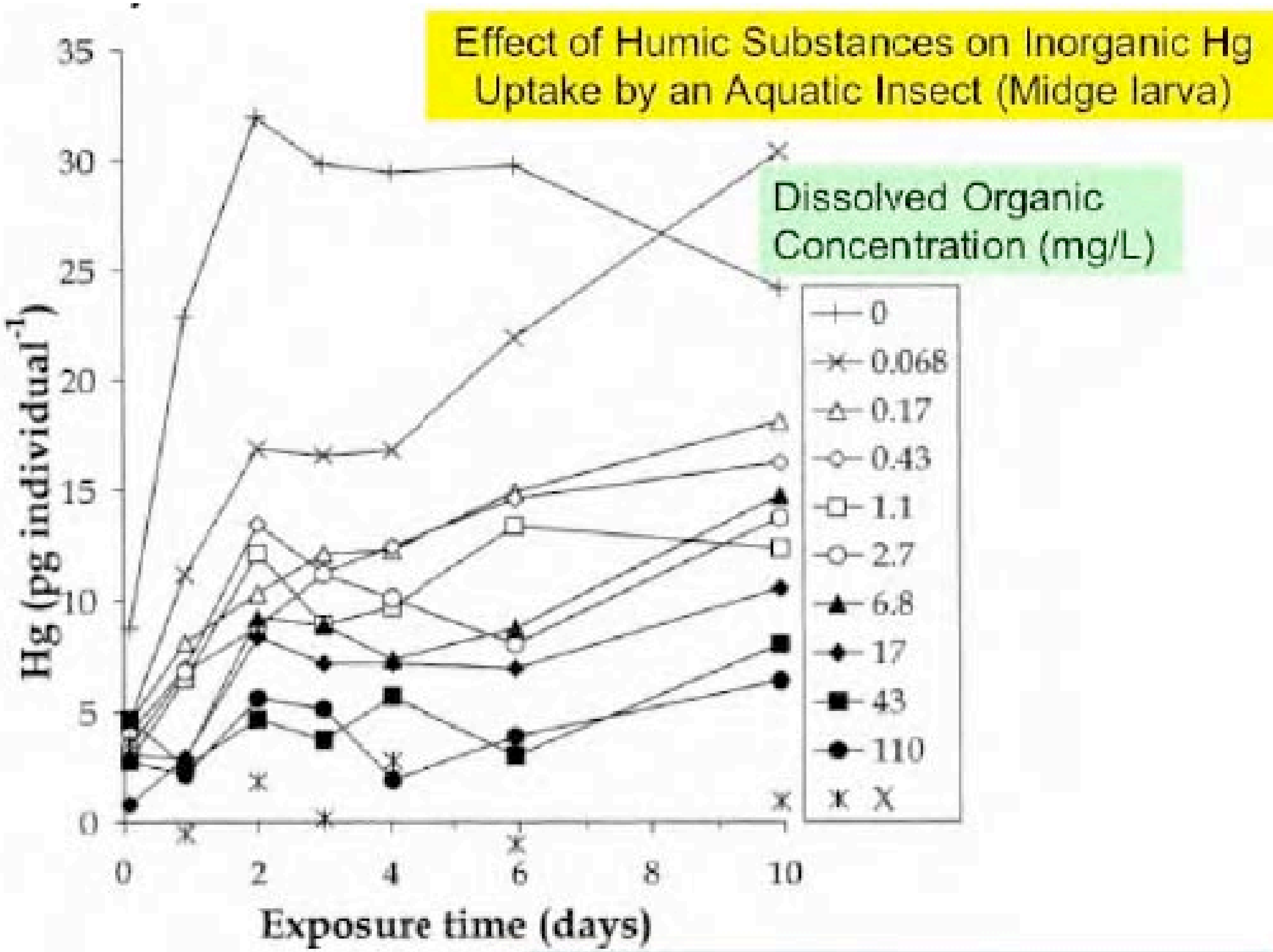


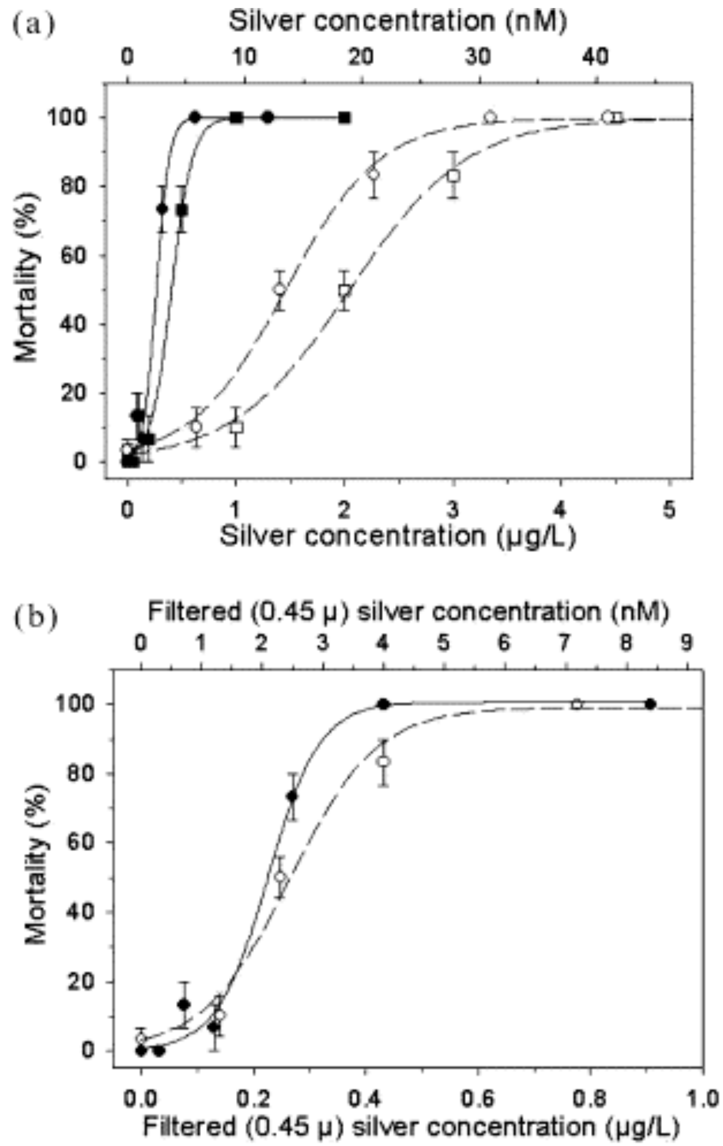
Photo courtesy of Phil Hageman

USGS

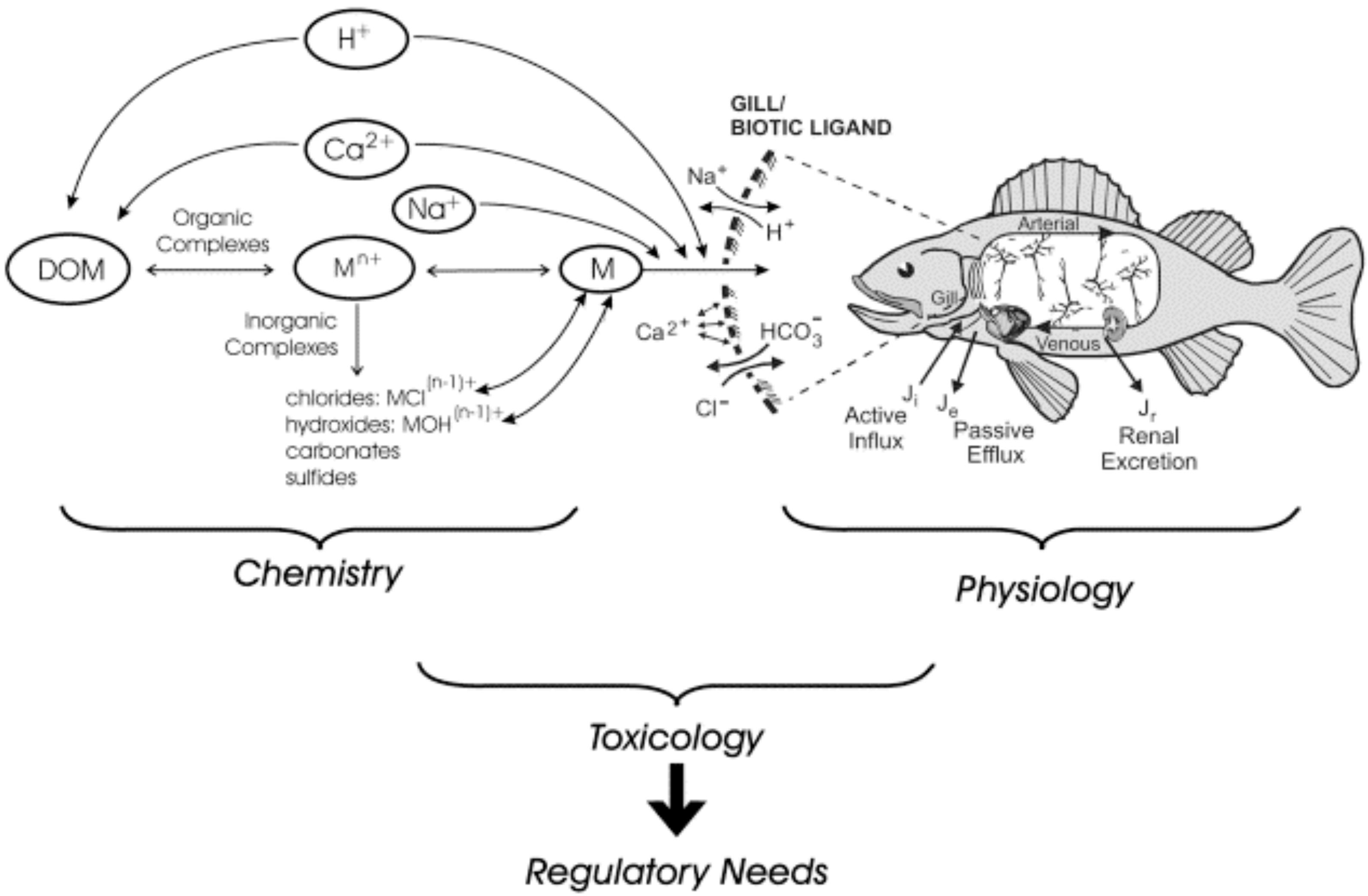


Sjoblom et al. (2000) Sci. Total Environ. 261:115

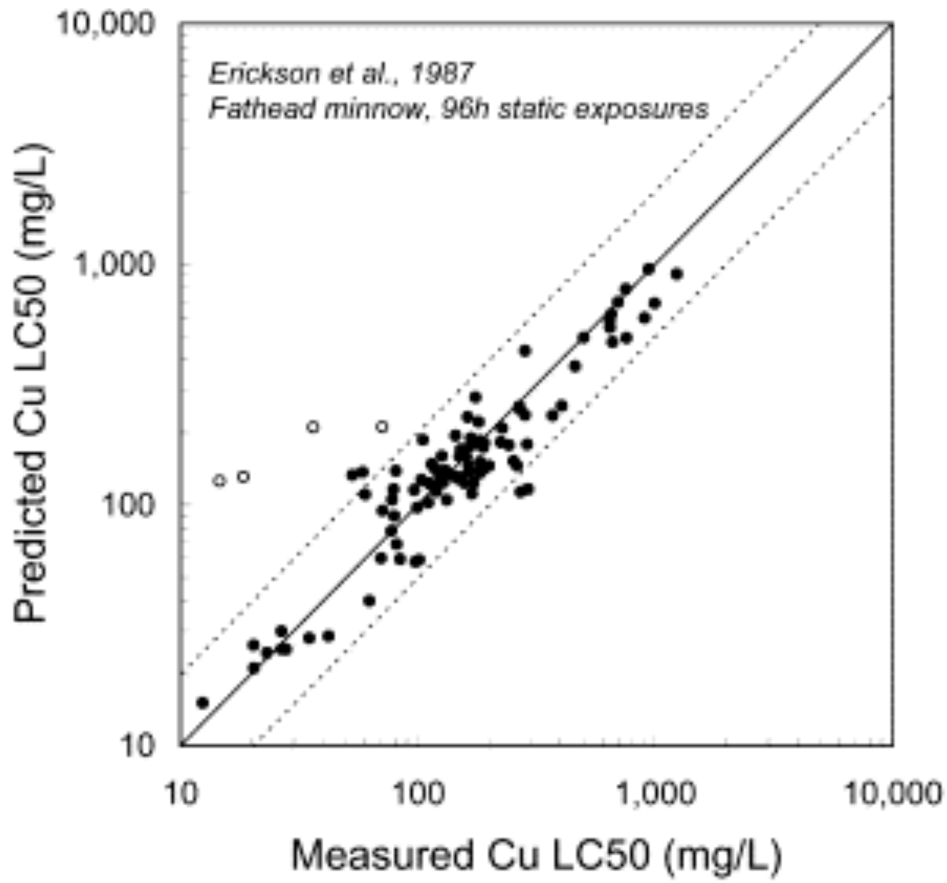
How sulfide affects toxicity



Biotic Ligand Model



BLM works for some metals

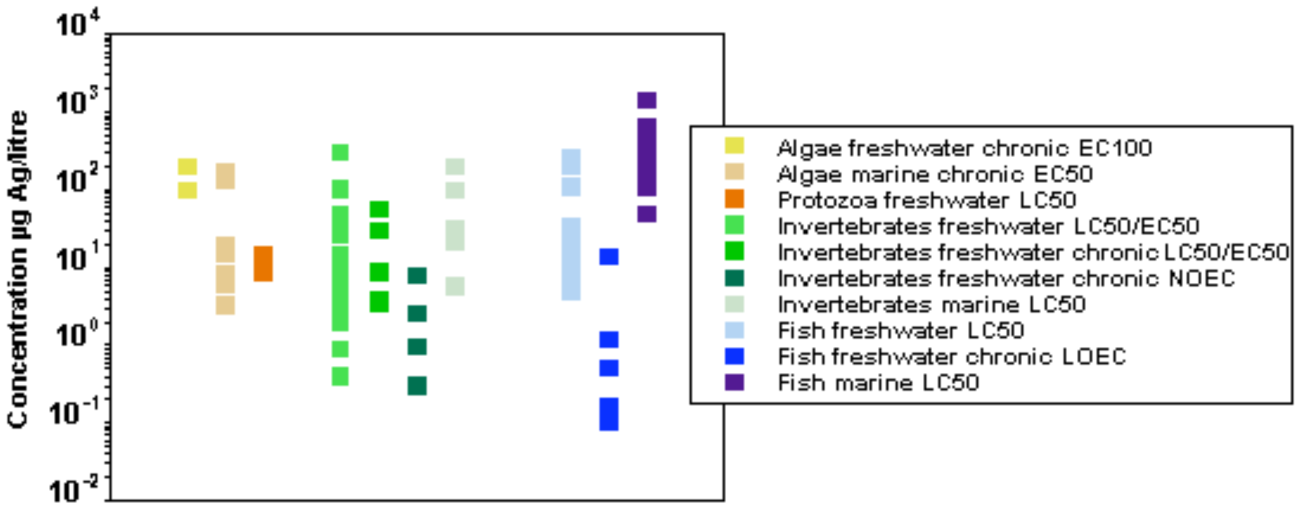


Silver

- ~15M kg of silver mined in 1999
- In US, ~2.5M kg enters the environment annually
  - ~30% to aqueous and 68% terrestrial
  - 30% of release is natural weathering
  - 30-50% is due to photography
- Sources of silver
  - Photographic processing waste
  - Metal smelting
  - Metal plating
  - Pharmaceuticals
  - biocides
  - Natural weathering

Silver toxicity

Figure 1: Plot of reported toxicity values
for silver (as the nitrate) in aquatic organisms



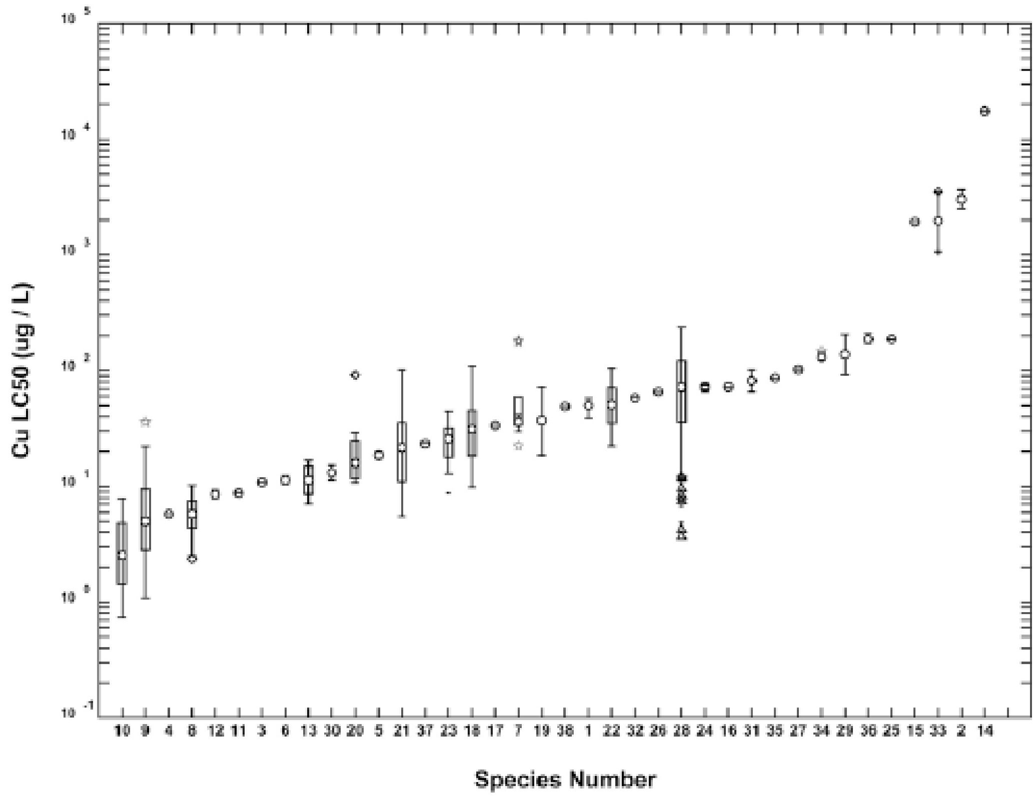
- Free silver ion is very toxic
- LC50 for FW invertebrates is often below 1 ug/L (daphnids and amphipods) and ragnes up to 300 for snails, FW fish usually range from 5-50 ug/L and leopard frogs are very sensitive with EC50 for growth and development of less than 1ppb
- Much less toxic in marine environments, due to high chloride concentration

Sources of Copper

- More than 19M metric tonnes (19B kg) of copper are used worldwide each year. ~30% comes from recycled materials.
- ~70 million pounds of copper are released into the environment in the US each year (~1.4B lbs/yr worldwide), mostly to terrrestrial sources
  - Mining and smelting
  - Printed Circuit board and metal finishing
  - Cooling water systems
  - Vehicle service facilities
  - Root control products (up to 25% copper)
  - Corrosion of copper pipes
  - Brake pads
  - Copper anti-fouling paints for ships

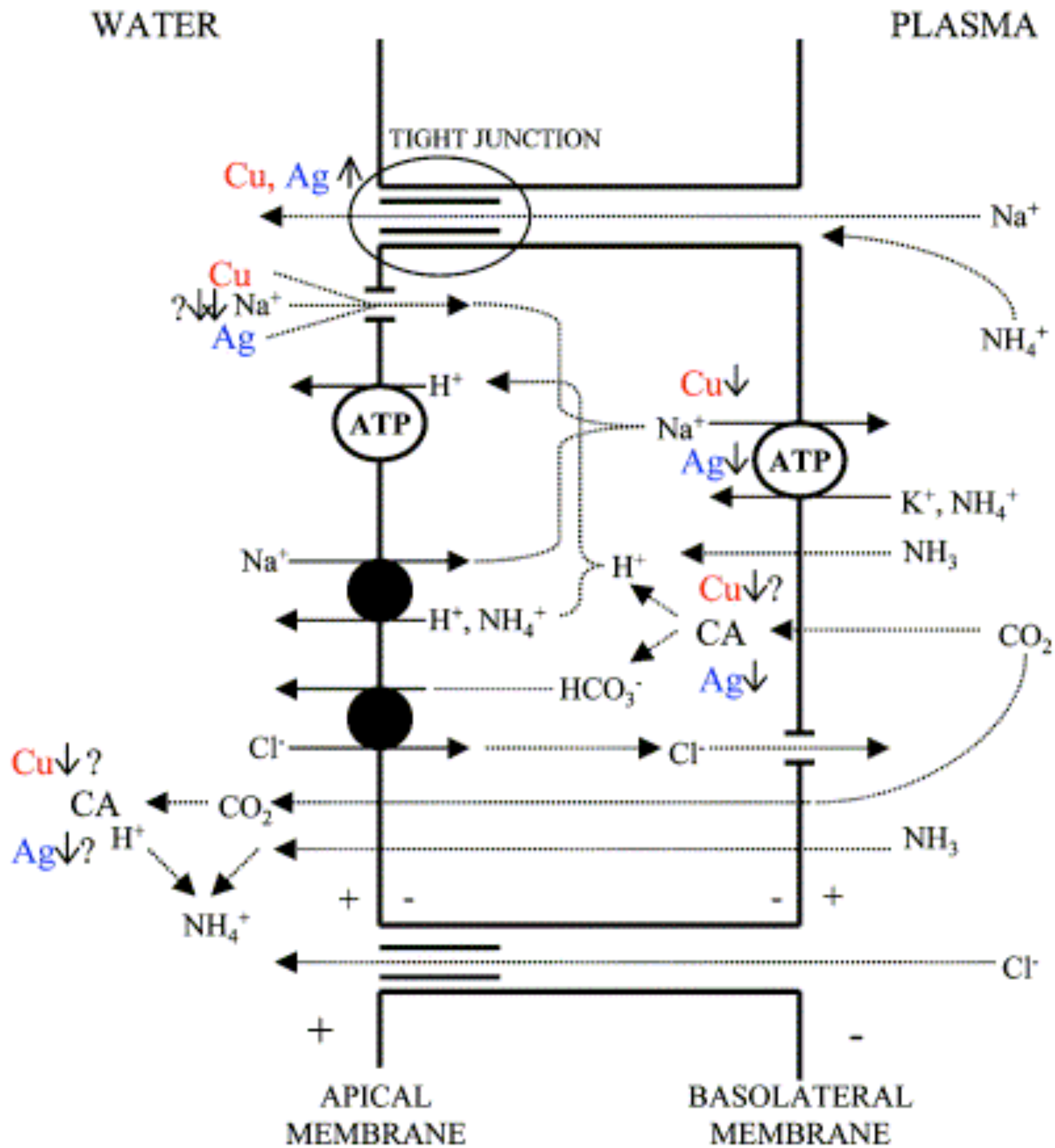
Copper toxicity

- LC50 values for most freshwater organisms are in the 10-200 ug/L range
- LC50 for marine organisms tends to be 100-1000+ ug/L



Mechanisms of silver and copper toxicity

- Silver and copper are ionoregulatory toxicants
- Inhibition of Na^+ uptake and Na^+/K^+-ATPase leads to loss of sodium from organism
- Freshwater organisms must take up sodium from the water to account for diffusive loss


WATER
PLASMA
TIGHT JUNCTION
Cu, Ag
Na+
Cu
?
Na+
Ag
NH4+
H+
ATP
Cu
Na+
Ag
ATP
K+, NH4+
NH3
Na+
H+
Cu ?
H+, NH4+
CA
CO2
HCO3-
Ag
Cl-
Cl-
Cu ?
CA
CO2
Ag ?
H+
NH3
NH4+
+
-
-
+
Cl-
+
-
APICAL
MEMBRANE
BASOLATERAL
MEMBRANE

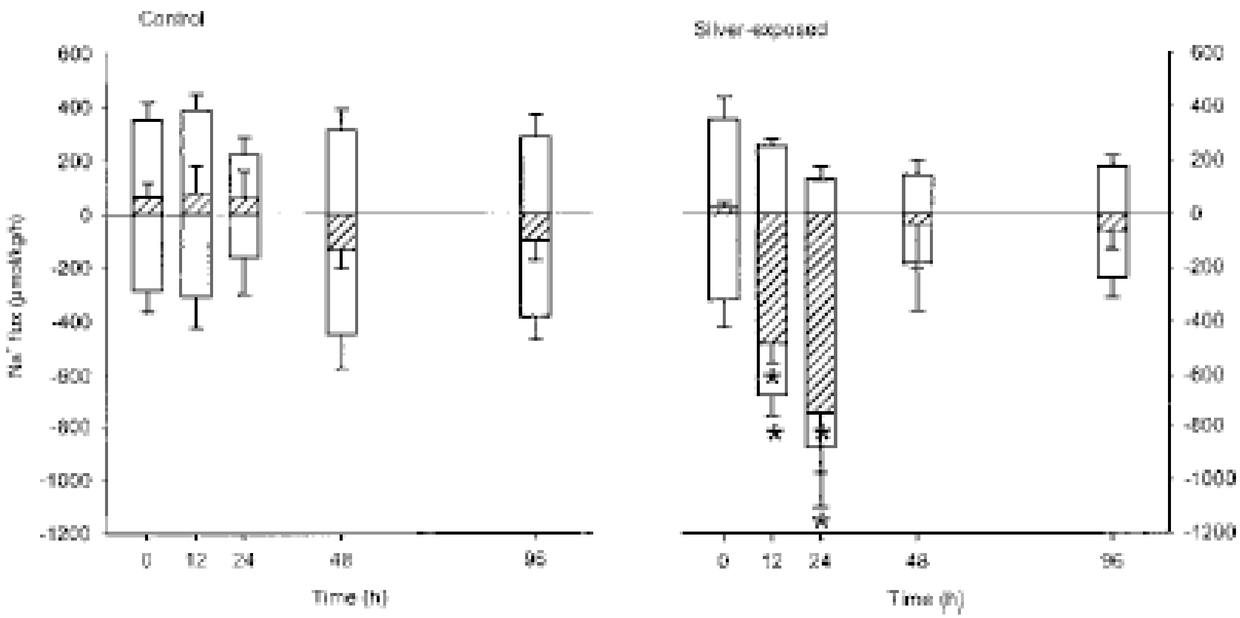


Fig. 1. Unidirectional Na^+ influx (open bars, positive values), efflux (open bars, negative values), and net flux (hatched bars) (μmol/kg/h) in control crayfish (left panel, $n = 8$) and silver-exposed (8.41 μg silver/L) crayfish (right panel, $n = 8$ for 0, 12, 24, and 48 h, $n = 7$ for 96 h). Means ± standard error of the mean (SEM). The asterisk indicates statistically significant difference from corresponding control at $p < 0.05$.

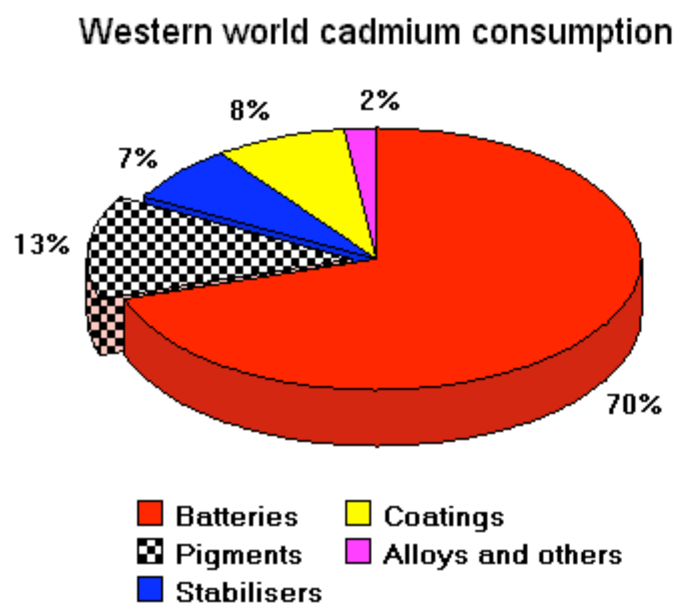
Grosell et al., 2001

Cadmium

- Weathering and erosion of parent rocks releases an estimated 15,000 metric tonnes (mt) per annum,
- Volcanic activity is also a major natural source of cadmium release to the atmosphere, and estimates on the amount have been placed as high as 820 mt per year
- Forest fires have also been reported as a natural source of cadmium air emissions, with estimates from 1 to 70 mt emitted to the atmosphere each year
- In the US, annual release of cadmium from industry ranges from 9-15M pounds, with ~80% released to land and 20% to water

Uses of Cadmium

- Nickel-Cadmium Batteries ·
- Cadmium Pigmented Plastics, Ceramics, Glasses, Paints and Enamels ·
- Cadmium Stabilised Polyvinylchloride (PVC) Products ·
- Cadmium Coated Ferrous and Non-ferrous Products ·
- Cadmium Alloys ·
- Cadmium Electronic Compounds
- Non-ferrous Metals and Alloys of Zinc, Lead and Copper ·
- Fossil Fuels (Coal, Oil, Gas, Peat and Wood) ·
- Cement ·
- Phosphate Fertilisers

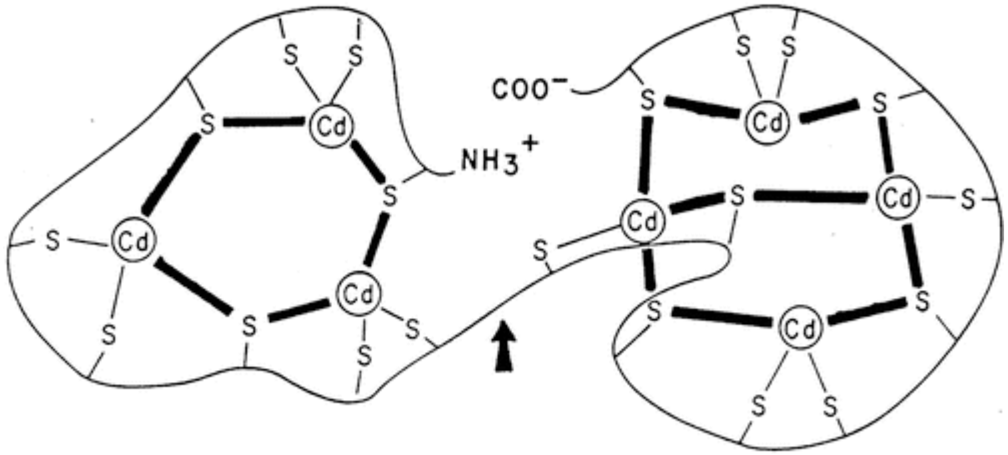


Cadmium inputs

Source	Input (thousand metric tons/yr)
Atmospheric deposition	0.9 - 3.6
Smelting and refining nonferrous metals	0.01 – 3.6
Manufacturing processes	
Chemicals	0.1 – 2.5
Metals	0.5 – 1.8
Domestic wastewater	
Central	0.2- 1.8
Non-central	0.3 – 1.2
Discharge of sewage sludge	0.1 – 1.3
Steam electricity production	0.01 – 0.24
Base metal mining and dressing	0 – 0.3
Total Input	2.1 – 17

Cadmium toxicity

- Cadmium is readily accumulated by microorganisms and molluscs; BCFs can be >1000
- Cadmium accumulates over the lifetime of most organisms due to very long half-life
- Most cadmium is bound to metallothionein and is stored in liver or kidney
- Acute toxicity occurs in most species between 5 and 30 ug/L
- Toxicity is reduced by increasing water hardness

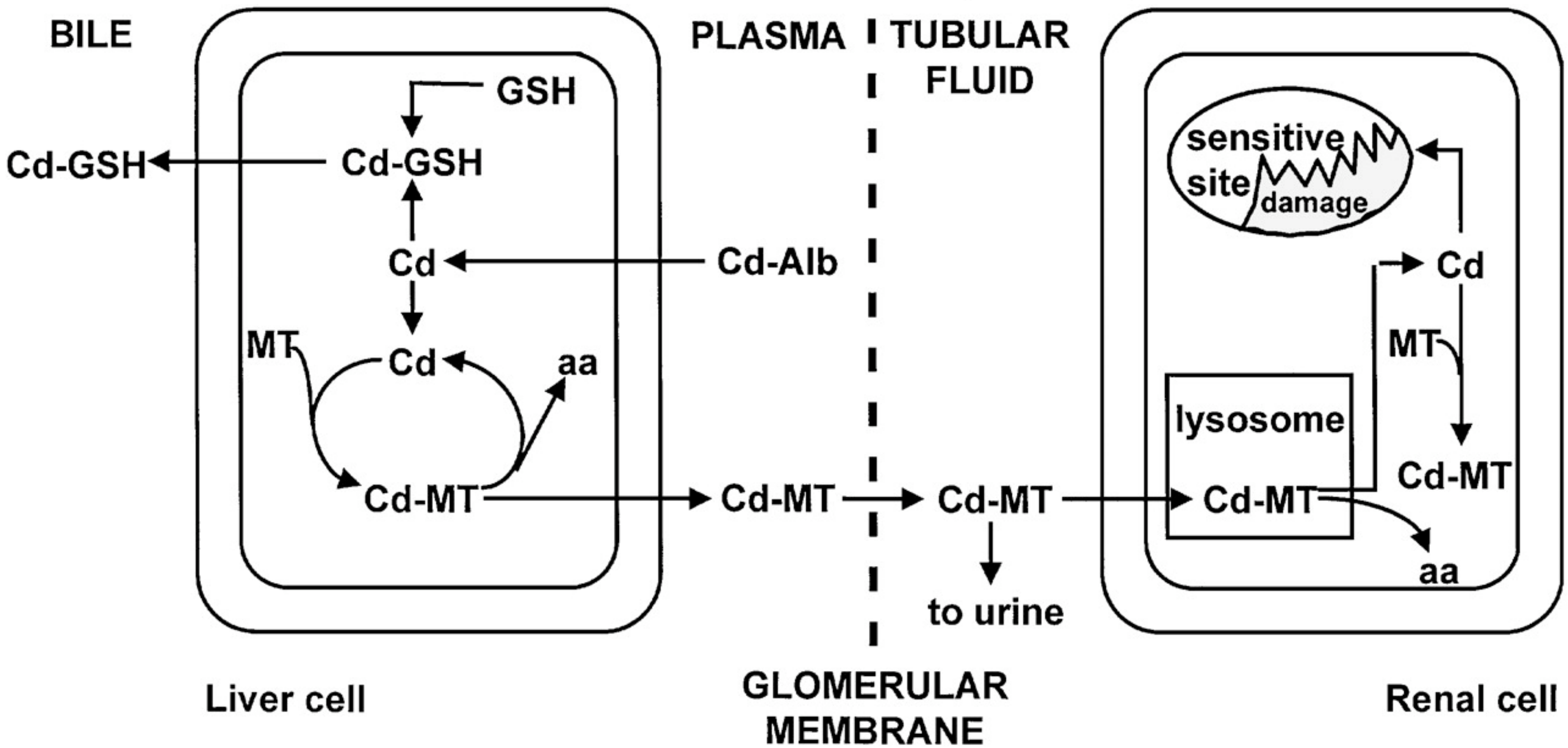


Cd_3 CLUSTER

(β-domain)

Cd_4 CLUSTER

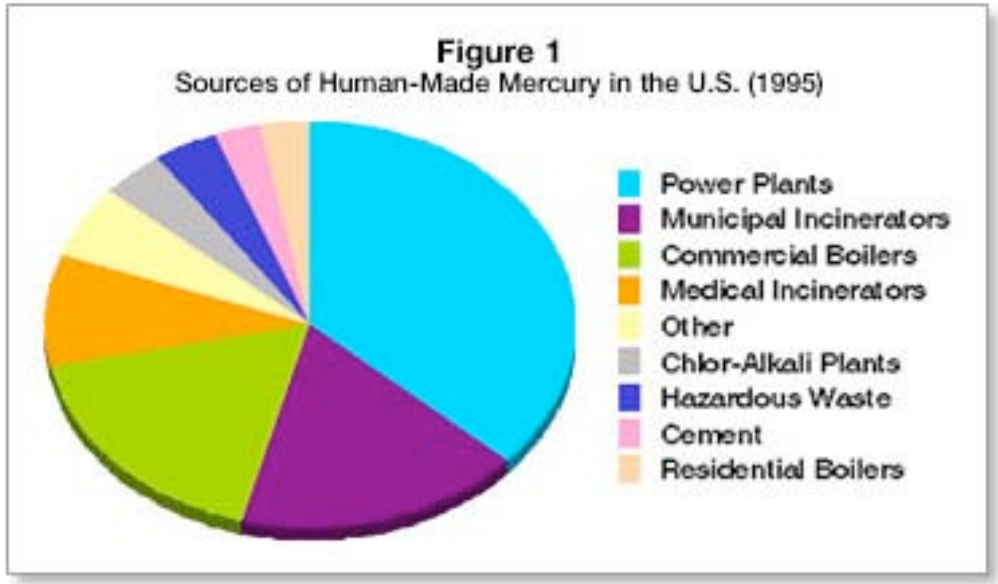
(α-domain)



- Cadmium binds to –SH groups on various enzymes, leading to inhibition
- Causes functional hypocalcemia, perhaps due to competition with Ca^{2+} or inhibition of Ca retention by kidney.

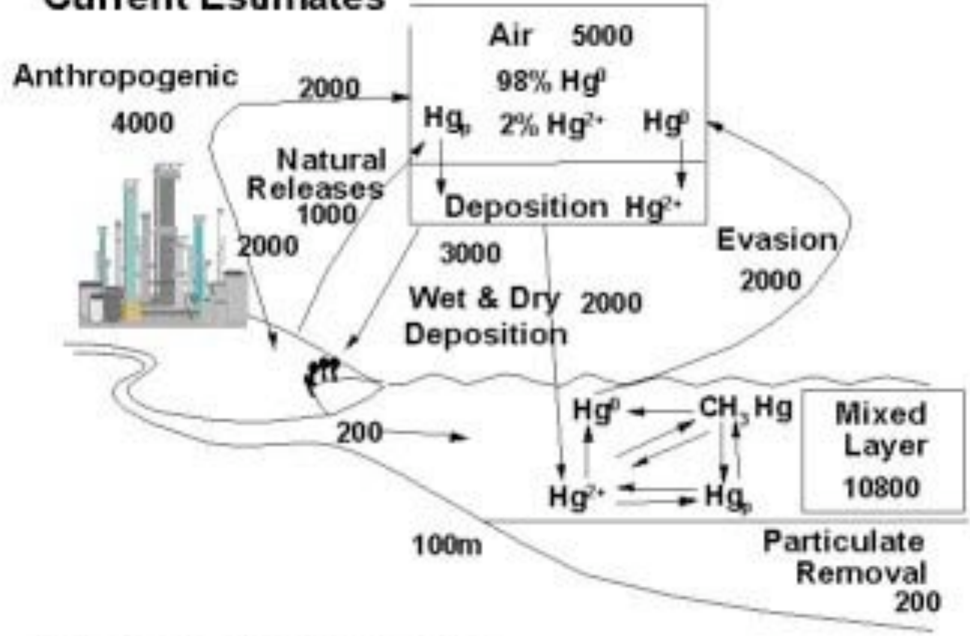
US Mercury emissions

- Anthropogenic sources of mercury (67%, 80 tons/yr)
  - Coal burning power plants (account for 40% of US anthropogenic emissions)
  - Waste incineration
  - Gold production
  - Cement production
  - Production of chlorine gas and caustic soda
  - Metal smelting
  - Broken fluorescent lights
- Forest fires, volcanoes (33%, `40 tons/year)

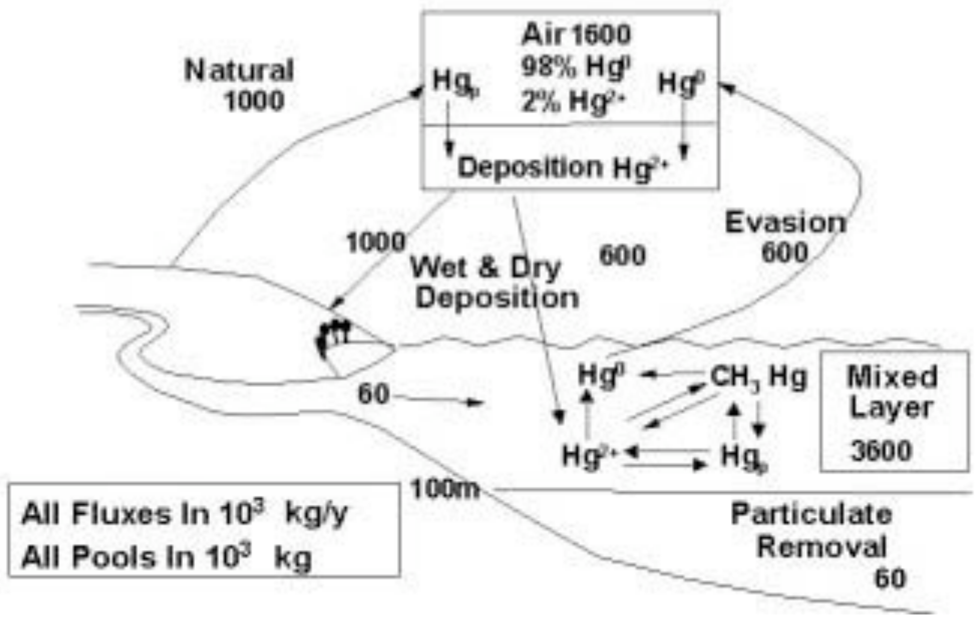


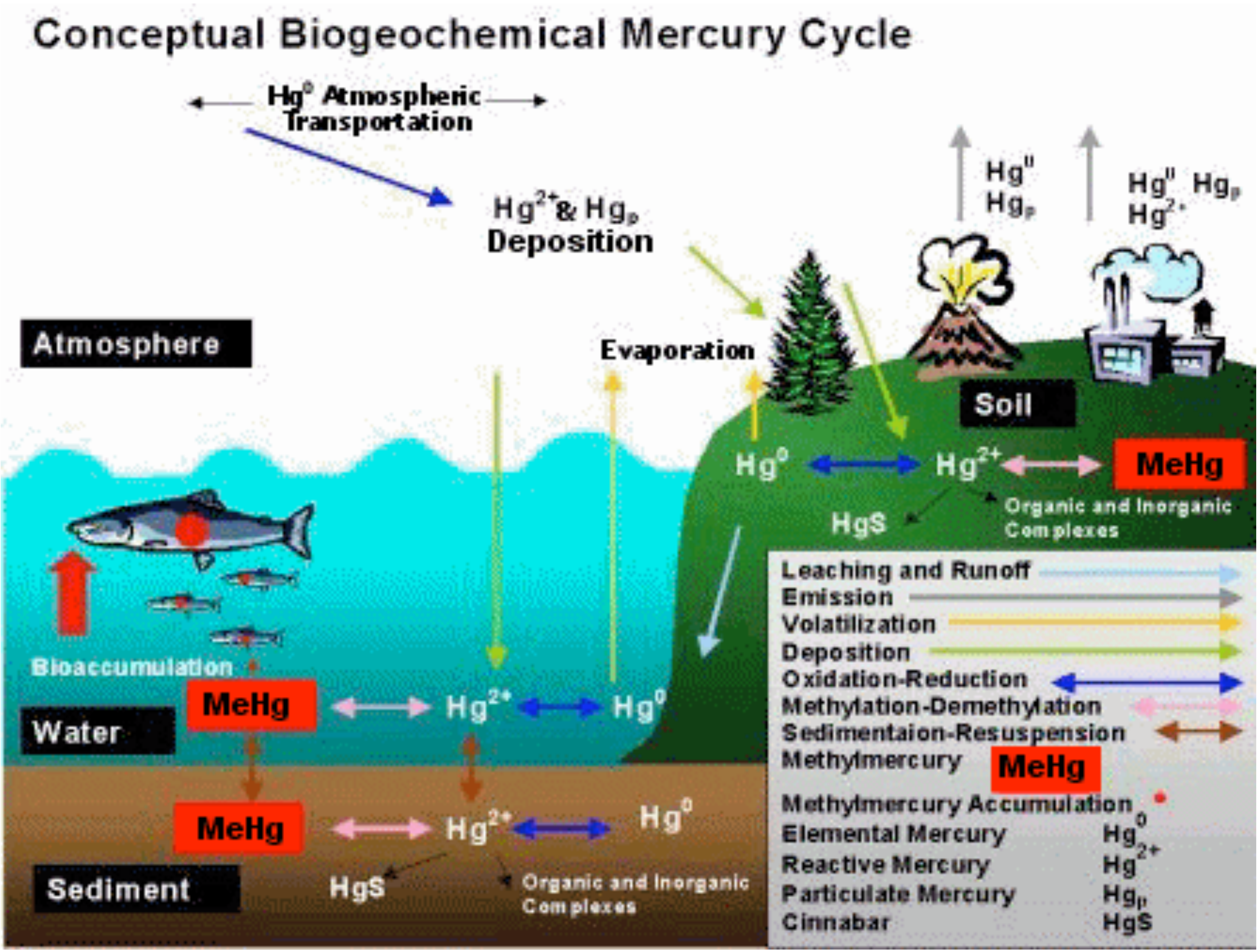
The Global Mercury Budget

Current Estimates

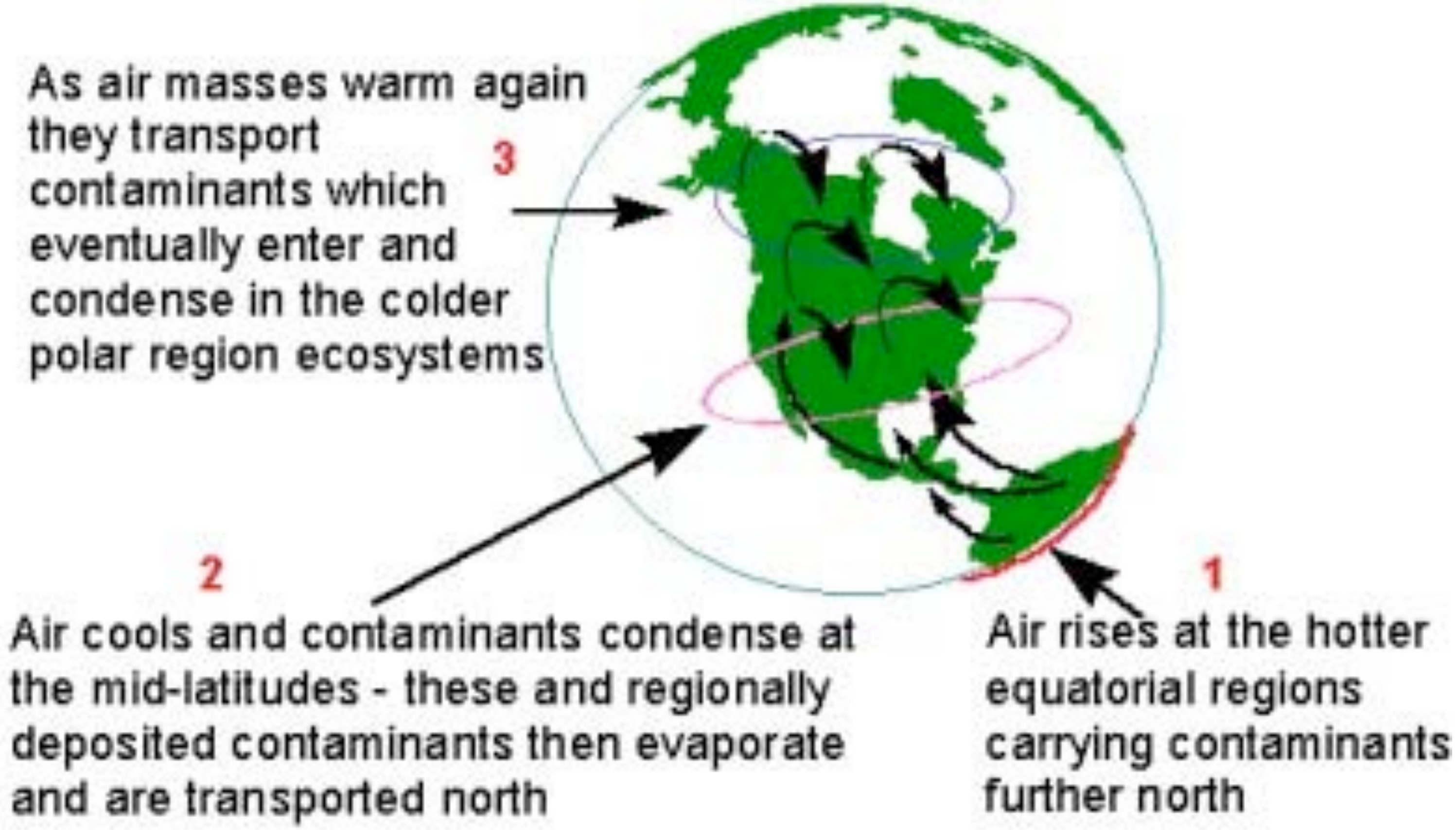


Pre-Industrial Estimates




Conceptual Biogeochemical Mercury Cycle
Hg⁰ Atmospheric Transportation
Hg²⁺ & Hgₚ Deposition
Hg⁰ Hgₚ
Hg⁰ Hgₚ Hg²⁺
Atmosphere
Evaporation
Soil
Hg⁰
Hg²⁺
MeHg
HgS
Organic and Inorganic Complexes
Bioaccumulation
MeHg
Hg²⁺
Hg⁰
Water
MeHg
Hg²⁺
Hg⁰
Sediment
HgS
Organic and Inorganic Complexes
Leaching and Runoff
Emission
Volatilization
Deposition
Oxidation-Reduction
Methylation-Demethylation
Sedimentaion-Resuspension
Methylmercury MeHg
Methylmercury Accumulation
Elemental Mercury Hg⁰
Reactive Mercury Hg²⁺
Particulate Mercury Hgₚ
Cinnabar HgS

Mercury in Canada's North and East: The Grasshopper Effect also known as Global Distillation



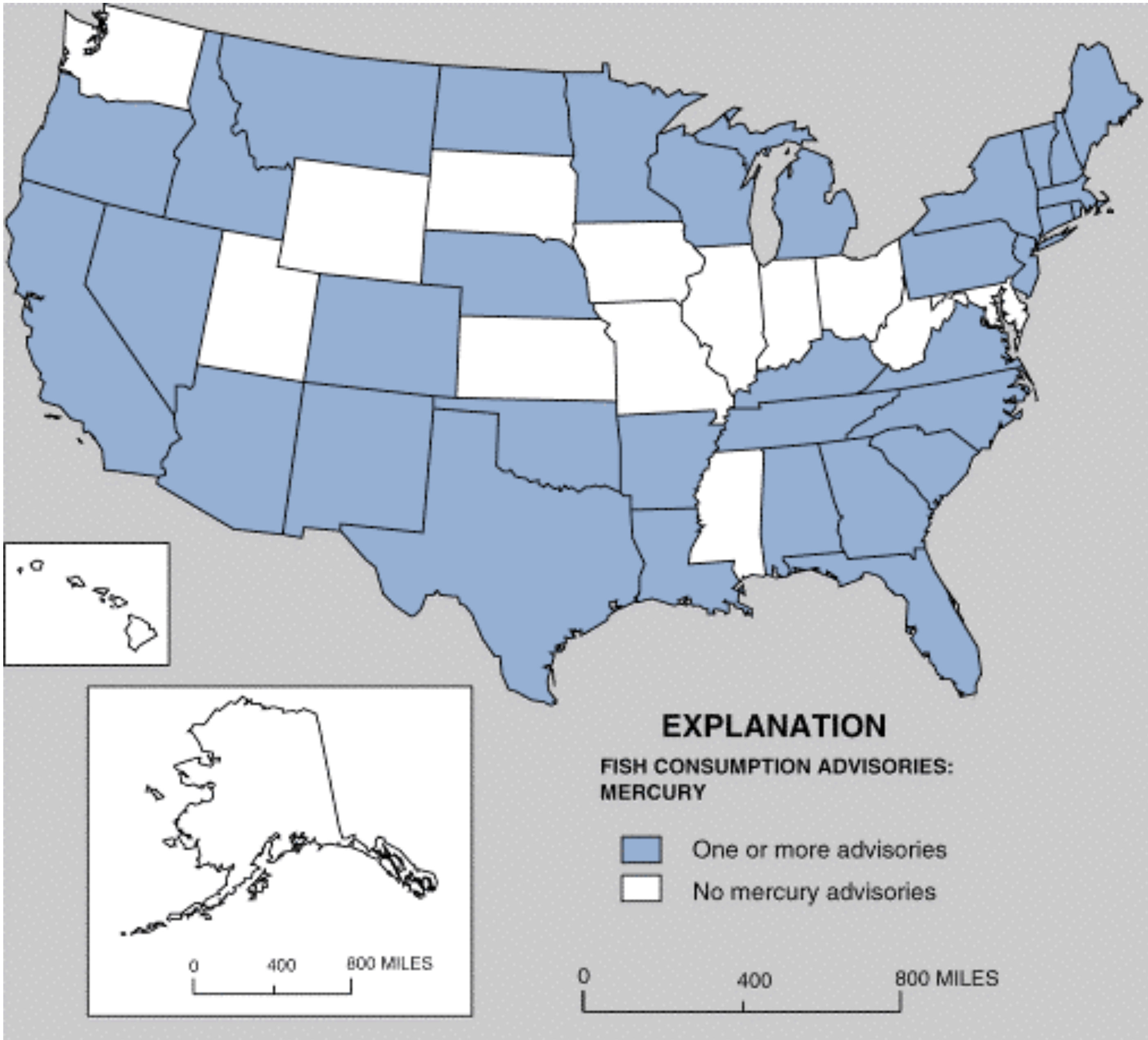


Figure 1. *States with at least one fish consumption advisory for mercury. Source: USEPA Fish Consumption Data Base*

Toxicity of Mercury

- Toxicity depends on form of mercury
- Inorganic mercury ($Hg2+$) causes toxicity primarily by binding to –SH groups and inhibiting enzymes. Generally larval or juvenile stages are most susceptible. Causes poor growth and development. Kidney damage is prominent. Plants are resistant to inorganic mercury toxicity
- Methylmercury causes primarily neurological damage. Developing organisms are very sensitive to methylmercury. It is bioaccumulated in the food chain.

Iron Mountain Mine

- 4400 acre mine near Redding, CA operated from 1890-1963, extracting copper (313M lbs), silver (24M oz), and zinc
- Largest Superfund site in US
- Mine is in huge pyrite deposit (iron sulfide)
- When sulfide reacts with oxygen and water, releases sulfuric acid

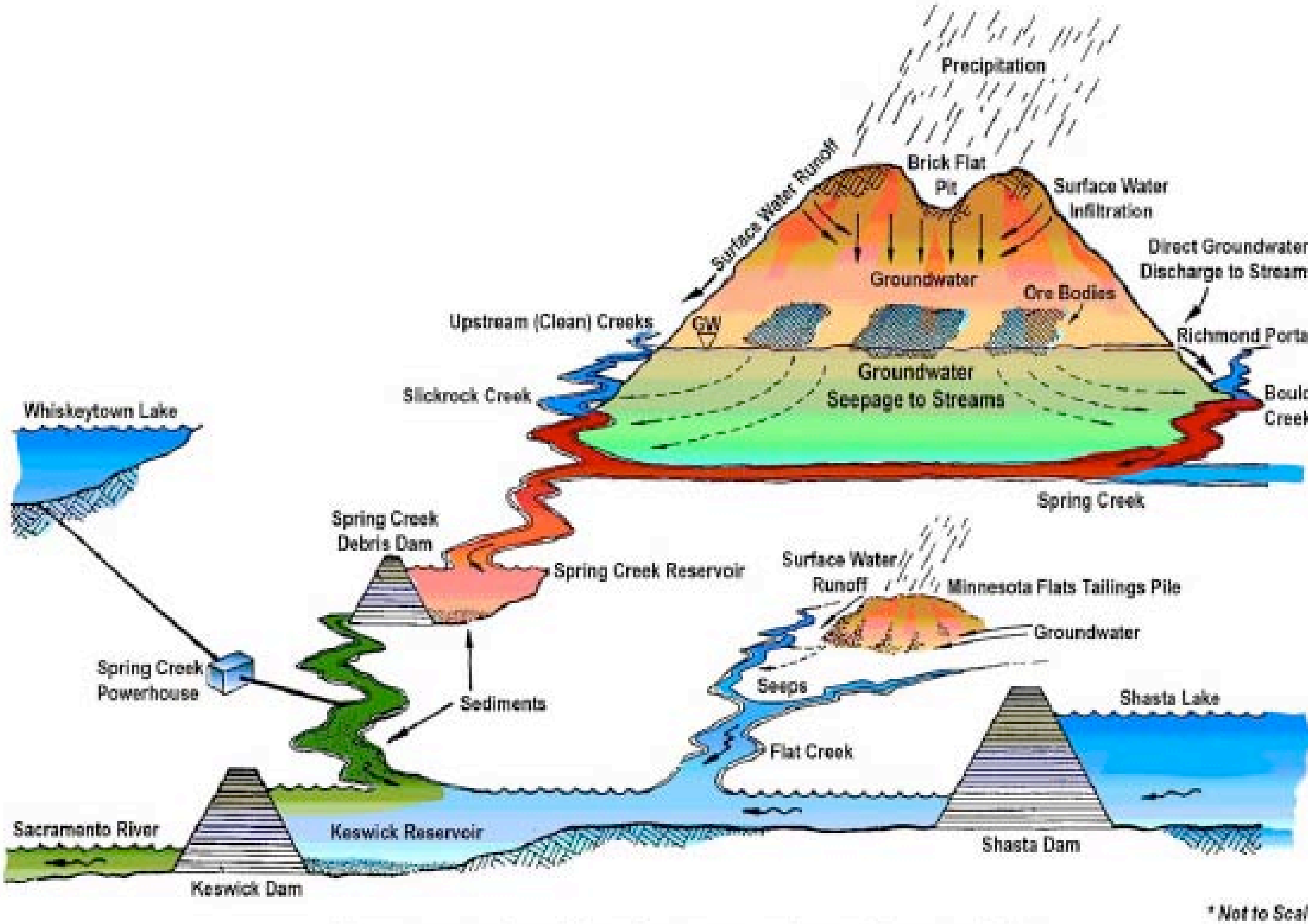


DIAGRAM OF ACID MINE DRAINAGE AT IRON MOUNTAIN MINE

- Water coming out of Iron Mountain is more acidic than battery acid
- Low pH dramatically increases dissolution of metals
- Prior to clean-up, site discharged 5 tons of Fe, 650 lbs of Cu and 1,800 lbs of Zn per day
- Accounted for 25% of entire US release of Cu
- More than 20 episodes were recorded where >100,000 fish were killed

Photo 5: According to EPA documents, workers once inadvertently left a shovel standing in the green liquid flowing from one of the mine portals. The next day half of the shovel had been eaten away.

Remediation of IMM

- Eventually a $950M settlement was reached with Aventis
- EPA constructed a lime neutralization facility with sludge collection
- 95% removal of metals from effluent
- Settlement has a balloon payment of $500M in 2030 for long term activities
- Will take 2,500 – 3,000 years for sulfide to be eliminated

Photo 6: Part of the lime neutralization/high-density sludge acid mine drainage treatment plant at Minnesota Flats. The large tank at center-left is one of two in which acid mine drainage is mixed with lime slurry.