# IMPACTS OF METALS ON AQUATIC ECOSYSTEMS AND HUMAN HEALTH

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# TOPICS TO BE COVERED

- Properties of metals
- How metals enter aquatic ecosystems
- Principles of metal toxicity
- Factors affecting metal toxicity
- Impacts of specific metals – mercury, cadmium, lead, copper

# PROPERTIES OF METALS

- Elements in rocks and mineral ores
- Released to environment by erosion, as well as generated by human activities.
- Form positively charged ions (cations).
- Solid at normal temperature and pressure
- Good conductors of heat and electricity
- Luster, malleability, and ductility

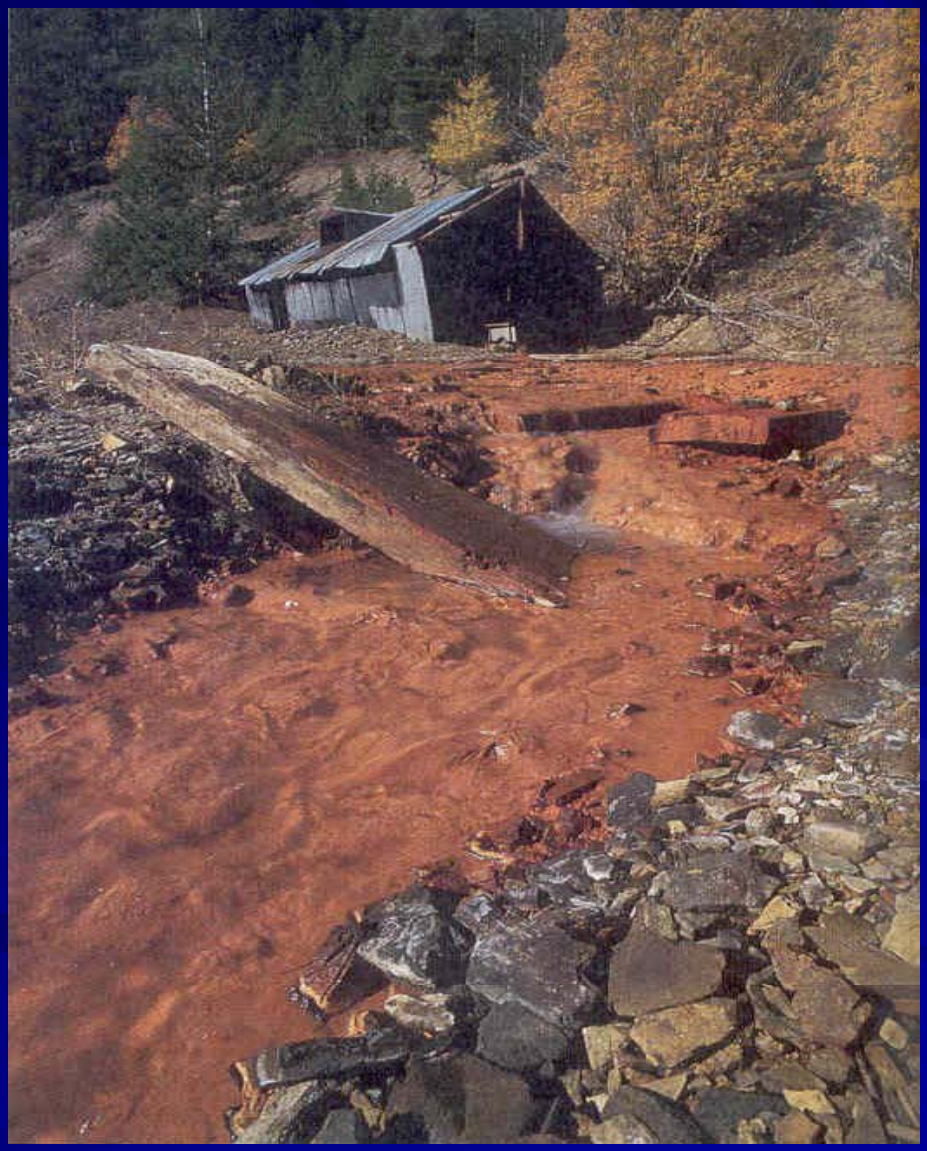
# PROPERTIES OF METALS

- Dissolve in water and are easily absorbed into fish and other aquatic organisms.
- Small concentrations can be toxic.
- Toxic metals contribute to point and nonpoint water pollution.

# MINING AND DISCHARGE OF METALS

- Direct disposal of mine tailings into waterbodies
- Production of acid rock drainage (ARD)
- Leaching of mine tailings and ARD from operating and abandoned mines into surface water and groundwater

# ACID ROCK DRAINAGE



# OTHER SOURCES OF METAL DISCHARGES

- Agricultural activities – fertilizers, soil amendments from biosolids
- Coal combustion – arsenic, cadmium, selenium, zinc
- Urban runoff – copper, lead, zinc
- Industrial waste
- Solid waste disposal – batteries, tires, appliances

# ESSENTIAL METALS

**Low concentrations are needed for good health. High concentrations are toxic.**

- **Chromium (Cr)**
- **Copper (Cu)**
- **Zinc (Zn)**
- **Nickel (Ni)**
- **Manganese (Mn)**
- **Selenium (Se)**

# NON-ESSENTIAL METALS

- Aluminum (Al)
- Arsenic (As)
- Cadmium (Cd)
- Gold (Au)
- Lead (Pb)
- Mercury (Hg)
- Silver (Ag)
- Tin (Sn)

# METAL TOXICITY

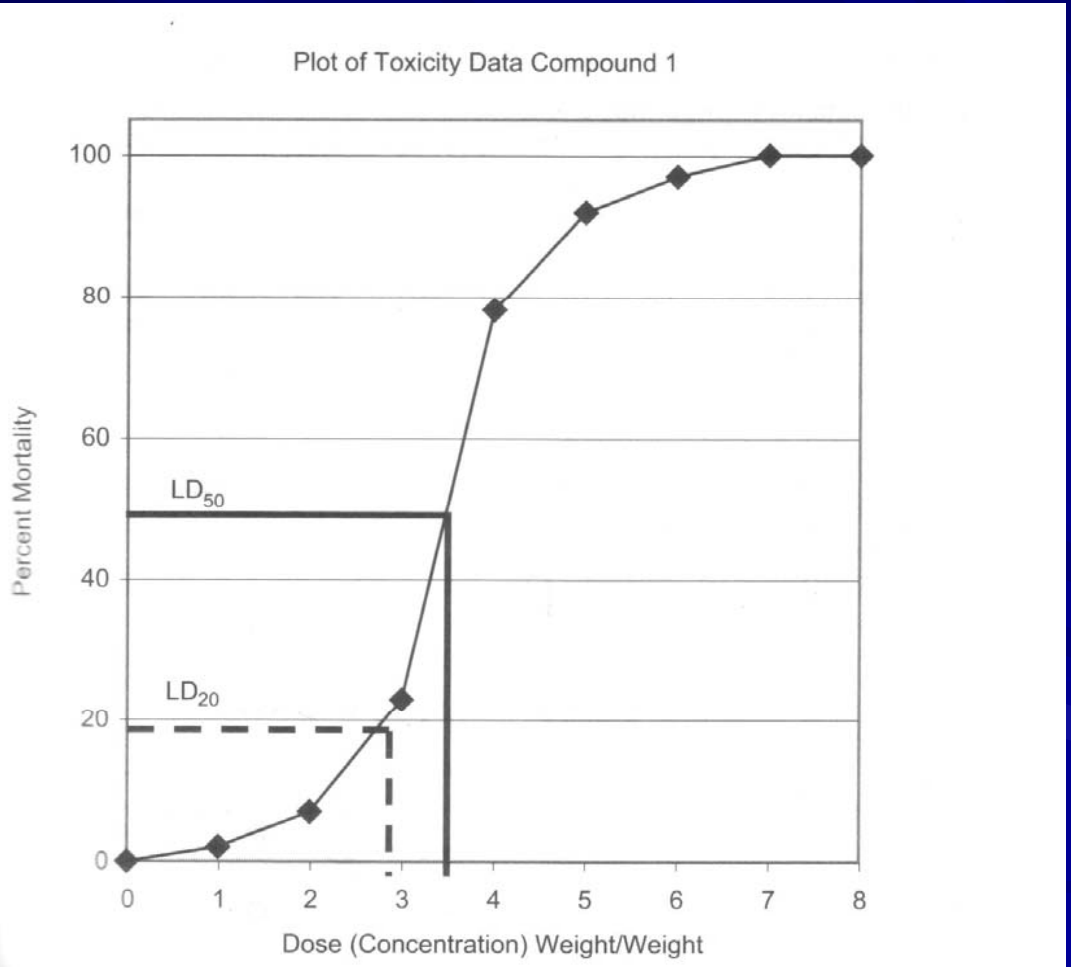
Adverse biological effects of a metal on an organism's

- Survival
- Activity
- Growth
- Metabolism
- Reproduction

# TOXICITY MEASUREMENTS

- $LC_{50}$ (lethal concentration 50) - causes death in 50% of the organisms in an exposed population.
- $EC_{50}$ (effective concentration 50) – causes nonlethal negative effect in 50% of the exposed organisms.
- The lower the $LC_{50}$ or $EC_{50}$, the more toxic the metal.

# DOSE-RESPONSE CURVE

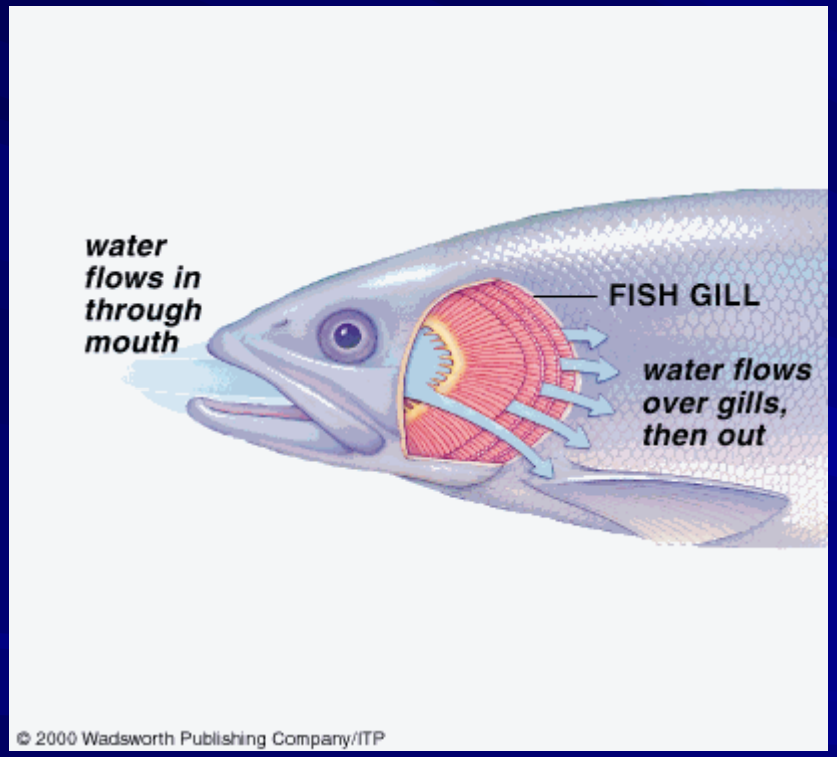



dose-response curve. Converted from the discontinuous bar graph of Figure 3.2 to
mortality is a continuous function of the toxicant, the result is the typical sigmoid

# METAL EXPOSURE PATHWAYS IN FISH

- Gills – diffusion across membranes into bloodstream
- Skin – diffusion into bloodstream
- Drinking water
- Ingestion of sediments
- Food chain

# FISH GILLS (www.sci.sdsu.edu; www.diatribune.com/marine-life-series)




# METAL EXPOSURE PATHWAYS IN HUMANS

- **Lungs – inhaled particulates**
- **Skin**
- **Drinking metal-polluted water**
- **Food chain – eating other animals or plants that have been exposed**

(Wright and Welbourn, 2002)

# MODES OF ACTION

- Metal injures an organ by causing structural damage (lesions) to the tissues (e.g., Hg damages brain).
- Metal inhibits or inactivates an enzyme or an enzyme cofactor.

# FACTORS AFFECTING METAL TOXICITY

- Concentration
- Mode and time of exposure
- Chemical factors
- Interaction of metals
- Water temperature
- Biological factors

# BIOCONCENTRATION (BIOACCUMULATION)

- Increase in concentration of a metal in an organism compared to its concentration in water or sediments
- Animals such as shellfish that live in sediments are especially vulnerable.
- All metals undergo bioconcentration.

# BIOMAGNIFICATION

- Increase in concentration of metals in successively higher trophic levels of a food chain
- Predators have higher concentrations than their prey.
- Animals at top of food chain have highest concentrations.
- Pertains to Hg and possibly Cd, Mn, Se

# CONCENTRATION AND EXPOSURE MODE AND TIME

- Exposure to high concentrations often results in acute effects.
- Exposure to low concentrations may result in chronic effects.
- Continuous exposure is more detrimental than intermittent exposure.

# CHEMICAL FACTORS

- Bioavailability/speciation
- pH
- Buffering capacity
- Salinity
- Hardness

# BIOAVAILABILITY/SPECIATION

- Concentration of a metal is not good predictor of its biological effect.
- Metal must be in form that can be "seen" by biological system (e.g., dissolved) and must interact with surface or interior of cells.
- Availability of a metal to enter and affect a biological system

# BIOAVAILABILITY/SPECIATION

- Speciation affects bioavailability.
- Refers to different chemical forms in which a metal exists: neutral element, ions, and organic forms
- Examples: organic and inorganic Hg, $Cr^{+6}$ and $Cr^{+3}$

# pH

- Metals are more toxic at lower pH.
- Hydrogen ion concentration affects metal speciation (e.g., Al).
- Lower pH releases metals from sediments.  Higher pH binds metals (e.g., Mn) in sediments

# BUFFERING CAPACITY

- Buffering capacity of a waterbody depends on concentration of carbonate and bicarbonate ions and affects vulnerability of an aquatic ecosystem to ARD.
- Metals are less toxic in a buffered waterbody.

# SALINITY

- Metals are more toxic in freshwater than in saltwater because they are more bioavailable in freshwater.
- Salinity affects chemical speciation, e.g., $Cd^{+2}$ is most bioavailable form of Cd and predominates in freshwater. In more saline water, Cd forms chloride complexes which are less bioavailable and therefore less toxic.

# WATER HARDNESS

- Depends on concentration of calcium ions ($Ca^{+2}$)
- Metals are more toxic in soft water.
- $Ca^{+2}$ may provide protective effect.
- U.S., Canada, and Europe base water quality criteria for metals on water hardness.

# INTERACTION OF METALS

- **Additivity (1+1=2) – two metals have twice the effect of either metal.**
- **Synergism (1+1=3) – two metals have more than twice the effect of either metal (e.g., Cd and Cu, Cd and Cr, Cu and Ag, Zn and Ag).**
- **Antagonism (1+1=1.5) – two metals have less than twice the effect of either metal (e.g., Zn and Cd, Zn and Pb, Hg and Se, Hg and Cd).**

# WATER TEMPERATURE

- Metal toxicity increases as water temperature increases.
- Q10 = 2 (metabolism rate in cold-blooded animals doubles with every 10°C increase in water temperature).
- Increased respiratory rate, membrane permeability, and absorption rates

# BIOLOGICAL FACTORS

- Species and individual differences
- Age/body size
- Persistence
- Biotransformation
- Detoxification

# SPECIES AND INDIVIDUAL DIFFERENCES

- Aquatic animals are more sensitive than aquatic plants.
- Daphnids are sensitive freshwater crustaceans.
- Shrimp are sensitive marine crustaceans.
- Salmon and trout are sensitive fish.
- Individual differences in sensitivity within each species

# AGE/BODY SIZE

**Developing and young animals are more sensitive than adults.**

- **Larger surface area/volume ratio, therefore faster toxic chemical uptake per unit weight**
- **Higher breathing and metabolic rates, therefore faster and more uptake of toxic chemicals.**
- **Young animals lack completely developed detoxification enzyme systems.**

# PERSISTENCE

- Biological half life = time required for 50% of the dose of the metal to be eliminated from the organism
- Some metals (e.g., Hg, Cd, Pb) have long half-lives in mammals and can cause serious long-term effects.

# BIOTRANSFORMATION

- Alteration of a metal by an organism
- Toxicity can be increased or decreased.
- Examples – Transformation of inorganic Hg to organic Hg increases Hg toxicity. But transformation of inorganic As to organic As decreases As toxicity.

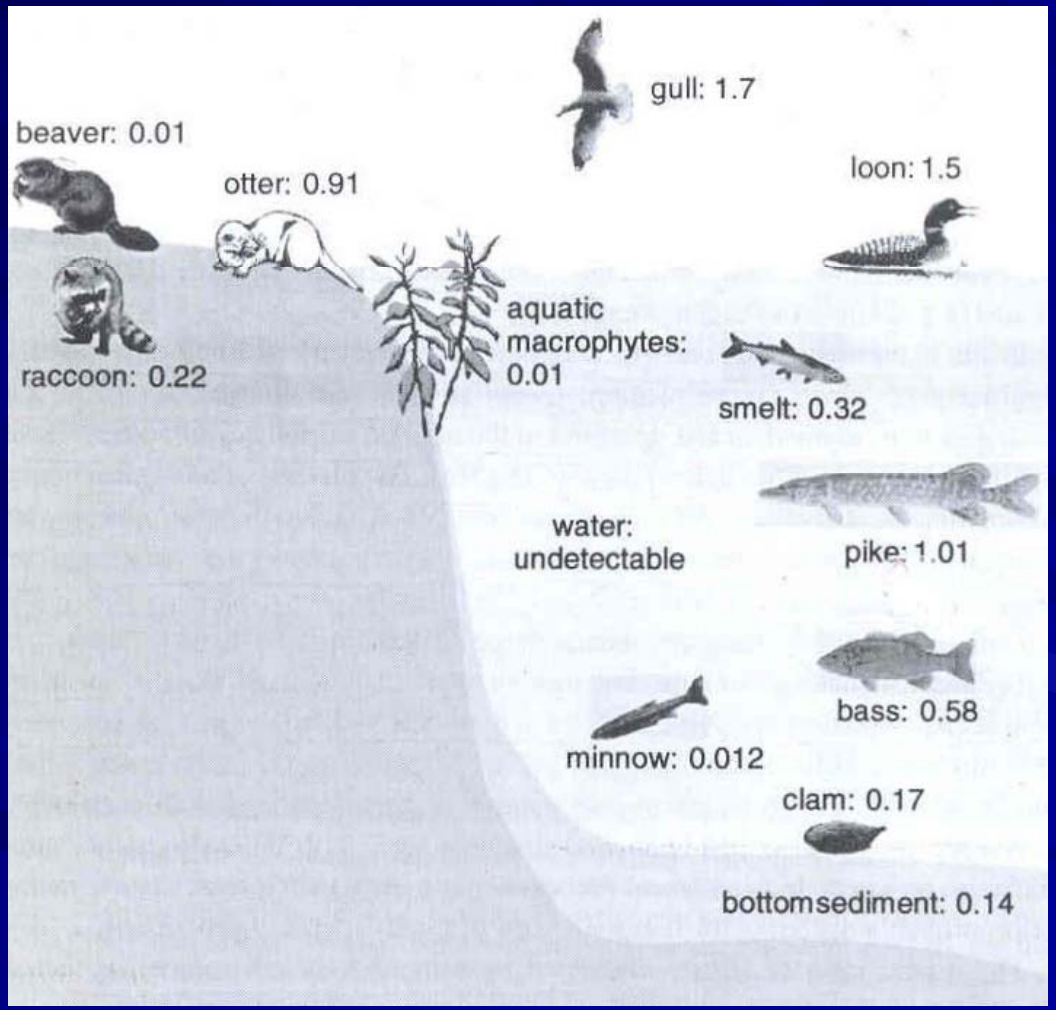
# DETOXIFICATION

- Exposure to metals induces metallothionen, a low molecular weight protein that can bind some metals (e.g., Cd, Cu, Zn) and decrease their toxicity.
- System can become overwhelmed if metal concentration is high or exposure is continuous.

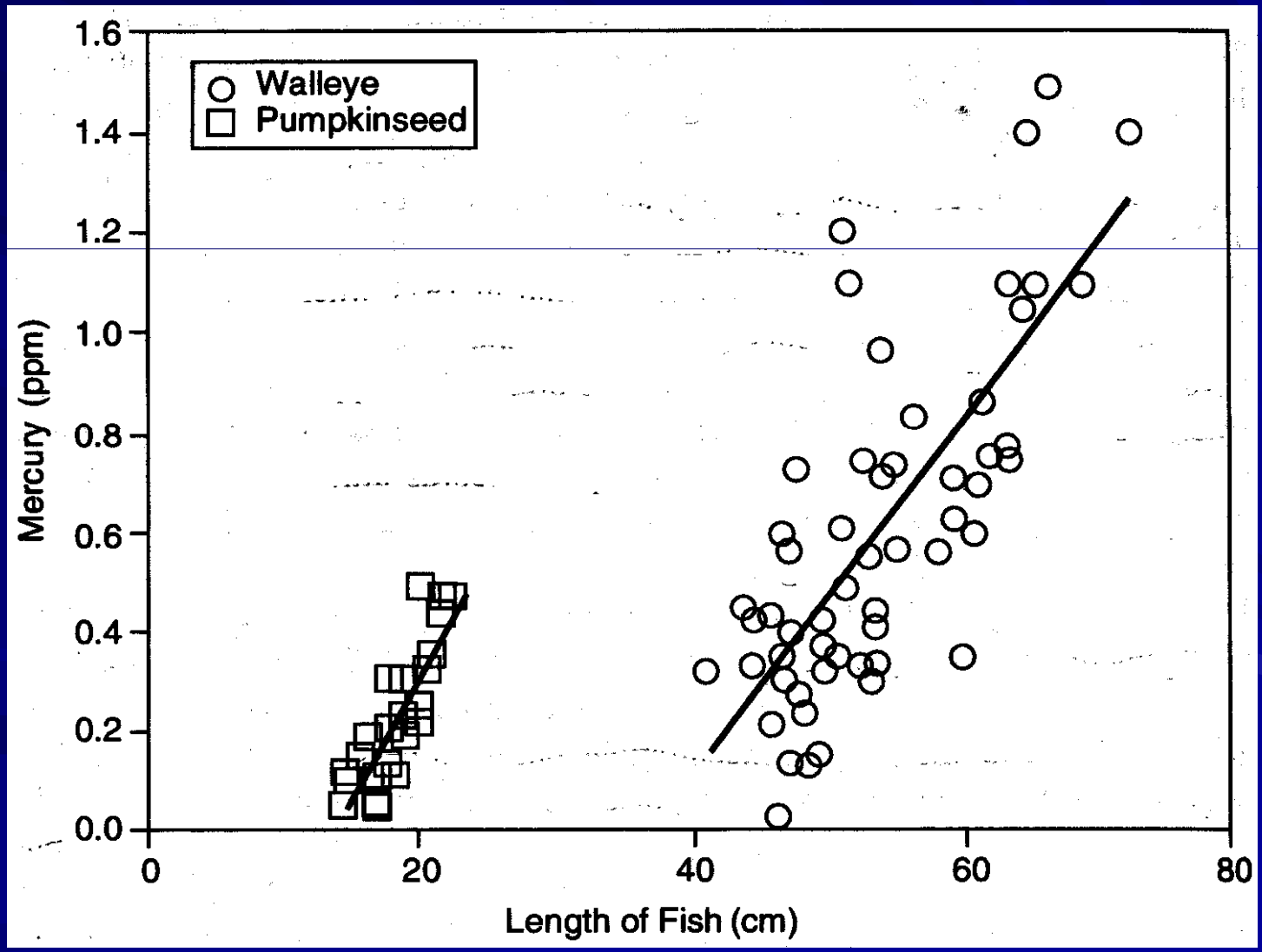
# MERCURY - SPECIATION

- Elemental Hg/metallic Hg ($Hg^0$), inorganic Hg ($Hg^{+2}$), organic Hg (methylmercury)
- Bacteria at water-sediment interface methylate $Hg^{+2}$.
- Methylation is promoted by low pH and high dissolved organic carbon (DOC).
- Methylmercury ($CH_3Hg^+$) is most persistent, toxic, and lipophilic form.

# MERCURY BIOMAGNIFICATION (parts per million - ppm)



# MERCURY CONCENTRATION AND FISH LENGTH



# METHYLMERCURY IMPACTS ON FISH

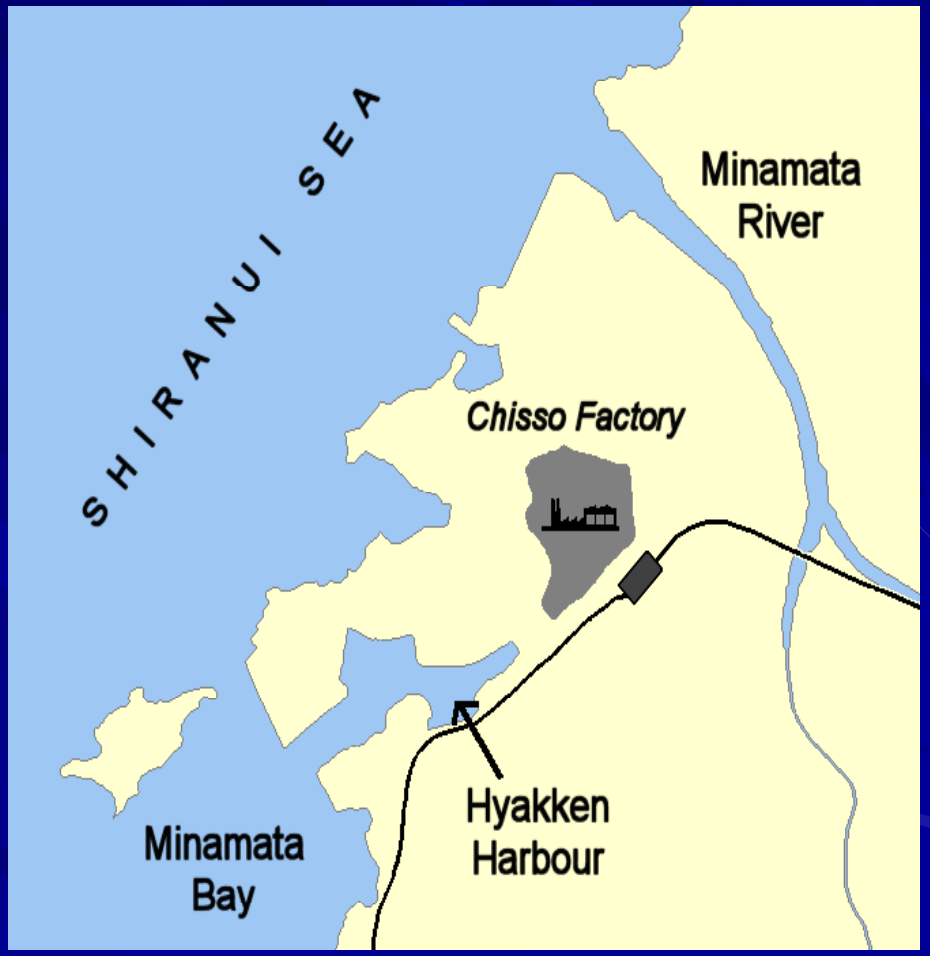
- Fish are ***relatively*** insensitive to toxic effects of $CH_3Hg^+$ and can tolerate 10 times as much $CH_3Hg^+$ as humans.
- Storage of $CH_3Hg^+$ in muscle tissue may detoxify $CH_3Hg^+$.
- If $CH_3Hg^+$ levels are high enough, then there will be adverse impacts, e.g., decreased hatching rate of eggs, impaired growth and development.

# MINAMATA BAY STORY

- Kyushu Island in southern Japan
- Mysterious neurological illness found in fishermen, their families, and seabirds in 1950s
- High concentrations of total Hg found in fish and shellfish in Minamata Bay
- Median concentration in fish was 11 mg/g (11,000 ppm = 11 parts per thousand = 1.1 percent).

# MINAMATA BAY STORY

- 1907 – Chisso began to produce acetaldehyde and vinyl chloride.
- 1932 – Mercuric oxide (HgO) catalyst began to be used.
- >150 tons of Hg discharged from 1932-1968

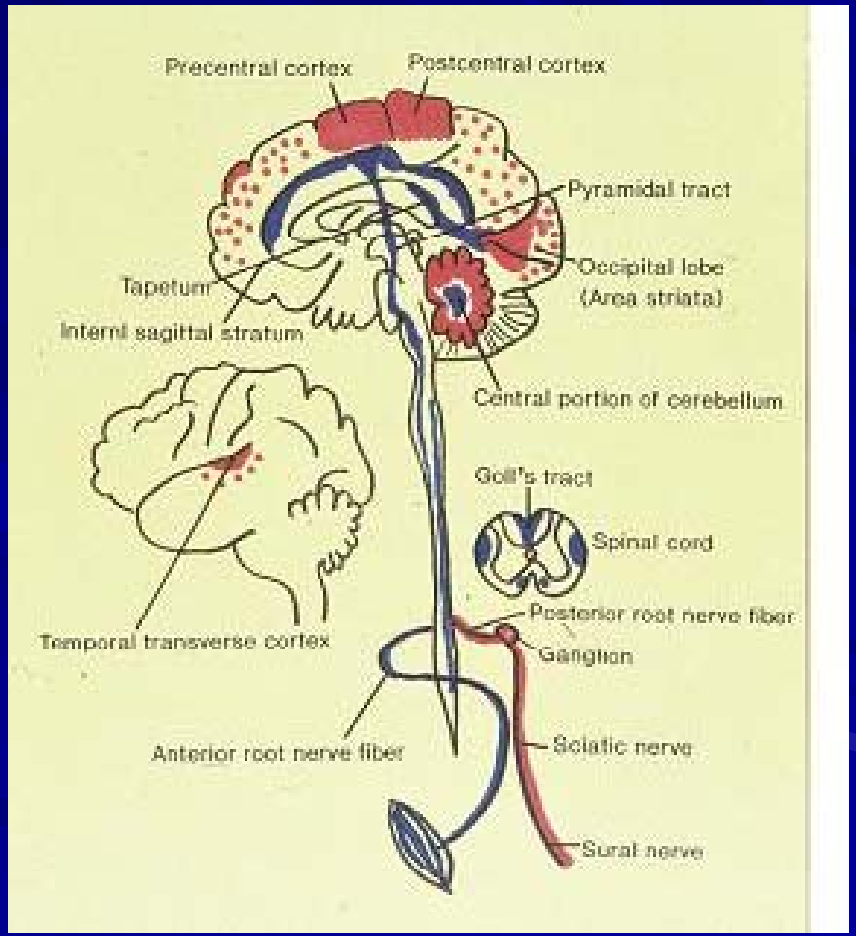


# WHAT HAPPENED IN MINAMATA BAY?

- Bacteria methylated $Hg^{+2}$.
- Seabirds and people ate fish.
- $CH_3Hg^+$ concentration at top of food chain is thousands or millions of times higher than in water.
- 1956 – linkage established between $CH_3Hg^+$ and Minamata Disease

# IMPACTS OF METHYLMERCURY ON HUMAN HEALTH

- Memory and speech loss
- Impaired hand-eye coordination
- Cognition impairment
- Vision loss



# IMPACTS OF METHYLMERCURY ON HUMAN HEALTH

- Weak muscles and spasms
- Hand paralysis
- Death

# IMPACTS OF METHYLMERCURY ON HUMAN HEALTH

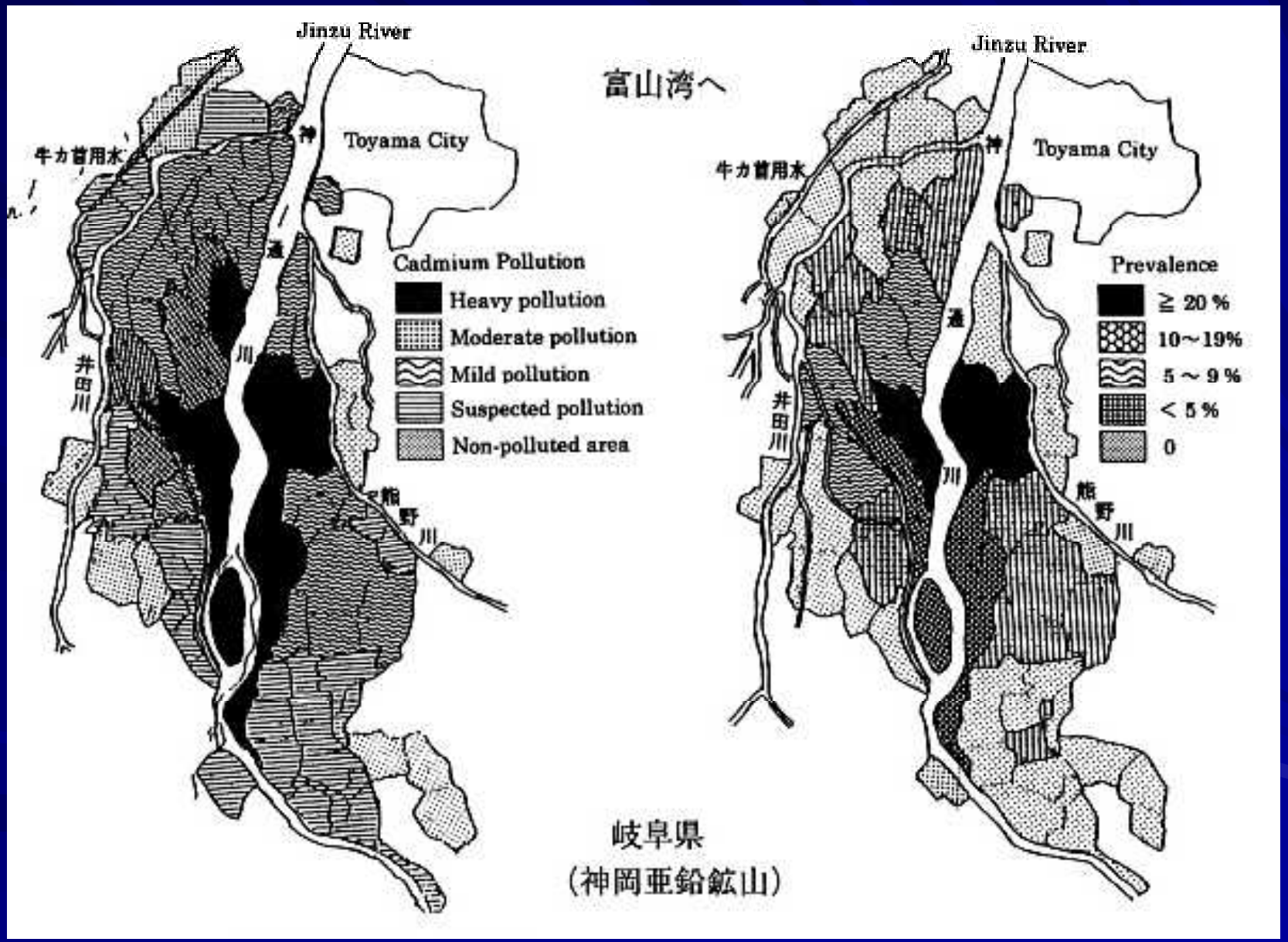
- Children, babies, and developing fetuses most at risk
- Birth defects
- Possible carcinogen - affects cell division and DNA content of cells
- Long-term exposure causes kidney damage.

# CADMIUM STORY
# ITAI-ITAI DISEASE

- In 1950s, people living in Fuchu, Japan (near Toyama City in Jinzu River Basin) complained of joint, bone, and muscle pains and also had symptoms of severe kidney dysfunction.
- Itai-itai (ouch-ouch) disease resulted in deaths of some residents.

# WHAT CAUSED ITAI-ITAI DISEASE?

- Kamioka Mine located 40 kilometers upstream of Fuchu had discharged untreated effluent, containing Cd, to rice paddies since 1920s.
- Rice plants absorb Cd easily.
- People ate contaminated rice and were exposed to 600-1000 micrograms of Cd daily – two to three times the toxic level, some for up to 30 years.


Jinzu River
富山湾へ
Toyama City
牛カ首用水
井田川
熊野川
Cadmium Pollution
Heavy pollution
Moderate pollution
Mild pollution
Suspected pollution
Non-polluted area
Jinzu River
Toyama City
牛カ首用水
井田川
熊野川
Prevalence
≧ 20 %
10～19%
5 ～ 9 %
< 5 %
0

岐阜県
(神岡亜鉛鉱山)

# CADMIUM EFFECTS ON HUMAN HEALTH

- Skeletal deformities and bone loss – blocks Vitamin D synthesis.
- Kidney dysfunction – inhibits enzymes responsible for absorption processes in kidney tubules.
- Anemia
- Generalized pain
- Carcinogen

# CADMIUM EFFECTS ON AQUATIC ORGANISMS

- Impaired aquatic plant growth
- Reduced survival and growth of shellfish and finfish larvae
- Impaired functioning of kidney tubules in fish
- Skeletal deformities in fish – Cd can replace calcium in bones.

# LEAD PROPERTIES

- Easy to find and mine, highly versatile
- Resists corrosion and discoloration
- Imparts brightness to paint pigments and helps them cling to wood.
- $Pb^{+2}$ is most bioavailable form and binds to sediments.

# IMPACTS ON AQUATIC ORGANISMS

>500 parts per billion (ppb) harms algae.

- Inhibits enzymes needed for photosynthesis.
- Reduces absorption of water.
- Interferes with cell division, thereby inhibiting growth

>50 ppb harms fish.

# HUMAN EXPOSURE PATHWAYS

- Inhalation of Pb dust
- Drinking water
- Contaminated food – Acidic foods and juices will solubilize Pb from containers.
- Children eating leaded paint that flakes off walls of old buildings and mouthing toys that contain lead paint

# IMPACTS ON HUMAN HEALTH

- Pb accumulates and persists in bones and teeth, which function as reservoirs for releasing Pb into bloodstream.
- Half-life of Pb in bones = 20 years.
- Pb toxicity is higher when diet is deficient in calcium.
- Target organs are brain and bone marrow.

# IMPACTS ON HUMAN HEALTH

- Pb exposure can be assessed by measuring Pb concentration in blood.
- 250 ppb was considered “safe” until 1970s. This is not “safe” for children.
- 50-100 ppb was revised recommended guideline.
- No “safe” level for children

# NEUROLOGICAL IMPACTS

- Hyperactivity, poor attention span, and low IQ, especially in children
- Mechanism of toxicity: interference with transport of calcium across membranes of neurons

# PHYSIOLOGICAL AND BIOCHEMICAL IMPACTS

- Inhibits enzymes that are needed for hemoglobin synthesis.
- Result is anemia (found in children with blood Pb > 400 ppb).
- Severely damages kidney function.
- Birth defects

# LEAD AND CHILDREN'S TOYS

(www.HealthyToys.org)



- **Tested 1200 toys and other products, using X-ray fluorescence analyzer.**
- **Worst Pb levels were 12 – 24 parts per thousand by weight.**
- **Worst Cd level was 1% by weight!**

# CHILDREN'S SAFE PRODUCTS ACT OF 2008

- **Passed by Washington State legislature and signed by governor on April 2.**
- **Prohibits sale of children's products containing Pb or Cd levels >40 ppm.**
- **Requires manufacturers to report what chemicals their products contain to Washington Department of Ecology.**
- **Takes effect on January 1, 2009.**
  (www.toxicfreelegacy.org, www.watoxics.org)

# COPPER - ESSENTIAL ELEMENT

Essential trace nutrient (5-20 ppm)

- Hemoglobin and hemocyanin formation
- Carbohydrate metabolism
- Functioning of >30 enzymes
- Healthy hair in humans

$Cu^{+2}$ is toxic at concentrations >20 ppm.

# COPPER TOXICITY - OVERVIEW

- Binds to sediments and organic matter.
- Highly toxic to aquatic organisms
- Shellfish and finfish: 10-100 times more sensitive than mammals
- Algae: 1000 times more sensitive than mammals
- Less toxic when DOC is present

# COPPER EFFECTS ON SHELLFISH

- Individual effects: lower rates of metabolism in clams in estuaries
- Population effects : lower production of sperm and eggs in sea scallops exposed to 10 – 20 ppb

# COPPER EFFECTS ON FINFISH

- Disrupts osmoregulation by interfering with sodium uptake in gills.
- Neurotoxic – interferes with olfaction
- Impaired olfaction impairs migration, salmon homing, and avoidance of predators.

# COPPER EFFECTS ON FINFISH

- Reduced appetite, food intake, growth
- Kidney damage
- Deformed vertebrae and fin rays
- Reduced sperm and egg production
- Abnormalities in newly hatched fish
- Reduced survival of young fish

# SUBLETHAL EFFECTS OF COPPER ON RAINBOW TROUT

Rainbow trout show stress at very low copper levels (1.4 ppb).

- Hyperactivity
- Increased levels of cortisol in blood
- Synthesis of metallothionens in liver

# ECOSYSTEM EFFECTS OF COPPER

- Decreased algae growth
- Disappearance of “good” insects (such as mayflies) and appearance of other insects that tolerate water pollution
- These changes will affect which species of fish are present.
- Reverberations throughout ecosystem

# COPPER EFFECTS ON HUMANS

- Low toxicity in humans due to detoxification of Cu by metallothionens in liver and kidney
- Drinking water standards for Cu are based on taste, not on risk of toxicity.

# FOR FURTHER INFORMATION

- On-line course (www.edumine.com)
- Landis, Wayne and Ming-Ho Yu (2003), "Introduction to Environmental Toxicology: Impacts of Chemicals Upon Ecological Systems," Lewis Publishers, Boca Raton, FL.
- Wright, David and Pamela Welbourn (2002), "Environmental Toxicology," Cambridge University Press, Cambridge, U.K.