Principles of environmental geochemistry as applied to research on medical geology, with a focus on metal contaminants

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"Everything is a poison, nothing is a poison, the dose alone is the poison"

P.A. Paracelus (1493-1541)

CNN interactive

HEALTH

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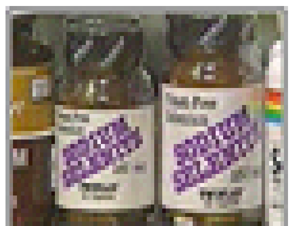
Selenium may lower several cancer risks

(CNN) -- A new study suggests selenium, a mineral found in grains, seafood and meat, may significantly lower the rate of some cancers.

The study was designed to look at selenium's effect on skin cancer, but researchers found that while it made no measurable difference there, the mineral did have effects on other types of cancers.

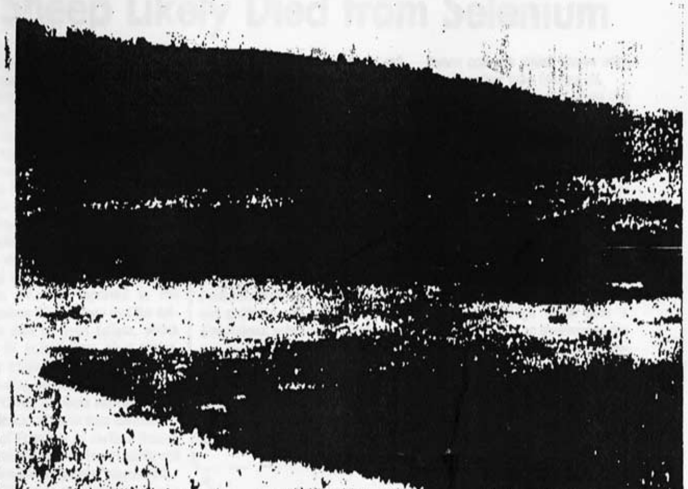


(CNN)

County Sun

...gs, Caribou County, Idaho 83276 (contact Mark Steele, editor 208/547-3260)

Thursday, November 11, 1999 — 50¢ PER COPY



TWO GROUPS of dead sheep were found in September near the old Stauffer Mine in Wooley Valley. Selenium toxicosis is the suspected cause of death because high levels of selenium were found in tissues and stomach contents. Experts said other variables may also have been an influence in the deaths and further testing by toxicologists is being conducted. Besides the two bunches, other suspected dead animals in the area brought the total between 60 and 80 sheep.

Toxicologist and Vet Say Dead Sheep Likely Died from Selenium

The cause of death of between 60 and 80 sheep on the Caribou National Forest is "reasonably and likely" selenium toxicosis, according to veterinarian and toxicology reports released this week by the ... Springs Animal Clinic, concurred with Dr. Talcott's findings, with whom he consulted. The sheep were owned by Cal Dredge of Soda Springs and grazed on the old Stauffer Mine site owned by ... rumen contents which shows what the sheep had been feeding on.

Dr. Cutler said certain plants and feed additives can also cause similar myocardial lesions independent of selenium, but "these plants ...

NEWSBRIEF FROM CHINA...

Red Beer: The Selenium-Enriched Brew From Taizhou

Red Beer—Se-enriched—is a unique new member of the beer family recently introduced in China following approval for commercial production by the provincial authorities. It is produced by the Boshi Brewing Co. in Taizhou and reportedly possesses "extraordinary Selenium supplementing qualities".

Cycling of potentially toxic elements and minerals in the environment

A complex mix of geological, geochemical, biological processes

Possible fates:

Dilution, sequestration;
bioaccumulation;
environmental and health effects;

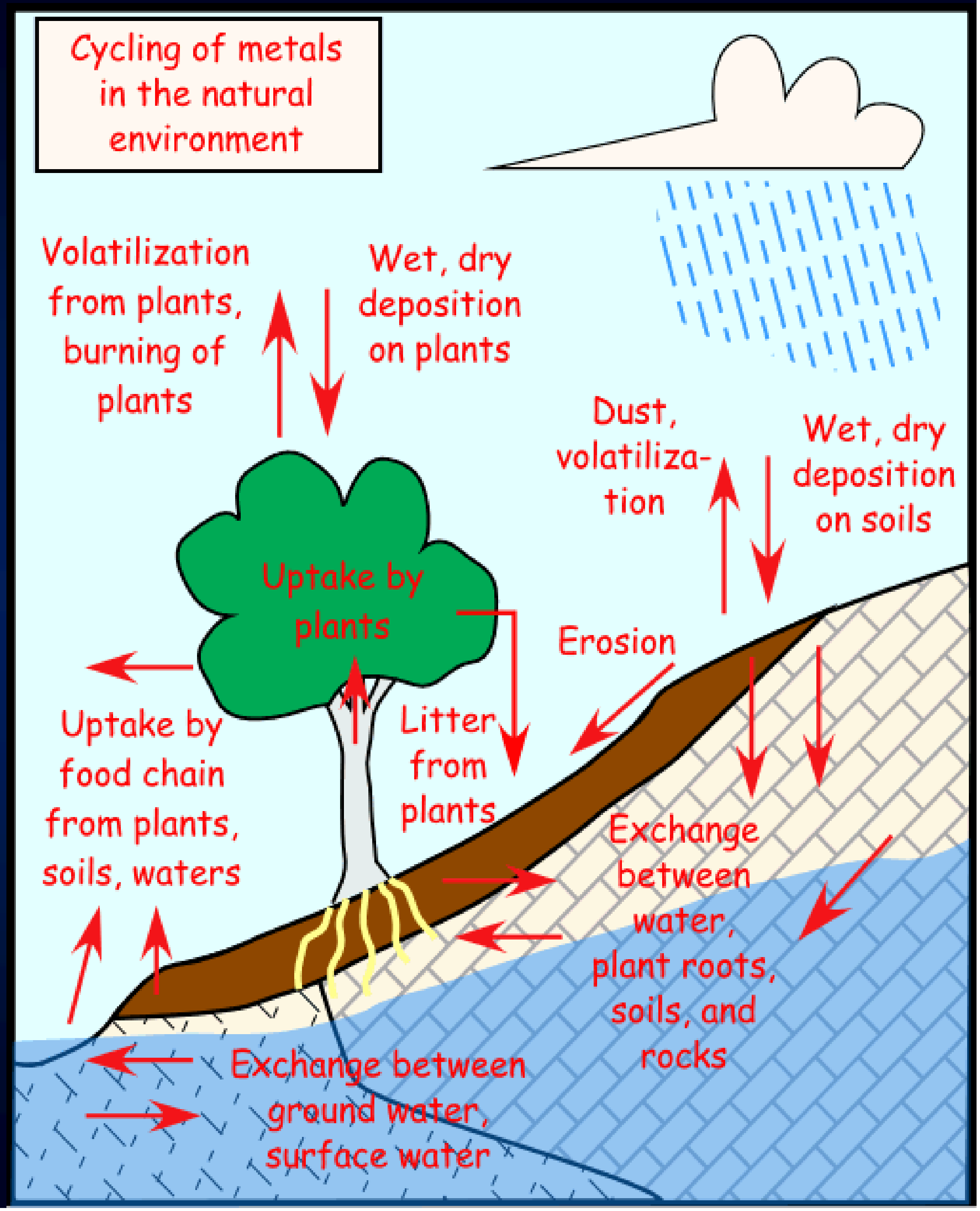
Mobilization, transport, uptake

Source:

Natural and (or) anthropogenic

Cycling of potentially toxic elements and minerals in the environment

A complex mix of geological, geochemical, biological processes



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A more complex model for the Hg cycle

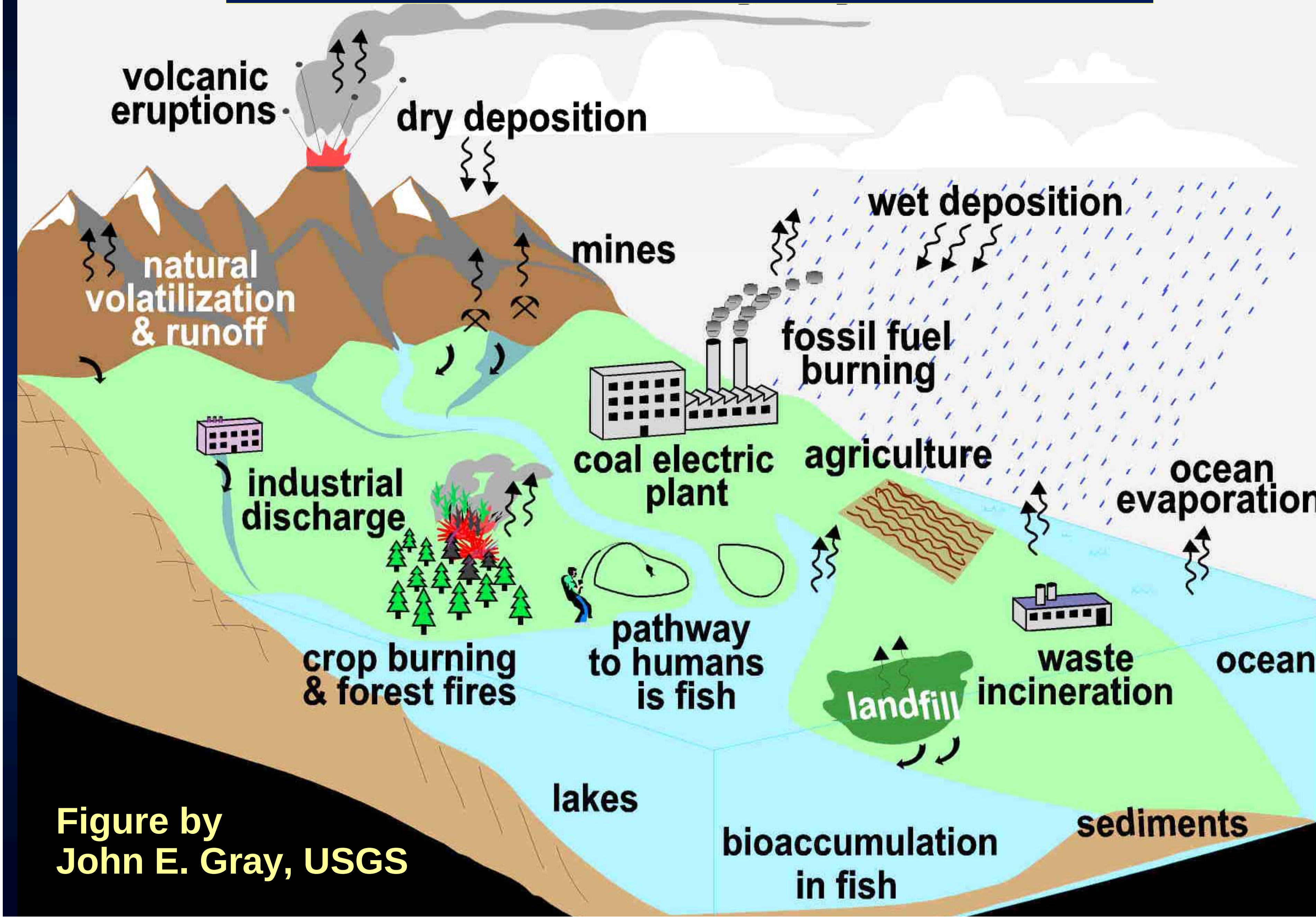
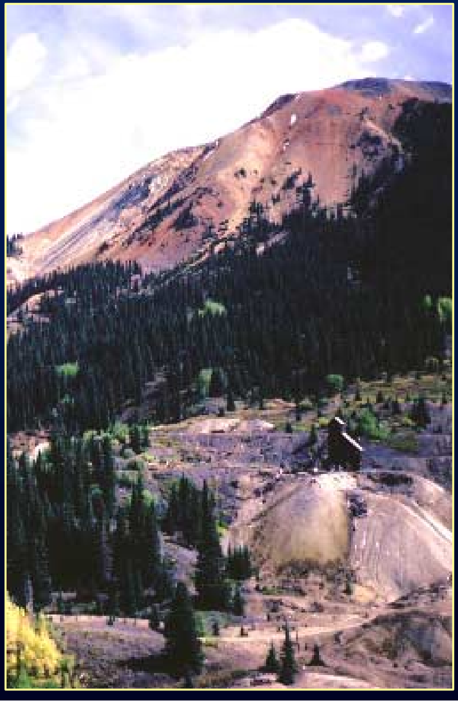


Figure by John E. Gray, USGS

Source

- Many different natural (geogenic) and anthropogenic sources contribute metal and mineral toxicants to the environment
- The mineralogical or chemical form of a mineral or metal toxicant in its source material greatly affects
  - how readily it is released into the environment, and
  - how readily it is taken up by organisms

Photograph by C. Coumans 1988

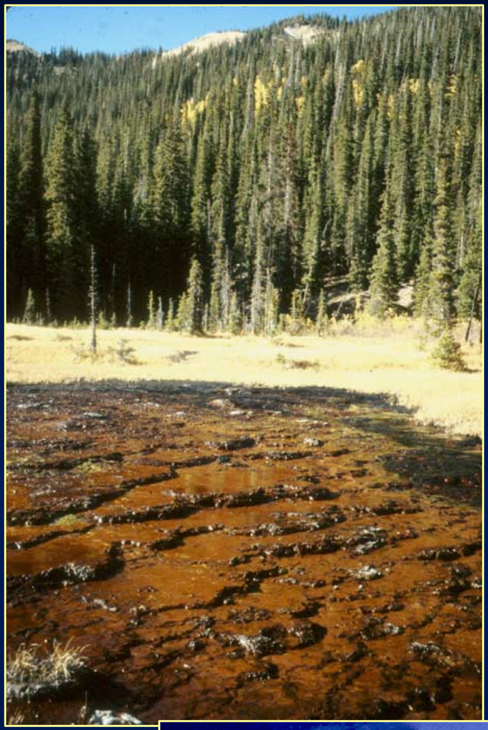


Photograph by C. Newhall, 9/15/94

Hayman wildfire, Colorado, June, 2002

Examples of Natural (Geogenic) Metal Sources in the Environment

- Weathering of rocks, mineral deposits
  - Produces metals in dusts, soils, sediments, ground waters, surface waters
- Geothermal systems: metals in waters, gases, precipitates
- Volcanoes: metals in atmospheric gases, aerosols, volcanic ash



Mt Pinatubo from Clark AFB, 1991

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Examples of Natural (Geogenic) Metal Sources in the Environment

- Plants: can naturally accumulate metals from soils, water, and deposition of atmospheric particulates
- Forest fires: metals in ash, mineral particulates, gases, aerosols
- “Edible” soils
- Natural hydrocarbon seeps


Natural oil seep


Hayman wildfire, Colorado, June, 2002

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Examples of Anthropogenic Metal Sources in the Environment

- Metal mining, mineral processing, smelting
  - Mine-drainage waters; mine waste piles; tailings impoundments and processing solutions; heap- leach impoundments and processing solutions; smelter slag and airborne emissions

Photograph by C. Coumans 1988

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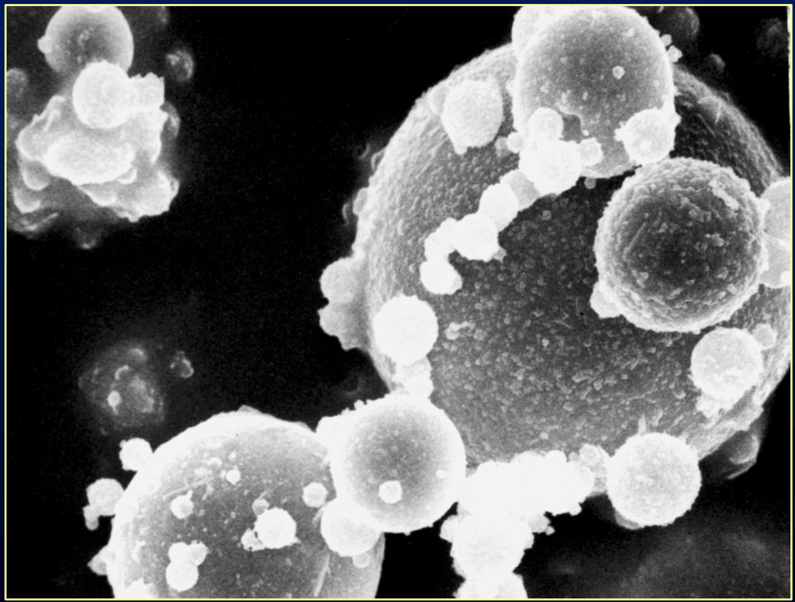
Examples of Anthropogenic Metal Sources in the Environment

- Coal mining, power generation
  - Coal mine drainage waters, waste piles; power plant emissions and fly ash



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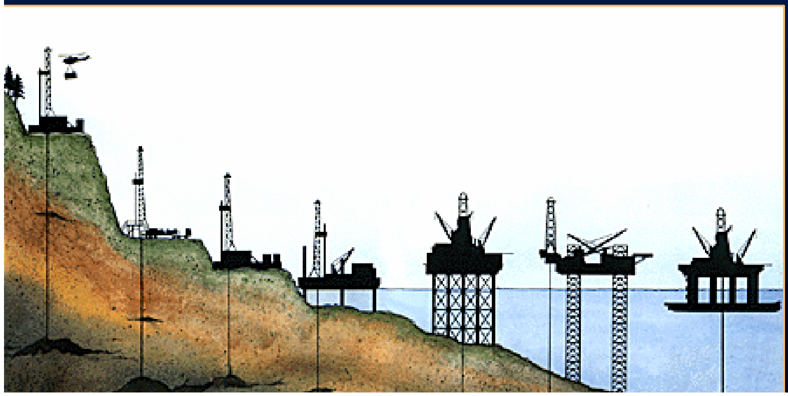
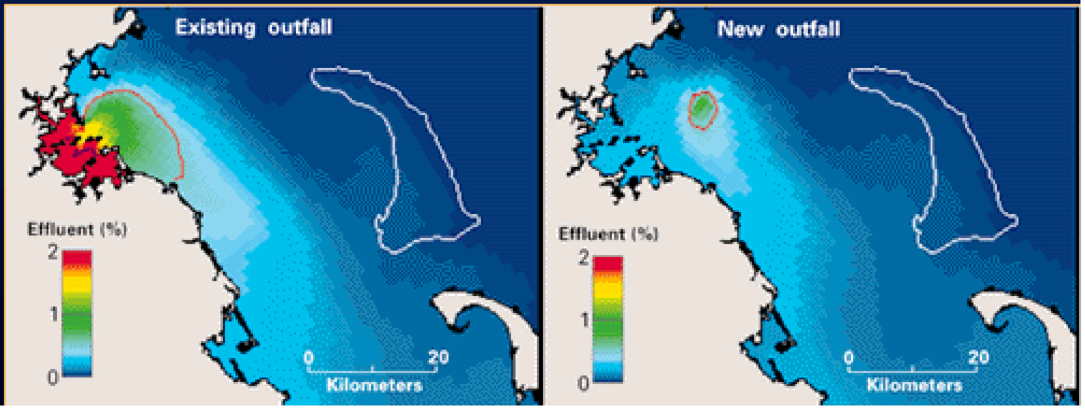
Examples of Anthropogenic Metal Sources in the Environment

- Oil, natural gas production, petroleum utilization
  - Produced waters; oil spills; additives and combustion products (ie, lead in gasoline prior to mid 1970's)
- Industrial — wide variety
  - Manufacturing / industrial wastes and byproducts; commercial products (ie, lead paint in houses), or spills of commercial chemicals
- Municipal waste incinerators, landfills, sewage sludge disposal





Examples of Anthropogenic Metal Sources in the Environment

- Agricultural
  - Pesticides, fertilizers; irrigation practices; crop burning
- Households – Ozzie and Harriet (or Ozzie and Sharon) effect
  - Chemicals spilled, disposed of, or volatilized; fireplaces; building products
- Urban settings
  - Particulates from petroleum combustion, building construction and demolition, vehicle tires, industrial emissions, many other sources

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Transport

- A complex variety of processes can help release metals from their sources, transport them in the environment, and remove them from the environment
- Physical processes:
  - physical erosion, landslides, debris flows
  - water transport of sediments
  - wind, atmospheric transport of dusts, aerosols

Owens dry lake bed, CA

Transport

- Geochemical processes (many can be bacterially catalyzed):
  - chemical weathering of rocks, minerals
  - oxidation - reduction reactions
  - formation of aqueous metal complexes
  - mineral precipitation
  - sorption of metals onto mineral, organic particulates
  - volatilization of gases
  - radioactive decay
  - partitioning of metals between water and immiscible liquids (ie oil or other organic liquids)

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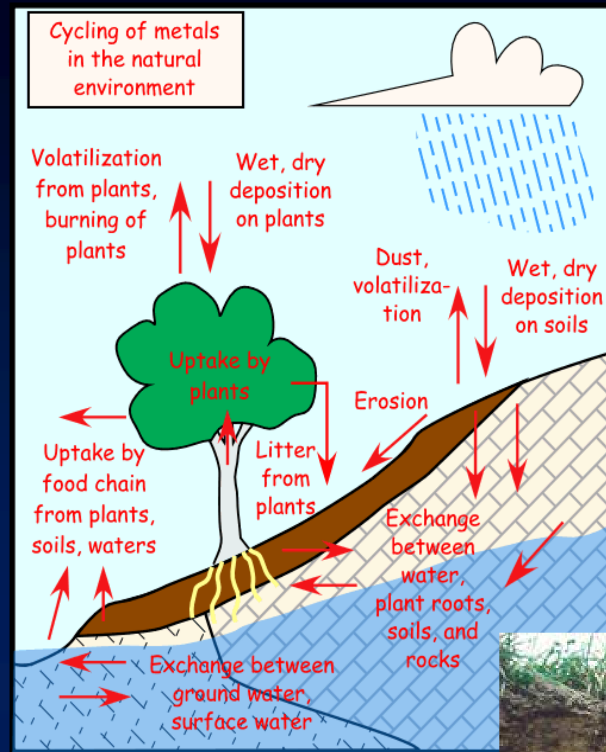
Weathering processes

- The minerals in most rocks are unstable under the ambient conditions at the Earth's surface
- Therefore they react with water and the atmosphere, either dissolving or forming progressively more stable mineral assemblages
- Plants contribute to the weathering, helping to create soils
- This weathering can result in the release of metals into and sequestering of metals from the environment.



Soil profile, Jim Turenne
nesoil.com/ images/haven.htm

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Fate

- Contaminants can be dispersed into or removed from the environment by a variety of physical and geochemical processes without affecting ecological or human health
  - "The solution to pollution is dilution"
  - Precipitation of metals in insoluble form
  - Accumulation of metals in sediments, which are then buried

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Fate

- Metals can be taken up from the environment by plants
  - through roots, atmospheric deposition on leaves
- Metals can be taken up from the environment by organisms
  - ingestion of waters, solids, plants
  - inhalation of dusts, gases, aerosols
  - absorption through skin
- Metals can be bio-accumulated up the food chain
- The chemical form and concentration of metals in the environment strongly influences their uptake by and toxicity to plants and organisms

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Geoavailability

- That portion of a metal's or a metal-bearing compound's total content in an earth material that can be liberated to the surficial or near-surface environment (or biosphere) through mechanical, chemical, or biological processes.
  - Smith and Huyck (1999)
  - In order for a metal in an earth material to be bioaccessible and bioavailable, it must first be geoavailable

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The geoavailability-bioavailability continuum

Total metal content of an earth material

The geoavailable fraction

The bioaccessible fraction – that which is soluble in various body fluids (gastrointestinal, respiratory, perspiration, etc.)

The bioavailable fraction – that which is absorbed by the body, and transported within the body to a site of toxicological action

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The geoavailability of lead

Trace lead in silicate minerals

Coarse-grained lead sulfide

Lead sorbed onto smelter particulates

The geoavailability of lead

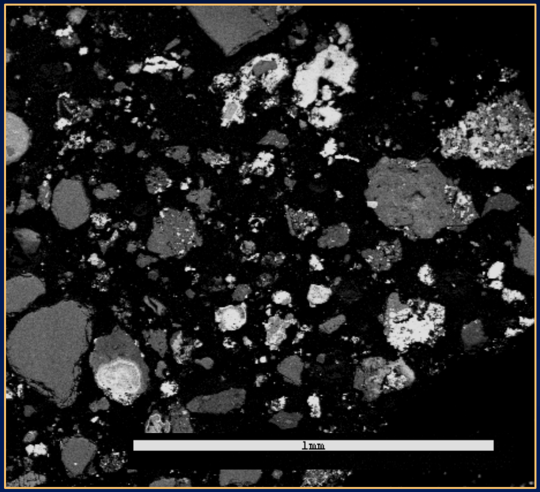
Coarse-grained
lead sulfide

Very High

Lead sorbed onto
smelter
particulates

Moderate

Fine-grained
lead carbonate



High

Lead Concentration

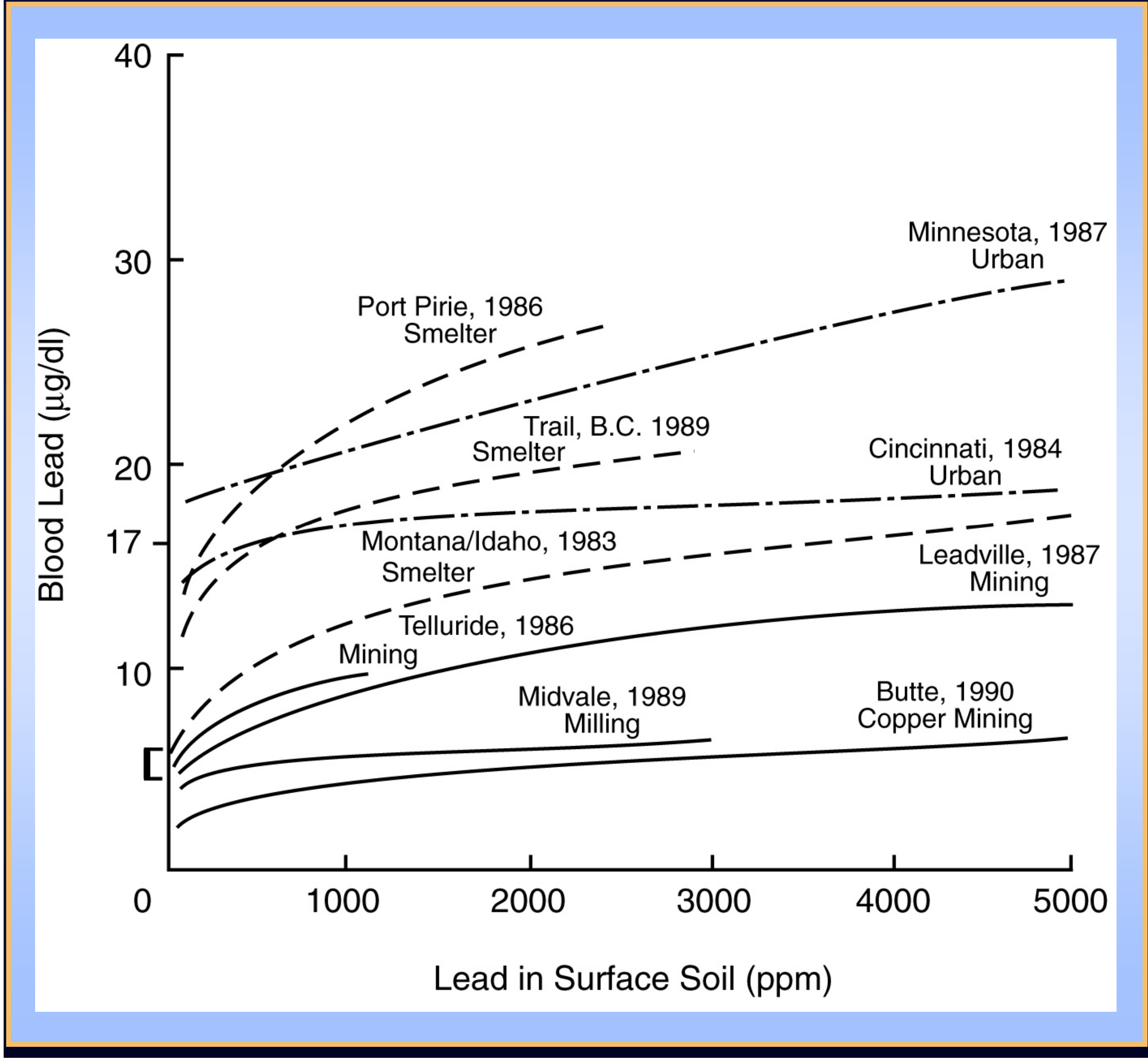
Low

Lead Geoavailability

Very High

Geoavailability and bioaccessibility of lead from mining

Not all forms of lead are readily geoavailable and bioaccessible

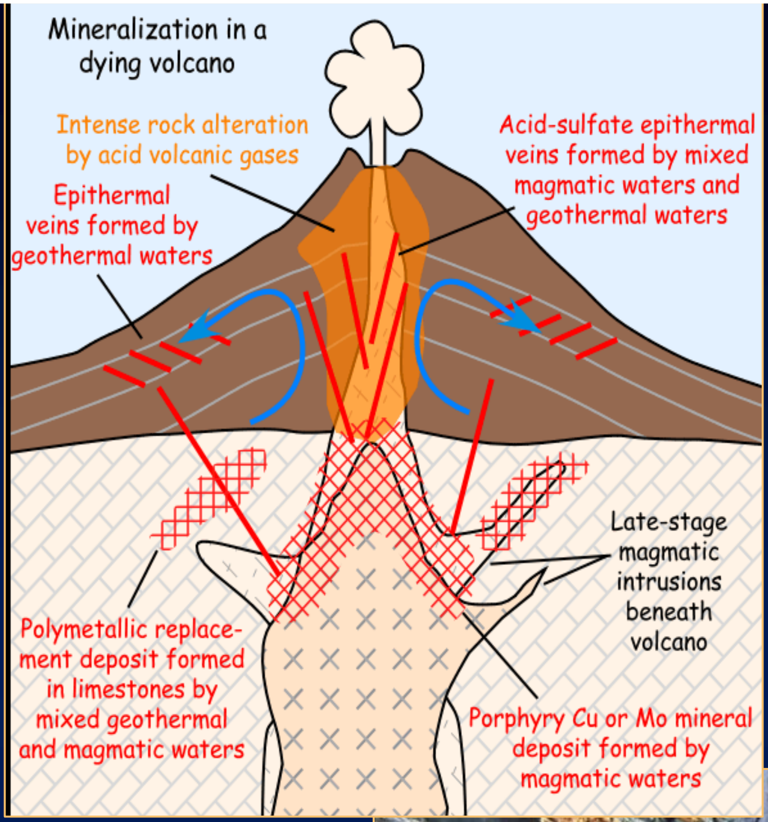


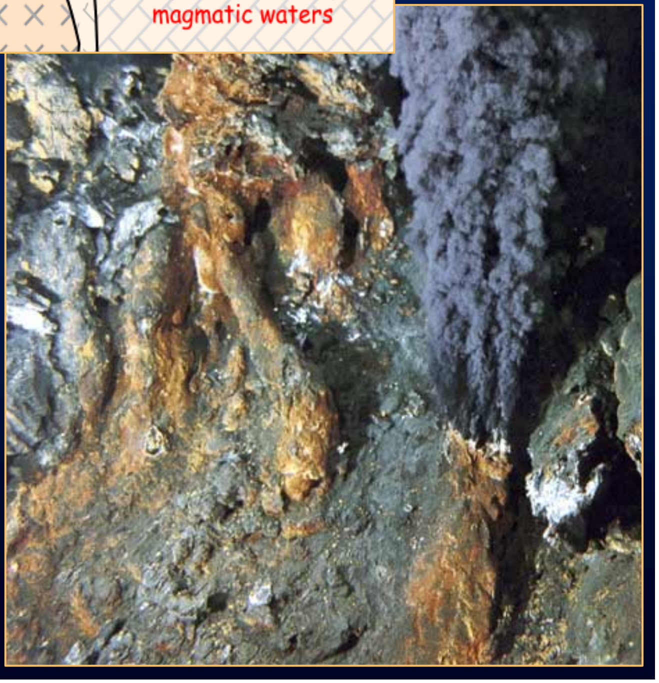
- Plot comparing soil lead to blood lead in children from mining (solid lines), smelter (dashed lines), and urban sites (dash-dot lines) in the United States. From Smith and Huyck (1999), reproducd from Gulson (1994)
- Declines in avg. blood lead from 17 µg/dL in 1980's to present 4-6 µg/dL due primarily to unleaded gas and solder.

Metals Released by Mineral Deposits, Metal Mining, and Mineral Processing

Metallic mineral deposits

- Concentrations of metallic elements and minerals in the earth's crust
- Form by:
  - Crystallization of magmas
  - Cooling, boiling, mixing of hydrothermal (also called geothermal) fluids in the earth's crust
  - Chemical precipitation of minerals on the sea floor or in sediments





Submarine "black smoker"

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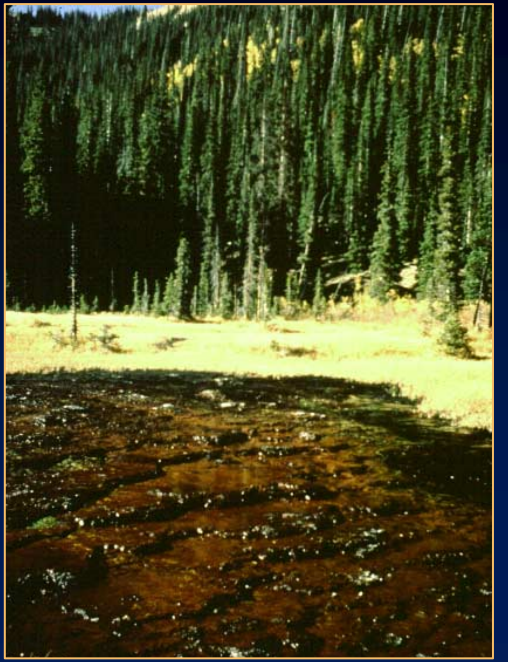
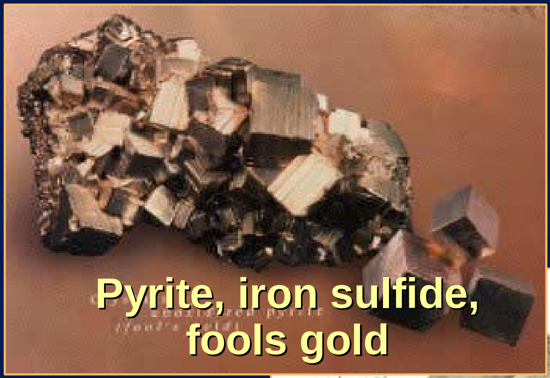
Weathering of metallic mineral deposits

- Weathering of the minerals in metallic mineral deposits commonly results in the release of metals into the environment.
    - ie, natural acidic and (or) metal-rich rock drainage
- Mining and mineral processing can accelerate or enhance this weathering process
    - Neutral to acidic mine drainage, mine wastes



Natural acid spring draining unmined mineralized area, Alamosa River, CO



Pyrite, iron sulfide, fools gold

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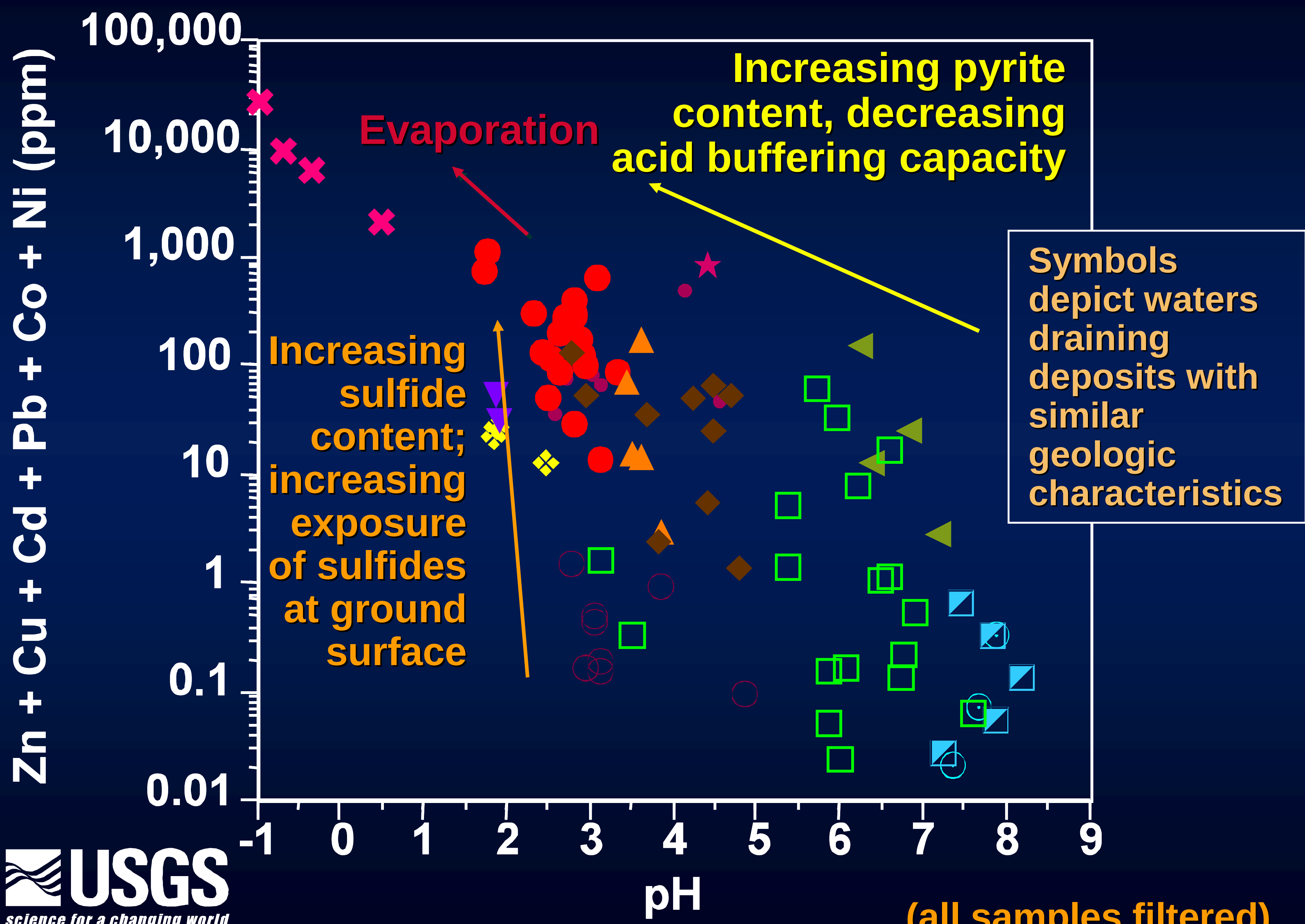
Acid-consuming minerals

- Carbonate minerals and some other minerals (some silicates, volcanic glasses) in mineral deposits, their host rocks, and watershed rocks:
  - Can react with and help consume acid generated by sulfide oxidation
  - Can also generate alkalinity in ground and surface waters, thereby increasing the waters' ability to buffer acid

Limestone

Calcite on pyrite, Silesia, Poland

Geologic controls on mine-drainage composition

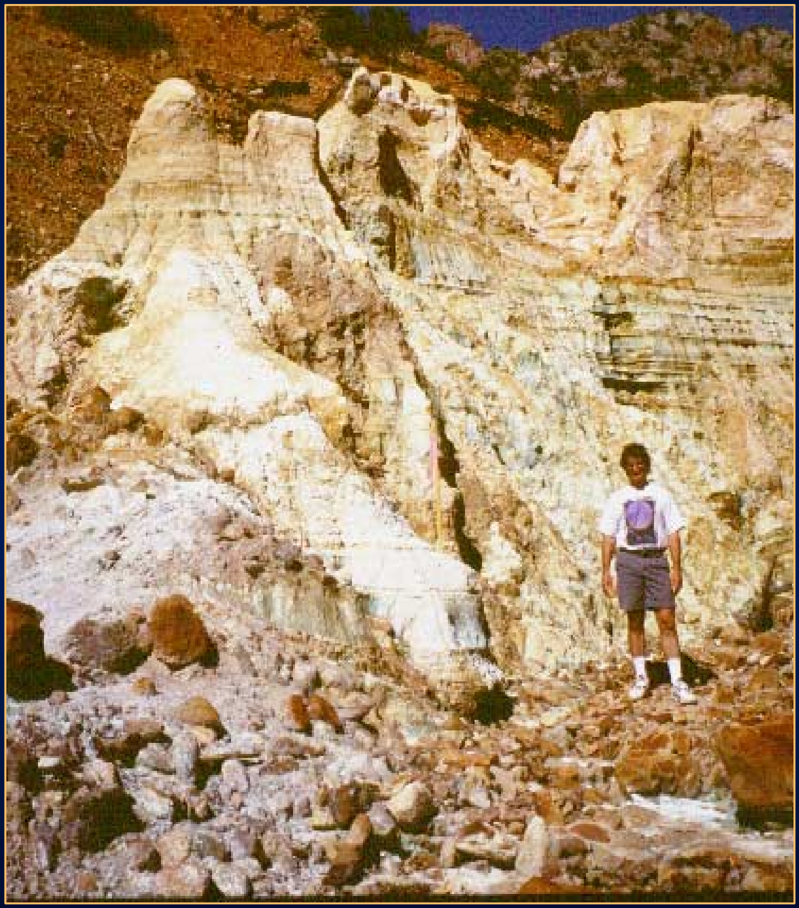


(all samples filtered)

Soluble secondary salts and acid-rock drainage

- Evaporation of acid waters during dry periods triggers the precipitation of soluble metal-sulfate salts such as copiapite, a ferrous iron sulfate, or chalcanthite, a copper sulfate.
- During the next wet period (ie rain storm or spring snow melt), these salts readily dissolve.
  - The resulting flush of acid and metals from mine dumps into local streams can be toxic to aquatic life

Mill tailings with abundant soluble salts, Arizona



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- Soluble salts from 3-R mine tailings (right) added to deionized water (left)
- ~20 parts water : 1 part solid
- pH rapidly drops to 3.5, conductivity jumps to 2500

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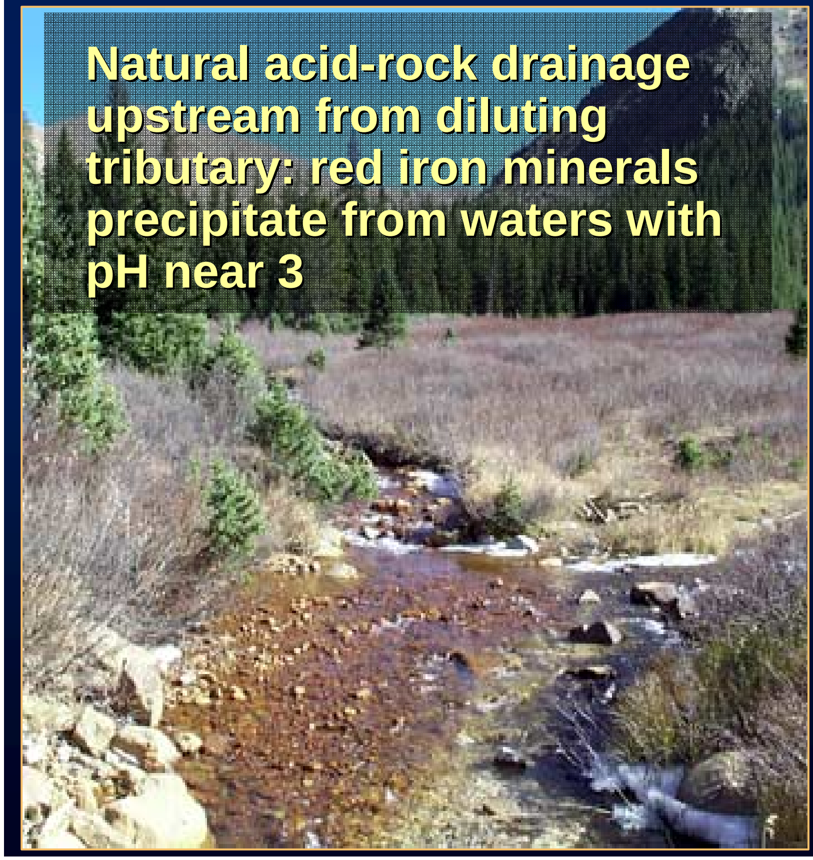
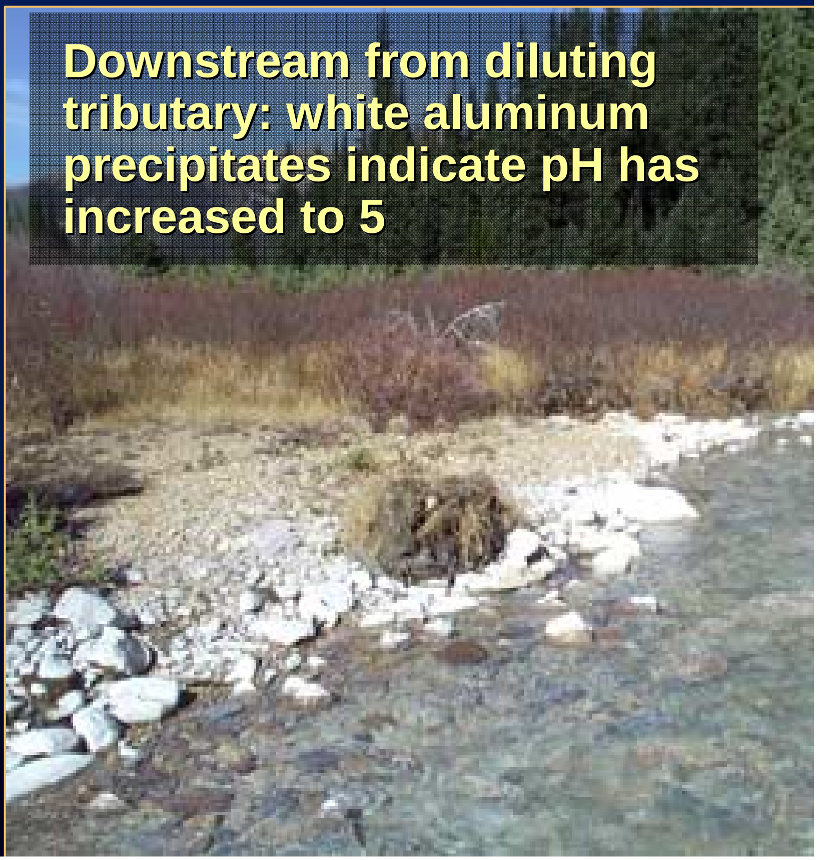
Controls on Metal Mobility from Mine Sites

- **Dilution by surface waters, ground waters**
  - **leads to increased pH—maximum effect in waters with high alkalinity (dry climates or drain carbonate rocks)**
- **Formation of colloids, particulates**
  - **Fe, Al hydrous oxides, hydroxysulfates, others**



Particulates can clog gills of fish



Controls on Metal Mobility from Mine Sites

Sorption of metals onto organic and inorganic particulates

- **Predictable function of the element, the pH, and the amounts of suspended particulates**
- **Settling of particulates from surface waters may remove the metals from the environment**
- **However, metals sorbed onto particulates may be quite bioavailable if ingested by aquatic life**

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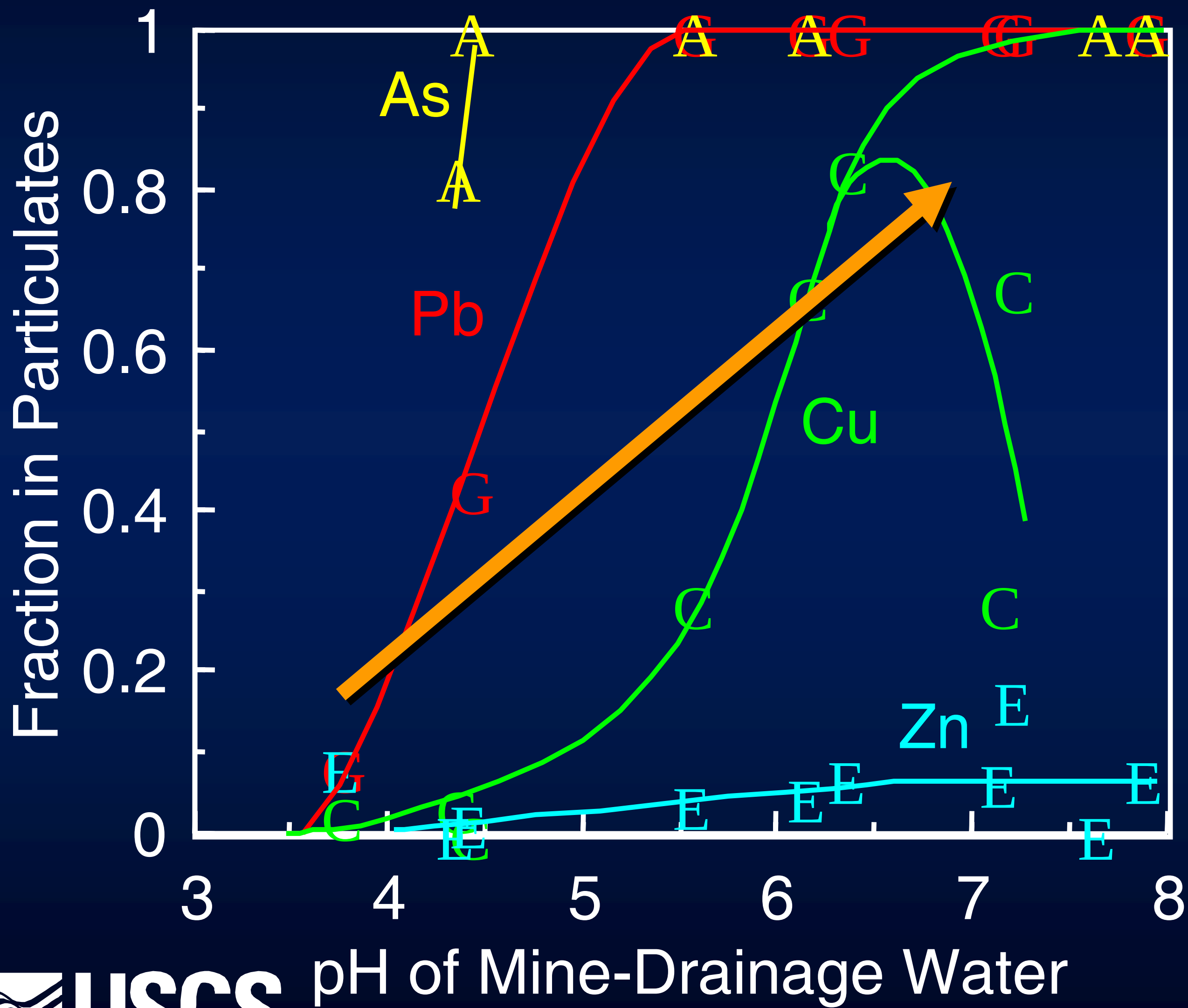
Metal fraction in suspended particulates, selected mine drainages



Orange arrow shows approx. pH-particulate trend for waters that are progressively diluted downstream from mine sites.

Data from K.S. Smith

Cd, Ni remain dissolved across entire pH range

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Arsenic oxidation state and its mobility in the environment

- In near-surface, oxidizing waters, Arsenic (V) is mobile at very low pH, and at alkaline pH. At near-neutral pH values, it strongly sorbs onto iron hydroxides
- In reducing ground waters out of contact with the atmosphere, arsenic (III) is very mobile at near-neutral pH values, especially when aqueous sulfide is absent
  - If aqueous sulfide is present, then As(III) tends to sorb onto pyrite (iron sulfide) surfaces

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Geogenic arsenic in drinking water

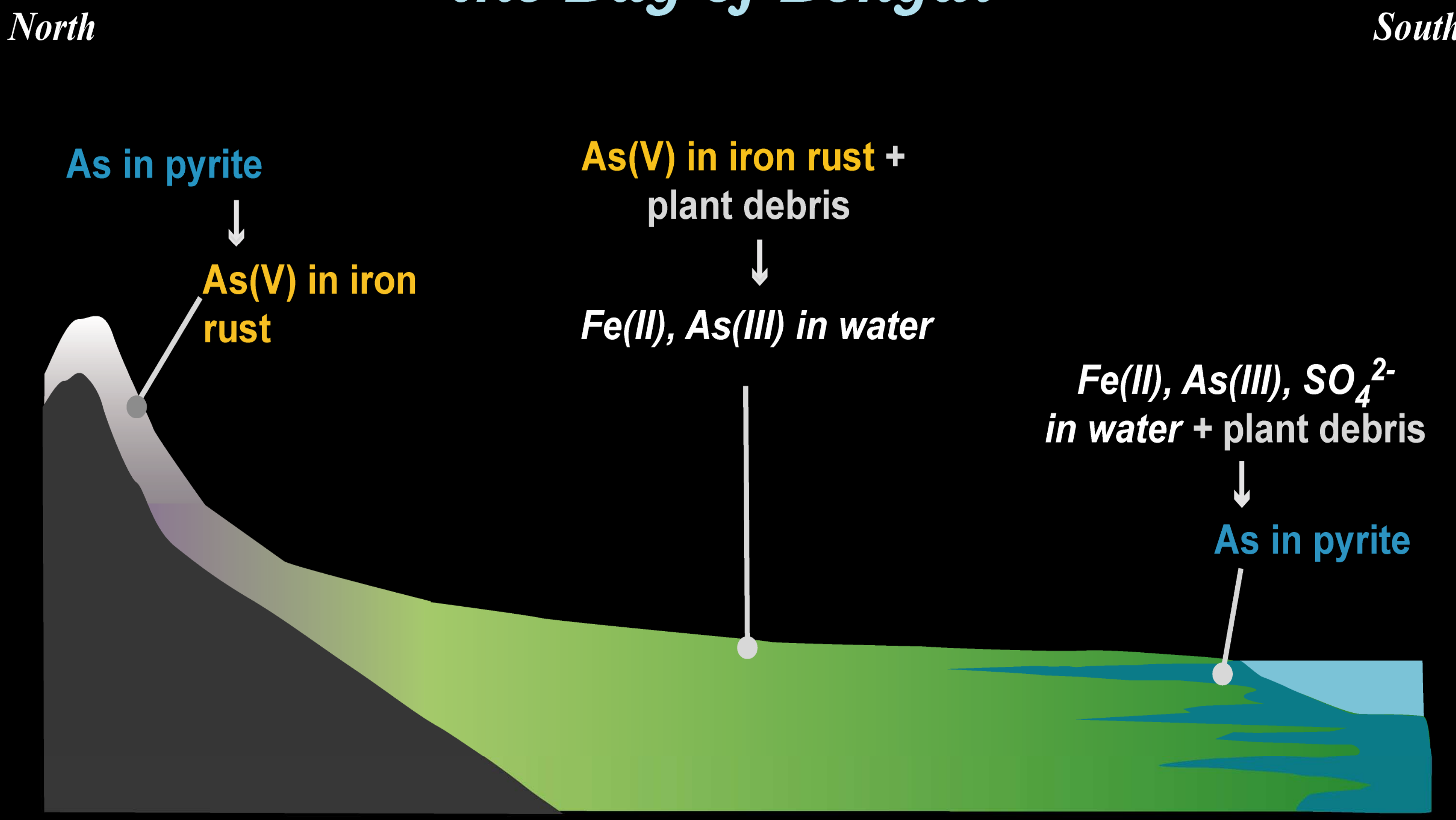
From: Smedley and Kinniburgh, in Selinus et al., 2005

Geogenic arsenic in drinking water, Bangladesh

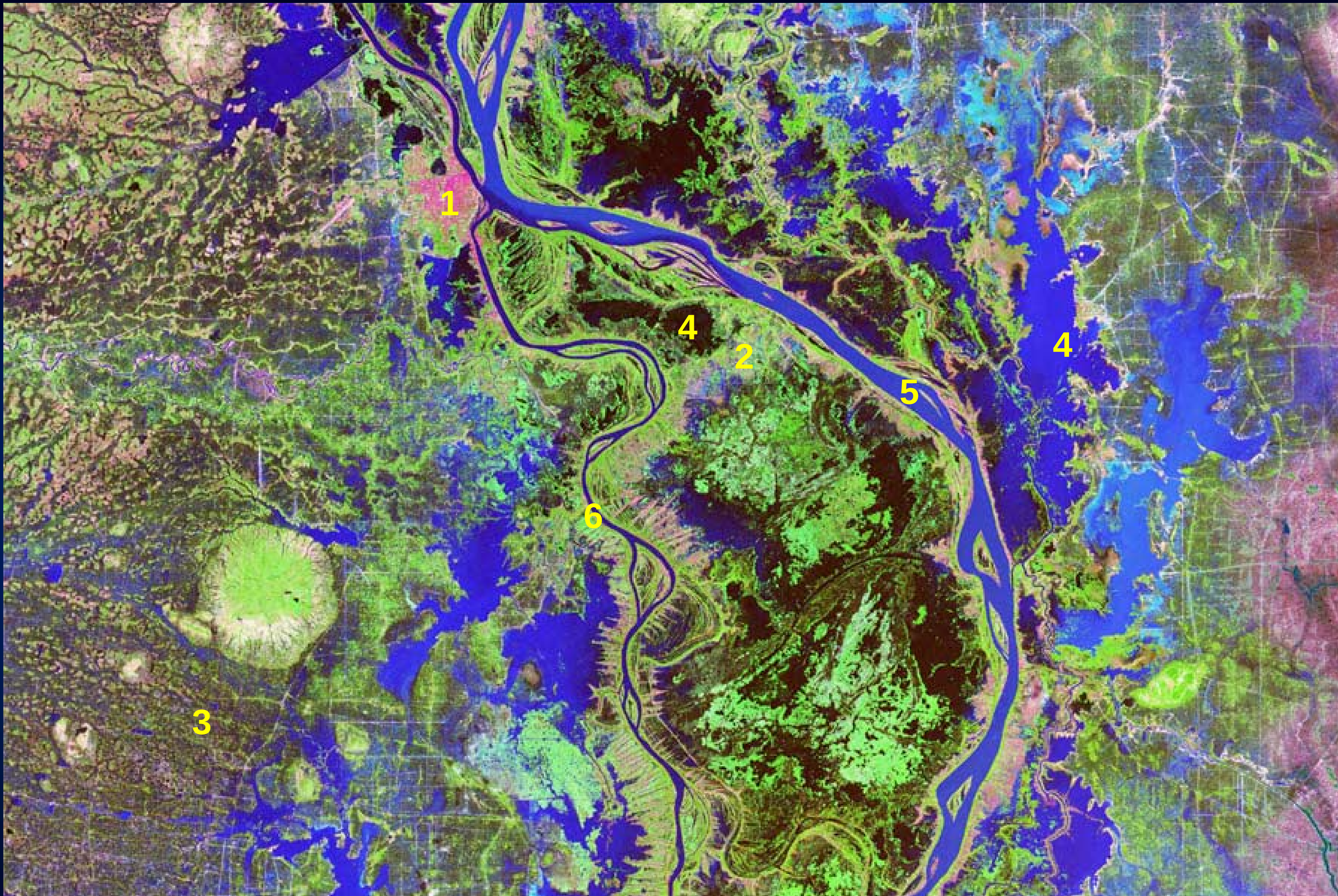
Arsenic patients in Bangladesh and West Bengal. (Photos by Prof. Richard Wilson of Harvard University)

- Consumption of ground water from shallow wells (installed originally to provide alternate source to pathogen-laden surface waters)
- Hyperkeratoses of skin, skin lesions, skin cancers, other problems
- As many as 200,000 people with arsenocosis

Arsenic changes form as rock in Himalayas is eroded and rivers carry sediment to the Bay of Bengal



Slide from George Breit, USGS, gbreit@usgs.gov



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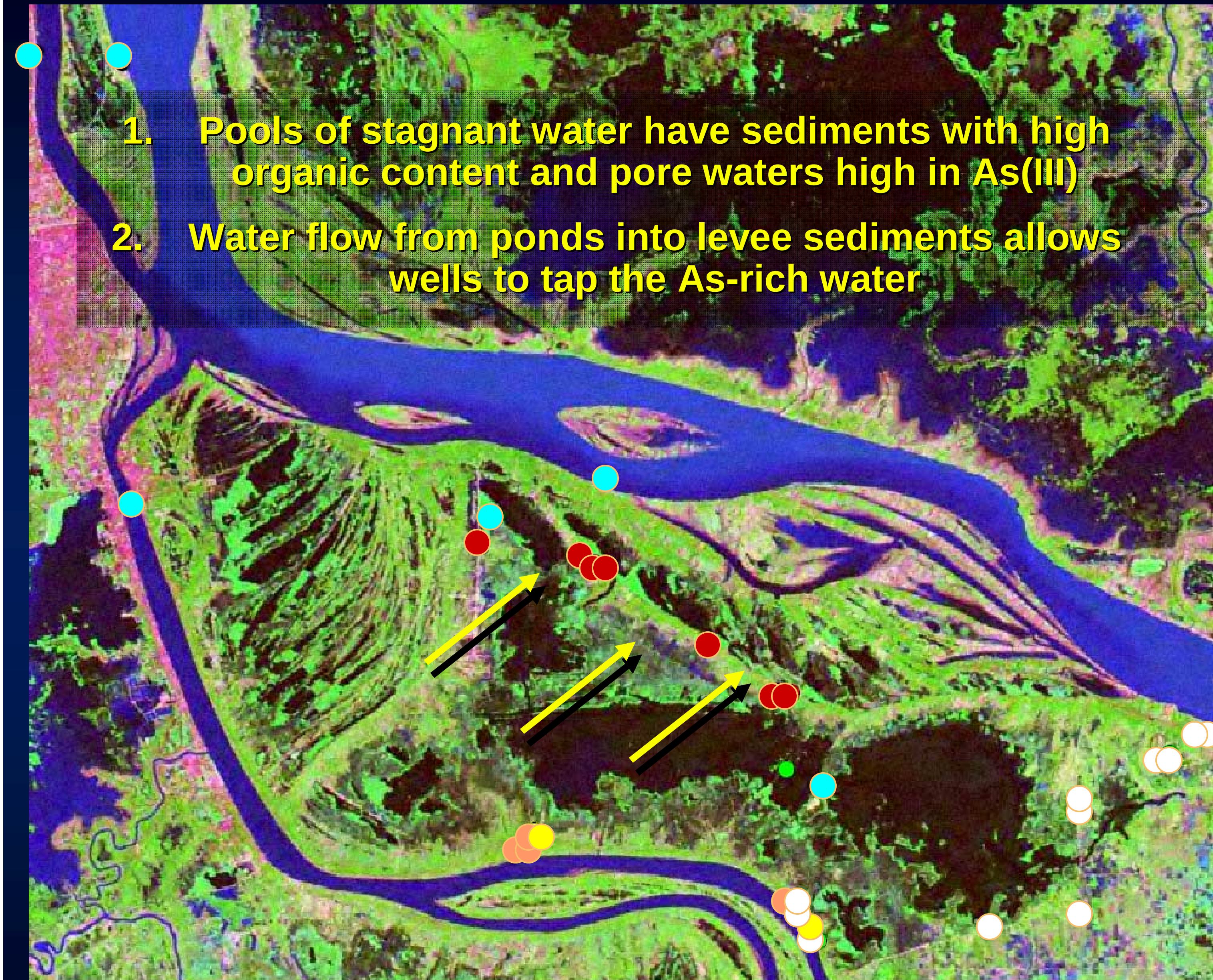
Satellite image of Phnom Penh and lower Mekong River

Slide from George Breit, John Whitney, USGS

USGS Water Data



Ground water

- <30 ug/L As
- 50-100 ug/L As
- 100-250 ug/L As
- >250 ug/L As

Surface Water

- <10 ug/L As

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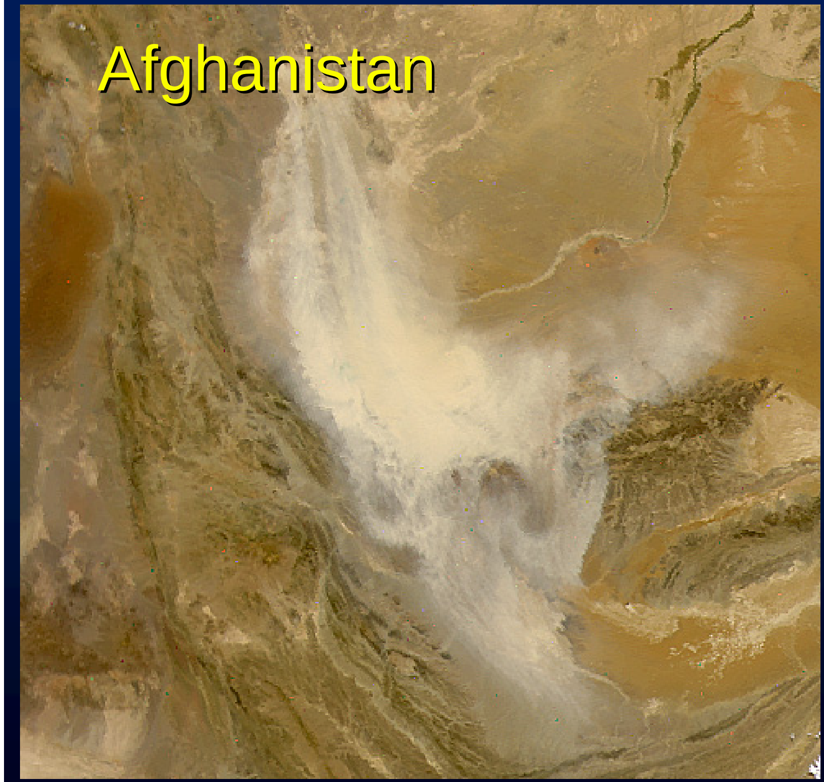
Iron-oxide-rich sediments with high sorbed As(V)
Organic-rich sediments with high mobile As(III)

Dusts from dry lake beds



Efflorescent salts build up on Mono's exposed lakebed and cause toxic dust storms when blown into the air.

Toxic elements in playa lakes, dry lake beds?

- Solutes and contaminants transported in by the waters are concentrated in the dry lake bed sediments
- The alkaline waters can leach elements from the detrital sediments
- A variety of elements, especially those that are geochemically mobile in alkaline waters, can be enriched in the lake waters and the lake bed sediments and highly soluble efflorescent salts

B, As, Al, Cr, Cd, U, V, W , Pb, Zn, Sb, Mo, …..

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Rocks as sources for potential toxicants

Some rock types may contain naturally elevated levels of potentially toxic trace elements:

- Black shales often contain elevated levels of S, Zn, Cu, As, Se, U, Mo, Ni
- Weathering of black shales releases these elements into the environment
  - May be accentuated by anthropogenic processes
  - Se in Kesterson Reservoir, San Joaquin Valley, CA

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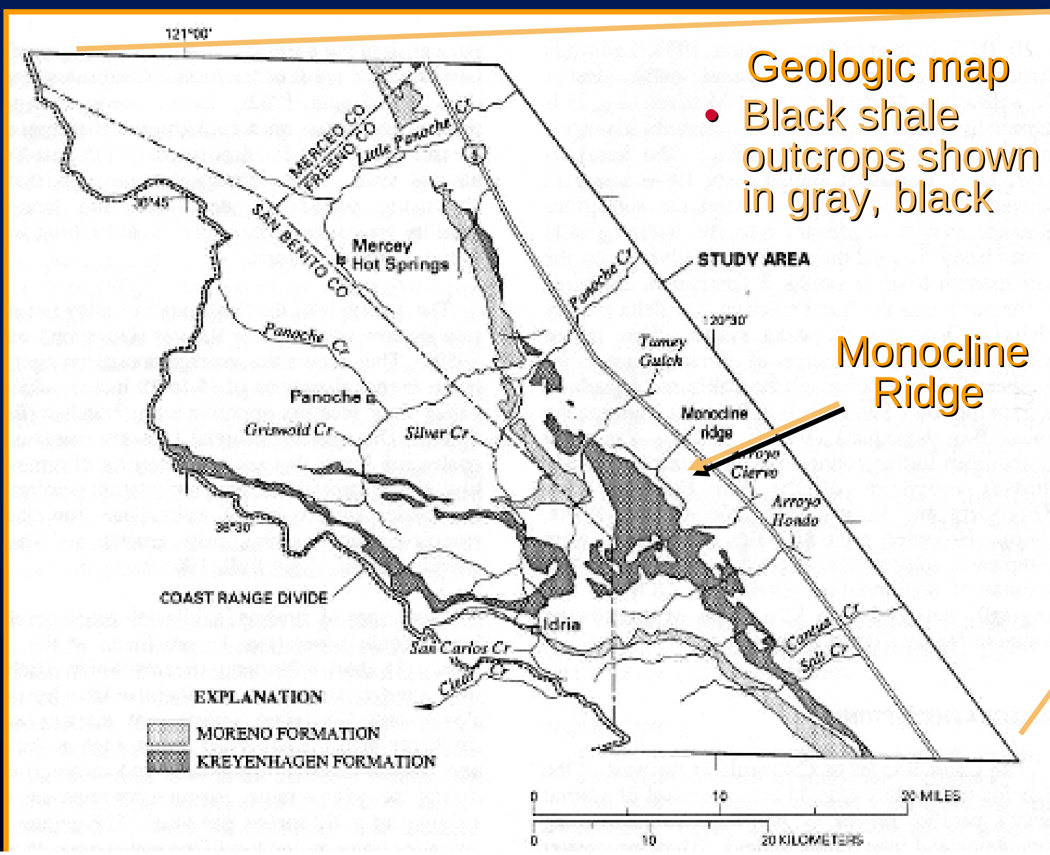
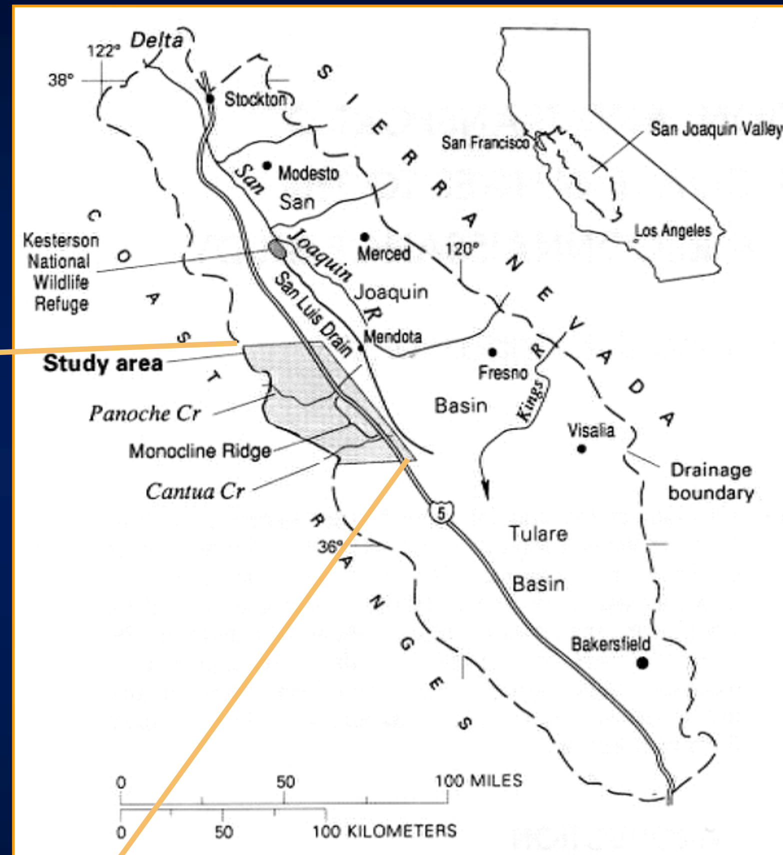
Sources of and processes leading to selenium toxicity in wildlife, Kesterson Reservoir, San Joaquin Valley, CA

- Late 1970's, early 1980's, dramatic increases in selenium-related wildfowl deformities, deaths at Kesterson Naitonal Wildlife Refuge.
- Leaching of selenium from soil into irrigation drain water was determined to be the cause

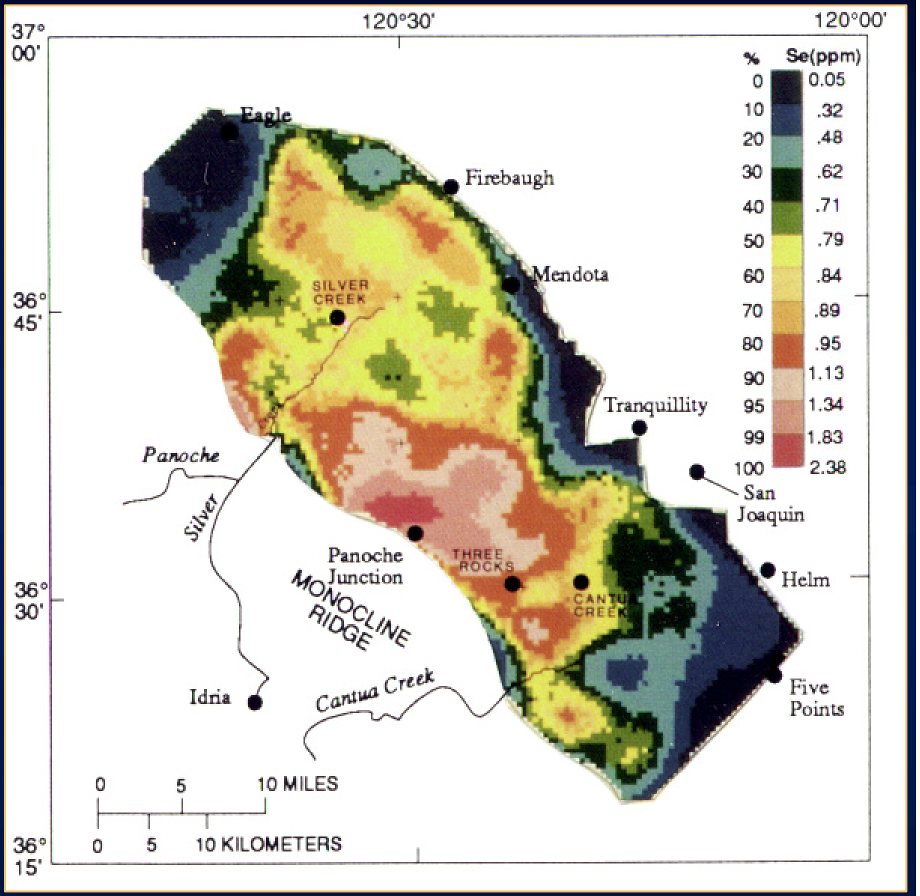




- Pyrite-bearing black shales occur in the foothills west of the valley

Sources of and processes leading to selenium toxicity in wildlife, Kesterson Reesrvoir, San Joaquin Valley, CA

- High Se concentrations in the Panoche fan soils are derived from erosion of the Se-rich, pyritic black shales in the foothills
- Se is present in sulfides, organics in the black shales. Oxidation during weathering releases Se(VI) into surface waters, which then flow into the valley and evaporate.
- Repeated application and evaporation of irrigation waters concentrated Se near the surface. Soluble Se-bearing salts formed by evaporation, then were leached by the next rain or irrigation water. Se was then transported via irrigation drains to Kesterson Reservoir.



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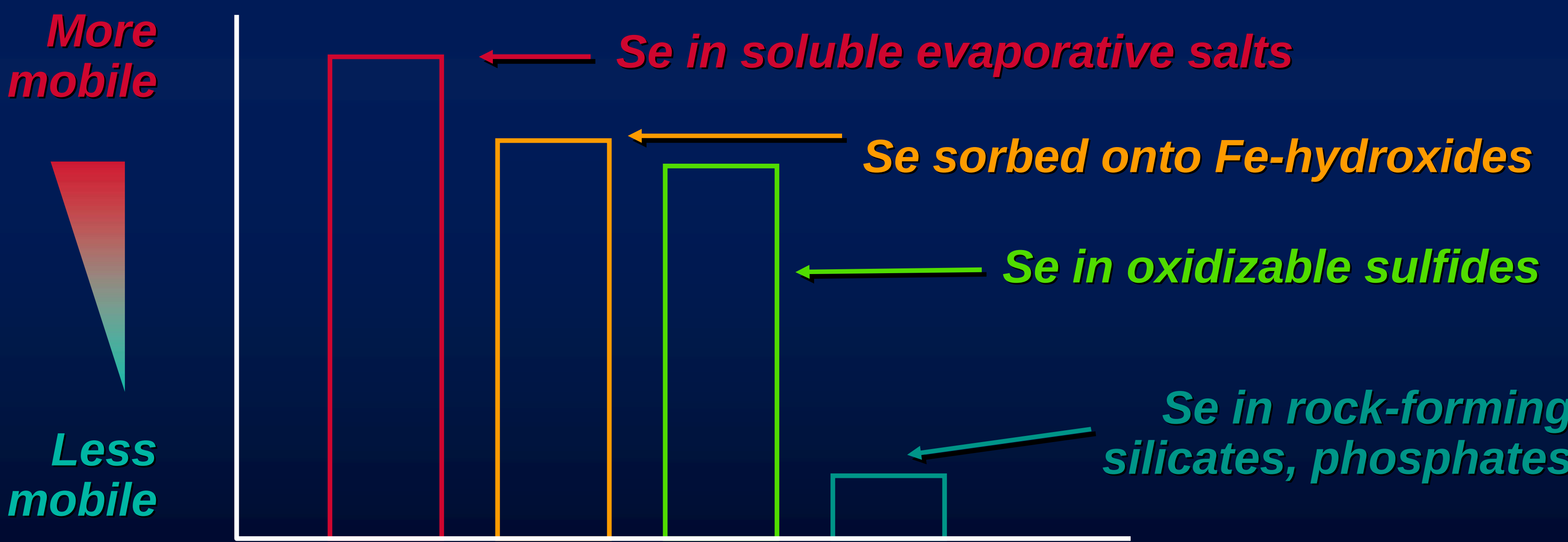
Rocks as sources for potential toxicants

The geologic occurrence of a trace element influences its environmental mobility

- Can be determined by mineralogical, geochemical studies



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Summary

"Everything is a poison, nothing is a poison, the dose alone is the poison"

- There are many sources for potential metal and mineral toxicants in the environment
- The environmental mobility as well as the health effects of metals are strongly controlled by:
  - The geological, mineralogical, or chemical form in which they occur in the source (ie, how readily liberated they are from the source by environmental processes)
  - The geological, geochemical, and biological processes that act to release them from the source, and transport them in the environment
  - The processes by which they are removed from the environment
- A large "dose" of geologic and geochemical knowledge is crucial to understand the potential origin and health implications of metals in the environment

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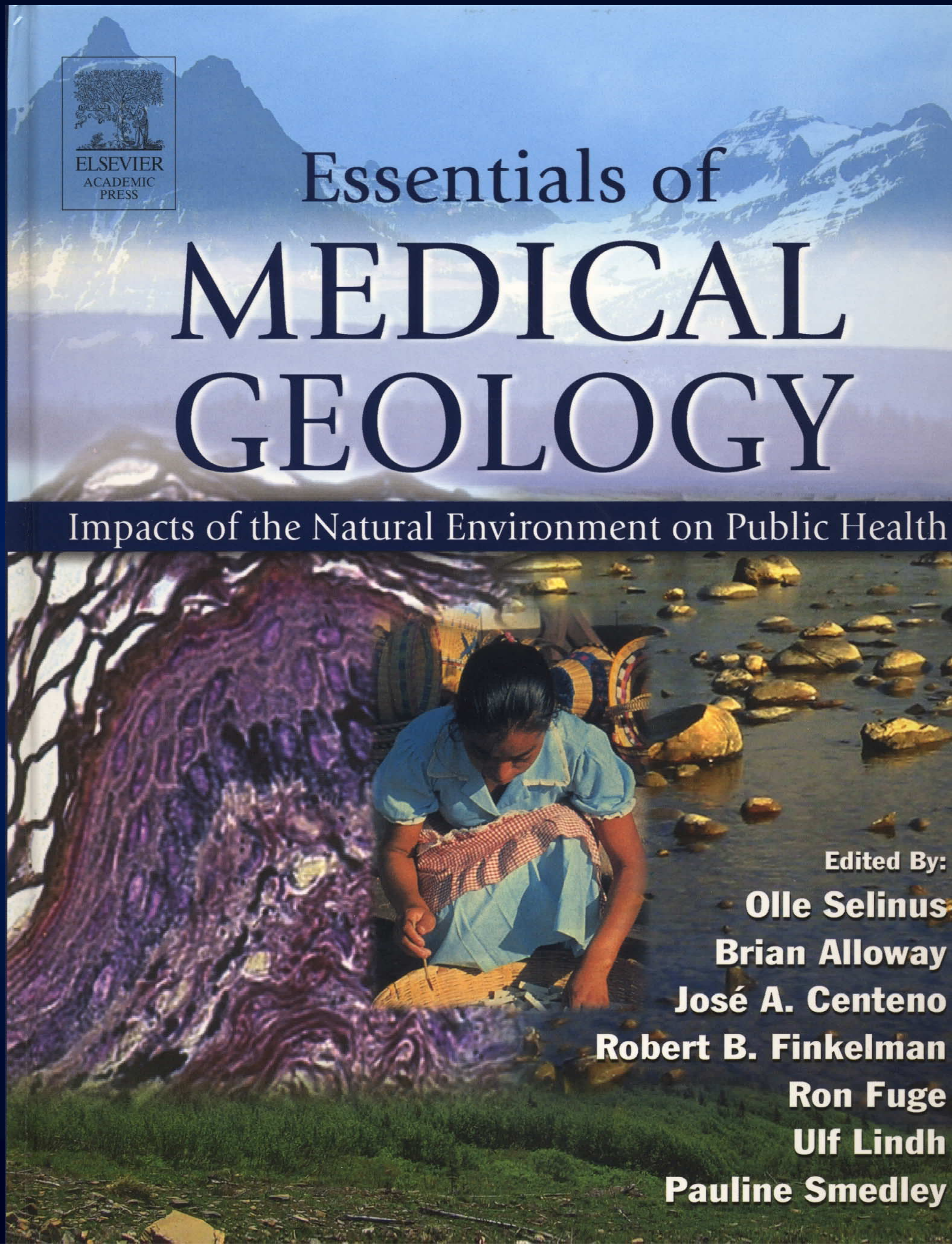
Useful references, cont.



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