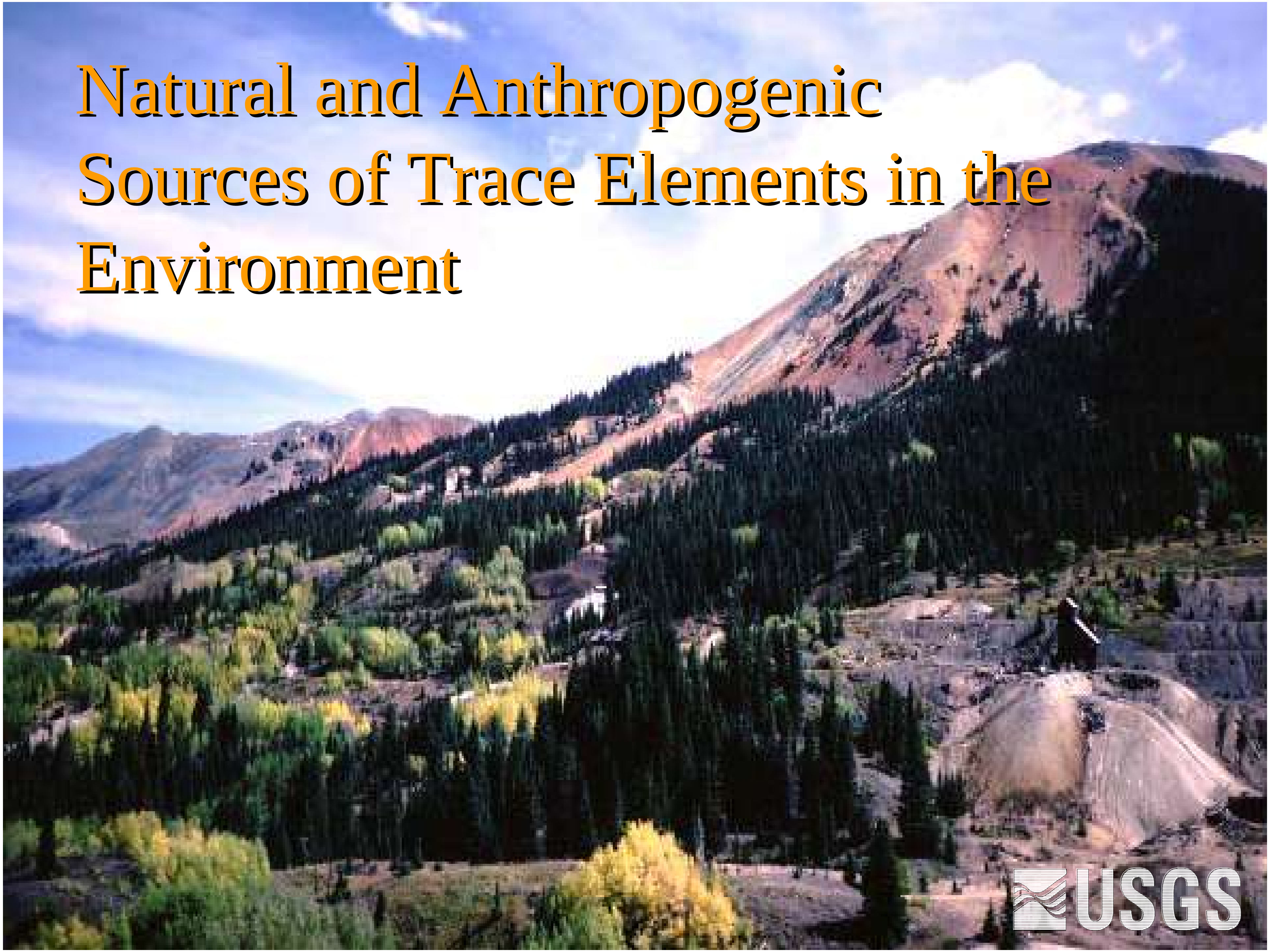
Natural and Anthropogenic Sources of Trace Elements in the Environment



A simple model for the cycling of potentially toxic elements and metals in the environment

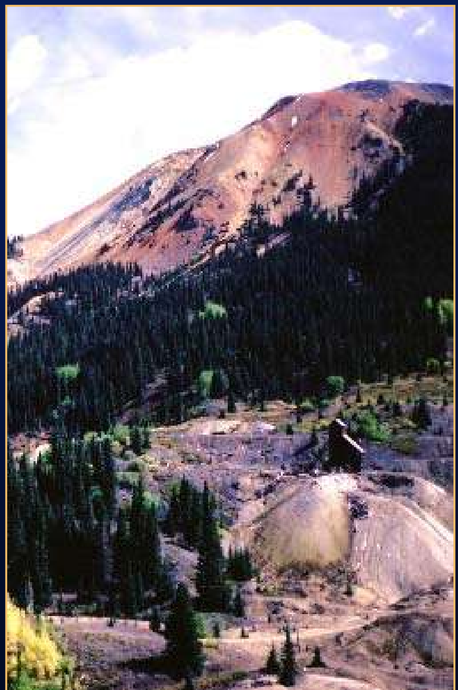
Fate:
Environmental and health effects

Transport (also mobilization, deposition):
Geological, geochemical, biological processes

Source:
Natural and (or) anthropogenic

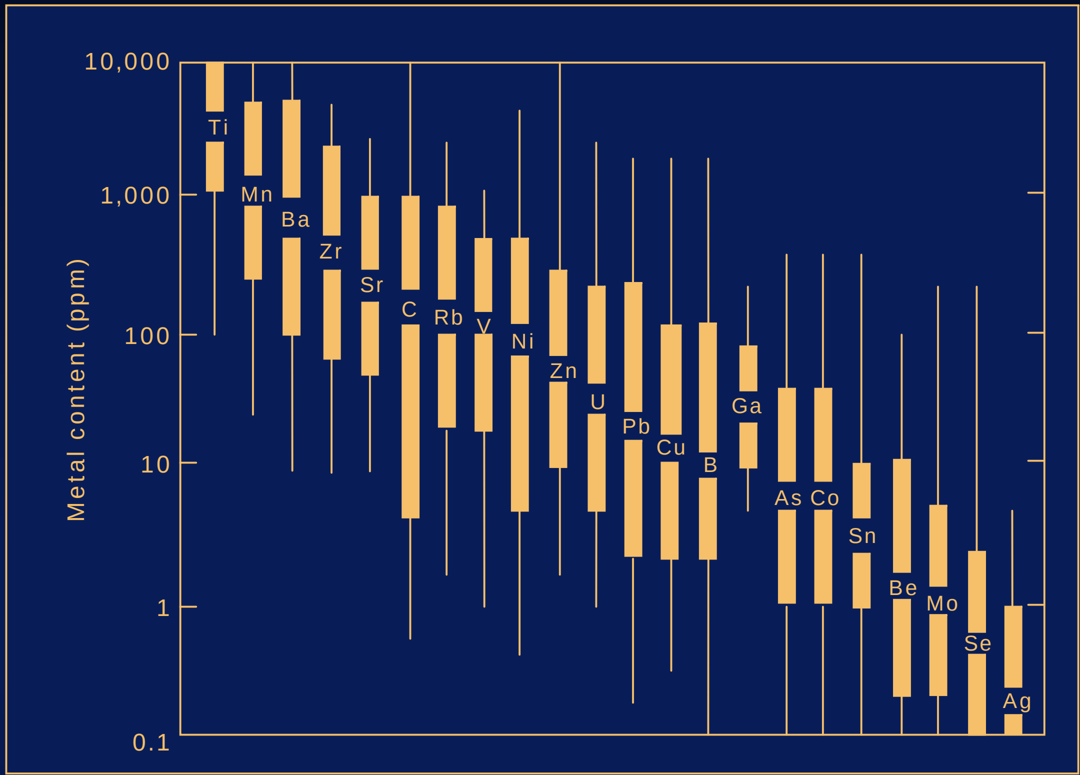
Source

- Many different sources contribute metals to the environment
  - Natural
  - Anthropogenic
- The mineralogical or chemical form in which a metal occurs in the source will greatly affect how readily it is released into the environment



NATURAL SOURCES

- ROCKS (SOIL)
- VOLCANIC EMISSIONS
- UNDERSEA SMOKERS
- EXTRA-TERRESTRIAL MATERIAL



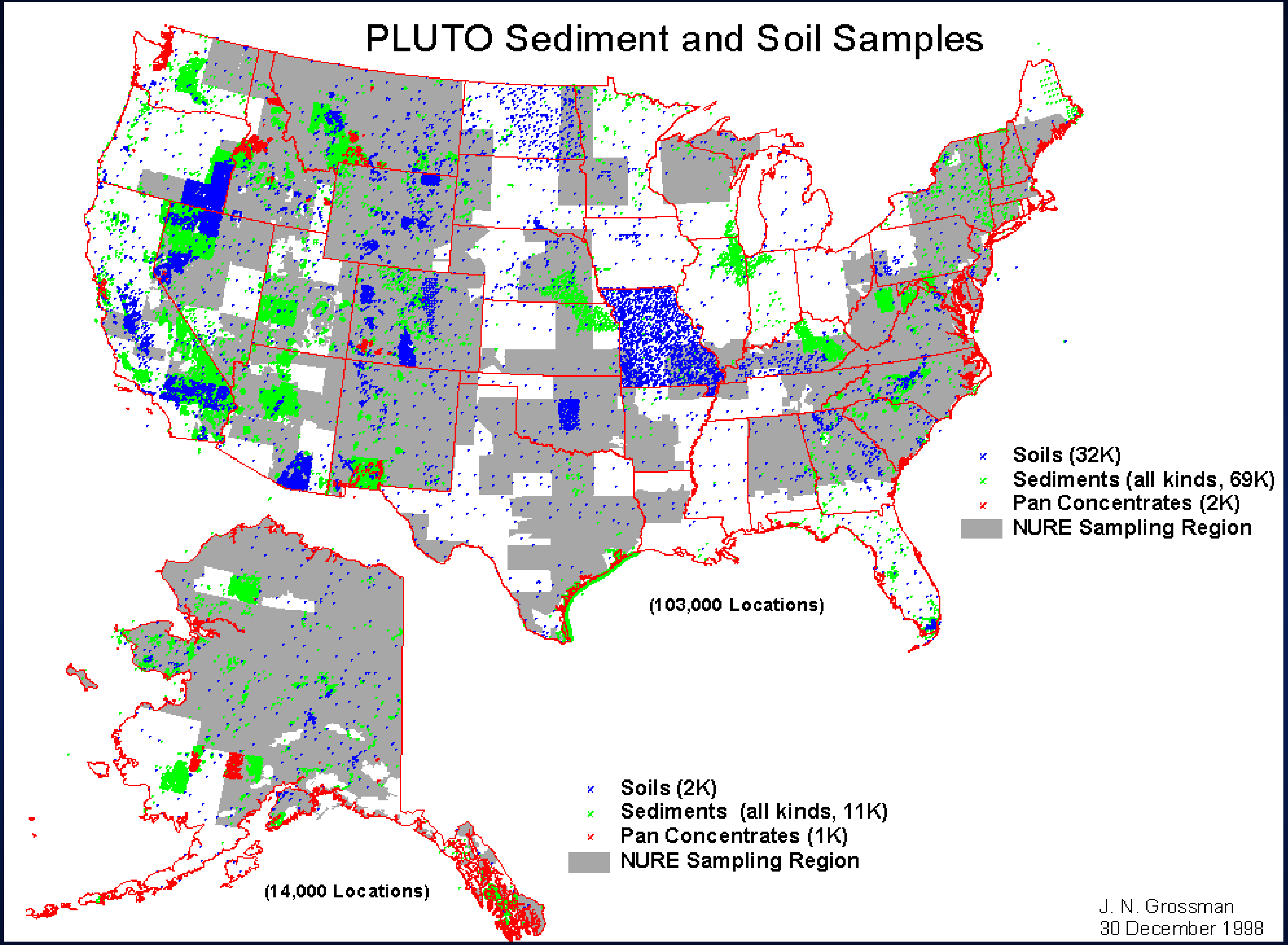
Range of the content of some minor elements in normal soils. Thin lines indicate more unusual values. (From Mitchell, in Bear, *Chemistry of the soil*.)

Examples of Metal Sources in the Environment

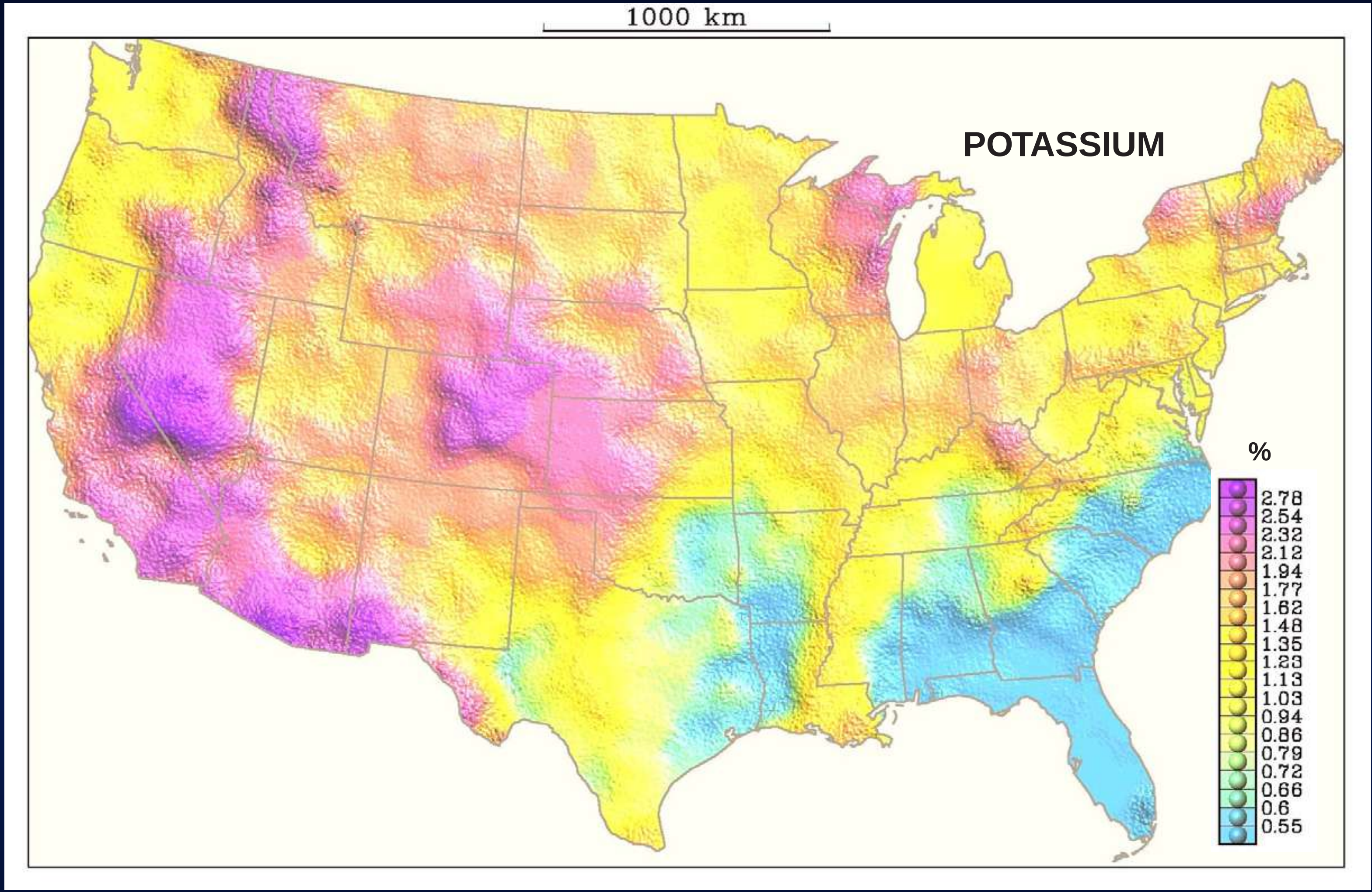
Natural sources (& processes)

- Weathering of rocks, mineral deposits
  - Produce metals in dusts, sediments, ground waters, surface waters
- Geothermal systems: metals in waters, gases, precipitates
- Volcanoes: metals in atmospheric gases, particulates, aerosols
- Sea spray: metals in water droplets, aerosols
- Forest fires: metals in ash, mineral particulates, gases, aerosols
- Biogenic emissions: relatively small contributions of metals in particulates, volatiles, waters
- Natural hydrocarbon seeps

Natural oil seep

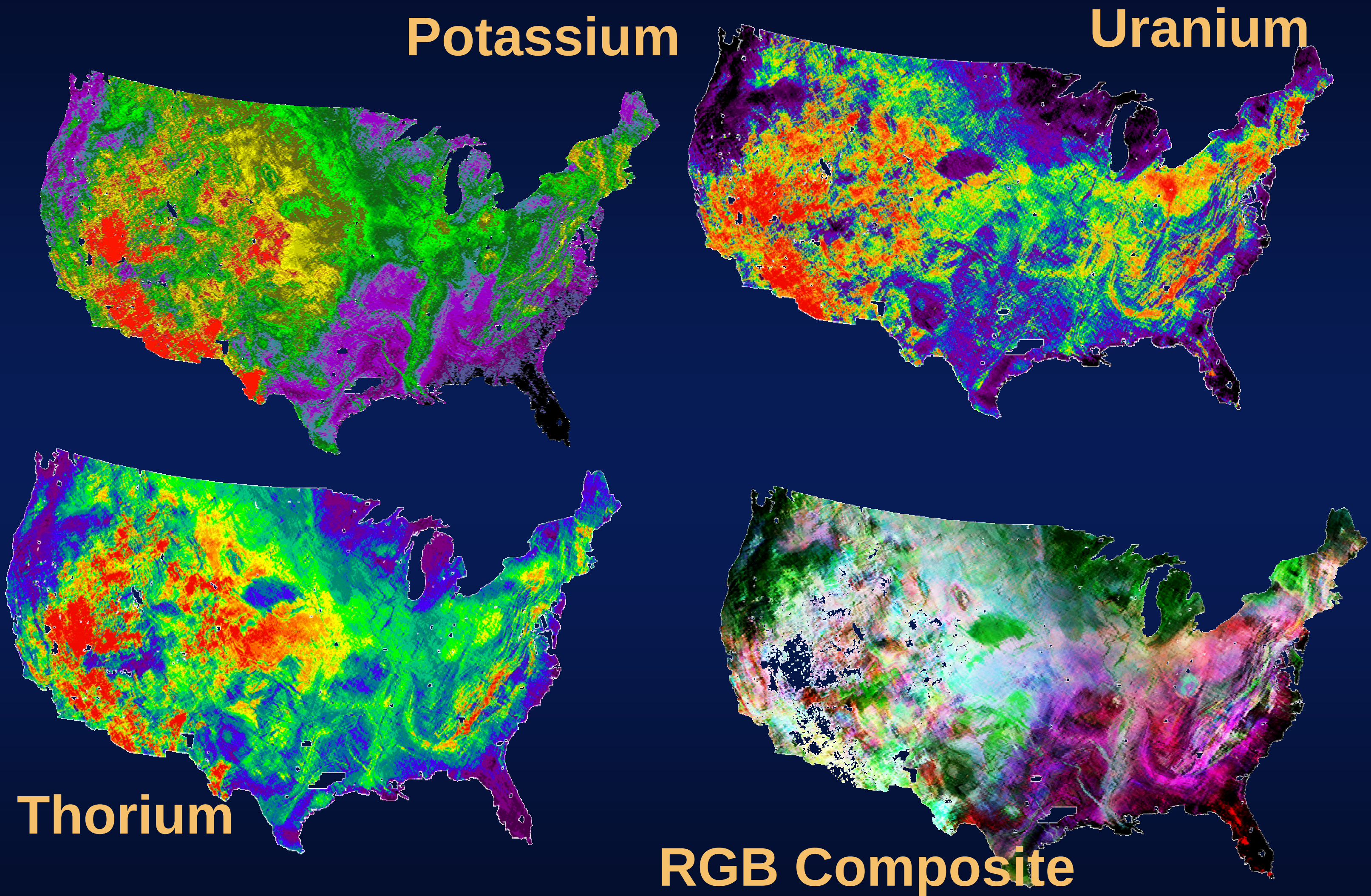


Current status of soil geochemistry—USGS



1000 km
POTASSIUM
%
2.78
2.54
2.32
2.12
1.94
1.77
1.62
1.48
1.35
1.23
1.13
1.03
0.94
0.86
0.79
0.72
0.66
0.6
0.55

GAMMA-RAY SURVEYS



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MANMADE SOURCES

- COMMERCIAL FERTILIZERS (Lime)
- PESTICUDES
- PAINT
- SEWAGE SLUDGE
- MUNICIPLE REFUSE
- MINING AND METAL SMELTING
- AUTO EMISSIONS
- COAL COMBUSTION & COAL WASTE
- ETC.

Examples of Metal Sources in the Environment

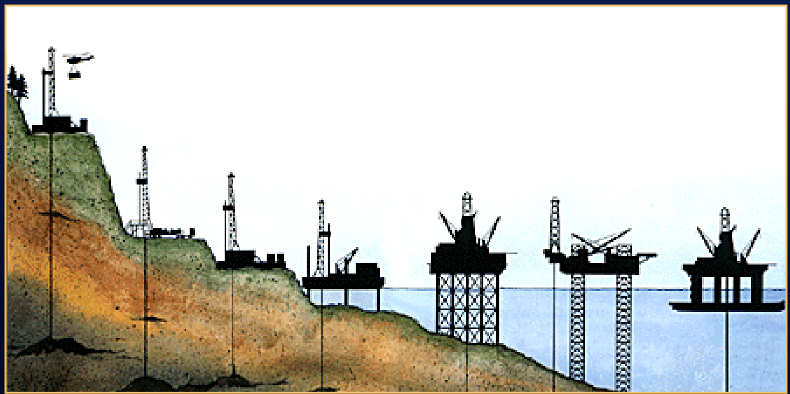
Anthropogenic sources (& processes)

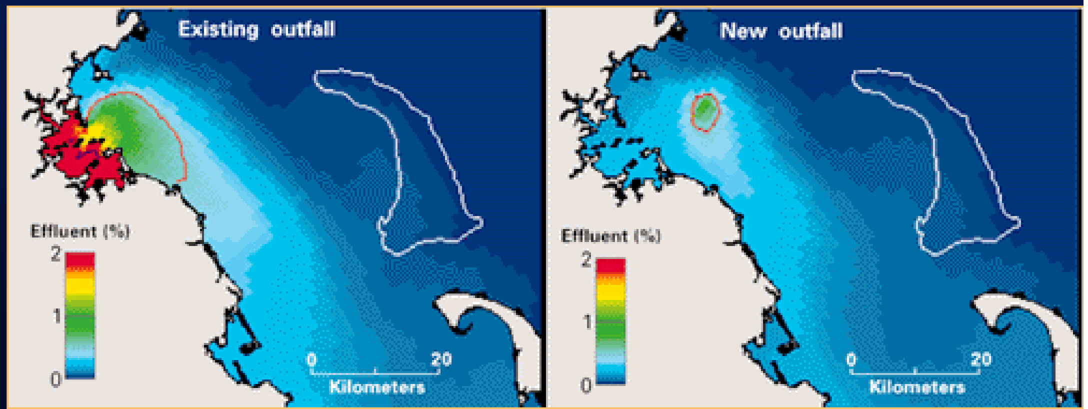
- Metal mining, mineral processing, smelting
  - Mine-drainage waters; mine waste piles; tailings impoundments and processing solutions; heap- leach impoundments and processing solutions; smelter slag and airborne emissions
- Coal mining, power generation
  - Mine drainage waters, waste piles; power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

Additional Examples of Metal Sources in the Environment

Anthropogenic sources

- 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 thereof (ie, commercial chemicals)
- Municipal waste incinerators, landfills, sewage sludge disposal





APPENDIX TABLE 1.13. Concentrations (ppm) of trace elements in surface soils impacted by smelters.

Pb smelter[a]								Cu and Ni smelter[b]								
Distance from smelter, km	Cd	Sb	Ag	Pb	Zn	Se	As	Distance from smelter, km	Cu	Ni	Co	Zn	Ag	Pb	Mn	V
0.4	83	155	30	7,900	13,000	4.6	100	1.1	2,892	5,104	199	96	7.9	82	255	103
1.1	25	5	9.3	3,200	870	0.76	49	1.6	2,416	1,851	80	65	3.5	53	202	63
2.4	—	32	6.0	1,700	970	—	69	2.2	2,418	2,337	92	82	7.8	58	174	115
3.2	32	260	31	6,700	1,400	5.1	94	2.9	1,657	1,202	41	50	3.3	48	143	25
3.7	—	28	2.7	2,000	200	—	24	7.4	1,371	1,771	46	87	2.9	46	299	165
5.3	18	18	2.8	1,000	940	—	36	10.4	287	282	54	72	2.3	28	364	137
8.1	—	20	3.6	300	320	—	53	13.5	233	271	42	100	4.3	23	602	151
12.6	—	20	3.7	890	804	—	24	19.3	184	306	24	61	ND[c]	28	264	55
19.0	—	40	10	2,200	3,000	—	37	24.1	45	101	18	46	5.5	19	207	33
								32.1	46	35	16	55	1.9	26	195	96
								38.6	2	39	29	62	ND	28	192	169
								49.8	26	35	22	83	1.0	20	168	23

Sources:

[a] In Kellogg, Idaho. Samples (0-2 cm surface soil) were not taken on a transect (Ragaini et al, 1977).

[b] In Sudbury Basin in Ontario, Canada. Samples (top 10 cm soil) were taken along a transect from smelter (Hutchinson and Whitby, 1974).

[c] Not detectable.

APPENDIX TABLE 1.7. Concentrations (ppm) of trace elements in sewage sludges.

	USA[a]		UK[b]		Sweden[c]		Canada[d]	New Zealand[e]
Element	Mean	Range	Mean	Range	Mean	Range	Mean	Mean
Ag	—	—	32	5-150	—	—	—	—
As	14.3	37345	—	—	—	—	—	—
B	37	22-90	70	15-1,000	—	—	1,950	480
Ba	621	272-1,066	1,700	150-4,000	—	—	—	580
Be	<8.5	—	5	1-30	—	—	—	—
Bi	16.8	<1-56	34	<12-100	—	—	—	—
Cd	104	7-444	<200	<60-1,500	13	2-171	38	4.5
Co	9.6	4-18	24	2-260	15	2-113	19	21
Cr	1441	169-14,000	980	40-8,800	872	20-40,615	1,960	850
Cu	1346	458-2,890	970	200-8,000	791	52-3,300	1,600	720
F	167	370-739	—	—	—	—	—	—
Hg	8.6	3-18	—	—	6.0	<0.1-55	—	—
Mn	194	32-527	500	150-2,500	517	73-3,861	2,660	610
Mo	14.3	1-40	7	2-30	—	—	13	8
Ni	235	36-562	510	20-5,300	121	16-2,120	380	350
Pb	1832	136-7,627	820	120-3,000	281	52-2,914	1,700	610
Sb	10.6	2-44	—	—	—	—	—	—
Se	3.1	1-5	—	—	—	—	—	—
Sn	216	111-492	160	40-700	—	—	—	80
Ti	2331	1,080-4,580	2,000	<1,000-4,500	—	—	—	4,700
V	40.6	15-92	75	20-400	—	—	15	80
W	20.2	1-100	—	—	—	—	—	—
Zn	2132	560-6,890	4,100	700-49,000	2,055	705-14,700	6,140	700

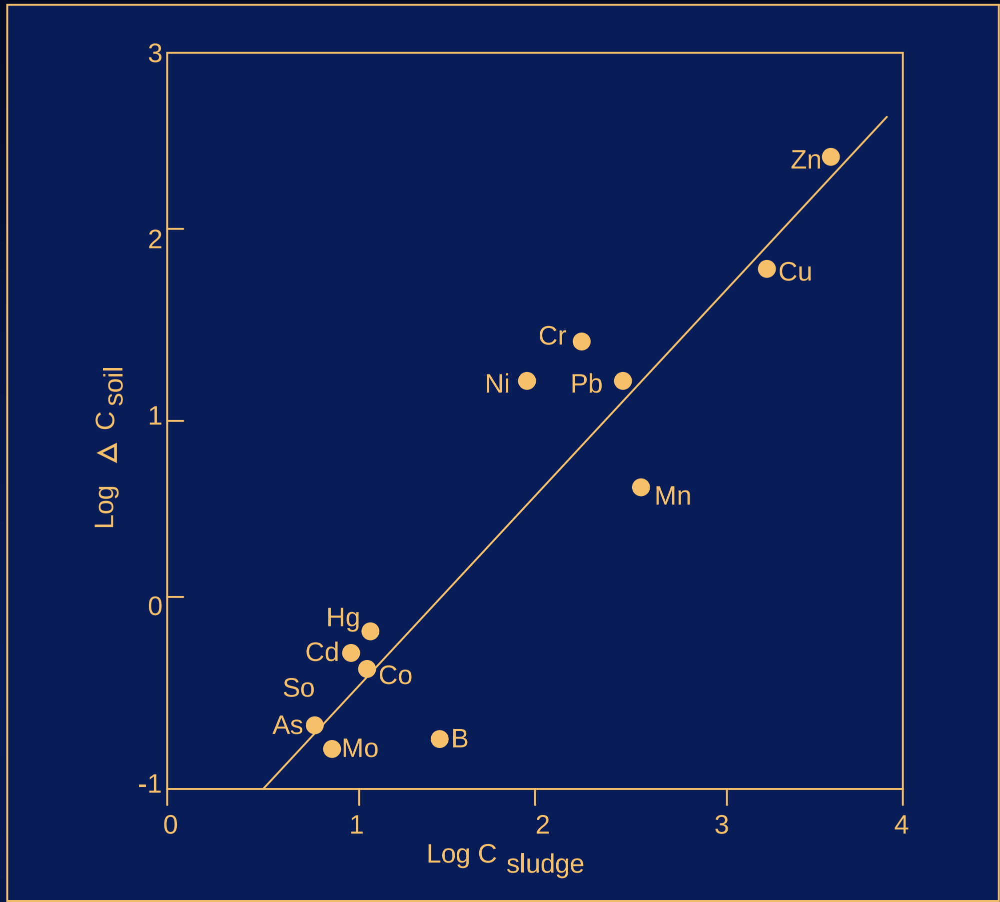
Sources: [a] Furr et al (1976); includes Atlanta, Chicago, Denver, Houston, Los Angeles, Miami, Milwaukee, Philadelphia, San Francisco, Seattle, Washington, DC, and five cities in New York.

[b] Berrow and Webber (1972); includes 42 samples from different locations in England and Wales.

[c] As summarized by Page (1974) from Berggren and Oden (1972); from 93 treatment plants.

[d] Oliver and Cosgrove (1975); from 10 sites in southern Ontario, Canada.

[e] Wells and Whitton (1977).



Relationship between concentration of trace elements in sewage sludge (C_{sludge}) and the increase of trace elements in the soil (C_{soil}) from using sewage Sludge. *Source*: Andersson and Nilsson, 1972.

More Examples of Metal Sources in the Environment

Anthropogenic sources

- Agricultural
  - Pesticides, fertilizers; irrigation practices; crop burning
- Households
  - Chemicals spilled, disposed of, or volatilized; fireplaces; building products

APPENDIX TABLE 1.3. Concentrations (ppm) of trace elements in fertilizers.

Fertilizer	Zn	Cu	Mn	B	Mo	Co	Cr	Ni	Pb
Diammonium phosphate (20-48-0)[a]:	—	—	—	—	—	—	—	—	—
Reagent grade	1.0	1.6	0.6	—	—	—	0.2	1.1	0.5
Idaho Phosphate rock	715	2.7	195	—	—	—	485	64	4.4
North Carolina phosphate rock	285	1.0	93	—	—	—	195	38	4.7
Rock phosphate[b]	187	32	975	72	555	109	184	—	962
Single superphosphate (0-16-0)[b]	165	15	890	132	335	77	87	—	488
Triple superphosphate (0-45-0)[b]	418	49	75	212	270	47	392	—	238
Diammonium phosphate[b]	112	7.2	307	396	75	16	80	—	195
Fluid fertilizer (0-15-0)[a]:	—	—	—	—	—	—	—	—	—
Idaho Phosphate rock	673	1.1	125	—	—	—	344	8.0	9.0
North Carolina phosphate rock	500	1.4	25	—	—	—	175	35	5.2
Urea (45-0-0)[b]	4.0	0.6	0.5	1.0	5.3	—	6.3	—	—
Calcium ammonium nitrate (25-0-0)[b]	7.6	2.8	25	9.0	56	6.6	8.5	—	116
Ammonium sulfate (21-0-0)[b]	11	0.8	3.5	—	6.0	24	4.0	—	—
Muriate of potash (0-0-60)[b]	10	3.1	3.5	16	26	22	13	—	117
N-P-K mixture (12-12-12)[b]	88	18	132	61	200	51	116	—	444
Superphosphate from apatite[c]	—	—	—	—	10	—	20	5	—

Sources: [a] Mortvedt and Giordano (1977); [b] Arora et al (1975); [c] Ermolenko (1972)

TABLE 2.9. Estimates of global arsenic emissions from natural and anthropogenic source. [a]

Source	Global production or consumption, 10^{12} g/yr	Arsenic emission factor, g/g source	Total arsenic emission ($d \leq 5$ μm), 10^9 g/yr
Natural			
Ocean			
Bubble bursting	1,000	5.7×10^{-7}	0.028
Gas exchange			0.11
Earth's crust			
Particle weathering	800	2.0×10^{-6}	0.24
Direct volatilization			0.0007
Volcanoes	25	2.8×10^{-4}	7.0
Forest wild fires	320	5.0×10^{-7}	0.16
Terrestrial biosphere			0.26
Total (natural)			7.8
Anthropogenic			
Coal	3,245	1.7×10^{-7}	0.55
Light fuels	585	1.2×10^{-10}	0.00007
Residual fuels	956	4.3×10^{-9}	0.0041
Wood fuel	1,200	5.0×10^{-7}	0.60
Agricultural burning	1,120	5.0×10^{-7}	0.56
Waste incineration	540	1.6×10^{-6}	0.43
Iron/steel production	1,220	7.0×10^{-6}	4.2
Copper production	8.7	3.0×10^{-3}	13
Lead/zinc production	9	5.0×10^{-4}	2.2
Mining mineral ore	2,500	1.0×10^{-8}	0.013
Arsenic/chemicals	0.040	1.0×10^{-2}	0.20
Arsenic/agriculture	0.037	5.0×10^{-2}	1.9
Cotton ginning	14	3.3×10^{-6}	0.023
Total (anthropogenic)			23.6
Grand Total (natural and anthropogenic sources)			31.4

[a] *Source:* Walsh et al, 1979, with permission of the authors, copyright by the Am Geophysical Union.

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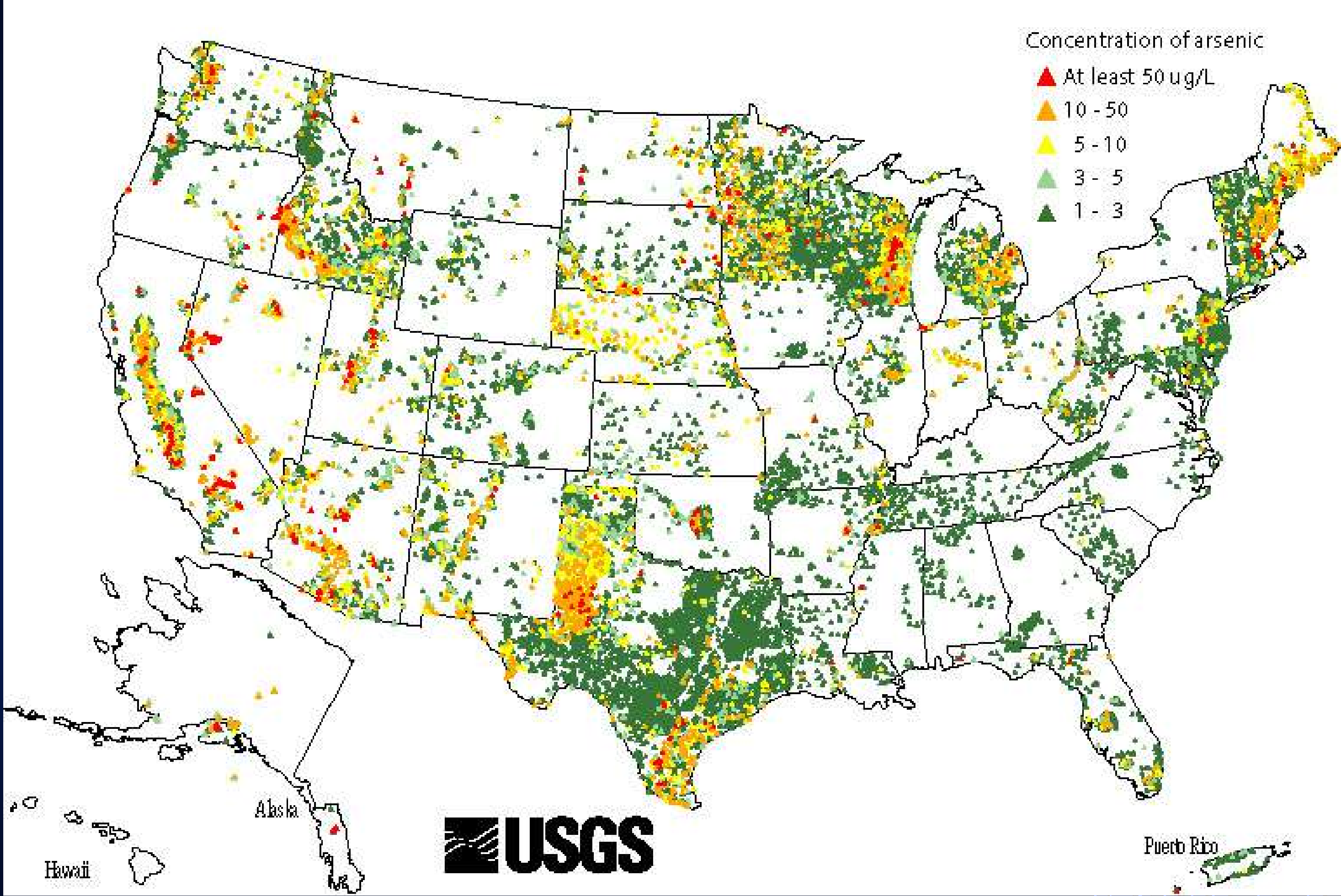

Concentration of arsenic
At least 50 ug/L
10 - 50
5 - 10
3 - 5
1 - 3
Alaska
Hawaii
Puerto Rico
USGS

TABLE 7.8. Global lead emissions from natural and anthropogenic sources.

Source	Production (109 kg/year)	Emission factor (g/kg)	Lead emission[b] (103 kg/year)
Natural			
Wind-blown and volcanic dust	200	1 x 10^{-2}	2,000
Sea spray	1000	<1 x 10^{-7}	<1,000
Forest foliage	100	<1 x 10^{-5}	<100
Volcanic sulfur	6	2 x 10^{-4}	1
Total			2,000
Anthropogenic			
Lead a1kyls	0.4	700	280,000
Iron smelting	780	0.06	47,000
Lead smelting	4	6	24,000
Zinc and copper smelting	15	2.8	42,000
Coal burning	3300	4.5 x 10^{-3}	15,000
Total			400,000

[a] Source: Settle and Patterson, 1980, with permission of the authors and the Am Assoc for Advancement of Science.
[b] Estimated as the product of production (in 10^9 kg/year) and emission factor (in g/kg).

Global Emissions of Hg to the Atmosphere per Year

- Total Emissions 6,000 to 8,000 metric tons
- Natural Sources of Hg 3,000 to 3,500 tons
  - Ocean may contribute as much as half
  - Erupting volcanoes
  - Soil Vapor Flux
  - Geothermal Systems/Hot Springs
  - Degassing Volcanoes and Fumaroles
  - Vapor Flux from Mineralized Areas
  - Active Faults

PINATUBO

2 days 1991

10 billion (miljarder) tons magma

20 milj ton SO2

2 milj ton Zn

1 milj ton Cu

5 500 ton Cd

100 000 ton Pb

300 000 Ni

550 000 ton Cr

800 ton Hg

60 Volcanoes/day

>3000 vent fields at midocean ridges

SGU

A more complex model for the Hg cycle

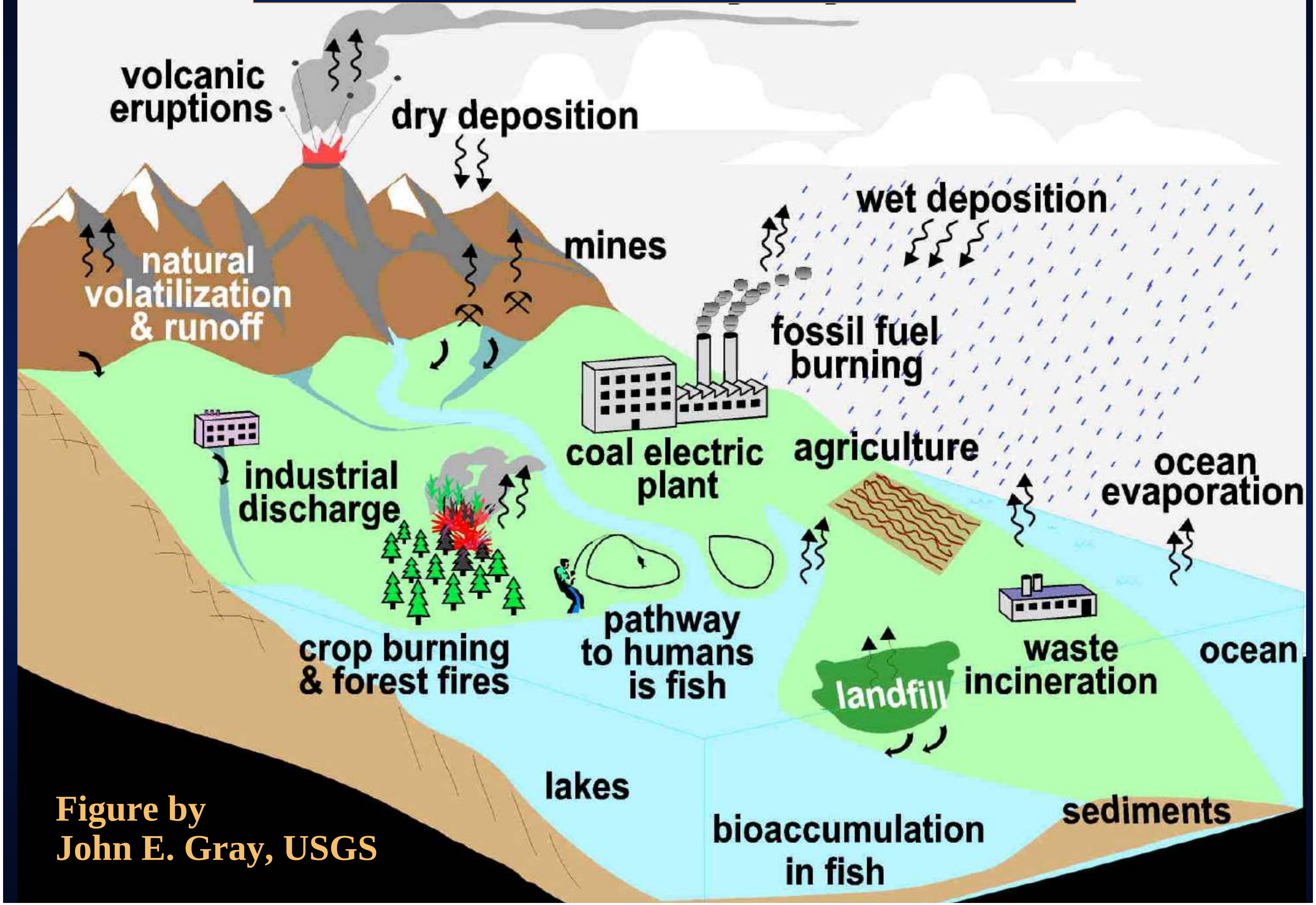


Figure by
John E. Gray, USGS

PRIMARY SOURCES

Cadmium-Mining and refining

Industrial and municipal wastes

Fertilizers

Sewage sludge

Coal combustion (1/3)

Chromium-Oxidation state important. Cr (VI) far more toxic than Cr (III).

Paper products

Chemicals

Fertilizers (up to 3,000 ppm)

Steel

Motor Vehicles

Chrome plating (10,000-50,000 ppm)

Municipal sludge

Coal combustion

PRIMARY SOURCES continued…

Mercury-Fungacides & Pestacides-now minor

Chemical and pulp mills

Coal combustion-important source

Ore smelting

Municipal wastes

Natural exhilation-importance?

Molybdenum-Sewage sludge

Coal combustion-primary source

Mining and milling

Selenium-Natural sources

Fertilizers

Coal combustion-important source in dry climates

Mining and smelting of sulfide ores

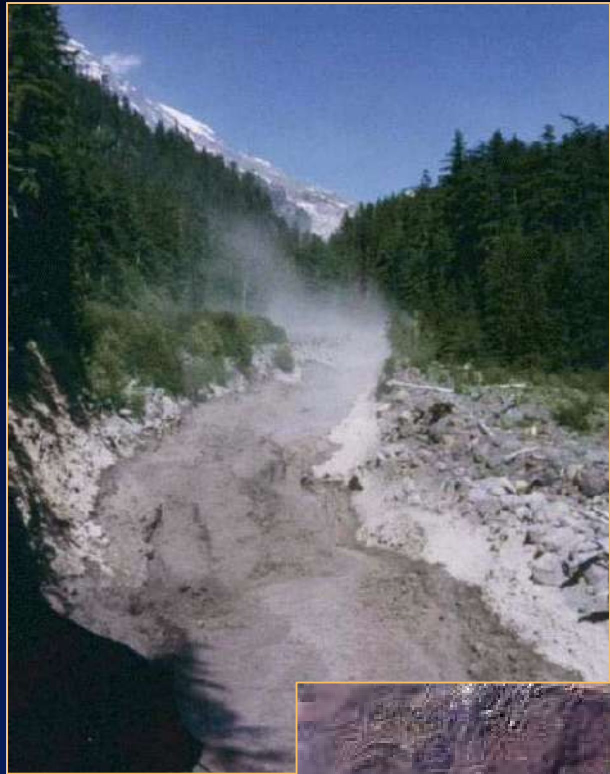
Processes That Affect Metal Mobility

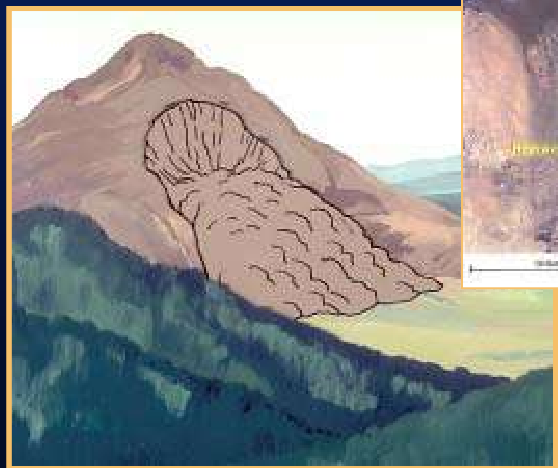
- Chemistry (inorganic, organic, physical)
- Microbiology (affects chemistry)
- Geology (lithology, structure, mineralogy)
- Hydrology (flow rates, permeability, flow paths)
- Gas transport (air permeability and flow paths)
- Weather and climate
- Solar cycles and photocatalysis

USGS

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



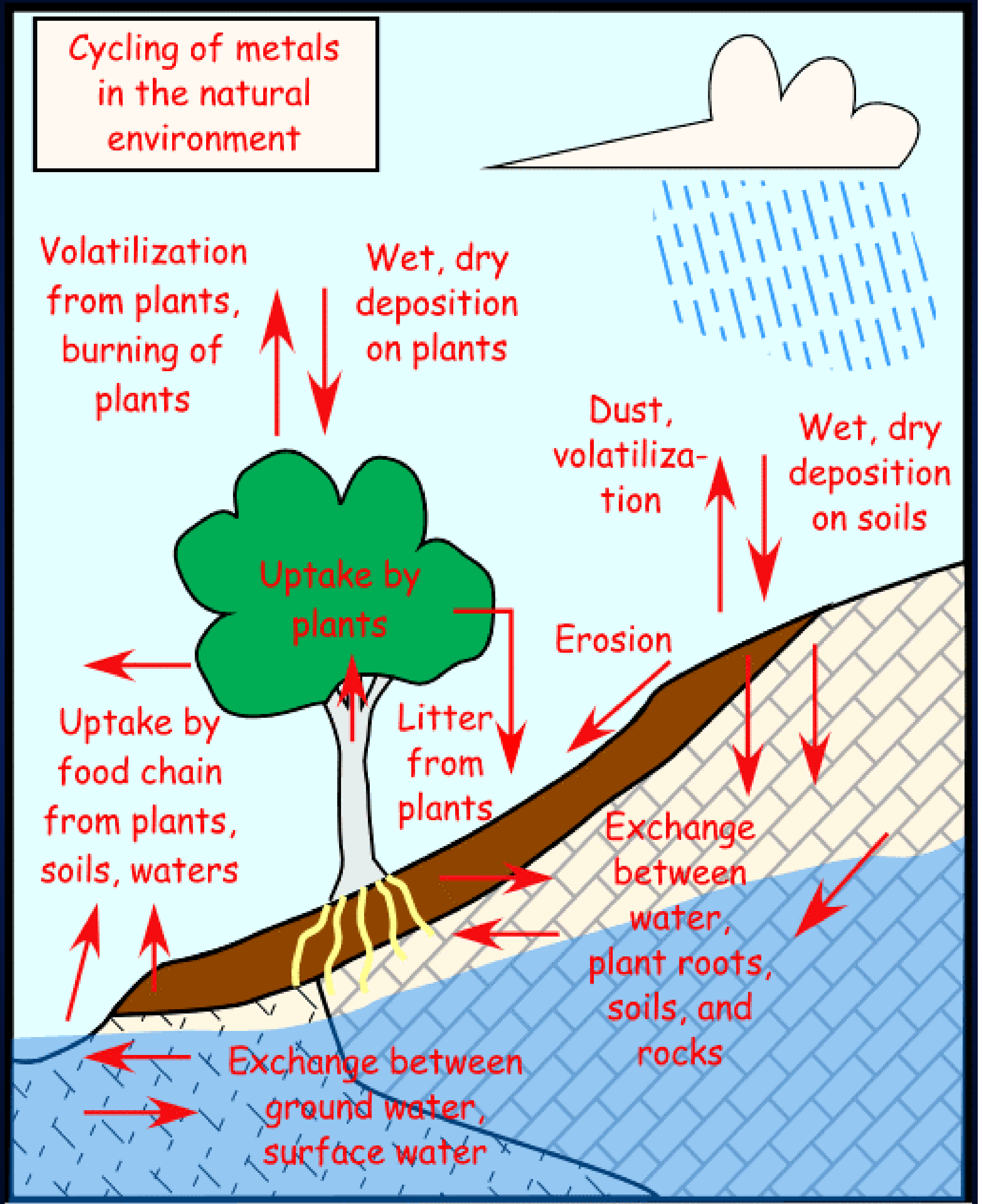


Transport

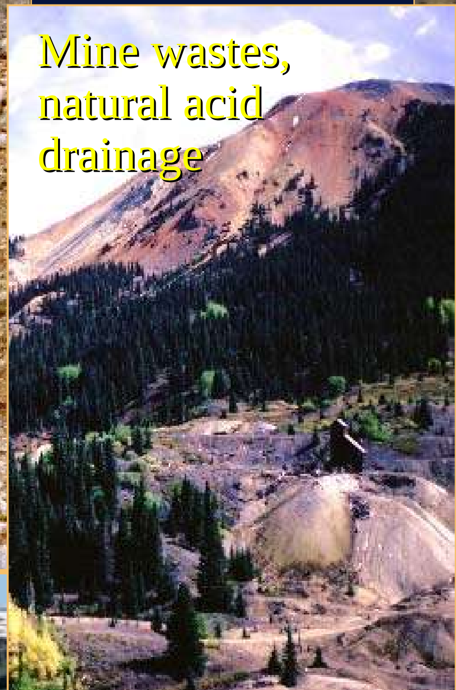
- Geochemical processes (many can bacterially catalyzed):
  - chemical weathering of rocks, minerals
  - oxidation - reduction reactions
  - acid/base reactions
  - formation of aqueous metal complexes
  - mineral precipitation
  - sorption of metals onto mineral, organic particulates
  - volatilization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

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.



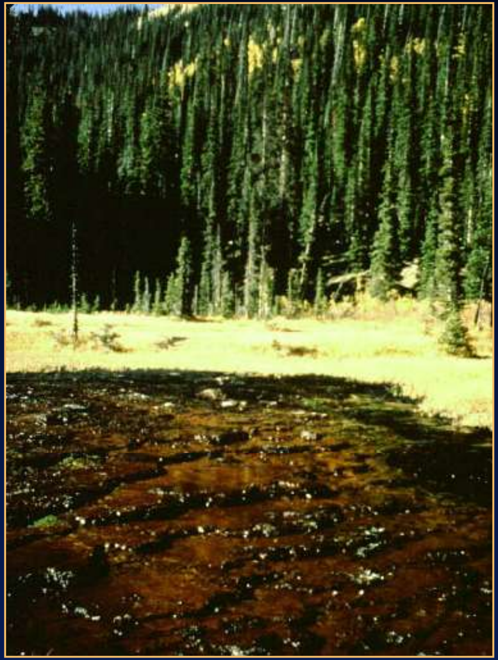
Metals Released by Mineral Deposits, Metal Mining, and Mineral Processing: Background and Case Studies



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



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Fate

- Metals can be removed from the environment by a variety of physical and geochemical processes without affecting ecological or human health, or…
- Metals can be taken up from the environment by plants
  - through roots, 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

- Geovailability
  - 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.
  - In order for a metal in an earth material to be bioavailable, it must first be geoavailable
- In order to predict, mitigate, and remediate the potential health effects of metals in the environment, it is crucial to understand:
  - The geologic, mineralogic, and chemical occurrences of metals in earth materials
  - The geochemical and biochemical processes that control metal mobility in the environment

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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 toxins 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

“Everything is a poison, nothing is a poison, the dose alone is the poison”

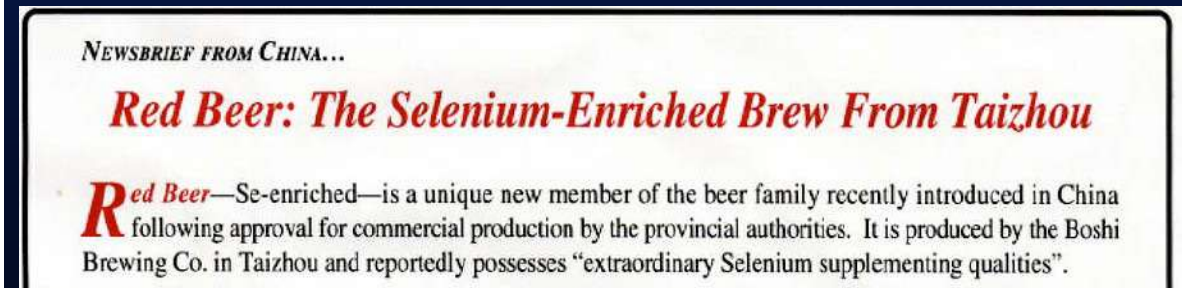
P.A. Parcelus (1493-1541)

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.

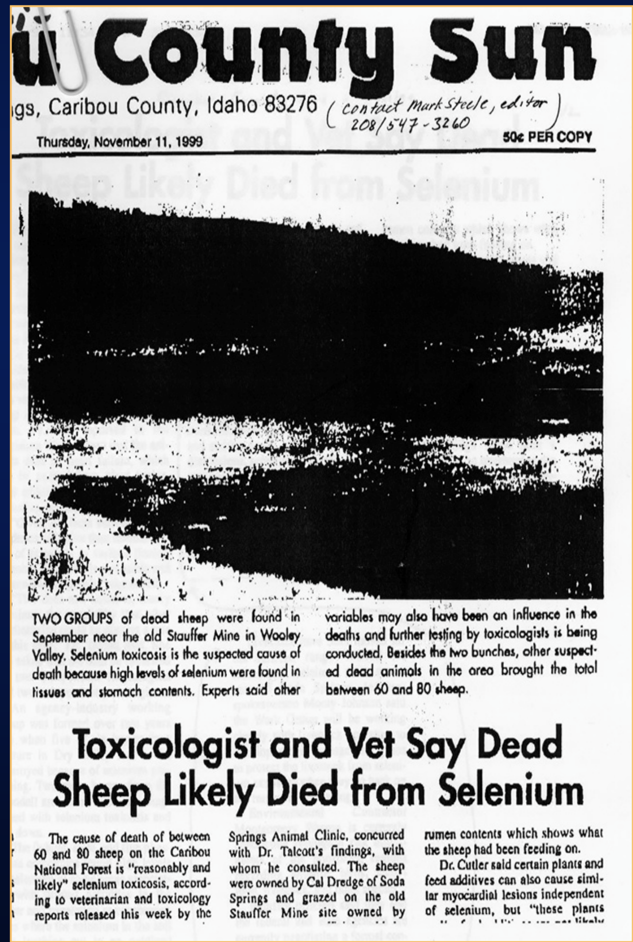
(CNN)



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”.



County Sun

...ngs, 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

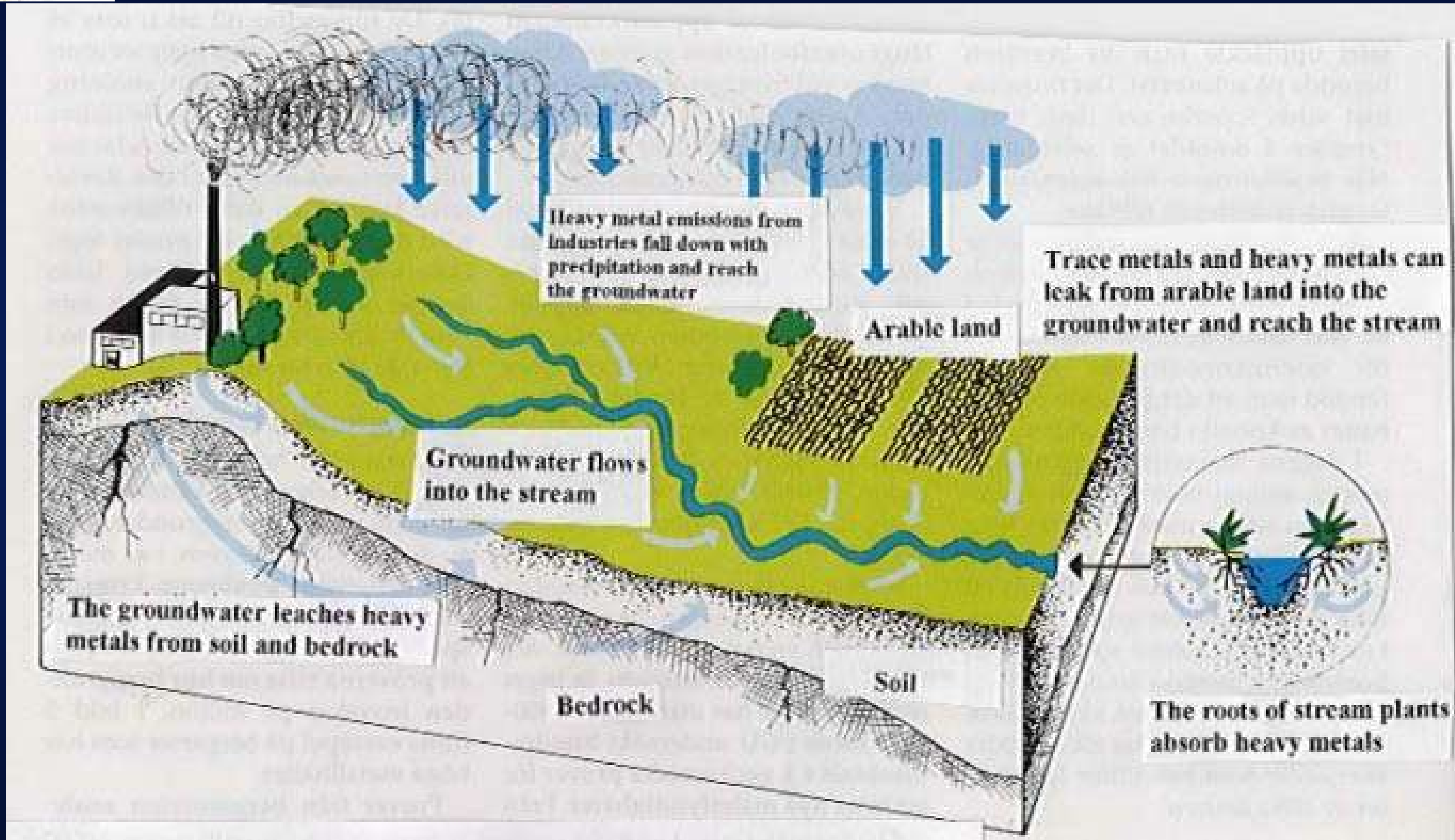
The cause of death of between 60 and 80 sheep on the Caribou National Forest is “reasonably and likely” selenium toxicosis, according to veterinarian and toxicology reports released this week by the Springs Animal Clinic, concurred with Dr. Talcott's findings, with whom he consulted. The sheep were owned 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

Fundamental Geochemical Processes

- Acid/base reactions (very common)
- Redox (Reduction-oxidation) reactions
- Complexation (inorganic and organic)
- Hydrolysis
- Sorption
- Evaporation (wet/dry cycles)
- Mineral precipitation/dissolution
- Gas reactions

United Nations Educational, Scientific and Cultural Organization.



The heavy metals in plant roots can be derived from bedrock and soils but also from industrial pollution and fertilization of arable land