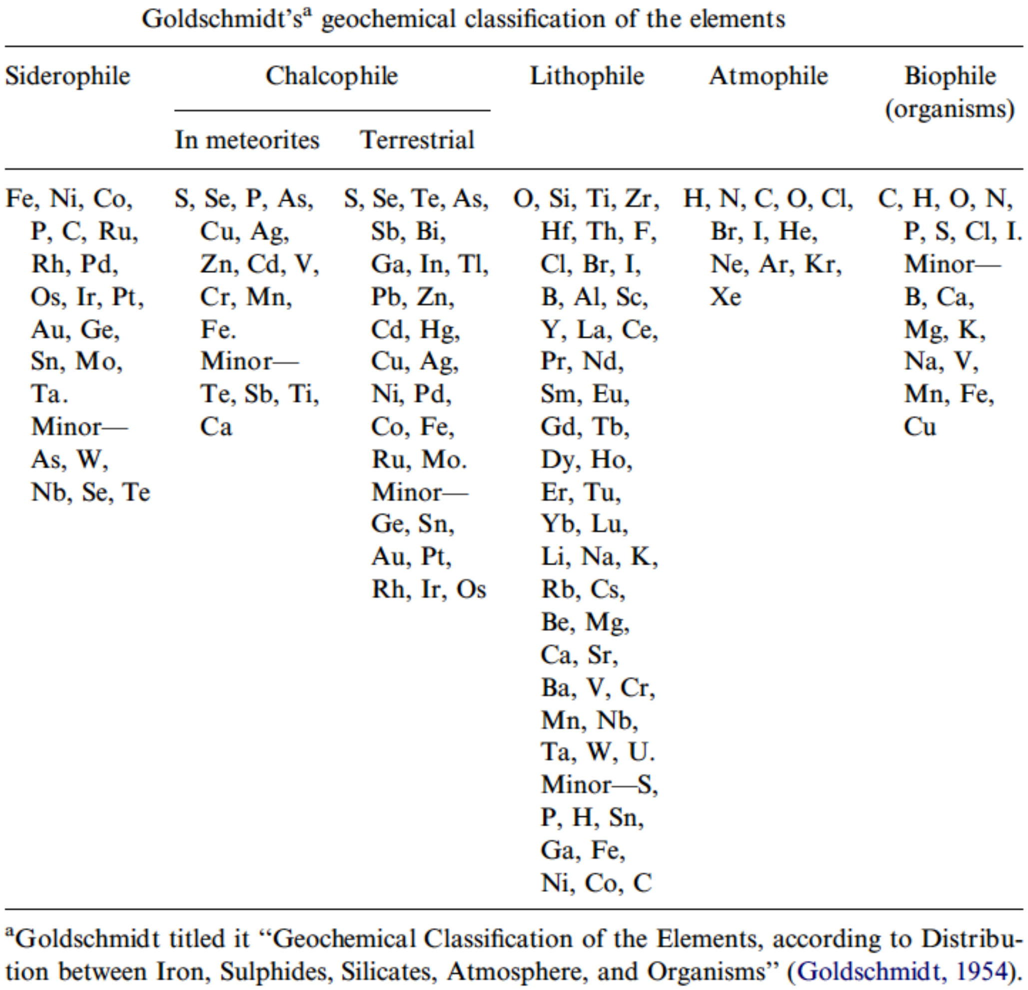
In 1923 **Victor Moritz Goldschmidt**, the father of modern geochemistry, proposed the ***geochemical classification of the elements*** (Goldschmidt, 1923 ; Mason, 1992 ).



Goldschmidt's[a] geochemical classification of the elements

| Siderophile | Chalcophile | | Lithophile | Atmophile | Biophile (organisms) |
|---|---|---|---|---|---|
| | In meteorites | Terrestrial | | | |
| Fe, Ni, Co, P, C, Ru, Rh, Pd, Os, Ir, Pt, Au, Ge, Sn, Mo, Ta. Minor—As, W, Nb, Se, Te | S, Se, P, As, Cu, Ag, Zn, Cd, V, Cr, Mn, Fe. Minor—Te, Sb, Ti, Ca | S, Se, Te, As, Sb, Bi, Ga, In, Tl, Pb, Zn, Cd, Hg, Cu, Ag, Ni, Pd, Co, Fe, Ru, Mo. Minor—Ge, Sn, Au, Pt, Rh, Ir, Os | O, Si, Ti, Zr, Hf, Th, F, Cl, Br, I, B, Al, Sc, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tu, Yb, Lu, Li, Na, K, Rb, Cs, Be, Mg, Ca, Sr, Ba, V, Cr, Mn, Nb, Ta, W, U. Minor—S, P, H, Sn, Ga, Fe, Ni, Co, C | H, N, C, O, Cl, Br, I, He, Ne, Ar, Kr, Xe | C, H, O, N, P, S, Cl, I. Minor—B, Ca, Mg, K, Na, V, Mn, Fe, Cu |

[a] Goldschmidt titled it "Geochemical Classification of the Elements, according to Distribution between Iron, Sulphides, Silicates, Atmosphere, and Organisms" (Goldschmidt, 1954).

The classification of the elements: **lithophile** (affinity for silicate), **siderophile** (affinity for iron–nickel), **chalcophile** (affinity for sulfide), and **atmophile** (affinity for the gaseous state)

Goldschmidt included in his classification the **biophile elements**. They are defined as *"those elements that are the most typical in organisms and organic material, or are concentrated in and by living plants and animals"* (Bates and Jackson, 1984 ).

The biophile elements all occur as lithophile and/or chalcophile elements. Biophile elements include carbon, hydrogen, oxygen, nitrogen, phosphorus, sulfur, chlorine, iodine, bromine, calcium, magnesium, potassium, sodium, vanadium, iron, manganese, and copper.

Tables of the distribution of the elements in leading geochemistry textbooks in 1982 and 1995

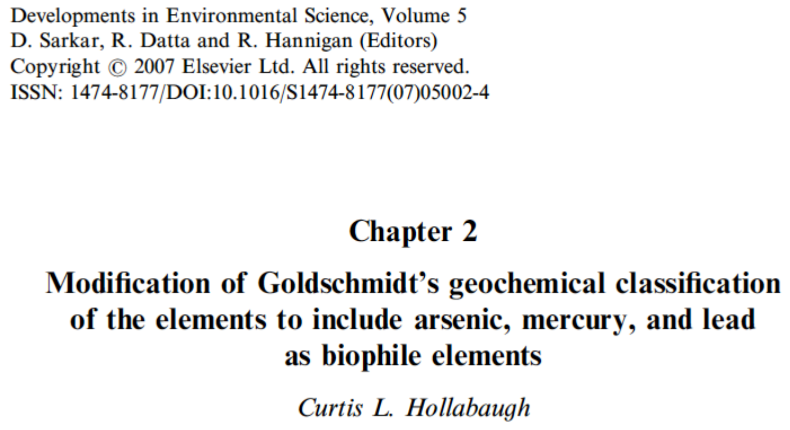
| Siderophile | Chalcophile | Lithophile | Atmophile |
|---|---|---|---|
| Mason and Moore (1982) | | | |
| Fe,[a] Co,[a] Ni,[a] Ru, Rh, Pd, Os, Ir, Pt, Au, Re,[b] Mo,[b] Ge,[a] Sn, W,[c] C,[c] Cu,[a] Ga,[a] Ge, As,[b] Sb[b] | Ag, Zn, Cd, Hg, Ga, In Tl, Pb, Bi, S, Se, Te, Mo. Minor—Cu, Ge, Sn, As, Sb, Fe, Os, Ru, Rh, Pd | Li, Na, K, Rb, Cs, Be, Mg, Ca, Sr, Ba, B, Al, Sc, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Si, Ti, Zr, Hf, Th, P, V, Nb, Ta, O, Cr, U, H, F, Cl, Br, I, Mn. Minor—Fe, Zr, Ga | N, He, Ne, Ar, Kr, Xe. Minor—H, O |
| Krauskopf and Bird (1995) | | | |
| Fe, Co, Ni, Ru, Rh, Pd, Re, Os, Ir, Pt, Au, Mo, Ge, Sn, C, P. Minor[d]—Pb, As, W | Cu, Ag, Zn, Cd, Hg, Ga, In, Tl, Pb, As, Sb, Bi, S, Se, Te. Minor[d]—Fe, Mo, Re | Li, Na, K, Rb, Cs, Be, Mg, Ca, Sr, Ba, B, Al, Sc, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Si, Ti, Zr, Hf, Th, V, Nb, Ta, O, Cr, W, U, Mn, F, Cl, Br, I. Minor[d]—Pb, C, P, Fe, H, Tl, Ga, Ge, N | H, N, He, Ne, Ar, Kr, Xe. Minor[d]—C, O, F, Cl, Br, I |

[a] Chalcophile and lithophile in the earth's crust.

[b] Chalcophile in the earth's crust.

[c] Lithophile in the earth's crust.

[d] Minor elements belong for the most part in another group but do occur in this group.



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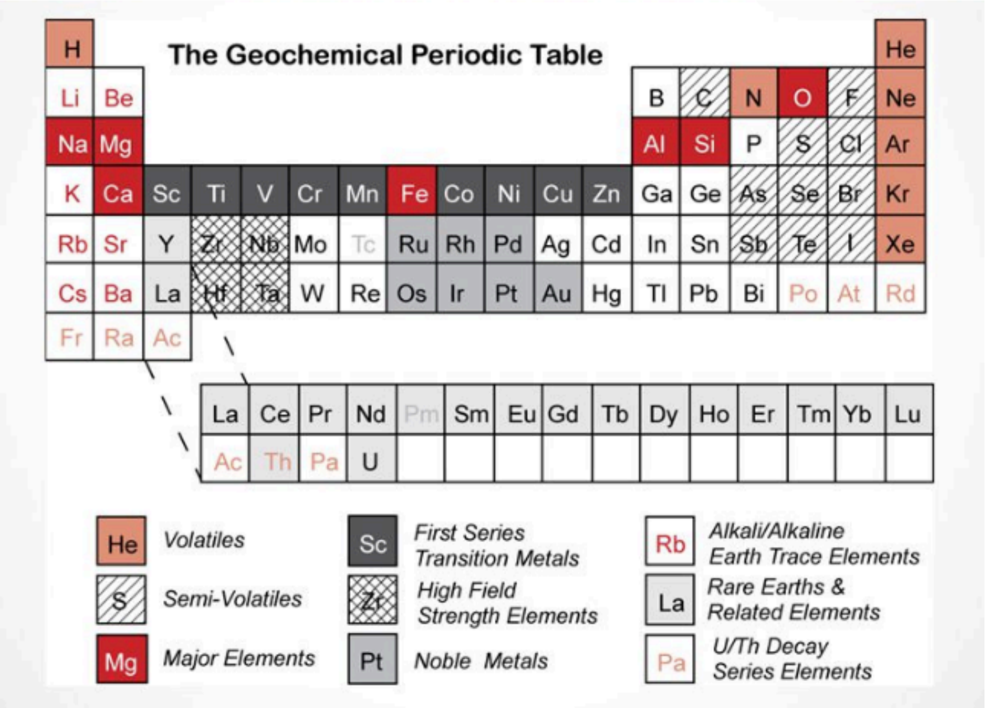
Chapter 2

**Modification of Goldschmidt's geochemical classification of the elements to include arsenic, mercury, and lead as biophile elements**

*Curtis L. Hollabaugh*



The Geochemical Periodic Table

| | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| H | | | | | | | | | | | | | | | | | He |
| Li | Be | | | | | | | | | | | B | C | N | O | F | Ne |
| Na | Mg | | | | | | | | | | | Al | Si | P | S | Cl | Ar |
| K | Ca | Sc | Ti | V | Cr | Mn | Fe | Co | Ni | Cu | Zn | Ga | Ge | As | Se | Br | Kr |
| Rb | Sr | Y | Zr | Nb | Mo | Tc | Ru | Rh | Pd | Ag | Cd | In | Sn | Sb | Te | I | Xe |
| Cs | Ba | La | Hf | Ta | W | Re | Os | Ir | Pt | Au | Hg | Tl | Pb | Bi | Po | At | Rd |
| Fr | Ra | Ac | | | | | | | | | | | | | | | |

| | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| La | Ce | Pr | Nd | Pm | Sm | Eu | Gd | Tb | Dy | Ho | Er | Tm | Yb | Lu |
| Ac | Th | Pa | U | | | | | | | | | | | |

He Volatiles
S Semi-Volatiles
Mg Major Elements
Sc First Series Transition Metals
Zr High Field Strength Elements
Pt Noble Metals
Rb Alkali/Alkaline Earth Trace Elements
La Rare Earths & Related Elements
Pa U/Th Decay Series Elements

Arsenic, lead, and mercury have great affinity to concentrate in the biosphere.

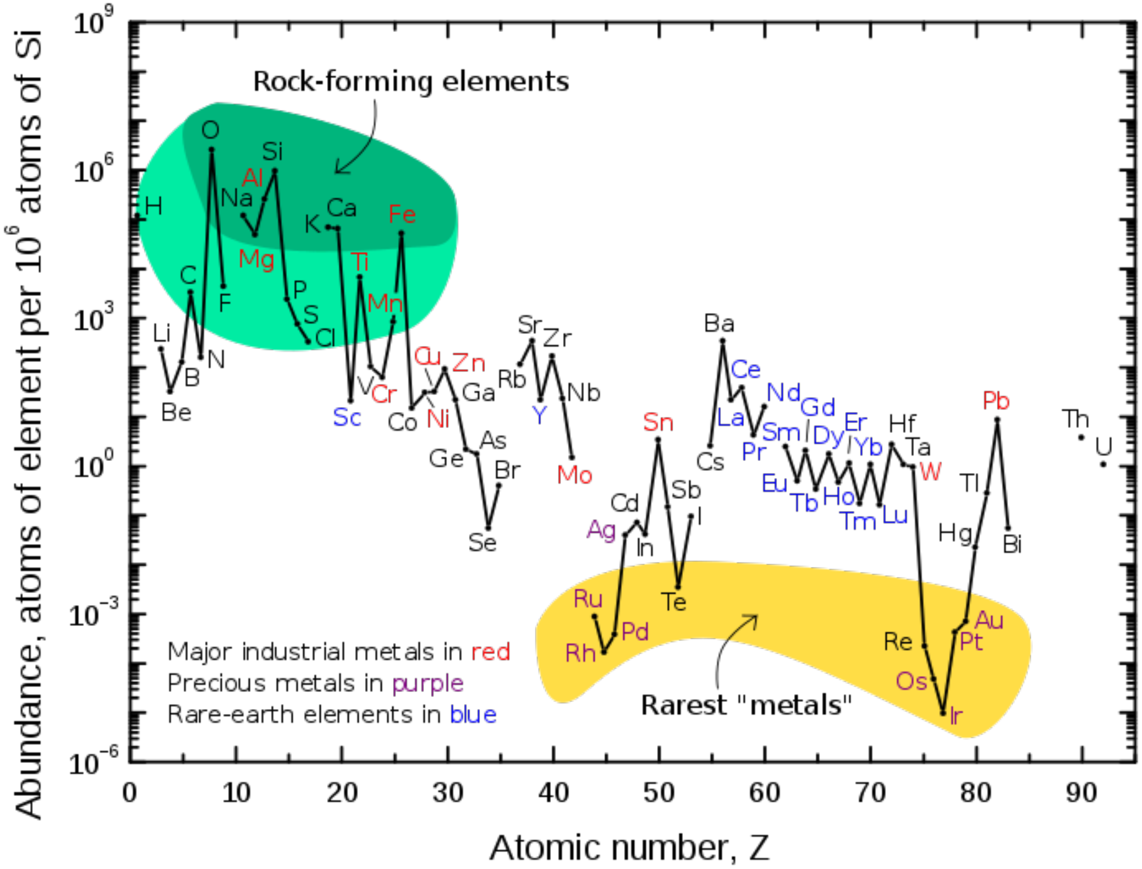
*<u>Under certain conditions</u>* they will reach relatively **high concentrations** in coal and humans.

They are **biophile** because of substitutions (lead for calcium), bioaccumulation (arsenic and mercury), and methylation (mercury).

Research indicates that additional classification of these traditional *<u>chalcophile elements</u>* as **biophile elements** is indispensable to future proper understanding and utilization of arsenic, lead, and mercury in the modern industrial, developing, and impoverished world.

# Biophile elements

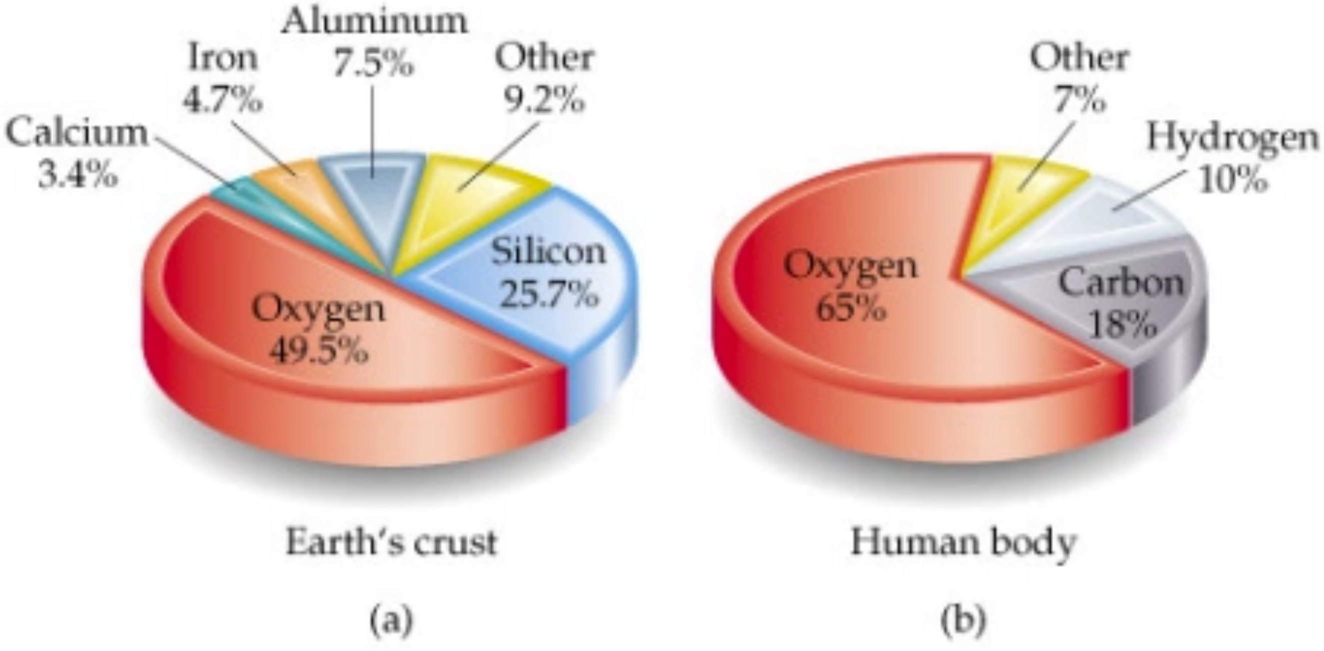
The beauty of Goldschmidt’s classification is that it is based on the distribution of the elements. The siderophile, chalcophile, lithophile, and atmophile elements are well described and long accepted (Garrett, 2005).



Goldschmidt’s original list of major biophile elements was C, H, O, N, P, S, Cl, and I. His list of minor biophile elements was B, Ca, Mg, K, Na, V, Mn, Fe, and Cu.

Biophile elements are enriched in the biosphere —life, organic waste, dead remains, and naturally processed materials from the biosphere (coal, oil, natural gas, and kerogen). The most significant biophile elements are carbon, hydrogen, oxygen, nitrogen, phosphorus, and sulfur.

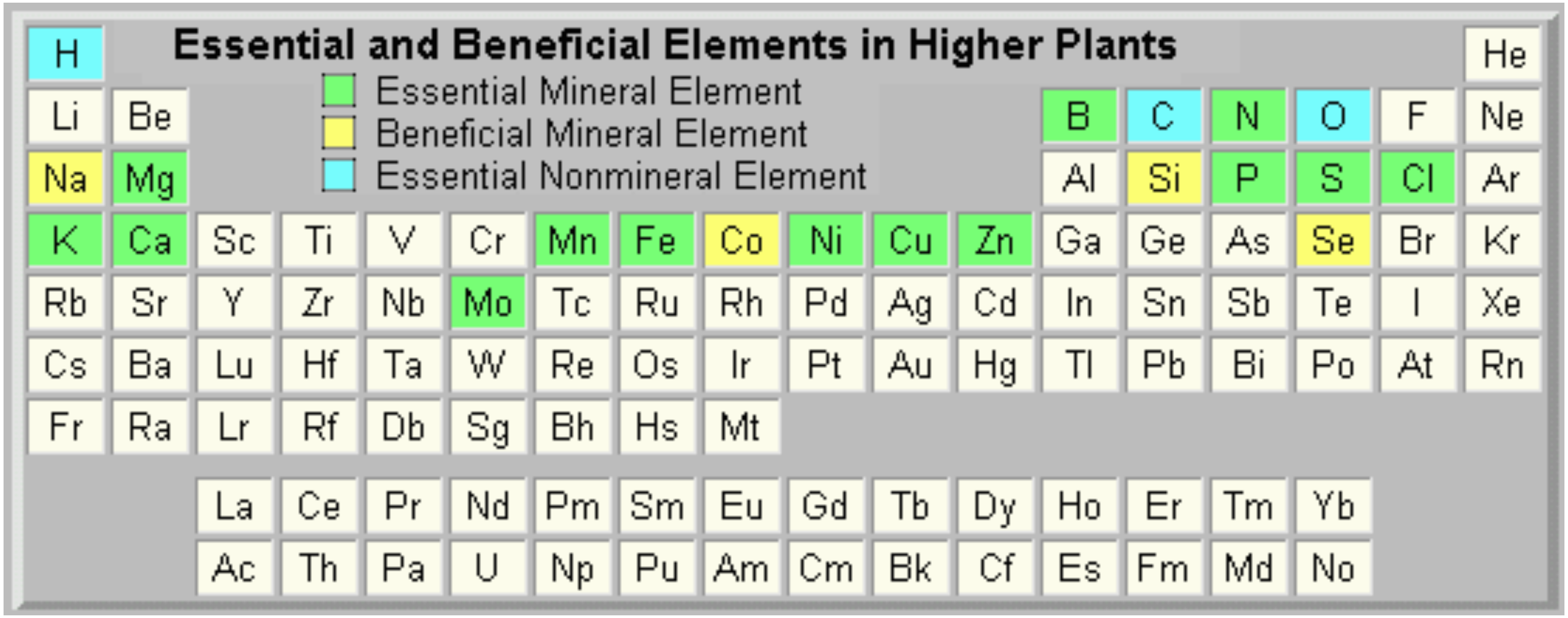
1. Elements that form bonds with organic carbon and are the major elements of life (i.e., Goldschmidt lists the major biophile elements C, H, O, N, P, S, Cl, and I). Lindh (2005) discusses the major and minor elements in the human body. Eleven elements make up 99.8% of the atoms in humans. These are oxygen (65%), carbon (18%), hydrogen (10%), nitrogen (3%), calcium (1.4%), phosphorus (1.0%), magnesium (0.5%), potassium (0.34%), sulfur (0.26%), sodium (0.14%), and chlorine (0.14%). Combs (2005) lists as macronutrient elements Ca, P, Mg, Na, K, and Cl.



2. Elements that function as skeletal structure (calcium phosphate in bones, calcium carbonate in shells, silica in some exoskeletons, and fluorine for OH in bones and teeth). Calcium phosphate in human bones is similar to the mineral apatite, $Ca_5(PO_4)_3(OH)$. The calcium content of the human body is more than 1 kg with 99% of this in the skeleton. About 85% of the bodies' 700 g of phosphorus occur in bone. Human bones also contain magnesium with 60–65% of the 20–28 g of Mg in the bones (Combs, 2005).

3. Fluid mediums (i.e., K, Na, Cl in blood) (Combs, 2005).

4. The elements that are in minor or trace amounts play a necessary role in life. Combs (2005) lists ten elements as accepted essential micronutrient elements (Fe, Cu, Zn, I, Se, Mn, Mo, Cr, F, and Co) and six as suspected essential elements (Ni, Pb, As, B, V, and Si). Lindh (2005) lists 18 essential and possible essential trace elements (Li, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, W, Mo, Si, Se, F, I, As, Br, and Sn).

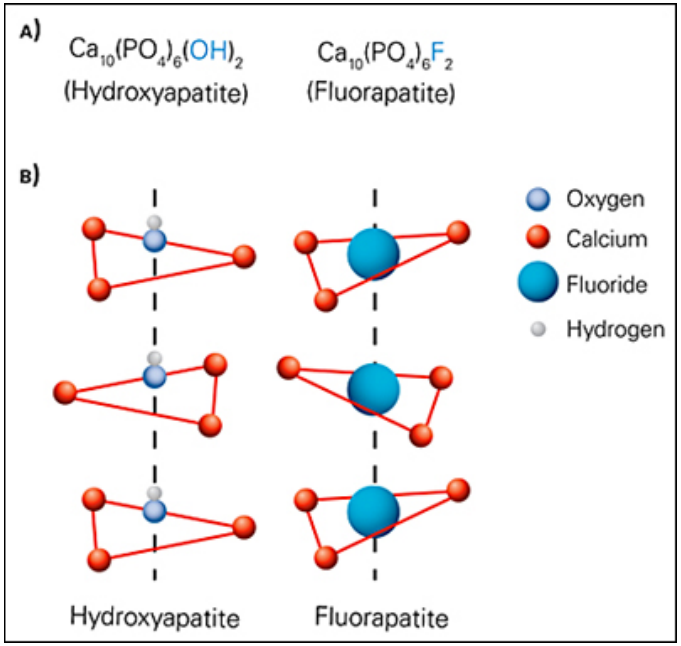


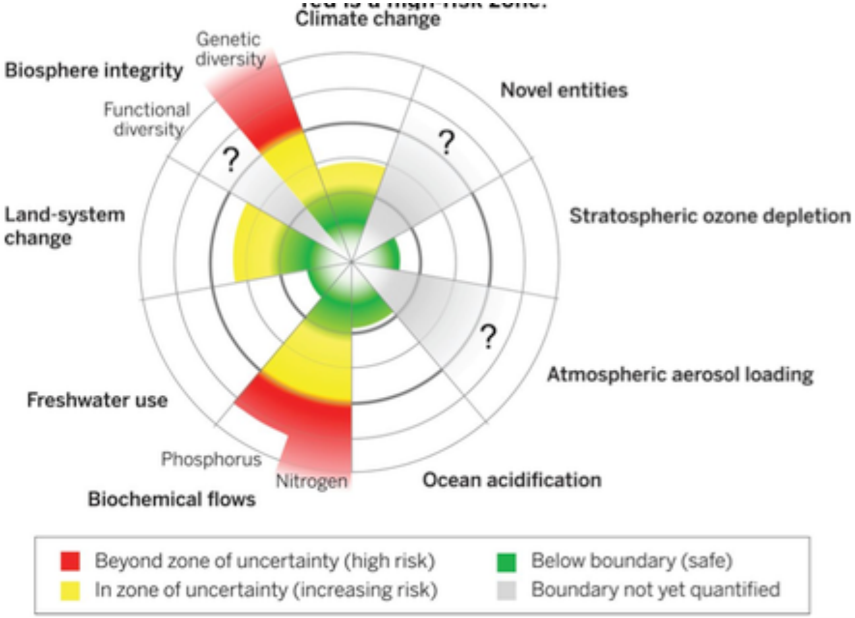
**Essential and Beneficial Elements in Higher Plants**

🟩 Essential Mineral Element
🟨 Beneficial Mineral Element
🟦 Essential Nonmineral Element

| | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 🟦 H | | | | | | | | | | | | | | | | | He |
| Li | Be | | | | | | | | | | | 🟩 B | 🟦 C | 🟩 N | 🟦 O | F | Ne |
| 🟨 Na | 🟩 Mg | | | | | | | | | | | Al | 🟨 Si | 🟩 P | 🟩 S | 🟩 Cl | Ar |
| 🟩 K | 🟩 Ca | Sc | Ti | V | Cr | 🟩 Mn | 🟩 Fe | 🟨 Co | 🟩 Ni | 🟩 Cu | 🟩 Zn | Ga | Ge | As | 🟨 Se | Br | Kr |
| Rb | Sr | Y | Zr | Nb | 🟩 Mo | Tc | Ru | Rh | Pd | Ag | Cd | In | Sn | Sb | Te | I | Xe |
| Cs | Ba | Lu | Hf | Ta | W | Re | Os | Ir | Pt | Au | Hg | Tl | Pb | Bi | Po | At | Rn |
| Fr | Ra | Lr | Rf | Db | Sg | Bh | Hs | Mt | | | | | | | | | |
| | | | | | | | | | | | | | | | | | |
| | | La | Ce | Pr | Nd | Pm | Sm | Eu | Gd | Tb | Dy | Ho | Er | Tm | Yb | | |
| | | Ac | Th | Pa | U | Np | Pu | Am | Cm | Bk | Cf | Es | Fm | Md | No | | |

5. Elements that because of functional similarities (size and charge) substitute for a biophile element (i.e., lead for calcium). Lead is the same charge as and is similar in size to calcium ($Pb^{2+}$ radii is 1.19 Å and $Ca^{2+}$ radii is 1.00 Å) and readily substitutes for calcium in bones. Skinner's (2005) proposed substitutes for calcium in bones and teeth are Pb, Cd, Mg, Sr, Ba, Mn, Na, and K. Substitutions for phosphate, $PO_4^{-3}$, in human bones can be $AsO_4^{-3}$, $SiO_4^{-4}$, $VO_4^{-3}$, $SO_4^{-2}$, $SbO_4^{-3}$, $CO_3^{-2}$, and $AlO_4^{-5}$. The hydroxyl site in apatite can have full substitution by fluorine and chlorine and limited substitution by Br and I. Carbonate can substitute for either phosphate or hydroxyl (Skinner, 2005).

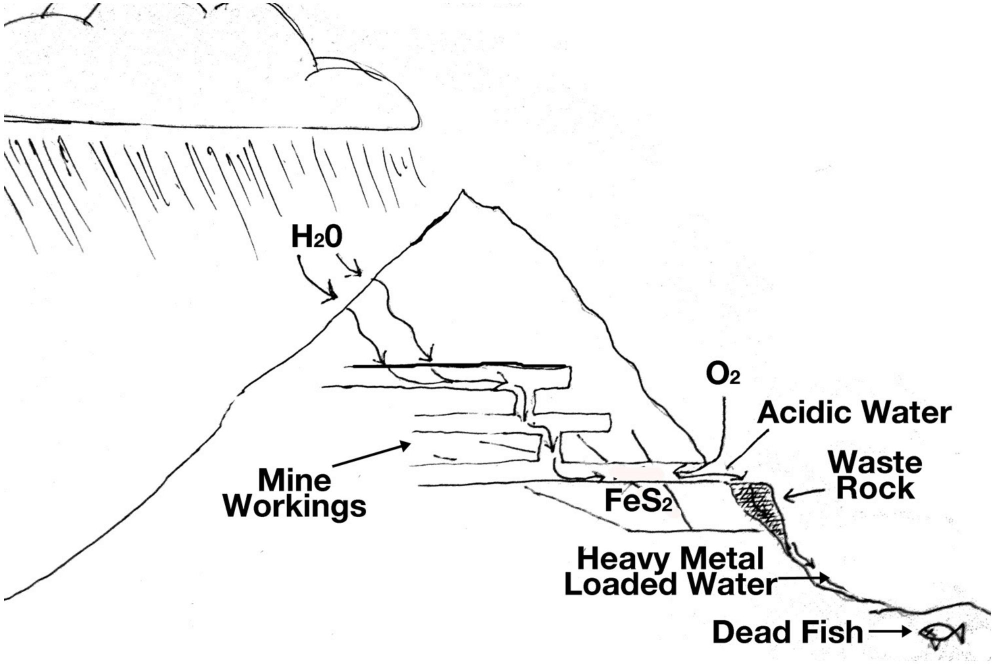


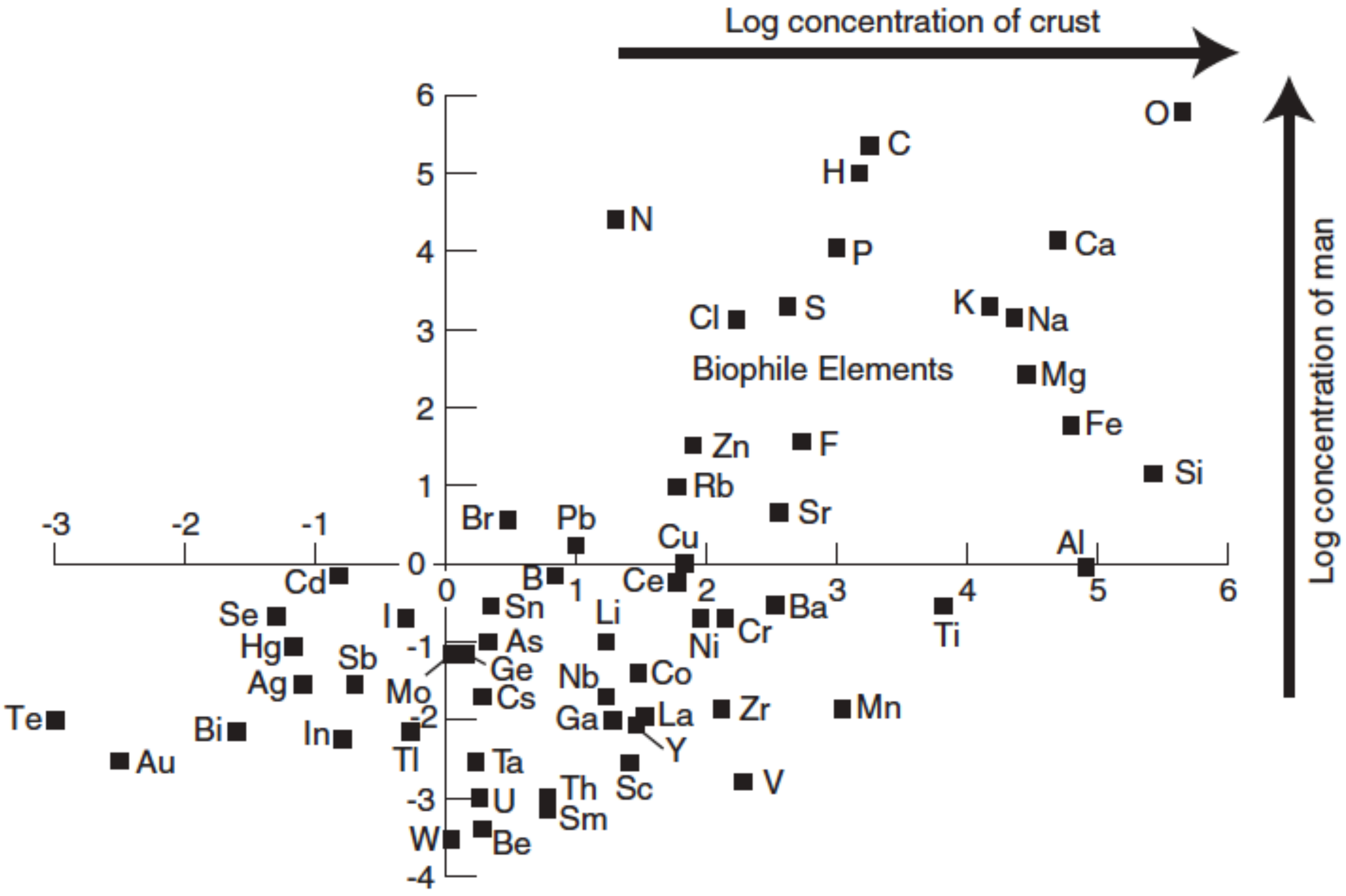


Will Steffen et al. Science 2015;347:1259855

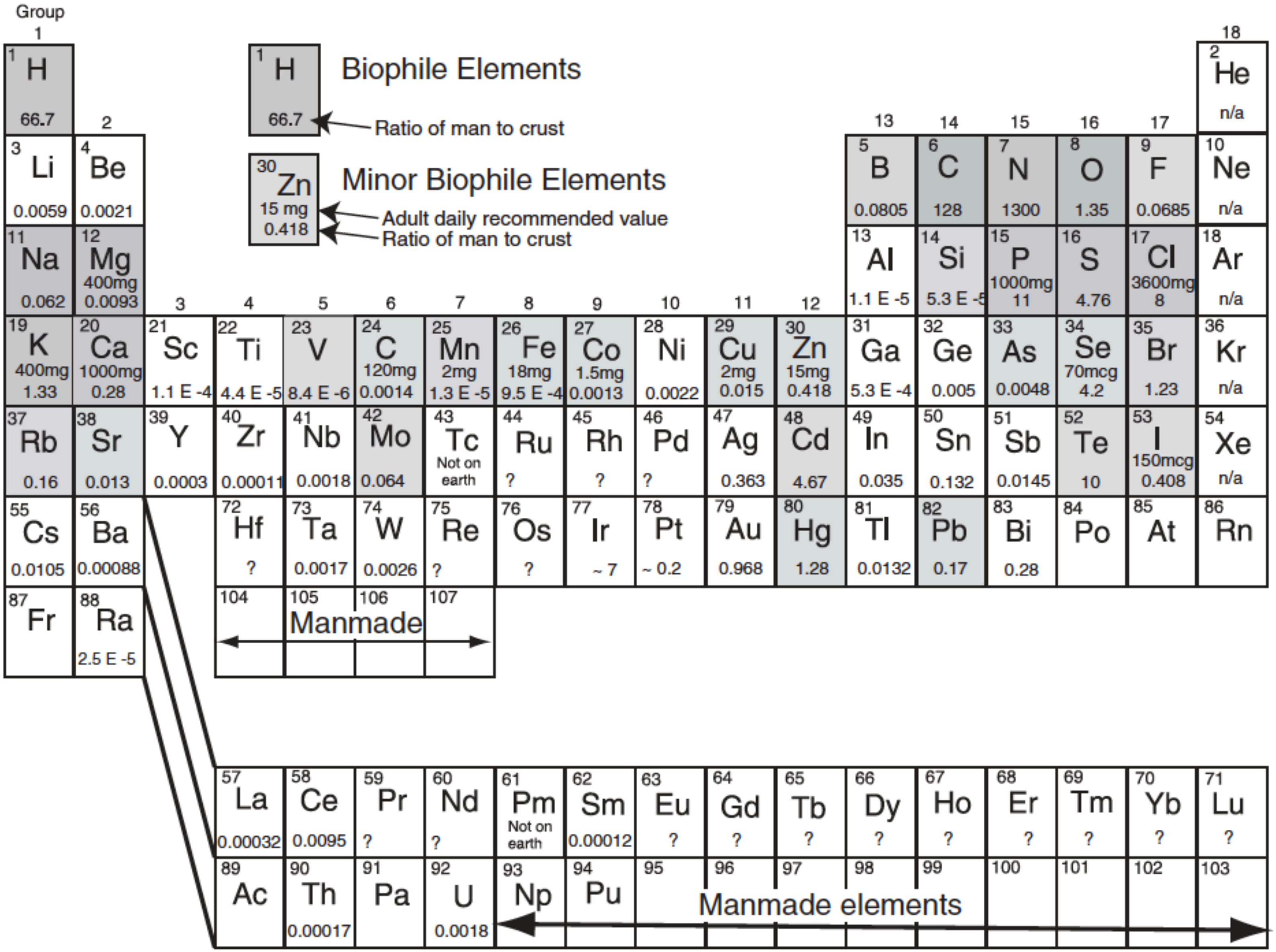
6. Rare or trace elements that will complex with carbon compounds and build up in the food chain (methylmercury and methylarsenic). The mercury added to the environment can be added as methylmercury, $Hg(CH_3)_2$, or in the metallic, Hg, form. Methylmercury can form readily within living organisms from metallic or inorganic mercury. Methylmercury species include $CH_3Hg^+$, $CH_3HgOH$, $CH_3HgCl$, $(CH_3)_2Hg$, and $(CH_3Hg)_2S$ (Turner, 1987). Bacteria in soil, sediment, or water readily transforms mercury into $(CH_3)_2Hg$ and $CH_3Hg^+$ with the latter compound going into solution (Stober et al., 2001). In the form of $CH_3Hg^+$ plants pick up the mercury. This can then work its way up the food chain from plants to small fish to large fish to humans because it builds up faster than it can be expelled. Typical unpolluted surface waters contain $0.5$–$4\ \mathrm{ng\ l^{-1}}$ mercury. Movement of mercury as methylmercury up the food chain is so great that contaminated fish occur even in remote lakes. Fish at the top of the food chain, because of bioaccumulation of methylmercury, may have 1–10 million times greater concentration of mercury than surrounding water.

7. Elements that can be reduced and deposited by organic waste and remains (S, As, Pb, Hg, and U in peat, coal, and oil). For example, the organic-rich peat that is buried to form coal originates in wet, reducing environments. Under these conditions and the diagenesis that forms coal, chalcophile elements precipitate sulfide minerals. Pyrite in coal may contain arsenic, mercury, thallium, selenium, nickel, lead, and cobalt (Davies et al., 2005). Additional elements in coal are cadmium, chromium, copper, vanadium, fluorine, and uranium (Fuge, 2005).

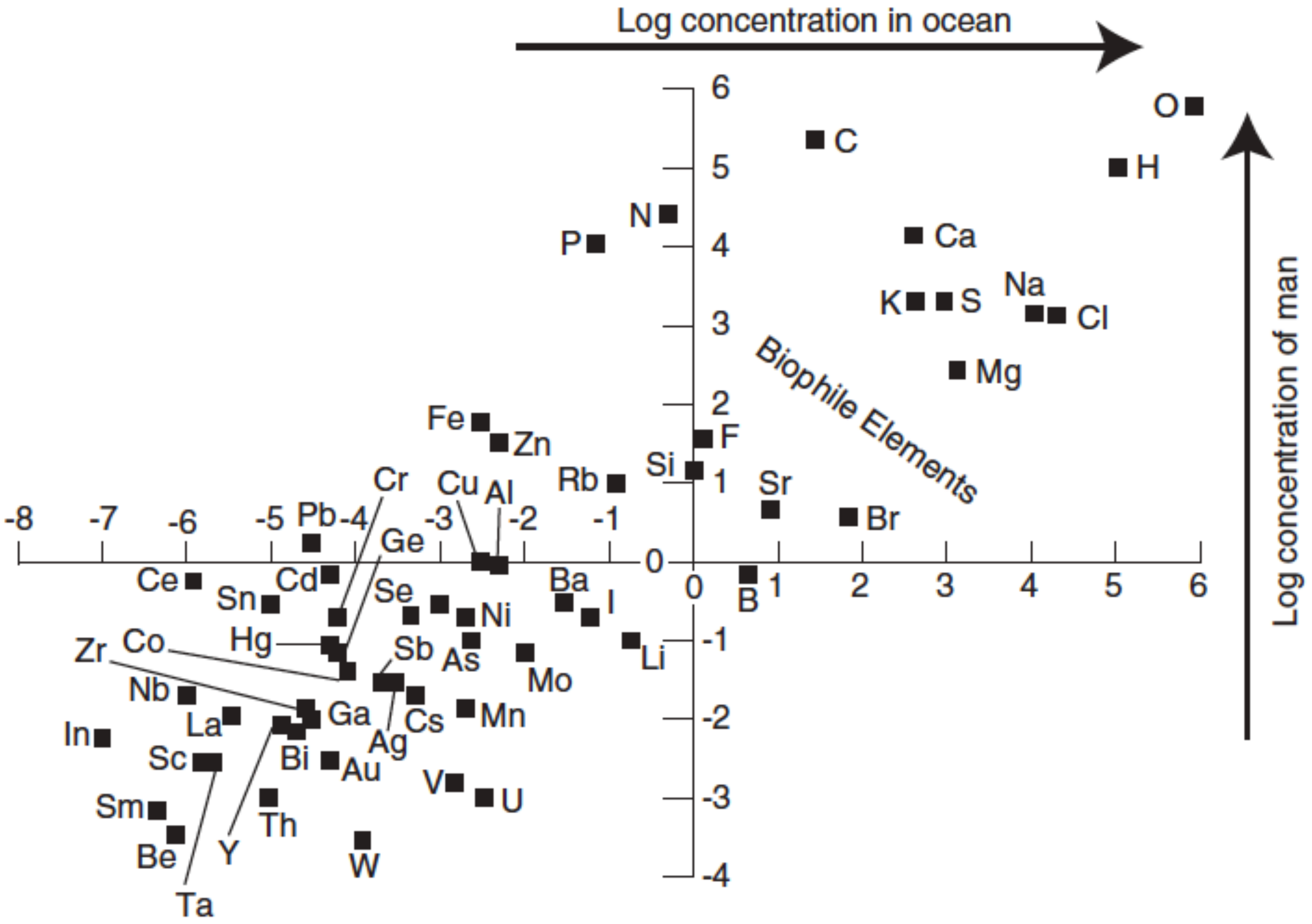




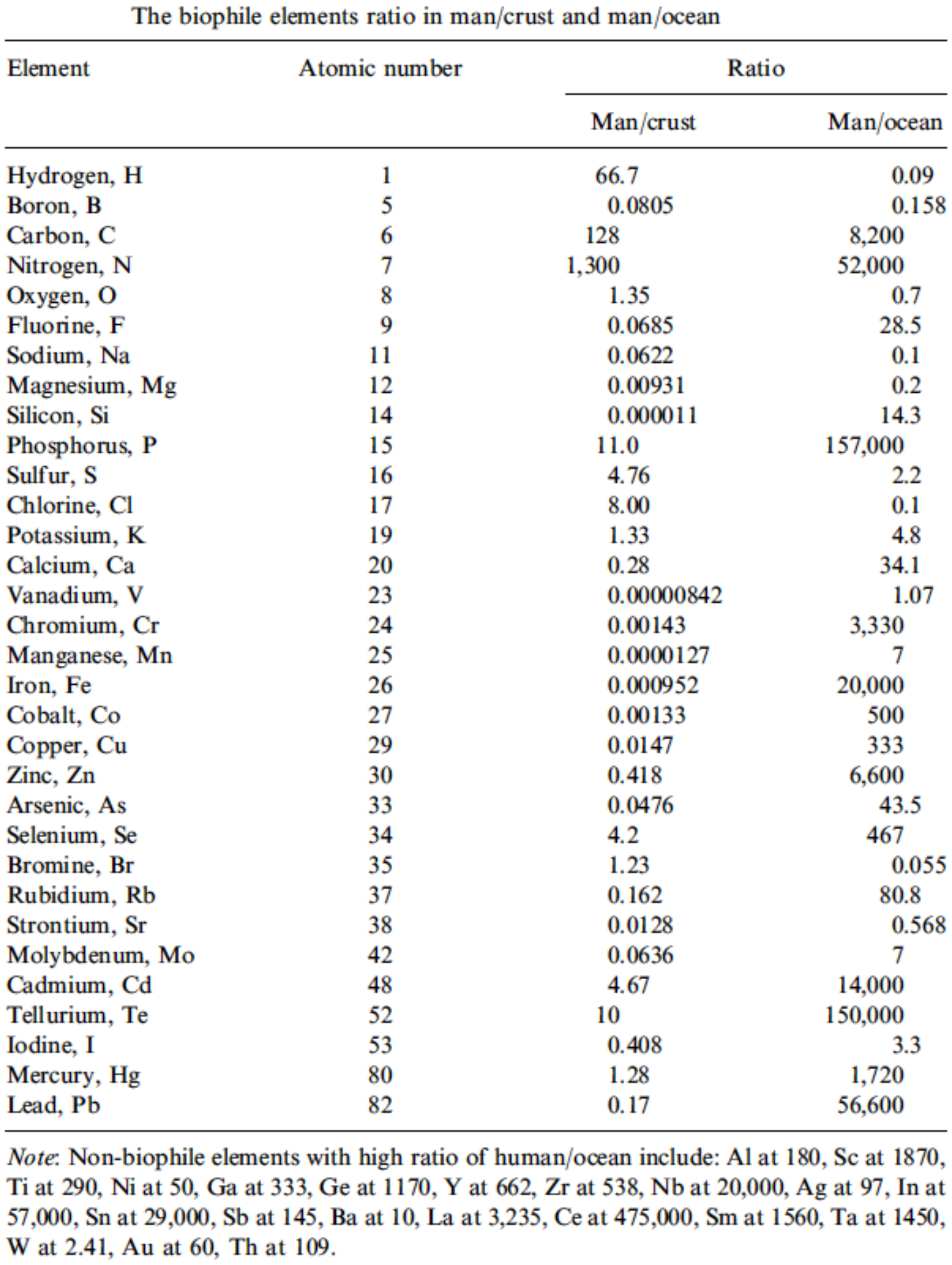
The abundance of elements in man versus the crust. Biophile elements are enriched in man relative to the crust.



Periodic table showing biophile elements (shaded) and the ratio of man to crust.



The abundance of elements in man versus the ocean. Some biophile elements (C, N, P) are enriched in man relative to the ocean while some biophile elements (Cl, Na, Mg, Br) are enriched in the ocean relative to man.



The biophile elements ratio in man/crust and man/ocean

| Element | Atomic number | Ratio | |
|---|---|---|---|
| | | Man/crust | Man/ocean |
| Hydrogen, H | 1 | 66.7 | 0.09 |
| Boron, B | 5 | 0.0805 | 0.158 |
| Carbon, C | 6 | 128 | 8,200 |
| Nitrogen, N | 7 | 1,300 | 52,000 |
| Oxygen, O | 8 | 1.35 | 0.7 |
| Fluorine, F | 9 | 0.0685 | 28.5 |
| Sodium, Na | 11 | 0.0622 | 0.1 |
| Magnesium, Mg | 12 | 0.00931 | 0.2 |
| Silicon, Si | 14 | 0.000011 | 14.3 |
| Phosphorus, P | 15 | 11.0 | 157,000 |
| Sulfur, S | 16 | 4.76 | 2.2 |
| Chlorine, Cl | 17 | 8.00 | 0.1 |
| Potassium, K | 19 | 1.33 | 4.8 |
| Calcium, Ca | 20 | 0.28 | 34.1 |
| Vanadium, V | 23 | 0.00000842 | 1.07 |
| Chromium, Cr | 24 | 0.00143 | 3,330 |
| Manganese, Mn | 25 | 0.0000127 | 7 |
| Iron, Fe | 26 | 0.000952 | 20,000 |
| Cobalt, Co | 27 | 0.00133 | 500 |
| Copper, Cu | 29 | 0.0147 | 333 |
| Zinc, Zn | 30 | 0.418 | 6,600 |
| Arsenic, As | 33 | 0.0476 | 43.5 |
| Selenium, Se | 34 | 4.2 | 467 |
| Bromine, Br | 35 | 1.23 | 0.055 |
| Rubidium, Rb | 37 | 0.162 | 80.8 |
| Strontium, Sr | 38 | 0.0128 | 0.568 |
| Molybdenum, Mo | 42 | 0.0636 | 7 |
| Cadmium, Cd | 48 | 4.67 | 14,000 |
| Tellurium, Te | 52 | 10 | 150,000 |
| Iodine, I | 53 | 0.408 | 3.3 |
| Mercury, Hg | 80 | 1.28 | 1,720 |
| Lead, Pb | 82 | 0.17 | 56,600 |

*Note*: Non-biophile elements with high ratio of human/ocean include: Al at 180, Sc at 1870, Ti at 290, Ni at 50, Ga at 333, Ge at 1170, Y at 662, Zr at 538, Nb at 20,000, Ag at 97, In at 57,000, Sn at 29,000, Sb at 145, Ba at 10, La at 3,235, Ce at 475,000, Sm at 1560, Ta at 1450, W at 2.41, Au at 60, Th at 109.

Goldschmidt (1954) had listed eight major (C, H, O, N, P, S, Cl, and I) and nine minor (B, Ca, Mg, K, Na, V, Mn, Fe, and Cu) **biophile elements**.

Based on the abundance of elements in humans (Lindh, 2005 ), Na, Mg, K, and Ca are included as major biophile elements and iodine is considered a minor biophile.

Additional elements included as minor biophile are the **essential micronutrient elements** Fe, Cu, Zn, I, Se, Mn, Mo, Cr, F, and Co. Functional similarities in size and charge and its ease of substitution for calcium in human bones place lead as a minor biophile element.

Other minor biophile elements that substitute into bone include Si, As, Br, Sr, and Cd. Another type of functional similarity is when an element located directly below an element on the periodic table readily substitutes for it. For example, the chalcophile mineral sphalerite, ZnS, has as a common substitute for zinc the element cadmium (Greenwood and Earnshaw, 1997 ).

Extending this type of functional similarity to biophile elements adds Rb, Sr, Cd, and Te as biophile elements because of their easy substitution for K, Ca, Zn, and Se, respectively.

# Environmental geochemistry and anthropogenic dispersion of arsenic, lead, and mercury

## Arsenic, As

At 1.8 ppm arsenic is the 53rd most abundant element in the earth's crust.

Arsenic's typical concentration in soil is 5 ppm, while its average concentration in the United States coal is 22 ppm. Arsenic's abundance in seawater is 3 ppb. The oxidation states of Arsenic are $As^{5+}$, $As^{3+}$, As, $As^{2-}$, and $As^{3-}$. Most arsenic used in industry is obtained as $As_2O_3$ from flue dust at lead and copper smelters, though it is also obtained from arsenopyrite, FeAsS, and lollingite, $FeAs_2$.

ALL'INQUINAMENTO

Metalli pesanti nel corpo uma

Test per

enuncia: «Alluminio

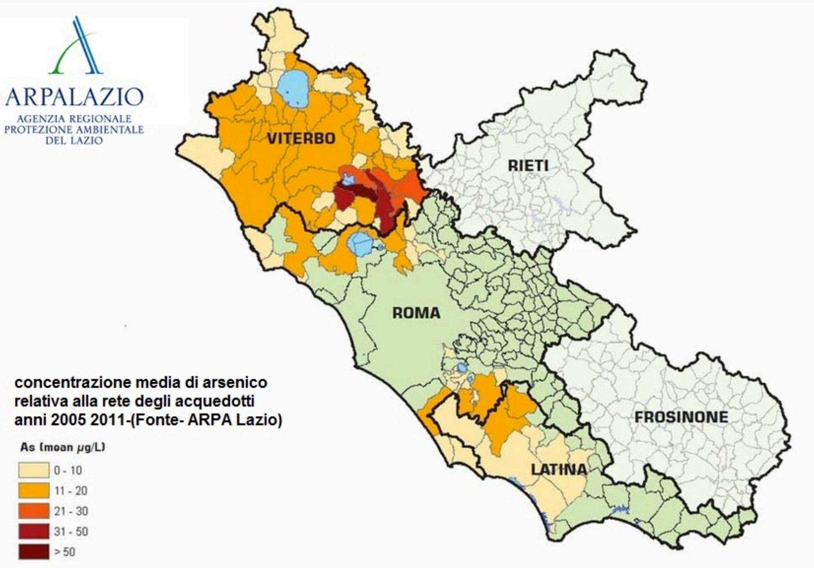
lopo analisi nei serbatoi della scuola "Pascoli"

il Resto del Carlino

LA RICERCA PREOCCUPANTI I RILIEVI DELLA MINERAL TEST SU UN CAMPIO

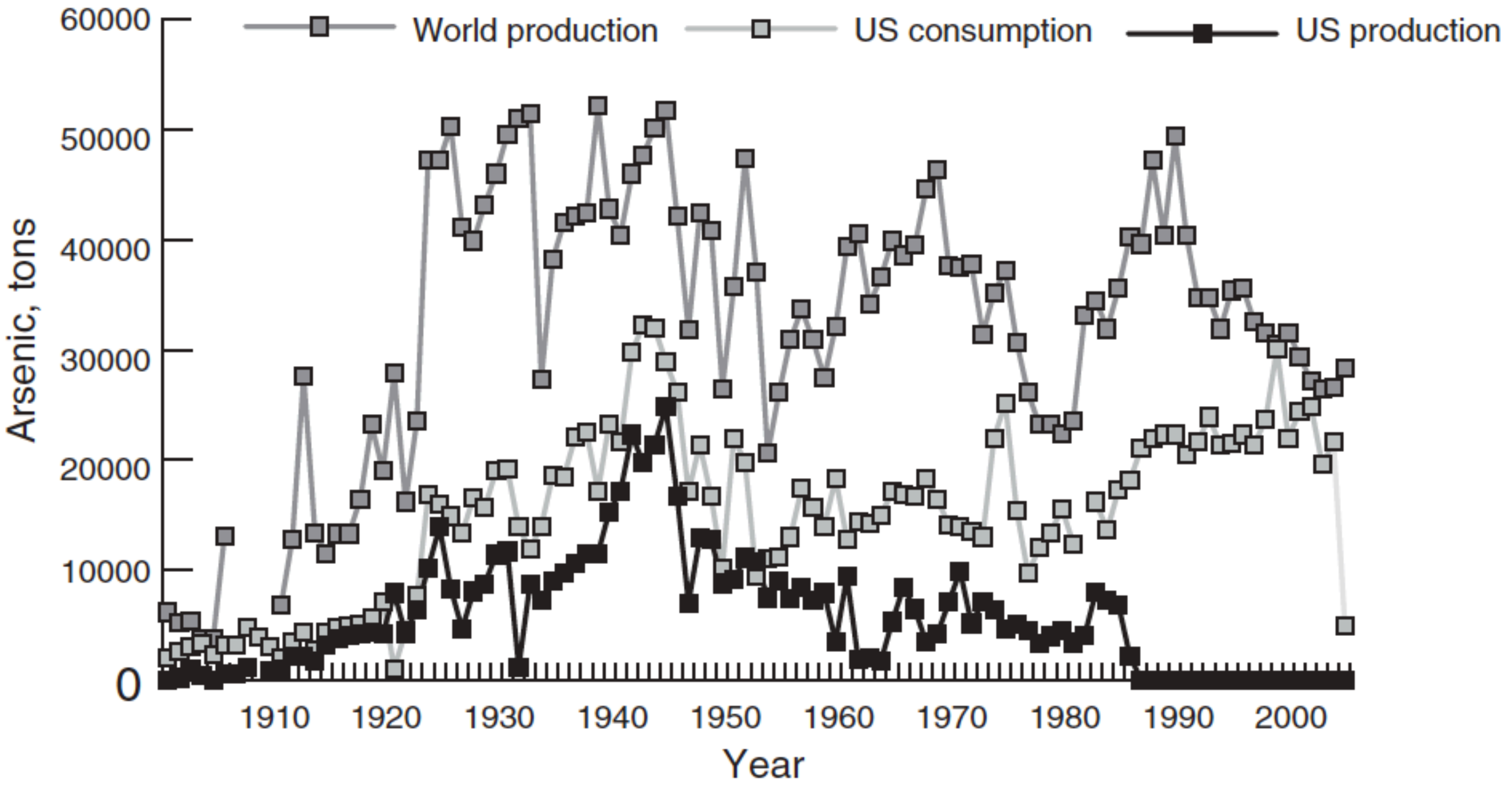
Alte dosi di mercurio, piombo

sono questi i veleni che abbia

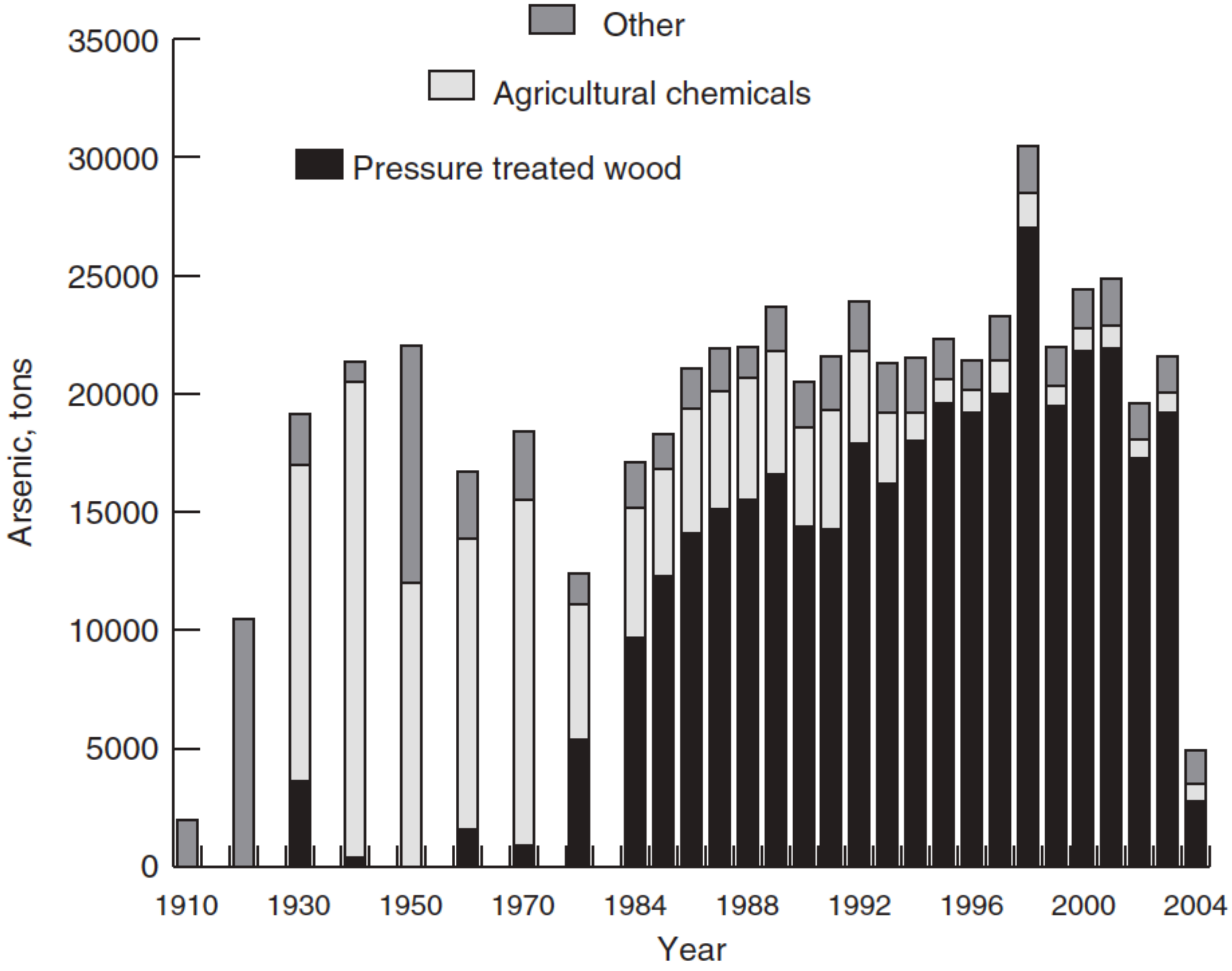


concentrazione media di arsenico relativa alla rete degli acquedotti anni 2005 2011-(Fonte- ARPA Lazio)

Arsenic is often considered the **classic example of a substance that is very toxic** (Fergusson, 1990 ; Thornton, 1996 ; ATSDR, 2000 ). The toxicity of ingested arsenic **varies with oxidation state** and whether it is **organic** or **inorganic**. Reduced forms are more toxic than oxidized forms and inorganic arsenic is more toxic than organic arsenic. The largest human intake of arsenic is from food (e.g., seafood). Organic arsenic is of low toxicity. $As^{5+}$ is more soluble than $As^{3+}$ . Inorganic forms of arsenic occurring in groundwater are most toxic.



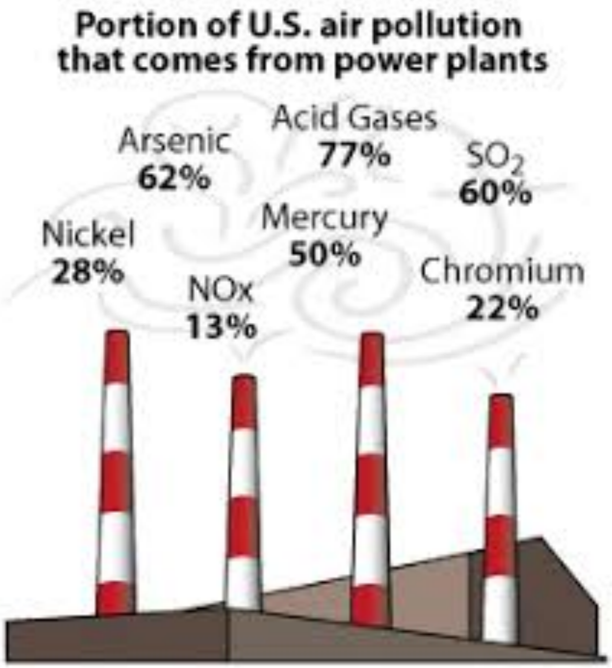
The world production and United States production and consumption of arsenic from 1900 to 2002. Arsenic production stopped by 1986 in the United States. Total world production of As from 1900 to 2002 was 3,250,000 tons. United States consumption was 1,500,000 tons. Data from USGS (2003, 2004).



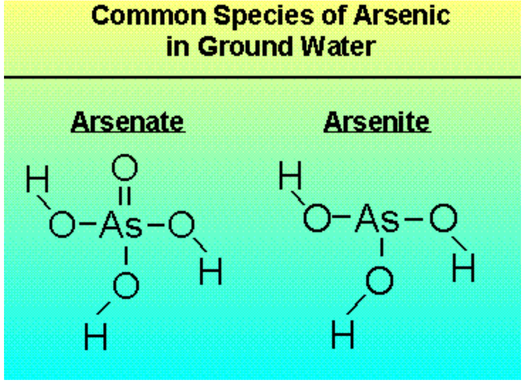
Use of arsenic in selected years in the United States after Bleiwas (2000) with additional data from USGS, Mineral Commodity Summaries and Loebenstein (1994). From 1960 to 2003 an estimated 420,000 tons of arsenic was used in the manufacture of pressure-treated wood and another 115,000 tons was used in agriculture. From 1910 to 1970 the largest usage of arsenic was in agriculture.

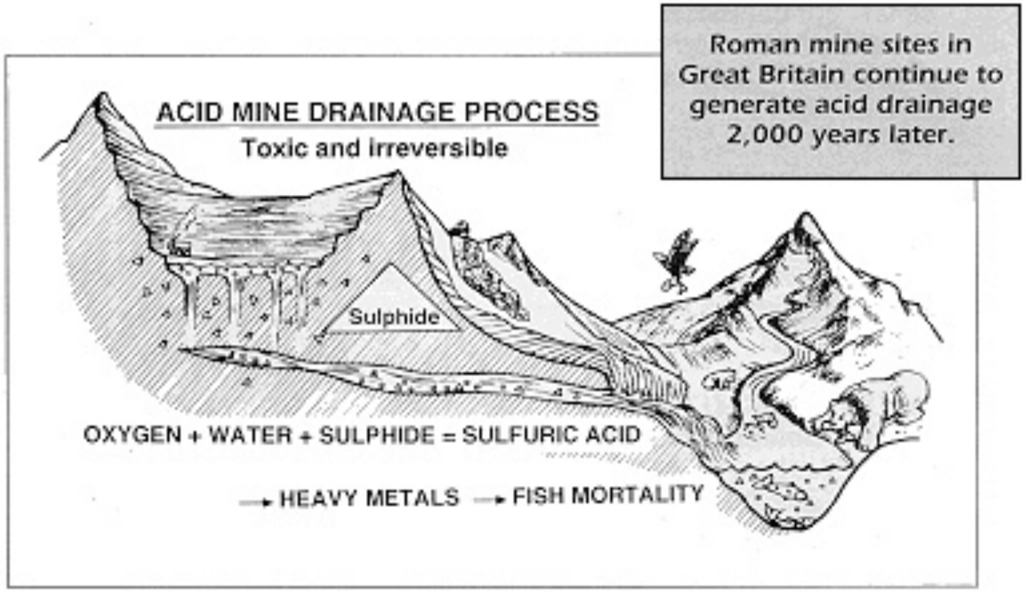
Arsenic is a semimetal that has both high natural (12,000 tons per year) and manmade (19,000 tons per year) emissions into the atmosphere. These emission values are estimates and there exists a range in estimates that vary with time and the methods used to determine the estimate. Arsenic's occurrence in sulfide ores causes its high emissions (12,000 tons per year) from ore smelters (Loebenstein, 1994).

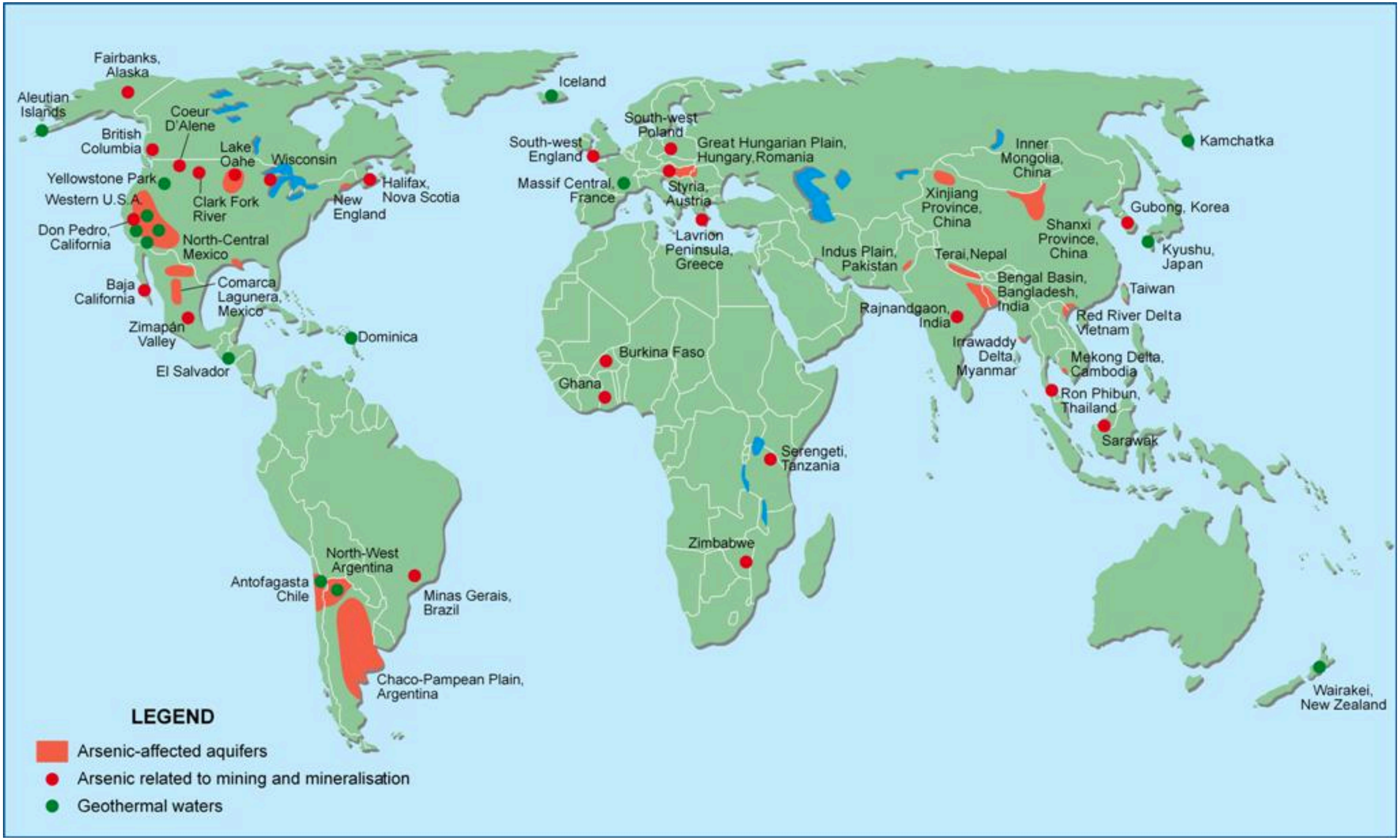
Total United States arsenic and arsenic compound emissions reported for 2002 by the EPA Toxic Release Inventory (TRI) are 89 tons. After emissions from electric utilities, metal mining and processing are the next major sources of arsenic emissions (EPA-TRI, 2004). Arsenic atmosphere emissions represent only 0.02% of total arsenic waste of 402,394 tons disposed of or released in 2002. Disposal of arsenic and arsenic compounds on land and on- and off-site were about 400,000 tons in 2002. Over 95% of this arsenic is from metal mining.



Arsenic in **groundwater** can be a risk because it is both reduced and inorganic and arsenic compounds **readily dissolve in water**. Drinking water has caused cases of chronic and acute arsenic poisoning in Taiwan, Argentina, China, and Mexico. A tragic modern epidemic of arsenic poisoning from groundwater is occurring in 17 nations including regions of Bangladesh, southern Nepal, China, Vietnam, and West Bengal and Bihar, India. Shallow tube wells were dug in these regions to provide drinking water free of the threats of diarrhea, dysentery, typhoid, cholera, and hepatitis common in surface water.

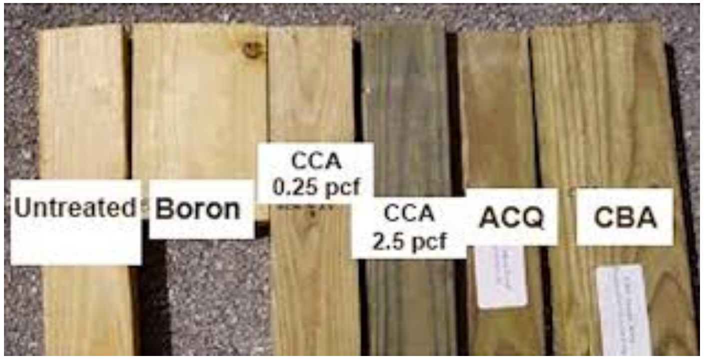


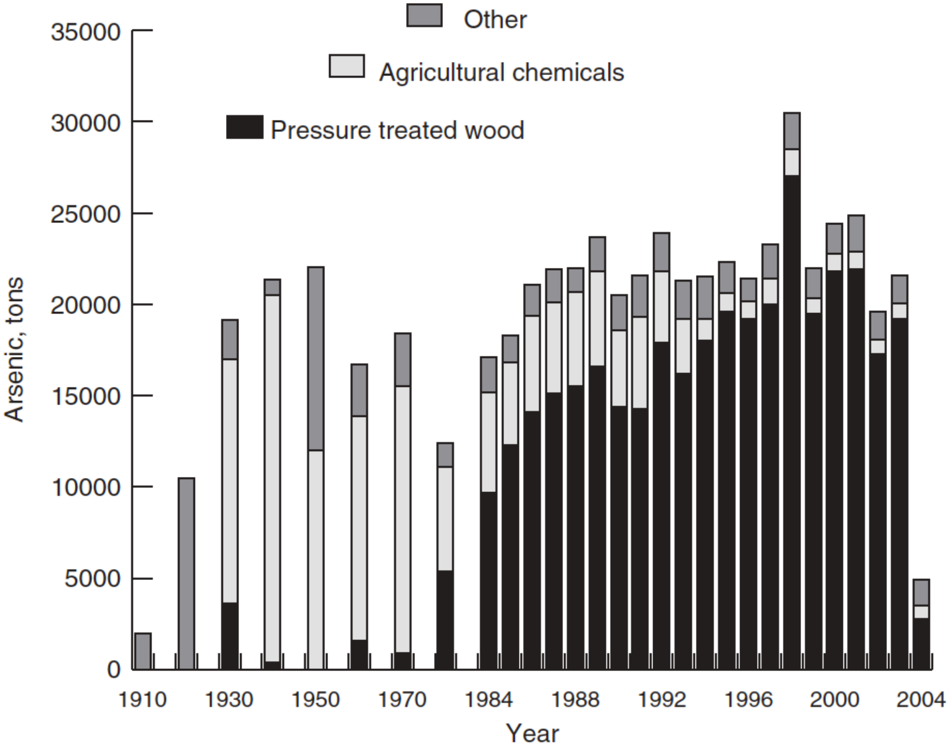



Fairbanks, Alaska
Aleutian Islands
British Columbia
Coeur D'Alene
Lake Oahe
Wisconsin
Yellowstone Park
Western U.S.A.
Clark Fork River
New England
Halifax, Nova Scotia
Don Pedro, California
North-Central Mexico
Baja California
Comarca Lagunera, Mexico
Zimapán Valley
Dominica
El Salvador
North-West Argentina
Antofagasta Chile
Minas Gerais, Brazil
Chaco-Pampean Plain, Argentina
Iceland
South-west England
South-west Poland
Great Hungarian Plain, Hungary, Romania
Massif Central, France
Styria, Austria
Lavrion Peninsula, Greece
Burkina Faso
Ghana
Serengeti, Tanzania
Zimbabwe
Inner Mongolia, China
Xinjiang Province, China
Shanxi Province, China
Indus Plain, Pakistan
Terai, Nepal
Bengal Basin, Bangladesh, India
Rajnandgaon, India
Irrawaddy Delta, Myanmar
Kamchatka
Gubong, Korea
Kyushu, Japan
Taiwan
Red River Delta Vietnam
Mekong Delta, Cambodia
Ron Phibun, Thailand
Sarawak
Wairakei, New Zealand
LEGEND
🟥 Arsenic-affected aquifers
● Arsenic related to mining and mineralisation
● Geothermal waters

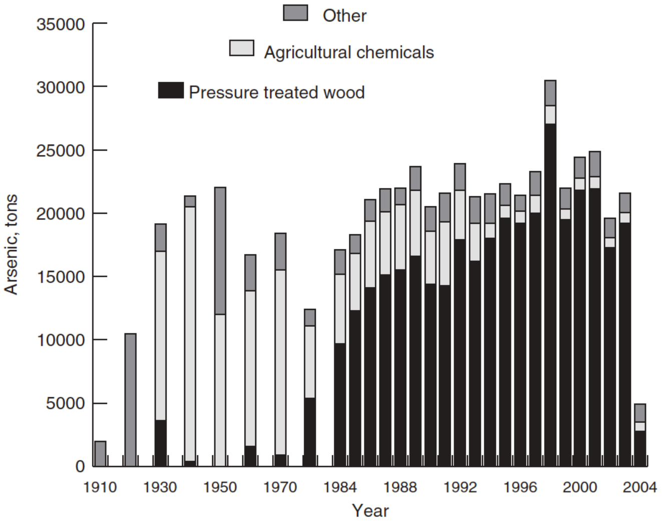
The high arsenic abundance in some coals is an important demonstration of the biophile nature of arsenic. Arsenic was concentrated in some coals during their formation; when the coal is burned As emissions are dispersed and can build up in humans. For example, high-arsenic lignite (500 ppm As) burned in Slovakia has resulted in arsenic emission from one power plant of 3000 metric tons since 1953 and nonmelanoma skin cancer (Ranft et al., 2003). An arsenic threat to human health is the burning of coal in the Guizhou Province of southwest China. Some coal samples from Guizhou Province contain up to 35,000 ppm As (3.5% As!), 50 ppm Hg, and 20 ppm Sb (USGS, 1998a; Liu et al., 2002). The coal is burned in un-vented ovens inside homes. The ovens can be used to dry crops such as chili peppers. The fresh chili peppers have less than 1 ppm arsenic whereas those dried over coal fires have more than 500 ppm As (USGS, 1998a; Schweinfurth, 2003). Over 3000 cases of arsenicosis have been reported. High levels of As, Hg, and F up to 181, 10.5 and 2259 ppm, respectively, occur in some locally used coals in China (Zhang et al., 2004).

A potential health problem of undefined proportions and dimensions is the several decade long usage of arsenic in pressure-treated wood Pressure-treated wood contains inorganic arsenic that protects it from decay and insects. The most common treatment is with chromated-copper-arsenate or CCA. One cubic foot (0.03 m$^3$) of CCA wood contains 1.15 oz (32.6 g) of arsenic. Such wood in an outdoor environment may resist termites and decay for 20–60 years. However, our research shows that in the warm humid southeastern United States, that framing timbers in contact with the ground may disintegrate after ten years (Hollabaugh, 2004, 2005). Over 420,000 tons of arsenic has been used in pressure-treated wood since 1960 in the United States. A voluntary agreement between the EPA and the manufacturers of pressure-treated wood removed arsenic in pressure-treated wood for residential uses in 2004 (Bleiwas, 2000; EPA, 2002; Brooks, 2003).

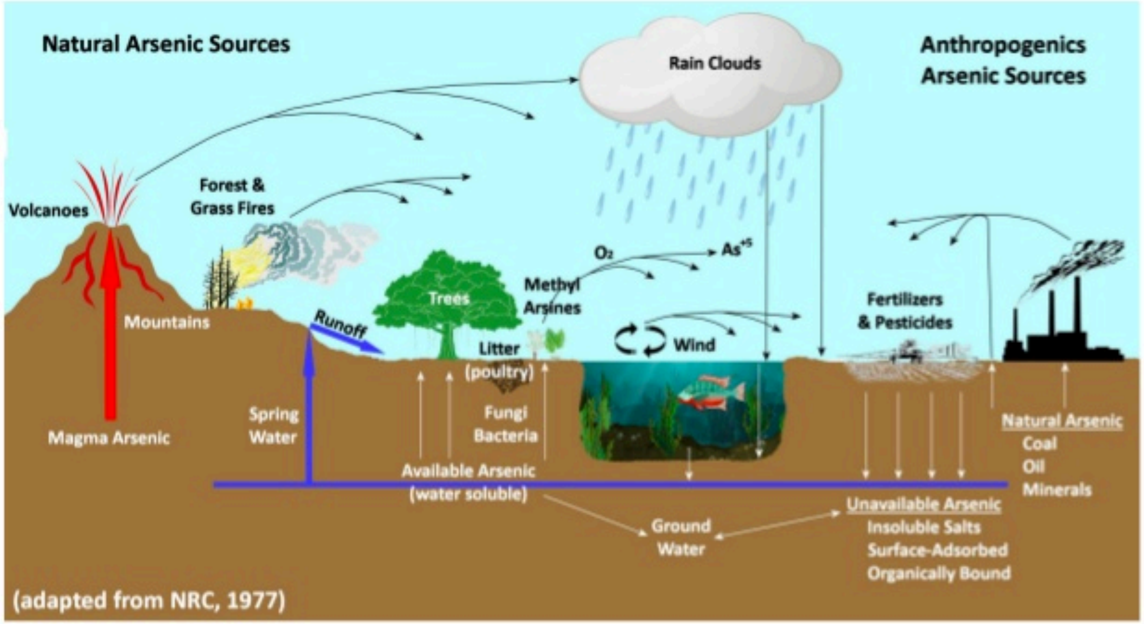




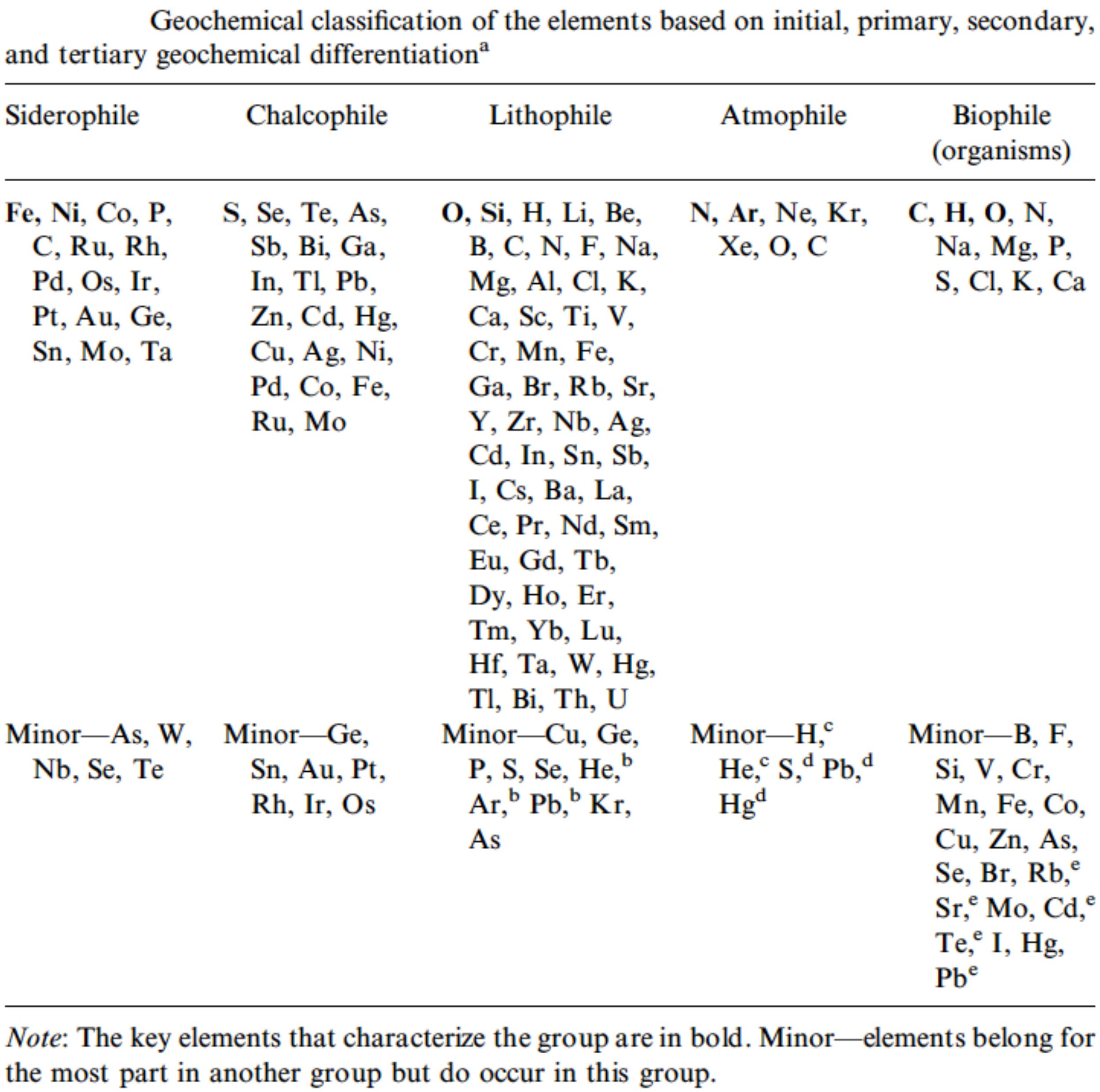
Another 350,000 tons of arsenic has been used since 1960 in the United States as agricultural chemicals In past decades arsenic-based agricultural chemicals were used for insecticides, selective plant killers, defoliants, rat poison, and parasitic control in chicken feed. Today arsenic as Roxarsone (4-hydroxy-3 nitrophenyl arsenic acid) is used as feed for broiler chickens to control intestinal parasites. This results in 3-fold greater arsenic concentrations in young chickens than in other meat and poultry (Lasky et al., 2004).



## Arsenic Sources & Transfer



(adapted from NRC, 1977)



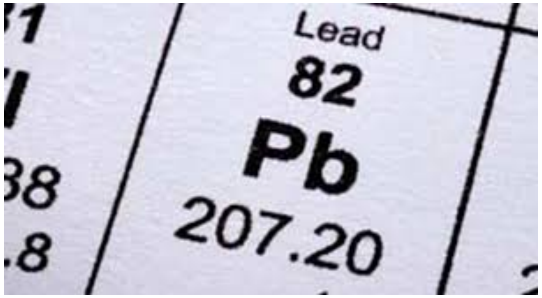
Geochemical classification of the elements based on initial, primary, secondary, and tertiary geochemical differentiation[a]

| Siderophile | Chalcophile | Lithophile | Atmophile | Biophile (organisms) |
|---|---|---|---|---|
| **Fe**, **Ni**, Co, P, C, Ru, Rh, Pd, Os, Ir, Pt, Au, Ge, Sn, Mo, Ta | **S**, Se, Te, As, Sb, Bi, Ga, In, Tl, Pb, Zn, Cd, Hg, Cu, Ag, Ni, Pd, Co, Fe, Ru, Mo | **O**, **Si**, H, Li, Be, B, C, N, F, Na, Mg, Al, Cl, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Ga, Br, Rb, Sr, Y, Zr, Nb, Ag, Cd, In, Sn, Sb, I, Cs, Ba, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, Ta, W, Hg, Tl, Bi, Th, U | **N**, **Ar**, Ne, Kr, Xe, O, C | **C**, **H**, **O**, N, Na, Mg, P, S, Cl, K, Ca |
| Minor—As, W, Nb, Se, Te | Minor—Ge, Sn, Au, Pt, Rh, Ir, Os | Minor—Cu, Ge, P, S, Se, He,[b] Ar,[b] Pb,[b] Kr, As | Minor—H,[c] He,[c] S,[d] Pb,[d] Hg[d] | Minor—B, F, Si, V, Cr, Mn, Fe, Co, Cu, Zn, As, Se, Br, Rb,[e] Sr,[e] Mo, Cd,[e] Te,[e] I, Hg, Pb[e] |

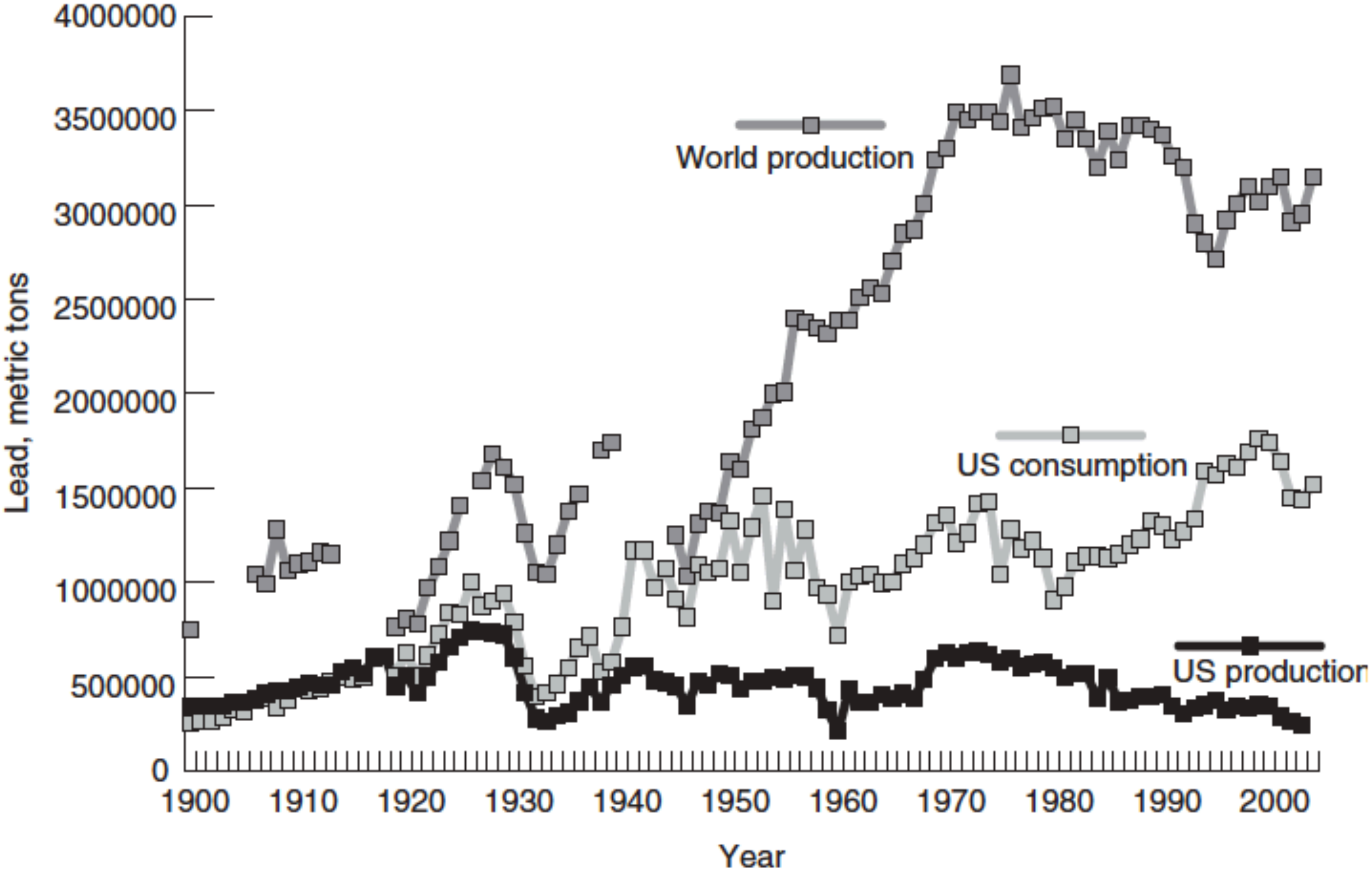
*Note*: The key elements that characterize the group are in bold. Minor—elements belong for the most part in another group but do occur in this group.

**Initial differentiation** is the formation of the earth and its separation from the solar system. **Primary differentiation** is the separation of earth into core and primitive mantle. **Secondary differentiation** is the formation of crust. **Tertiary differentiation** is the process of formation and development of hydrosphere and biosphere, and lithophile enrichment of crust by plume and plate tectonic activity.

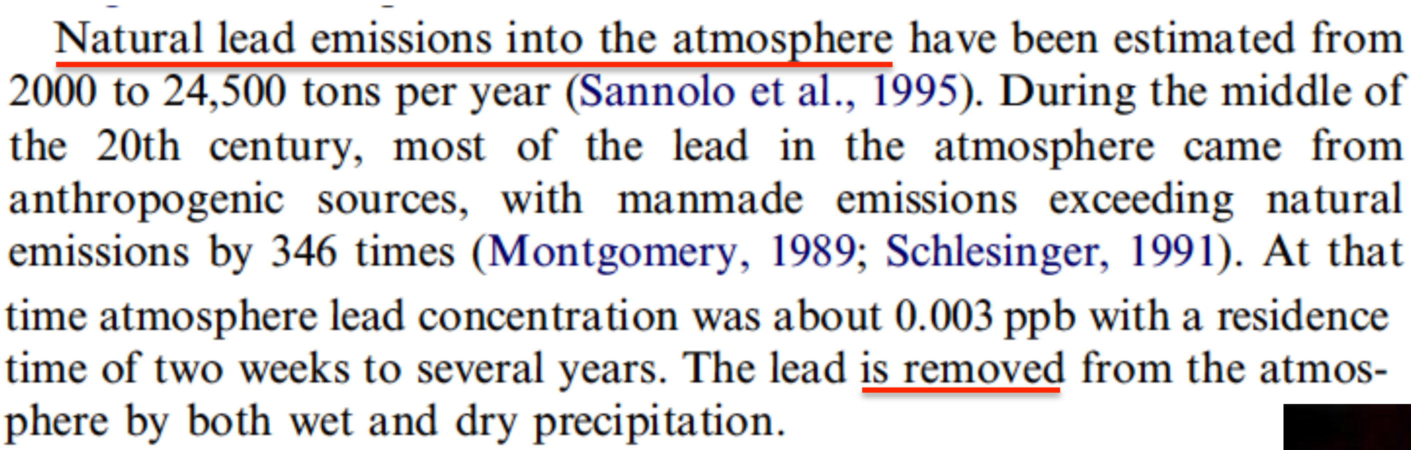
### *2.2.2. Lead, Pb*



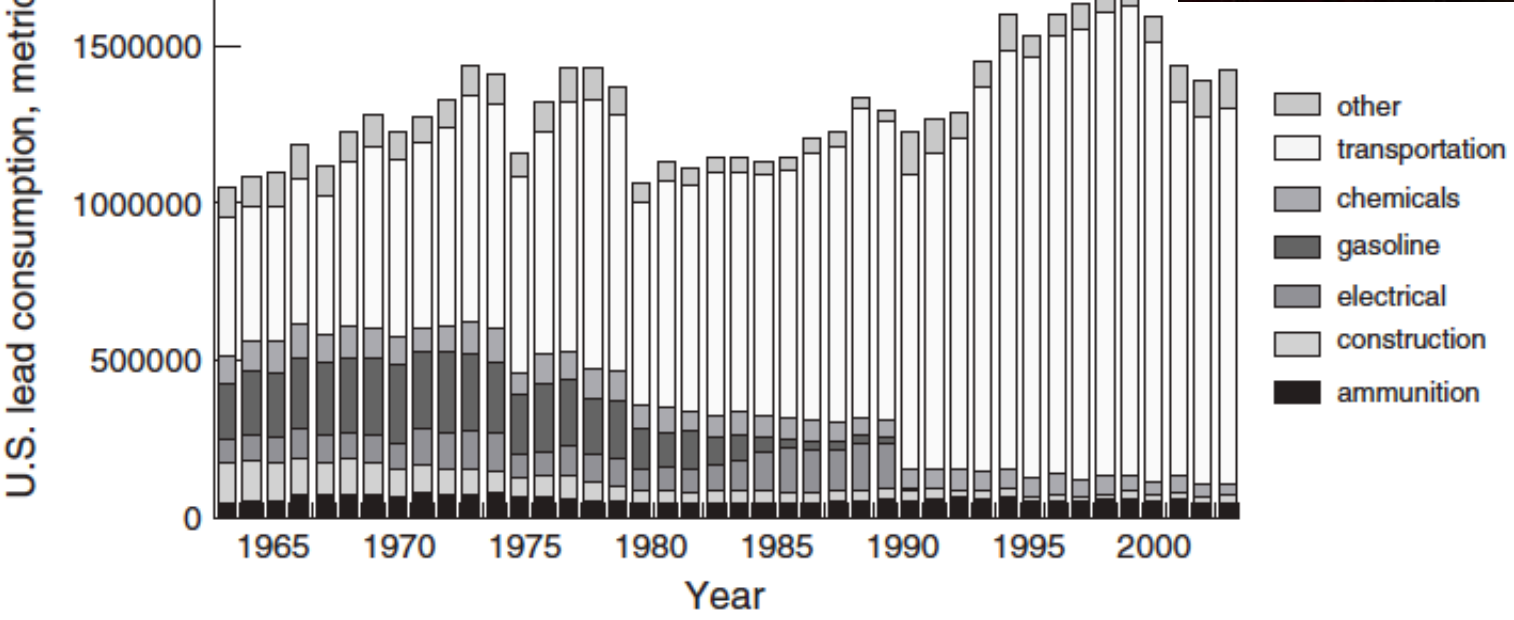
Lead is the 36th most abundant element in the earth's crust. Most geochemists report lead's crustal abundance to be between 12.5 and 16 ppm, although a detailed study by Taylor and McLennan (1985) determined that continental crust contains 8 ppm lead and ocean floor crust contains 0.8 ppm lead. Lead is the most abundant heavy metal in the earth's crust; some of this enhanced abundance is the product of the decay of extreme lithophile uranium and thorium into lead (Greenwood and Earnshaw, 1997). Oxidation states of lead are Pb, Pb$^{2+}$, Pb$^{3+}$ (rare), and Pb$^{4+}$ (rare). Common lead minerals are galena, PbS, cerussite, PbCO$_3$, and anglesite, PbSO$_4$. Lead concentration in seawater is 0.003 ppb. Figure 2.6 shows the United States production and consumption and world production of lead. Some human uses of lead shown in Table 2.5 and plotted



The world production and United States production and consumption of lead from 1900 to 2002. Total world production of Pb from 1900 to 2002 is estimated to be 214,000,000 tons. United States consumption was 97,000,000 tons. Data from USGS (2003, 2004).

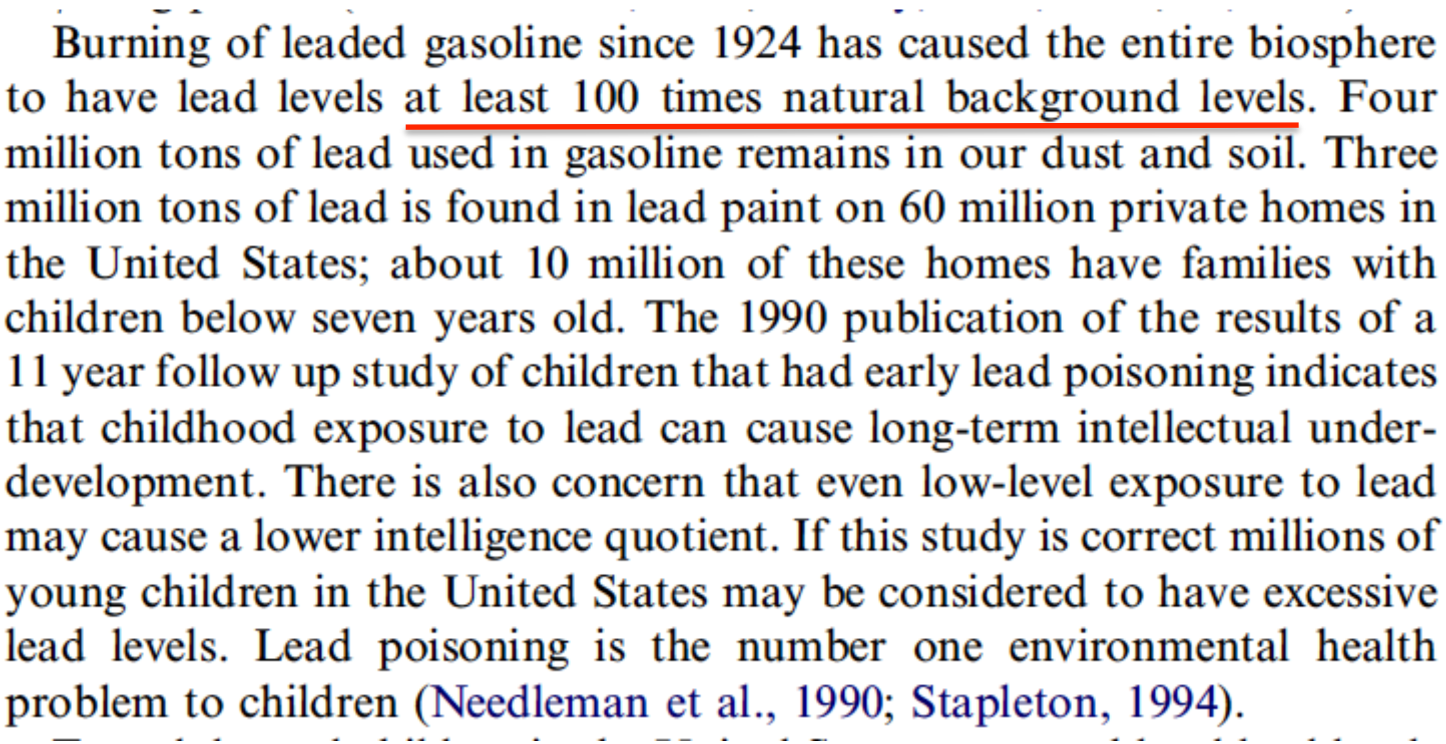


Natural lead emissions into the atmosphere have been estimated from 2000 to 24,500 tons per year (Sannolo et al., 1995). During the middle of the 20th century, most of the lead in the atmosphere came from anthropogenic sources, with manmade emissions exceeding natural emissions by 346 times (Montgomery, 1989; Schlesinger, 1991). At that time atmosphere lead concentration was about 0.003 ppb with a residence time of two weeks to several years. The lead is removed from the atmosphere by both wet and dry precipitation.



Lead is a classic siderophile element, occurring as galena in many sulfide deposits. Under oxidizing conditions the sulfur is removed or oxidized and lead behaves as a lithophile element forming cerussite and anglesite. Lead is a biophile element because of its close size and the same charge as calcium ($Pb^{2+}$ radii is 1.19Å and $Ca^{2+}$ is 1.00Å). Calcium in the brain plays a role in "converting an electrical neural signal into a chemical signal" however "Pb does not function as a neurotransmitter, effectively creating permanent neural differentiation defects resulting in mental retardation, learning disorders, and attention deficit hyper-activity disorder (ADHA)" (Filippelli et al., 2005).

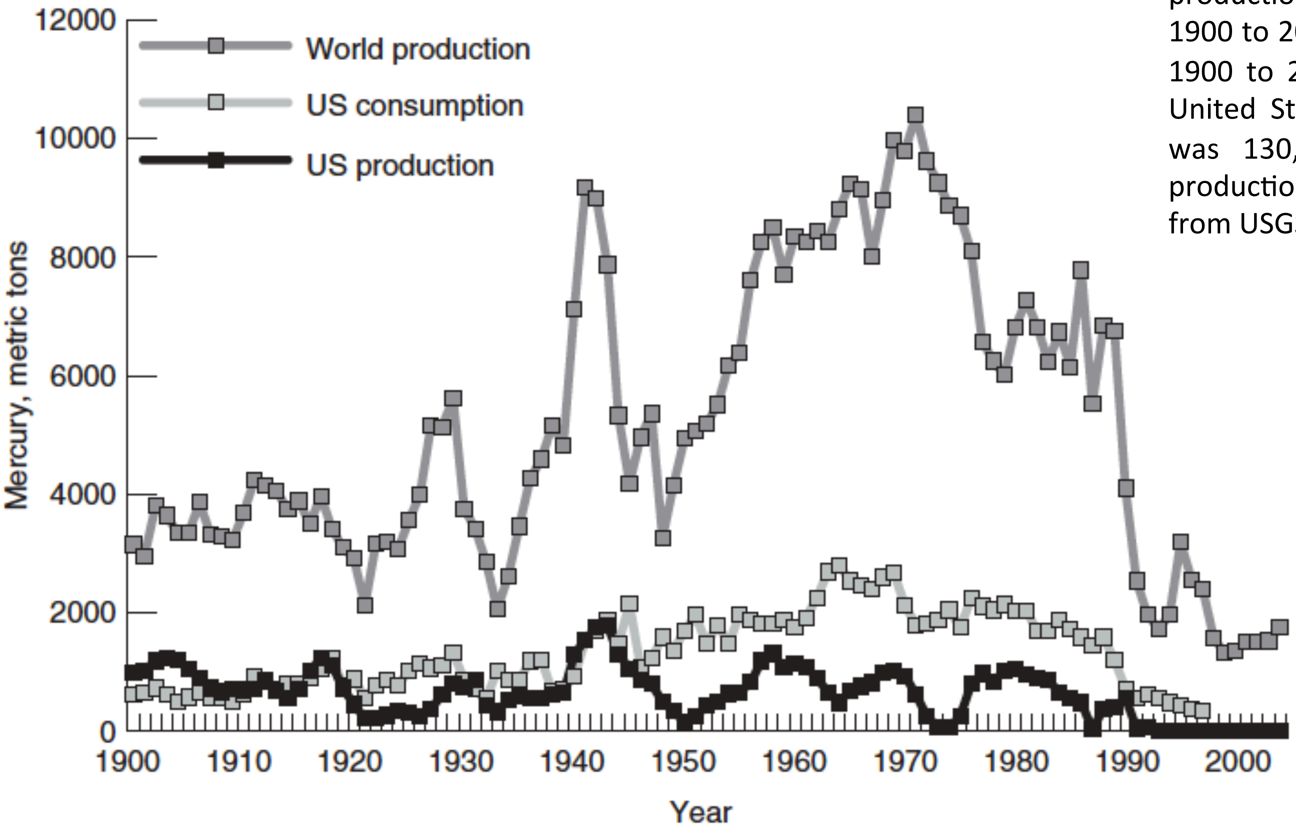
Much of the lead in a human body is stored in the bone. Modern human bones contain 3–30 ppm Pb. Concentration of lead in soft tissue is about 0.18 ppm. Before the common and widespread burning of leaded gasoline, human bones contained from 0.05 to 0.08 ppm, and before heavy industrial development occurred after 1750 human bones contained 0.01 ppm Pb (Sannolo et al., 1995). However, during the peak of the Roman Empire lead production (80,000 tons Pb per year) when lead emissions into the atmosphere are estimated to have reached 4000 tons per year, analyses of 1st to 4th centuries AD Romano-Britons bones and teeth show 10 times more Pb than a 1960s British city-dweller (Keys, 2003). The body burden of an adult in the United States is 120–400 mg Pb/70 kg person (Sannolo et al., 1995; Emsley, 1998, 2001; Li, 2000).



Burning of leaded gasoline since 1924 has caused the entire biosphere to have lead levels at least 100 times natural background levels. Four million tons of lead used in gasoline remains in our dust and soil. Three million tons of lead is found in lead paint on 60 million private homes in the United States; about 10 million of these homes have families with children below seven years old. The 1990 publication of the results of a 11 year follow up study of children that had early lead poisoning indicates that childhood exposure to lead can cause long-term intellectual underdevelopment. There is also concern that even low-level exposure to lead may cause a lower intelligence quotient. If this study is correct millions of young children in the United States may be considered to have excessive lead levels. Lead poisoning is the number one environmental health problem to children (Needleman et al., 1990; Stapleton, 1994).

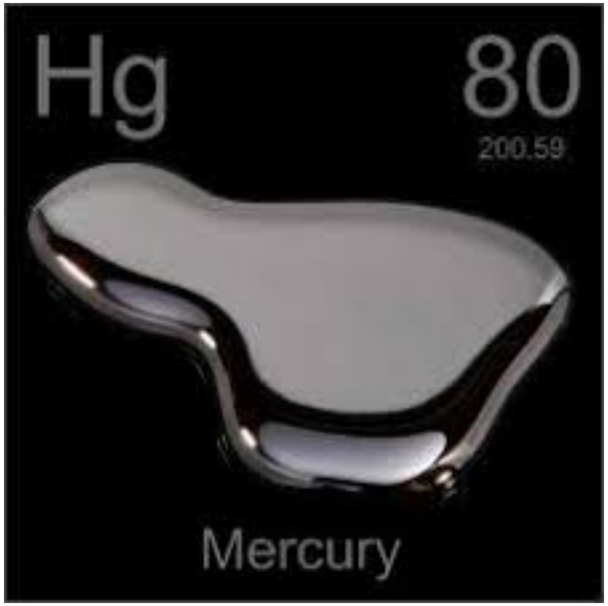
# Mercury, Hg

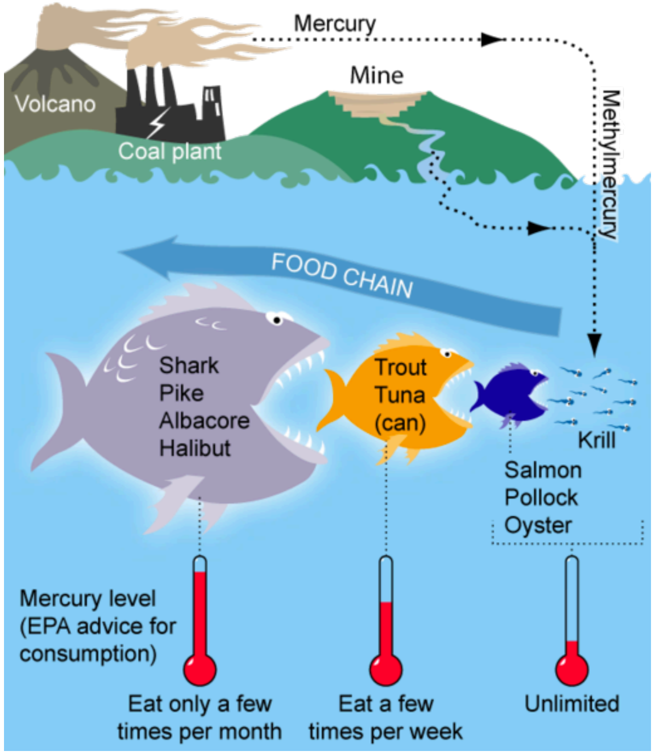
Mercury is a classic **chalcophile element** occurring most commonly as cinnabar, HgS. Natural occurrences of high mercury concentrations are limited to a few areas in the crust where hydrothermal processes have **concentrated** cinnabar with lesser amounts of native mercury. Outside of these mineral deposits mercury is a rare substance; Hg is 68th in abundance at 80 ppb in the earth's crust, while the concentration in seawater is 0.03 ppb Hg. Oxidation states of mercury are Hg, $Hg^{+}$ , and $Hg^{2+}$ .

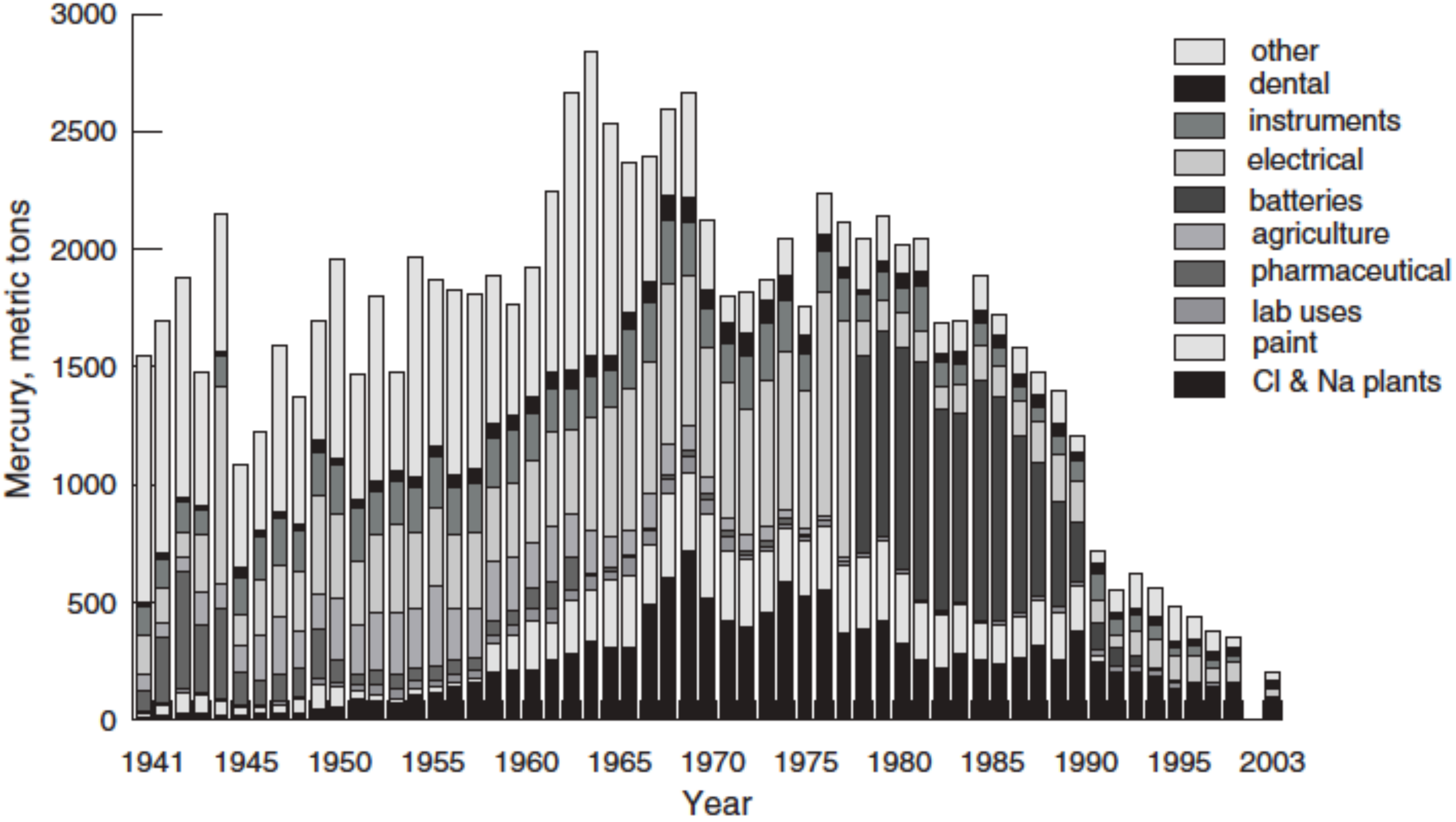


The world production and United States production and consumption of mercury from 1900 to 2002. Total world production of Hg from 1900 to 2002 is estimated to be 530,000 tons. United States consumption from 1900 to 1997 was 130,000 tons. There has been no Hg production in the United States since 1992. Data from USGS (2003, 2004).

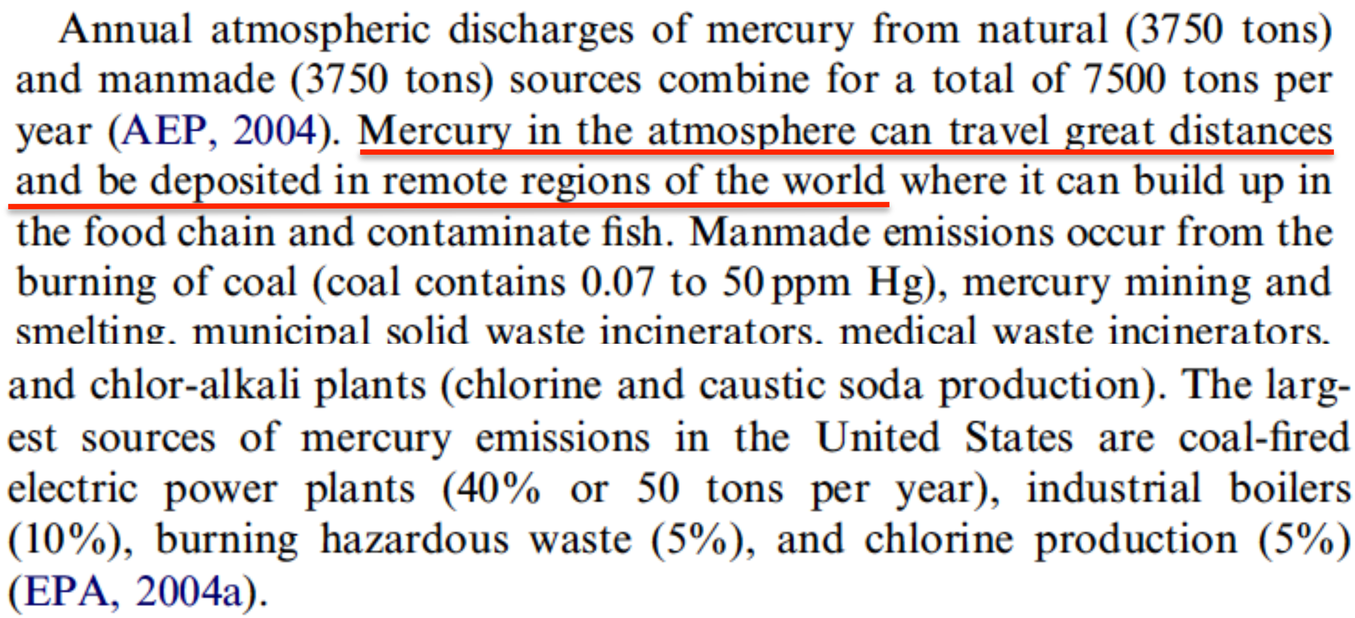
Mercury differs from other heavy toxic metals in many ways: (1) elemental mercury is a liquid with high volatility and readily vaporizes into the atmosphere (melting point = −38.9°C and boiling point = 357°C); (2) mercury vapor travels throughout the atmosphere; (3) mercury can undergo reduction with free mercury liquid produced in soils; (4) mercury is the most soluble metal; (5) mercury dissolves gold and silver and is dissolved in minor amounts in naturally occurring Au and Ag; (6) biomethylation of mercury produces very toxic and volatile compounds such as $(CH_3)_2Hg$; and (7) methylmercury bioaccumulates in the food chain (Fergusson, 1990; Sznopek and Goonan, 2000).



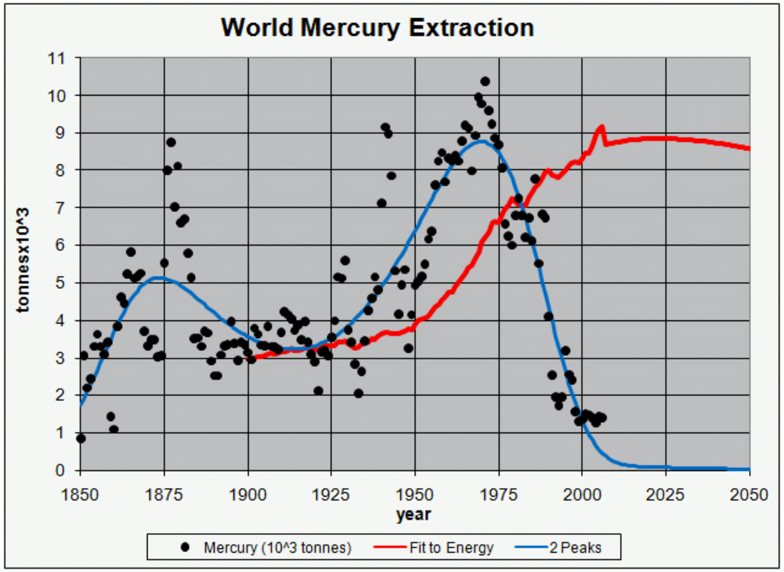


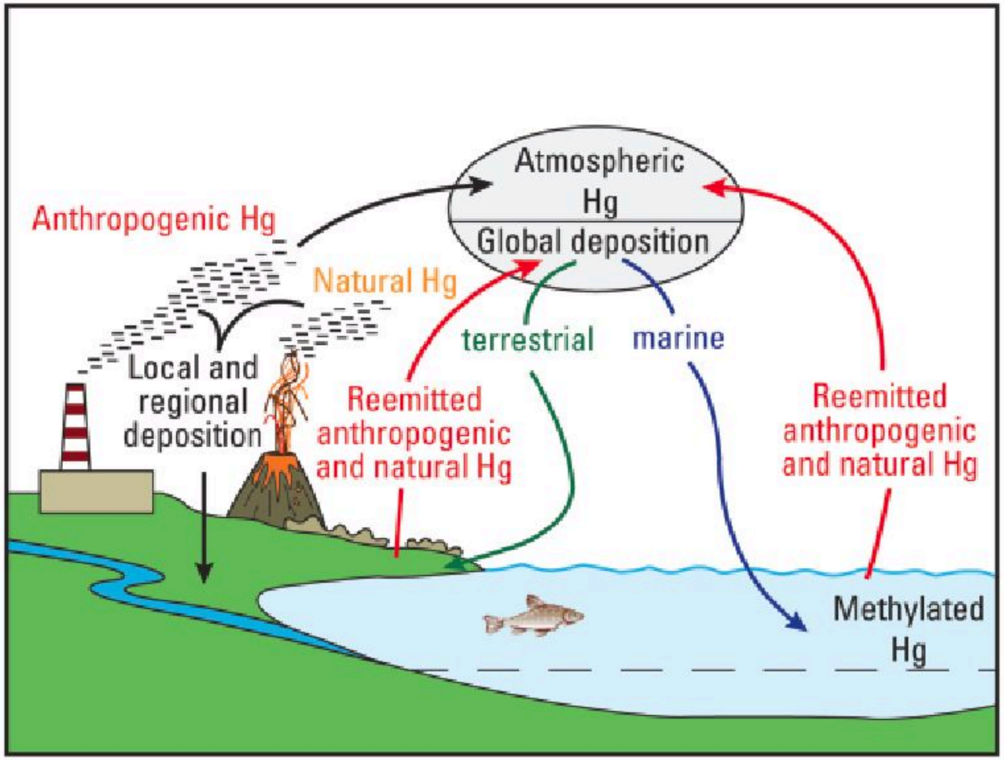


Use of mercury in selected years in the United States (Jasinski, 1994; Sznopek and Goonan, 2000). From 1941 to 1996 an estimated 93,000 tons of Hg was used in the United States. Major uses were for electrical (18,000 tons, including batteries, wiring devices and switches, and lighting), chlorine and caustic soda manufacture (12,500 tons), paint (8400 tons), laboratory and measuring and control instruments (8700 tons), pharmaceutical (3400 tons), agricultural chemicals (5500 tons) and dental (2700 tons). Recovery by amalgamation of gold and silver is part of ‘‘other’’. Before 1978 mercury in batteries was included
within electrical.

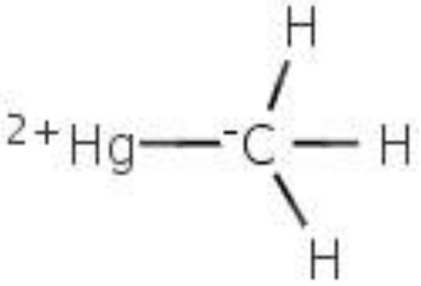


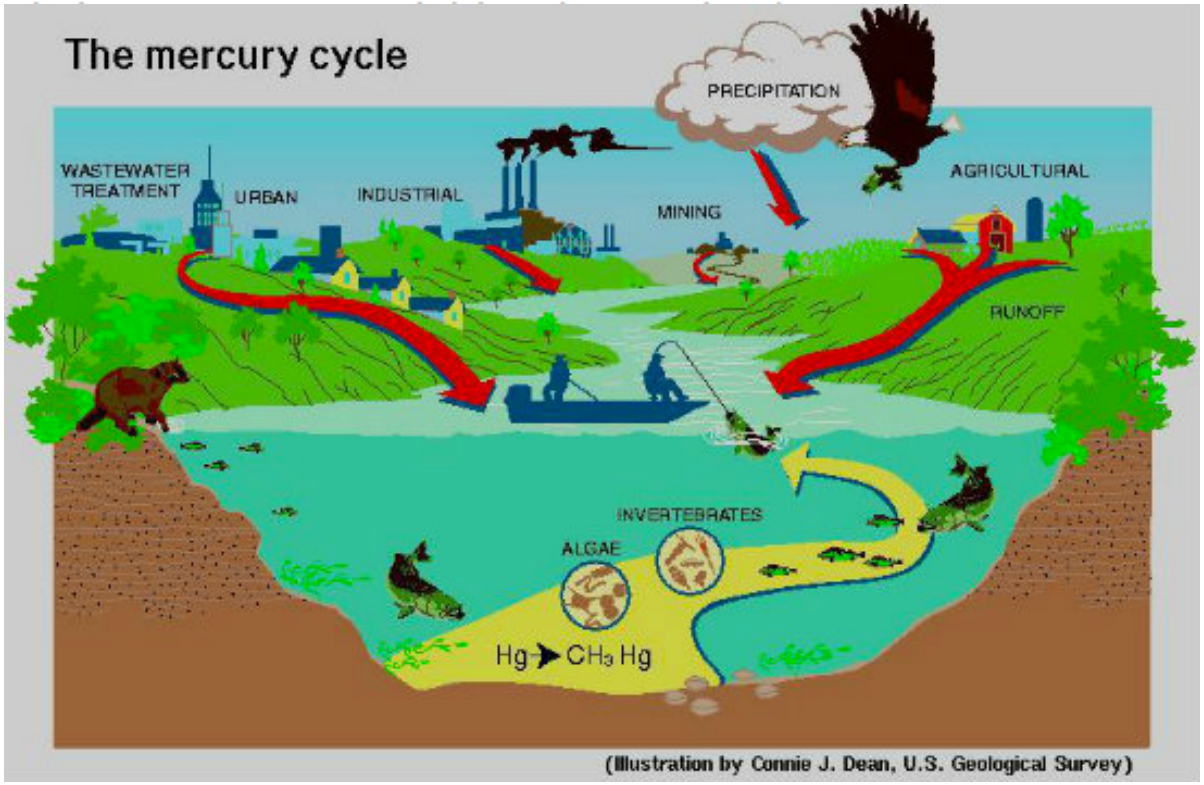
Annual atmospheric discharges of mercury from natural (3750 tons) and manmade (3750 tons) sources combine for a total of 7500 tons per year (AEP, 2004). Mercury in the atmosphere can travel great distances and be deposited in remote regions of the world where it can build up in the food chain and contaminate fish. Manmade emissions occur from the burning of coal (coal contains 0.07 to 50 ppm Hg), mercury mining and smelting, municipal solid waste incinerators, medical waste incinerators, and chlor-alkali plants (chlorine and caustic soda production). The largest sources of mercury emissions in the United States are coal-fired electric power plants (40% or 50 tons per year), industrial boilers (10%), burning hazardous waste (5%), and chlorine production (5%) (EPA, 2004a).





Methylmercury is the most dangerous form of mercury. Fish and shellfish are the usual methods of mercury intake by humans. They contain 1000 to 10,000 times more methylmercury than other foods (cereals, potatoes, vegetables, fruits, meats, poultry, eggs, and milk). Most fish contain 0.001 to 0.5 ppm Hg and the average amount of methylmercury in commercial saltwater fish is less than 0.3 ppm. A few species of large predatory fish commonly have higher levels. Fish to be avoided by mothers and small children include shark, swordfish, king mackerel, and tilefish (EPA, 2004b).





(Illustration by Connie J. Dean, U.S. Geological Survey)