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Chapter 2

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

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Abstract

The geochemical distribution and classification of the elements was determined and described by Victor Moritz Goldschmidt. This paper describes proposed modifications of Goldschmidt's classification of the elements in the light of geochemical and environmental data obtained in the last 70 years. Arsenic, lead, and mercury have great affinity to concentrate in the biosphere. Under certain conditions they will reach relatively high concentrations in coal and humans. Arsenic and mercury form methyl compounds with carbon and can build up in the food chain. Lead, because it has the same charge and a similar ionic radius to calcium, builds up in the human body when ingested. This is especially true in young children (below 6 years old) that require high levels of calcium to grow. Toxic levels of As, Pb, and Hg can result in death to all ages. Less than toxic levels can cause birth defects and brain damage (Hg), cancer and skin warts (As), and brain damage and lower IQ (Pb). Research indicates that additional classification of these traditional chalcophile elements as biophile elements is indispensable to future proper understanding and utilization of arsenic, lead, and mercury in the modern industrial, developing, and impoverished world.

2.1. Introduction

In 1923 Victor Moritz Goldschmidt, the father of modern geochemistry, proposed the geochemical classification of the elements (Goldschmidt, 1923; Mason, 1992). The classification of the elements (Table 2.1) into lithophile (affinity for silicate), siderophile (affinity for iron–nickel), chalcophile (affinity for sulfide), and atmophile (affinity for the gaseous

Table 2.1. 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).

state) has withstood the test of time (Cox, 1989; Emsley, 1998; Li, 2000; Railsback, 2003). 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. Sixty years after the publication many geochemistry textbooks had dropped the biophile elements from tables showing the geochemical classification of the elements (Table 2.2) (Mason and Moore, 1982; Krauskopf and Bird, 1995).

The purpose of this paper is to update the classification of the elements and to suggest that arsenic, lead, and mercury should be included in the biophile elements. Our research consists of determining the distribution

Table 2.2. 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.

ratio of arsenic, lead, and mercury in humans versus lithosphere and hydrosphere. This paper will discuss how humans have historically distributed arsenic, mercury, and lead around the world and the toxic effects of this distribution.

2.1.1. 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. A complete listing of all biophile elements is compiled from:

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).
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).

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).

Figure 2.1 shows that humans have high (>1) ratios of man to crust for H, C, O, N, P, S, Cl, Br, Cd, Se, Hg, and Te. Figure 2.2 shows that most elements have high (>1) ratios of man to ocean with Pb having a ratio less than that of C, N, and P but more than that of Ca, Zn, and Fe. Table 2.3 and Fig. 2.3 show the proposed list of biophile elements. 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

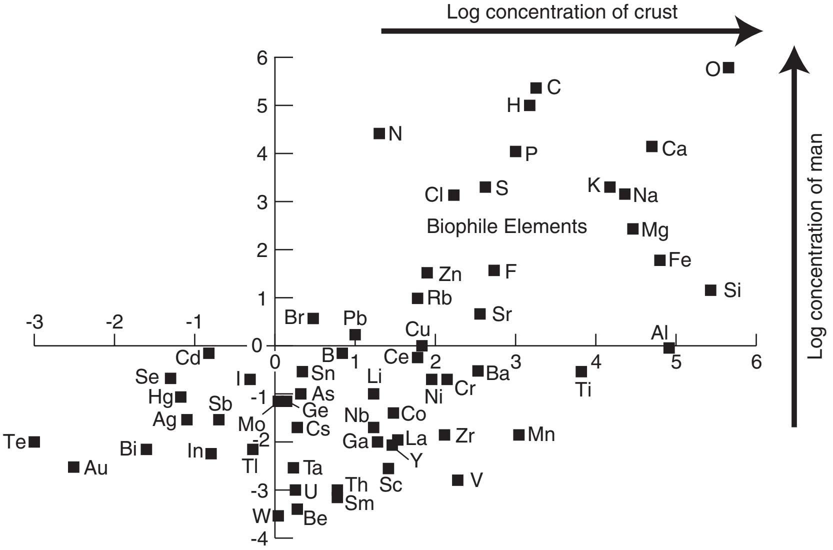

Figure 2.1. The abundance of elements in man versus the crust. Biophile elements are enriched in man relative to the crust.

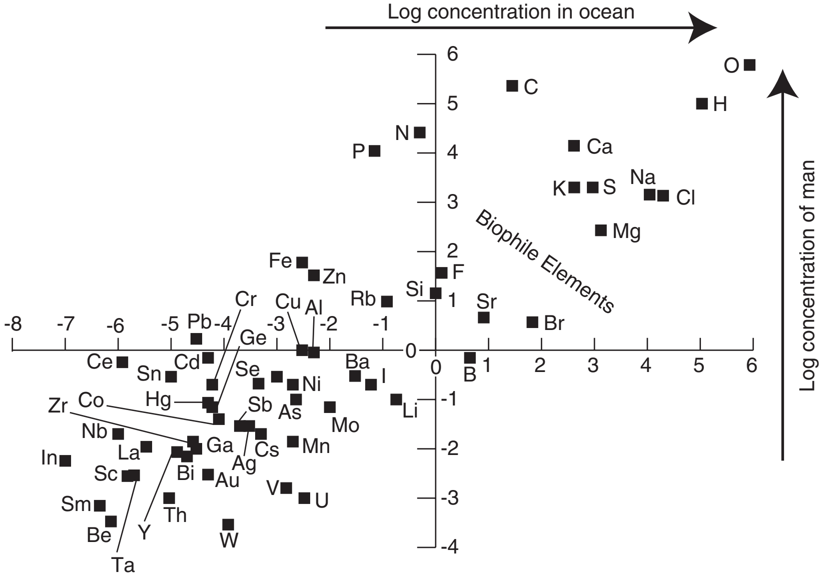

Figure 2.2. The abundance of elements in man versus the ocean. Some biophile elements (C, N, P) are enriched in man relative to the ocean while some biophile elements (Cl, Na, Mg, Br) are enriched in the ocean relative to man.

Table 2.3. 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.

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.

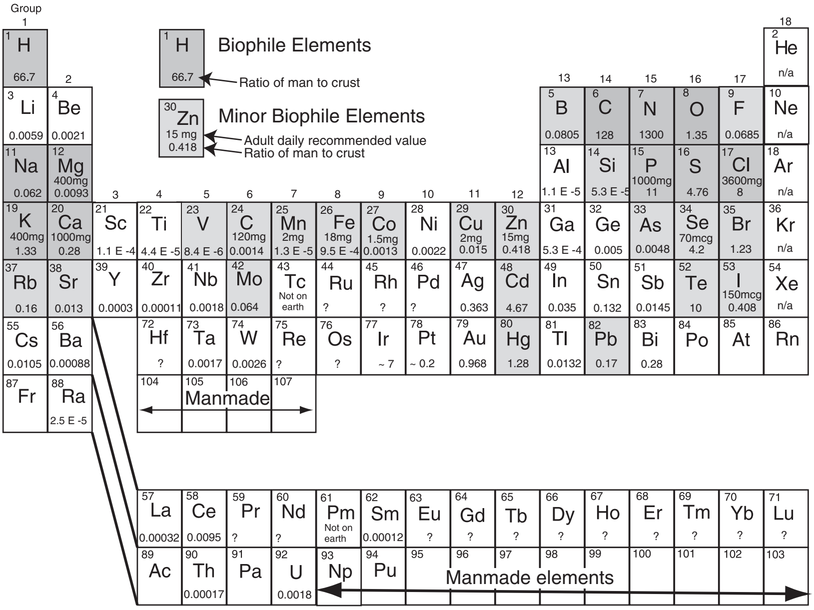

Figure 2.3. Periodic table showing biophile elements (shaded) and the ratio of man to crust.

2.2. Environmental geochemistry and anthropogenic dispersion of arsenic, lead, and mercury

2.2.1. 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, $FeAs_2$. Figures 2.4 and 2.5 are plots of the human production and usage of arsenic (Table 2.4) that have spread arsenic around the world.

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

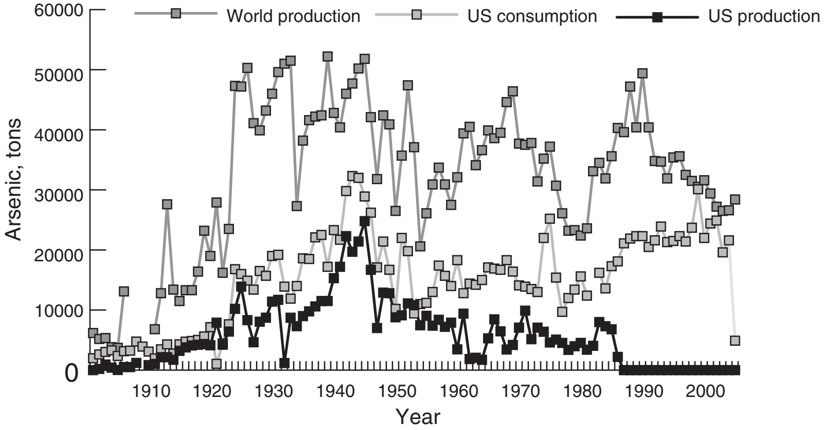

Figure 2.4. The world production and United States production and consumption of arsenic from 1900 to 2002. Arsenic production stopped by 1986 in the United States. Total world production of As from 1900 to 2002 was 3,250,000 tons. United States consumption was 1,500,000 tons. Data from USGS (2003, 2004).

low toxicity. As^{5+} is more soluble than As^{3+}. Inorganic forms of arsenic occurring in groundwater are most toxic.

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

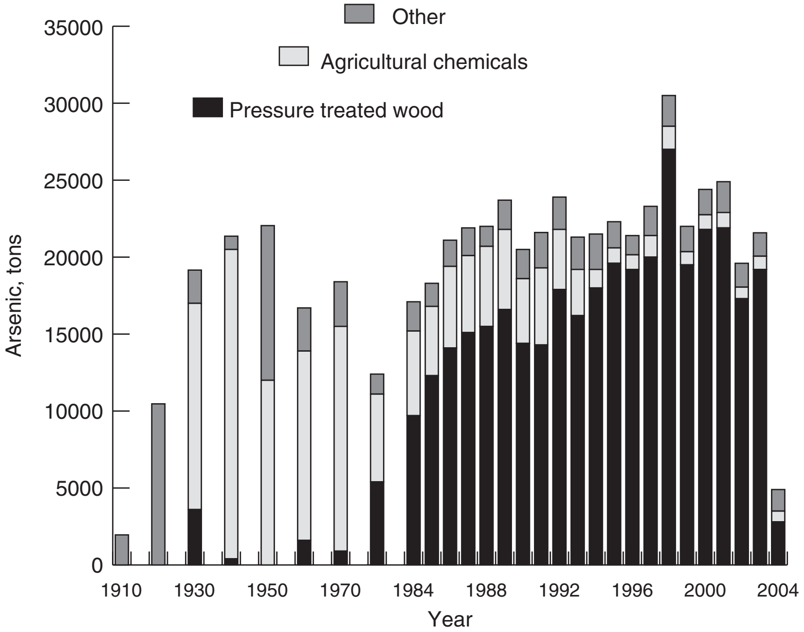

Figure 2.5. Use of arsenic in selected years in the United States after Bleiwas (2000) with additional data from USGS, Mineral Commodity Summaries and Loebenstein (1994). From 1960 to 2003 an estimated 420,000 tons of arsenic was used in the manufacture of pressure-treated wood and another 115,000 tons was used in agriculture. From 1910 to 1970 the largest usage of arsenic was in agriculture.

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. In Bangladesh since 1971, 8–12 million shallow tube wells were dug, providing drinking water for 90% of a population of 140 million. In 1993 arsenic was discovered in the well water. Groundwater in one million of the wells has arsenic concentrations above 50 ppb with some wells containing over 1,000,000 ppb As. Chakraborti et al. (2003) in a study done in Bihar, India found 19.9% of tube wells had >300 ppb As. The study was done in a 4 km^2 area in a remote agricultural village of 5000 people. In some regions of south Asia, 50% of the wells have arsenic levels exceeding the USEPA maximum drinking water level of 10 ppb As (Frisbie et al., 2002). Arsenic threatens 40–60 million people in Bangladesh and has caused skin lesions (arsenical dermatitis) in over 100,000 people with tens of thousands of people

Table 2.4. 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.

[a] 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.

[b] Radioactive decay of U and Th to He and Pb, and K to Ar places these elements into this group, He and Ar are trapped in silicate structures.

[c] H and He escape from the earth's atmosphere into space.

[d] Volcanic eruptions, forest fires, burning fossil fuels, smelting metal ores, and incineration of waste places these elements into this group. Mercury is in this group because of its high vapor pressure.

[e] Biophile elements because of easy substitution; Rb for K, Sr and Pb for Ca, Se and Te for S, and Cd for Zn.

displaying hyperkeratosis and chronic and acute arsenicosis (McArthur et al., 2001; WHO, 2001; Brooks, 2003; USGS International Program, 2004; Meharg, 2005). Children exposed to wells with >50 ppb As have reduced intellectual function relative to children with exposures to <5.5 ppb As (Wasserman et al., 2004). In Bangladesh an estimated 9000 deaths per year are arsenic related (Lokuge et al., 2004).

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 (Fig. 2.5). 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 (Fig. 2.5). 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).

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 in Fig. 2.7 have dispersed lead around the world.

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

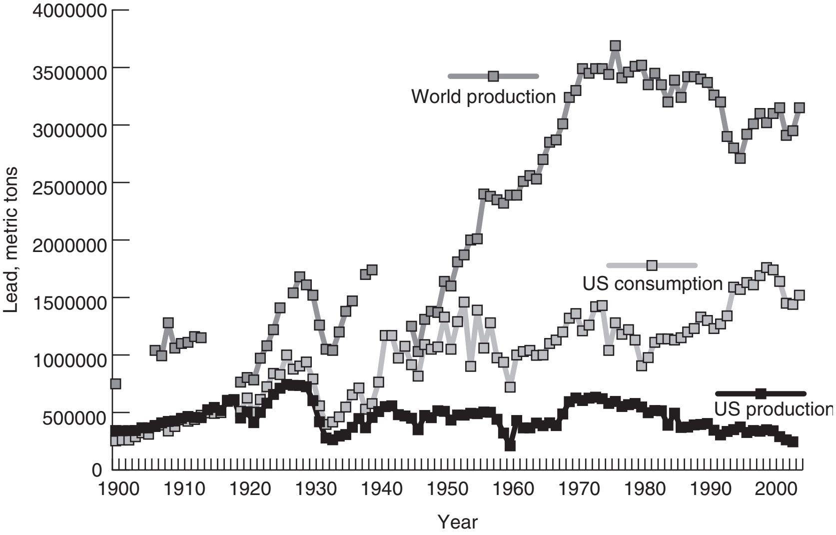

Figure 2.6. The world production and United States production and consumption of lead from 1900 to 2002. Total world production of Pb from 1900 to 2002 is estimated to be 214,000,000 tons. United States consumption was 97,000,000 tons. Data from USGS (2003, 2004).

Table 2.5. The major uses of arsenic, lead, and mercury during the last 140 years[a]

Metal	Usage
Arsenic Before 1900	Insecticides, herbicides, fungicides, glass and ceramics, folk remedies, metal alloys
1900–1985	Insecticides, herbicides, fungicides, leathering, tanning, paint pigments, treatment of syphilis and psoriasis until 1940s, glass making, metal alloys (in solder, with lead in ammunition, in bearings)
1985–present	Pressure-treated wood, metal alloys (additive to increase strength of posts on batteries), pesticide, desiccant on cotton fields, insecticides, herbicides (weed control), fungicides, fertilizers, semiconductors (computers, wireless phones, solar cells), light emitting diodes, animal feed (promote growth), glass making, paint pigment
Lead Before 1900	Ammunition, brass, burial vault liners, ceramic glazes, roofs, plumbing, soldering, paint and pigment, batteries, leaded glass and crystal, pewter, water lines and pipes
1900–1985	Batteries, gasoline additive, paint and pigment, ammunition, crystal glass, flint glass, insecticides, herbicides, fungicides, bearing metals, cable covering, caulking lead, solders, type metals, terne metal for gas tanks, radiation shielding, ballast and counter weights, brass, bronze, foil, wire
1985–present	Batteries (84% of US usage in 2003), ammunition (3%), glass and ceramics (3%), casting metals (2%), sheet lead (1%), radiation shielding, radiation shielding in medical analysis and video display equipment, covering for power and communication cables, building materials, solders for motor vehicles, metal containers
Mercury Before 1900	Gold and silver mining (amalgamation), medical, pharmaceutics, insecticides, herbicides, fungicides, electrical instruments, paint and pigment, wool and felt, antibacterial, batteries, mirrors, laboratory chemicals, thermometers, catalysts, explosives, dental amalgams
1900–1985	Batteries, gold mining, medical, electrical instruments, catalysts, insecticides, herbicides, fungicides, dental amalgams, paper industry for control of slime, laboratory chemicals, thermometers, chlorine and caustic soda production, explosives, preservative in cosmetics, antifungal agricultural products, pharmaceutics
1985–present	Chlorine and caustic soda production (33–50% of US usage in 2003), paint (anti-mildew marine paint, and fungicide and biocide additive), batteries, electrical instruments, fluorescent lights and Hg vapor lamps, dental amalgams, catalysts, laboratory chemicals, thermometers, barometers, thermostats, pigment, pharmaceutics, medical.[b] Globally—gold and silver mining, button-type batteries, cleansers, folk medicine, pesticides, skin-lightening cream and soap

[a] After Ayres and Rod (1986), Fergusson (1990), Jasinski (1994), ATSDR (2000), Bleiwas (2000), USGS (2005) and EPA (2004c and 2004d).

[b] See Appendix A and B of EPA (2004c).

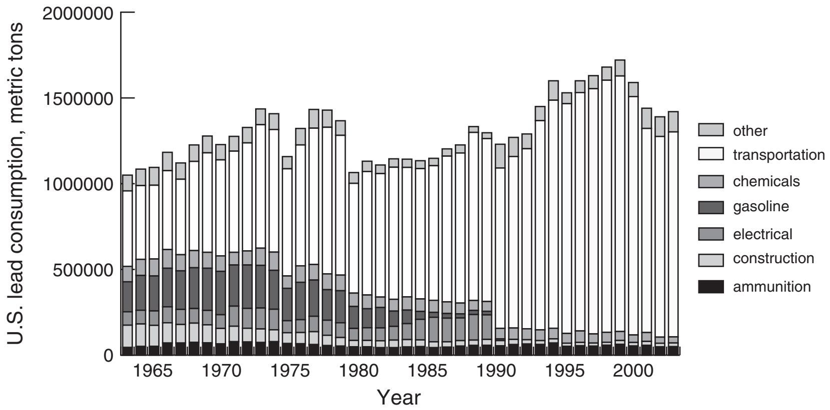

Figure 2.7. Use of lead in selected years in the United States. Data from USGS, Mineral Commodity Summaries (USGS, 1998a, 2004). Lead usage in gasoline in the United States ended in 1993. Transportation includes lead in car and truck batteries. Exports of ammunition and imports of glass, ceramics, and batteries cause an increase in lead consumption because of net imports of manufactured products (Biviano et al., 1999).

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.

Total United States lead and lead compound emissions reported for 2002 by the EPA Toxic Release Inventory (TRI) were 732 tons. TRI reports that metal mining and metal processing result in 351 tons of emissions (EPA-TRI, 2004). Lead atmosphere emissions are 0.17% of total Pb waste of 426,469 tons in 2002. Disposal of Pb and Pb compounds on land and on- and off-site were about 410,000 tons in 2002. Over 92% of this is from metal mining and primary metal processing. Industries in 2002 discharged 69 tons of lead into surface waters, 3589 tons into underground wells, 196,897 tons onto land, and 225,181 tons to on- and off-site disposal.

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).

For adults and children in the United States, average blood lead levels have dropped as major uses of lead have declined—lead in paint, gasoline, drinking water systems, and food cans. The geometric mean blood lead level in children ages 1–5 has fallen from 14.9 $\mu g\,dl^{-1}$ in 1976–1980 to 2.0 $\mu g\,dl^{-1}$ in 1999 (Koller et al., 2004). In spite of good progress there are still areas of concern with lead. The first of these is well described by Filippelli et al. (2005). The number of children in the United States with lead poisoning has been lowered from 88% to 2.2%. However, in urban centers 15 to 29% of children can have unsafe blood lead levels ($>10\,\mu g\,dl^{-1}$). The 2.2% is still too high because it means 434,000 children in the United States have elevated blood lead levels (EPA, 2004a).

2.2.3. *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+}.

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).

Figure 2.8 shows United States production and consumption and world production of mercury from 1900 to 2003. Before 1900 much usage of mercury was for extracting gold and silver from ore. The principle uses of mercury (Table 2.4) from 1941 to 2003 in the United States are shown in Fig. 2.9. Many of these uses have spread mercury throughout the

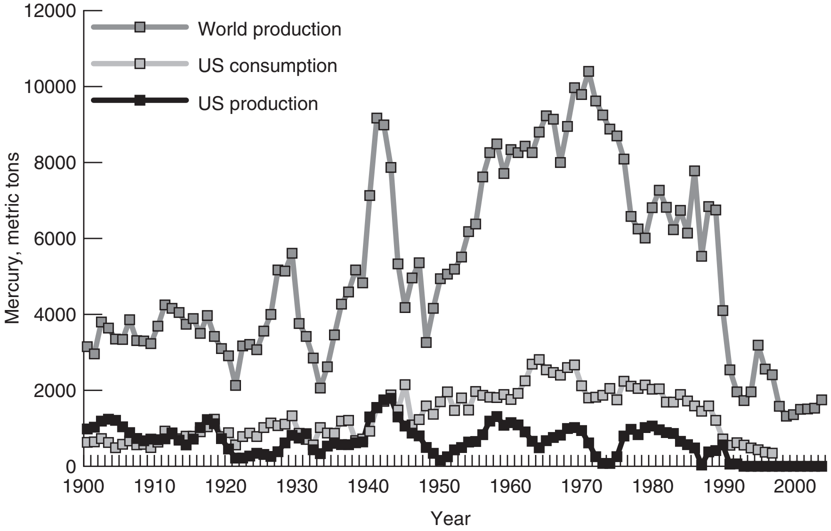

Figure 2.8. The world production and United States production and consumption of mercury from 1900 to 2002. Total world production of Hg from 1900 to 2002 is estimated to be 530,000 tons. United States consumption from 1900 to 1997 was 130,000 tons. There has been no Hg production in the United States since 1992. Data from USGS (2003, 2004).

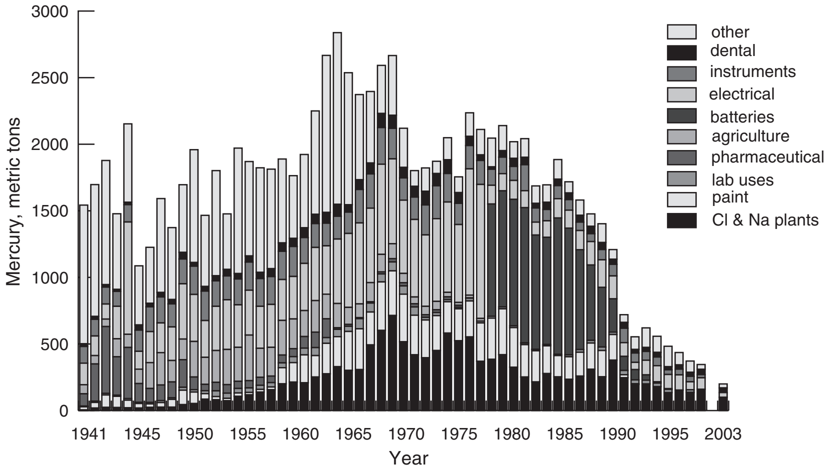

Figure 2.9. Use of mercury in selected years in the United States (Jasinski, 1994; Sznopek and Goonan, 2000). From 1941 to 1996 an estimated 93,000 tons of Hg was used in the United States. Major uses were for electrical (18,000 tons, including batteries, wiring devices and switches, and lighting), chlorine 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.

environment—gold and silver mining, escape of mercury from chlorine and caustic soda production, batteries, paint, dental, insecticides, herbicides, and fungicides. Mercury usage in the United States has steadily declined since a high of 2800 tons in 1964 with environmental restrictions such as elimination of mercury from paint and most batteries (Sznopek and Goonan, 2000). In 2005 the principle uses of mercury in the United States are in the chlorine and caustic soda industry, fluorescent lights, Hg vapor lamps, and dental amalgams. Of these uses only dental amalgams appear to be safe for healthy working adults (Factor-Litvak et al., 2003). Worldwide, considerable mercury is still lost to the environment from gold mining.

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). Avoiding consumption of certain top predatory freshwater fish is necessary; within the United States 48 states had issued 3089 fish advisories by 2003 with 76% of the advisories including mercury (EPA, 2004b). Large fish that may be on local consumption advisories (with mean and range of mercury in ppm) are eastern chain pickerel (0.61, 0.014–2.81), largemouth bass (0.52, 0.0005–8.94), walleye (0.43, 0.005–16), northern pike (0.36, 0.005–4.4), smallmouth bass (0.32, 0.005–3.34), lake trout (0.27, 0.005–2), yellow perch (0.25, 0.005–2.14) (EPA, 2001; Burger et al., 2005).

Mahaffey et al. (2004) discuss results of the 1999 and 2000 National Health and Nutrition Examination Survey that measured blood methylmercury concentration in 1709 women. The methylmercury concentration was 0.6 ppb at the 50th percentile. The concentration was 6.7 ppb at the 95th percentile. An estimated 7.8% of U.S. women have blood methylmercury levels greater that 5.8 ppb (EPA recommends whole blood levels be below 5 ppb), and a 1:1 ratio of mother to baby blood methylmercury concentrations. Mahaffey et al. (2004) conclude that over 300,000 newborns out of 4,058,814 births in the U.S. per year are at risk for problems in neurodevelopment. Hair mercury levels yielded similar results (McDowell et al., 2004).

2.3. Conclusion

Modifications of Goldschmidt's geochemical classification of the elements are made based on distribution and tendency of the elements. The biophile elements have tendencies that uniquely distinguish them. These tendencies are well demonstrated by arsenic, lead, and mercury. They are biophile because of substitutions (lead for calcium), bioaccumulation (arsenic and mercury), and methylation (mercury). In Bangladesh an estimated 9000 deaths per year are arsenic related and 40–60 million people are threatened by arsenic in drinking water. In the United States an estimated 434,000 children have their intellectual development threatened by elevated blood lead levels. Mercury from fish consumption in the United States threatens the neurodevelopment of an estimated 300,000 newborns each year. Today's world of rapid development necessitates the classification of As, Pb, and Hg as toxic biophile elements to avoid making future environmental mistakes.

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REFERENCES

AEP (American Electric Power Company), 2004. Environmental. Accessed on 2-21-2005 at http://www.aep.com/environmental/emissionscontrol/rtk/mercury.htm

ATSDR, 2000. Public health statement for arsenic. Agency for Toxic Substances and Disease Registry. Assessed on 7-18-2003 at http:astsdr1.cdc.gov/toxProfilesphs8802.html

Ayres, R.U., Rod, S.R., 1986. Patterns of pollution in the Hudson–Raritan Basin. Environment, 28(4), 14–20, 39–43.

Bates, R.L., Jackson, J.A., 1984. Dictionary of Geological Terms, third ed. American Geological Institute, Anchor Press, Garden City, New York, p. 571.

Biviano, M.B., Sullivan, D.E., Wagner, L.A., 1999. Total materials consumption: An estimation methodology and example using lead—a materials flow analysis. U.S. Geological Survey Circular 1183, p. 22. Accessed on 2-7-2005 at http://greenwood.cr.usgs.gov/pub/circulars/c1183/

Bleiwas, D.I., 2000. Arsenic and old waste. US Geological Survey. Accessed on 8-6-2004 at http://minerals.usgs.gov/minerals/mflow/d00-0195/

Brooks, W.E., 2003. Arsenic. U.S. Geological Survey Minerals Yearbook – 2003.

Burger, J., Stern, A.H., Gochfeld, M., 2005. Mercury in commercial fish: Optimizing individual choices to reduce risk. Environ. Health Perspect. 113, 1–6.

Chakraborti, D., Murkherjee, S.C., Pati, S., Sengupta, M.K., Rahman, M.M., Chowdhury, U.K., Lodh, A.D., Chanda, C.R., Chhakraborti, A.K., Gautam, 2003. Arsenic groundwater contamination in Middle Ganga Plain, Bihar, India: A future danger. Environ. Health Perspect. 111, 1194–1201.

Combs Jr., G.F., 2005. Geological impacts on nutrition. In: Selinus, O. (Ed.), Essentials of Medical Geology: Impacts of the Natural Environment on Public Health. Elsevier, Amsterdam, The Netherlands, pp. 161–178.

Cox, P.A., 1989. The Elements Their Origin, Abundance and Distribution. Oxford Science Publications, Oxford, England, p. 207.

Davies, B.E., Bowman, C., Davies, T.C., Selinus, O., 2005. Medical geology: Perspectives and prospects. In: Selinus, O. (Ed.), Essentials of Medical Geology: Impacts of the Natural Environment on Public Health. Elsevier, Amsterdam, The Netherlands, pp. 1–16.

Emsley, J., 1998. The Elements. third ed. Oxford University Press, p. 292.

Emsley, J., 2001. Nature's Building Blocks: An A–Z Guide to the Elements. Oxford University Press, Oxford, England, p. 538.

EPA, 2001. Fact Sheet. Mercury Uptake: Impact on fish advisories. EPA-823-F-01-011 p. 9.

EPA, 2002. Manufacturers to use new wood preservatives, replacing most residential uses of CCA. Accessed on 6-7-2004 at http://www.epa.gov/pesticides/factsheets/chemicals/cca_transition.htm

EPA, 2004a. Mercury Frequent Questions. Assessed on 9-3-2004 at http://www.epa.gov/air/mercury/information1.htm

EPA, 2004b. Fish Advisories: What you need to know about mercury in fish and shellfish. Assessed on 9-2-2004 at http://www.epa.gov/waterscience/fishadvice/advice.htm

EPA, 2004c. Reducing mercury use in healthcare promoting a healthier environment. Assessed on 9-3-2004 at http://www.epa.gov/getlakes/bnsdocs/merchealth/

EPA, 2004d. Lead in paint, dust, and soil. Assessed on 2-2-2005 at http://www.epa.gov/opptintr/lead/index.html

EPA-TRI, 2004. Data obtained from Toxic Release Inventory. Assessed on 3-1-2005 at http://www.epa.gov/triexplorer/trends/htm

Factor-Litvak, P., Hasselgren, G., Jacobs, D., Begg, M., Kline, J., Geier, J., Mervish, N., Schoenholtz, S., Graziano, J., 2003. Mercury derived from dental amalgams, and neuropsychologic function. Environ. Health Perspect. 111, 719–723.

Fergusson, J.E., 1990. The Heavy Elements: Chemistry, Environmental Impact and Health Effects. Pergamon Press, New York, p. 614.

Filippelli, G.M., Laidlaw, M.A.S., Latimer, J.C., Raftis, R., 2005. Urban lead poisoning and medical geology: An unfinished story. GSA Today 15, 4–11.

Frisbie, S.H., Ortega, R., Maynard, D.M., Sarkar, B., 2002. The concentrations of arsenic and other toxic elements in Bangladesh's drinking water. Environ. Health Perspect. 110, 1147–1153.

Fuge, R., 2005. Anthropogenic sources. In: Selinus, O. (Ed.), Essentials of Medical Geology: Impacts of the Natural Environment on Public Health. Elsevier, Amsterdam, The Netherlands, pp. 43–60.

Garrett, R.G., 2005. Natural distribution and abundance of elements. In: Selinus, O. (Ed.), Essentials of Medical Geology: Impacts of the Natural Environment on Public Health. Elsevier, Amsterdam, The Netherlands, pp. 17–42.

Goldschmidt, V.M., 1923. Geochemische Verteilungsgesetze der Elemente (1). Vidensk. skrifter. I. Mat.-naturv. klasse. No. 3, p. 17.

Goldschmidt, V.M., 1954. Geochemistry. Oxford University Press, Oxford, England, p. 730.

Greenwood, N.N., Earnshaw, A., 1997. Chemistry of the Elements. second ed. Butterworth-Heinemann, p. 1341.

Hollabaugh, C.L., 2004. The inclusion of arsenic, lead, and mercury as biophile elements. Geol. Soc. Am. Abstracts with Programs 36(5), 333.

Hollabaugh, C.L., 2005. Toxic biophile elements arsenic, lead, and mercury: From personal to professional undergraduate research in environmental geochemistry. Geol. Soc. Am. Abstracts with Programs 37(2), 8.

Jasinski, S.M., 1994. The materials flow of mercury in the United States. Bureau of Mines Information Circular 9412. p. 27.

Keys, D., 2003. How Rome polluted the world. Geographical 75, 45–48.

Koller, K., Brown, T., Spurgeon, A., Levy, L., 2004. Recent developments in low-level lead exposure and intellectual impairment in children. Environ. Health Perspect. 112, 987–994.

Krauskopf, K.B., Bird, D.K., 1995. Introduction to Geochemistry, third ed. McGraw-Hill, New York, p. 647.

Lasky, T., Sun, W., Kadry, A., Hoffman, M.K., 2004. Mean total arsenic concentrations in chicken 1989–2000 and estimated exposures for consumers of chicken. Environ. Health Perspect. 112, 18–21.

Li, Y-H., 2000. A Compendium of Geochemistry: From Solar Nebula to the Human Brain. Princeton University Press, Princeton, New Jersey, p. 475.

Lindh, U., 2005. Biological functions of the elements. In: Selinus, O. (Ed.), Essentials of Medical Geology: Impacts of the Natural Environment on Public Health. Elsevier, Amsterdam, The Netherlands, pp. 115–160.

Liu, J., Zheng, B., Aposhian, H.V., Zhou, Y., Chen, M.-L., Zhang, A., Waalkes, M.P., 2002. Chronic arsenic poisoning from burning high-arsenic-containing coal in Guizhou, China. Environ. Health Perspect. 110, 119–122.

Loebenstein, J.R., 1994. The materials flow of arsenic in the United States. Bureau of Mines Information Circular 9282, p. 12.

Lokuge, K.M., Smith, W., Caldwell, B., Dear, K., Milton, A., 2004. The effect of arsenic mitigation interventions on disease burden in Bangladesh. Environ. Health Perspect. 112, 1172–1177.

Mahaffey, K.R., Clickner, R.P., Bodurow, C.C., 2004. Blood organic mercury and dietary intake: National Health and Nutrition Examination Survey, 1999 and 2000. Environ. Health Perspect. 112, 562–570.

Mason, B., 1992. Victor Moritz Goldschmidt: Father of Modern Geochemistry. Special Publication No. 4. The Geochemical Society, New York, p. 184.

Mason, B., Moore, C.B., 1982. Principles of Geochemistry, fourth ed. John Wiley and Sons, New York, p. 344.

McArthur, J.M., Ravenscroft, P., Safiullah, S., Thirlwall, M.F., 2001. Arsenic in groundwater: Testing pollution mechanisms for sedimentary aquifers in Bangladesh. Water Resour. Res. 37, 109–117.

McDowell, M.A., Dillon, C.F., Osterloh, J., Bolger, P.M., Pellizzari, E., Fernando, R., de Oca, R.M., Schober, S.E., Sinks, T., Jones, R.L., Mahaffey, K.R., 2004. Hair mercury levels in U.S. children and women of childbearing age: Reference range data from NHANES 1999–2000. Environ. Health Perspect. 112, 1165–1171.

Meharg, A.A., 2005. Venomous Earth: How arsenic caused the world's worst mass poisoning. Macmillan, New York, p. 192.

Montgomery, C.W., 1989. Environmental Geology, second ed. Wm. C. Brown Publishers, Dubuque, Iowa, p. 476.

Needleman, H.L., Schell, A., Bellinger, D., Leviton, A., Allred, E.N., 1990. The long-term effects of exposure to low doses of lead in childhood. An 11-year follow-up report. N. Engl. J. Med. 322, 83–88.

Railsback, L.B., 2003. An Earth scientist's periodic table of the elements and their ions. Geology 31, 737–740.

Ranft, U., Miskovic, P., Pesch, B., Jakubis, P., Fabianova, E., Keegan, T., Hergemoller, A., Jakubis, M., Nieuwenhuijsen, M.J., 2003. Association between arsenic exposure from a coal-burning power plant urinary arsenic concentrations in Prievidza District, Slovakia. Environ. Health Perspect. 111, 889–894.

Sannolo, N., Carelli, G., De Lorenzo, G., Castellino, N., 1995. Environmental exposure. In: Castellino, N., Sannolo, N., Castellino, P. (Eds.), Inorganic Lead Exposure and Intoxications. CRC-Press, Boca Raton, Florida, p. 544.

Schlesinger, W.H., 1991. Biogeochemistry: An Analysis of Global Change. Academic Press, San Diego, p. 443.

Schweinfurth, S.P., 2003. Coal—A complex natural resource. U.S. Geological Survey Circular 1143, p. 39.

Skinner, H.C.W., 2005. Mineralogy of bone. In: Selinus, O. (Ed.), Essentials of Medical Geology: Impacts of the Natural Environment on Public Health. Elsevier, Amsterdam, The Netherlands, pp. 667–694.

Stapleton, R.M., 1994. Lead is a Silent Hazard. Walker and Company, New York, p. 224.

Stober, Q.J., Thornton, K., Jones, R., Richards, J., Ivey, C., Welch, R., Madden, M., Trexler, J., Gaiser, E., Scheidt, D., Rathbun, S., 2001. South Florida Ecosystem Assessment: Phase I/II—Everglades stressor interactions: Hydropatterns, eutrophication, habitat, alteration, and mercury contamination (Summary). EPA 904-R-01-002. p. 63.

Sznopek, J.L., Goonan, T.G., 2000. The materials flow of mercury in the economies of the United States and the world. U.S. Geological Survey Circular 1197, p. 28.

Taylor, S.R., McLennan, S.M., 1985. The Continental Crust: Its Composition and Evolution. Blackwell Scientific Publications, London, p. 312.

Thornton, I., 1996. Sources and pathways of arsenic in the geochemical environment: Health implications. In: Appleton, J.D., Fuge, R., McCall, G.J.H. (Eds.), Environmental Geochemistry and Health. Geological Society Special Publication No. 113, pp. 153–161.

Turner, D.R., 1987. Speciation and cycling of arsenic, cadmium, lead and mercury in natural waters. In: Hutchinson, T.C., Meema, K.M. (Eds.), Lead, Mercury, Cadmium and Arsenic in the Environment. SCOPE 31. John Wiley and Sons, Chichester, Great Britain, pp. 175–186.

United States Geological Survey, 1998a. Lead Statistical Compendium. Accessed on 2-7-2005 at http://minerals.usgs.gov/minerals/pubs/commodity/lead/stat/

United States Geological Survey, 2003. Mercury in the Environment Fact Sheet 146-00 (October, 2000). Accessed on 8-6-2003 at: http://www.usgs.gov/themes/factsheet/146-00/

United States Geological Survey, 2004. Minerals Database. Accessed on 2-2-2005 at: http://minerals.usgs.gov/minerals/pubs/commodity/lead/380303.pdf; http://minerals.usgs.gov/minerals/pubs/commodity/arsenic/160303.pdf; http://minerals.usgs.gov/minerals/pubs/commodity/mercury/430303.pdf

United States Geological Survey, 2005. Lead Statistics and Information. Accessed on 2-1-2005 at /minerals.usgs,gov/minerals/pubs/commodity/leadl/

USGS International Programs, 2004. Geologic, hydrologic, and geochemical characterization of the deep ground water aquifer system in the Bengal Delta of Bangladesh. Accessed on 1-5-2005 at http://international.usgs.gov/project/bg_arsenic.htm

Wasserman, G.A., Liu, X., Parvez, F., Ahsan, H., Factor-Livak, P., van Green, A., Slavkovich, V., Lolacono, N.J., Cheng, Z., Hussain, I., Momotaj, H., Graziano, J.H., 2004. Water arsenic exposure and children's intellectual function in Araihazar, Bangladesh. Environ. Health Perspect. 112, 1329–1333.

WHO, 2001. Arsenic in drinking water. Revised May 2001, World Health Organization. Accessed on 1-6-2005 at http://www.who.int/mediacentre/factsheets/fs210/en/

Zhang, J., Ren, D., Zhu, Y., Chou, C.-L., Zeng, R., Zheng, B., 2004. Mineral matter and potentially hazardous trace elements in coals from Qianxi Fault deposition area in southwestern Guizhou, China. J. Coal Geol. 57, 59–61.