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Environmental Significance of elevated natural
levels of Arsenic

By:

Jose M. Azcue

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**ENVIRONMENTAL SIGNIFICANCE OF ELEVATED NATURAL
LEVELS OF ARSENIC**

José M. Azcue

Lakes Research Branch - National Water Research Institute

P.O.Box 5050 - Burlington - ON L7R 4A6 - Canada

ABSTRACT

Globally, arsenic introduced into the biosphere by human activities has greatly surpassed arsenic from natural sources, the abundance of the element from these two sources being 77 and 33%, respectively. However, numerous regions of the world have elevated concentrations of arsenic from natural sources. Arsenopyrite may contain up to 6,000 $\mu\text{g.g}^{-1}$ of arsenic, and the weathering of such geological materials can increase the levels of arsenic in groundwater. Long-term consumption of groundwater containing elevated concentrations of arsenic has caused "natural chronic arsenic intoxication" in local populations in Taiwan, Mexico, Chile, Argentina, and other countries. An endemic disease commonly called blackfoot disease which is also caused by arsenic in drinking water, was documented in Taiwan in 1963. For more than 80 years local populations had consumed well water with arsenic concentrations as high as 1,829 $\mu\text{g.L}^{-1}$. The widespread geographical distribution of minerals with high arsenic content suggests that many new regions with "natural arsenic contamination" will be identified in the near future.

INTRODUCTION

Arsenic, in both natural and synthetic forms, has been a cause of serious concern since ancient times because of its toxic properties. The word Arsenic (As) has made its way through history by virtue of its "killing" properties. Currently it belongs to the general vocabulary, surrounded by mystery and myth, as a synonym of "poison". Yet in low doses has been prescribed as a remedy (Frost, 1984) or as a deadly poison (Azcue and Nriagu, 1994). Few elements have a more controversial place in human history.

Anomalously high levels of As have been observed in the vicinity of anthropogenic sources in many parts of the world. Arsenic pollution has resulted from pesticide manufacture in the USA (Faust *et al.*, 1983), mining activities in Canada (Mudroch and Clair, 1986), wood treatment in Nigeria (Ndiokwere, 1985), semiconductor manufacture in the USA (Edelman, 1990), copper smelting in the USA (Binder *et al.*, 1987), and glass production in Sweden (Andren *et al.*, 1988). Chronic and acute intoxication by As from anthropogenic sources has been extensively reported in the literature. On the other hand, very few data are available for areas with elevated natural levels of As. Arsenic is widely distributed in many types of mineral deposits in trace, minor, and major amounts, and is not confined to any particular metallogenic epoch or province (Boyle and Jonasson, 1973). Arsenic may accompany Au, Cu, Zn, Hg, Sb, Pb, Mo, Fe, Co, Ni, and the Pt minerals in most

types of their deposits and can often be used as an indicator of metal deposits, particularly Au, in geochemical prospecting. There are well defined local and regional arseniferous metallogenic provinces in rocks of practically all ages in the earth's crust (Boyle and Jonasson, 1973).

NATURAL SOURCES OF ARSENIC

Figure 1 shows the global biogeochemical cycle of As from natural sources. The estimated global release of As from natural sources is approximately 8×10^6 kg per year (Walsh et al., 1979). Arsenic occurs in nature as a free element and in different compounds, and it is widely distributed in sulphide ores. Arsenic is a major constituent of no fewer than 245 mineral species (Boyle and Jonasson, 1973), with arsenopyrite (FeAsS) being the most common As-containing mineral; arsenopyrite may contain as much as 5% As.

Microorganisms have been shown to increase the rate of As release from sulfide ores by catalyzing the oxidation of sulfide to sulfate and ferrous to ferric iron (Tamaki and Frankerberger, 1992). Microorganisms, including bacteria, fungi, and yeast, form volatile methylated derivatives of As under both aerobic and anaerobic conditions. Weathering of As-containing rocks is considered one of the major causes of high natural levels of As.

This process is estimated to release 45,000 metric tons of As per year (Ferguson and Gavis, 1972). The weathered As compounds may be retained in soils or dissolved in water and subsequently transported and redistributed.

Approximately 60% of the emission of As into the atmosphere is from natural sources. Walsh et al. (1979) identified seven main natural sources of atmospheric As: 1) ocean bubble bursting, 2) ocean gas exchanges, 3) rock weathering, 4) direct volatilization from the earth's crust, 5) volcanism, 6) forest wildfires, and 7) the terrestrial biosphere. Estimates of the global atmospheric cycle of As indicated that 20% and 65% of the As emissions are of natural origin in the Northern and Southern Hemisphere, respectively (Buat-Menard, 1984). The most important natural source may be volcanoes, from which As volatilised. The total As emission resulting from all of these volatilization processes is about 120 times greater than emissions from primary particle sources, i.e., sea salt and ordinary crustal rocks undergoing weathering (Buat-Menard, 1984). Walsh et al. (1979) suggested that As concentrations are predominantly natural in the Southern Hemisphere and predominantly industrial in the Northern Hemisphere. The global tropospheric residence time of As appears to be about 9 days (Walsh et al., 1979). Despite biological volatilization of As from the ocean surface, mass balance models indicate that the ocean is a net sink for As (Walsh et al., 1979).

ARSENIC CONCENTRATIONS IN ENVIRONMENTAL SAMPLES

Table 1 summarises As concentrations in different environmental compartments in uncontaminated regions. Arsenic in the form of inorganic As compounds is present in the earth's crust at an average concentration of 1.5 to 5 $\mu\text{g.g}^{-1}$ and is primarily associated with igneous and sedimentary rocks. The mean concentration of As in shales is 13 $\mu\text{g.g}^{-1}$, the range being 0.3 to 490 $\mu\text{g.g}^{-1}$. Uncontaminated soils generally contain less than 15 $\mu\text{g.g}^{-1}$ of As with an average of about 7 $\mu\text{g.g}^{-1}$ (NRCC, 1978). The degree of As uptake in plants is apparently related to the concentration of soluble As in the soil, the chemical composition of the soil, and the species of plants (Walsh et al., 1977). Natural As levels in plants seldom exceed 1 $\mu\text{g.g}^{-1}$ (Nriagu and Azcue, 1990).

Arsenic concentrations in seawater are relatively homogeneous ranging between 1.5 to 5.0 $\mu\text{g.L}^{-1}$ with an average of 1.7 $\mu\text{g.L}^{-1}$ (Chilvers and Peterson, 1987). Concentrations in uncontaminated freshwaters are more variable, ranging from 1.0 to 10 $\mu\text{g.L}^{-1}$. Arsenic concentrations in freshwaters are very dependent on bedrock, runoff, evaporation, and condensation rates. Arsenate is generally the dominant form of As in natural waters, although arsenite, methylarsonic acid and dimethylarsinic acid, and methylated forms have been identified as well. Concentrations of total As in freshwater fish, ranging from 0.07 to 2.7 $\mu\text{g.g}^{-1}$ wet

weight, in most cases are lower than those found in marine species. Arsenic concentrations in marine organisms and seaweed are in general about ten times greater than those in other foods (Edmonds and Francesconi, 1993). Many species of bony fish contain between 1 and 10 $\mu\text{g.g}^{-1}$, while certain bottom-feeding fish, crustaceans and seaweed may contain over 100 $\mu\text{g As.g}^{-1}$ (Fowler et al., 1979). The As in marine organisms seems to be in different organic forms, mainly arsenobetaine and arsenocholine.

Atmospheric concentrations of As are considerably greater over land masses than over oceans. Moreover, the estimated tropospheric burden of As is partitioned between the northern and southern hemispheres, 74% being in the former and 26% in the latter. The atmospheric concentration of As over oceans is dependent on proximity to land, approaching $6.0 \times 10^{-4} \mu\text{g.m}^{-3}$ over the North Atlantic and $1.8 \times 10^{-5} \mu\text{g.m}^{-3}$ over oceans in the Southern hemisphere (Chilvers and Peterson, 1987). Atmospheric As concentrations in rural areas are $<0.01 \mu\text{g.m}^{-3}$. The much higher As concentration in the air of Prague, Czech Republic in winter ($0.56 \mu\text{g.m}^{-3}$) than in summer ($0.07 \mu\text{g.m}^{-3}$) has been attributed to the use of coal with a high As content for heating (Fowler et al., 1979).

In Scotland, As concentrations ($\mu\text{g.g}^{-1}$ dry weight) in organs of healthy people killed in accidents ranged from 0.012 in brain to 0.46 in hair (Leibscher and Smith, 1968). The concentration of urinary As in persons with no known exposure has been reported to

range from 4.3 to 60 $\mu\text{g}\cdot\text{L}^{-1}$ (Table 1). The same authors found that the major form of As was dimethylarsenic acid, which accounted for 40 to 85% of the total As. Leibscher and Smith (1968) observed As levels from 0.02 to 8.17 $\mu\text{g}\cdot\text{g}^{-1}$ in hair from 1250 persons without known exposure to As. Arsenic concentrations of about 4 $\mu\text{g}\cdot\text{L}^{-1}$ in whole blood are considered normal for people not exposed to As. However, because the clearance of As from blood is very rapid, the time lapse between exposure and sampling is critical in the assessment of effects of exposure on blood levels (Fowler et al., 1979).

REGIONS WITH ELEVATED NATURAL LEVELS OF ARSENIC

Figure 2 shows several areas of the world characterized by abnormally high levels of As from natural sources. The extremely high concentrations of As in well water from these regions (Table 2) provided the motivation for most of the studies in these areas. However, in some cases (in Taiwan, Mexico, and Chile) the study of chronic mass As poisoning of humans revealed that drinking water was the main source of As. Some of these high-As areas are described in more detail below.

a) The West Coast of Taiwan

Over 110,000 inhabitants of the "endemic area" - the region supplied by artesian wells with high concentrations of As - have been identified as being at risk (Tseng, 1989). The endemic area is located along the western coast of Taiwan just south of the Tropic of Cancer, extending approximately 20 km north and south along the coast and extending to 15 km eastward from the sea (Figure 2). It is a flat alluvial plain, the highest elevation being only a few meters above sea level; the surface soil is primarily saline yellow clay of low fertility (Ch'i and Blackwell, 1968). Fresh water sources are limited in the endemic area; in some places shallow wells provide fresh water almost free of As, but in most areas waters from shallow wells are too salty for human consumption (Yeh, 1974). In most parts of the area the artesian wells are between 120 and 280 meters deep. Well water with concentrations as high as $1,829 \mu\text{g}\cdot\text{L}^{-1}$ had been consumed by the local population for more than eighty years.

A high percentage of the inhabitants have suffered from skin lesions caused by chronic arsenicism, i.e. hyperpigmentation, keratosis, and cancer. In addition, an endemic peripheral vascular disease has been found among the inhabitants of this region of Taiwan. The disease is locally known as "Wu chia ping" (blackfoot disease) owing to characteristic discoloration of the affected extremities, which become black and sharply demarcated from

adjacent unaffected tissues. Blackfoot disease was first observed in 1954, and the induction period of the disease has been estimated as 20-30 years (Chen et al., 1985).

A dose-response relationship between blackfoot disease and the As level of drinking water was observed in a study of over 40,000 people (Tseng, 1989). In 1956 a supply of tap water was established in the affected area, and no new cases of blackfoot disease have been found among young inhabitants who had only consumed the tap water. Chen and Lien (1963) unsuccessfully tried to reproduce the blackfoot changes in animals fed with high-As artesian well water from the endemic area. However, the discrepancies have been explained by differences in absorption, methylation, and/or excretion of As (Chen, 1990).

Owing to the large number of people affected, the long term of exposure, and the low migration rates into and out of the endemic area, this is one of the few situations where it has been possible to establish environmental-related epidemiologic studies (Ch'i and Blackwell, 1968; Yeh et al., 1968; Tseng, 1977; Wu et al., 1989; Brown et al., 1989; Chen et al., 1992). Chen et al. (1990) studied the toxic effects of various As concentrations on cultured human umbilical vein endothelial cells. Brown et al. (1989), assuming that the skin cancer risk from ingested As in the American population would be similar to that in the Taiwan population, calculated that an American male would have a lifetime risk of

developing skin cancer of 1.3×10^{-3} if exposed to $1 \mu\text{g} \cdot \text{kg}^{-1} \cdot \text{day}^{-1}$ for a 76 year lifespan.

b) Region Lagunera (Mexico)

Aquifers in the Region Lagunera in northern Mexico (Figure 2) are heavily contaminated with As. Most of this region is reported to have a substratum rich in As, which is known to produce high As levels in well waters (Tovar et al., 1964). The basin called Region Lagunera is a large plain with extensive land production based on irrigation by surface water from approximately 3,000 wells that over-exploit a granular aquifer in which the water level is dropping gradually with a consequent decline in the productivity of the land (Latorre et al., 1981). Total As concentrations in water samples ranged from 8 to $949 \mu\text{g} \cdot \text{L}^{-1}$ (Table 2).

Approximately 400,000 inhabitants of the rural areas have been exposed to As via drinking water with concentrations greater than $50 \mu\text{g} \cdot \text{L}^{-1}$, which is the current WHO drinking water standard (Del Razo et al., 1990). In all the 128 wells sampled, As was present mainly in its inorganic form, and in 93% of the samples As(V) was the predominant species (Del Razo et al., 1990). However, the samples may not truly represent the oxidation state of As within the aquifer because they were not protected from changes occurring during the extraction process prior to analysis. Organic arsenicals were reported in very small concentrations in the well waters from

this region.

Various pathological effects attributed to As exposure have been reported in this area, including cutaneous manifestations (skin pigmentation changes, keratosis, and skin cancer), gastrointestinal disturbances, peripheral vascular disease (blackfoot disease), chromosomal aberrations, and alterations in the coproporphyrin/uroporphyrin excretion ratio (Albores et al., 1979; Cebrian et al., 1983; Garcia et al., 1984, 1991; Vargas et al., 1991; Wegman et al., 1991). Several cases of dental fluorosis in this area motivated Del Razo et al. (1993) and Valentine et al. (1994) to study the concentrations of fluoride in well water and its relationship with As. Fluoride concentrations ranged from less than 500 to 3,700 $\mu\text{g.L}^{-1}$, and about 20% of the samples from 129 water wells had levels above the WHO drinking water standard. Del Razo et al. (1993) suggested that some of the pathological effects may have been caused by interaction between fluoride and As, since both elements affect enzyme activity in the glycolytic and tricarboxylic acid pathways and depress succinate dehydrogenase activity in yeast and liver slices.

c) Province of Cordoba (Argentina)

Contamination of water with As in the Pampa region of Argentina was reported in the beginning of the century. Anomalously high death rates due to cancer were recorded during the period

1949-1959 (Fowler et al., 1979). The continued consumption of this type of water caused several pathological conditions generally known as HACRE (hidroarsenicismo cronico regional endemico, i.e. Chronic Endemic Regional Hydroarsenicism) (Nicolli et al., 1989). The occurrence of the disease is so common that ^{it} is also known as the "Bell Ville disease" after the name of one of the most important cities in the region. The most common manifestation of this disease is cancer of the epithelium, described as symmetrical palmar and plantar hyperkeratosis (Astolfi et al., 1981). Arsenic concentrations in sixty water samples ranged from 18.7 to 3,810 $\mu\text{g.L}^{-1}$ (Table 2), and 82% of the samples exceed the WHO drinking water standard for As. High concentrations of fluorine (up to 6,290 $\mu\text{g.L}^{-1}$) have been observed as well (Nicolli et al., 1989). Forty two percent of the samples exceeded the drinking standards for fluorine. Other trace elements were present at very high concentrations in groundwater from the Pampa region -for instance selenium (up to 24.2 $\mu\text{g.L}^{-1}$), vanadium (up to 1,715 $\mu\text{g.L}^{-1}$), and molybdenum (up to 6,280 $\mu\text{g.L}^{-1}$). The combined effects of the high concentrations of these trace elements in the water of the province of Cordoba have not been studied, since the pathological manifestations of HACRE have been attributed exclusively to high concentrations of As.

In order to investigate the origin of the contamination, Nicolli et al. (1989) analyzed 54 loess samples collected in wells at depths ranging from the surface down to the water table. The

loess and volcanic glass showed anomalously high concentrations of all trace elements, mainly As (geometric mean $16.7 \mu\text{g.g}^{-1}$ in loess and $8.71 \mu\text{g.g}^{-1}$ in volcanic glass) and selenium (geometric mean $1.53 \mu\text{g.g}^{-1}$ from loess and $1.79 \mu\text{g.g}^{-1}$ from volcanic glass). For that reason they were considered the most important contaminants of groundwater in the area.

d) City of Antofagasta (Chile)

The city of Antofagasta (population approximately 130,000) had a water supply with high concentrations of As (up to $800 \mu\text{g.L}^{-1}$) between 1958 and 1970. The source of the As was the Toconce River, whose waters come from the Andes mountains. In 1960 the first dermatological manifestations were observed, especially in children. By 1969, 180 Antofagasta inhabitants were diagnosed as suffering from symptoms of arsenicism. Among the clinical manifestations were bronchiectasis, Raynaud's syndrome and other peripheral vascular phenomena, ischemia and myocardial infarction, and mesenteric thrombosis (Rosenberg, 1974). Clinical and epidemiological findings showed a possible cause-and-effect relationship between high As content in the water supply and the dermatologic lesions noted in a high percentage of Antofagasta's inhabitants.

Indications of chronic As poisoning were found in autopsy-tissue samples from five children (Rosenberg, 1974). In addition,

the As content of hair and nail clipping samples of inhabitants collected before 1970 averaged 9.2 and 28.6 $\mu\text{g.g}^{-1}$, respectively (Borgoño et al., 1977). In 1970 a water treatment plant started operation in the city of Antofagasta. Six years after its installation, the average As levels in hair and nails of the local population had decreased to 2.7 and 14.1 $\mu\text{g.g}^{-1}$, respectively. The same authors observed an absence of cutaneous lesions in school children after the water treatment plant began operation. However, the fact that the As contamination problem continued, though greatly diminished, suggested that continued investigations were desirable to follow up the clinical manifestations and to understand the geochemical sources of the As.

Natural Abundance of As in regions of United States

High levels of As in well water and in biological samples were found in Ester Dome (Alaska), a residential area just outside Fairbanks (Figure 2). The Ester Dome area covers approximately 250 km^2 and 500 homes are located there, all with individual wells. Arsenic has been associated with gold mineralization in the Fairbanks area and is believed to reach the waters of the area through weathering of As-containing rocks (Wilson and Hawkins, 1978). Total As concentrations in well water ranged from 1 to 478 $\mu\text{g.L}^{-1}$ (Table 2). In Ester Dome area, the most toxic form, As(III), varied from 3 to 64% (mean = 34%) of the total concentration of As (Harrington et al., 1978). Gold was discovered in this area in 1902

and by 1974 only a few small placer operations remained active. The As content of streams in the vicinity of former mining operations surpass considerably the natural levels. The As concentration in suspended sediments reached values up to $17,700 \mu\text{g.g}^{-1}$ in a stream near a placer mining operation (Wilson and Hawkins, 1978).

Kreiss et al. (1983) calculated that the As intake of a population exposed to As in Alaskan well water ranged from 1 to $4,521 \mu\text{g.day}^{-1}$. For their study they selected 149 Ester Dome residents on the basis of well water As concentrations and no occupational exposure to As. The concentrations of As in urine ranged from 6 to $4,964 \mu\text{g.L}^{-1}$ with a median of $51 \mu\text{g.L}^{-1}$ (Table 2). The concentrations of As in nails ranged from 2.66 to $7.58 \mu\text{g.g}^{-1}$ (Table 2) and correlated poorly with exposure to As in well water. No dose-response relationship was found between As ingestion and symptoms or physical findings compatible with peripheral neuropathy. Thirteen people with elevated As intake but no signs or symptoms of neuropathy had one or more abnormal nerve conduction velocity (Kreiss et al., 1983). No dose-response relationship, however, existed between As ingestion and nerve conduction velocities. The authors concluded that As ingestions from well water at the concentrations found in this Alaskan community did not result in clinical or subclinical neuropathy.

High As levels have been found in several water sources in Oregon, ranging from <1 to $2,150 \mu\text{g.L}^{-1}$ (Table 2). Lane County, in

Western Oregon midway between the Columbia River and the northern boundary of California (Figure 2), has received the most attention because it is a highly populated area. In 1962 a widespread investigation of the As content in groundwater in Lane County was undertaken. The As-rich groundwater problem is due to the volcanic events leading to the formation of the Cascade and Pacific Coast Mountain ranges (Whanger et al., 1977). The As-rich groundwater is underlain by a group of sedimentary and volcanic rocks named the Fisher Formation. Mineralogical and chemical changes within rocks of the Fisher Formation subsequent to their deposition most likely resulted in soft, arsenic- and boron-rich groundwater of high pH. Inorganic As comprised 51 to 100% of the total As analyzed in well water (Wagner et al., 1979). In general, the water from deeper wells contained more As than that from shallow ones. Hot springs in Oregon contained As levels of up to $900 \mu\text{g.L}^{-1}$ (Whanger et al., 1977).

Blood As levels of some Oregon residents ranged from 10 to $360 \mu\text{g.L}^{-1}$ (Table 2). Skin biopsy from a local patient presented As levels ranging from 0.002 to $0.012 \mu\text{g.L}^{-1}$ (Table 2). Very little information is available to indicate that As levels in the waters of Lane County caused acute toxicity, but sufficient evidence is available to indicate some chronic problems (Morton et al., 1976; Wagner et al., 1979; Whanger et al., 1977). No relationship between the As levels in water and incidence of skin cancer was found in this area (Morton et al., 1976).

Goldsmith et al. (1972) studied the health implications of well water supplies with As concentrations ranging from 100 to 1,400 $\mu\text{g.L}^{-1}$ in the residents of Lassen County, California (Figure 2). The same authors observed statistically significant association of water As and As concentrations in hair of the residents. However, As intake did not seem to be associated with any medical condition of the local population. Goldsmith et al. (1972) concluded that above 50 (± 30) $\mu\text{g.L}^{-1}$ of As in drinking water, there was evidence of increased storage of the material in the body, as evidenced increasing levels of As in hair. Concentrations of inorganic As ranging from <1 to 96 $\mu\text{g.L}^{-1}$ were found in groundwater of northeastern Ohio (Matisoff et al., 1982). It has been estimated that more than 350,000 people in the United States may be supplied with water containing more than 50 $\mu\text{g.L}^{-1}$ As and more than 2.5 million people may be supplied with water with As concentrations greater than 25 $\mu\text{g.L}^{-1}$ (Smith et al., 1992).

Natural Abundance of As in Canadian regions

Groundwater containing As in excess of the WHO international standard of 50 $\mu\text{g.L}^{-1}$ occurs in large areas of southwestern New Brunswick and southern Nova Scotia in east maritime Canada (Figure 2). In the gold deposits of the Meguma Series of Nova Scotia some beds carry up to 2% of As along the strike for distances measured in miles (Boyle, 1966). The occurrence of As contaminated groundwaters in both regions is primarily the result of natural

weathering of As-bearing minerals and can be anticipated to be encountered whenever a new well is drilled into these formations (Bottomley, 1984). Groundwater samples from 50 privately owned wells in Nova Scotia showed that >80% of the total As was present in the oxidized As(V) form (Subramanian et al., 1984). Merager et al. (1984) observed that 70% of the 94 samples analyzed exceeded the drinking water guideline ($50 \mu\text{g.L}^{-1}$) for As.

In Nova Scotia As concentrations greater than $1,000 \mu\text{g.L}^{-1}$ have been reported (Grantham and Jones, 1977), and clinical features of chronic arsenicalism in the population have been attributed to consumption of As-contaminated groundwater (Hindmarsh et al., 1977). Clinical features of chronic arsenicalism have not been identified in New Brunswick. The As-contaminated groundwater ranges in age from less than 10 yr to greater than 10^4 yr, and is characterised by both oxidizing and reducing conditions (Bottomley, 1984). As in the case of Estern Dome, Alaska, the problem in Nova Scotia has been accentuated by mining activities, which have increased the rate of oxidation of arsenopyrite and other As-minerals present in mine tailings (Bottomley, 1984).

Three post-active acid sulfate soils derived from weathered pyritic shale in Alberta, Canada (Figure 2) were analyzed for total As (Dudas and Pawluk, 1980; Dudas, 1984). They found that As levels in the B- and C-horizons of soils were nearly 10 times greater than normal background abundances. The greatest concentrations of As

were measured in samples of segregated iron oxides, ranging up to 500 $\mu\text{g.g}^{-1}$ (Dudas, 1984). Pyrite is believed to be the source of the elevated levels of As. Secondary iron oxides formed from the weathering of pyrite acted as scavengers of As. Unfortunately, there are no data for the As levels in groundwater from this area.

Other regions

The natural concentration of total As in high carbonate spring waters in Romania, Kamchatka (in the former USSR), in Yellowstone National Park, USA, and New Zealand, ranged from 160 to 8,500 $\mu\text{g.L}^{-1}$ (Ritchie, 1961; Schroedere and Balassa, 1966; Reay, 1972; Stauffer and Thompson, 1984). In Japan concentrations of up to 6,400 $\mu\text{g.L}^{-1}$ have been recorded in hot-spring water (Kawakami, 1967; Nakahara et al., 1978). Most recently, other areas with elevated natural levels of As have been identified in several parts of the world, such as in Kumasi and Obuasi, (Ghana) (Neizer and Amekor, 1993), in Doetinchem, Netherlands (van den Hazel et al., 1993), in Xinyang, China (Huang et al., 1992). Unfortunately, very few data are available for these regions.

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Table 1. Arsenic concentrations in different environmental compartments of uncontaminated areas

		Arsenic (range)
Crustal materials: ($\mu\text{g}\cdot\text{g}^{-1}$)		
Earth crust		1.5-5.0
-Igneous rocks		
	ultrabasic	0.3-16
	basalts	0.06-113
	andesites	0.5-5.8
	granitic	0.2-13.8
	silicic, volcanic	0.2-12.2
-Sedimentary rocks		
	limestones	0.1-20
	sandstones	0.6-120
	shales and clays	0.3-490
	phosphorites	0.4-188
	evaporites	0.1-10
-Metamorphic rocks		
Metamorphic rocks		0.4-17.6
Meteorites:		
	chondrites	0.3-11
	irons	3.2-8.0
Air ($\mu\text{g}\cdot\text{m}^3$)	rural areas	0.001-0.01
Freshwater ($\mu\text{g}\cdot\text{L}^{-1}$)		1.0-10
Freshwater fish ($\mu\text{g}\cdot\text{g}^{-1}$)		0.07-2.7
Vegetation ($\mu\text{g}\cdot\text{g}^{-1}$)		0.01-5
Seawater ($\mu\text{g}\cdot\text{L}^{-1}$)		1.0-5.0
Marine fish ($\mu\text{g}\cdot\text{g}^{-1}$)		1-100
Human samples:		
	hair ($\mu\text{g}\cdot\text{g}^{-1}$)	0.02-8.17
	nails ($\mu\text{g}\cdot\text{g}^{-1}$)	0.28-5.5
	blood ($\mu\text{g}\cdot\text{L}^{-1}$)	0.04-4.0
	skin ($\mu\text{g}\cdot\text{g}^{-1}$)	0.08
	urine ($\mu\text{g}\cdot\text{L}^{-1}$)	4.3-60

Sources: Braman and Foreback, 1973; Fowler et al., 1979; Leibsher and Smith 1968; NAS, 1977; Pershagem, 1978; Vahter and Lind, 1986; Welch et al., 1988; WHO, 1981.

Table 2. Range of reported arsenic concentration in well water and in biological samples of local population of regions with elevated natural levels of arsenic

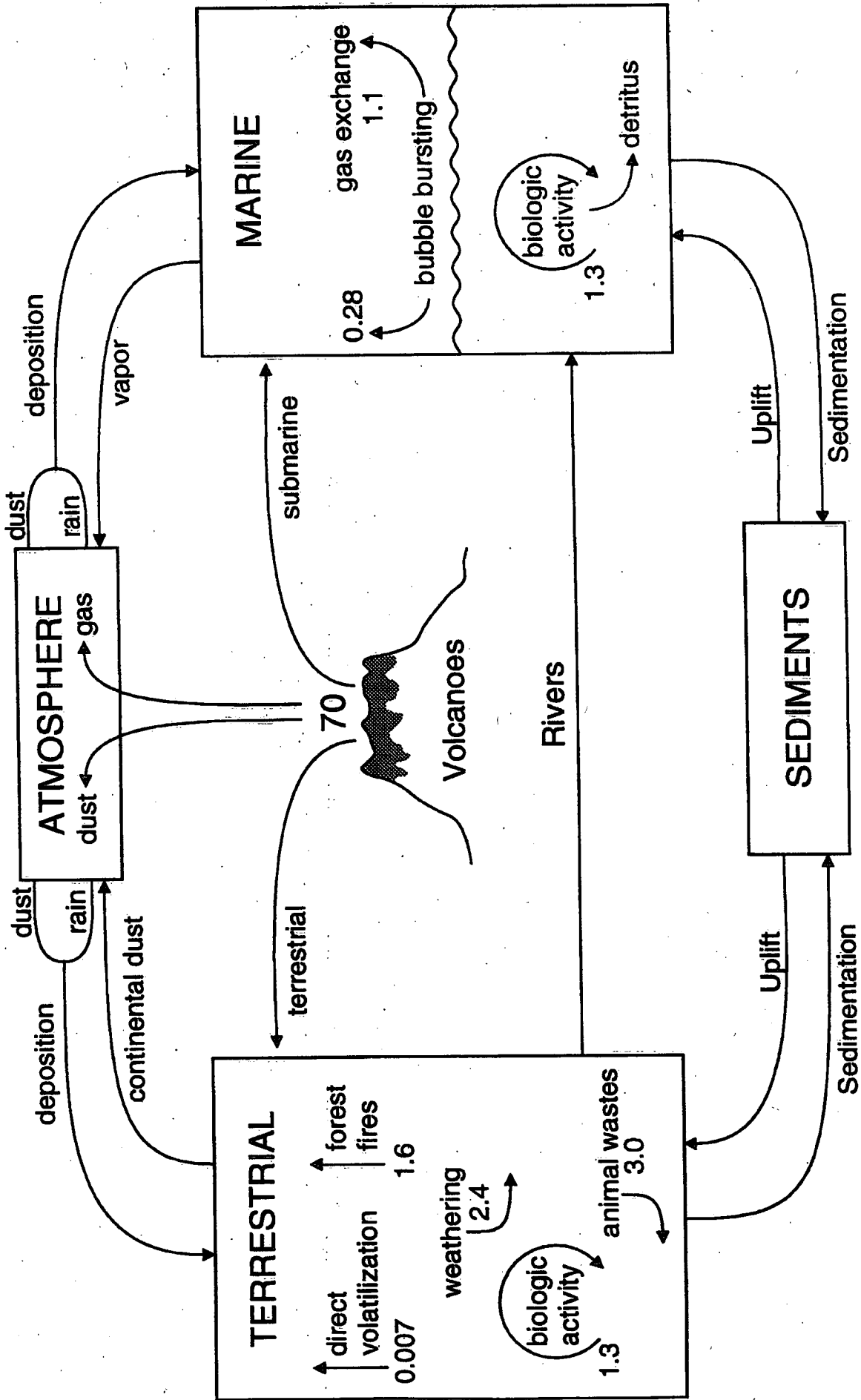
Region	Arsenic in well water	Clinical information	References
Southwest coast (Taiwan)	100-1,820	Blackfoot disease	Chen et al. 1988 Chi and Blackwell 1968 Tseng 1989 Wu et al. 1989 Yeh et al. 1968
Region Lagunera (Mexico)	8-949	hair (0.5-2.33) nail (0.82-3.5)	Chaves et al. 1964 Cortes et al. 1974 Del Razo et al. 1990
Cordoba (Argentina)	18.7-3,810	HACRE disease	Castolfi et al. 1981 Nicolli et al. 1989
Antofagasta (Chile)	up to 800	hair (0-18) nail (0-75)	Borgoño et al. 1977
Ester Dome (Alaska)	1-4,781	urine (6-4,964) hair (0.43-5.74) nail (2.66-7.58)	Kreis et al. 1983 Harrington et al. 1978 Wilson and Hawkins 1978
Ohio (USA)	0-96	n.a.	Matisoff et al. 1982
Lane County-Oregon (USA)	<1-2,000	blood (10-360) skin (0.002-0.012)	Morton et al. 1976 Wagner et al. 1979 Whanger et al. 1977
Lassen County-California (USA)	100-1,400	hair (0.01-2.0)	Goldsmith et al. 1972
Nova Scotia (Canada)	1.0-1,000	hair (0.25-60)	Granham and Jones 1977 Merangen et al. 1984 Hinmarsh et al. 1977
Alberta (Canada)	490(*)	n.a.	Dudas 1987 Dudas and Pawluk, 1980
New Brunswick (Canada)	3-193	n.a.	Bottomley 1984

n.a. = not available

(*) $\mu\text{g.g}^{-1}$ subsoil sample

Arsenic concentration in hair, skin, and nails in ($\mu\text{g.g}^{-1}$)

Arsenic concentrations in water, urine and blood in ($\mu\text{g.L}^{-1}$)



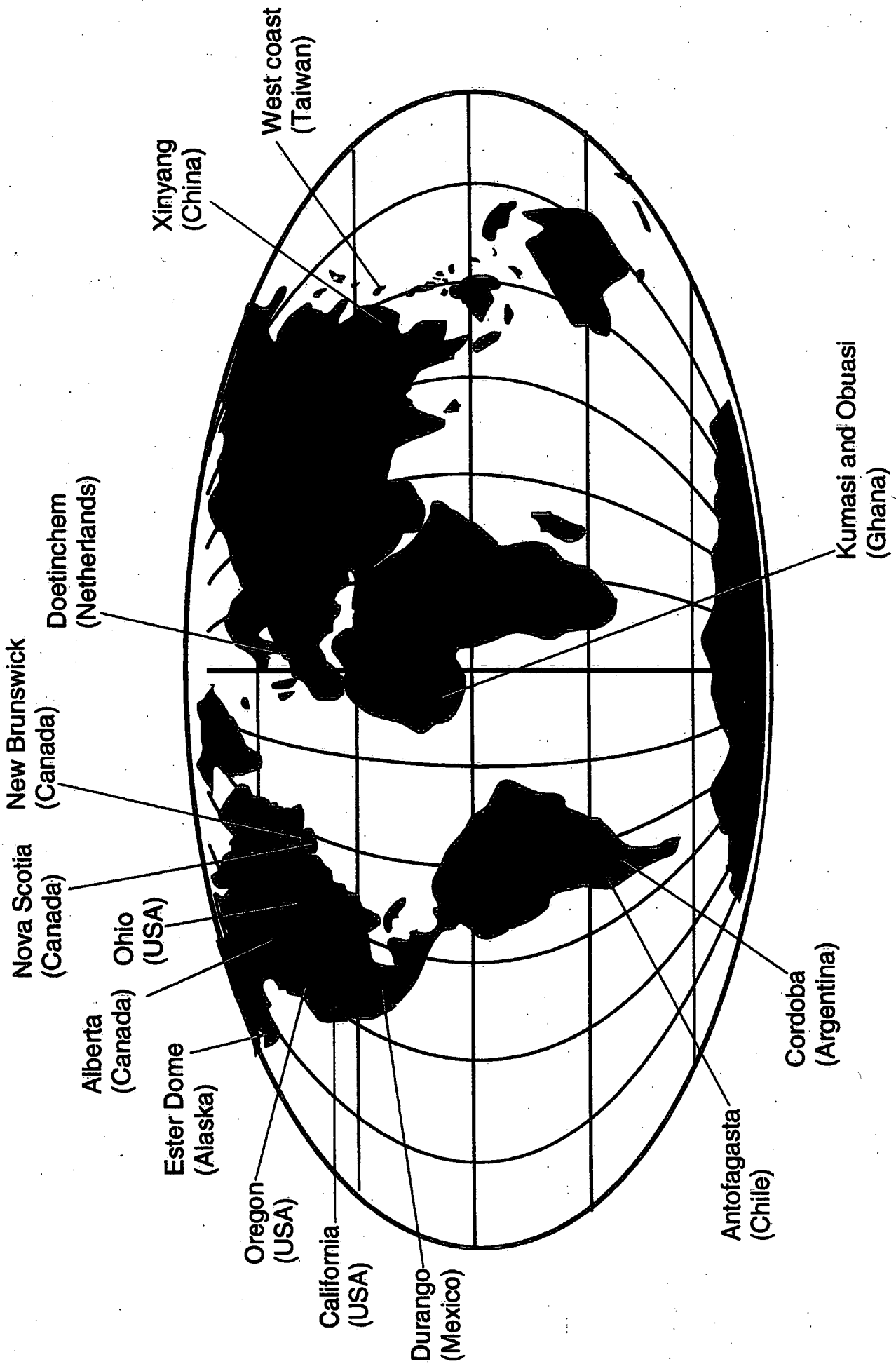


Figure Captions:

Figure 1. Global biogeochemical cycle of arsenic from natural sources

Figure 2. Areas of the world characterized by abnormally high levels of arsenic from natural sources

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