Jose A. Centeno, Chin-Hsiao Tseng, Gijsbert B. Van der Voet and Robert B. Finkelman

Global Impacts Of Geogenic Arsenic: A Medical Geology Research Case

INTRODUCTION

Arsenic (As) is a ubiquitous element, and it is the 20th most abundant element in the Earth's crust. Humans can be exposed to As through the diet or from natural environmental sources, such as contaminated groundwater, soils, or burning coal. Anthropogenic (man-made) sources of exposure to As may include the use of As in medicine (e.g., Fowler's solution or AsO_3), industrial pollution, mining, and the burning of chromate-copper-arsenate–treated wood.

Inorganic As (In-As), found in surface and groundwater sources, is generally composed of pentavalent arsenate (As^V) and/or trivalent arsenite (As^{III}). Upon ingestion, in humans, In-As is metabolized in a 2-step process that involves reduction and oxidative methylation reactions to produce the monomethylarsonic acid (MMA^V) and the dimethylarsenic acid (DMA^V) before it is excreted in the urine. Because these methylated species are easily excreted in the urine (i.e., in most populations exposed to As, total urinary As is composed of approximately 60–80% DMA^V, 10–20% MMA^V, and 10–20% In-As), they are generally considered to be less toxic than In-As species. Thus, methylation is generally thought as a "detoxification" pathway of As in humans. Inorganic As^{III} forms are generally considered to be much more toxic than the pentavalent methylated forms; however, recent laboratory findings suggested the formation of intermediate methylation species in the form of monomethylarsonous acid (MMA^{III}) and dimethylarsinic acid (DMA^{III}) (1), which may be more toxic than arsenite for certain deoxyribonucleic acid–damage end points (2). Accordingly, not only is the measurement of total As required, but, also, quantification of the individual metabolites is necessary to assess the toxicity and health risk of this element.

The health effects of chronic exposure to As are well established in countries with high levels of As in their drinking water; however, such evidence is not readily available in countries with lower levels of environmental As or with drinking water treatment systems. Of more relevance to developed countries, e.g., United States, are the potential health consequences of long-term low-level exposures via drinking water or through occupation, or wood treatments. This paper is aimed at providing an overview of and a brief discussion of the available literature on global distribution of As as a research case on medical geology.

BACKGROUND AND GLOBAL IMPLICATIONS

Chronic As toxicity from drinking As-contaminated groundwater has recently been reported from many Asian countries (3). Of these, the catastrophic health problems caused by As in the well waters of Bangladesh and West Bengal, India, have been front page stories in mass media and in scientific journals. Although estimates of how many people are at risk vary, there is no question that it runs into the tens of millions in Bangladesh alone, and, in West Bengal, it is suspected that about 6 million people are exposed to As-contaminated drinking water above the 50 $\mu g\ L^{-1}$ As level. This situation was called the "greatest mass poisoning in history" (4). What is often not reported is that the tens of millions of people exposed to As in Bangladesh represent only a portion of the people who are at risk worldwide. Elevated levels of As were reported in water supplies of communities in Argentina, Austria, Brazil, Canada, China, Ghana, Greece, Hungary, Iceland, India, Japan, Korea, Malaysia, Mexico, Inner Mongolia, Nepal, Romania, Taiwan, Vietnam, Zimbabwe, and the United States (see Fig. 1).

Geoscientists are working with public health officials to seek solutions to these problems. By studying the geological and hydrological environment, geoscientists are trying to determine the source rocks from which As is being leached into the ground water. They are also trying to determine the conditions under which the As is being mobilized. For example, is the As being desorbed and dissolved from iron oxide minerals by anaerobic (oxygen-deficient) groundwater, or is the As derived from the dissolution of As-bearing sulfide minerals, e.g., pyrite, by oxygenated waters? The answers to these questions will allow the public health communities around the world to identify aquifers with similar characteristics and to more accurately determine which populations may be at risk from As exposure.

GEOLOGICAL SOURCES OF EXPOSURE

As indicated previously, exposure to As may come from both natural and anthropogenic activities, including industrial sources, mining, medicinal sources, food, and beverages. However, exposure to natural geological sources of As, including groundwater, geothermal springs, volcanic sediments, and As-rich coal led to the largest incidence of reportable poisoning cases in different parts of the world (3). For example, As mobilized through coal combustion caused severe health problems in China (5) and Slovakia (6).

In China's Guizhou Province, the situation is exacerbated by the villagers' domestic use of coal. The coal in this region has extraordinarily high concentrations of As (up to 35 000 $\mu g\ g^{-1}$ As). Thousands of people in this region are suffering from severe As poisoning. Those affected exhibit typical symptoms of As poisoning, including hyperpigmentation (flushed appearance, freckles), hyperkeratosis (scaly lesions on the skin, generally concentrated on the hands and feet), Bowen's disease (dark, horny precancerous lesions of the skin (see Fig. 2). Chili peppers dried over open coal-burning stoves may be a principal route for the As poisoning. Fresh chili peppers have less than 1 $\mu g\ g^{-1}$ As. In contrast, chili peppers dried over high-As coal fires in this region can reach up to 500 $\mu g\ g^{-1}$ As. Significant amounts of As may also come from other tainted foods, ingestion of dust (samples of Guizhou kitchen dust contained as much as 3000 $\mu g\ g^{-1}$ As), and from inhalation of indoor air polluted by As derived from coal combustion. Interesting, in Guizhou Province, the relatively low As content in drinking water did not appear to make it as important a route of exposure as in other parts of the world, e.g., Bangladesh. To understand the form, mobility, and transport of As from these natural geological sources, as well as to develop solutions to these problems, it is of critical importance to emphasize the need to obtain detailed chemical characterization of those natural geological sources where As may be present. In the case of the coal samples from China, detailed chemical and mineralogical characterization demonstrated that much of the As in these Chinese coal samples is bound to the organic

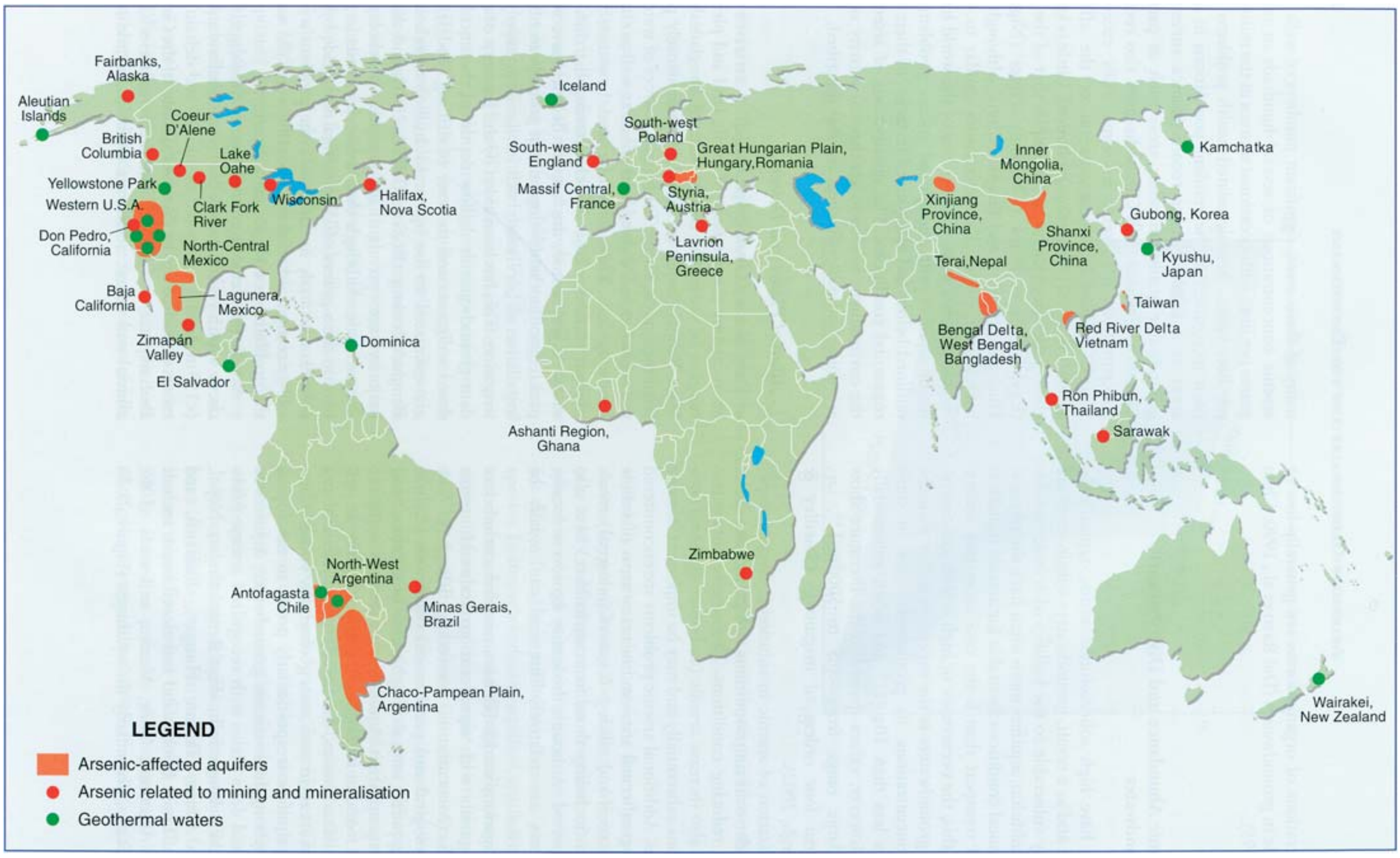

Figure 1. World map illustrating regions with documented arsenic problems in groundwater (As $> 50\ \mu g\ L^{-1}$). Adapted from Ref. 22.

component of these coals and not in pyrite as is typically found worldwide (7). Accordingly, traditional methods of reducing As, e.g., physical removal of heavy minerals, primarily As-bearing pyrite, would not be effective.

In the West Bengal delta, the source of As is also known to be geogenic, but the exposure is through contaminated drinking water. Although the mechanism and the cause by which As may leach from its source has not been fully established, geochemical studies suggested procedures involving oxidation, reduction, and carbon reduction as potential mechanisms for the mobilization of As to the groundwater (3).

In Mexico, chronic As poisoning from contaminated drinking water was reported in 6 areas of the Lagunera region in the central part of north Mexico, with a population of ~200 000 (8). The source of As in this region was suggested to come from volcanic sediment (9). Geogenic As in the soils and groundwater of Zimapan in the Hidalgo area poses an environmental risk for human exposure via the drinking water (10).

In Argentina, elevated levels of As in surface water, shallow wells, and thermal springs have been reported. This natural contamination was associated with volcanic deposits (tertiary-quaternary sediments), together with postvolcanic geysers and a thermal spring. Case studies in the Chaco-Pampean plain report on elevated groundwater As from geogenic sources (11, 12). Groundwater contamination with As was also reported in the Province of Cordoba, Argentina, with As concentrations exceeding 100 $\mu g\ L^{-1}$ (13).

In Antofagasta, Chile, several epidemiological studies document the As-related health problems from years of drinking water with As levels as high as 800 $\mu g\ L^{-1}$ (14). In this region, tertiary-quaternary sediments, minerals, and soils were suggested as the sources of As (15).

Arsenic exposure through drinking well water in Taiwan was initially recognized in the 1960s, and it was stopped in the late 1970. Pyrite occurring in the black shales underlying geological strata was suggested to be the source of As (16).

HEALTH IMPACTS FROM CHRONIC ARSENIC EXPOSURE

Inorganic As is well documented as a human carcinogen of the skin and lungs. Significantly high prevalence of skin cancer was observed in all arseniasis-endemic areas around the world, particularly in Asia. Inorganic-As was demonstrated to also affect many other organ systems, including the gastrointestinal, hepatic, cardiovascular, nervous, renal, and hematopoietic systems. Arsenic is a systemic toxicant known to induce cardiovascular diseases; developmental abnormalities; neurologic and neurobehavioral disorders; diabetes mellitus; mental retardation; ischemic heart disease; peripheral polyneuritis and polyneuropathy; peripheral vascular disease and limb gangrene; hypertension; hearing loss; and hematologic, gastrointestinal, renal, and respiratory disorders. The severity of adverse health effects is related to the source of exposure (natural and/or anthropogenic), the chemical form of the element (i.e., speciation), as well as the dose and duration of As exposure, although nutritional status and As methylation capacity may be involved in the determination of individual susceptibility to develop As poisoning.

Perhaps the single most characteristic effect of long-term oral exposure to In-As is a pattern of skin changes. These include a darkening of the skin and the appearance of nodular and diffuse lesions on the palms, soles, and torso (see Fig. 2) (17). Chronic As exposure from oral ingestion and inhalation has been associated with a variety of internal cancers involving the gastrointestinal tract, urinary bladder, lung, liver, and kidney

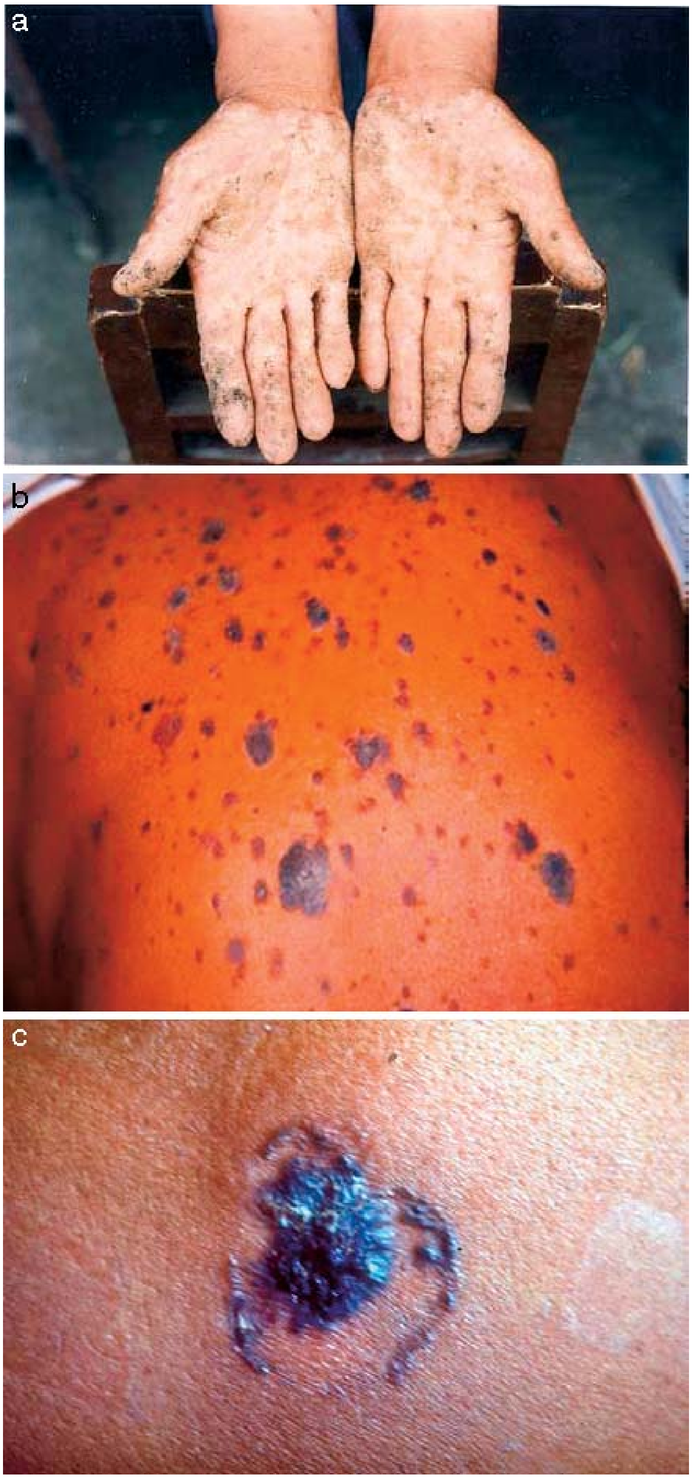

Figure 2. Arsenical-induced skin lesions. (a) The palms show multifocal hyperkeratotic lesions. (b) Skin of back with raindrop-liked chronic arsenic-induced hyperkeratotic lesions. (c) Arsenic-induced Bowen's disease.

(18, 19). Research has also pointed to significantly higher standardized mortality rates for cancers of the bladder, kidney, skin, and liver in many areas of As pollution (20).

Early recognition of As exposure and health effects may contribute to timely consideration of the As health risk and preventive measures. Being aware of these health impacts it seems important to communities and individuals relying on groundwater sources for drinking water to monitor the As levels to ensure that supplies are safe (20). Communities with water As levels >5 g L^{-1} should consider a program to regularly monitor diagnostic [e.g., As in urine, nails, hair, and, recently, blood (21)] and clinical effect markers (e.g., skin lesions) for As in the population. Research efforts, therefore, should focus on environmental and human markers for early recognition of exposure and poisoning, and on risk assessment.

CONCLUSION

Arsenic contamination through natural (geogenic) and anthropogenic sources is a serious threat to humans all over the world. Natural sources of As exposure may include contaminated groundwater, volcanic sediments, coal, and spring thermal waters. The number of people affected by As is staggering, the problems are life threatening, the scope is global, and the potential for medical geology interventions is enormous. In this manuscript, we provide an overview of the global health impacts from chronic As exposure. There is sufficient evidence from human epidemiological studies in Taiwan, Chile, Argentina, and Bangladesh to conclude that ingestion of As in drinking water poses a hazard of cancer of the lung and the bladder, in addition to cancer of the skin. However, no human studies of sufficient statistical power or scope have examined whether consumption of As in drinking water at the current World Health Organization standard of 10 ppb results in an increased incidence of cancer or noncancer effects. Therefore, research efforts are urgently needed to better understand the health risk assessment from chronic low-exposure levels to As, as well as speciation studies to better define the distribution of As in the natural environment, food, and other sources of exposure.

Medical geology has the objectives of identifying harmful geologic agents; determining exposure relating to deteriorating health conditions; and developing sound principles, strategies, programs, and approaches to eliminate or minimize health risks, with particular focus on the naturally occurring physical and chemical agents in the environment. Interaction and communication should be encouraged between the geoscience and biomedical/public health communities to seek novel solutions to better protect human health from the damaging effects of As exposure.

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Jose A. Centeno is Senior Research Scientist and Chief, Division of Biophysical Toxicology, Department of Environmental and Infectious Disease Sciences, Armed Forces Institute of Pathology, Washington DC, 20306-6000. Dr. Centeno's research interests are on the area of environmental health, medical geology, inorganic toxicology, and speciation of metals, metalloids, and trace elements.
centeno@afip.osd.mil

Chin-Hsiao Tseng is a physician and an epidemiologist with the Division of Endocrinology and Metabolism of the Department of Internal Medicine and Department of Medical Research and Development, National Taiwan University, Hospital Yun-Lin Branch, Yun-Lin, Taiwan. Dr. Tseng's research interests include the epidemiology, health effects and clinical toxicology of arsenic.
ccktsh@ms6.hinet.net

Gijsbert Van der Voet is a toxicologist and research fellow with the Division of Biophysical Toxicology, Department of Environmental and Infectious Disease Sciences, Armed Forces Institute of Pathology, Washington, DC 20306-6000. Dr. Van der Voet's research interests are in the area of clinical toxicology of metals and metalloids, environmental health, and inorganic analysis.
Gijsbert.VanderVoet@afip.osd.mil

Robert B. Finkelman is a geologist and Emeritus Professor at the University of Texas at Dallas, Department of Geosciences, Richardson, TX 75083-0688. Dr. Finkelman's research interests are in the area of coal geochemistry and medical geology.
rbf@usgs.gov