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Abstract	To a larger degree than most others, North Americans are shielded from the natural environment. Nevertheless, health problems caused by geologic material and geologic process do occur in North America. In contrast to the acute health problems caused by the geologic environment in developing countries, in North America these problems are generally chronic, caused by long-term, low-level exposures. Among these health problems are exposure to trace elements such as fluorine, arsenic, and radon; exposure to naturally occurring asbestos-form minerals; occupational and community exposure to trace elements and mineral dust; and ingestion of naturally occurring organic compounds in drinking water. This chapter provides North American examples of each of these environmental health problems and suggestions as to how the earth sciences can be an integral part of multi-disciplinary teams working to mitigate these problems.
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Medical Geology Issues in North America

Robert B. Finkelman, Heather Gingerich, Jose A. Centeno, Goeffry Plumlee,
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Abstract To a larger degree than most others, North Americans are shielded from the natural environment. Nevertheless, health problems caused by geologic material and geologic process do occur in North America. In contrast to the acute health problems caused by the geologic environment in developing countries, in North America these problems are generally chronic, caused by long-term, low-level exposures. Among these health problems are exposure to trace elements such as fluorine, arsenic, and radon; exposure to naturally occurring asbestos-form minerals; occupational and community exposure to trace elements and mineral dust; and ingestion of naturally occurring organic compounds in drinking water. This chapter provides North American examples of each of these environmental health problems and suggestions as to how the earth sciences can be an integral part of multi-disciplinary teams working to mitigate these problems.

Keywords United States · Canada · Fluorosis · Cancer · Asbestos · Black lung disease · BEN · Organic compounds · Radon · Arsenic · Diabetes · Fluorine

Introduction

To a larger degree than most other people, North Americans are shielded from the natural environment. North Americans commonly live, work, and travel in air-conditioned environments; in supermarkets they purchase foods grown all over the world; most drink

municipal water that has been purified; and many take daily vitamins to supplement dietary deficiencies. Despite this shielding from the natural environment, health problems caused by geologic material and geologic process do occur in North America. In contrast to the acute health problems caused by the geologic environment in developing countries, in North America these problems are generally chronic, caused by long-term, low-level exposures.

There is a rich medical geology history in North America dating back to 1792 when John Rouelle described the medicinal properties of mineral water in Virginia (Rouelle, 1792). The 1970 s enjoyed a renaissance marked by the appearance of a series of publications focused on the impacts of trace elements on human health. These publications included Geological Society of America (GSA) Memoir 123 (Cannon and Hopps, 1971); GSA Special Paper 140 (Cannon and Hopps, 1972); Annals of the New York Academy of Sciences Volume 199 (Hopps and Cannon, 1972); U.S. Geological Survey Professional Paper 574-C (Shacklette et al., 1970); GSA Special Paper 155 (Freedman, 1975); and National Research Council (1979).

Changes in staffing and priorities resulted in a hiatus in North American medical geology activities from the 1980 s until the mid-1990s. The past decade has seen a resurgence of interest in medical geology evidenced by the inclusion of human health issues in the USGS Strategic Plan (U.S. Geological Survey, 2007), the formation of GSA's Geology and Health Division and strong North American leadership, and representation in the International Medical Geology Association.

This chapter is not intended to be a compendium of geology and health issues in North America. Rather,

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our objective is to highlight some of the more prevalent issues such as exposure to selected trace elements, dust, naturally occurring organics, and occupational health issues providing both historical and current examples of health issues caused by geologic materials.

With renewed interest in the links between geology and health, natural elemental hazards are an important consideration in the rural areas as well as the densely populated urban centers of North America where cumulative, low-dose, and long-term exposures can lead to some of the chronic illness that consumes moderate percentages of the national incomes (as GDP) of the United States (15.9%), Canada (9.7%), and Mexico (6.7%), respectively (*The Economist*, July 19, 2007).

Trace Element Exposure

One of the major themes of the geology and health story involves acquiring an understanding of the consequences of both natural and perturbed cycling of elements between and within the lithosphere, the atmosphere, the hydrosphere, and the biosphere. In some cases, human settlement on our increasingly crowded landscape has expanded to include environments that are “naturally impaired” by either an over-abundance or a deficiency of elements relative to human and animal biological requirements.

Where elemental exposures create toxicity, safeguarding health becomes a matter of finding the “point(s) of intervention” in the Source–Path–Trap relationship, whether it be in air, water, earth materials or the food chain, and adapting appropriately to the natural environment in sustainable ways. In other instances, the challenge is to distinguish natural elemental occurrences, which we generally can only avoid through awareness, from “anthropogenic overprinting.” Naturally occurring elements such as fluorine, radon, and arsenic have had variable impacts on different communities in North America as a function of route of exposure and dose. For example, US EPA considers that radon, “... is the leading cause of lung cancer among non-smokers. Radon is the second leading cause of lung cancer in America and claims about 20,000 lives annually.” (<http://www.epa.gov/radon/>). Similarly, naturally occurring arsenic levels in ground water sources can be a significant issue in many parts of the United States

especially in the western mountain regions where ground water levels often exceed regulatory standards (<http://www.epa.gov/safewater/arsenic/index.html>).

Fluorine

Owing to its extensive use in preventive dentistry in the post-World War II era, fluorine (F), which is commonly referred to as its ionic form, *fluoride*, is one of the most familiar and controversial elements of the Periodic Table. Safe, responsible, and sustainable use of fluorides is dependent on decision makers (whether they be politicians or parents) having a firm grasp on three key principles: (i) fluorine is not so much “essential” as it is “everywhere,” (ii) recent human activities have significantly increased fluorine exposures to the biosphere, and (iii) fluorine has biogeochemical effects beyond bones and teeth.

Some of the fluorine that is ingested, imbibed, inhaled, or absorbed through the skin is excreted via the kidneys after having spent time in the circulatory system (WHO, 1997), whereas the balance is integrated into the body’s mineralized tissues of teeth, bone (Ledbetter et al., 1960), the pineal gland (Luke, 2001), and sometimes as constituents of calculi or “stones” in the kidney, gallbladder, and tonsils. The easily identified and irreversible cosmetic, and sometimes structural, damage of *dental fluorosis* (see photo in Box 1) is caused by ingestion of excessive fluoride prior to the eruption of the tooth through the gum-line in childhood (Ruan et al., 2007). *Skeletal fluorosis* (see photo in Box 2) mimics a host of osteological disorders, including osteoarthritis and osteoporosis, and primarily affects adults in middle age although earlier incidence can occur in severe cases (Skinner, 2005). The full range in dysfunction associated with *systemic fluorosis* is still not well understood, although research has found correlations with thyroid disorders (National Research Council, 2006), certain cancers (Bassinet al., 2006), and deleterious effects on the brain (Mullenix et al., 1995).

Fluorine is ubiquitous in the natural environment. At the atomic level, fluorine is not only the 14th most abundant element in the Earth’s crust –more abundant than any other halogen and even the “Basic Building Block of Life”, carbon (C) –but also supremely reactive and oxidative, with the highest Pauling value for electronegativity of 4.0 and an unusually low

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dissociation energy, which means that it has the tendency to “steal” electrons from most other elements or at least “share” them by forming strong bonds. The fluoride ion (F^-) has a charge of (-1) and a similar ionic radius (1.33 \AA) to that of the anions of oxygen (O^{2-} , 1.40 \AA) and the hydroxyl group (OH^- , 1.32 \AA), but being so much more electronegative, it often substitutes for the hydroxyl group in mineral complexes and increases the stability of the crystal lattice structure. The resulting resistance to dissolution in acid of fluorapatite as compared with hydroxylapatite is the basis of fluoride’s use in preventive dentistry.

Earth materials that are characteristically rich in fluorine are organic clays and shales, carbonatites, phosphates, hydrothermal ores, and silicic igneous rocks like rhyolites, dacites, and granites—especially the Rapakivi and alkali type (Boyle, 1976). In short, every geologic environment in the lithosphere—igneous, metamorphic, sedimentary—contains fluorine, though the amount that is bioavailable can vary considerably.

By volume, the greatest amount of naturally occurring fluorine in the atmosphere occurs as HF gas related to volcanic activity. Fluoride also regularly makes its way into the atmosphere as marine aerosols and by the diffusion from the surface of the water-soluble fluoride mineral *fluorspar* (CaF_2), which is common to the non-volcanic subsurface environment of the Mississippi Valley of the United States and some parts of Ontario and Québec in Canada (Boyle, 1976).

Within the biosphere, plants appear to be relatively tolerant to high fluoride in groundwater and soils (Kabata-Pendias, 2001) and respond by accumulating this element in the leaves (which is why tea is a fluoride-rich foodstuff). While not obviously toxic to the plant itself, fluorine-laden particulates associated with volcanic activity can accumulate on forage materials that are ingested by herbivores and then concentrated along the food chain (Fleming et al., 1987).

Aside from the rare instances when one of North America’s many active volcanoes like Mount St. Helen’s or Popocatepetl erupts, drinking water is the primary route of fluoride exposure for individuals and communities. The average concentration of fluoride in seawater is 1.35 mg/l , but with the exception of alkali lakes, other surface waters and precipitation are generally naturally low in dissolved fluoride ion ($0.01\text{--}0.3 \text{ mg/l}$), depending on atmospheric inputs

and the geochemistry of the earth materials contacted (Edmunds and Smedley, 2005). Groundwater, on the other hand, can vary tremendously with respect to fluoride content.

Dental Fluorosis: A Century of “Colorado Brown Stain”

Nestled at the foot of the Pikes Peak at the eastern end of the Rocky Mountain Chain, Colorado Springs at the turn of the last century was a breathtakingly beautiful, albeit challenging, first posting for the young dentist, Dr. Frederick McKay. Fresh out of dental school and far from his native Massachusetts, McKay was puzzled by the mottled and sometimes pitted appearance of many of his new patients’ teeth, locally referred to as “Colorado Brown Stain” that reminded him of a phenomenon that was prevalent in the local population in St. Louis, Missouri, in the heart of the Mississippi River Valley, where he completed his training in orthodontia. Upon further investigation, it was found that 87.5% of surveyed school children that were born in the Pikes Peak region had some degree of what is now known as *dental fluorosis* that residents attributed to “something in the water.” It was the Spring of 1909. (Paraphrased from the Pierre Fauchard Academy International Hall of Fame of Dentistry induction speech.) (Fig. 1).

In 1931, US Public Health Service researcher Henry Trendley Dean concluded that the “something” that caused Colorado Brown Stain was naturally elevated levels of fluoride (F^-) in the local water supply, which



Fig. 1 *Colorado Brown Stain*. Dental fluorosis that would be classified as “moderate” on Dean’s Index. All enamel surfaces of the teeth are affected, and the surfaces subject to attrition show wear. Brown stain is frequently a disfiguring feature that lasts for life. Source: Photo courtesy of Hardy Limeback

In the decades that followed, dental data have been instrumental in identifying fluoride-rich environments, as children are especially susceptible to developing the tell-tale sign of mottled teeth that they carry into adulthood due to high fluoride exposure relative to their low body weight during critical phases in enamel formation. H. Trendley Dean became the first director of the National Institute of Dental Research in 1948 and was able to identify several other geochemical environments that are associated with high naturally occurring fluoride resulting in adverse biological effects within the continental United States. Notable among them are the petroleum-rich Lone Star State which is home to “Texas Teeth” (a southern cousin of “Colorado Brown Stain”), the fault- and fracture-riddled bedrock that hosts the metal-sulfide ore deposits of the Upper Mississippi River Valley (noted by Frederick McKay during his time in St. Louis), the highly metamorphosed coal-bearing hills of Virginia, Maryland, and Pennsylvania along the eastern seaboard, and the phosphate-rich Florida Panhandle (Fig. 3).

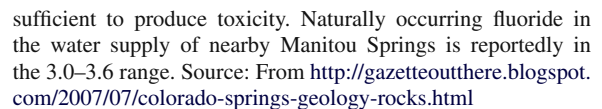
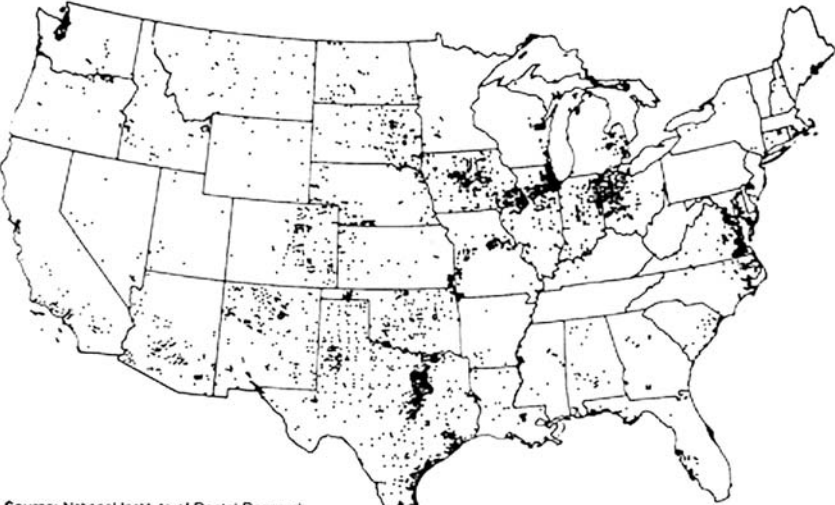


Fig. 3 Many US communities have 0.7 ppm or more natural fluoride in their water supply

Many U.S. communities have 0.7 ppm or more natural fluoride in their water supply



Source: National Institute of Dental Research

Recent Human Activities Have Perturbed Natural Fluorine Cycling

While volcanic eruptions do not happen every day, and few people live in close proximity to an economically significant mineral deposit, the fluorine exposures of modern North American residents have increased dramatically since the end of World War II when industrial fluorine use became commonplace. Today, the primary sources of anthropogenic fluorine emissions include phosphate fertilizer production, aluminum and magnesium smelting, coal burning, oil refining, steel production, chemical production, primary copper and nickel production, clay production, lead and zinc smelting, glass and enamel making, brick and ceramic manufacturing, glues and adhesives production, fluoridation of drinking water, waste from sewage sludge, and the production of uranium trifluoride (UF₃) and uranium hexafluoride (UF₆) for the nuclear industry (Environment Canada, 2001). Most of these new sources of fluorine to the atmosphere and hydrosphere are the result of processing Earth materials that had previously been largely biologically unavailable as little as 60 years ago.

Taken together with the advent of fluorinated agricultural chemicals and phosphate fertilizers introduced to the food chain via intensive agricultural practices

(Hudlicky and Pavlath, 1995), the development and marketing of an FDA-approved fluoridated toothpaste by Procter and Gamble Company, and the application of deep well drilling technology to groundwater resources (Bailey, 2006, personal communication) that also coincided with the post-war era, it is perhaps not too much of an exaggeration to say that consumer choices (i.e., what you eat, where you live, where you get your drinking water) now play a bigger role in determining overall fluorine exposures than Nature. And whether water in particular is considered to be “high” or “low” in fluoride is relative only to established benchmarks that seem to vary considerably depending on its intended use but not its eventual fate.

In broad terms, it can be said that groundwater supplies in arid climates in North America are more fluoride rich than those in temperate climates; that aquifers influenced by certain igneous and metamorphic earth materials are generally more fluoride-enriched than aquifers pumping from sedimentary rock (although sedimentary aquifers are more widespread); that deep-source bedrock water wells produce more fluoriferous water as compared to shallow overburden wells; and that bedrock aquifers that are highly fractured due to nuclear or industrial blasting, meteorite impacts, seismicity, and/or glacial isostasy are higher in fluoride than undisturbed formations (Boyle, 1976).

Skeletal Fluorosis: The Danger of Drilling Deeper

In the 1970 s, when the shallow dug wells of a small town in Canada’s Gaspé Peninsula were no longer able to meet their needs, the residents of Maria, Québec, did what most rural residents would do –they drilled deeper. This has become standard practice in most parts of Canada, where 33% of the population currently rely on groundwater resources, especially with mounting concerns over the vulnerability of shallow wells to dropping water table levels associated with climate change and susceptibility to anthropogenic surface contaminants like road salt run-off, landfill and septic system leachate, fertilizers, pesticides, floodwaters, and manure. What the residents did not anticipate when they drilled through the 10–30 m (30–100 feet) of Quaternary glacial tills, whose mean fluoride concentration was 0.1 mg/l, was that they had been exposing themselves to 100 times more fluoride from “fossil waters” extracted from the highly mineralized and naturally softened Carboniferous sedimentary bedrock aquifer (Fig. 4).

Although it took several years, eventually the dramatically increased incidence of osteoarthritis-like symptoms among Maria residents caught the attention of local public health authorities who, with the help of a geoscientist well versed in fluoride geochemistry, diagnosed *skeletal fluorosis* resulting

from the consumption of fluoride-enriched drinking water for as little as 6 years (Boyle and Chagnon, 1995). X-rays of the affected individuals would have been familiar to Dr. Kaj Roholm, who had observed similar effects in the skeletons of Danish cryolite (Na₃AlF₆) workers in Greenland in the 1930 s, documenting his findings in the landmark publication, *Fluorine Intoxication: A Clinical-Hygienic Study* in 1937 (Roholm, 1937: source of photos below) (Fig. 5).

Dental fluorosis was not prevalent in either the cryolite workers in Greenland, whose primary route of exposure was via inhaled dust particles, or the mostly adult population of 2,500 in the town of Maria because the critical period of exposure in the biomineralization of enamel occurs before a tooth erupts through the gum-line during early childhood. The human skeleton is continuously being re-modeled through the action of osteoclasts and osteoblasts, replacing itself completely three times over the course of an average lifespan. Therefore, skeletal fluorosis is the most obvious sign of pathology in adults exposed to high levels of fluorine but there is some hope of recovery once fluoride inputs have been significantly reduced, whereas dental fluorosis is irreversible.

Fluorine from any source has biological effects beyond human bones and teeth that are consistent with its unique chemical characteristics. From a geology and health perspective, it is important to realize that

Fig. 4 British postage stamp showing the glaciated terrain of the Gaspé Peninsula and its location on the brackish waters of the St. Lawrence Seaway. The overburden is under the influence of meteoric waters, whereas the presence of sodium increases the solubility of fluoride minerals in the cement of the Carboniferous bedrock sediments



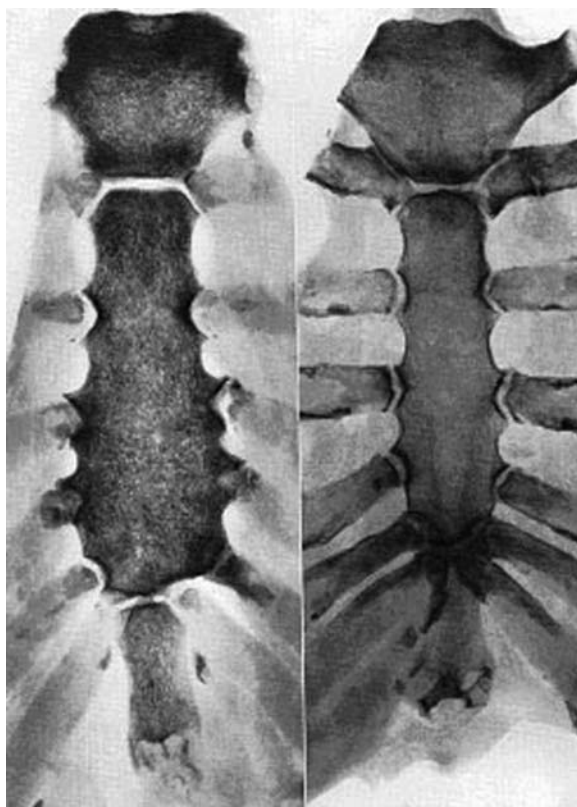


Fig. 5 Chest X-rays of a 51-year-old Danish cryolite worker (*left*) and a 50-year-old non-worker (*right*). The sternum is thickened and misshapen and the articular surfaces of the costal (rib) bones are sclerosed, making inhalation difficult

fluorine's function in nature is to facilitate chemical reactions. It lowers the energy required to both bring certain elements together and break molecules apart – its behavior remains the same across the lithosphere, atmosphere, biosphere, and hydrosphere. This raises questions regarding the extent of the effects of anthropogenic fluorine exposures in the human system as well as the ecosystem, as municipal and industrial wastewaters are discharged into surface water bodies at levels that are greater than 10 times what sensitive aquatic species can tolerate (Environment Canada, 2001).

The combination of natural and man-made fluorine compounds in the upper atmosphere is resulting in “greenhouse powerhouse” gases like trifluoromethyl sulfur pentafluoride (SF_5CF_3) (Sturges et al., 2000) and fluoride-facilitated mineralization in the pineal gland early in life is thought to be contributing to the premature sexual maturation (Luke, 1997) with all of

its associated “social system” implications related to early parenting. Infancy appears to be a critical time with regard to fluorine exposures and the development of symptoms of systemic fluorosis in adulthood, an aspect that was not captured in the early water fluoridation studies that lasted only 10 years (Bast et al., 1950).

One of fluorine's often over-looked effects in the hydrosphere is that it makes lead-, copper-, and cadmium-containing compounds in plumbing pipes and fixtures and cookware more soluble in water, particularly at the higher temperatures that might be experienced from the water heater to the tap or while cooking with copper pots (Boyle, 1976). Geochemistry tells us that the corrosivity of a low pH solution (i.e., surface water) is further enhanced when Na^+ and Cl^- ions are also present (Barnes, 1979), as is the case when certain disinfecting agents like sodium hypochlorite or chlorine bleach (NaClO) and chloramine (NH_2Cl) are added to naturally or artificially softened water. Many naturally low-fluoride North American municipal water supplies are now artificially fluoridated to levels of between 0.6 and 1.2 mg/l using fluoride salts (NaF , villiaumite also known as sodium fluoride) or, more commonly, with fluorine-rich by-products of phosphate fertilizer processing like hydrofluosilicic acid (H_2SiF_6) that also contain other elemental constituents like lead, arsenic, and natural radionucleotides because phosphate mineral deposits are never 100% pure (Wedepohl, 1978).

Systemic Fluorosis: The Catalyst of the Universe

Lead is among the handful of elements that are known to have adverse neurological effects to which unborn and young children are the most vulnerable due to their low body weight and susceptible stage of brain development (Gavaghan, 2002). Aside from updating old infrastructure, recommending to homeowners that lead plumbing be replaced, and incorporating the use of lead-free materials into the building code, managers of municipal water supplies can also control corrosion in the system by using some additives that adjust pH and alkalinity and others that are meant to inhibit leaching through the formation of an inorganic film on the inside of the pipes. The effectiveness of this last measure will depend heavily on the purity of the corrosion inhibitors (typically orthophosphate, polyphosphate and sodium silicate), as phosphate rock

contains between 10,400 and 42,000 mg/kg of fluorine (Boyle, 1976) and some sodium silicate minerals contain up to 5% fluorine by weight (Wedepohl, 1978), possibly doing more harm than good in the cases where artificial fluoridation is the cause of the corrosion (Fig. 6).

High lead exposures in childhood can have significant long-term neurological effects that can range from extremely subtle to gross impacts on motor function. Some research data indicate that high early childhood exposures are associated with significant long-term effects including lower intellectual performance

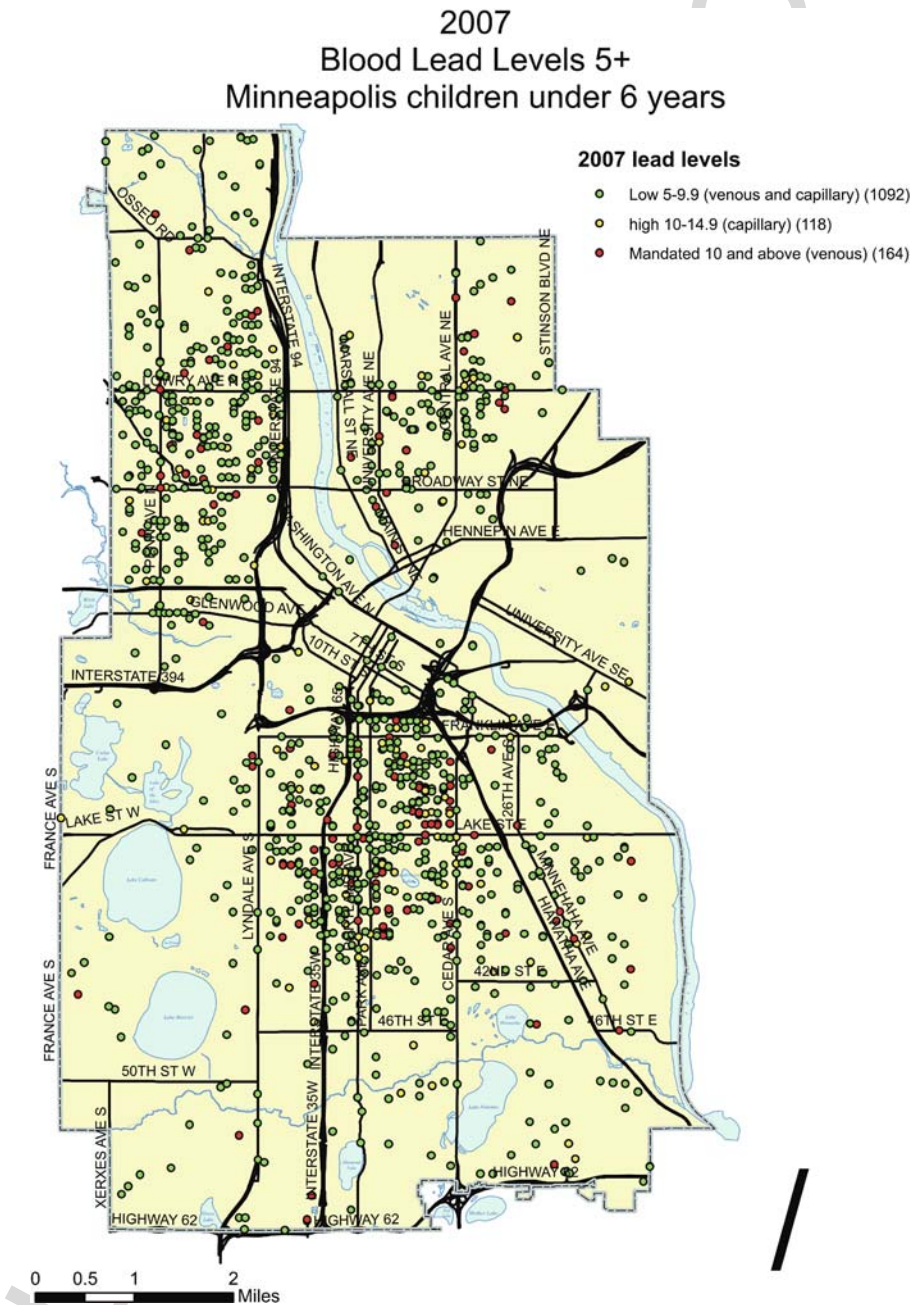


Fig. 6 Blood levels in children in Minneapolis

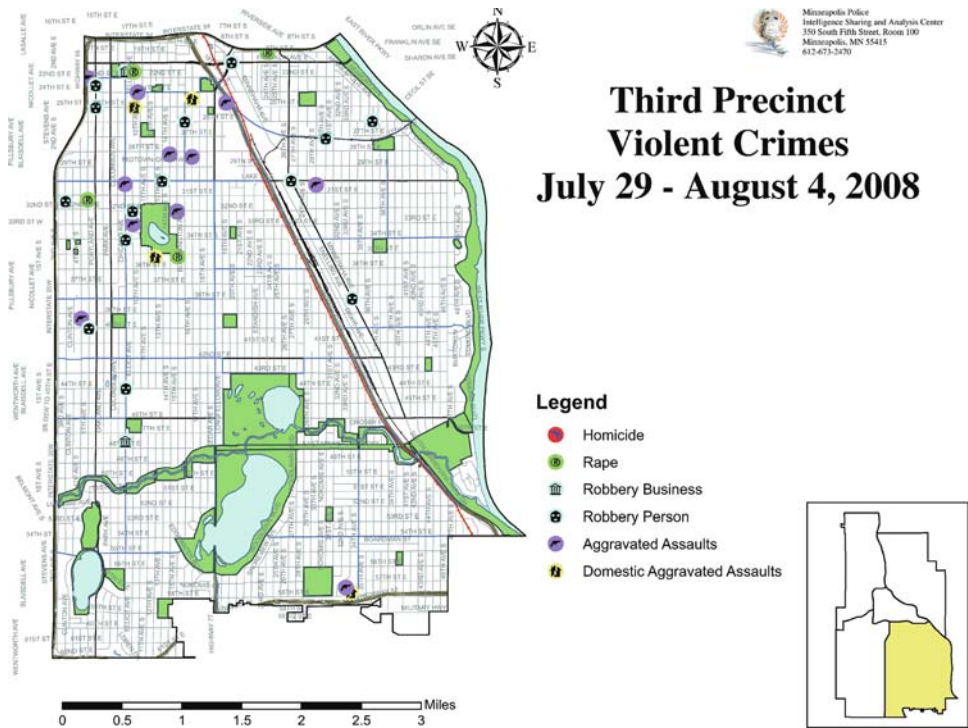


Fig. 7 Violent crimes 2008 in US cities

and higher rates of delinquency. Large and long-established communities like Minneapolis, Minnesota (incorporated in 1867), are particularly at risk because of the metals in the pipes of the old infrastructure that is common to the more densely populated and poorer parts of town where nutritional status is also low. Residences closest to the treatment and distribution centers might also be receiving higher doses of chlorine and fluorine (up to 1.2 mg/l) added to Mississippi River water as compared to those at “the end of the line.” Though there are more questions than answers at this point, aided by GIS technology, a multi-disciplinary team of researchers is currently investigating different aspects of the relationship between fluoride-enhanced lead exposures via drinking water and violent crime rates in major US cities (Fig. 7).

Prior to the Industrial Revolution, overly fluorine-rich “provinces” were generally restricted to specific natural environments like coastal, volcanic, and arid areas, or to places with deposits of soluble fluoride minerals like fluorite (CaF_2), villiaumite (NaF), and cryolite (Na_3AlF_6) and/or rifted, faulted, and fractured terrain (Edmunds and Smedley, 2005). Given its chemical properties, it becomes clear that sufficient fluorine

exposure to meet the biological requirements of a particular organism is easily obtained from a variety of sources—even outside of these “fluoriferous” natural environments—without any effort, and so attention needs to be focused on avoiding toxicity.

Fluoride’s geochemical associations with some “bad company” in the public health world, together with the enhanced solubility of certain metals found in plumbing and fixtures in the presence of fluoridated water (particularly with a low pH and low calcium–magnesium content as is common to surface water sources), make it a perfect tool for identifying communities in environments that are naturally prone to arsenicosis, heavy metal toxicity, and radon gas exposure from the radioactive decay of uranium in earth materials.

Radon

The harmful isotope-222 of the noble gas, *radon*, is produced from the natural radioactive decay of radium-226 and uranium-238, but this was not known when Czech silver miners were suffering from Bergkrankheit

or “mountain sickness” in 1550 (Witschi, 2001). The ultimate cause of this pulmonary illness that was the cause of death among miners 75% of the time, now diagnosed as lung cancer, was not identified until 1924 –almost 3 decades after Becquerel had discovered radioactivity (in 1896) and the husband and wife team of Pierre and Marie Curie had isolated radium (in 1898), and well over a century after Martin Klaproth extracted uranium from the mineral pitchblende (in 1789) or uraninite (UO_2) (Porter and Ogilvie, 2000). The carcinogenicity of radon gas is associated with its decay products, primarily polonium-218 and polonium-214, which deliver a radiologically significant dose of alpha and gamma rays to pulmonary epithelium as inhaled aerosols of short-lived progeny on the way to eventually becoming the stable isotope of lead-206 –a process that takes about 22 years (National Research Council, 1999).

Between the mid-1940 s and 1990 in North America, several cohorts of more than 3,500 fluorspar and uranium miners receiving high occupational exposures of radon-222 were followed. But before these studies had concluded, public health researchers were already looking at the carcinogenicity of radon gas exposures in North American residential settings (National Research Council, 1999). By the mid-1990 s it was concluded that 10–15% of lung cancers in the United States and Canada were caused by radon gas, 90% of which were also smokers.

Radiation in the Navajo Nation

Being primarily engaged in agriculture and other “open-air” activities and originally having low smoking rates, lung cancer among Native American Indians in the southwest was once a rare occurrence (Gottlieb and Luverne, 1982). But when vast uranium deposits were discovered beneath their territory in the years leading up to World War II, many male members of the Navajo Nation were eager for work in the mines so close to their homes, despite the fact that they would be paid less than minimum wage (between \$0.81 and 1.00) for their back-breaking labor. Although they were doing most of the work by hand in an enclosed space, they were not provided with any protective equipment, as ventilation measures developed from the European experience with “mountain sickness” were purported to have drastically reduced radon exposures.

As is common, the greatest public health failure seems to have been related to poor communication and lack of education, as there is no word for “radiation” in the Navajo language, and few Navajo miners spoke much English. Adding to the constellation of factors were the high rates of smoking among all miners, particularly during wartime and the period immediately following, and lack of clear legislation that required employers and public health researchers to inform workers of the occupational hazard (Brugge et al., 2006) (Fig. 8).



Fig. 8 Source: <http://www.ehponline.org/docs/2007/115-12/mining.jpg>

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The radon story parallels that of fluorine. The earth materials that may produce radon are also similar to those that are known to be high in fluorine, namely silicic igneous rocks, organic-rich clays and shales, phosphates, carbonates, and hydrothermal or metasomatic ore deposits in “structural discontinuities” such as are found in Canada’s Athabasca Basin and various locations in the United States (Fig. 9).

The atmosphere and the hydrosphere provide subsurface pathways for radon into the biosphere, where human exposures occur in the home. Depending on its location and construction, radon may be inhaled as it vaporizes from running water and drains, or as it seeps through ground-level windows, foundation cracks, and gaps created by fittings and footings. Like fluoride, uranium (and therefore, dissolved radon) concentrations tend to be higher in groundwater as opposed to surface water (Wedepohl, 1978) but unlike fluoride, where bioaccumulation and the “halo effect” of processing must always be borne in mind, there is little

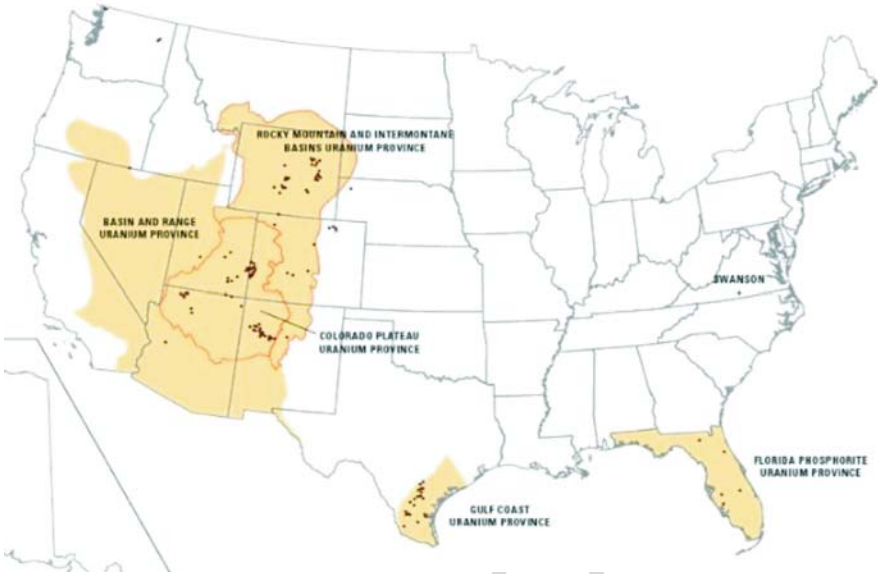
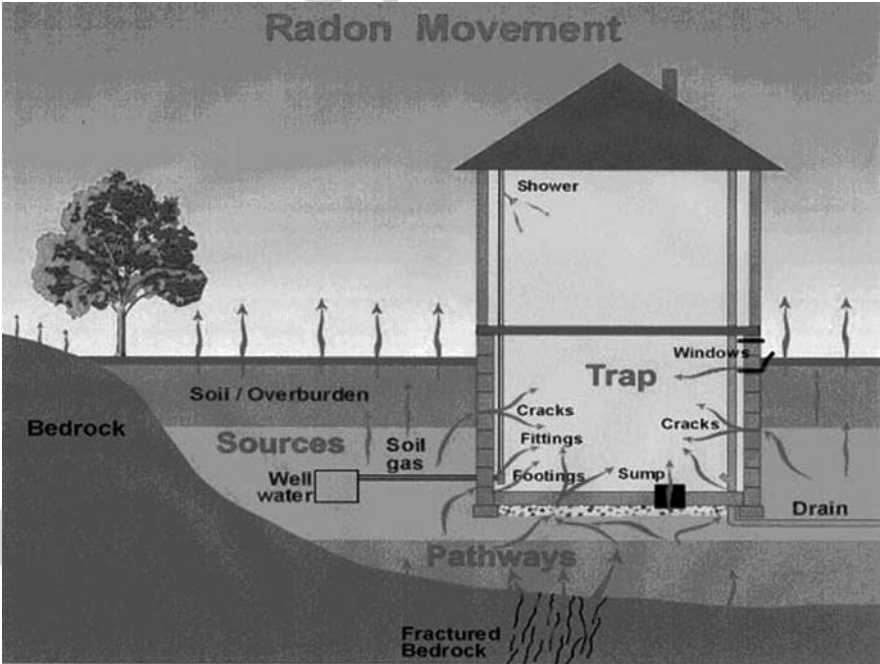


Fig. 9 Map of uranium deposits in the United States. Note the areas of overlap with the drinking water fluoride map in Box 1. Source: USGS (<http://www.energy-net.org/01NUKE/u-mining/us-uranium-usgs.jpg>)

Fig. 10 Diagram of the many pathways radon gas can employ in migrating from its source in uranium-rich earth materials to its trap within the home. Source: Zielinski (2008)

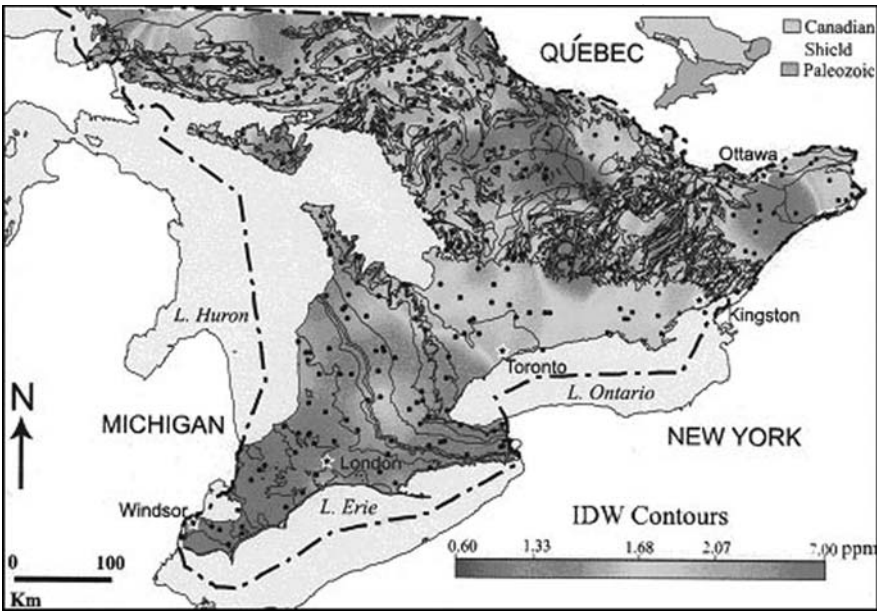


evidence that food chain exposures of radon are much of a concern (Kabata-Pendias, 2001) (Fig. 10).

The pathways that allow the migration of radon gas into homes with foundations are primarily controlled by rock mechanics and climate, which determine the number and “connectedness” of potential conduits,

mineral surface area, atmospheric pressure, and permeability of the channels due to saturation with water. In this way, radon gas hazards may present intermittently in a wide variety of geochemical environments, making geologic hazard identification difficult, especially when considering the effects of global climate

Fig. 11 Map of uranium (U) in the A horizon of southern Ontario. Dark gray “hot spots” of higher U concentrations in soil are indicative of a potential radon gas hazard. Source: Geological Survey of Canada (unpublished data)



change. It is conceivable that dropping water table levels and the “drying up” of clay- and organic-rich soils will create new pathways for the liberation of significant amounts of radon gas into existing homes or that soils relocated by extreme weather events like hurricanes or airborne dusts from dried-up lakebeds and deforestation could lay dangerous foundations for new construction in areas that are not currently considered to be radon gas prone.

Lung Cancer Hot Spots

Thick Palaeozoic sedimentary bedrock units underlie the most densely populated parts of Ontario, and so it is not surprising that lung cancer rates in this province lag significantly behind those of Nova Scotia, New Brunswick, and Québec (Canadian Cancer Society, 2008) where more of the Canadian Shield is exposed. However, the influence of uranium-rich clays becomes apparent when looking at the intra-provincial lung cancer statistics. Both lung cancer morbidity and mortality rates for the province are highest in areas underlain by heavy clay (zone 1 below) and Canadian Shield (zones 10, 12, 13, and 14). Predictably, the lowest rates of incidence and death from lung cancer are reported for the Central zone (8) which covers the highlands formed by the Algonquin Arch but which is underlain by a thick blanket of coarse Quaternary sediments



Fig. 12 Map of local health integration networks in the province of Ontario. Source: <http://www.lhins.on.ca/FindYourLHIN.aspx>

that are low in uranium content and Palaeozoic bedrock (Cancer Care Ontario, 2006 2004 data) (Fig. 12). Internationally, the generally accepted guideline for residential exposures is 200 Bq/m³. If this threshold is exceeded, the recommended remedial measures are inexpensive, simple to implement, and can generally be completed in a short period of time. In so doing, it is estimated that hundreds of cases of lung cancer per year could be prevented in North America, thus significantly reducing the burden on the health-care system.

Arsenic

Arsenic contamination through natural (geogenic) and anthropogenic sources is a serious threat to humans all over the world. Several epidemiological studies have documented the global impact of arsenic contamination and the characterization of the sources of exposure. The health effects of chronic exposure to arsenic are well established in countries with high arsenic in drinking water; however, such evidence is not so readily available in countries with lower levels of environmental arsenic, or treated drinking water systems. Of more relevance to developed and industrialized countries, such as the United States, are the potential health consequences of long-term, low-level exposure via drinking water or through occupation or medical use although the relationship between health effects and exposure to drinking water arsenic is not well established in US populations (Lewis et al., 1999). We provide here an overview of the state of arsenic studies in the United States and a discussion of the available epidemiological and human health literature in the United States.

Epidemiological and Environmental Health Studies on Arsenic Exposure

Areas of the United States have been affected by arsenic in drinking water, especially in areas close to mining sites, for example, Twisp, Okanogan County, Washington (Peplow and Edmonds 2004) and New Hampshire (Karagas et al., 2002). Recently, the US Geological Survey (USGS) published an updated version of a map illustrating “Arsenic in Ground Water of the United States.” The map was generated from the most recent arsenic measurements from 31,350 wells and springs showing national level patterns of naturally occurring arsenic in ground water resources of the United States and Puerto Rico. The data set displayed on this map is a moving 75th percentile, which is the maximum arsenic concentration found in 75% of samples within a moving 50 km radius (the median size of a US county; USGS, 2005). The USGS map shows that there are parts of many states affected by high levels of arsenic in groundwater, following the new USEPA MCL for 10 $\mu\text{g/l}$.

Several recent studies have been published concerning the distribution of arsenic levels in the US drinking water supplies. A study by Frost et al. (2003) identified 33 counties in 11 states with an estimated mean drinking water arsenic concentration of 10 $\mu\text{g/l}$ or greater. A total of 11 of these counties have an estimated mean arsenic concentration of 20 $\mu\text{g/l}$ or more, and two have an estimated mean arsenic concentration of 50 $\mu\text{g/l}$ or more. Domestic wells are a particular issue, for example, in New Hampshire, domestic wells serve roughly 40% of the population, and about 10% of these contain arsenic concentrations in the controversial range of 10–50 $\mu\text{g/l}$ (Karagas et al., 2002). Based on census data, between 1950 and 1999 there were approximately 51.1 million person-years of exposure to drinking water arsenic at levels of 10 $\mu\text{g/l}$ or more, 8.2 million at levels of 20 $\mu\text{g/l}$ or more, and 0.9 million at levels of 50 $\mu\text{g/l}$ or more (Frost et al., 2003).

Although several studies have described the distribution of arsenic within the US drinking water supplies, there is a lack of epidemiologic data to indicate disease associations within the United States (Brown and Ross, 2002). It has been suggested that the mortality and incidence of diseases known to be associated with arsenic exposure should be examined in other high exposure State/Counties as part of an assessment of arsenic health effect in US populations (Frost et al., 2003).

Cardiovascular Effects

The association of drinking water arsenic and mortality outcome was investigated in a cohort of residents from Millard County, Utah. Median drinking water arsenic concentrations for selected towns ranged from 14 to 166 ppb and were from public and private samples. Standard mortality ratios (SMRs) were calculated. Statistically significant findings included increased mortality from hypertensive heart disease among males (SMR 2.20, 95% CI (confidence interval) 1.36–3.36), increased mortality for hypertensive heart disease among females (SMR 1.73, 95% CI 1.11–2.58), and for the category of all other heart disease (SMR 1.43, 95% CI 1.11–1.80) (Lewis et al., 1999).

A case-control study in the United States investigated the association between chemicals in maternal drinking water consumed during pregnancy and

congenital heart disease in the offspring. Two hundred and seventy affected children and 665 healthy children took part in the study. Data included information on contaminant levels in maternal drinking water and on health, pregnancy management, and demographic characteristics. Nine inorganic metals were analyzed for detection of an association with congenital heart disease. Arsenic exposure at any detectable level was associated with a threefold increase in occurrence of contraction of the aorta (OR (odd ratios) 3.4, 95% CI 1.3–8.9) (Zierler et al., 1988).

A recent US study analyzed water samples and used self-report format for 1,185 people who reported drinking arsenic-contaminated water for more than 20 years. They found that respondents with arsenic levels of >2 $\mu\text{g/l}$ were statistically more likely to report a history of depression, high blood pressure, circulatory problems, and heart bypass surgery (Zierold et al., 2004).

Diabetes Mellitus

Diabetes is a major source of morbidity and mortality in the United States and recent studies have reported an increase in the incidence and prevalence of this disease. For example, the overall prevalence rose from 4.9% in 1990 to 6.5% in 1998 (Mokdad et al., 2001). As discussed, diabetes has recently been found to be associated with arsenic exposure in some epidemiologic studies, predominantly on studies conducted in Taiwan (Lai et al., 1994; Tseng et al., 2002). However, no work to date has been undertaken examining the relationship between diabetes mellitus with lower chronic doses of arsenic in drinking water in the United States.

Skin Cancer

A case-control study examining the association between drinking water and cutaneous melanoma in Iowa was undertaken. This study found an increased risk of melanoma for participants with elevated toenail arsenic concentrations (OR 2.1, 95% CI 1.4, 3.3). This is the first study to find a significant association between arsenic and melanoma in the United States and warrants further investigation (Beane Freeman et al., 2004).

Lung, Stomach, and Colon Cancer

Increased risk for lung cancer with arsenic exposure has been consistently observed in ecological, case-control, and cohort studies in Taiwan, Japan, Chile, and Argentina, but not yet in the United States (WHO, 2004). Significant excess mortality from cancers of the digestive tract has been observed among copper smelter workers in Anaconda, Montana, with a standardized mortality ratio of 1.3 (Enterline et al., 1987) only a slight excess in mortality from digestive tract cancer was observed among smelter workers in Tacoma, Washington. Colon cancer mortality has also been significantly associated with chronic exposures to inorganic arsenic among copper smelter workers in Tacoma, Washington, with a significant standardized mortality ratio of 2.1 for those who were employed before respirators were implemented in the smelter exposure areas (Enterline et al., 1987).

Breast Cancer

An association between arsenic exposure and breast cancer has been investigated but not confirmed. The associations between toenail levels of five trace elements and breast cancer risk were studied among a cohort of 62,641 US women who were free from diagnosed breast cancer in 1982. Among 433 cases of breast cancer identified during 4 years of follow-up and their matched controls, the OR comparing the highest with the lowest quintiles was 1.12 (95% CI 0.66–1.91). Even though breast cancer is examined as part of this epidemiological exercise, results to date do not provide evidence for an effect of arsenic on breast cancer risk (Garland et al., 1996).

Bladder Cancer

New Hampshire is known to have high arsenic in groundwater and along with other States in New England has among the highest bladder cancer mortality rates in the country. These facts prompted a large case-control study to be undertaken in this region examining toenail arsenic levels and their association with skin and bladder cancer (Karagas et al., 1998). The OR for squamous cell carcinoma (SCC) and basal

cell carcinoma (BCC) were close to unity in all but the highest arsenic percentile category. Among individuals with toenail arsenic concentrations above the 97th percentile, the adjusted ORs were 2.07 (95% CI 0.92–4.66) for SCC and 1.44 (95% CI 0.74–2.81) for BCC, compared with those with concentrations at or below the median (Karagas et al., 2002). Among smokers, an elevated OR for bladder cancer was observed for the uppermost arsenic category (OR 2.17, 95% CI 0.92–5.11) (Karagas et al., 2004). However, because the 95% CI includes the value 1.0, arsenic levels cannot be considered a useful predictor variable, thus these results merely suggest an association between arsenic and the cancers examined and indicate that smoking may act as a co-carcinogen.

Ayotte et al. (2006) found a statistically significant positive correlation between residential bladder cancer mortality rates and private water supply use in New England. Previous studies (Montgomery et al., 2003) found elevated levels of arsenic in the well water.

Prostate Cancer

Epidemiologic studies have suggested a possible association between exposure to inorganic arsenic and prostate cancer (Wu et al., 1989; Chen and Wang, 1990), including a recent study of populations residing in the United States, in which SMR analysis by low-, medium-, and high-arsenic exposure groups indicated a dose relationship for prostate cancer (Lewis et al., 1999). Prostate cancer SMR was 1.45 (95% CI 1.07–1.91). A study by Achanzar et al. (2002) which found human prostate epithelial cells are directly susceptible to the transforming effects of inorganic arsenite. Another study on the effect of chronic oral exposure to arsenic on male mouse testicular and accessory sex organ weights, sperm parameters, testicular marker enzymes, and distribution of arsenic in reproductive organs, found a significant accumulation of arsenic in testes, epididymis, seminal vesicle, and prostate gland in treated animals (Pant et al., 2004). These laboratory studies show biological plausibility in the relationship between arsenic and prostate cancer.

The health effects of chronic exposure to arsenic are well established in countries with high levels of drinking water arsenic; however, such evidence is not so readily available in countries with lower levels of arsenic, such as the United States. The research that

has been undertaken in the United States is limited and much of what has been undertaken is not definitive.

From the studies that have been carried out in the United States, some have found a statistically significant association between disease and arsenic levels, most consistently the cardiovascular studies (Lewis et al., 1999, Zierler, et al., 1988, Zierold et al., 2004). Prostate cancer also showed a significant association with arsenic levels (Lewis et al., 1999), which has been found to be biologically plausible in laboratory studies (Achanzar et al., 2002, Pant et al., 2004). Finally, a study on the risk of melanoma found a significant association with elevated toenail arsenic concentrations (Beane Freeman et al., 2004). In the United States the arsenic-related environmental etiology of several chronic diseases warrants further investigation.

Naturally Occurring Organic Compounds

Long-term exposure to low levels of organic substances leached from low-rank coal aquifers has been hypothesized to be linked to kidney disease and urinary system cancers (Orem et al., 2007). This link has been most firmly established in the case of Balkan Endemic Nephropathy (BEN), a fatal kidney disease with associated renal/pelvic cancer that occurs in restricted areas of the Balkans where Pliocene lignites deposits are present (Tatu, et al., 1998). In northwestern Louisiana, where lignites underlie a region having an elevated incidence of renal pelvic cancers, recent studies have shown that a suite of coal-derived organic substances occur in drinking water supplies, resembling those observed in drinking water supplies from areas impacted by BEN (Bunnell et al., 2006). Recently (Peterson et al., 2009) collected water samples from two counties in East Texas reported to have relatively high incidences of renal/pelvic cancer. Dichloromethane extractable organic compounds in the water samples were identified by gas chromatography/mass spectrometry. Compounds present in the water samples included some substituted polycyclic aromatic hydrocarbons (mostly lower molecular weight), heterocyclic and substituted aromatics, phenols, terpenoids, and aliphatic hydrocarbons at sub-microgram/liter levels. This suite of organic compounds is similar to those observed in other coal containing aquifers. These results suggest

that a BEN-like health problem may exist in the Gulf Coast region of the United States.

Evolving Concerns About Asbestos

Asbestos is a term applied to a group of fibrous silicate minerals that were mined and used commercially for centuries, primarily because of their flexibility, weavability, high tensile strength, and resistance to heat, chemicals, and electricity. The potential health effects of exposure to asbestos have been recognized for decades and include diseases such as asbestos, mesothelioma cancer, lung cancer, pleural plaques, pleural thickening, and others (Roggli et al., 2004; Dodson and Hammar, 2006). These diseases are known to result from occupational exposures to high levels of asbestos dusts. As a result, mining and processing of asbestos ceased in the United States in 2002, and US commercial use of asbestos has plummeted since the 1970 s; however, some asbestos is still imported for use in some commercial applications such as roofing (Virta, 2009).

In spite of decades of research into the health effects of asbestos, substantial debate continues as to the exact mechanisms of toxicity, the potential health effects of low-level exposures, potential health effects of elongated mineral particles that do not fit compositional or morphological definitions of asbestos, and other aspects (NIOSH, 2009; Plumlee et al., 2007; Roggli et al., 2004; Dodson and Hammar, 2006). Further, the last decade has seen a substantial increase in public health concern about potential health effects resulting from occupational and environmental exposures to dusts generated by mining of mineral deposits that contain asbestos as a natural contaminant, or by natural weathering or human disturbance of rock types that contain naturally occurring asbestos (Van Gosen, 2009; Harper, 2008; Pan et al., 2005).

Vermiculite deposits mined at Libby, Montana, from 1923 to 1990 provided the bulk of the Nation's vermiculite used commercially during that time period. High rates of asbestos-related disease are noted in Libby vermiculite miners and workers exposed occupationally, in their family members, and in Libby townspeople with no occupational connection to the mine (Peipins et al., 2003; Sullivan, 2007). Elevated rates of asbestos-related disease are also noted in communities elsewhere in the United States that received

and processed vermiculite ore from Libby (Horton et al., 2008). It is generally agreed that the source of these diseases was exposure to asbestiform and fibrous amphiboles intergrown with the Libby vermiculite that were released into the air as the vermiculite was mined, processed, or otherwise disturbed.

Rocks that contain natural chrysotile and tremolite asbestos are found in 35 of the 50 United States (Van Gosen, 2009). As these rocks are weathered naturally, mined for aggregate or industrial mineral commodities, or exposed by earth moving for road and building construction, there is the potential for release of asbestos-containing dusts into the environment. In the last decade, substantial debate has developed as to whether these dusts pose a health risk to residents and workers alike. The debate has been particularly intense in the area around El Dorado Hills, California, an area that is underlain by serpentinites and other ultramafic rocks that contain chrysotile and tremolite-actinolite asbestos (Harper, 2008; Van Gosen, 2007; USEPA, 2006). Asbestos occurrences in or released from their original geologic source rocks, or soils derived naturally from those rocks have been termed "naturally occurring asbestos," or "NOA" (Harper, 2008).

How Earth Sciences Can Help

Earth sciences investigations are providing important contributions on a wide variety of asbestos issues, ranging from policy-making to fundamental health research. On a local to regional scale, fundamental geologic mapping, remote sensing, geophysical, and related characterization studies are helping map the distribution and mineralogical characteristics of asbestos-containing rocks (Churchill and Hill, 2000; Clinkenbeard et al., 2002; Swayze et al., 2009). In some jurisdictions such as California and Fairfax County, Virginia, geologic mapping forms the basis of policies requiring enhanced dust control measures and other practices in areas underlain by asbestos-containing rocks.

Studies are underway to inventory asbestos localities and map the distribution of geologically favorable rock types containing asbestos across the United States (Van Gosen, 2007, 2009). These studies are needed to aid in the interpretation of regional to national scale epidemiological data on asbestos-related diseases, with the ultimate goal of understanding better the health

risks associated with living on or rocks containing NOA (Pan et al., 2005).

Mineralogical characterization studies are essential to help understand the nature of the particles to which affected populations have been exposed. For example, mineralogical characterization has shown that the Libby amphiboles occur in a range of morphologies and chemical compositions, only a subset of which has been traditionally regulated as “asbestos” (Meeker et al., 2003). In El Dorado Hills, California, mineralogical studies also documented a wide range of elongated particle types in air samples that would all be counted as potentially hazardous under current regulations, but only a subset of these particles is truly asbestiform (Meeker et al., 2006).

Other areas in which earth scientists work in collaboration with health scientists can contribute include (Plumlee et al., 2006; Plumlee and Ziegler, 2007; NIOSH, 2009) characterization of dosing materials used in asbestos-related toxicity testing; characterizing particles to which various worker cohorts having elevated asbestos-related disease rates were exposed; examining dissolution rates of asbestos and other mineral particles in body fluids encountered along inhalation and ingestion exposure pathways; examining other chemical interactions of particles with the body, and how these interactions (such as oxidation–reduction reactions that generate free radicals and oxidative stress) may influence toxicity in the body.

A Growing Role for Earth Sciences in Environmental Disaster Response and Planning

Natural and anthropogenic disasters (e.g., earthquakes, volcanic eruptions, wildfires, urban fires, landslides, hurricanes, tsunamis, floods, industrial spills, terrorist attacks) can produce copious solid, gaseous, or liquid materials of potential environmental and public health concern. Examples include contaminated and/or pathogen-bearing waters, dusts, soils, and sediments; liquids; gases; smoke; ash; and debris. Many of these materials are derived from the earth, geochemical processes influence how they evolve in the environment, and their geochemical characteristics can strongly influence their potential impacts on the environment and health (Plumlee and Ziegler, 2007). As a

result, there is a growing role for process-focused earth science expertise and methods applied to environmental disaster response and planning.

Volcanologists have had a long history of helping assess impacts of volcanic ash and gases on the environment and health, and Mt. St. Helens and Kilauea volcanoes in the United States have played prominently in these studies. Water leach studies of ash have documented that rain waters falling onto fresh ash could become quite acidic, due to the liberation of acidic gas species that had condensed onto the ash particles in the eruption cloud (Hinkley and Smith, 1987; Witham et al., 2005). Studies of other eruptions from around the world have regularly demonstrated that fluoride can be leached in sufficient quantities from ash to trigger fluorosis in humans and other animals that consume water affected by ash, or animals that eat vegetation coated by ash (Weinstein and Cook, 2005). Volcanology collaborations with the public health community have helped elucidate and communicate to the public the health hazards associated with exposure to volcanic fog (vog) emanating from volcanoes, and laze (lava haze) produced when lava flows into seawater (USGS, 2008). Recent articles provide excellent summaries of the potential health hazards associated with respiratory exposure to volcanic ash (Hansell et al., 2006; Horwell and Baxter, 2006; Weinstein and Cook, 2005), and toxicologically important reactions involving ash (Horwell et al., 2007). Other information on volcanic ash can be found through web sites of the US Geological Survey (<http://volcanoes.usgs.gov/ash/health/>) and International Volcanic Health Hazards Network (<http://www.ivhnn.org>).

The outbreak of the fungal disease Valley Fever in humans and sea otters immediately following the 1994 Northridge, California, earthquake is often cited as an example of the links between earth processes, geophysical disasters, and health. Landslide specialists worked directly with public health experts to help examine the timing and spatial distribution of sickened people and were able to determine that the outbreak originated through exposures to dust clouds generated during earthquake-triggered landslides (Jibson et al., 1998; Schneider et al., 1997). The landslides had disturbed soils that contained spores of the pathogenic soil fungus *Coccidioides immitis*, the etiological agent of Valley Fever that is endemic to soils in much of the US desert southwest. Since 1994, substantial research has

focused on determining potential geological and other controls on the habitat of *C. immitis* in soils (Bultman et al., 2005; Fisher et al., 2007).

In the last decade, interdisciplinary earth science studies have helped provide insights into the potential environmental- and health-hazard characteristics of materials produced by a number of natural and anthropogenic disasters in addition to volcanic eruptions, including

- dust and debris produced by the attacks on and collapse of the World Trade Center towers (Clark et al., 2001, 2005; Plumlee et al., 2005; Meeker et al., 2005; Swayze et al., 2005);
- flood waters and flood sediments left in the greater New Orleans area by 2005 hurricanes Katrina and Rita (e.g., Pardue et al., 2005; Plumlee et al., 2006; Presley et al., 2006; Van Metre et al., 2006; Cobb et al., 2006; Plumlee et al., 2007a; Farris et al., 2007; USEPA, 2005–2008; Griffin et al., 2009 in press);
- ash and burned soils from wildfires (Plumlee et al., 2007b; Wolf et al., 2008);
- mud from the ongoing LUSI, East Java mud volcano eruption (Plumlee et al., 2008).

How Earth Sciences Can Help

These studies collectively demonstrate that important contributions can be made in disaster response from across the earth science disciplines, including geology, geophysics, geochemistry, hydrology, remote sensing, geomicrobiology, and others. For example, during a disaster, earth scientists can, in collaboration with emergency managers, public health experts, microbiologists, and ecologists, help to

- characterize the physical, chemical, and microbial makeup of materials generated by the disaster;
- identify source(s) of the materials;
- monitor, map, and/or model dispersal and evolution of materials in the environment;
- understand how the materials are modified by environmental processes;
- identify key characteristics and processes that influence the materials' toxicity to exposed humans and ecosystems; and

- estimate shifts away from pre-disaster environmental baseline conditions.

The key goal of all these studies is to help define the magnitude and nature of the environmental and health risks posed by a specific disaster, both spatially and over time.

In addition, results from past responses can be used to anticipate and plan for future disasters. As part of disaster preparedness, earth scientists can

- measure and compile data on pre-disaster environmental baseline conditions;
- develop models for the environmental behavior and effects of materials generated by similar types of disasters;
- develop a resource of appropriate data and methods that can be used to enhance and guide responses to future environmental disasters; and
- work with emergency planners to help mitigate effects of and improve resiliency to future disasters.

Occupational Health Issues

Occupational health issues associated with metals exposure are both industry and metal specific. While there are a large number of metals that are important in a workplace setting, there are six "heavy metals" that are considered to be the most significant in terms of potential toxicity to exposed workers. These are arsenic, beryllium, cadmium, hexavalent chromium, lead, and mercury. The other metals of significance include Al, Sb, Co, Cu, Fe, Mn, Mo, Ni, Se, Ag, Sn, Vn, and Zn. Each of these metals can also produce potentially significant dose-related health effects.

Unlike the situation associated with community exposures where either the food pathway or direct soil ingestion routes dominate, in an industrial setting, the dominant pathway is air. Occupational exposure standards are primarily focused on the air pathway, as neither the dermal nor direct ingestion routes of exposure are typically as significant in comparison to the air route. The exceptions to this observation are beryllium and hexavalent chromium where dermal exposures are important potential routes of exposure and health effects.

In general, there are several important questions that should be considered when analyzing the potential for adverse effects from workplace exposures to metals:

1. What industrial operations are typically associated with workplace exposures to the metal under consideration?
2. What health effects are associated with exposure dose to the specific metal?
3. How are exposure and/or dose evaluated?
4. What are the relevant regulatory exposure standards?
5. What are some of the typical strategies utilized to minimize or prevent exposure?

The first four questions tend to be substance specific and will be briefly summarized for each of the most important “heavy metals.” However, regulatory standards are country specific and the reader should always consult the most current available guidance. Health effects are metal and dose specific. Simply listing observed generic clinical effects, e.g., rash, cough, fatigue, provides little or no useful information as health effects are strongly dose related. Exposure minimization strategies apply to all of the metals. Excellent sources of information for both toxicology and occupational exposures, including regulatory considerations are (i) Agency for Toxic Substance and Disease Registry (ATSDR) site, <http://www.atsdr.cdc.gov/toxpro2.html>; (ii) Occupational Health and Safety Administration (OSHA) site, <http://www.osha.gov/SLTC/metalsheavy/index.html>; and (iii) Canadian Centre for Occupational health and Safety (CCOHS) site, <http://www.ccohs.ca/>

Arsenic: Potential exposures to inorganic arsenic and its compounds include coke oven emissions, smelting, wood preservation, glass production, nonferrous metal alloys, and electronic semiconductor manufacturing industries.

Chronic long-term exposure can lead to specific forms of dermatitis, mild pigmentation keratosis of the skin, vasospasticity, gross pigmentation with hyperkeratinization of exposed areas, and wart formation. These health effects are not due to direct dermal exposure but instead can be observed in individuals exposed by inhalation or ingestion, particularly via contaminated drinking water. Arsenic-related skin lesions have been well described when exposures were due to high levels, either anthropogenic or naturally occurring, in

drinking water. Arsenic is considered to be a known human carcinogen via chronic high-dose inhalation exposure.

Exposures are determined by a combination of (i) airborne industrial hygiene sampling, e.g., personal and/or area and/or (ii) biological monitoring which can include blood and urine sampling.

Beryllium: Occupational exposure can occur in mining, extraction, and in the processing of alloy metals containing beryllium. There are significant applications in the aerospace, nuclear, and manufacturing industries. Beryllium is extremely light weight and stiff; hence it has wide usage in dental appliances, golf clubs, non-sparking tools, wheel chairs, and electronic devices.

The adverse health effects of beryllium exposure are due to an immunological reaction that produces an allergic-type response. According to OSHA, approximately 1–15% of all people occupationally exposed to beryllium in air become sensitive to beryllium and may develop chronic beryllium disease (CBD), an irreversible and sometimes fatal scarring of the lungs.

Air, wipe, and bulk sampling techniques can be used to measure occupational exposures. A specific blood test, the beryllium lymphocyte proliferation test (BeLPT), is an important screening tool that has been developed in order to determine which workers have become sensitized to beryllium.

Cadmium: Most cadmium exposures are associated with workplaces where ores are processed or smelted. Exposures in electroplating, and welding operations have also been observed. Cadmium is also a component of certain industrial paints and is utilized in the manufacture of nickel–cadmium batteries.

Cadmium toxicology is quite complex with target organs primarily centered on the lung and kidney. Cadmium is considered to be a potential lung human carcinogen via inhalation exposures. The kidney is an important target that exhibits threshold effects, i.e., an overall “critical concentration” is observed prior to development of observable adverse effects.

Both industrial hygiene (air) and biological monitoring (urine) are used for determining exposures and as regulatory compliance monitors.

Chromium-hexavalent (Cr+6): Toxicity to chromium is directly related to valence state, i.e., the more common naturally occurring trivalent form (Cr+3) has an extremely low toxicity profile.

According to OSHA, occupational exposures are associated with workers who handle pigments containing dry chromate, spray paints and coatings containing chromate, operate chrome-plating baths, and weld or cut metals containing chromium, such as stainless steel. Hexavalent chromium compounds include chromate pigments in dyes, paints, inks, and plastics; chromates added as anticorrosive agents to paints, primers, and other surface coatings; and chromic acid electroplated onto metal parts to provide a decorative or protective coating. Hexavalent chromium can be created during “hot work” i.e., welding on stainless steel or melting chromium metal. In these situations the high temperatures involved in the process oxidize the Cr+3 to the hexavalent state.

Exposures can occur via inhalation, dermal exposure, and ingestion. The most significant routes are inhalation and dermal (skin and eye) and the upper respiratory tract and lung are the most important target organs for toxicity with increased lung cancer rates observed in a dose-related exposure pattern.

Both industrial hygiene (air) and biological monitoring (urine) are used for determining exposures. Air exposures are used for regulatory compliance monitors. Biological exposure indices can be performed; however, pre- and post-shift monitoring of urine is necessary as the urine test measures Cr+3 a normal dietary intake component.

Lead: Lead exposures are one of the most common in an industrial setting. OSHA considers lead exposure as a leading cause of chemical-related workplace illness. Aside from mining and smelting, lead is found in numerous industrial settings. In addition, workers can be exposed to lead while working at certain hazardous waste sites or during remediation of older housing stock where lead-based paints were commonly used. According to OSHA, standard particulate sampling techniques are used to evaluate lead exposures. Wipe sampling can indicate potential for lead ingestion.

Toxicity in workers can be acute or chronic and is typically dose related. Symptoms of lead toxicity include loss of appetite, nausea, vomiting, stomach cramps, constipation, difficulty in sleeping, fatigue, moodiness, headache, joint or muscle aches, anemia, and decreased sexual drive. However, these symptoms are non-specific and can be commonly elicited during a history and physical examination. Hence the use of biological monitoring is extremely important, i.e., measuring the blood lead level.

Target organs include blood-forming, nervous, renal, and reproductive systems. Both air sampling and biological monitoring are mainstays for exposure determination and are also used for regulatory compliance.

Mercury: Exposure can occur during mining and refining of gold and silver ores. Unlike commercial gold miners who use cyanide-based processes, “artisanal” miners commonly use mercury in their small-scale extraction efforts. Mercury can be found in thermometers, manometers, barometers, gauges, valves, switches, batteries, and high-intensity discharge (HID) lamps. Mercury is also used in amalgams for dentistry, preservatives, heat transfer technology, pigments, catalysts, and lubricating oils.

In the workplace, mercury can be found in three forms (i) elemental (metallic); (ii) inorganic, i.e., typically combined with chlorine, sulfur, and oxygen; and (iii) organic, i.e., combined with carbon or carbon-containing substances into straight (alkyl) or aromatic (aryl) ring forms. In general the alkyl forms are the most toxic although all forms exhibit a dose-related toxicity pattern.

Both air sampling and biological monitoring are mainstays for exposure determination. Regulatory agencies have issued specific standards for the major mercury compounds; hence, it is critical to determine which category a compound belongs to before comparing it with a standard or determining its relative toxicity.

Regardless of the specific chemical, workplace exposure control strategies are based on engineering controls, administrative controls, (i.e., good work practices and training), and the use of personal protective equipment (PPE), e.g., clothing and respirators, where required. According to OSHA, engineering controls include material substitution, isolation, process/equipment modification, and local ventilation. Administrative controls include good housekeeping, appropriate personal hygiene practices, periodic inspection and maintenance of process and control equipment, proper procedures to perform a task, and appropriate supervision to ensure that the proper procedures are followed.

North America, United States, and Canada have a 100+ year history of mining activity. While overall base metal mining and smelting has declined, particularly in the United States, mining activity continues to be an extremely important economic driver

in many discrete geographic areas. In Canada, as opposed to the United States, mining is far more important economically as a percent of the overall Gross Domestic product (GDP). In the United States, mining is extremely geographically focused and often centered on gold mining as opposed to more “traditional” base metals, e.g., lead, copper, zinc.

As discussed in this chapter, the medical geology of mining activity is minimally a function of the (i) specific suite of metals in the ore and their chemical speciation and mineralogy; (ii) the type of extractive procedures used on the ore, i.e., smelting, flotation, leaching, or closed circuit cyanide extraction processes; (iii) background environmental characteristics of the mine site; (iv) the fate-transport (chemodynamics) characteristics of the individual metals (e.g., existing relationship between surface and ground water, air patterns,); and (v) demographic characteristics of the potentially exposed populations, e.g., socio-economics, age distributions, housing stock ages. All of these elements influence the degree in which source → exposure → dose → potential health effects. Various complex conceptual models have been developed by the regulatory agencies and risk assessment professionals to illustrate this fundamental sequence. Each historic and active site has a unique set of circumstances that should be considered.

Despite these site-specific difference, over the last 30 years there has been a substantial regulatory history of evaluating and managing the environmental and human health effects from mining activity, particularly legacy sites that are no longer actively operating. Many of these “legacy sites” are extremely complex and are often referred to as “mining megasites.” In 2005, the US National Academy of Sciences (NAS) published a large monograph, entitled “Superfund and Mining Megasites: Lessons form the Coeur d’Alene River Basin” (<http://www.nap.edu/catalog/11359.html>). While there are a large number of US-centric features about the monograph these are entirely related to the legal context of managing sites as opposed to the medical geology of a complex megasite. From a scientific perspective, the NAS analysis is an extremely useful and detailed road map of the twists and turns of analyzing large legacy mining sites. While focused on inactive or legacy issues, the technical analysis is easily applicable to active locations.

One of the critical insights of the report is that approaches to evaluating sites, including their ultimate remediation, are constantly evolving. The disposition and effects of contaminants within a geographical location have evolved significantly over the last 30+ years; hence, decisions are always made based on limited technical information. The information database grows and evolves in sophistication and complexity. In addition, the medical/health effects database does not remain static. For example, background levels of blood lead in US children under age 7 have dramatically fallen almost sevenfold over the last 35 years. Blood lead levels that were considered “normal” in the 1970 s and 1980 s now trigger intense regulatory and medical investigation. The medical toxicology has clearly shifted from a consideration of gross effects to subtle often sub-clinical considerations, i.e., findings not observable on physical examination but instead requiring sophisticated longitudinal testing procedures. At many of the US megasites, e.g., Bunker Hill lead site in the Coeur d’Alene basin, this has been the situation. Medically site investigations have evolved from gross exposure in emergency rooms to long-term medical monitoring protocols for both previous workers and exposed community residents. Similarly, the environmental assessment has transitioned from “hot spot” analysis of gross contamination to concerns over low-level exceedances of background or calculated “safe” soil levels. For example, at the Tacoma smelter in Washington State, United States, arsenic levels in soil greater than 20 ppm are considered a “public health concern.” (“Dirt Alert: Arsenic and lead in Soils” Washington State Department of Ecology, www.ecy.wa.gov/programs/tcp/sites/tacoma_smelter/ts_hp.htm). Similarly, lead in soils above 250 ppm is also considered a “public health concern.” As previously noted in the chapter, background arsenic and lead soil levels often significantly exceed these administrative levels of “public health concern.”

The history of megasite remediation indicates that decades of effort and hundreds of millions of dollars are spent on remediation. Critics often ask whether this concerted effort is “worth it.” As pointed out by the NAS, this question goes beyond matters that science alone can address. Complex economic and societal values tend to dominate the megasites and while “science” is necessary it rarely seems “sufficient” based on the historic record. Thus, medical geology practitioners need to realize that the process may be more art

than science and framed by a heavy dose of legal and political considerations. Megasites, whether Bunker Hill Idaho, Leadville Colorado, Tacoma smelter site, Washington, copper sites in the Gaspé Region of Quebec Canada, all illustrate these observations.

Black Lung Disease

Although the incidence of Coal Worker's Pneumoconiosis (CWP: Black Lung Disease), a progressive, debilitating respiratory problem caused by inhalation of coal dust has decreased dramatically in the United States, it still takes a heavy toll on former miners coal miners. For more than 100 years it has been assumed that black lung disease was caused by the inhalation of the black pulverized particles of coal. Recent research (Huang et al., 2004), however, has shown that CWP may be initiated not by the coal particles but by inhalation of pulverized pyrite, a common coal mineral. The pyrite dissolves in the lung fluids releasing strong acids that irritate the lung tissues. Particles (coal dust, quartz, clay, pyrite, etc.) that then contact the irritated tissues will cause the fibrosis leading to decreased oxygen exchange capacity. Thus, knowledge of the mineral composition of the coal may be a key parameter in anticipating the incidence of CWP. Information on the mineralogy of the coal being mined may provide essential data needed to protect the health of the miners in cost-effective ways thus reducing the enormous financial burden of health care and lost productivity.

Community Effects

Community level exposures to metals generically occur in two forms: (i) anthropogenic, i.e., man-made activity and (ii) natural, i.e., low-level concentrations found in soils. The anthropogenic exposures to metals are generally related to industrial activity, either legacy (e.g., past mining and smelting) or current operations with releases to air, water, and soils. For example, coal combustion associated with electrical power generation is a common source of atmospheric metals emissions, e.g., mercury and selenium. Depending upon the specific form, naturally occurring soil levels of virtually all of the metals

is easily demonstrated. These "background" levels exhibit significant heterogeneity as a function of geography. Hence, background is invariably presented as a wide range as variation in natural mineralization is extremely common. In many situations it is important to fully understand the local and regional background levels of a specific metal as the variability can easily span a factor of 10, i.e., an order of magnitude. This variability becomes important at the two ends of the concentration distribution profile and both critical micronutrient deficiencies, e.g., iodine and selenium, and over exposures, e.g., lead, arsenic, and cadmium are well documented in the literature. A convenient source of high-quality information describing the most important metals can be found at the Agency for Toxic Substance and Disease Registry (ATSDR) site, <http://www.atsdr.cdc.gov/toxpro2.html>. ATSDR has published extensive "Toxicological Profiles" for a wide variety of chemicals, including the medically most significant chemicals.

From a medical toxicology perspective, community exposures are typically focused on four common "heavy metals": (i) arsenic, (ii) cadmium, (iii) lead, and (iv) mercury. Each of these metals has a distinctive fate-transport (how it moves in the environment in air, water, and soil) profile that influences how and where the metal accumulates once released from an anthropogenic source. For example, all of these metals exist in multiple forms that preferentially accumulate in soils, sediments, and biota. The geochemistry of each metal is the key factor and must be understood in order to anticipate whether a potential human health problem actually exists. Many metals are present in forms that have very low bioavailability; hence, while an individual is exposed to the metal, the actual internal dose is quite low and may have little or no discernable clinical effects. Therefore, it is extremely important that specific chemical forms of the metal under consideration are evaluated and characterized. For example, legacy issues (arsenic, cadmium, lead, and mercury) associated with mining and smelting have been a major focus of the regulatory agencies in the United States with development of extensive and multi-million dollar remediation effects. Much of this effort is driven by the observation that some metals, e.g. lead, do not have a known physiological function in humans. In contrast, certain forms of arsenic do have an essential biochemical function in humans.

In general, exposure to the heavy metals is dominated by two routes: inhalation and ingestion. The third pathway, dermal (skin), is usually considered to be extremely minor. Unless there is an ongoing industrial operation, e.g., smelting, incineration, power plant emissions, the inhalation or air pathway is usually quite small relative to ingestion. Ingestion is dominated by food, water, and direct contact with soils. In a non-legacy situation, i.e., significant concentrations above naturally occurring background are not present, overall human exposures are primarily driven by dietary intake. Overall diet intake is a function of the natural level found in soils, the geochemistry of the soils, e.g., pH, carbon content, cationic exchange capacity, and the specific types of crops and/or livestock that are in local or regional production. In addition, some personal choice habits, e.g., smoking, dramatically influence the daily exposure level to specific metals, e.g., cadmium. Smokers have twice the body burden of cadmium versus a non-smoker. In situation associated with daily intake of cadmium from food, the margin of safety becomes significantly narrower for an individual who smokes.

In the northern hemisphere, the legacy problems associated with heavy metals have often dominated the discussion surrounding medical geology. However, the micronutrient deficiency burden of disease at a community level is significantly larger in terms of overall attributable morbidity (illness) and mortality (death). A low daily intake (usually less than 100 µg/day) of a wide variety of metals, e.g., Fe, I, Se, Cu, Zn, CO, Mn, and Mo, is essential for normal health and wellness. The normal daily intake of these metals comes from diet. In areas that have naturally occurring deficiencies in these metals a variety of gross and subtle clinical effects can be found. Iron and iodine deficiency are two of the most common micronutrient deficiencies, particularly. In rural sub-Saharan Africa, geographically distributed pockets of micronutrient deficiencies can be found where there is a largely rural subsistence economy and soils are deficient in one or more of the essential metals.

For example, selenium serves an extremely important role in number of important physiologically important processes, particularly enzymes involved in antioxidant defense mechanisms, thyroid hormone metabolism, and redox control of intracellular reactions (ATSDR, Toxicological Profile for Selenium,

2003). Both excessive intake and deficiency scenarios are possible and have been clinically documented. The creation of an excess or deficiency risk is largely a function of background soil concentration, specific soil geochemistry, and daily diet. For humans, meat products generally contain the highest concentration of selenium, while vegetables and fruits contain the lowest. In some areas of the world, e.g., foothills of the Andes Mountains, soils contain elevated levels of selenium and local agricultural products, such as Brazil nuts, can have extremely high levels of selenium (ATSDR, 2003). In the United States, the highest levels of selenium in soil are found in certain areas of the West and Midwest.

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Chapter 1

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