Recent Developments on Arsenic: Contamination and Remediation

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Abstract

Arsenic (As) is widely known for its adverse effects on human health, affecting millions of people around the world. In Asia the consumption of groundwater (through wells) in an attempt to replace polluted surface water supplies has resulted in widespread As poisoning. Both, the United States Environmental Protection Agency (US-EPA) and the World Health Organization (WHO) have established the As level for drinking water at 10 μg L^{-1}. Unfortunately, some developing countries still use the old standard of 50 μg L^{-1}, primarily because of economical factors that prevent access to new technologies. Given the importance of As as a global environmental toxicant to bioorganisms, we present a brief review about its origin, anthropogenic sources, chemistry, and concentration in soils and waters around the world. The review also discusses the latest analytical methodologies for As determination and some removal mechanisms – with emphasis on phytoremediation.

Origin of Arsenic in soil

Arsenic (As) can be present in soils, air and water as a metalloid and as chemical compounds of both inorganic and organic forms (Matschullat, 2000; Miteva, et al., 2005). Arsenic ranks twentieth in abundance of elements in the earth's crust, fourteenth in seawater and is the twelfth most abundant element in the human body (Mandal and Suzuki, 2002). Despite its abundance, it is one of the most toxic elements encountered in the environment (Cullen and Reimer, 1989, Dermatas, et al., 2004; Hudson-Edwards, et al., 2004). Arsenic can enter terrestrial and aquatic environments through both natural geologic processes (geogenic) and human (anthropogenic) activities. The natural pool of As in surface soils arose from the net of geological, hydrological and soil-forming biogeochemical processes. Under typical soil-forming conditions, the nature of soil As is controlled by the lithology of the parent rock materials, volcanic activity, weathering history, transport, sorption, biological activity and precipitation (Kabata-Pendias and Adriano, 1995). The average As content in the earth's crust was estimated to be about 1.8 mg Kg^{-1} (Greenwood and Earnshaw, 1984). A similar value of 1.5 mg Kg^{-1} was suggested by Onishi (1969) for igneous rocks. Higher As levels were detected in sedimentary rocks and values as high as 13 mg Kg^{-1} (Onishi, 1969) are common for clay-rich rocks. Since As accumulates due to weathering and translocation in colloid fractions, its concentration is usually higher in soils than in parent rocks (Yan-Chu, 1994). More recently, Smith, et al. (1998a) and Zhang, et al. (2002) suggested that as a result of the variability in these processes, the distribution of As in sedimentary rocks is highly variable. Arsenic concentrations range from 1.7 to 400 mg Kg^{-1} in sedimentary rocks, and from 1.3 to 3.0 mg Kg^{-1} in the igneous rocks. The national academy of sciences, medical

and biological effects of environmental pollutants (2000), established the average of As content of the Earth's crust as 2.5 mg Kg^{-1}. However, more recently, Nagy, et al. (2005) proposed that the total As in the earth's crust ranged from 45 to 3275 mg Kg^{-1}. Concentrations of As in non-contaminated soils range from 0.1 to 40 mg Kg^{-1} (Kabata-Pendias and Pendias, 1992), and Fitz and Wenzel (2002) suggested a new value of <10 mg Kg^{-1}. Arsenic is also commonly associated with sulfides, e.g. in sulfidic ore deposits. Other natural sources of As include volcanic activities, wind-born soil particles, sea salt sprays and microbial volatilization of As (Nriagu, 1990; Frankenberger and Arshad, 2002). Arsenic is also a typical component of the thermal waters, its concentration can reach up to 47 mg L^{-1} in carbonaceous chloride mineral springs (Baskov and Surikow, 1989). Arsenic in the environment is often associated with other elements, such as gold (Au), silver (Ag), copper (Cu) and uranium (U). Uranium mining and processing activities can raise As concentrations in the vicinity of mining sites (Pichler, et al., 2001; Moldovan, et al., 2003). Arsenic concentrations in environmental media are presented in Table 1. Arsenic occurs as a major constituent in more than 200 minerals, including elemental As, arsenides, sulphides, oxides, arsenates and arsenites. A list of some of the most common As minerals is given in Table 2. Arsenopyrite (FeAsS), realgar (As_2S_2) and orpiment (As_2S_3) are the most important of these minerals. They may be considered as As ores because of the high amount of As in these compounds (Hossain, 2005). Arsenic may be released to soil, surface water, groundwater, and the atmosphere from sulfide ores of other metals including Cu, Pb, Ag and Au. (Ning, 2002). Where arsenopyrite is present in sulphide ores associated with sediment-hosted Au deposits, it tends to be the earliest-formed mineral, derived from hydrothermal solutions and formed at temperatures typically of 100°C or more (Smedley and Kinniburgh, 2002).

Table 1. Arsenic concentrations in environmental media (USEPA, 2000).

Environmental media	Arsenic concentration range
Air, ng m^{-3}	1.5-53
Rain from unpolluted ocean air, ugL^{-1} (ppb)	0.019
Rain from terrestrial air, ugL^{-1}	0.46
Rivers, ugL^{-1}	0.20-264
Lakes, ugL^{-1}	0.38-1000
Ground (well) water, ugL^{-1}	1.0-1000
Seawater, ugL^{-1}	0.15-6.0
Soil, $mgKg^{-1}$	0.1-1000
Stream/river sediment, $mgKg^{-1}$	5.0-4000
Lake sediment, $mgKg^{-1}$	2.0-300
Igneous rock, $mgKg^{-1}$	0.3-113
Metamorphic rock, $mgKg^{-1}$	0.0-143
Sedimentary rock, $mgKg^{-1}$	0.1-490

| Biota – green algae, mgKg^{-1} | 0.5-5.0 |
| Biota – brown algae, mgKg^{-1} | 30 |

Table 2. Major arsenic minerals occurring in nature (Smedley and Kinniburgh, 2002).

Mineral	Composition	Occurrence
Native arsenic	As	Hydrothermal veins
Niciolite	NiAs	Vein deposits and norites
Realgar	AsS	Vein deposits, often associated with orpiment, clays and limestones, also deposits from hot springs.
Orpiment	As_2S_3	Hydrothermal veins, hot springs, volcanic sublimation products.
Cobaltite	CoAsS	High-temperature deposits, metamorphic rocks.
Arsenopyrite	FeAsS	The most abundant As mineral, dominantly in mineral veins.
Tennantite	$(Cu, Fe)_{12}As_4S_{13}$	Hydrothermal veins.
Enargite	Cu_3AsS_4	Hydrothermal veins.
Arsenolite	As_2O_3	Secondary mineral formed by oxidation of arsenopyrite, native arsenic and other As minerals.
Claudetite	As_2O_3	Secondary mineral formed by oxidation of realgar, arsenopyrite and other As minerals.
Scorodite	$FeAsO_4.2H_2O$	Secondary mineral
Annabergite	$(Ni,Co)_3(AsO_4)_2.8H_2O$	Secondary mineral
Hoernesite	$Mg_3(AsO_4)_2.8H_2O$	Secondary mineral, smelter wastes.
Haematilite	$(Mn,Mg)_4Al(AsO_4)(OH)_8$	
Conichalcite	$CaCu(AsO_4)(OH)$	Secondary mineral
Pharmacosiderite	$Fe_3(AsO_4)_2(OH)_3.5H_2O$	Oxidation product of arsenopyrite and other As minerals.

The primary anthropogenic contributions of As to soils are from the combustion of municipal solid waste, application of arsenical pesticides (herbicides, fungicides and insecticides) (Matera and Le Hecho, 2001), land application of solid waste/sewage sludge, river and irrigation waters (Kabata-Pendias and Adriano, 1995), mining and

smelting of As-containing ores, combustion of fossil fuels (especially coal), land filling of industrial wastes, release or disposal of chemical warfare agents (Goh and Lim, 2005), manufacturing of metals and alloys, petroleum refining, and pharmaceutical manufacturing (Ning, 2002). Another potential contributing source of As in soil is the current use of chromated copper arsenate (CCA) as wood preservative (Dobran and Zagury, 2005). Most agricultural uses of As have been banned in the USA, however, sodium salts of methylarsonic acid are still used in cotton fields as herbicides and for golf course pest maintenance. Organic As is also a constituent of feed additives for poultry and swine for the control of coccidian intestinal parasites and to improve feed efficiency (Wershaw, et al., 1999), and appears to concentrate in the resultant animal wastes. There is a significant use of As in the production of lead-acid batteries, while small amounts of very pure As metal are used to produce gallium arsenide, which is a semiconductor used in computers and other electronic applications (Ning, 2002).

Historically, the mining and smelting of trace elements has created soil contamination problems of greatest magnitude. Fine particles selectively eroded from the mining waste-rock, tailings and slag have the potential to contaminate nearby soils or migrate as sediments in surface waters, greatly enlarging the area affected by the original mining activities. Secondary contamination often occurs in groundwater beneath or down gradient open pits and ponds. Sediments in river channels and reservoirs, and floodplain are also affected by As derived from mining operations (Pierzynski, et al., 2005).

Even though industrial use of As has decreased in recent years, it remains a significant source for some human health problems (Karim, 2000). In an effort to better protect public health, and based on recent toxicological data the US-EPA promulgated a reduction in the Safe Drinking Water Act Maximum Contaminant Level (MCL) for As from 50 to 10 $\mu g\ L^{-1}$ (USEPA, 2002). This standard became effective in January 2006. The World Health Organization (WHO) As drinking water limit is also set at 10 $\mu g\ L^{-1}$ (Le, 2002). Table 3 shows various regulatory standard for drinking water and soils (Matschullat, et al., 2000).

Table 3. Drinking water limits and soil threshold values for As (Matschullat, et al., 2000).

Water ($\mu g\ L^{-1}$)	WHO*	EU	NL	TVO-D	DVGW
As	10	50	10-60	10	10-30
Soil (mg Kg^{-1})	Cal.Ass	EU	NL	KSVO-D	D-Test
As	500	-	29-55	20	20-130

* WHO World Health Organization, drinking water guidelines; EU: European Union drinking water guidelines and soil threshold values; NL: Dutch standards for groundwater concentrations and permissible soil concentrations (the first numbers refer to reference values, the second to maximum permissible levels); TVO-D: German drinking water standards; DVGW: German surface water (raw water) guidelines (for ranges see NL); Cal.Ass.: Californian Assessment Manual Standards (threshold value for dangerous total concentrations TTLC); KSVO-D: German threshold values for maximum permissible soil concentrations; D-Test: German threshold values for different soil uses (low= children playground, high= industrial area).

Arsenic chemistry

Arsenic, with atomic number 33, and situated in Group 15 (or VA) of the periodic table, may exist in four different oxidation states: (-III), (0), (III), and (V), however, oxidized As(III) and As(V) are the most widespread forms in nature. Arsenate, As(V), is a form of As with many industrial/commercial applications such as agricultural pesticides, glass manufacturing, and Cu refining (Conner, 1990; Dutré, et al., 1999). Arsenate is also the prevalent form in soils under oxidizing conditions (Pongratz, 1998; Smith, et al., 1998a; Turpeinen, et al., 1999, 2002), and dominates the soil solid phase (Montperrus, et al., 2002). Arsenite, As(III), on the other hand, is expected to be the primary form of As encountered in waste environments (Dermatas, et al., 2004) and under reducing conditions, such as water-saturated soils or soils with significant organic matter or waste (Smith, et al., 1998a). Arsenite, is known to be more toxic and mobile than arsenate (Panstar-Kallio and Manninen, 1997; Stronach, et al., 1997). In general, inorganic As species are more mobile and toxic than organic forms to living organisms, including plants, animals and humans (Meharg and Hartley-Whitaker, 2002). Chemical structures of some common As compounds are listed in Figure 1 (Goessler and Kuehnelt, 2002).
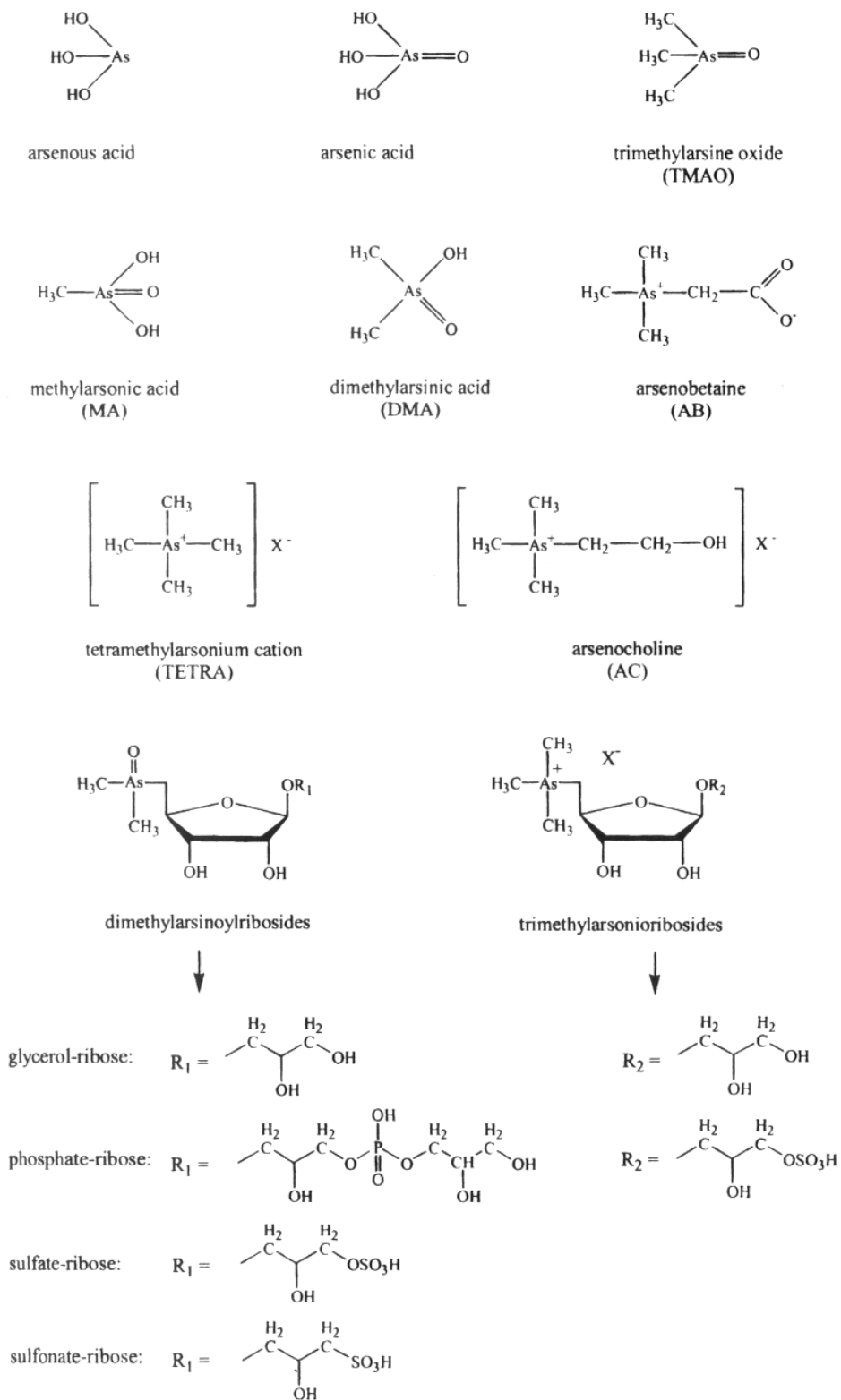
Figure 1. Arsenic compounds commonly detected in the environment (Abbreviations are in parenthesis) (Goessler and Kuehnelt, 2002).

Important factors affecting As chemistry, and its mobility in soils, are soil solution chemistry (pH and redox conditions), solid composition, As-bearing phases, adsorption and desorption, and biological transformations, volatilization, and cycling of As in soil (Sadiq, 1997). Metal sulfide and sulfide concentrations, temperature, salinity and distribution and composition of biota appear to be significant factors that determine the fate and transport of As (Ning, 2002). In surface waters, additional factors include total suspended sediment, seasonal water flow volumes and rates, and time of day. Sorption of As to suspended sediment may strongly affect the fate and transport of As in surface water systems (Nimick, et al., 1998). However, in situations where suspended sediment loads are higher, or As concentrations and pH levels are lower; As is more likely to be present in a suspended particulate phase than the dissolved phase (Ning, 2002). Soil organic matter may be also an important factor affecting As chemistry (Goh and Lim, 2005), and specifically influences the formation of As(III) in aerobic environments, by mediating the reduction of As(V) to As(III). Organic matter, as an important surface soil component, may impact on the redox transformations of As and its biomethylation, thus, affecting As toxicity and its fate in soils (Dobran and Zagury, 2005).

Arsenic in soils may have different physicochemical forms, which are associated with various soils constituents. It is the chemical forms of As associated with various soil phases, rather than its total concentration, that affects its mobility, bioavailability and toxicity to the biosphere (Culler and Reimer, 1989; Goh and Lim, 2005). A number of studies have reported the mobilization and attenuation of As in the fine and coarse soil fractions (Lombi, et al., 2000; Bhattacharya, et al., 2002; Cai, et al., 2002). According to Lombi, et al. (2000), the coarse textured soils are likely to yield a higher fraction of readily mobile As, while As in the fine textured soils is relatively immobile, but can be released upon changes in the subsurface geochemical environment.

Inorganic As (arsenate and arsenite) is highly toxic to plants because it uncouples phosphorylation and inhibits phosphate uptake. At higher concentrations, As interferes with plant metabolic processes and inhibits growth. Under severe conditions it may lead to plant death (Dermatas, et al., 2004).

Adsorption of arsenate ($HAsO_4^{2-}$) onto soil particles is dependent on various parameters, such as Al and Fe oxides, clay content of soils (Jian, et al., 2005) and soil pH (Baroni, et al., 2004). According to Elkhatib, et al. (1984), the pH, redox conditions and Fe-oxide content in soil are the most important features controlling arsenate adsorption. Its availability for uptake by plants is affected by several factors, such as the source, chemical speciation and soil parameters (pH, EC, organic matter, and colloid contents, soil texture and drainage conditions) (Eisler, 1994; Mitchell and Barr, 1995). Arsenate, the dominant form of As in aerated conditions, is taken up by plants via the phosphate transport system in plant roots, because of the chemical similarity between arsenate and phosphate (Dixon, 1997). In *Pteris vittata* (brake fern), As(V) is converted to As(III) shortly before or after it is rapidly translocated from root to shoot, where arsenite accumulates in the epidermal cell of the fronds (Gumaelius, et al. 2004) and interferes with metabolic processes (Meharg, et al., 1994; Meharg and Macnair, 1992). In some other plants, As inhibits plant growth and fruit yield (Miteva, et al., 2005).

In addition to geochemical factors, microbial agents can influence the oxidation state of As in water, and can mediate the methylation of inorganic As to form organic As

compounds (Ning, 2002). Microorganisms can oxidize arsenite to arsenate; reduce arsenate to arsenite or even arsine (AsH_3). Bacteria and fungi can reduce arsenate to volatile methylarsines. Marine algae transform arsenate into non-volatile methylated As compounds such as methylarsionic acid ($CH_3AsO(OH)_2$) and dimethylarsinic acid (($CH_3)_2AsO(OH)$)) in seawater.

Arsenic concentrations in surface water and groundwater depend on daily and seasonal variations in raw water input (McNeill, et al., 2002). For example, Fuller, et al. (1991) reported diurnal variations in As of 39 – 50 and 57 – 83 µg L^{-1} in a stream. One possible reason for seasonal As concentration variations is uptake and release of As by aquatic plants. These plants may absorb As in the spring and summer, causing a slight decrease in As concentrations in the water (Shibata, et al., 1996). Some concentration variations are 11 – 21 and 16 – 63 µg L^{-1} in surface waters (McLaren and Kim, 1995) and 10 – 220 µg L^{-1} in groundwater (Gibbs and Scanlan, 1994). Variations in As concentration and speciation is becoming increasingly important to understand in ensuring attainment of water quality standards, especially for drinking water.

Arsenic Concentration in Soils Around the World

Arsenic, is a significant contaminant of soils and groundwater in many regions of the world, see Figure 2. Depending on the country, exposure to As has come from natural sources, from industrial sources or from food and beverages, see Table 4. High concentrations of As in drinking water (above 50 µg L^{-1}) have been reported in several countries, including Argentina, Chile, China, Japan, Mexico, Poland, Mongolia, Nepal, Taiwan, Vietnam, and some parts of the United States. The world's largest As health issues are the contamination of drinking water aquifers in Bangladesh and West Bengal, India, potentially affecting millions of people (Anawar, et al., 2002; Roychowdhury, et al., 2002; Mitra, et al., 2002; Pandey, et al., 2002; Chakraborti, et al., 2001; Smith, et al., 2001; Mudur, 2000; Chowdhury et al, 2000; Tchounwou, et al., 1999). Localized groundwater As problems are being reported by some countries and new cases are continuing to be discovered. Many countries, particularly developing ones, still use the 50 µgL^{-1} of As standard, in part because of lack of adequate testing facilities for lower As concentrations (Narcise, et al., 2005). Until recently, As was not traditionally on the list of analytes routinely tested by water-quality laboratories. Thus, many water sources with high As might have been missed (Smedley and Kinniburgh, 2002). Paradoxically, high As levels in groundwater are not necessarily related to areas of high As concentrations in the source rocks or sediments. Distinctive groundwater As problems occur under both reducing and oxidizing conditions in both humid/temperate and arid climates (Smedley and Kinniburgh, 2002).
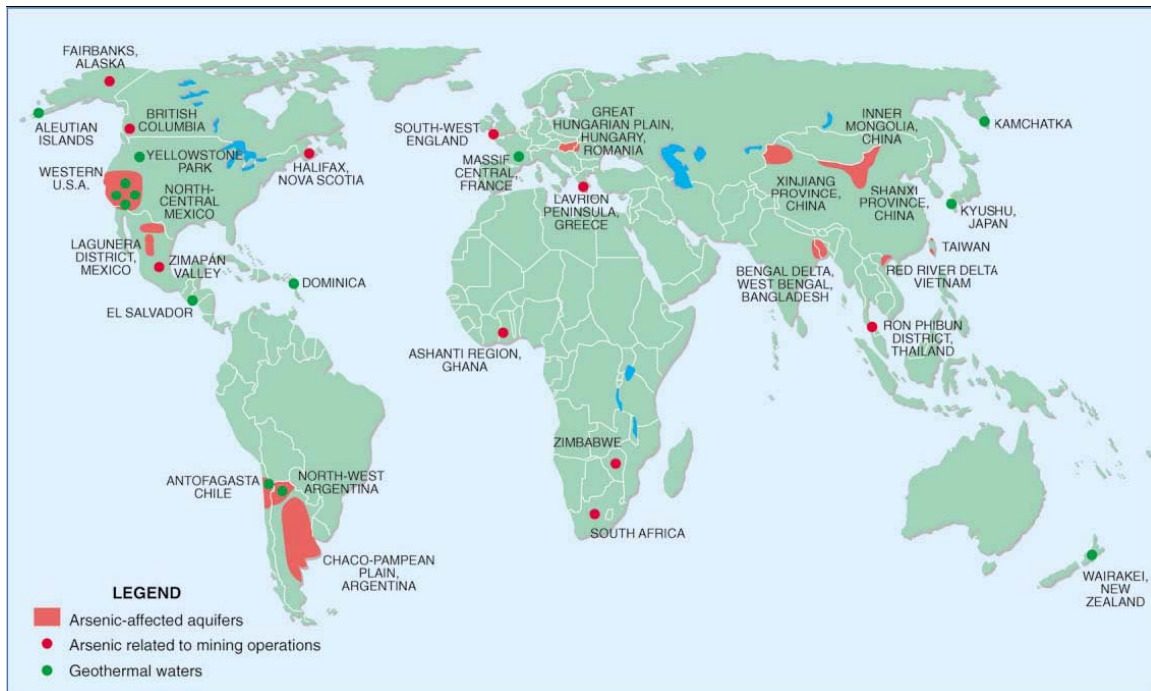
Figure 2. Distribution of documented world problems with As in groundwater in major aquifers as well as water and environmental problems related to mining and geothermal sources. Areas in blue are lakes. (Adapted from Smedley and Kinniburgh, 2002).

Table 4. Arsenic concentrations from different sources in the world (Hossain, 2005).

Location	Natural groundwater As contamination (mgL^{-1})	As contamination from industrial sources (mgKg^{-1})	As contamination in food (mgKg^{-1}) and beverages (mgL^{-1})
Taiwan	0.01-1.82		
Chile	0.8		
West Bengal	0.05-0.55		
Mexico	0.5-3.7	4.0-6.0	
Argentina	0.1		
USA (Utah)	0.18-0.21		
USA (Oregon)	0.05-1.7		
USA (California)	0.05-1.4		
Canada (Ontario)	0.10-0.41	20.0-82.0	
Canada (Nova Scotia)	>3.00		
Hungary	0.06-4.0		
New Zealand	8.5		
USA (Alaska)	0.05-0.07		

China			Ghizhou: 100-9600
	2.20-20.0		Yunan: 300-1100
Japan	0.01-0.29	0.025-4.0	Soysauce: 5.6-71.6
			Milk: 13.5-21
Vietnam	0.01-3.05		
Thailand		0.05-5.0	
Philippines		0.1	
India (Calcuta Mitra)		0.05-58.0	
India (Madhya Pradesh)		0.88	
Czechoslovakia		900-1500	
Greece		1480-3800	
Ghana		<0.002-0.18	
Scotland		0.52-64.0	
Bulgaria		0.75-1.50	
England			Milk: 1.14-9.12

The following discussion will present relevant As soil and water studies from around the world. We will first discuss the Bengal Delta area of Bangladesh and West Bengal, India, where the As contamination is a serious problem affecting millions of people.

Bengal Delta Region

The As calamity in Bangladesh, and adjacent West Bengal, India can be described as one of the largest known mass poisoning in human history, with an estimated 35 – 77 million people being exposed to As-contaminated drinking water (Rabbani, et al., 2002). A map of the affected region showing the range of As concentration in groundwater is provided as Figure 3. Most rural Bangladesh derive their drinking water from shallow tube wells drilled into the alluvial and deltaic deposits that constitute a large portion of the country. The greatest concentration of affected wells is in the south and east of Bangladesh, with a median As concentration in groundwater of 135 μg L^{-1}. Over 60% of the wells in seriously affected districts contain As concentrations exceeding 1000 μg L^{-1} (Kinniburg and Kosmus, 2002). Low As concentrations are most common in groundwater from northern Bangladesh and the aquifers in Plio-Pleistocene sediments of the uplifted Barind and Madhupur Tracts of North Central Bangladesh (Smedley and Kinniburgh, 2002). Populations in rural Bangladesh are likely to be affected by drinking and cooking with contaminated water from the tube wells and through consumption of contaminated foods. However, the bioavailability of As in cooked foods, and the As risks to human health remain to be determined (Das, et al., 2004).

Arsenic occurs naturally in the sediments of Bangladesh bound to amorphous iron oxyhydroxide. Due to the strongly reducing nature of groundwater in Bangladesh, this

compound tends to break down and release As into the groundwater (Nickson et al., 1998). Although As occurs in alluvial sediments, its origin must be the outcrops of hard rocks higher up the Ganges catchments that were eroded in the recent geological past and then re-deposited in West Bengal and Bangladesh by the ancient courses of the Ganges. At present, these source rocks have not been identified. It is also important to understand that As does not occur at all depths in the alluvial sediments (Jakariya, 2000). High concentrations of As are often restricted mainly to the shallow aquifer (less than 50 meters deep) (BGS and DPHE, 2001).
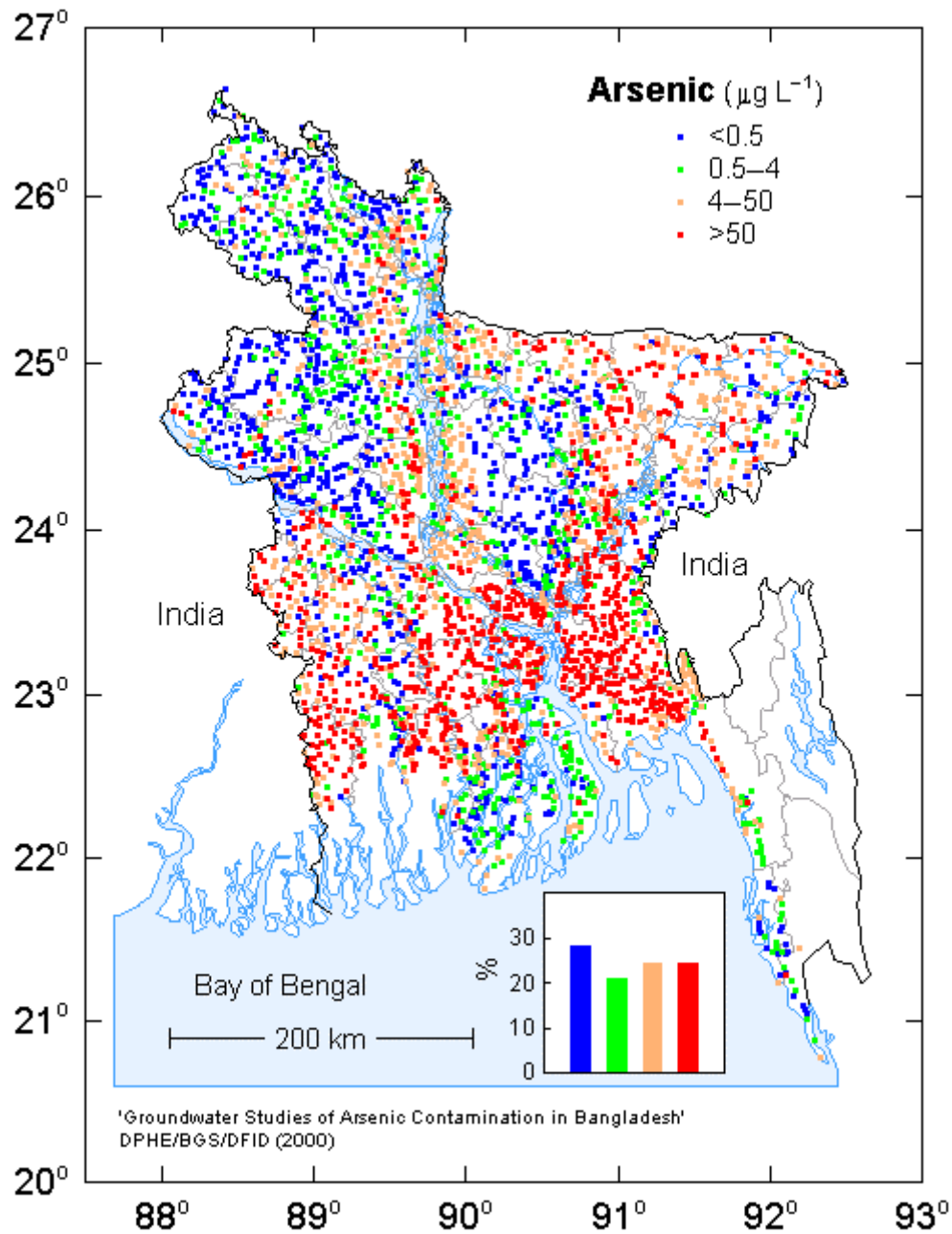
Figure 3. Arsenic concentrations in groundwater in Bangladesh (BGS and DPHE, 2001).

However, the origin of As in the groundwater is more complex. Indiscriminate use of agro-chemicals in the agricultural field for higher rice production and excessive use of groundwater for irrigation (an oxidation process), may also release As to groundwater (Jakariya, 2000). Nevertheless, most authorities believe that long-term geochemical changes led to the release of As from its core compound (arsenopyrites) via oxidation by reaching the underground aquifers through the tube well conduits (Mandal, et al., 1996). The other theory indicates that reduction of iron and manganese oxyhydroxides and their subsequent dissolution are associated with As release to groundwater (Kinniburg and Smedley, 2001). Swartz, et al. (2004) hypothesize that past or ongoing reductive dissolution of ferric hydroxide minerals has diminished the As sorption capacity of the shallow aquifer, leading to increased soluble As levels. According to BGS (2000), the groundwater As problem in Bangladesh arises from a combination of many factors: a source of As (As is present in the aquifer sediments), mobilization (As is released from the sediments to the groundwater) and transport (As is flushed in the natural groundwater circulation). The main cause of As contamination should be illuminated, so different remediation options can be implemented (Jakariya, 2000).

In the past (40 to 45 years ago), agriculture in West Bengal, India, relied on rain. Each year, there was only one crop following the monsoon. At present, to meet the food demands of the increasing population, the growing season has been expanded from one to four or five crops per year. Rain alone can no longer meet the water demand of such intensive agriculture. Thus, groundwater is being used to supplement the rainwater supplies (Roychowdhury, et al., 2005). West Bengal and Bangladesh rely heavily on groundwater for public drinking water supply. Groundwater development has been actively encouraged in the region over the past few decades by government and other agencies as an alternative to polluted surface water, which may cause water-borne diseases (Smedley and Kinniburgh, 2002). Big cities like Calcutta and Dhaka fortunately draw their water from older sediments that do not have As contamination problems. Although available data are difficult to assess, indications are that As enrichment is not as severe in West Bengal as in most affected districts of Bangladesh. The affected groundwater in Bengal Basin is associated with sediments having total As concentrations 2-20 mg Kg^{-1}.

Other Asian Areas

Active volcanoes in Indonesia, in the area of Kawah Putih –West Java, are capable of producing natural environments where concentrations of many elements far exceed common geological background levels. Acid crater lakes can be prime sources of volcanogenic pollutants, as they may contain heavy metals and other toxic elements in extremely high concentrations, including As (up to 1170 mgL^{-1}), Cu and other trace metals (Sriwana, et al., 1998).

In Vietnam, the aquifers under large deltas of the Mekong and Red Rivers are now widely exploited for drinking water. The total number of tube wells in Vietnam is unknown but could be over one million, and perhaps 150,000 in the Red River delta alone (Smedley and Kinniburgh, 2002). High concentrations of As, Mn and Ba were

found in tube-well water and human hair in suburban areas of Hanoi, Vietnam. In the Red River delta, Berg et al. (2001) found As concentrations up to 3050 µgL^{-1} in groundwater. These high levels are comparable to those observed in Bangladesh and West Bengal, India. The Red River delta is home to 11 million people, and therefore the potential health risk to the population consuming As-contaminated groundwater is of great concern, yet little or no information o the extent of the problem is available (Agusa, et al., 2006). Similarly, little is known about the As concentrations in groundwater from the middle and upper parts of the Mekong Delta (and into adjacent Cambodia and Laos) and other smaller alluvial aquifers in Vietnam (Smedley and Kinniburgh, 2002).

Thailand is one of several countries in the Southeast Asia that mines tin (Sn). The waste piles from tin mining are high in As (as arsenopyrite) which leaches out and contaminates local soil and groundwater (Williams, et al., 1996; Francesconi, et al., 2002). The groundwater serves as a water source for local people, in the Ron Phibun District (Nakorn Si Thammarat Province) and the Bannang Sata District (Yala Province) of southern Thailand (Visoottiviseth, et al., 2002). In 1996, more than 1000 people in the Ron Phibun District were diagnosed with As-related skin disorders, and the population at risk was estimated at 30,000 (Williams, et al., 1996). Arsenic concentrations up to 5000 µg L^{-1} have been found in shallow groundwaters overlying Quaternary alluvial sediments affected by Sn-mining operations (Smedley and Kinniburgh, 2002).

High As concentrations have been found in groundwater from Inner Mongolia, Xinjiang and Shanxi Provinces, China (Smedley, et al., 2001; Niu, et al., 1997). The first cases were recognized in Xinjiang Province in the early 1980s (Smedley and Kinniburgh, 2002). Wang (1984) found As concentrations up to 1200 µg L^{-1} in groundwater from the province. Wang and Huang (1994) reported As concentrations of between 40 and 750 µg L^{-1} in deep artesian groundwater from Dzungaria Basin on the north of the Tianshan Mountains. Artesian groundwater has been used for drinking in the region since 1960, and chronic health problems have been identified as a result (Wang and Huang, 1994). It is reported that in the vicinity of an As mine in Hinan, China, nearly 35% of the local population had severe arsenism, and that percentage increased with age (Geng, et al., 2005). It is believed that the soil-plant transfer pathway is mainly responsible for human exposure to As (Geng, et al., 2005).

Oceania

In Australia, As-based pesticides were historically used to control ticks, fleas and lice in the cattle and sheep, resulting in high As contamination in soils up to 5,000 mg Kg^{-1} at former cattle dip sites in Northern New South Wales (McLaren, et al., 1998; Smith, et al., 1999). Inorganic As-based herbicides were historically used as non-selective soil sterilants and weed killers in Australia. In the state of South Australia, As-based herbicides were widely applied to railway tracks and sidings to control plant growth as a part of fire prevention maintenance programs. Such repeated applications resulted in the contamination of a large area with As concentrations ranging between 20 and 1000 mg Kg^{-1} (Smith, et al., 2005). Although supplied water to cities is treated to remove As, large numbers of people in peri-urban areas do not have access to public water supplies and

rely on their own wells for drinking water. Residents in urban areas may also use domestic wells for garden irrigation (Appleyard, et al., 2006). A combination of increasing population in urban areas, increasing groundwater abstraction and low rainfall has contributed to elevated As levels in groundwater in the North of Perth, Australia, where concentrations of As in peat commonly exceed 100 mg Kg^{-1}, and over 1000 mg Kg^{-1} in some localities (Appleyard, et al., 2006).

Europe

There are potentially 1.4 million sites within the European Community contaminated by organic and/or trace metal/metalloid pollutants (ETCS, 1998), especially in Eastern Europe (Kramer, 2005). Concentrations of As above 50 $\mu g\ L^{-1}$ have been identified in groundwater from alluvial sediments in the southern part of the Great Hungarian Plain of Hungary and neighboring Romania (Smedley and Kinniburgh, 2002).

Africa

In Africa, As has only been identified as a water-quality problem in some localized areas associated with sulfide mining activities (Smedley, 1996). William and Smith (1994) found concentrations up to 72 mg L^{-1} As in acidic waters of a Au mining area in Zimbabwe. Smedley (1996) reported As concentrations up to 350 $\mu g\ L^{-1}$ in stream waters affected by mining pollution in the Obuasi area of southern Ghana. However, no regions in Africa have been identified with high concentrations of As in groundwater, and no health problems related to groundwater As are yet known. Ghana is the main Au producing country in West Africa, and Au often is in close association with sulfide As minerals, especially arsenopyrite (Smedley, 1996). Groundwater in the Au belt of Ghana is therefore vulnerable to potential As problems as a result of oxidation of sulfide minerals (Smedley, 1996).

South Africa is the world's 6th largest producer of coal; it produces around 220 Mt of coal per year (Wagner and Hlatshwayo, 2005). However, As levels in these Highveld coals are low compared to values from US coals. Nevertheless, US risk-based health studies have not reported health effects from As emissions from their coals (Wagner and Hlatshwayo, 2005).

America

Unrestrained industrialization and urbanization, together with insufficient measures of emission control and pollution abatement have caused serious environmental problems in Brazil (Klumpp, et al., 2003). The hydrothermal Au deposits in the Iron Quadrangle in Brazil (Minas Gerais State) contain As-bearing sulfides such as arsenopyrite, pyrite and pyrrhotite (Vieira, 1988). Mining activities dating back to the 1700s, have yielded an estimated 1.3 million metric tons tailings containing as much as 14,000 mg Kg^{-1} of As (Deschamps, et al., 2002). These mining activities have released As into surface and groundwater, and via atmospheric emissions onto the soils (Deschamps, et al., 2005). Average total soil As concentration above 100 mg Kg^{-1} and As concentrations in local

waters up to several 100 µg L^{-1} are not uncommon (Matschullat, et al., 2000; Deschamps, et al., 2002).

Health problems related to As in drinking water were first recognized in Northern Chile in early 1960s (Borgoño, et al., 1977). This region is a volcanic zone, with a population of approximately 4,000 people (CODEFF, 1990). It is one of the world's most arid zones (Atacama Desert), thus its ecological systems are very fragile (Queirolo, et al., 2000a). Very high As levels (in some cases higher than 2000 µg L^{-1}) in the surface water of rivers in the pre-Andes have been reported (Queirolo, 2000b). Several scattered villages devoted to agriculture, have their irrigation system depending on the availability of water (Queirolo, et al., 2000a). High As concentrations are often accompanied by high salinity and high B concentrations, because of the high evaporation rate, augmented by geothermal As input from the El Tatio field. Arsenic concentrations below 100 µg L^{-1} in either surface waters or ground waters are apparently quite rare, and concentrations up to 21,000 µg L^{-1} have been found (Smedley and Kinniburgh, 2002). It has been estimated that around 7% of all deaths occurring in Antofagasta between 1989 and 1993 were due to past exposure to As in drinking water at concentrations about 500 µg L^{-1} (Smith, et al., 1998b).

The Chaco-Pampean Plain of Central Argentina constitutes perhaps one of the largest regions of high As groundwater known, covering around one million km^2, with As concentrations between 10 – 11500 µg L^{-1} (Smedley and Kinniburgh, 2002). The groundwater often has high salinity and elevated As and other elements (F, V, HCO$_3$, B, Mo). Sediments containing As along with Fe and Mn oxides and hydroxides are thought to be the main source of dissolved As, yet dissolution of volcanic glass has also been cited as a potential source (Nicolli, et al., 1989).

Arsenic in groundwater is becoming a problem in many Mexican regions, La Comarca Lagunera, San Luis Potosi, Salamanca, Andocutin, Zimapán and others (Parga, et al., 2005). Arsenic contamination has been found in well water from several communities ranging from 240 to 1000 µgL^{-1}. This region has substrata rich in As, therefore, As in groundwater is largely the result of minerals dissolving naturally from weathered rocks and soils, resulting in high As in well water (Parga, et al., 2005). Other possible sources of contamination are organoarsenical pesticides (Del Razo, et al., 1997; Loffredo, et al., 2003). In La Comarca Lagunera, thousands of people already have symptoms of As poisoning, and at least two millions are at risks of As contamination from drinking well water (Parga, et al., 2005). In San Luis Potosi, a smelter producing Cu, Pb, and As is located within the urban area. The accumulation of metals in soil (the industry has been operating since 1890) may be a risk to children in the area (Carrizales, et al., 2006). Zimapán Valley is a semiarid area located in Hidalgo State, and is one of the most important mining districts. In 1992 and 1993, the National Commission of Water carried out a water monitoring campaign to detect cholera vibron and included As analysis for the first time in the region (Rodriguez, et al., 2004). Arsenic concentrations greater than the 45 µg L^{-1} Mexican standard for drinking water were found in some wells.

A number of regions of North America are enriched with As, with levels greater than 8 – 10 mgKg^{-1}. The total range of regional As concentrations is from less than 0.5 mgKg^{-1} in Florida and across much of the continental shield from Labrador to Saskatchewan and south into Wisconsin to 50 – 100 mgKg^{-1} in the east central Yuko and on Central Baffin Island to 100 – 200 mgKg^{-1}. Most of the continent has less than 5 mg As Kg^{-1} (Grosz, et al., 2004). Both the Geological Survey of Canada (GSC) and the United States Geological Survey (USGS) have geochemical databases for stream sediments, lake sediments and soils used to produce a map of As concentrations in these materials for the two countries, Figure 4 (GSC, 2002 and USGS, 2002).
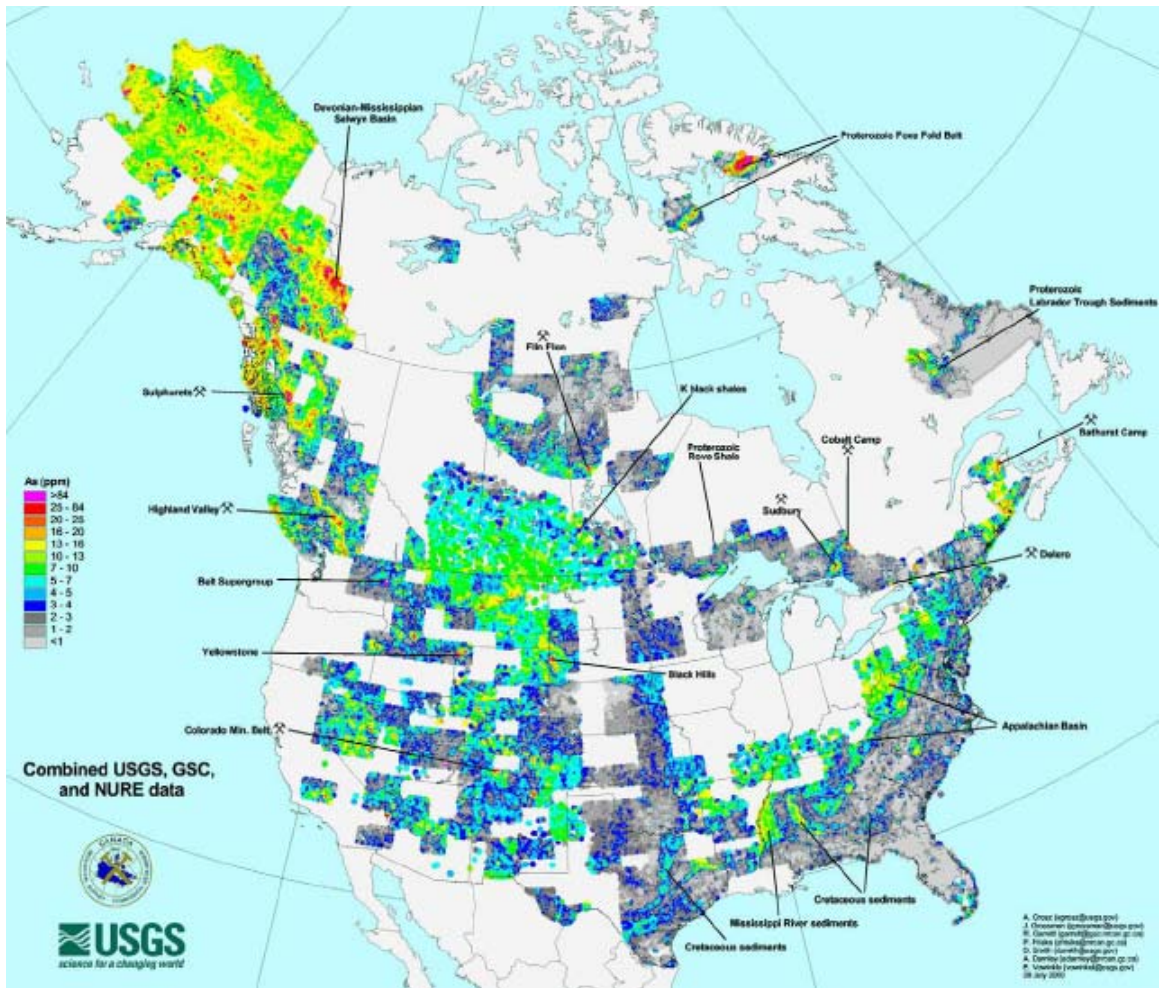

Figure 4. Preliminary map of As in North American soils and sediments

About half of the continental United States drinking water comes from groundwater. Nearly 2.5 million people in the US might be supplied with water with more than 25 µg L^{-1}As (Rasul, et al., 2002). The southeastern US have been cultivated intensively for cotton, sod, and citrus, and contain areas of elevated As suggesting anthropogenic input.

This may be the result of past application of arsenical herbicides such as monosodium metharsenate (MSMA), di-sodium metharsenate (DSMA), and lead arsenate. The upper Coastal Plains throughout the eastern US has also been extensively cultivated and treated with agrochemicals over long periods of time. In New Jersey, for example, it is estimated that 15 million tons of As (contained in 49 million tons of lead arsenate and 18 million tons of calcium arsenate) were applied to soils from 1900 to 1980 (Grosz, et al., 2004). The use of organic and inorganic As as pesticides in the US began in the 1850s and peaked in the 1950s, although As use as a wood preservative has recently been increasing (Welch, et al., 2000).

In Hawaii, chemical controls of weeds on sugar cane lands began in 1913 with sodium arsenite as the choice until about 1945. In the 1930's, sodium chlorate found some use but was limited due to its fire hazard (Hance, 1938; Hanson, 1959). Decades of use of synthetic organic nematicides and herbicides on pineapple and sugar cane cultivation in Hawaii have resulted in the contamination of some groundwater aquifers, however to date, elevated As in Hawaiian aquifers has not been quantified. Groundwater is uniquely important to Hawaii as the source of more than 95% of the drinking water. The discovery of synthetic organic agricultural chemicals in drinking water has led the state to implement a more progressive and proactive approach to pesticide control and registration (Ray, 2005).

Although geogenic background levels of As in Hawaiian soils are typically less than 20 mg Kg^{-1} (average 5 mg As Kg^{-1}), significantly elevated As levels have been identified at a number of locations. On former sugar cane lands in the Kea'au area south of Hilo, Hawaii, soil As levels up to 800 mg Kg^{-1} have been identified (HDOH, 2005). These lands are being used for residential buildings, as well as commercial agriculture (papaya, bananas, macadamia nuts), small business organic farming and family gardening. However, As in these soils, as determined by standard in vitro bioaccessibility tests, (Drexler, 2003; Ruby et al, 1993) indicates that only 2 to 20 percent of total As is bioaccessible (HDOH, 2005). On Oahu and Kauai, soils from former sugar cane locations have been evaluated with As concentrations averaging 80 and 120 mg Kg^{-1}.

Analytical methods for the determination of Arsenic

In order to be able to properly understand the global distribution of As in soils and sediments and its pathways to water, plants and animals, it is important to collect accurate values of total and solid – phase As at both high and low concentrations (Hudson-Edwards, et al., 2004). This is because of As in soils may distribute among various soil components in different physicochemical forms.

European Commission has recommended colorimetry for the analysis of As in soils. X-ray fluorescence spectrometry (XRS) is also used (Black and Craw, 2001). A wide variety of methods exist for extracting and analyzing total As and operationally defined solid fractions of As in soils and sediments (Hudson-Edwards, et al., 2004). The most common methods for extracting total As from soils and sediments involve wet ashing of the sample using one or a combination of acids such as H_2SO_4, HNO_3, HCl, H_3BO_3, HF

and H_2O_2. Ashing can be carried out using hotplate or microwave –digestion ovens (Mucci, et al., 2003).

Different analytical techniques include liquid chromatography systems for separation of various As forms, atomic absorption spectrometry (AAS) equipped with a graphite furnace, inductively coupled plasma-mass spectrometry (ICP-MS) and electroanalytical techniques (Jain and Ali, 2000; Garcia-Manyes, et al., 2002). By coupling liquid chromatography - ultraviolet - hydride generation - and atomic fluorescence spectrometry different As species can be detected. Moreover, the coupling of ICP-MS is quite sensitive, reaching the ng L^{-1} range of As in solution (Garcia-Manyes, et al., 2002).

It is the form of As associated with various soil solid phases, rather than its total As concentration that affects its mobility, bioavailability and toxicity (Goh and Lim, 2005; Cepriá, et al., 2005). This is a major challenge for analytical chemists since the difficulty lies in the extraction of the species from the sample without disturbing equilibrium and changing the physical form (Cepriá, et al., 2005).

Arsenic fractionation or distribution in different soil solid phases can be examined by surface analytical techniques or perhaps a selective sequential extraction (SSE). The SSE has sufficient sensitivity to quantify concentrations of an element in different fractions based on the target binding phases (Keon, et al., 2001). SSE has been successfully employed to determine the source of As in the widespread Bangladesh aquifer system (Swartz et al, 2004). More recently, flow injection (FI) on-line sequential extraction coupled with HG-AFS has been used to demonstrate rapid, automatic and sensitive fractionation of As in soils. Compared with traditional batch-mode sequential extraction and currently available flow though sequential extraction schemes with off-lime detection and quantification, the present methodology offers several advantages, such as minimization of re-adsorption/redistribution, improvement of accuracy, high speed, less sample/reagent consumption, less risk of contamination and analyte loss (Dong and Yan, 2005).

Electroanalytical techniques have been of great interest in monitoring contamination on site (Wang, et al.1996a, b) due to their versatility, and miniaturization possibilities of the electrodes and instruments (Cepriá, et al. 2005). Problems due to sample dissolution or extraction when dealing with solid samples can be overcome with electroanalysis.

In general, a wide variety of methods exist for extracting and analyzing total As and operationally defined solid fractions of As in soils and sediments. Hudson-Edwards, et al. (2004) recommend that complementary techniques (mineralogical and spectroscopic analysis, pore water analysis, and platinum-electrode potential) be carried out to validate the operationally defined sequential extraction results for As.

Remediation of Arsenic Contaminated Soils

Remediation refers to the process or methods for treating contaminants in soil or water such that they are contained, removed, degraded, or rendered less harmful (Pierzynski, et al., 2005). There are several subcategories of remediation. *Site remediation* is often used for processes that contain (i.e. restrict movement) a contaminant but do not necessarily directly affect the contaminant. In contrast, soil and water remediations generally refer to processes that directly treat the medium and affect the contaminant in some way. *In situ*

remediation refers to treatment or stabilization of soil or water contaminants in place, whereas *ex situ remediation* involves physical removal and treatment of either soil or water at another location (Pierzynski, et al., 2005).

Soil contaminated with As has traditionally been addressed with conventional cleanup technologies such as removal (excavation and landfilling) and containment (capping). Due to the high cost of removal, and loss of land use by containment, cost-effective *in-situ* remedies are being explored. It is believed that geochemical fixation and phytoremediation can be developed for cost-effective treatments of As contamination. In fact, phytoremediation has been applied to different contaminants from soil, surface and groundwater, leachate and municipal and industrial waste water (US-EPA, 2002; Terry and Banuelos, 1999; US-EPA, 2000; Dahmani-Muller, et al., 2000; Raskin and Ensley, 2000).

Phytoremediation involves the cultivation of tolerant plants that concentrate soil contaminants in their above ground tissues. At the end of a growth period, plant biomass is harvested, dried or incinerated, and the contaminant-enriched material is deposited in a landfill or added to smelter feed (Kramer, 2005). Cautions must be taken, because combustion of such a waste may release toxic As_2O_3 (Cullen and Reimer, 1989). Marine systems on the other hand, have a particular ability to bio-transform and detoxify inorganic As, presumably as a consequence of their evolving in an As containing environment. Seawater contains approximately 1 μg As L^{-1}, primarily as arsenate (Francesconi and Edmonds, 1997). Arsenite added to seawater, is likely to be quickly converted to arsenate, the more thermodynamically stable form. The first stage of this detoxification process is the formation of arsenosugars by algae, and perhaps other organisms as well, and the final As metabolite appears to be arsenobetaine, a stable non-toxic form of As found in all marine animals (Francesconi and Edmonds, 1997). Some marine unicellular algae can carry out this biotransformation at arsenate concentrations 1000 – fold ambient levels (i.e. at 1000 μg As L^{-1}) (Edmonds, et al., 1997).

Phytoremediation for As (and other toxic elements) can be categorized into five fundamental processes (Salt, et al., 1998; Wenzel et al., 1999; Garbisu, et al., 2002; Raskin and Ensley, 2000): 1) Phytoextraction, which uses pollutant-accumulating plants to extract and translocate pollutants to the harvestable parts. It can be sub-divided into phytoextraction using hyperaccumulator plants and chemically-induced phytoextraction for the accumulation of metals to plants. Induced phytoextraction, however, has not yet been applied to As (Fitz and Wenzel, 2002; Salt, et al., 1998); 2) Phytostabilization, uses pollutant-tolerant plants to mechanically stabilize polluted land in order to prevent bulk erosion, reduce air-borne transport and leaching of pollutants. In contrast to phytoextraction, plants are required to take up only small amounts of As and other metals in order to prevent transfer into the wild-life food chain (Fitz and Wenzel, 2002); 3) Immobilization is the use of plants to decrease the mobility and bioavailability of pollutants by altering soil factors that lower pollutant mobility by formation of precipitates and insoluble compounds and by sorption on roots (Fitz and Wenzel, 2002); 4) Volatilization is the use of plants to volatilize pollutants. Volatilization of As is known to occur in natural environments (Frankenberger and Arshad, 2002); and 5) Rhizofiltration, the use of plant with extensive root systems and high accumulation capacity for contaminants, to absorb and adsorb pollutants, mainly metals, from water

and streams (Salt, et al., 1998; Chen, et al., 2005). The phytoremediation of As contaminated water by rhizofiltration is a relatively new idea, its full scale viability is still unknown (Ma, et al., 2003).

A number of plants have been identified as hyperaccumulators of a variety of metals including Cd, Cr, Cu, Hg, Pb, Ni, Se and Zn (Reeves, et al., 2001). The brake fern (*Pteris vittata*), an efficacious As hyperaccumulator, was discovered in an abandoned wood treatment site in Central Florida, USA (Ma, et al., 2001). Subsequently four other fern species, *Pityrogramma calomelanos* (Visoottiviseth, et al., 2002), *Pteris cretica*, *P. longifolia* and *P. umbrosa* are also been identified as As accumulators (Francesconi, et al., 2002; Zhao, et al., 2002). Table 5 provides an overview on reported shoot, root and substrate concentrations of As hyperaccumulators and As tolerant plants (Fitz and Wenzel, 2002). The brake fern can accumulate between 1442 – 7526 mg As Kg^{-1} in fronds from contaminated soils (Ma, et al., 2001), and up to 27,000 mg As Kg^{-1} in its fronds in hydroponics culture (Caille, et al., 2004). This plant is not only efficient in taking up large amounts of As (up to 2.3% dry plant weight) from soil but also in translocating As to its aboveground biomass (up to 90% of the total As uptake) (Cao, et al., 2004). In hydroponics batch studies, *Pteris* ferns have been shown to rapidly reduce As concentrations from spiked drinking water from as high as 500 µg L^{-1} to less than 2 µg L^{-1} even in the presence of sulfate, nitrate and phosphate (Huang, et al., 2004; Poynton, et al., 2004). However, the phytoremediation potential of *Pteris vittata* has not been tested in soils naturally contaminated with As, which are likely to have a much lower bioavailability of As than soils amended with soluble As (Caille, et al., 2004).

Table 5. Arsenic concentrations in hyperaccumulator and As tolerant plants. (Adapted from Fitz and Wenzel, 2002).

Plant species	As in plants (mg Kg^{1})		As in soil (mg Kg^{-1})	References*
	Frond/shoot	Root		
Hyperaccumulators				
P. vittata	22630		1500	1
	7234	303	97	1
	755		6	1
P. calomelanos	8000	88	135	2
Tolerant plants (non-accumulators)				
Agrostis capillaries	3470		26500	3
Agrostis catellana	170	1000	1700	4
Agrostis delicatula	300	1800	1700	4
Cynodon dactylon	1600	10850	9530	5
Paspalum tuberosum	1130		7670	6
Spergularia grandis	1175		7670	6

*1. Ma, et al., 2001; 2. Francesconi, et al., 2002; 3. Porter and Peterson, 1975; 4. DeKoe, 1994; 5. Jonnalagadda and Nenzou, 1996, 1997; 6. Bech, et al., 1997.

Conclusions

Arsenic, from both anthropogenic and geologic sources, has been considered one of the most toxic elements, affecting millions of people around the world. More sound information related to As is definitely needed. Treatments of residues from smelting or mining; the avoidance of use of agrochemicals containing As; reliable and simple methods for soil/water arsenic testing in field or laboratory, that would allow decision making for remediation; and an adequate disposal plan in the case of phytoremediation are some of the issues that need urgent attention.

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