ARSENIC CONTAMINATION AND ITS RISK MANAGEMENT IN COMPLEX ENVIRONMENTAL SETTINGS

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Contamination of terrestrial and aquatic ecosystems by arsenic (As) is a very sensitive environmental issue due to its adverse impact on human health. Although not anthropogenic in origin, the problem of As contamination in

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groundwaters of West Bengal (India) and Bangladesh has been considered of calamitous proportion because significant segment of the population is at high risk, with untold numbers already suffering from irreversible effects of As poisoning. Elsewhere, indiscriminate disposal of industrial and mining wastes has led to extensive contamination of lands, thereby exacerbating the potential for food chain contamination. With greater public awareness of As poisoning in animal and human nutrition, there has been a growing interest in developing regulatory guidelines and remediation technologies for mitigating As-contaminated ecosystems. Although the immediate needs revolve around the stripping of As from domestic water supplies as exemplified by the affected areas in Bangladesh and West Bengal, a remediation scheme should also be explored to be able to cope with pivotal needs to abate the contamination of soils, sediments, and water and the potential to compromise the quality of the food chain. A range of technologies, including bioremediation, has been applied with varying levels of success either to remove As from the contaminated medium or to reduce its biotoxicity. This review provides general overview of the various biogeochemical processes that regulate As bioavailability to organisms, including microbes, plants, animals and humans. In turn, the role of the source term, chemical form, and chemical species of As are discussed as an overture to As bioavailability. Having laid the fundamental mechanisms and factors regulating As bioavailability, we then assembled the various physical, chemical, and biological mitigative methods that have been demonstrated, some being practical, highlighting their special strengths and potential for more effective and economical widespread applications. Because of the complexity involved in dealing with contaminated sites, exacerbated by site characteristics, nature of hydrogeology, source term, chemical form, land use, and so on, no one remedial technology might suffice. Therefore, we have attempted to offer an "integrated" approach of employing a combination of technologies at multiscalar levels, depending on extenuating circumstance, with the aim of securing viable methods, economically and technologically. Future research needs, especially in the area of As bioavailability and remediation strategies, are identified.

> Arsenic is a unique carcinogen. It is the only known human carcinogen for which there is adequate evidence of carcinogenic risk by both inhalation and ingestion. While arsenic is released to the environment from natural sources such as wind-blown dirt and volcanoes, releases from anthropogenic sources far exceed those from natural sources. Oral exposure of arsenic to human beings however, is usually not the result of anthropogenic activity as it is with many carcinogens, but the result of natural contamination of well-water supplies by arsenic-rich geologic strata.
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> Centeno *et al.* (2002)

I. INTRODUCTION

Arsenic (As) is a toxic metalloid found in rocks, soil, water, sediments, and air. It enters into the terrestrial and aquatic ecosystems through a combination of natural processes such as weathering reactions, biological activity, and volcanic emissions, as well as a result of anthropogenic activities. Excessive use of As-based pesticides and indiscriminate disposal of domestic (sewage) and industrial (timber, tannery, paints, electroplating, etc.) wastes, as well as mining activities, have resulted in widespread As contamination of soils and waterways. Arsenic in terrestrial and aquatic ecosystems attracts worldwide attention primarily because of its adverse impact on human health. The general population may be exposed to As from air, food, and water (Adriano, 2001; Sparks, 1995). Of the various sources of As in the environment, drinking water probably poses the greatest threat to human health (Smedley and Kinniburgh, 2002). People drinking As-contaminated water over prolonged periods often show typical arsenical lesions, which are a late manifestation of As toxicity. Arsenic has been unequivocally demonstrated to be both toxic and carcinogenic to humans and animals.

Although trace levels of As have been shown to be beneficial in plant and animal nutrition (Leonard, 1991; Smith *et al.*, 1998; USEPA, 1993), no comparable data are available for humans (Adriano, 2001), and elevated concentrations of As in the biosphere pose a significant threat to mankind. Arsenic contamination of surface and groundwaters occurs worldwide and has become a sociopolitical issue in several parts of the globe. For example, several million people are at risk from drinking As-contaminated water in West Bengal (India) (Chakraborti *et al.*, 2002; Chatterjee *et al.*, 1995) and Bangladesh (Smith *et al.*, 2000). Scores of people from China (Wang, 1984), Vietnam (Berg *et al.*, 2001), Taiwan (Lu, 1990), Chile (Smith *et al.*, 1998), Argentina (Hopenhayn-Rich *et al.*, 1998), and Mexico (Del Razo *et al.*, 1990) are likely at risk as well.

The problem of As contamination in groundwaters of West Bengal and Bangladesh has been considered of calamitous proportion because a significant segment of the population is at high risk, with untold number already suffering from irreversible effects of As poisoning (Chatterjee *et al.*, 1995). “For many people in Bangladesh it can sometimes literally be a choice between death by arsenic poisoning and death by diarrhea,” says Timothy Claydon, country representative of Water Aid (http://Phys4.Harvard.Edu/~Wilson/Arsenic). Elsewhere, indiscriminate disposal of industrial and mining wastes has led to extensive contamination of lands. Consequently, thousands of As-contaminated sites have been reported around the world (Eisler, 2004; ETCS, 1998; Smith *et al.*, 1998; USEPA, 1997). The economic consequences of As contamination include loss of productivity, healthcare costs, and, most importantly, imposition of As contamination as a nontariff trade barrier, preventing export sales to some countries.

With greater public awareness of As poisoning in animal and human nutrition, there has been growing interest in developing guidelines and remediation technologies for mitigating As-contaminated ecosystems. A range of technologies, including chemical immobilization and bioremediation, has been applied with varying levels of success either to completely remove As from the system or to reduce its biotoxicity. Phytoremediation, an emerging form of bioremediation technology that uses plants to remove or stabilize contaminants, may offer a low-cost and ecologically viable means for the mitigation of As toxicity in the environment.

There have been a number of reviews on As in soil (Matschullat, 2000; Smith *et al.*, 1998) and aquatic (Korte and Fernando, 1991; Smedley and Kinniburgh, 2002) environments. However, there has been no comprehensive review on the biogeochemistry and transformation of As in relation to its remediation. The present review, therefore, aims to integrate fundamental aspects of As transformation and recent developments on As speciation in relation to remediation strategies for the risk management of As-contaminated terrestrial and aquatic ecosystems. The review first discusses the various sources and distribution of As in soil, sediments, and water. The transformation of As in these systems is examined in relation to As speciation and bioavailability. The detrimental effects of As on plant growth, microbial functions, and animal and human health are discussed with relevant examples. Various physical, chemical, and biological techniques available for remediation of As-contaminated sites are synthesized with an aim to develop integrated practical strategies at multiscalar levels to manage As-contaminated sites. Future research needs, especially in the area of As bioavailability and long-term remediation strategies, are identified. The review encourages greater interaction among soil scientists, agronomists, aquatic biogeochemists, and environmental and resource engineers in devising risk management strategies to resolve one of the worst environmental calamities of the 21st century.

II. ORIGIN AND SOURCES OF ARSENIC CONTAMINATION

A range of As compounds, both organic and inorganic, are introduced into the environment through geological (geogenic) and anthropogenic (human activities) sources (Fig. 1). Small amounts of As also enter the soil and water through various biological sources (biogenic) that are rich in As (Table I). Although the anthropogenic source of As contamination is increasingly becoming important, it should be pointed out that the recent episode of extensive As contamination of groundwaters in Bangladesh and West Bengal is of geological origin, transported by rivers from sedimentary rocks in the Himalayas over tens of thousands of years, rather than anthropogenic.

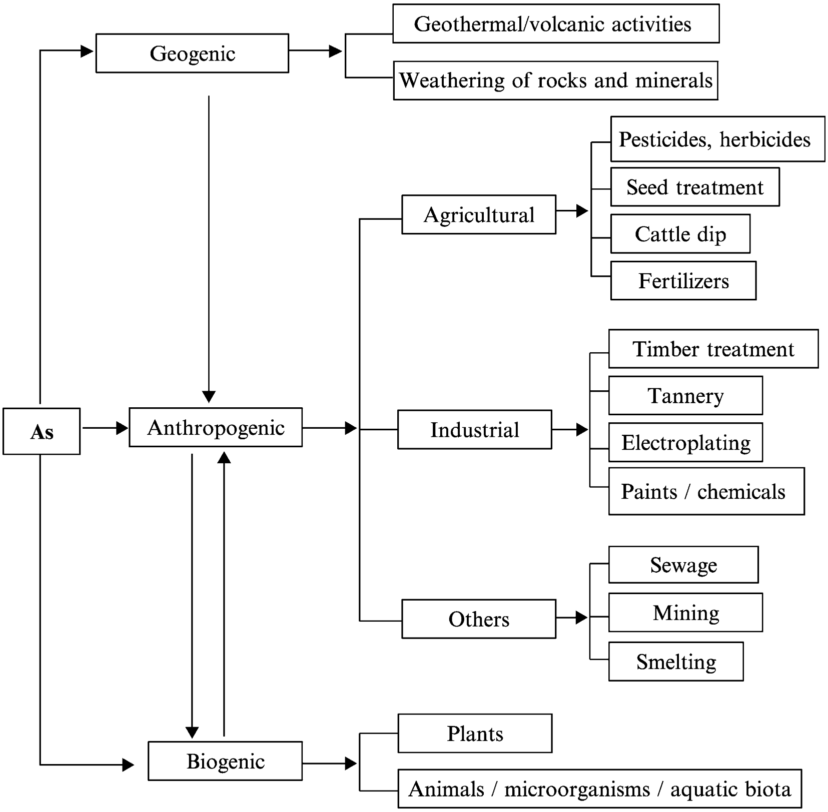

Figure 1 Major sources and routes of arsenic in soil and aquatic ecosystems.

A. GEOGENIC

Arsenic is widely distributed in all geological materials at varying concentrations. An average concentration of 1.5 to 2.0 mg As kg^{-1} is expected in the continental crust of the earth. The mean concentrations of As in igneous rocks range from 1.5 to 3.0 mg kg^{-1}, whereas in sedimentary rocks range from 1.7 to 400 mg kg^{-1} (Smith *et al.*, 1998). Arsenic ranks 52nd in crustal abundance and it is a major constituent in more than 245 minerals (O'Neill, 1995). These are mostly sulfide-containing ores of copper (Cu), nickel (Ni), lead (Pb), cobalt (Co), zinc (Zn), gold (Au), or other base metals. The most important ores of As include pyrites, realgar, and orpiment. Arsenic is introduced into soil and water during the weathering of rocks and minerals followed by subsequent leaching and runoff. Therefore, the primary source of As in soil is the parent (or rock) materials from which it is derived (Yan-Chu, 1994). Geogenic contamination of As in soils (Table II)

Table I
Selected References on Sources of Arsenic in Soil and Aquatic Environments

Source	Concentration (mg kg^{-1})	Reference
Broiler litter	34.6	Jackson and Miller (2000)
Cattle manure (composted)	3.0–5.2	Raven and Loeppert (1997)
Coal	2–825	Adriano *et al.* (1980)
	15,005	Bencko and Symon (1977)
Cow manure	6–8.5	Raven and Loeppert (1997)
Dikes and ores	1242–30,800	Ongley *et al.* (2003)
Earthworms	1358	Langdon *et al.* (2002)
Fly ash	2–6300	Page *et al.* (1979)
FYM from cattle	0.8–2.6	Nicholson *et al.* (1999)
Lake weeds	83–1262	Aggett and Aspell (1980)
Metallurgical ore waste	52,700–63,000	Magalhaes *et al.* (2001)
Mine spoils	>20,000	Porter and Peterson (1975)
Mine tailing	62,350	Kim *et al.* (2002)
	7000	Roussel *et al.* (2000)
Mushroom (edible) from contaminated soil	1420	Larsen *et al.* (1998)
Poultry manure	50	Arai *et al.* (2003)
	16.8	Jackson and Bertsch (2001)
Rice straw	91.8	Abedin *et al.* (2002)
Sewage sludge	11.9–21.0	Department of Health (NZ) (1992); Ross *et al.* (1991)
	8.1–14.3	Caper *et al.* (1978); Raven and Loeppert (1997)

and water (Table III) has been reported in many parts of the world. One typical example is the extensive As contamination of groundwaters in Bangladesh and West Bengal in India.

Based on As geochemistry, three probable mechanisms have been offered for As mobility in groundwaters of West Bengal and Bangladesh (Bose and Sharma, 2002):

i. Mobilization of As due to the oxidation of As-bearing pyrite minerals. Insoluble As-bearing minerals such as arsenopyrite (FeAsS) are rapidly oxidized [Eq. (1)] when exposed to atmosphere, releasing soluble arsenite [As(III)], sulfate (SO_4^{2-}), and ferrous iron [Fe(II)] (Mandal *et al.*, 1996). The dissolution of these As-containing minerals is highly dependent on the availability of oxygen and the rate of oxidation of sulfide (Loeppert, 1997). The released As(III) is partially oxidized to arsenate [As(V)] by microbially mediated reactions (Wilkie and Hering, 1998).

Table II
Selected References on Arsenic Concentration in Contaminated Soils

Country	Source of contamination	As content (mg kg^{-1})	Reference
Australia	Tannery wastes	<1–435	Sadler *et al.* (1994)
Australia	Arsenical pesticides	9.8–124	Bishop and Chisholm (1961)
Australia (NSW)	Mining and processing of arsenopyrite ore	9300	Ashley and Lottermoser (1999)
Australia (NSW)	Cattle dip	37–3542	McLaren *et al.* (1998)
Austria	Ore vein	700–4000	Geiszinger *et al.* (2002)
Bangladesh	Geological	1.7–56.7	Alam and Sattar (2000)
Belgium	Metal alloy and metallurgical industries	36,000	Cappuyns *et al.* (2002)
Belgium	Arsenic factory	25,000–35,000	Dutre *et al.* (1998)
Brazil	Metallurgical plant wastes	636–748	Magalhaes *et al.* (2001)
China	Wastewater	40–120	Jiang and Ho (1983)
England	Tin, copper, and arsenic mining	120–52,600	Kavanagh *et al.* (1997)
England (southwest)	Geological	110	Mitchell and Barr (1995)
Germany	Storage of organoarsenic-based chemical warfare agents	Up to 250,000 (mean 923)	Pitten *et al.* (1999)
Ghana	Mining	2.1–48.9	AmonooNeizer *et al.* (1996)
Ghana	Mining	189–1025	Bowell *et al.* (1994)
India (West Bengal	Geological (through irrigation water)	11.5–28.0	Amit *et al.* (1999); Chatterjee and Mukherjee (1999)
India (West Bengal)	Disposal from arsenical pesticides manufacturing	20,100–35,500	Roychowdhury *et al.* (2002)
Japan	Arsenic mine and smelter	391–459	Hiroki (1993)
Mexico	Mining activities	14,700	Ongley *et al.* (2003)
Mexico	Runoff from mining waste	>2.0	Naranjo-Pulido *et al.* (2002)
New Zealand	Timber treatment with CCA	6100	CMPS & F (1995)
		161–790	Yeates *et al.* (1994)
		376–10,440	Armishaw *et al.*(1994)
		80–5475	McLaren (1992)
Slovakia	Coal-burning power station	8.8–139	Keegan *et al.* (2002)
Thailand (southern)	Geologcal	Up to 5000	Williams *et al.* (1996)
USA	Mine tailing	48–3421	Jones *et al.* (1997)
USA (Colorado)	Pesticide spray	>1000	Folkes *et al.* (2001)
USA (Florida)	Industrial activities	0.2–660	Chirenje *et al.* (2003)
USA (Louisiana)	Arsenic dipping vat	555	Masscheleyn *et al.* (1991)
USA (southern California)	Crude oil storage facility	30–2300	Wellman *et al.* (1999)

Table III
Selected References on Arsenic Concentration in Contaminated Aquatic Media

Country	Water source	Source of contamination	As content (μg liter^{-1})	Reference
Argentina	Groundwater	Geological	3000	Sbarato and Sanchez (2001)
Australia	River sediments	Mining	32.8–42.7	Taylor (1996)
Australia (NSW)	Water sample from a mine shaft and waste dump seepage	Geological	13,900	Ashley and Lottermoser (1999)
Bangladesh	Tube wells	Geological	260–830	Ali and Tarafdar (2003)
Bangladesh	Tube wells	Geological	>50	Yokota *et al.* (2002)
Bangladesh	Groundwater	Geological	0.7–640	Frisbie *et al.* (2002)
Bangladesh	Tube wells	Geological	1–535	Watanabe *et al.* (2001)
Bangladesh	Tube well water	Geological	0.01–0.071	Alam and Sattar (2000)
Brazil	River sediments	Metallurigical plant	347 mg kg^{-1}	Magalhaes *et al.* (2001)
Chile	Natural water	Geological	950–13,080	Munoz *et al.* (2000)
Chile	Drinking water	Geological	750–800	Smith *et al.* (2000)
Chile (north)	Drinking water	Geological	600	Hopenhayn-Rich *et al.* (1996)
China (inner Mongolia)	Groundwater	Geological	1088–1354	Guo *et al.* (2001)
England (SW)	River	Tin mine drainage	Dissolved As(III) 240	Hunt and Howard (1994)
Germany (northern Bavaria)	Deep water wells	Geological	10–150	Heinrichs and Udluft (1999)
India (West Bengal)	Groundwater	Geological	0.5–135.9	Nag *et al.* (1996)

India (West Bengal)	Tube well water	Geological	22–2000	Mazumder *et al.* (1988)
India (West Bengal)	Drinking water	Geological	212	Mahata *et al.* (2003)
India (West Bengal)	Tube well water	Geological	82–170	Roychoudhury *et al.* (2002a)
India (West Bengal)	Tube well water	Geological	85	Roychoudhury *et al.* (2002b)
India (West Bengal)	Tube well water	Geological	2.7–170	Tokunaga *et al.* (2002)
India (West Bengal)	Groundwater	Geological	200–3700	Mandal *et al.* (1996)
Japan	Groundwater	Geological	293	Kondo *et al.* (1999)
Mexico	Well water	Geological	267–1070	Gomez-Arroyo *et al.* (1997)
Nepal	Tube wells	Geological	>10	Neku and Tandukar (2003)
Nepal	Tube wells	Geological	>50	Shrestha *et al.* (2003)
New Zealand	River, Waikato	Geothermal release	3–121	Robinson *et al.* (1995)
New Zealand	Lake Ohakuri	Geothermal release	37–60	Aggett and Aspell (1980)
New Zealand	Sediments from Waikato river	Geothermal	8700–156,100	Robinson *et al.* (1995)
Taiwan	Deep well water	Geological	>10	Wai *et al.* (2003)
Taiwan	Well water	Geological	671	Chen *et al.* (1995)
Turkey	Geothermal water	Geological	1135	Buyuktuncel *et al.* (1997)
USA (California)	Lake	Geological	200 μmol liter^{-1}	Oremland *et al.* (2000)
USA (eastern Wisconsin)	Groundwater from a confined sandstone aquifer	Geological	12,000	Schreiber *et al.* (2000)
USA (Madison)	Groundwater	Natural hydrological and geochemical	16–176	Nimick (1998)
USA (New England)	Groundwater	Geological	>10	Ayotte *et al.* (2003)
USA (New Hampshire)	Well water	Geological	0.003–180	Peters *et al.* (1999)
Vietnam	Tube well water	Geological	1–3050	Berg *et al.* (2001)

$$FeAsS + 13Fe^{3+} + 8H_2O \rightarrow 14Fe^{2+} + SO_4^{2-} + 13H^+ + H_3AsO_4(aq) \quad (1)$$

ii. Dissolution of As-rich iron oxyhydroxides (FeOOH) due to onset of reducing conditions in the subsurface. Under oxidizing conditions, and in the presence of Fe, inorganic species of As are predominantly retained in the solid phase through interaction with FeOOH coatings on soil particles. The onset of reducing conditions in such environments can lead to the dissolution of FeOOH coatings. Fermentation of peat in the subsurface releases organic molecules (e.g., acetate) to drive reductive dissolution of FeOOH, resulting in the release of Fe(II), As(III), and As (V) present on such coatings [Eq. (2)] (McArthur *et al.*, 2000; Nickson *et al.*, 2000).

$$\begin{aligned} &8FeOOH - As_{(s)} + CH_3COOH + 14H_2CO_3 \rightarrow 8Fe^{2+} + As_{(d)} \\ &+ 16HCO_3^- + 12H_2O \end{aligned} \quad (2)$$

where $As_{(s)}$ is sorbed As and $As_{(d)}$ is dissolved As.

iii. Release of As sorbed to aquifer minerals by competitive exchange with phosphate ($H_2PO_4^-$) ions that migrate into aquifers from the application of fertilizers to surface soil (Acharya *et al.*, 1999).

However, the second mechanism involving dissolution of FeOOH under reducing conditions is considered to be the most probable reason for excessive As accumulation in groundwater (Harvey *et al.*, 2002; Smedley and Kinniburgh, 2002).

Relatively high concentrations of naturally occurring As can appear in some areas as a result of inputs from geothermal sources or As-rich groundwaters (Smedley and Kinniburgh, 2002). For example, Robinson *et al.* (1995) found high As concentrations (3800 μg liter^{-1}) in waste geothermal brine from the main drain at Wairakei geothermal field in New Zealand. River and lake waters receiving inputs of geothermal waters were found to contain up to 121 μg As liter^{-1}.

Arsenic concentration is usually higher in soil and shales than in earth crust because of its continuous accumulation during weathering and translocation in colloidal fractions. Arsenic may also be coprecipitated with Fe hydroxides and sulfides in sedimentary rocks. Therefore, Fe deposits and sedimentary Fe ores are rich in As, and the soils derived from such sedimentary rocks may contain as high as 20 to 30 mg As kg^{-1} (Zou, 1986). Arsenic in the natural environment occurs in soil at an average concentration of about 5 to 6 mg kg^{-1} (i.e., background level), but this varies among geological regions (Peterson *et al.*, 1981). Volcanoes are also considered as a geogenic source of As to the environment with the total atmospheric annual emissions from volcanoes being estimated at 31,000 mg (Smith *et al*., 1998; Walsh *et al*., 1979).

B. ANTHROPOGENIC

Arsenic is also being introduced into the environment through various anthropogenic activities. These sources release As compounds that differ greatly in chemical nature (speciation) and bioavailability. Major sources of As discharged onto land originate from commercial wastes (~40%), coal ash (~22%), mining industry (~16%), and the atmospheric fallout from the steel industry (~13%) (Eisler, 2004; Nriagu and Pacyna, 1988). Arsenic trioxide (As_2O_3) is used extensively in the manufacturing of ceramic and glass, electronics, pigments and antifouling agents, cosmetics, fireworks, and Cu-based alloys (Leonard, 1991). Arsenic is also used for wood preservation in conjunction with Cu and chromium (Cr), i.e., copper–chromium–arsenate (CCA). Some important physicochemical properties of As compounds are presented in Table IV.

Industries that manufacture As-containing pesticides and herbicides release As-laden liquid and solid wastes that, upon disposal, are likely to contaminate soil and water bodies. For example, indiscriminate discharge of industrial effluents from the manufacturing of Paris Green (copper acetoarsenite, an arsenical pesticide) resulted in the contamination of soil and

Table IV
Physicochemical Properties of Arsenic Compounds[a]

Compounds	Density ($g\ cm^3$)	Water solubility ($g\ liter^{-1}$)	Melting point (°C)	Boiling point (°C)
Arsenic–As (element)	5.727	Insoluble	613	–
Arsenic trioxide or arsenous oxide–As_2O_3	3.738	37 at 20 °C	312.3	465
Arsenic oxide or arsenic pentoxide–As_2O_5	4.32	1500 at 16 °C	315 (decomposes)	–
Arsenic sulfide or arsenic trisulfide–As_2S_3	3.43	5×10^{-4} at 18 °C	300	707
Dimethylarsinic acid or cacodylic acid $(CH_3)_2AsO(OH)$	–	829 at 22 °C	200	–
Arsenate or salts of arsenic acid–$HAsO_4$	5.79	Very slightly	720 (decomposes)	–

[a] From Lide (1992) and IARC (1980).

groundwater in residential area of Calcutta, India (Chatterjee *et al.*, 1999). Similarly, in New Zealand, timber treatment effluent is considered to be the major source of As contamination in aquatic and terrestrial environments (Bolan and Thiyagarajan, 2001). Because As is widely distributed in the sulfide ores of Pb, Zn, Au, and Cu, it is released during their mining and smelting processes. The flue gases and particulate from smelters can contaminate nearby ecosystems downwind from the operation with a range of toxic metal(loid)s, including As (Adriano, 2001). Coal combustion not only releases gaseous As into the atmosphere, but also generates fly and bottom ash containing varied amounts of As. Disposal of these materials often leads to As contamination of soil and water (Beretka and Nelson, 1994).

Arsenic is present in many pesticides, herbicides, and fertilizers. The use of horticultural pesticides, lead arsenate ($PbAsO_4$), calcium arsenate ($CaAsO_4$), magnesium arsenate ($MgAsO_4$), zinc arsenate ($ZnAsO_4$), zinc arsenite [$Zn(AsO_2)_2$], and Paris Green [$Cu(CH_3COO)_2.3Cu(AsO_2)_2$] in orchards has contributed to soil As contamination in many parts of the world (Merry *et al.*, 1983; Peryea and Creger, 1994). Soil contamination due to the use of organoarsenical herbicides such as monosodium methanearsonate (MSMA) and disodium methanearsonate (DSMA) was also reported (Gilmore and Wells, 1980; Smith *et al.*, 1998). The use of sodium arsenite ($NaAsO_2$) to control aquatic weeds has contaminated small fish ponds and lakes in several parts of United States with As (Adriano, 2001). Arsenic contamination in soil was also reported due to the arsenical pesticides used in sheep and cattle dips to control ticks, fleas, and lice (McBride *et al.*, 1998; McLaren *et al.*, 1998). A study of 11 dip sites in New South Wales indicated considerable surface soil (0–10 cm) contamination with As (37–3542 mg kg^{-1}) and significant movement of As (57–2282 mg kg^{-1}) down the soil profile at 20–40 cm depth (McLaren *et al.*, 1998). Continuous application of fertilizers that contain trace levels of As also results in As contamination of soil, thereby reaching the food chain through plant uptake (McLaughlin *et al.*, 1996).

C. BIOGENIC REDISTRIBUTION

Biological sources contribute only small amounts of As into soil and water ecosystems. However, plants and micro- and macroorganisms affect the redistribution of As through their bioaccumulation (e.g., biosorption), biotransformation (e.g., biomethylation), and transfer (e.g., volatilization). Arsenic accumulates readily in living tissues because of its strong affinity for proteins, lipids, and other cellular components (Ferguson and Gavis, 1972). Aquatic organisms are particularly known to accumulate As, resulting in considerably higher concentrations than in the water in which they live (i.e., biomagnification). Upon disposal or consumption they subsequently become a source of environmental contamination. Arsenic could be transferred from soil to plants and then to animals and humans, involving terrestrial and aquatic food chains. For example, poultry manure addition is considered to be one of the major sources of As input to soils. In the Delaware–Maryland–Virginia peninsula along the eastern shore of the United States, 20–50 mg of As is introduced annually to the environment through the use of As compounds (e.g., Roxarsone, ROX) in poultry feed (Christen, 2001). However, in many situations the soil–plant transfer of As is low (Smith *et al.*, 1998) and it is important to recognize that metal(loid)s loading through manure application may overestimate their actual net accumulation in soil, as a substantial portion of the metal(loid)s in manure originate in crop uptake and are therefore being recycled within a production system (Bolan *et al.*, 2004).

III. DISTRIBUTION AND SPECIATION OF ARSENIC IN THE ENVIRONMENT

A. DISTRIBUTION IN SOIL

Generally, As concentrations in uncontaminated soils seldom exceed 10 mg kg^{-1}. However, anthropogenic sources of As have elevated the background concentration of As in soils (Adriano, 2001). For example, in areas near As mineral deposits, As levels in soils may reach up to 9300 mg kg^{-1} (Ashley and Lottermoser, 1999). The distribution of As in contaminated soils around the world is presented in Table II. Depending on the nature of the geogenic and anthropogenic sources, As concentration in soils can range from <1 to 250,000 mg kg^{-1}. However, there is a large fluctuation among countries due to variation in soil parent material, for example, calcareous soils can be expected to have higher levels of As than noncalcareous soils (Aichberger and Hofer, 1989). As discussed in Section II,B, although the dominant source of As in soils is geological, additional inputs may also be derived locally from industrial sources, such as smelting and fossil-fuel combustion products and agricultural sources, namely pesticides and phosphatic fertilizers.

In soils, As forms a variety of inorganic and organic compounds (Vaughan, 1993). Arsenic forms solid precipitates with Fe, aluminium (Al), calcium (Ca), magnesium (Mg), and Ni. A number of studies involving solid-phase speciation have shown that As is prevalent mostly in the oxalate fractions associated with amorphous and crystalline Fe and Al oxides, indicating the strong affinity of As for these soil components (Wenzel *et al.*, 2001). The soluble As concentration in soil is largely determined by redox conditions, pH, biological activity, and adsorption reactions. The adsorption and mobility of As in soil are affected more strongly by the presence of $H_2PO_2^-$ ion than any other anions. Arsenic is subject to both chemical and biological transformations in soils, resulting in the formation of various species.

B. DISTRIBUTION IN THE AQUATIC ENVIRONMENT

Arsenic in an aquatic environment is distributed in both the aqueous solution and sediments. Elevated concentrations of As in natural waters are usually associated with As-rich sedimentary rocks of marine origin, weathered volcanic rocks, fossil fuels, geothermal areas, mineral deposits, mining wastes, agricultural use, and irrigation practices (Korte and Fernando, 1991). Uncontaminated waters usually contain less than 0.001 μg As liter^{-1}. In contaminated areas, however, high levels of As have been reported in water bodies (Table III). It should be noted that considerable variation in As concentration exists within the same geological area as reported by different researchers. The World Health Organization (WHO, 1981) recommends that the As concentration in drinking water not exceed 10 μg liter^{-1}. However, the limit in many countries, including Bangladesh and the United States, is still 50 μg As liter^{-1}. The widespread occurrence of high concentrations of As in water in many parts of the world caused the U.S. President George W. Bush to state "Arsenic is a natural substance that sometimes causes problems," and to reverse the previous government's decision to accept a five times lower WHO standard (i.e., 10 μg liter^{-1}) (Kaiser, 2001).

As discussed earlier, one of the principal causes of high As concentrations in subsurface waters is the reductive dissolution of hydrous Fe oxides and/or the release of adsorbed As (Smedley and Kinniburgh, 2002). Deuel and Swoboda (1972) proposed that the release was primarily due to reduction (and dissolution) of "ferric arsenates" instead of changes in the As speciation. The high As in groundwater can be associated with reducing conditions, resulting from the presence of dissolved organic carbon, particularly in alluvial and delta environments. The groundwater of the Bengal basin is the most notable example. While the exact mechanisms responsible for this remain uncertain, it is possible that both reductive dissolution and desorption of As from oxides and clay play an important role in elevating As concentration (Smedley and Kinniburgh, 2002).

A significant proportion of As in aquatic environment is derived from the sediments, and the relative distribution of As in water and sediments depends mainly on the nature and amounts of sediments (Table III). Arsenic in river sediments is highly variable, ranging from 32.8–42.7 mg kg^{-1} (Australia) (Taylor, 1996) to 8700–156100 mg kg^{-1} (New Zealand)

(Robinson *et al*., 1995). The As-rich sediments act as a buffer in maintaining the As concentration in water bodies, thereby controlling the dynamics and bioavailability of As in the aquatic environment.

C. CHEMICAL FORM AND SPECIATION

Speciation of metal(loid)s can be achieved by both analytical processes and on the basis of theoretical consideration. The analytical processes involved in the speciation of metal(loid)s in soils can be grouped into solid-phase speciation and solution-phase speciation. In view of the limitations of many of the analytical procedures used in speciation, often species distribution is predicted using a number of speciation models (e.g., GEOCHEM by Mattigod and Sposito, 1979; MINTEQ2 by Allison *et al*., 1991) that are based on theoretical chemical (thermodynamic) concepts. Although the fundamental thermodynamic principles that drive these models are based on scientific facts, problems arise when these principles are applied to complex natural matrixes.

A large number of sequential extraction schemes have been used for soils, generally attempting to identify metal(loid)s held in any of the following fractions: soluble, exchangeable, sulfide/carbonate bound, organically bound, oxides bound, and residual or lattice mineral bound. The bioavailability of metal(loid)s in soils has been examined using the physiologically based *in vitro* chemical fractionation schemes that include the physiologically based extraction test (PBET), potentially bioavailable sequential extraction (PBASE), and gastrointestinal (GI) test. These innovative tests predict the bioavailability of metal(loid)s in soil/sediments when ingested by animals and humans.

A vast number of analytical techniques are available for solution-phase characterization and quantification of metal(loid)s. These include electroanalytical techniques, cation/anion-exchange resins and chemical adsorbents to fractionate ionic and nonionic forms, ultrafiltration, dialysis, and gel permeation techniques for molecular size fractionation, spectroscopic techniques measuring the oxidation state of elements, X-ray techniques to measure trace element distribution, and chromatographic techniques to measure the phase distribution of metal(loid)s.

Arsenic speciation is determined by both biotic and abiotic variables. Arsenic speciation is important not only for understanding the biogeochemical cycling of As in different ecosystems and mechanisms of As accumulation and detoxification, but also for designing safe disposal options of As-rich biomass (Tu *et al*., 2003; Watt and Le, 2003).

In soil, As occurs both as inorganic [As(III) and As(V)] and as organic forms. Trivalent As can exist as arsenous oxide (As_2O_3), arsenious acid

($HAsO_2$), arsenite ($H_2AsO_3^-$, $HAsO_3^{2-}$, AsO_3^{3-}) ions, arsenic trichloride ($AsCl_3$), arsenic sulfide (AsS_3), and arsine (AsH_3). Pentavalent As commonly occurs as arsenic pentoxide (As_2O_5), orthoarsenic acid (H_3AsO_4), metaarsenic acid ($HAsO_3$), and arsenate ($H_2AsO_4^-$, $HAsO_4^{2-}$, AsO_4^{3-}) ions. The presence of different forms of organic As, such as monomethylarsonic acid [MMA, $CH_3AsO(OH)_2$], dimethylarsenic acid [DMA, $(CH_3)_2AsO(OH)$], trimethylarsine oxide [$(CH_3)_3AsO$], methylarsine (CH_3AsH_2), dimethylarsine [$(CH_3)_2AsH$] and trimethylarsine [TMA, $(CH_3)_3As$], has also been observed in contaminated soil and water (Gao and Burau, 1997).

The most common forms of As in the environment are the inorganic oxyions of As(III) and As(V). Arsenite [As(III)] is more toxic and relatively mobile in contaminated soils, whereas arsenate [As(V)] is relatively less toxic. Both As(III) and As(V) compounds are highly soluble in water and may change valency states depending on the pH and redox conditions.

Results of a literature search on the speciation of As in environmental and biological samples are presented in Table V. In contaminated soils, generally As(V) predominates over As(III), whereas in waters, the relative proportion of these two species varies depending on a number of factors, including As sources, redox potential, pH, and microbial activity.

Masscheleyn *et al.* (1991) studied the influence of redox potential and pH on As speciation and solubility in a contaminated soil. They observed that alterations in the oxidation state of As, as influenced by redox potential and pH, greatly affected its solubility in soil. At oxic redox levels (500–200 mV), As solubility was low and the major part (65–98%) of the As in soil solution was present as As(V). At alkaline pH, the reduction of As(V) to As(III) released substantial proportions of As into solution. Under moderately reducing conditions (0–100 mV), As solubility was controlled by the dissolution of Fe oxyhydroxides. At an anoxic redox level of −200 mV, soluble As increased 13-fold as compared to an oxic redox level of 500 mV. The apparent slow kinetics of the As(V) to As(III) transformation and the high concentrations of manganese (Mn) present indicate that, under reducing conditions, As solubility could be controlled by the $Mn_3(AsO_4)_2$ phase.

In a study conducted in New Zealand, Aggett and Aspell (1976) showed that with the occasional exception of a few summer months, over 90% of the As in water of the Waikato River and dams was present as As(V). Freeman (1985) detected As(III) in the Waikato River only when cyanobacteria (*Anabaena oscillaroides*) reduced As(V) to As(III).

While reviewing the As cycle in natural waters, Ferguson and Gavis (1972) suggested that As(III) is stable and mobile only in a narrow range of Eh and pH conditions. Conditions must be reducing enough to produce dissolved As(III) but not so reducing as to produce sulfide, which could precipitate As(III). Under conditions where sulfide is formed, realgar (AsS) and orpiment (As_2S_3) occur as stable solids. At low pH, $HAsS_2$(aq) is the

Table V
Selected References on Chemical Speciation of Arsenic in Various Media

Environment	Speciation technique[a]	Fraction/concentration	Reference
Acid mine drainage	LC-ICP-MS	As(III) = 13,000 μg liter^{-1} As(V) = 3700 μg liter^{-1}	Bednar *et al.* (2002)
Coal fly ash	IC-ICP-MS	As(V) $\gg$ As(III)	Jackson and Miller (1998)
Drinking water (Natural water)	–	Particulate and soluble As contributed 11.4 and 88.6% of the total As, respectively. In the case of soluble As, As(III) and As(V) were 47.3 and 52.7%, respectively	Thirunavukkarasu *et al.* (2001)
Geothermal waters	HPLC/GFAS and HPLC/HGAAS	Na_2HAsO_4 was predominant	Buyuktuncel *et al.* (1997)
Groundwater	LC-ICP-MS	As(III) = 720 μg liter^{-1} As(V) = 1080 μg liter^{-1}	Bednar *et al.* (2002)
Groundwater	FI-HG-AAS	As(III) and As(V) were present in 1:1 ratio	Samanta *et al.* (1999)
Groundwater	FI-HGAAS	As(III) was present at about 50% of the total As	Chatterjee *et al.* (1995)
Groundwater close to cattle tick dip sites	ICP-AES	As(V) was dominant	Kimber *et al.* (2002)
Human urine (Bangladesh)	IC-FI-HG-AAS	As (III) was the major species	Alauddin *et al.* (2003)
Mine tailings	AAS	Total As = 62350 mg kg^{-1} 63–99% as As(V)	Kim *et al.* (2002)
Mine tailings	XANES and EXAFS	As(V) was dominant	Foster *et al.* (1997)
Mung bean seedlings	LC-ICP-MS	Roots: As(III) > As(V) Leaves: As(V) $\gg$ As(III)	Van den Broeck *et al.* (1998)
Mushroom (edible)	HPLC-ICP-MS	DMA 68–74% Methylarsonic acid 0.3–2.9% Trimethylarsine oxide 0.6–2.0% Arsenic acid 0.1–6.1%	Larsen *et al.* (1998)
Plant—Chinese brake (*Pteris vittata* L.)	HPLC - AFS	94% of As in fronds was primarily as As(III)	Tu *et al.* (2003)

(*continued*)

Table V (*continued*)

Environment	Speciation technique[a]	Fraction concentration	Reference
Polluted urban watercourse	IC-ICP-MS	Dissolved As mostly as As(V) 130 μg liter^{-1}	Gault *et al.* (2003)
Poultry wastes	IC-ICP-MS	Organoarsenic compounds (Roxarsone) was dominant with trace levels of DMA and As(V)	Jackson and Bertsch (2001)
Rice grain	IC-ICP-MS	Total As 0.11–0.34 mg kg^{-1} Inorganic As 11–91% remaining DMA	Heitkemper *et al.* (2001)
Rice straw	HPLC-ICP-MS	As(V) > As(III)	Abedin *et al.* (2002)
River waters	HGAAS using Na-tetrahydro borate(III) reductant	As(V) was the principal species	Quinaia and Rollember (2001)
Sewage sludge	HG-CT-AAS	At pH 5.0 inorganic-As > organic-As At pH 6.5 organic-As > inorganic-As	Carbonell-Barrachina *et al.* (2000)
Soil (contaminated)	HPLC-ICP-MS	Total As = 10000 mg kg^{-1} As(V) = >90%	Matera *et al.* (2003)
Soil (contaminated)	Extraction with 1 *M* phosphoric acid plus 0.1 *M* ascorbic acid and measurement in LC-UV-HG-ICP/MS	As(V) was the major species	Garcia-Manyes *et al.* (2002)
Soil (contaminated)	XAFS	$Mg_3(AsO_4)_2 \cdot 8H_2O$	Foster *et al.* (1997)
Well waters	AAS	670 μg liter^{-1} total dissolved arsenic; As(III) was dominant: As(III)/As(V) ratio = 2.6	Chen *et al.* (1994)
Wetlands	XANES	As(III) > As(V)	La Force *et al.* (2000)

[a] HPLC, high-performance liquid chromatography; ICP, inductively coupled plasmanalysis; MS, mass spectroscopy; LC, liquid chromatography; HG, hydride generation; XAFS, X-ray absorption fine structure spectroscopy; FI, flow injection; AAS, atomic absorption spectrometry; GFAAS, graphite furnace atomic absorption spectrometry; XANES, X-ray absorption near edge structure (XANES) spectroscopy; EXAFS, extended X-ray absorption fine-structure spectroscopy; AFS, atomic florescence spectrometry; CT, cold trapping.

predominant species if sulfide is present, whereas AsS_2^- species predominate at pH greater than 3.7. Studying a stratified lake, Seyler and Martin (1989) showed that Mn, which has a higher redox potential than Fe and As, was reduced before the complete depletion of dissolved oxygen, and any dissolved As was present predominantly in the form of As(V). As conditions became more reducing, there was a rapid and concomitant increase of Fe and As and a reversal of As speciation such that as As(III) became more dominant, As_2S_3 and As concentrations correspondingly decreased.

In groundwater, As is predominantly present as As(III) and As(V). The major As species in freshwater are As(III) and As(V), and small amounts of MMA, DMA, and methylated As(III) have also been detected. In seawater, As speciation differs in the surface and deep zones, with As(V) and As(III) species dominating the respective zone. In addition to the aforementioned species, Watt and Le (2003) noticed that an array of uncharacterized As species also appeared to constitute a significant portion of the total As present in water. The identification of these compounds is necessary to fully understand the As biogeochemistry in water.

IV. BIOGEOCHEMISTRY OF ARSENIC IN THE ENVIRONMENT

The biogeochemistry and dynamics of As and other metal(loid)s vary between soil and aquatic environments. In the case of soil environment, a substantial proportion of the metal(loid)s is associated with the solid phase and their fate is strongly influenced by physicochemical interactions (e.g., adsorption–desorption) with the solid phase. Whereas in the case of aquatic environment, depending on the sediment content, a substantial proportion of metal(loid)s remains in solution and their fate is controlled largely by biological transformation.

A. Biogeochemistry of Arsenic in the Soil

Smith *et al.* (1998) presented a comprehensive review on the biogeochemistry of As in the soil environment. Here we include a brief discussion on various biogeochemical reactions of As in soil, which is helpful in understanding its behavior and in developing remediation strategies. As already discussed, As can exist in soil in different oxidation states but mostly as inorganic species, As(V) or As(III) (Adriano, 2001; Masscheleyn *et al.*, 1991). In addition to inorganic species, microbial methylation of As in soil results in the release of organic methylarsenic compounds, such as MMA and

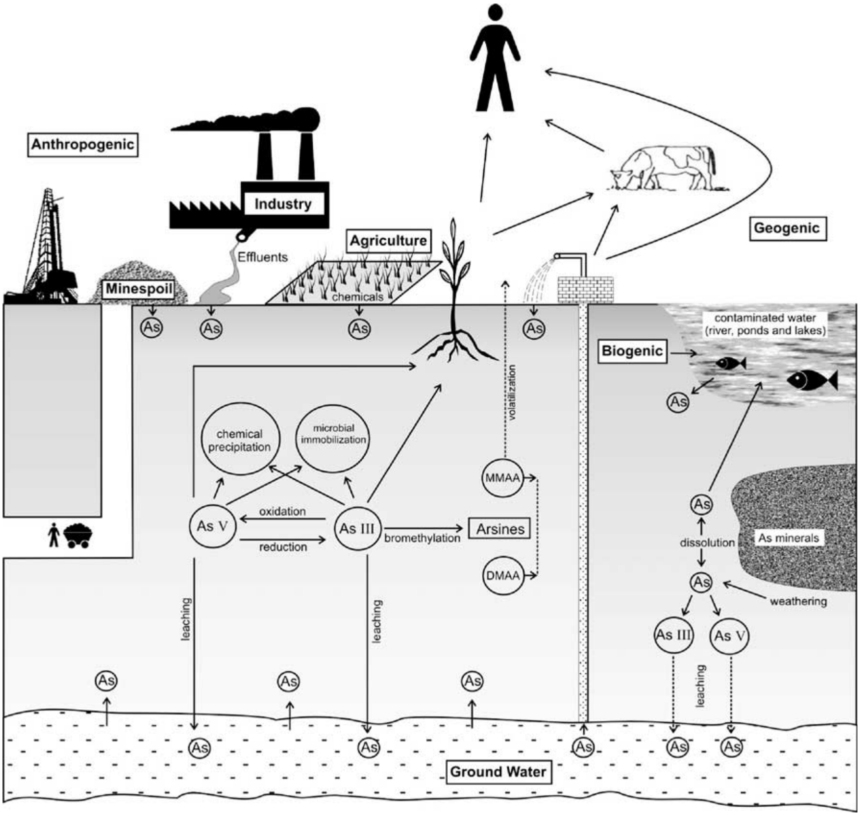

Figure 2 Arsenic dynamics in contaminated soil and aquatic ecosystems.

DMA, and ultimately arsine gas (Smith *et al.*, 1998; Vaughan, 1993). Both inorganic and organic species of As undergo various biological and chemical transformations in soils, including adsorption, desorption, precipitation, complexation, volatilization, and methylation (Fig. 2). Some important biogeochemical reactions of As and their significance in soil and aquatic environments are given in Table VI. The most thermodynamically stable species of As(III) (i.e., H_3AsO_3 and $H_2AsO_4^-$) and As(V) (i.e., $HAsO_4^{2-}$) occur over the normal soil pH range of 4 to 8.

1. Adsorption and Surface Complexation

The adsorption and retention of As by soils determine its persistence, reactions, movement, transformation, and ecological effects (toxicity). As in the case of most other metal(loid)s and nonmetals, one of the most

Table VI
Some Important Biochemical Reactions of Arsenic and their Environmental Significance

Process	Reactions	Eq. No.	Significance	Reference
Acid–base reactions	$AsO_4^{3-} + H^+ = HAsO_4^{2-} (\log K_a = 11.60)$	3	As(V), a less toxic As species, can exist in solution as H_3AsO_4, $H_2AsO_4^-$, $HAsO_4^{3-}$, and AsO_4^{3-} As(III), a highly toxic As species, exists at natural pH values as H_3AsO_3, and $H_2AsO_3^-$	Wilkie and Hering (1996)
	$AsO_4^{3-} + 2H^+ = H_2AsO_4^- (\log Ka = 18.35)$	4		
	$AsO_4^{3-} + 3H^+ = H_3AsO_4 (\log Ka = 20.60)$	5		
	$AsO_3^{3-} + H^+ = HAsO_3^{2-} (\log K_a = 13.41)$	6		
	$AsO_3^{3-} + 2H^+ = H_2AsO_3^- (\log K_a = 25.52)$	7		
	$AsO_3^{3-} + 3H^+ = H_3AsO_3^- (\log K_a = 34.74)$	8		
Oxidation	Chemical			
	$2HFe(VI)O_4^- + 3H_3As(III)O_3 \rightarrow 2Fe(III) + 3HAs(V)O_4^{2-}$	9	As(III) is more toxic and mobile and hence it is desirable to oxidize to As(V), which is less toxic and relatively immobile. Chemical oxidation of As(III) may occur via Fe, or H_2O_2, or MnO_2(VI) and Fe(VI) and is found very effective in the removal of As from water	Kocar and Inskeep (2003); Lee *et al.* (2003); Oscarson *et al.* (1981)
	$2Fe_3^+ + HAsO_2 + 2H_2O \rightarrow 2Fe^{2+} + H_3AsO_4 + 2H^+$	10		
	$H_3AsO_3^o + OH^- + O_2(g) \rightarrow H_2AsO_4^- + O_2^- + 2H^+$	11		
	$MnO_2 + 2H^+ + AsO_3^{3-} \leftrightarrows Mn^{2+} + AsO_4^{3-} + H_2O$	12		
	$MnO_2 + HAsO_2 + 2H^+ \rightarrow Mn^{2+} + H_3AsO_4$	13		
	Microbial			
	$Fe_2O_3 + 4H^+ + AsO_3^{3-} \leftrightarrows 2Fe^{2+} + AsO_4^{3-} + 2H_2O$	14	Competition of Fe(III) as a terminal electron acceptor in microbial respiration results in the oxidation of As(III)	Masscheleyn *et al.* (1991)
	$(CH_3)_2AsH \rightarrow (CH_3)_2AsO(OH)$	15	Arsine (di- and trimethyl) compounds can be oxidized by bacteria and fungi in the methylation process	O'Neill (1995)
	$(CH_3)_3As \rightarrow (CH_3)_2AsO(OH)$	16		
Reduction	$AsO_4^{3-} + 2H^+ + 2e^- \rightarrow AsO_3^{3-} + H_2O (\log K = 5.293)$	17	In waters reduction of As(V) to As(III) is possible at low pH and pE	Bose and Sharma (2002)
	$H_2AsO_4^- + 2Fe^{2+} + 5H_2O \rightarrow H_3AsO_3 + 2Fe(OH)_3(_s) + 3H^+$	18	Reduction of As(V) to As(III) is possible in the presence of Fe even at a pE value of 0.5 at pH 7, while at pH 8 such reduction is not possible unless pE is <-1.5	Bose and Sharma (2002)
	$HAsO_4^{2-} + 2Fe^{2+} + 5H_2O \rightarrow H_3AsO_3 + 2Fe(OH)_3(_s) + 2H^+$	19		
	$H_2AsO_4^- + 3H^+ + 2e^- \rightarrow H_3AsO_3 + H_2O$	20	The formation of sulfides in reducing environment facilitates the reduction of As(V) to As(III) with the latter species dominating in the porewater	Moore *et al.* (1988)
	$2H_3AsO_3 + 6H^+ + 3S_2^- \rightarrow As_2S_3 + 6H_2O$	21		
	$2As_2S_3 + 4e^- \rightarrow 4AsS + 2S^{2-}$	22		

(*continued*)

Table VI (*continued*)

Process	Reactions	Eq. No.	Significance	Reference
	$(CH_3)_2AsO(OH) \rightarrow (CH_3)_2AsH$	23	Dimethylarsinic acid can be reduced by bacteria to dimethyl arsine	O'Neill (1995)
Methylation	$H_3AsO_4 \leftrightarrows H_3AsO_3 \rightarrow (CH_3)AsO(OH)_2 \rightarrow (CH_3)_2AsO(OH)$	24	Biochemical transformations are mediated by microorganisms in terrestrial and aquatic environments. Biomethylation of inorganic and organic As is considered a major detoxification process	O'Neill (1995)
	$(CH_3)_2AsO(OH) \leftrightarrows (CH_3)_2AsH$	25		
	$(CH_3)_2AsO(OH) \leftrightarrows (CH_3)_3As$	26		
Adsorption	$FeOH + AsO_4^{3-} + 3H^+ \rightarrow FeH_2AsO_4 + H_2O$	27	Arsenic removal from water and wastewater is governed by sorption processes. Hydrous ferric oxide (FeOH) is an important sorbent in natural and engineered aquatic systems. Adsorption of As(III) increases with decreasing As/Fe ratios. As(V) adsorption is higher at high pH	Wilkie and Hering (1996)
	$FeOH + AsO_4^{3-} + 2H^+ \rightarrow FeHAsO_4^- + H_2O$	28		
	$FeOH + AsO_4^{3-} \rightarrow FeOHAsO_4^{3-}$	29		
	$FeOH + AsO_3^{3-} + 3H^+ \rightarrow FeH_2AsO_3 + H_2O$	30		
	$AlOH + AsO_4^{3-} \rightarrow AlOHAsO_4^{3-}$	31	Natural Boehmite (monohydrates of trivalent aluminium oxide) is found to adsorb large amounts of As(V) and thus is suitable for As removal from water and wastewaters	Dousova *et al.* (2003)
	$AlOH + AsO_4^{3-} + H^+ \rightarrow AlAsO_4^{2-} + H_2O$	32		
	$AlOH + AsO_4^{3-} + 2H^+ \rightarrow AlHAsO_4^- + H_2O$	33		
Precipitation	$Fe_2(SO_4)_3 + 2H_3AsO_4 \rightarrow 2FeAsO_4 + 3H_2SO_4$	34	A molar ratios (FeAs) of 4, and an optimum pH of 5 at 33 °C achieved less residual As in solution	Papassiopi *et al.* (1996)
	$H_3AsO_4 + Ca(OH)_2 \rightarrow CaHAsO_4.2H_2O$	35	Liming results in the precipitation of As as calcium arsenate, which is unstable in aqueous environment and becomes insoluble	Stefanakis and Kontopoulos (1988)
	$Fe(OH)_3 + H_3AsO_4 \rightarrow FeAsO_4.2H_2O + H_2O$	36	As(V) can be immobilized through coprecipitation with hydrous Fe oxide or hydrous Mn oxide	Masscheleyn *et al.* (1991)
	$3MnOOH + 2HAsO_4^{2-} + 7H^+ + 3e^- \rightarrow Mn_3(AsO_4)_2 + 6H_2O$	37		

commonly reported, and perhaps the first reaction to occur in soils, is As adsorption onto soil particles. Numerous studies have dealt with As sorption on to specific minerals and uncontaminated soils. Ferrous oxides/hydroxides are involved most commonly in the adsorption of As in both acidic and alkaline soils. Carbonate minerals adsorb As in calcareous soils. In acidic soils, Mn oxides and biogenic particles play a dominant role in the adsorption of As (Arai *et al.*, 2003; Oscarson *et al.*, 1981).

Arsenic is known to have high affinity for oxide surfaces, and several biogeochemical factors are found to play a major role in adsorption. Soil particle size, organic matter, type and nature of constituent minerals, pH, redox potential, and competing ions have all been shown to influence As adsorption (Chiu and Hering, 2000; Jones *et al.*, 2000; Smith *et al.*, 1998).

In general, adsorption of As(V) decreases with increasing pH. In contrast, adsorption of As(III) increases with increasing pH. The effect of pH on As adsorption varies considerably among soils and is dependent on the nature of mineral surface. In soils containing low oxidic minerals, increasing the pH has little effect on the amount of As(V) adsorbed, whereas in highly oxidic soils, adsorption of As(V) decreases with increasing pH (Smith *et al.*, 1998). This decrease is attributed to two interacting factors: (i) the increasing negative surface potential on the plane of adsorption and (ii) the increasing concentration of negatively charged As(V) species present in the soil solution.

Brookins (1988) observed that amorphous Al and Fe hydroxides adsorbed more As(V) than As(III). The surface charge properties of variable charge soil components are strongly influenced by pH. At acid pH these soil components contain large amounts of positive charges, and adsorption of As (V) may become important. Arsenate ions are attracted to positively charged colloidal surfaces either at broken clay lattice edges where charged Al^{3+} groups are exposed or on surfaces of Fe and Al oxides and hydroxide films. Many researchers have investigated As(III) and As(V) adsorption reactions and surface speciation on major soil minerals (i.e., metal oxyhydroxides and phyllosilicate minerals) using various macroscopic and spectroscopic techniques. Arsenate is strongly adsorbed at acidic pH values on amorphous $Al(OH)_3$, α-Al_2O_3, ferrihydrite, and hematite (Arai *et al.*, 2001; Raven *et al.*, 1998; Xu *et al.*, 1988). Several spectroscopic [e.g., extended X-ray adsorption fine structure spectroscopy (EXAFS)], macroscopic [e.g., electrophoretic mobility (EM)], and thermodynamic modeling (e.g., surface complexation model) have revealed innersphere bidentate binuclear and/or monodentate As(V) complexes on ferrihydrite, goethite, amorphous Fe and Al oxides, and the bayerite polymorph (Arai *et al.*, 2001; Fendorf *et al.*, 1997) and on both inner sphere and outer sphere As(III) complexes on Al oxides (Arai *et al.*, 2001; Goldberg and Johnston, 2001). In general, As(V) sorption on amorphous Al and Fe oxides is characterized by an apparent sorption maximum at pH 4, whereas As(III) sorption maximum occurs in the pH range of 7 to 8.5.

The type and quantity of silicate clay minerals present in soil also influence the retention of As. Soils having higher clay content retain more As than sandy soils with low clay content. The degree of As sorption onto silicate clay minerals decreases in the order of kaolinite > vermiculite > montmorillonite (Goldberg and Glaubig, 1988; Manning and Goldberg, 1997). The silicate clay minerals also generally adsorb more As(V) than As (III), and adsorption by clay minerals is affected by pH (Lin and Puls, 2000).

Arsenic and P belong to the same chemical group and both have comparable dissociation constants for their acids and solubility products for their salts. Therefore, $H_2AsO_4^-$ and $H_2PO_4^-$ ions compete for the same sorption sites in soils, although some sites are preferentially available for the sorption of either $H_2PO_4^-$ or $H_2AsO_4^-$ ions. A number of studies have shown that among the competing anions, the $H_2PO_4^-$ suppresses As(V) sorption by soil more significantly than chloride (Cl^-), nitrate (NO_3^-), and sulfate (SO_4^{2-}) (Matera and LeHecho, 2001; Manful *et al.*, 1989; O'Neill, 1995; Thanabalasingam and Pickering, 1986).

Soil organic matter content also affects the adsorption of As and thus its bioavailability as organic molecules compete with As for sorption to surface sites. Thanabalasingam and Pickering (1986) showed that the maximum adsorption of As(V) on humic acids occurred around pH 5.5, whereas adsorption of As(III) increased up to pH 8. At high pH, the solubilization of humic substances reduces As retention. While there is very little information available on the effects of organic matter on As adsorption, Grafe *et al.* (2001) have shown that humic acid reduces both As(V) and As(III) adsorption on geothite between pH 3 and 9. Several functional groups present on these complex organic polymers may be responsible for binding As. Further, dissolved organic carbon substances are capable of increasing the mobility and bioavailability of As in soil and water ecosystems through redox reactions and soluble complex formation.

Depending on various factors affecting the adsorption of As, part of the As adsorbed onto soil constituents is desorbed and released into the soil solution. Soil pH and phosphate addition are the most important factors that control the desorption of As. For example, Woolson *et al.* (1973) observed that phosphate addition to an As-contaminated soil displaced about 77% of the total As in the soil. Although phosphate addition increases As solubility, Peryea (1991) reported that desorption of As was dependent on the soil type, as no increase in As concentration in soil solution from a volcanic soil (with high anion-fixing and pH-buffering capacity) was observed. This suggests that only large additions of P (>400 mg kg^{-1}) would affect the As solubility in these soils (Chen *et al.*, 2002; Smith *et al.*, 1998). In long-term poultry litter-amended agricultural soils, Arai *et al.* (2003)

observed that the extent of As desorption from the litter increased with increasing pH from 4.5 to 7, but only 15% of the total As was released at pH 7, indicating the presence of insoluble phases and/or strongly retained soluble compounds. Elkhatib *et al.* (1984) suggested that the sorption of As (III) is not reversible in soil.

One of the important factors affecting the adsorption/desorption characteristics of As is the contact time (residence time) in soils and sediments. For example, Arai and Sparks (2002) reported that the longer the residence time (1 year), the greater the decrease in As(V) desorption at pH 4.5 and 7.8, suggesting nonsingular reactions. The surface transformation processes, such as rearrangement of surface complexes and conversion of surface complexes into aluminum arsenate-like precipitates, might be responsible for the decrease in As(V) reversibility with aging. Thus, the fate and transport of the contaminants must be predicted/modeled not only on short-term adsorption and desorption studies, but also on long-term reactions.

Although the desorption process is important in relation to the bioavailability and mobility of As, only a few studies have focused on desorption of As from soil constituents. Further studies on desorption are needed to fully understand the chemistry of As in soils, which might help in developing appropriate remediation technologies.

2. Redox Reactions

In soil and aquatic environments, redox reactions not only determine the nature of chemical species, but also the solubility and mobility of As and thus its environmental significance. Arsenic in soils is subject to both abiotic and biotic redox reactions [Eqs. (9–23) in Table VI]. The Fe(III) oxides, Mn (III) oxides, and organic compounds in soils play a major role in catalyzing the abiotic oxidation of As(III) through an electron transfer mechanism (Adriano, 2001; Oscarson *et al.*, 1981). Similarly, abiotic redox reactions are also responsible for the release of As from arsenopyrite through oxidation by Fe(III), considered to be a predominating process inducing the release of As into the groundwater in areas where well waters are highly contaminated with As [Eq. (1)].

Under moderately reducing conditions, As(III) is often found to be the predominant species in soil solution (Marin *et al.*, 1993; Masscheleyn *et al.*, 1991; Onken and Hossner, 1995). Studies by Deuel and Swoboda (1972) showed that there was an increase of As(III) in soil solution over time under flooded conditions. This was attributed to the release of As(V) during reductive dissolution of Fe oxyhydroxide minerals that have a strong affinity for As(V) and the subsequent reduction of As(V) to As(III).

Biotransformation of As, involving the oxidation of As(III) to As(V) and the reduction of As(V) to As(III) by a variety of microorganisms, may occur in contaminated soil. For example, *Alcaligenes faecalis* was found to oxidize As(III) to As(V) (Osborne and Ehrlich, 1976; Phillips and Taylor, 1976). Bacteria, fungi, and algae are also able to reduce As(V) to As(III) and subsequently to arsine (Frankenberger and Losi, 1995). However, the effect of microbial activity on the transformation and movement of As in soil is difficult to quantify (Smith *et al.*, 1998).

3. Biomethylation

Arsenic in soil is also subject to biological transformation resulting in the formation of organo-arsenicals and other compounds [Eqs. (24–26) in Table VI]. Inorganic As can undergo microbially mediated biochemical transformation, i.e., the hydroxyl group of arsenic acid [$AsO(OH)_3$] is replaced by the CH_3 group to form MMA, DMA, and TMA (Maeda, 1994). The pathway of As(V) methylation initially involves the reduction of As(V) to As(III), with the subsequent methylation of As(III) to dimethylarsine by coenzyme *S*-adenosylmethionine (Frankenberger and Losi, 1995). Methylation is often enhanced by sulfate-reducing bacteria. In addition to bacteria, several fungal species also have shown their ability to reduce As. Inorganic As is incorporated by autotrophic organisms such as algae and is then transported through the food chain. Arsenic becomes progressively methylated during this transfer. Therefore, methylation of As is considered a major detoxifying processes for these microorganisms (Adriano, 2001). The methylated As species is also subject to volatilization and photochemical reactions that may eliminate As from soil.

Demethylation of methylarsenicals can occur under both aerobic and anaerobic conditions. Anaerobic demethylation reactions may result in the formation of toxic and reactive AsH_3 from less toxic DMA, whereas aerobic demethylation of DMA is likely to yield As(V), thereby retaining As in the system. Although AsH_3 undergoes rapid chemical oxidation under oxic conditions, it can exist for long periods in an aerobic environment. Because the demethylation process often produces CO_2 in addition to CH_4, it is preceded by oxidative assimilatory pathways used in substrate metabolism rather than by dissimilatory lyses.

Methylation, demethylation, and reduction reactions are also important in controlling the mobilization and subsequent distribution of arsenicals in soils. These transformations are promoted by microbes; however, it is still not clear if *in situ* biomethylation is a common phenomenon. Although the presence of organic forms of As in soil can be associated with the application of anthropogenic compounds, such as fertilizers and pesticides (O'Neill, 1995), their presence is often linked to biomethylation. However, biomethylation reactions occur readily in aquatic environment and these reactions are discussed in Section IV.B.

4. Leaching

Due to its strong adsorption onto organic and clay colloids, As(V) is likely to persist in soils for a long time, especially in fine-textured soils with high Fe contents (Woolson, 1983). In these soils, leaching of As(V) is low and therefore As contamination of groundwater is considered unlikely (Woolson, 1983). However, under certain environmental conditions (i.e., low pH and low Eh), As would leach in the soil profile, thereby contaminating the surface and groundwaters (Hingston *et al.*, 2001; Ruokolainen *et al.*, 2000).

Considerable amounts of solubilized As could move downward in the soil profile with leaching water, especially in coarse-textured soils. It is for this reason that abandoned wood preservative (CCA) sites may threaten groundwater quality. For example, in examining the leaching of Cu, Cr, and As from CCA solution through free-draining, coarse-textured surface and subsurface soils using undisturbed soil lysimeters, McLaren *et al.* (1994) observed that the cumulative amounts of As leached ranged from 4 to 30% of the total As applied. Arsenic is present as a simple salt (soluble Na_2HAsO_4) in CCA, which is liable for leaching losses, especially in coarse-textured soils. Whereas when As is present as an organically complexed form (e.g., in sewage sludge), it is not readily leached in soils (McLaren *et al.*, 1994).

Again the role of $H_2PO_4^-$ ions in enhancing the mobility of As, especially AsO_4^{2-} ions, should be noted. For example, Qafoku *et al.* (1999) noticed that the leaching of As in a column containing mineral soil incorporated with As-rich poultry manure increased with the addition of a phosphate compound. The arsenic concentration in the leachate was approximately 10 times higher when $Ca(H_2PO_4)_2$ was used to leach the soil column as compared to the $CaSO_4$ solution. In the presence of the $Ca(H_2PO_4)_2$ solution, a maximum As concentration of 800 μg liter^{-1} was found in the leachate, much higher than the WHO maximum permissible limit of 10 μg liter^{-1} for drinking water.

B. BIOGEOCHEMISTRY OF ARSENIC IN AQUATIC ENVIRONMENTS

As in the case of soil systems, the environmental and ecological significance of As dynamics in aquatic ecosystem is largely determined by its biogeochemical reactions, which are discussed in this section.

1. Adsorption and Desorption

Arsenic is stable in four oxidation states (+5, +3, 0, −3) under the Eh conditions that occur in aquatic systems. At high Eh values (mostly exist in oxygenated waters), arsenic acid species (i.e., H_3AsO_4, $H_2AsO_4^-$, $HAsO_4^{2-}$, and AsO_4^{3-}) are stable. At mildly reducing conditions, arsenious acid species (i.e., H_3AsO_3, $H_2AsO_3^-$, and $HAsO_3^{2-}$) become stable (Korte and Fernando, 1991; Penrose, 1974; Smith, 1986). The speciation of As in aquatic environment is critical in controlling the adsorption/desorption reactions with sediments. Adsorption to sediment particles may remove As(V) from contaminated water, as well as inhibiting the precipitation of As minerals such as scorodite ($FeAsO_4{\cdot}2H_2O$) that control the equilibrium aqueous concentration (Foster *et al*., 1997).

Under the aerobic and acidic to near-neutral conditions (typical of many aquatic environments), As(V) is adsorbed very strongly by oxide minerals in sediments. The highly nonlinear nature of the adsorption isotherm for As(V) in oxide minerals ensures that the amount of As adsorbed is relatively large, even when dissolved aqueous concentrations of As are low. Such adsorption occurring in natural environments protects water bodies from widespread As toxicity problems. Adsorption of As species by sediments are as follows: As(V) > As(III) > As (II) > DMA (Smedley and Kinniburgh, 2002).

In As-contaminated sediments, Clement and Faust (1981) found that a significant portion of the As was bound in organo-complex forms and indicated that adsorption–desorption equilibrium must be considered as well as the redox effects in examining the dynamics of As in aquatic environment. As pH increases, especially above pH 8.5, As desorbs from the oxide surfaces, thereby increasing the concentration of As in solution. Desorption of As from As-contaminated sediments at high pH is the most likely mechanism for the development of groundwater As problems under the oxidizing conditions (Robertson, 1989; Smedley *et al*., 2002). These adsorption and desorption reactions of As in the aquatic environment have not been studied in detail under varied ecological conditions and therefore require greater attention.

2. Biotransformation

Arsenic undergoes a series of biological transformations in the aquatic environment, yielding a large number of compounds, especially organoarsenicals. Certain reactions, such as oxidation of As(III) to As(V), may occur both in the presence and in the absence of microorganisms, whereas other reactions, such as methylation, are not thermodynamically favorable in water and can occur only in the presence of organisms. In neutral oxygenated waters, As(V) is the thermodynamically favored form, whereas As(III) is stable under reducing conditions (Ferguson and Gavis, 1972). Some bacteria and marine phytoplankton are capable of reducing As(V) to As(III) or oxidizing As(III) to As(V) (Andreae, 1977). Biological reduction of As(V) to As(III) reportedly occurs most easily at a pH between 6 and 6.7 (Korte and Fernando, 1991). For example, Aggett and Aspell (1980) noticed that As was usually found as As(V) in the Waikato River of New Zealand, but during the spring and summer months, As(III) was often found to predominate. The reduction of As(V) to As(III) has been attributed to biological components of the river ecosystem. This biotransformation has been reported to occur in various aquatic systems, mediated by bacteria (Johnson, 1972; Myers *et al.*, 1973) and algae (Andreae and Klumpp, 1979; Sanders 1983; Sanders and Windom, 1980). A cyanobacteria (*Anabaena oscillaroides*)–bacteria assemblage was also found to reduce As(V) to As (III) (Freeman, 1985).

Benthic microbes are capable of methylating As under both aerobic and anaerobic conditions to produce methylarsines and methyl-arsenic compounds with a generic formula $(CH_3)_nAs(O)(OH)_{3-n}$ where n may be 1, 2, or 3. MMA and DMA are the common organoarsenicals in river water. Methylated As species could result from direct excretion by algae or microbes or from degradation of the excreted arsenicals or more complex cellular organoarsenicals. Methylation may play a significant role in the mobilization of As by releasing it from the sediments to aqueous environment. The presence of organoarsenicals in river sediments is evidence that methylation occurs in the sediments (Anderson and Bruland, 1991). The rate of methylation/demethylation reactions and the consequent mobilization of arsenicals are affected by adsorption by sediments and soils.

Primary producers such as algae take up As(V) from solution and reduce this to As(III) prior to methylation of the latter to produce MMA and DMA; the methylated derivatives are then excreted. This may be considered to represent a detoxification process in respect to the organism involved. Arsenic is taken up by algae due to its chemical similarity to phosphate. Although the detoxification of As by microorganism can be achieved through methylation, the element may be of significant toxicity to phytoplankton and periphyton communities in marine environments.

Both macro- and microorganisms accumulate As in their tissues. Concentrations in organisms may be considerably higher than in the water in which they live, but unlike mercury (Hg), there is little, if any, concentration upward through the food chain (i.e., bioaugmentation). The toxicity of As to aquatic organisms is similar to its effects on terrestrial life, i.e., As(V) is much less toxic than As(III) (Ferguson and Gavis, 1972).

Arsenate can replace $H_2PO_4^-$ uptake in phosphate-deficient waters and can then be accumulated by algae. In a study of As accumulation in the food chain, it has been reported that most of the As accumulated by algae was in a nonmethylated form, which was bound strongly to protein or polysaccharides in the algal cell (Maeda *et al.*, 1990). Such transformation can be stimulated by adding nutrients. Microbial formation of volatile arsine or other volatile-reduced compounds may play a role in the discharge of As to the atmosphere. Arsenite can be reduced and methylated to DMA, which can be further methylated or reduced and may eventually volatilize (Korte and Fernando, 1991).

V. BIOAVAILABILITY AND TOXICITY OF ARSENIC TO BIOTA

Arsenic is used as an additive in various metal alloys and in wood preservation. Its toxic properties are exploited in the formulation of arsenical herbicides and insecticides. To date, however, geogenic As is largely responsible for most human poisoning (Smith *et al.*, 2000). Due to its environmental and human health impact, As toxicity has been researched and documented more extensively than any other metal(loid)s.

A. TOXICITY TO PLANTS AND MICROORGANISMS

Arsenic contamination of soil and water poses a serious threat to plants and animals. Plants and microorganisms are known to accumulate As in their tissues and exhibit a certain degree of tolerance. However, at high concentrations, As is toxic to nearly all forms of life. Some selected references on toxicity (risks) of As in microorganisms, higher plants, and animals are presented in Table VII.

Biotoxicity is mostly determined by the nature and bioavailability of As species present in the contaminated habitat. An average toxicity threshold of 40 mg kg^{-1} has been established for crop plants (Sheppard, 1992). At high concentrations, As in plants inhibits plant metabolic processes, such as photosynthesis through interference of the pentose–phosphate pathway, thereby inhibiting growth and often leading to death (Marques and Anderson, 1986; Tu and Ma, 2002). Arsenite penetrates the plant cuticle to a greater degree than As(V) and generally results in the loss of turgor (Adriano, 2001).

Biomass production and yields of a variety of crops have been shown to reduce significantly at high concentrations of As in soils (Carbonell-Barrachina *et al.*, 1997). For example, significant yield reductions of barley (*Hordeum vulgare* L.) and ryegrass (*Lolium perenne* L.) have been reported

Table VII
Potential Risks of Arsenic to Terrestrial Biota

Medium	Concentration[a]	Effect	Reference
Soil	360	Yield reduction in barley; plants showed symptoms of As toxicity and P deficiency	Lambkin and Alloway (2003)
	50–100	Reduction in growth of vegetative and root system in tomatoes	Miteva (2002)
	70–100	As contents in rice cultivars exceeded the WHO standard	Xie and Huang (1998)
Soil	0, 15, 20, 30, 50, and 100 as power station fly ash or disodium hydrogen arsenate	50% yield reduction in wheat, barley, and oats. Sensitivity to As was in the order: oats > wheat > barley	Toth and Hruskovicova (1977)
Soil	100	Decreased the height of the apple tree: 100% growth inhibition at above 100 mg kg^{-1}	Benson (1976)
Seedling beds	1000 and 2000	Substantial growth reduction in white spruce seedlings	Rosehart and Lee (1973)
Soil	0–280 kg As ha^{-1} (fine sandy loam soil) 0–560 kg As ha^{-1} (clay soil).	Significant growth reduction in cotton and soyabean	Deuel and Swoboda (1972)
Soil	$NaAsO_2$ applied at rates up to 720 kg As ha^{-1}	As toxicity persisted for four growing seasons in potatoes and peas	Steevens *et al.* (1972)
Water & nutrient solutions	0.01, 0.1, or 1.0 m*M* $PbCl_2$ or Na_2HAsO_4 in 1% agar + modified Arnon and Hoagland solution.	Growth inhibition of pea seedlings at all concentrations. As resulted in more growth inhibition than Pb	Paivoke (1979)
Soilless culture	1.0–5.5	No phytotoxic effect on radish	Carbonell-Barrachina *et al.* (1999a)
Soilless culture	1.0–5.0	Organic arsenicals (MAA > DMA) more phytotoxic than inorganic As to turnip, accumulating above the threshold for As in food crops (1.0 mg kg^{-1})	Carbonell-Barrachina *et al.* (1999b)

(*continued*)

Table VII (*continued*)

Medium	Concentration[a]	Effect	Reference
Nutrient solution	0–10	Significant yield reduction in tomato (no tissue chlorosis or necrosis was observed)	Carbonell-Barrachina *et al.* (1997)
Growth medium	0.5–50 μM As	Growth inhibition of mung bean above 2.2 μg g^{-1} of As in the dry mass	Van den Broeck *et al.* (1997)
Water culture	0, 0.04, 0.4, 4.0, and 20	Increasing As decreased plant dry weight in cabbage. Most As remained in the roots with only 10–25% transported to the tops, ~2% entered the inner leaves	Hara *et al.* (1977)
Green algae in culture medium	78.7 μg liter^{-1} As(III) 159.3 μg liter^{-1} As(V) 12.4 (MMA) 35.7 (DMA)	Raising phosphate concentration in the medium increased As(V) toxicity to freshwater green alga *Scenedesmus obliguus*	Chen *et al.* (1994)
Earthworms	>400	Caused total fatality to earthworms	Yeates *et al.* (1994)
	Up to 8000	Tolerated by *Lumbricus rubellus* and *Dendrodrilus rubidus* tolerated	Langdon *et al.* (1999)
	PDA (phenyldichloroarsine), As(III) and As(V) at varied concentrations	Toxicity follows: PDA > As(III) > As(V) and 24 h LD_{50} values 189.5, 191.0, and 519.4 μmol kg^{-1}, respectively	Li *et al.* (1994)

[a] mg kg^{-1} or mg liter^{-1} unless specified.

with the application of only 50 mg As kg^{-1} soil (Jiang and Singh, 1994). Plant uptake of As is greatly influenced by its species in soil. As has already been discussed, different species have different solubility and mobility, thereby differing in their bioavailability to plants. Marin *et al.* (1992) reported that the order of As availability to rice (*Oryza sativa* L.) is as follows: As(III) $>$ MMA $>$ As(V) $>$ DMA. They observed that upon absorption, DMA is readily translocated to the plant shoot, whereas As (III), As(V), and MMA accumulate primarily in the roots. While the application of As(V) and DMA did not affect rice growth, both As(III) and MMA were found to be phytotoxic to rice. Burlo *et al.* (1999) noted that both MMA and DMA in tomato plants (*Lycopersicon esculentum* Mill.) had a greater upward translocation than As(III) and As(V).

In general, the accumulation of As in the edible parts of most plants is low (O'Neill, 1995), which is attributed to a number of reasons, including (Wang *et al.*, 2002) (i) low bioavailability of As in soil; (ii) restricted uptake by plant roots; (iii) limited translocation of As from roots to shoots; and (iv) phytotoxicity and subsequent premature plant death at relatively low As concentrations in plant tissues. Apart from chemical forms, it has been shown that the phytotoxicity of As varies with the soil conditions. For example, Reed and Sturgis (1963) reported that As inhibits rice plant growth more strongly under submerged soil conditions than under upland soil conditions, because As(V) is reduced to As(III), which is more soluble and more toxic to plants in submerged soil. Arsenic phytotoxicity is expected to be greater in sandy soils than in other soil types, as the former soils generally contain low amounts of Fe and Al oxides and silicate clays, which have been implicated in the adsorption of As from soil solution (Sheppard, 1992; Smith *et al.*, 1998).

The antagonistic and synergistic effects of various nutrient anions also determine the phytotoxicity of As to some extent. For example, Davenport and Peryea (1991) reported a reduction of As uptake by plants with the application of phosphate, which was attributed to $H_2PO_4^-$ ion-induced inhibition of As(V) uptake by plant roots. In contrast, Woolson (1973) observed that a phosphate application increased As availability and As uptake by plants, which was attributed to the $H_2PO_4^-$ ion-induced release of As(V) to the soil solution. Most plants do not accumulate enough As to be toxic to animals and humans. Growth reductions and crop failure are the main consequences of soil As contamination (Walsh and Keeney, 1975). Thus the major hazard for animal and human systems is derived from direct ingestion of As-contaminated soil or water (Smith *et al.*, 1998).

Arsenic contamination of soil and water has a direct impact on microbial community and structure. At high concentrations, a reduction in the soil microbial population has been reported by a number of researchers (Bisessar, 1982; Van Zwieten *et al.*, 2003). In general, as in the case of higher plants, As(III) is more toxic to microorganisms than As(V) (Maliszewska *et al.*, 1985). Hiroki (1993) has shown that As(III) is more toxic to bacteria and actinomycetes than As(V) and that fungi not only display a higher tolerance to As(III) than bacteria and actinomycetes, but also show the same tolerance to both As(V) and As(III). Arsenite also inhibits enzyme activities in soil (Tabatabai, 1977). However, many bacterial communities are found to adapt to As-contaminated environments by developing resistance and tolerance mechanisms (Smith *et al.*, 1998).

Earthworms usually have a high capacity for accumulating toxic elements; however, the extent of accumulation is dependent on the type of element and on soil properties (Ma, 1982). Earthworms are known to inhabit As-rich metalliferous soils (Langdon *et al.*, 1999). They are likely to accumulate As present in soils through ingestion of solid-phase As and dermal contact with pore water As. Yeates *et al.* (1994) observed a complete elimination of earthworms in soils contaminated by As derived from timber preservatives at concentrations of 400 and 800 mg As kg^{-1}, but few earthworms at 100 mg As kg^{-1}. In contrast, Langdon *et al.* (1999) found populations of *Lumbricus rubellus* and *Dendrodrilus rubidus* resistant to As(V) and Cu present in mine spoil containing up to 8000 mg As kg^{-1} and 750 mg Cu kg^{-1}. The difference in the threshold levels of As for earthworms between these two experiments may be attributed to the difference in the bioavailability of As, which is a function of speciation and substrate matrix. Earthworms generally show resistance to As toxicity; however, the mechanisms of such resistance are not fully understood (Langdon *et al.*, 2003).

B. Risk to Animals and Humans

Drinking water is the most important source of dietary intake of As by animals and humans (Fitz and Wenzel, 2002). However, food also forms a source of As exposure (Adriano, 2001). The occurrence of inorganic As in drinking water has been identified as a source of risk for human health even at relatively low concentrations. As a consequence, more stringent safer limits for As in drinking water have been proposed (Wenzel *et al.*, 2001). Soluble As compounds are rapidly absorbed from the gastrointestinal tract (Hindmarsh and McCurdy, 1986). Several studies in humans indicate that both As(III) and As(V) are well absorbed across the gastrointestinal tract (USDHHS, 2000). Studies involving the measurement of As in fecal excretion in humans indicated that almost 95% of oral intake of As(III) is absorbed (Bettley and O'Shea, 1975). This was supported by studies in which urinary excretion in humans was found to account for 55–80% of daily intakes of As(III) or As(V) (Buchet *et al.*, 1981; Crecelius, 1977; Mappes, 1977). It has also been reported that both MMA and DMA are also well absorbed (75–85%) across the gastrointestinal tract (Buchet *et al.*, 1981).

Once absorbed, simultaneous partial oxidation of As(III) to As(V) and partial reduction of As(V) to As(III) occur, yielding a mixture of As(III) and As(V) in the blood. The As(III) may undergo enzymatic methylation primarily in the liver to form MMA and DMA, but the rate and relative proportion of methylation production vary among animal species. Most As is promptly excreted in the urine as a mixture of As(III), As(V), MMA, and DMA, and relatively smaller amounts are excreted in the feces. Some As may remain bound to tissues, depending on the rate and extent of methylation. Monomethylarsonic acid may be methylated to DMA, but neither MMA nor DMA is demethylated to yield As(III) or As(V). Arsenic may accumulate in skin, bone, and muscle and its half-life in humans is between 2 and 40 days (USDHHS, 2000).

Teratogenic effects of As in chicks, golden hamsters, and mice have been reported. Arsenic does not appear to be mutagenic in bacterial and mammalian assays, although it can induce chromosomal breakage, chromosomal aberration, and chromatid exchange. Studies have shown that As may be an essential element at trace concentrations for several animals such as goats, rats, and poultry, but there is no evidence that it is essential for humans (USEPA, 1988). The acute toxicity of As compounds in humans is a function of their rate of removal from the body. Arsine is considered to be the most toxic form, followed by As(III), As(V) and organic As compounds (MMA and DMA). Lethal doses in humans range from 1.5 mg kg^{-1} (diarsenic trioxide) to 500 mg kg^{-1} of body weight (DMA). Acute As intoxication associated with the ingestion of contaminated well water has been reported in many countries (Table VIII).

The single most characteristic effect of long-term exposure to As is a pattern of skin changes, including hyperkeratosis (a darkening of the skin and appearance of small "corns" or "warts" on the palms, soles, and torso; Fig. 3). A small number of the "corns" may ultimately develop into skin cancer (USDHHS, 2000).

Early symptoms of As poisoning in humans include abdominal pain, vomiting, diarrhea, muscular pain, and weakness, with flushing of the skin (Armstrong *et al*., 1984; Cullen *et al*., 1995; Moore *et al*., 1994). These symptoms are often followed by numbness and tingling of the extremities, muscular cramping, and the appearance of an erythematous rash. Further symptoms may appear within a month, including burning paraesthesias of the extremities, hyper/hypopigmentation (mottled or multicolor skin), Mee's lines on fingernails, and progressive deterioration in motor and sensory responses (Fennell and Stacy, 1981; Murphy *et al*., 1981).

Acute oral As poisoning at doses of 8 mg As kg^{-1} and above have been reported to affect the respiratory system (Civantos *et al*., 1995). A number of studies in humans have shown that As ingestion may lead to serious effects on the cardiovascular system (Cullen *et al*., 1995). Anemia and leukopenia

Table VIII
Selected References on Effect of Arsenic on Human Health

Effect and/or symptoms	Countries	Reference
Neoplasia and induce DNA damage and inhibit DNA hypermethylation	France USA	Burnichon *et al.* (2003) Goering *et al.* (1999)
Malanosis, melanokeratosis (malignancy) in adults	Bangladesh and India	Saha (2003)
Hyper pigmentation, keratosis, weakness, anemia, burning sensation of eyes, solid swelling of legs, liver fibrosis, chronic lung disease, gangrene of toes, neuropathy	Bangladesh Bangladesh Bangladesh and India Bangladesh Bangladesh	Karim (2000) Mazumder (2003) Rahman *et al.* (2001) Kadono *et al.* (2002) Karim (2000)
Chromosomal aberrations and chromatid exchanges	India	Mahata *et al.* (2003)
Skin cancer	Bangladesh India USA USA USA Bangladesh India	Mazumder (2003) Mukherjee *et al.* (2003) Brown and Ross (2002) Hamadeh *et al.* (2002) Hall (2002) Kadono *et al.* (2002) Das *et al.* (1996)
Bladder cancer	USA	Brown and Ross (2002)
Lung cancer	USA USA	Brown and Ross (2002) Hall (2002)
Peripheral vascular, cardiovascular, cerebrovascular diseases	USA	Brown and Ross (2002)
Diabetes	USA	Brown and Ross (2002)
Adverse reproductive outcome	USA	Brown and Ross (2002)
Neuropathy	Bangladesh and India India	Mazumder (2003) Mukherjee *et al.* (2003)
Paresthesias and pains in the distal parts of extremities	India	Mukherjee *et al.* (2003)
Dysfunction of sensory nerve	India	Mukherjee *et al.* (2003)
Apoptosis and necrosis in developing brain cells	India	Chattopadhyay *et al.* (2002)
Inducement of oxidative stress, activating stress gene expression	Taiwan USA	Yih *et al.* (2002) Hughes (2002)
Altered DNA methylation and cell proliferation	USA	Hughes (2002)
Bone marrow depression	USA	Hall (2002)
Hypertension	India	Rahman *et al.* (1999)
Gastrointestinal disturbances	USA	Cullen *et al.* (1995); Hall (2002)
Hepatocellular carcinoma	China	Liu *et al.* (2001)

(*continued*)

Table VIII (*continued*)

Effect and/or symptoms	Countries	Reference
Hepatic fibrosis	India	Santra *et al.* (2000)
Blackfoot disease	Taiwan	Wang *et al.* (1997)
	Bangladesh, China, India, Taiwan, and USA	Wai *et al.* (2003)
Acute intake results: vomiting, diarrhea, low blood pressure, and high heart beat	USA	Cullen *et al.* (1995)
Teratogenesis in unborn children	Bangladesh	Karim (2000)

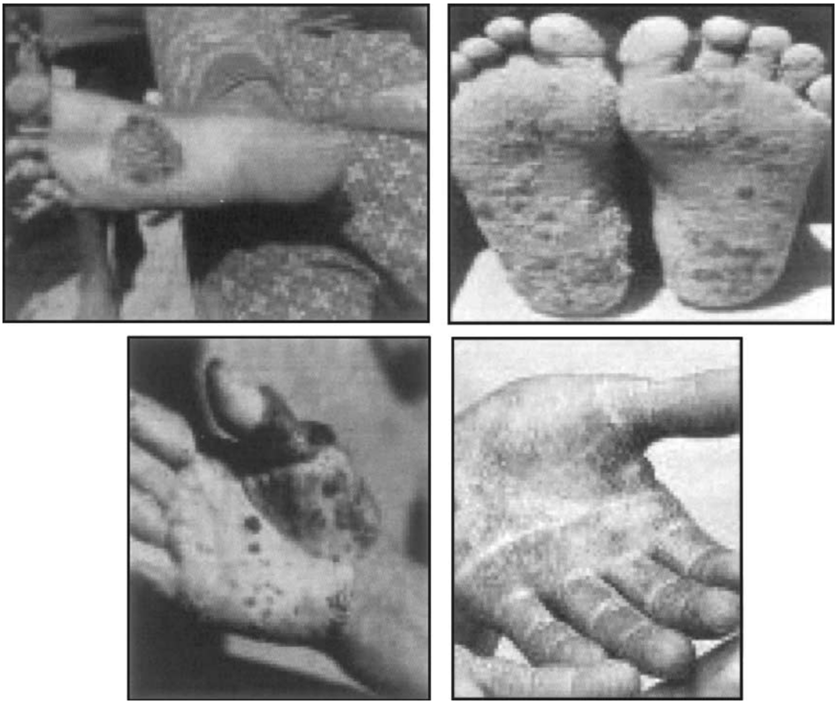

Figure 3 Skin lesions (hyperkeratosis) at various stages due to arsenic poisoning.

were also found to be the common effects of As poisoning in humans resulting from prolonged oral exposure at doses of 0.05 mg As kg^{-1} day^{-1} or more (Armstrong *et al.*, 1984; Mazumder *et al.*, 1988; Saha *et al.*, 2003).

Studies have also revealed hepatic effects of As poisoning (USDHHS, 2000), as indicated by swollen and tender liver with elevated levels of hepatic enzymes in blood (Armstrong *et al.*, 1984).

VI. RISK MANAGEMENT OF ARSENIC IN CONTAMINATED ENVIRONMENTS

Risk management of contaminated sites includes source reduction, site remediation, and environmental protection. Selection of optimal risk management strategies requires consideration of core objectives such as technical practicability, feasibility, and cost effectiveness of the strategy and wider environmental, social, and economic impacts. Arriving at an optimal risk management solution for a specific contaminated site involves three main phases of the decision-making process. These include problem identification, development of problem solving alternatives (i.e., remediation technologies), and management of the site. The next section discusses the various remediation technologies considered suitable for managing As-contaminated soil and aquatic environments.

A. REMEDIATION OF ARSENIC-CONTAMINATED SOIL

Remediation of As-contaminated soil involves physical, chemical, and biological approaches that may achieve either the partial/complete removal of As from soil or the reduction of its bioavailability in order to minimize toxicity (Fig. 4). A large variety of methods have been developed to remediate metal(loid)s-contaminated sites. These methods can also be applicable for the remediation of As-contaminated soils. The selection and adoption of these technologies depend on the extent and nature of As contamination, type of soil, characteristics of the contaminated site, cost of operation, availability of materials, and relevant regulations.

1. Physical Remediation

Major physical *in situ* treatment technologies to remediate metal(loid)-contaminated sites include capping, soil mixing, soil washing, and solidification. The simplest technique for reducing the toxic concentration of As in soils is mixing the contaminated soil with uncontaminated soil. This results in the dilution of As to acceptable levels. This can be achieved by importing clean soil and mixing it with As-contaminated soil or redistributing clean

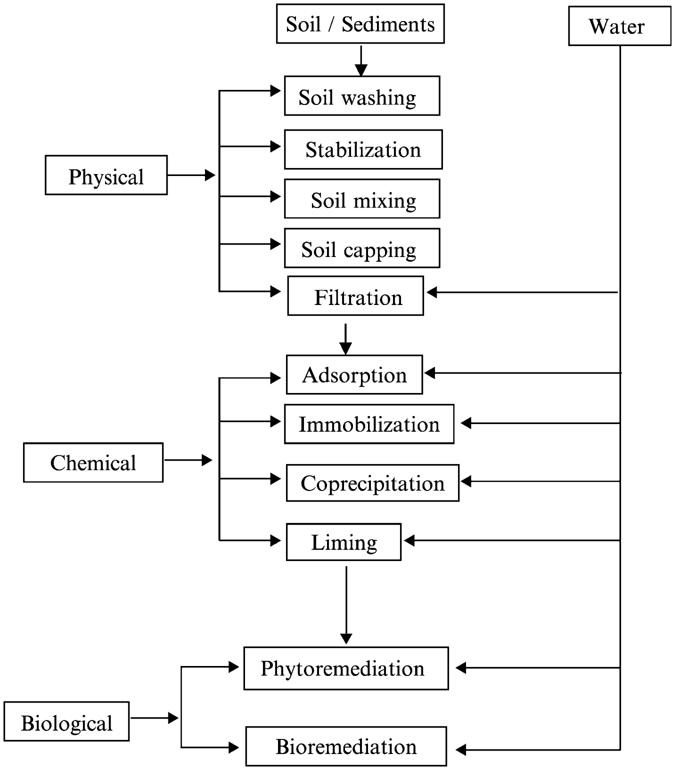

Figure 4 Viable remediation technologies for arsenic-contaminated soil/sediment and aquatic ecosystems.

materials already available in the contaminated site. Another dilution technique, especially in cultivated soils, relies on deep ploughing, during which the vertical mixing of the contaminated surface soil with less contaminated subsoil reduces the surface contamination, thereby minimizing the potential for As uptake by plants and ingestion of As by grazing animals. However, in this method the total concentration of As in soil will remain the same.

Soil washing or extraction has also been used widely for the remediation of metal(loid)-contaminated soils in Europe (Tuin and Tels, 1991) and this method may be applicable for As-contaminated soils to some extent. Tokunaga and Hakuta (2002) evaluated an acid-washing process to extract the bulk of As(V) from a highly contaminated (2830 mg As kg^{-1} soil) Kuroboku soil (Andosol) so as to minimize the risk of As to human health and the environment. The contaminated soil was washed with different concentrations of hydrogen fluoride, phosphoric acid, sulfuric acid, hydrogen chloride, nitric acid, perchloric acid, hydrogen bromide, acetic acid, hydrogen peroxide, 3:1 hydrogen chloride–nitric acid, or 2:1 nitric acid–perchloric acid. Phosphoric acid proved to be most promising as an extractant, attaining 99.9% As extraction at 9.4% acid concentration. Sulfuric acid also attained a high percentage extraction. The acid-washed soil was further stabilized by the addition of lanthanum (La), cerium (Ce), and Fe(III) salts or their oxides/hydroxides, which form an insoluble complex with dissolved As. Both salts and oxides of La and Ce were effective in immobilizing As in the soil attaining less than 0.01 mg liter^{-1} As in the leachate.

The success of soil washing largely depends on speciation of As present in the contaminated soils, as it is based on the desorption or dissolution of As from the soil inorganic and organic matrix during washing with acids and chelating agents. Although soil washing is suitable for off-site treatment of soil, it can also be used for on-site remediation using mobile equipment. However, the high cost of chelating agents and choice of extractant may restrict their usage to only small-scale operations.

Arsenic-contaminated soil may be bound into a solid mass by using materials such as cement, gypsum, or asphalt. However, there are issues associated with the long-term stability of the solidified material. Capping the contaminated sites with clean soil is used to isolate contaminated sites as it is less expensive than other remedial options (Kookana and Naidu, 2000). Such covers should obviously prevent upward migration of contaminants through the capillary movement of soil water. The depth of such cover or “cap” required for contaminated sites should be assessed carefully. Using a simulated experiment, Kookana and Naidu (2000) demonstrated that when the water table is deeper than 2 m from the surface of cap, the upward migration of As through the cap is likely to be less than 0.5 m in 5 years. Where the water table is shallow enough to supply water to the surface (i.e., 1.5 to 2 m in most soils), dissolved As could take <10 years to reach the surface. They have also indicated that when the cap is of a different soil type than the underlying contaminated soil, a coarse-textured cap is very effective in reducing the capillary rise and therefore the cap should always be designed to include a coarser layer to break the capillary continuity.

2. Chemical Remediation

Remediation, based on chemical reactions, is becoming increasingly popular largely because of a high rate of success. A number of methods have been developed mainly involving adsorption, immobilization, precipitation, and complexation reactions [Eqs. (27–37) in Table VI]. However, such methods are often expensive for the remediation of large areas. Two approaches are often used in the chemical remediation of metal(loid)-contaminated soils: (i) immobilization of metal(loid)s using inorganic and organic soil amendments in order to reduce their bioavailability and (ii) mobilization of metal(loid)s and their subsequent removal through plant uptake (phytoremediation) or soil washing. This section discusses the immobilization techniques used for the remediation of As-contaminated soil. The second approach is discussed in Section VI.A.3.

Chemical immobilization is achieved mainly through adsorption/precipitation of As in contaminated sites through the addition of soil amendments. The mobilization of metal(loid)s in soils for plant uptake and leaching to groundwater can be minimized by reducing their bioavailability through chemical and biological immobilization (Bolan *et al.*, 2004). There has been interest in the immobilization of metal(loid)s using a range of inorganic compounds such as lime, P fertilizers (e.g., phosphate rocks) and alkaline waste materials, and organic compounds such as biosolids (Basta *et al.*, 2001; Knox *et al.*, 2000). Depending on the source, the application of P compounds can cause direct adsorption of As onto these materials, promote As complex formation, or induce desorption of As through competition. This method is considered more economical and less disruptive than the conventional remediation option of soil removal (Bolan *et al.*, 2003).

Immobilization of As may be achieved by (i) changing the physical properties of the soil so that As is more tightly bound and therefore becomes less bioavailable; (ii) chemically immobilizing As either by sorption onto a mineral surface or by precipitation as a discrete insoluble compound; and/or (iii) mixing the contaminated soil with uncontaminated soil, thereby increasing the number of As-binding sites (Naidu *et al.*, 2003).

A number of organic and inorganic amendments are known to immobilize a range of metal(loid)s including As by chemical adsorption. These include ion-exchange resin, ferrous sulfate, silica gel, gypsum, clay minerals such as bentonite, kaolin, and zeolite, green sand, and liming materials. These materials are naturally occurring and nontoxic with a large specific surface area and a significant amount of surface charge. The use of naturally occurring clay minerals such as zeolite as adsorbents is a novel method for the remediation of metal(loid)-contaminated soils (Minato *et al.*, 2000). The advantages of zeolite application are its high efficiency for retention of metal(loid)s in soils, low cost, and easy application. Naidu *et al.* (2000) examined the potential for using strongly weathered oxidic soils as reactive barriers and found a strong affinity for As as it retains almost 5000 mg As kg^{-1}.

Boisson *et al.* (1999) assessed the effectiveness of soil additives in reducing contaminant mobility. Their results indicated that the lowest amount of As was extracted when the soil was amended with beringite, steel shots, and their combination. Although the addition of hydroxyapatite decreased the mobility of metals such as Cd and Pb, it increased the mobility of As mainly due to H_2PO_4–AsO_4 competition for the sorption sites. Therefore, the use of hydroxyapatite at multimetal(loid)-contaminated sites requires careful attention.

Liming is increasingly being used as an important soil management practice in reducing the toxicity of certain metal(loid)s in soils. In addition to the traditional agricultural lime, a large number of studies have examined the potential value of other liming materials as immobilizing agents in reducing the bioavailability of a range of metal(loid)s in soils (Bolan *et al.*, 2003). However, the effect of liming soils on As mobility has been rather inconsistent. Lime addition to As-contaminated soil induces the formation of $CaH(AsO_4)_2$ [Eq. (35) in Table VI], thereby reducing the soluble As in the soil solution for plant uptake and leaching. However, the solubility product of this compound is greater than that for Fe and Al arsenates, which are readily formed in most soils. For this reason, liming is not practiced widely to overcome As toxicity in soils (Jones *et al.*, 1997), although liming has been reported to increase the immobilization of As (Bothe and Brown, 1999) and to decrease the plant uptake of As (Jiang and Singh, 1994; Tyler and Olsson, 2001).

Naidu *et al.* (2003) evaluated the potential value of the chemical immobilization technique in the remediation of an As-contaminated site under field conditions in Australia. The site was a former railway depot that had previously been shown to be extensively contaminated with As. The As levels in the soil exceeded both ecological (20 mg kg^{-1}) and health investigation levels (100 mg kg^{-1}) and was appreciably water soluble, indicating that large amounts of As were potentially mobile at this site. The historical source of the contamination appears to be the ubiquitous use of As-based herbicides. Exposure pathway analyses showed that the highly mobile As posed a risk to both the groundwater and the residents living in the area. The contaminated site was identified for industrial development with Australian industrial guidelines for As set at 500 mg kg^{-1} soil. Options for managing contaminated soil included *in situ* cleanup, excavation, and transport to landfill sites or application of risk-based land management strategy. Both *in situ* cleanup and excavation and transport to landfill were found to be prohibitively expensive and ranged from ~\$500,000 to \$1,000,000.

A risk reduction strategy was adopted with the aim to reduce the mobility of As through chemical immobilization. Ferrous salt was used to generate *in situ* mineral phases to immobilize As [Eq. (38)]. This reaction requires oxygen to be available to the soil and also generates considerable amounts of acid, which may be counterproductive to As immobilization in poorly buffered soils. The increased acidity could be neutralized by the amendment with lime [Eq. (39)]. The redox conditions of the soil also influence the speciation of As, and an example of two possible redox couples is given later [Eqs. (40) and (41)]. Following initial detailed laboratory studies, a mixture of Fe/Mn/gypsum was used as the stabilizing chemical. As shown in

Fig. 5, application of the mixed chemical led to a significant decline in mobile As. Subsequent studies involving aging of the treated soil showed complete elimination of risk posed by As. The total cost using this strategy was < \$100,000, thus providing significant savings to the client.

$$4FeSO_4 + O_{2(g)} + 6H_2O \leftrightharpoons 4FeOOH_{(s)} + 4SO_4^{2-} + 8H^+ \tag{38}$$

$$2FeSO_4 + \frac{1}{2}O_{2(g)} + 2CaCO_3 + 5H_2O \leftrightharpoons 2FeOOH_{(s)} + 2CaSO_4 \cdot 2H_2O + 2CO_{2(g)} \tag{39}$$

$$Fe_2O_{3(s)} + 4H^+ + AsO_3^{3-} \leftrightharpoons 2Fe^{2+} + AsO_4^{3-} + 2H_2O \quad E_o = 0.21\ V \tag{40}$$

$$MnO_{2(s)} + 2H^+ + AsO_3^{3-} \leftrightharpoons Mn^{2+} + AsO_4^{3-} + H_2O \quad E_o = 0.67\ V \tag{41}$$

Results of a field experiment conducted by Xie and Huang (1998) on an As-polluted soil (*Typentiaqualf*) in China have shown that the application of Fe (as $FeCl_3$ at 25 mg Fe kg^{-1} soil) or Mn (as MnO_2 at 25 mg Mn kg^{-1} soil) markedly lowered the total water- soluble As [As(III) + As(V)] (24–26%) and As(III) (17–82%) in the soil and made the rice plants grow better than the control treatment, resulting in a higher rice grain yield and lesser As content in rice husk. This was attributed to the oxidation of As(III) to As(V) by MnO_2 and the subsequent strong adsorption of As(V) by Fe and Mn oxides.

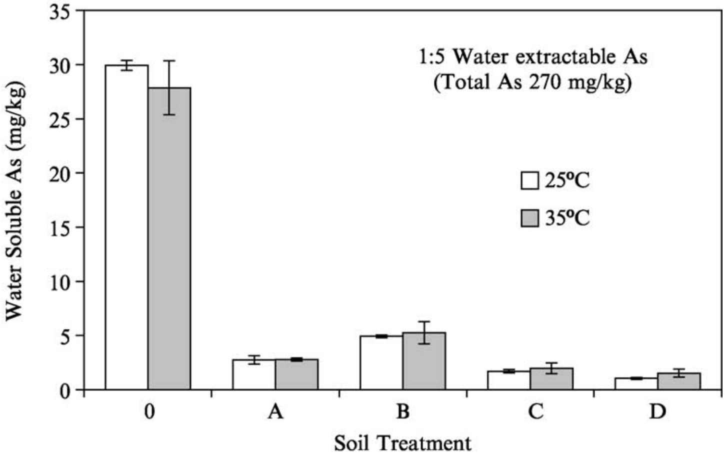

Figure 5 Variation of water-extractable As (1:5) for a subsurface-contaminated soil with soil treatment and incubation temperature. Treatments were (0) control soil; (A) Fe; (B) Fe + lime; (C) Fe + Mn; and (D) Fe + Mn + Al (Naidu *et al.*, 2003).

3. Biological Remediation

a. Bioremediation. Bioremediation of soils contaminated with organic compounds such as pesticides and hydrocarbons is widely accepted in which native or introduced microorganisms and/or biological materials, such as compost, animal manures, and plant residues, are used to detoxify or transform contaminants. There has been increasing interest in the application of this technology for the remediation of metal(loid)-contaminated soils, especially for those metal(loid)s that undergo biological transformation. Although it has several limitations, this technology holds continuing interest because of its cost effectiveness. The unique aspect in bioremediation is that it relies mainly on natural processes and does not necessarily require the addition of chemical amendments other than microbial cultures and biological wastes. Because As undergoes biological transformation in soil, appropriate microorganisms may be used for the remediation of As-contaminated soils. Existing and developing *in situ* bioremediation technologies may be grouped into the following two broad categories (NRC, 1997).

i. Intrinsic bioremediation is where the essential materials required to sustain microbial activity exist in sufficient concentrations that naturally occurring microbial communities are able to degrade the target contaminants without the need for human intervention. This technique is better suited for remediation of soils with low levels of As over an extensive area.
ii. Engineered bioremediation relies on various approaches to accelerate *in situ* microbial degradation rates. This is accomplished by optimizing the environmental conditions by adding nutrients and/or an electron donor/acceptor, thus promoting the proliferation and activity of existing microbial consortia. It is favored for highly contaminated localized sites.

Three approaches could be used in the bioremediation of As-contaminated soils: (i) As could be immobilized into microbial cells through biosorption (bioaccumulation), (ii) toxic As(III) could be oxidized to less toxic As(V), and (iii) As compounds could be removed from the soil by volatilization.

i. Bioaccumulation: Microorganisms exhibit a strong ability to accumulate (bioaccumulation) As from a substrate containing very low concentrations of this element. Bioaccumulation is activated by two processes, namely biosorption of As by microbial biomass and its byproducts and physiological uptake of As by microorganisms through metabolically active and passive processes. Factors such as soil pH, moisture and aeration, temperature, concentration and speciation of As, soil amendments, and rhizosphere are known to influence the process of bioaccumulation of As in microbial cells. While a number of bacterial and fungal species have been known to bioaccumulate As, some algal species (*Fucus gardneri* and *Chlorella vulgaris*) are also known to accumulate As (Granchinho *et al.*, 2001; Maeda *et al.*, 1985). This technique has often been used successfully to remove metal(loid) ions from the aquatic environment and is therefore discussed further in Section VI.B.2.

ii. Microbial redox reactions: Heterotrophic bacteria have been found to oxidize toxic As(III) in soils and sediments to less toxic As(V) and thus could play an important role in the remediation of contaminated environment (Wakao *et al.*, 1988). Because As(V) is strongly adsorbed onto inorganic soil components, microbial oxidation could result in the immobilization of As. Strains of *Bacillus* and *Pseudomonas* spp. (Frankenberger and Losi, 1995) and *Alcaligenes faecalis* (Phillips and Taylor, 1976) and *Alcaligenes* spp. (Osborne and Ehrlich, 1976) were found capable of oxidizing As(III) to As(V).

A dissimilatory metal(loid) reduction has the potential to be a helpful mechanism for both intrinsic and engineered bioremediation of contaminated environments. Arsenic can be reduced to As^o, which is subsequently precipitated as a result of microbial sulfate reduction. *Desulfototomaculum auripigmentum*, which reduces both As(V) to As(III) and SO_4^{2-} to H_2S leads to As_2S_3 precipitation (Newman *et al.*, 1997). Because arsenite is more soluble than As(V), the latter can be reduced to As(III) using bacteria in soil and subsequently leached.

iii. Methylation of As: A variety of microbes could transform inorganic As into its metallic hydride or methylated forms. Due to their low boiling point and/or high vapor pressure, these compounds are susceptible for volatilization and could easily be lost to the atmosphere (Braman and Foreback, 1973). Methylation is considered a major biological transformation through which As is volatilized and lost. As discussed earlier, biomethylation of As in soils and aquatic systems is well documented, as it is important in controlling the mobilization and subsequent distribution of arsenicals in the environment (Frankenberger and Losi, 1995; Gao and Burae, 1997; McBride and Wolfe, 1971; Tamaki and Frankenberger, 1992).

Methanogenic bacteria, commonly present in sewage sludge, freshwater sediments, and composts, are capable of methylating inorganic As to volatile DMA. Arsenate, As(III), and MAA can serve as substrates in DMA formation. Inorganic As methylation is coupled to the CH_4 biosynthetic pathway and may be a widely occurring mechanism for As removal and detoxification (Frankenberger and Losi, 1995). In addition to bacteria, certain soil fungi also are able to volatilize As as methylarsine compounds, which are derived from inorganic and organic As species.

Woolson (1977) demonstrated the release of alkylarsines in a number of soils. Dimethylarsine and trimethylarsine are produced when soils were amended with inorganic and methylated arsenic herbicides. The organisms responsible for volatilization of As originate from diverse environments, suggesting that a number of species have the capacity to produce alkylarsines (Frankenberger and Losi, 1995; Woolson, 1977). Some examples of the organisms involved in the biomethylation of As are given in Table IX. In most cases, these organisms were tested in laboratory conditions; however, their performance should be assessed under field conditions in contaminated sites.

b. Phytoremediation. Phytoremediation is considered a subset of bioremediation that employs plants and their associated root-bound microbial community to remove, contain, degrade, or render environmental contaminants harmless (Raskin *et al.*, 1997; Robinson *et al.*, 2003b). This terminology applies to all plant-influenced biological, chemical, and physical processes that aid in the remediation of contaminated medium (Cunningham and Lee, 1995). It involves soil–plant systems in which metal(loid)s-accumulating plants are grown in contaminated sites. It is considered an economically feasible and environmentally viable technology for remediating metal(loid)-contaminated systems. The effectiveness of this technology is, however, variable and highly site dependent.

In phytoremediation, plants are exploited as a biopump that use the energy of the sun to remove water and contaminants from the soil to the aboveground portion and return some of the products of photosynthesis back into the root zone in the form of root exudates involved in the (im)mobilization of contaminants. Transpiration is the driving force for phytoremediation. By removing water from the medium, plants help reduce erosion, runoff, and leaching, thereby limiting the movement of contaminants off-site. Some contaminants are taken up in the transpiration stream, where they may be metabolized, and may be eventually volatilized. By removing excess water from the soil profile, plant roots may also create an aerobic environment where metal(loid) mobility is reduced and biological activity is enhanced. Plants stimulate microbiological activity in the root zone by providing a carbon source from root exudates and decaying root materials (Robinson *et al.*, 2003b).

Phytoremediation technologies have been grouped into various categories that include phytostabilization, rhizofiltration, and phytoextraction (Cunningham *et al.*, 1995). In phytostabilization, transpiration and root growth are used to immobilize contaminants, including As by reducing leaching, controlling erosion, creating an aerobic environment in the root zone, and adding organic matter to the substrate that binds As. It involves the establishment of metal(loid)-tolerant vegetation on the contaminated site

Table IX
Microorganisms Proven Capable of Biomethylating Arsenic Compounds in Soil and Aquatic Environments

Organisms	Mechanism	Reference
Scopulariopsis koningii *Fomitopsis pinicola* *Penicillium gladioli*	Methylate As to trimethylarsenic(V) species, precursors to volatile trimethylarsine	Lehr *et al.* (2003)
Fusarium oxysporum meloni	Accumulates As(V) and converts to dimethylarsine	Granchinho *et al.* (2002)
Fucus gardneri	Methylates As(V) to dimethylarsine	Granchinho *et al.* (2001)
Closterium aciculare	Methylates As(V) to methylarsenic(III) species	Hasegawa *et al.* (2001)
S. brevicaule	Transforms As(V) to $(CH_3)_3As$ species	Andrewes *et al.* (2000)
Chlorella vulgaris	Biosorption and accumulation of As and converting into compound of $(CH_3)_2AsO(OH)$	Kaise *et al.* (1997)
Polyphysa peniculus	Methylates As(V) to dimethylarsine	Cullen *et al.* (1994)
Penicillium sp.	At pH 5 to 6 methylates $CH_3AsO(OH)_2$ and $(CH_3)_2AsO(OH)$ to $(CH_3)_3As$.	Huysmans and Frankenberger (1991)
Aeromonas sp.	Methylates $(CH_3)_2AsO(OH)$ to $(CH_3)_3AsO$	Baker *et al.* (1983)
Alcaligenes sp. *Pseudomonas* sp.	Methylates AsO_2^- or AsO_4^{3-} into AsH_3 under aerobic condition	Cheng and Focht (1979)
Flavobacterium sp.	Methylates $(CH_3)_2AsO(OH)$ to $(CH_3)_3AsO$	Chau and Wong (1978)
Candida humicola	Methylates As(V) into a volatile As species	Cullen *et al.* (1984)
Methanobacteriaum	Methylates As(V), As(III) and $CH_3AsO(OH)_2$ to $(CH_3)_2AsH$ under anaerobic condition	McBride and Wolfe (1971)
C. humicola *Gliocladium roseum* *Penicillium* sp.	Methylates $CH_3AsO(OH)_2$ and $(CH_3)_2AsO(OH)$ acid to $(CH_3)_3As$. [*C. humicola* uses AsO_2^- and AsO_4^{3-} as substrates to produce $(CH_3)_3As$]	Cox and Alexander (1973)

that is left in perpetuity. The stabilization of As in the root zone could be achieved through the addition of organic matter as well as soil amendments. In rhizofiltration, the roots can be used to adsorb or absorb metal (loid)s, which are subsequently removed by harvesting the whole plant. In this case, metal(loid) tolerance and translocation of the metal(loid)s to aerial parts are largely irrelevant. In phytoextraction, plants can be grown on contaminated soil and the aerial parts [and the metal(loid)s they contain] harvested. In this case, plants need to be tolerant only if the soil metal(loid) content is very high, but they need to accumulate very high concentrations in their aerial parts. Phytoextraction involves repeated cropping of plants until the metal(loid) concentration in the soil has reached the acceptable (targeted) level.

Certain plants, termed "hyperaccumulators" (Brooks *et al.*, 1977), accumulate an inordinate concentration of metal(loid)s in their aboveground biomass. These plants may even accumulate metal(loid)s that are nonessential and often toxic to plants. The minimum concentration of As required for a plant to be classified as a hyperaccumulator of As was set at 1000 mg kg^{-1} (0.1%) on a dry weight basis (Ma *et al.*, 2001). The hyperaccumulation of metal(loid)s involves uptake of the soluble metal(loid) species by the root system, translocation to the aerial parts, and storage in a nontoxic form in the aerial portions. Chaney *et al.* (1997) suggested that this process necessarily requires tolerance to high concentrations of metal (loid)s.

Using a combination of techniques, including X-ray absorption spectroscopy, Pickering *et al.* (2000) studied the biological mechanisms involved in the accumulation of As in Indian mustard (*Brassica juncea*) and established the biochemical fate of As taken up by this plant. Arsenic was taken up by roots as oxyanions [As(V) and As(III)], possibly via the $H_2PO_4^-$ transport mechanism, and a small fraction was exported to the shoot via xylem. Once in the shoot, the As is stored as an As-III-tris-thiolate complex. The majority of the As remains in the roots as an As-III-tris-thiolate complex, which is indistinguishable from that found in the shoots and from As-III-tris-glutathione. The thiolate donors are thus probably either glutathione or phytochelatins. Addition of the dithiol arsenic chelator dimercaptosuccinate to the hydroponic culture medium caused a fivefold increase in the As level in the leaves, although the total As accumulation was increased only marginally. This indicates that the addition of dimercaptosuccinate to As-contaminated soils is likely to facilitate As bioaccumulation in plant shoots, a prerequisite for efficient phytoremediation strategy. The high cost of this compound, however, would be an economic concern unless the plants would be able to synthesize it.

At present there are about 400 species of known terrestrial plants that hyperaccumulate one or more of several metal(loid)s (Robinson *et al.*, 1995). However, until recently no As-hyperaccumulating plants were reported. Ma *et al.* (2001) discovered an As-hyperaccumulating plant, ladder brake (*Pteris vittata* L.), a terrestrial fern, which accumulates large amounts (23,000 mg kg^{-1}-dry weight basis) of As from soils. The unique property of As hyperaccumulation by the Chinese brake fern is of great significance in the phytoremediation of As-contaminated soils. Therefore, the potential of this fern for phytoremediation of As-contaminated soil was assessed by Tu *et al.* (2002) in a glasshouse experiment using soils from an abandoned wood preservation site. Results have shown that the Chinese brake accumulated huge amounts of As from soil and that its As concentration increased with the growth period. The As concentration in the fronds was 6000 mg kg^{-1} dry mass after 8 weeks of transplanting and increased to 7230 mg kg^{-1} after 20 weeks. The As concentration increased as fronds aged, with old fronds accumulating as much as 13,800 mg As kg^{-1}. Another silver fern [*Pityrogramma calomelanos* (L.) Link] has also been reported to hyperaccumulate As up to 8350 mg kg^{-1} dry mass from soil containing 135 mg kg^{-1} (Francesconi *et al.*, 2002). It occurs in tropical and subtropical regions of the world and is widely distributed in Thailand where it favors open, high rainfall areas. Some of the studies involving phytoremediation of As in the soil are presented in Table X.

Arsenic uptake by plants is associated with the $H_2PO_4^-$ uptake mechanism, where presumably As(V) is taken up as a $H_2PO_4^-$ analogue (Pickering *et al.*, 2000). Therefore, there is a growing interest in using P fertilizer to enhance As uptake by plants. Tu and Ma (2003) suggested that phosphate application may be an important strategy for the efficient use of Chinese brake (*Pteris vittata* L.) to phytoremediate As-contaminated soils. The addition of P fertilizer to As-contaminated soil was found to increase As solubility and mobility and thus increase plant uptake of soil As (Creger and Peryea, 1994). Some selected references on the mobilization of As by phosphate compounds are reported in Table XI.

In an hydroponic experiment, Wang *et al.* (2002) investigated the interactions of As(V) and $H_2PO_4^-$ on the uptake and distribution of As and P, and As speciation in *P. vittata*. They found that the plants accumulated As in the fronds up to 27,000 mg kg $^{-1}$ dry weight, and the frond As to root As concentration ratio varied between 1.3 and 6.7. Increasing the phosphate supply decreased the As uptake markedly, with the effect being greater on root As concentration than on shoot concentration. They concluded that As(V) is taken up by *P. vittata* via the $H_2PO_4^-$ transporters, reduced to As (III), and sequestered in the fronds primarily as As(III). In a fly ash-amended soil, Qafoku *et al.* (1999) observed that $H_2PO_4^-$ displaced both As(III) and As(V), thereby increasing the mobility of As in soils. Thus, the $H_2PO_4^-$-induced plant uptake of As could be employed in the phytoremediation of As-contaminated sites.

Table X
Selected References on Phytoremediation of Arsenic-Contaminated Soil

Plant used	Result and remark	Reference
Chinese brake ferns (*Pteris vittata*)	As concentration in shoot as high as 20 times the soil As concentration under field condition. Increasing soil pH improved As uptake by plant	Salido *et al.* (2003)
	Fern transfers As rapidly from soil to aboveground biomass with only minimal As in roots	Zhang *et al.* (2002)
	Hyperaccumulation of As enhanced by P addition	Chen *et al.* (2002)
	Fronds accumulated as much as 13,800 mg As kg^{-1} (∼90% As transported to the fronds)	Tu *et al.* (2002)
White lupin (*Lupinus albus*)	As(V) uptake was high. Roots accumulated As under P deficiency. Potentially a good candidate due to rapid growth and adaptability to varying edaphic status	Esteban *et al.* (2003)
Arabidopsis thaliana	Plants accumulated large amounts of As showing some tolerance	Dhankher *et al.* (2002)
Ladder brake (*P. vittata* L.)	Removal of ∼26% of soil As within 20 weeks after transplanting	Tu and Ma (2002)
Silver fern (*Pityrogramma calomelanos*)	Accumulating in fronds up to 8350 mg kg^{-1}	Francesconi *et al.* (2002)
Herb (*Mimosa pudica*)	Tolerated high soil As (∼5200 mg As kg^{-1}), accumulating in leaves ∼77 mg As kg^{-1}	Visoottiviseth *et al.* (2002)
Shrub (*Melastoma malabrathriccum*)	Tolerated high soil As (∼5200 mg As kg^{-1}), accumulating in leaves up to 43 mg As kg^{-1}	Visoottiviseth *et al.* (2002)
Rice (*Oryza sativa*)	Plants grown on As-treated soil had higher As uptake than plants grown on untreated soil; at concentrations >1500 mg As kg^{-1} plants died	Onken and Hossner (1995)

Table XI
Selected References on the Mobilization of Arsenic by Phosphate Compounds

Phosphate compound	Method of investigation	Proposed mechanism	Reference
$Ca(H_2PO_4)_2$	Transport and leaching	Desorption	Qafoku *et al.* (1999)
NaH_2PO_4	Chemical fractionation; transport and leaching studies	Competitive adsorption	Creger and Peryea (1994)
NaH_2PO_4	Chemical fractionation	Competitive adsorption	Reynolds *et al.* (1999)
NaH_2PO_4	Phytoavailability bioassay		Woolson *et al.* (1973)
NaH_2PO_4	Phytoavailability bioassay	Competitive adsorption	Livesey and Huang (1981)
$NH_4H_2PO_4$ $Ca(H_2PO_4)_2$	Adsorption and desorption	Competitive adsorption	Peryea (1991); Peryea and Kammereck (1997)
$NH_4H_2PO_4$	Transport and leaching	Competitive adsorption	Davenport and Peryea (1991)
Hydroxyapatite	Chemical fractionation	Competitive adsorption	Boisson *et al.* (1999)

Davenport and Peryea (1991) observed that high rates of monoammonium phosphate (MAP) or monocalcium phosphate (MCP) fertilizers significantly increased the amount of As leached from the soil. Mixing high rates of MAP or MCP fertilizers with orchard soil, Peryea (1991) reported that As release from lead–arsenate-contaminated soil was positively related to the level of P input but was not significantly influenced by the P source. Arsenic solubility was regulated by specific $H_2PO_4^-$ –AsO_4 exchange, whereas $H_2PO_4^-$ solubility was controlled by the equilibria of metastable P minerals. Results indicate that the use of P fertilizers on such soils has the potential to greatly enhance the downward movement of As (Peryea and Kammereck, 1997). Thus the increased mobilization of As resulting from phosphate input can result in its increased leaching to groundwater, especially in the absence of active plant growth. Hence attempts to use plants to remove As from soils need to take the multiple effects of phosphate into consideration.

Phytoremediation has several advantages over other remediation and metal(loid) extraction technologies. The cost involved in phytoremediation is much lower than other technologies, such as soil removal, capping, and *ex situ* cleansing. Other advantages include the ultimate fertility of the cleaned site, the high public appeal of "green" technology, and the possibility of producing secondary products that offset the cost of the operation or even produce a small profit. However, some of the basic plant physiological processes, such as low biomass production and shallow root growth, nonetheless limit the scope of phytoremediation. Only surface contamination can be removed or degraded and the cleanup is restricted to areas that are amenable to plant growth. Most importantly, it may take a long time for site remediation to be effective. Phytoremediation can only be used if it meets environmental regulation during the operation as well as its end point.

B. REMOVAL OF ARSENIC FROM AQUATIC ENVIRONMENTS

As discussed earlier, because most cases of As toxicity in humans have resulted from the consumption of As-contaminated water, there have been intensive research efforts in developing technologies aimed at stripping As from water. A plethora of methods suitable for the removal of As from water at both household and community levels are currently available. These methods are primarily based on (i) removal of solid-phase As through coagulation, sedimentation, or filtration; (ii) removal of solution-phase As through ion exchange, osmosis, or electrodialysis; (iii) oxidation of As(III) to As(V) and its subsequent removal through adsorption and/or precipitation; (iv) biosorption using microorganisms; and (v) rhizofiltration using aquatic plants. Some of the methods that have been tested for the removal of As from water are presented in Table XII.

1. Physicochemial Methods

Filtration, adsorption, and chemical precipitation are the most common physicochemical methods used for stripping As from water. While the particulate As in water can be removed by simple filtration, the aqueous As can be removed through adsorption or precipitation followed by filtration.

a. Filtration. Most of the domestic drinking water treatment systems for As removal involve filtration. For example, the "Pitcher filter" involving porous ceramics (Neku and Tandukar, 2003) and sand filters (Yokota *et al.*, 2001) have been found to be effective in stripping As from water. Seidel *et al.* (2001) noticed that the porous nanofiltration anion-exchange membrane removed about 90% of As(V) present in water at a concentration of 316 μg liter^{-1}. Although this technology could achieve a high degree of As removal, it involves a high initial investment and high operation and maintenance costs.

Table XII
Selected References on Methods of Arsenic Stripping from Water

Method	Remark	Reference
3-Gagri (Pitcher) filter	Removed 76–95% of As. Suitable for household use	Neku and Tandukar (2003)
Aeration and sand filtration	Removed 62–92% of As containing ~240–320 μg liter^{-1}	Berg *et al.* (2001)
Pond sand filter system	Removed >99 % of 5 mg As liter^{-1}	Yokota *et al.* (2001)
Negatively charged porous nanofiltration (NF) membrane	60–90% removal of As(V) from water containing ~10–316 μg liter^{-1}	Seidel *et al.* (2001)
Using rare earth oxides	Adsorbed As(V) rapidly and effectively; >90% of adsorption occurred within the first 10 min, adsorbed As (V) could be desorbed by washing with pH 12 solution	Raichur and Panvekar (2002)
Iron oxide-coated sand (IOCS)	Very effective in removing As (III) and As(V) from drinking water containing 200 to 1700 μg liter^{-1}; about 94% removal efficiency	Yuan *et al.* (2002)
Coprecipitation with Fe	Bench scale test showed ~88% of As(III) in water removed by settlement over 24 h	Mamtaz and Bache (2000)
Porous NF membrane	As removal by 60–90 % from drinking water containing As from 10 to 316 μg liter^{-1}	Vrijenhoek and Waypa (2000)
Iron oxide-coated sand and ferrihydrite (IOCS and FH)	~90% removal of As from natural water containing 325 μg liter^{-1}; adsorption of IOCS and FH estimated at 18.3 and 285 μg g^{-1}, respectively	Thirunavkukkarasu *et al.* (2001)
Iron-sulfide minerals (pyrite and pyrrhotite)	Fe-sulfides are very effective in removing As [both As(III) and As(V)] from water	Han and Fyfe (2000)
Kimberlite tailing (mineral waste from diamond mining)	Removed As at a rate of 270 μg g^{-1}; more efficient at near neutral pH. 90–94% removal in 12 h	Dikshit *et al.* (2000)
Mesoporous anions traps (metal-chelated ligands immobilized on anion-binding silica material)	Most As removed from water containing >120 mg liter^{-1}; adsorption at 120 mg g^{-1}	Fryxell *et al.* (1999)
Aquifer materials (composed of quartz, feldspar, calcite, chlorite, illite, and magnetite/hematite)	Removed As(III) from water through adsorption	Carrillo and Drever (1998)

b. Adsorption. A number of compounds, including activated alumina, Fe-coated sand, and ion-exchange resins are used to adsorb As. In most geologic environments, Fe_2O_3 carries a positive surface charge that preferentially adsorbs As. Similarly, $Al(OH)_3$ and silicate clays also adsorb large amounts of As. Yoshida *et al.* (1976) investigated the removal of As from water using "brown gel," which is a silica gel containing 6% of $Fe(OH)_3$, and observed that the maximum adsorption (17 g As kg^{-1}) of both As(III) and As(V) occurred at pH 6.

Rothbaum and Buisson (1977) found that synthetic Fe-floc [$Fe(OH)_3$], prepared by treating $FeSO_4$ with NaOCl at pH 3.5–5.0, removed a large percentage of As from geothermal discharge water through coprecipitation. Similarly, Yuan *et al.* (2002) examined the potential value of several Fe-treated natural materials such as Fe-treated activated carbon, Fe-treated gel beads, and Fe oxide-coated sand in removing As from drinking water under both laboratory and field conditions. The Fe oxide-coated sand consistently achieved a high degree (>94%) of As(III) and As(V) removal. When the pH was increased from 5 to 9, As(V) adsorption decreased slightly, but As(III) adsorption remained relatively stable. Kimberlite tailings (Dikshit *et al.*, 2000) and iron-sulfide minerals such as pyrite and pyrrhotite (Han and Fyfe, 2000) were also found to be very effective adsorbents in stripping both As(III) and As(V) from water.

Hlavay and Polyak (1997) developed and tested novel adsorbents for As stripping. Porous support materials were granulated using Al_2O_3 and/or TiO_2 and then $Fe(OH)_3$ was freshly precipitated onto the surface of these particles. The resulting $Fe(OH)_3$-impregnated porous adsorbent was dried at room temperature and packed into an ion-exchange column. These columns were found to remove >85% of As in water. The As(III) ions can primarily be adsorbed by chemical reaction on the surface of $Fe(OH)_3$. The neutral functional group of $\{{=}FeOH\}$ reacts with $H_2AsO_3^-$ ions, and surface compounds of $\{{=}FeAsO_3H_2\}$, $\{{=}FeAsO_3H^-\}$, and $\{{=}FeAsO^{2-}\}$ can be formed.

Das *et al.* (1995) demonstrated the practical application of the adsorption technique in stripping As by developing a simple household device to remove As from groundwater used for drinking and cooking purposes. The system consists of a filter, tablet, and two earthen or plastic jars. The tablet contains Fe(III) salt, an oxidizing agent, and activated charcoal. The filter is made of mainly purified fly ash with binder. When the tablet is added to water (one tablet for every 20 liters), the As(III) ions are catalytically oxidized to As(V) ions in the presence of Fe(III), which are subsequently adsorbed onto activated charcoal and hydrous ferric oxide ($Fe_2O_3.2–3H_2O$). In addition to As(V), As(III) ions are also strongly adsorbed by Fe(III) oxides. The water is allowed to settle for about an hour and is then filtered. This stripping system has been installed in several locations in Bangladesh and

West Bengal, and analytical results have shown that generally 93–100% of the total As in water (with an initial concentration of 149–463 μg liter^{-1}) is removed.

Khan *et al.* (2000) evaluated the efficiency of a simple three-pitcher filter system consisting of ceramic filters (locally known as 3-kalshi) in stripping As from groundwater. In the 3-kalshi assembly, the first kalshi (pot) contains Fe chips and coarse sand, the second contains wood charcoal and fine sand, and the third is the collector for the filtered water. Depending on the size of the filtering units, this system has been shown to be capable of reducing the As concentration in water from an initial level of 1100 μg liter^{-1} to below the detection limit of 2 μg liter^{-1} with a corresponding decrease in dissolved Fe concentration (from 6000 to 200 μg liter^{-1}).

Similarly, Kim *et al.* (2004) have shown that mesoporous alumina with a wide surface area (307 m^2 g^{-1}), high pore volume (0.39 m^3 g^{-1}), uniform pore size (3.5 nm), and interlinked pore system is efficient in stripping As from domestic water. The mesoporous alumina is insoluble and stable within the range of pH 3–7. The maximum As adsorption was seven times higher [121 mg As(V) g^{-1} and 47 mg As(III) g^{-1}] than that of conventional activated alumina, and the kinetics of adsorption are also rapid with complete adsorption in less than 5 h as compared to conventional alumina (about 2 days to reach half of the initial concentration). Fryxell *et al.* (1999) used metal-chelated ligands immobilized on mesoporous silica as a novel anion-binding material to remove As from water. Nearly complete removal of As(V) has been achieved from solutions containing more than 100 mg As (V) liter^{-1}.

c. Precipitation. Arsenate can be removed by precipitation/coprecipitation using Fe and Al compounds [Eqs. (27–33) in Table VI]. Gulledge and O'Connor (1973) achieved a complete removal of As(V) from water using $Fe_2(SO_4)_3$ at a pH range of 5 to 7.5 [Eq. (34)]. Hydrolyzing metal salts such as $FeCl_3$ and alum [$Al_2(SO_4)_3$] have been shown to be effective in stripping As by coagulation. Hering *et al.* (1997) achieved >90% removal of As(V) from water containing an initial concentration of 100 μg As liter^{-1}. Shen (1973) removed As from drinking water by dosing with chlorine (Cl_2) and $FeCl_3$. Oxidation of As(III) to As(V) by Cl_2 and the subsequent removal by precipitation were considered the mechanisms involved in this process.

Treating drinking water with Fenton's reagent (ferrous ammonium sulfate and H_2O_2) followed by passing through elemental Fe, Krishna *et al.* (2001) achieved As removal below the USEPA maximum permissible limit of 50 μg liter^{-1} from an initial concentration of 2000 μg liter^{-1} of As(III). This method is simple and cost effective for use at community levels. Using a bench scale test, Mamtaz and Bache (2000) demonstrated that up to 88% of the As(III) in water could be removed by coprecipitation with naturally occurring Fe found in groundwater. One of the advantages in chemical precipitation method is that this can be used at both household and community levels. The materials are readily available and generally inexpensive. However, a problem of disposal of toxic sludge exists and it also requires trained operators.

2. Biological Methods

a. Phytoremediation using Aquatic Plants. Phytoremediation of As-contaminated waters may be readily achieved by the use of aquatic plants because unlike soil, most of the As in water is available for plant uptake. In the case of soils, the plant must first solubilize the metal(loid)s in the rhizosphere and then should have the ability to transport it to the aerial tissue (Brooks and Robinson, 1998). The use of freshwater vascular plants for the removal of metal(loid)s from water has been long established. There are two approaches in using these plants for the remediation of polluted water: The first involves monospecific pond cultures of free-floating plants such as water hyacinth. The plants accumulate the metal(loid)s until a steady state of equilibrium is achieved. They are then harvested by removal from the pond. The second approach involves growing rooted emergent species in trickling bed filters. Rhizosphere microbes usually facilitate the removal of metal(loid)s in these systems. Rhizofiltration usually involves the hydroponic culture of plants in a stationary or moving aqueous environment wherein the plant roots absorb metal(loid)s from the water (Brooks and Robinson, 1998). Ideal plants for rhizofiltration should have extensive root systems and be able to remove metal(loid)s over an extended period. Some of the aquatic plants capable of accumulating large amounts of As are presented in Table XIII.

Robinson *et al.* (2004) undertook a field survey in which a number of terrestrial and aquatic plant samples were taken at several sites within the Taupo volcanic zone (TVZ) in New Zealand. The TVZ covers an area of 600,000 ha in the central North Island of New Zealand and the area is rich in geothermal activity. There have been previous reports of elevated As concentrations in some waterways and associated lands in the TVZ (Liddle, 1982). The known sources of As pollution in the TVZ include (i) As arising from naturally occurring geothermal activity; (ii) geothermal bores that release As-rich water into the aquatic biosphere; (iii) runoff of As-based pesticides; (iv) As from timber treatment sites such as the pulp and paper mill at Kinleith; and (v) As added to lakes to control weeds (e.g., $NaAsO_2$ added to Lake Rotorua).

The mean As concentrations in all the plants tested from the TVZ are given in Fig. 6. Data clearly display the difference of As accumulation

Table XIII
Selected Aquatic Plants for Potentially Stripping Arsenic from Water

Name of plant	Level of As accumulation (mg kg^{-1})[a]	Reference
Agrostis capillaris	3470	Porter and Peterson (1975)
Ceratophyllum demersum	650	Reay (1972)
C. demersum	265–1121	Liddle (1982)
C. demersum	44–1160	Robinson *et al.* (1995)
Egeria densa	94–1120	Robinson *et al.* (1995)
Lagarosiphon major	11–1200	Robinson *et al.* (1995)
Rorippa naturtium (subsp. *Aquaticum*)	>400	Robinson *et al.* (1995)
Cynodan dactylon	1600	Jonnalagadda and Nenzou (1997)
Spergularia grandis	1175	Bech *et al.* (1997)
Paspalum tuberosum	1130	Bech *et al.* (1997)
Fern *(Pteris vittata)*	22,630	Ma *et al.* (2001)
Fern *(P. vittata)*	8960–27,000	Wang *et al.* (2002)
Silver fern *(Pityrogramma calomelanos)*	8350	Visoottiviseth *et al.* (2002)
Fern *(Pteris cretica)*	6200–7600	Zhao *et al.* (2002)
Fern *(P. longifolia)*		
Fern *(P. umbrosa)*		
Watercress (*Lepidium sativum*)	12–1766	Robinson *et al.* (2003a)
Myriophyllum propinquum	974–3900	Machetti (2003)
Elodea canadensis	1628–1857	Machetti (2003)
Agrostis sp	800	Machetti (2003)

[a] Dry weight basis.

between aquatic and terrestrial plants. Aquatic plants, grouped on the left-hand side of Fig. 6, had As concentrations up to 4000 mg kg^{-1} on a dry matter basis. In contrast, terrestrial plants, on the right-hand side of Fig. 6, showed much lower As concentrations. All the aquatic plants tested accumulated As at concentrations greater than 5 mg kg^{-1} on a dry matter basis, and none of the terrestrial plants tested had As concentrations surpassing 11 mg kg^{-1}. Most of the terrestrial plants tested were below the detection limit for As (0.5 mg kg^{-1}) even when growing in soil containing up to 89 mg As kg^{-1}.

The difference in metal(loid) accumulation between aquatic and terrestrial plants was noticed by Outridge and Noller (1991) in their review of hyperaccumulation of elements by aquatic plants. Although they did not provide an explanation of this phenomenon, various reasons could be

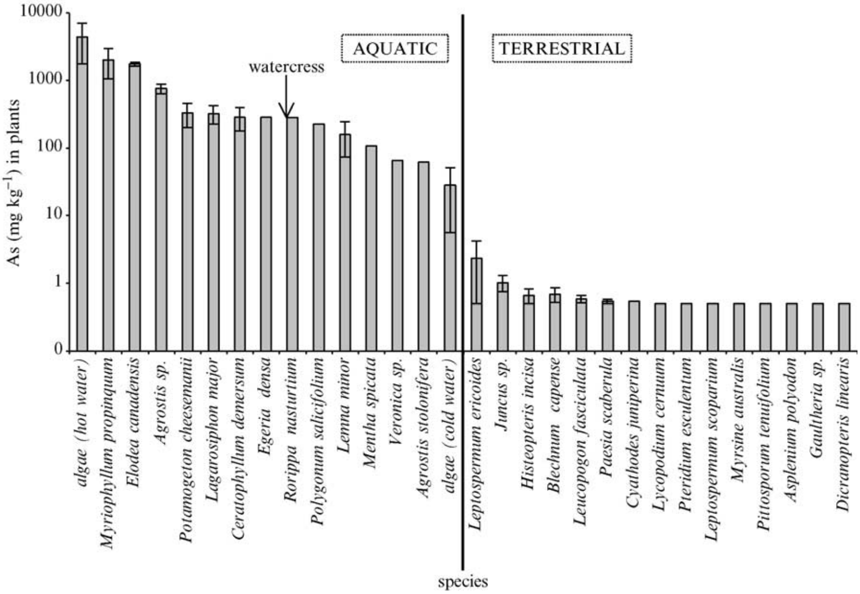

Figure 6 Mean arsenic concentration in plants collected from the Taupo volcanic zone (TVZ) (Robinson *et al.*, 2004).

attributed for the difference in As accumulation between aquatic and terrestrial plants. For instance, in terrestrial systems, the solubilization of As in the rhizosphere is necessary to allow the plant roots to take up and transport this element to the aerial parts of the plant. This is not the case when the plant grows in an aqueous medium, where the metal(loid) is already present in a bioavailable form (Brooks and Robinson, 1998).

b. Microbial Removal of Arsenic. Biosorption and biomethylation are the two important processes by which metal(loid)s, including As, are removed from water using microorganisms.

The biosorptive process generally lacks specificity in metal(loid) binding and is sensitive to ambient environmental conditions, such as pH, solution composition, and the presence of chelators. Genetically engineered microorganisms (e.g., *Escherichia coli*) that express a metal(loid)-binding protein (i.e., metallothionein) and a metal(loid)-specific transport system have been found to be successful in their selectivity for accumulation of a specific metal(loid) in the presence of a high concentration of other metal(loid)s and chelating agents in solution (Chen and Wilson, 1997). These organisms also have potential application to remove specific metal(loid)s from contaminated soil and sediments.

Biosorption is one of the promising technologies involved in removing As from water and wastewater. Several chemically modified sorbents have been examined for their efficiency in removing metalloids. Loukidou *et al.* (2003) examined the potential of *Penicillum chrysogenum*, a waste by-product from antibiotic production, for the removal of As(V) from wastewaters. They reported that the pretreatment of biomass with common surfactants (as hexadecyl-trimethylammonium bromide and dodecylamine) and a cationic polyelectrolyte was found to remove a significant amount of As(V) from waters. At pH 3, the removal capacities of modified biomass ranged from 33.3 to 56.1 mg As g^{-1} biomass.

Methylation is the most reliable biological process through which As can be removed from aquatic medium. Certain fungi, yeasts, and bacteria are known to methylate As to gaseous derivatives of arsine. Commercial application of biotransformation of metal(loid)s in relation to the remediation of metal(loid)-contaminated water was documented by Bender *et al.* (1995). They examined the removal and transformation of metal(loid)s using microbial mats, which were constructed by combining cyanobacteria with a sediment inoculum from a contaminated site. When water containing high concentrations of metal(loid)s was passed through the microbial mat, there was a rapid removal of the metal(loid)s from the water. The mat was found to be tolerant of high concentrations of toxic metal(loid)s such as Cd, Pb, Cr, Se, and As (up to 350 mg $liter^{-1}$). Management of toxic metal(loid)s by the mat was attributed to the deposition of metal(loid) compounds outside the cell surfaces, as well as chemical modification of the aqueous environment surrounding the mat. Large quantities of metal(loid)-binding polysaccharides were produced by the cyanobacterial component of the mat. Photosynthetic oxygen production at the surface and heterotrophic consumption in the deeper regions resulted in steep gradients of redox condition in the mat. Additionally, sulfur-reducing bacteria colonized the lower strata, removing and utilizing the metal(loid) sulfide. Thus, depending on the biochemical characteristics of the microzone of the mat, the sequestered metal(loid)s could be oxidized, reduced, and precipitated as sulfides or oxides.

C. MULTISCALAR-INTEGRATED RISK MANAGEMENT

A number of challenging issues need to be taken into consideration when devising strategies to manage As contamination of the environment. These include the following.

i. Complexity of As contamination—the severity and long-term persistence of As contamination are influenced by factors such as medium characteristics, site hydrogeology, land and water use, source term, chemical form and speciation, and target organism.

ii. Presence of multichemical species—As undergoes several biogeochemical transformation processes, resulting in the release of an array of chemical species that differ in their biogeochemical reactions, bioavailability, and biotoxicity.
iii. Extent and magnitude of As contamination of groundwater resource—for example, in Bangladesh, As in groundwater is derived from geological weathering of parent rock materials from the Indo-Gangetic alluvial plains spread over an area of millions of hectares
iv. Multipurpose end use of contaminated resources—water is used for drinking, cooking, and other household purposes and for irrigation; similarly, soil is used for agricultural production and recreational activities.

It is therefore important to formulate and/or devise integrated risk management strategies involving source avoidance, source reduction, and remediation. Source avoidance, which refers to avoiding the most contaminated source of the groundwater relative to certain geological strata, can be practiced to minimize the risk resulting from As contamination of soil and water resources. For example, in Bangladesh, shallow dug wells are increasingly becoming popular as an alternative to pump water from deeper strata. In some cases, the relatively contaminant-free strata are below 250-m deep zones. However, sanitation of these shallow wells is paramount to avoid gastroenteritis and other pathogenic-borne diseases. Another strategy is source reduction, which refers to removing or stopping the source of contamination. Source reduction can be achieved easily when the contamination source is of anthropogenic origin, such as those in landfills or similar point sources. As discussed earlier, in most regions, As contamination of groundwater is largely of geogenic origin, and source reduction may not be a feasible option to manage As contamination.

Remediation of contaminated soil and water resources requires both short-term and long-term solutions to the As problem. Therefore, the remediation strategies should be aimed at multiscalar levels, i.e., household level to community and regional levels, representing the various levels of complexity. Depending on the efficiency and cost effectiveness of the system, a combination of technologies may be required at certain levels. The potential technologies for remediation of As-contaminated soil and water resources at different scales in relation to the end use of the resources are depicted in Fig. 7. For example, at the least complex household level, remediation strategies involving only a simple filter (sorptive) system can be used to remove As (i.e., As stripping) from water used for drinking and cooking purposes, whereas at a more complex community level, more sophisticated precipitation technologies should be used to strip As from the community water supply so that cost can be shared and the system can be managed

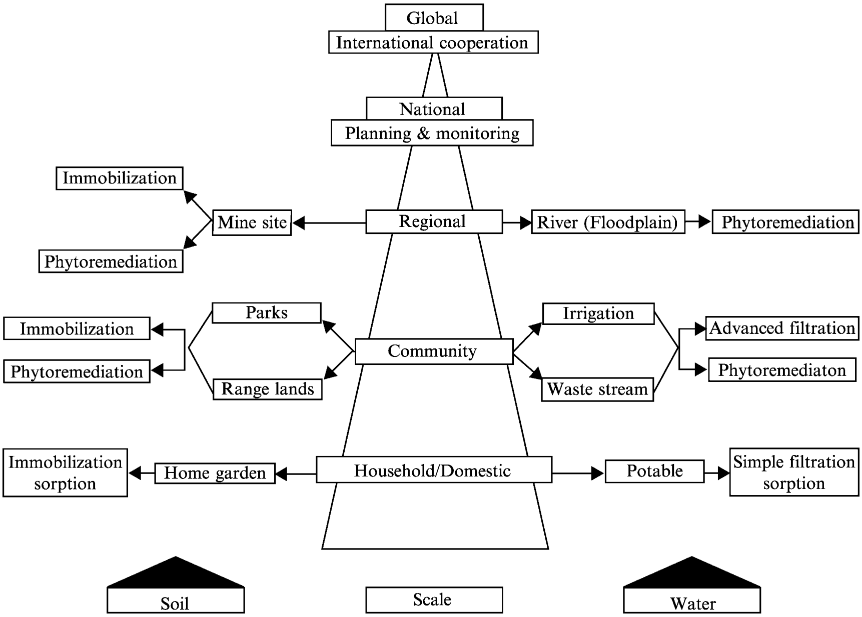

Figure 7 Multiscalar risk management for arsenic-contaminated soil and aquatic ecosystems.

efficiently. More sophisticated stripping methods, which may require a series of a filtering–sorptive (precipitation) setup, are necessary in order to cope with the enormous volume of groundwater that needs to be treated before distribution to the community. Even at the community scale, the situation becomes even more complex when dealing with impacted soils, especially those geared for food production. In this case, land use is a very important factor to address. For example, in parks, applying soil amendments such as those high in Fe_2O_3 may suffice to mitigate As risk. In contrast, technologies might be paired in a situation when the food chain might be compromised, as typified by rangeland, rice paddy, and so on. A viable approach in this circumstance is to apply phytoremediation during the initial period (1 to 2 years) to strip the "bioavailable" fraction, subsequently followed by soil amendments before committing to the intended land use. It is very important to observe that as the level of contamination becomes more complex, a monitoring scheme should be in place. Hence, a successful remediation scheme for an As-contaminated environment should aim for an integrated approach involving the possible combination of physical, chemical, and/or biological mechanisms.

It is essential that the integration of remediation technologies should enhance efficiency, both technologically and economically, resulting in a

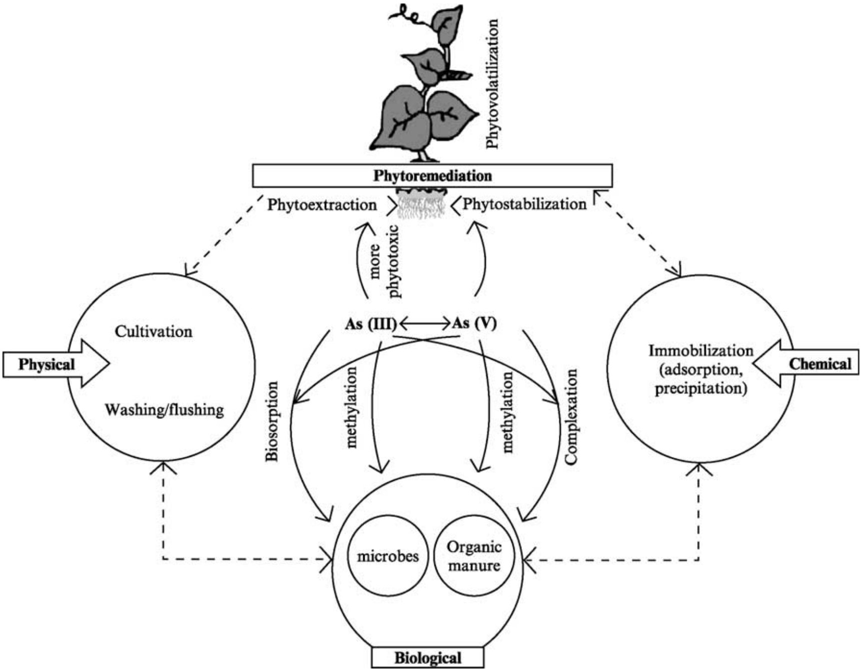

Figure 8 Conceptual integrated approach for remediation of arsenic-contaminated soil and aquatic ecosystems, focusing on phytoremediation.

reduction in the time required for achieving targeted levels of As. For example, phytoremediation is a promising new technology, which is relatively inexpensive and has been proven effective in the large–scale remediation of both soil and water resources. Further, it would also add “green” value (aesthetic) to the environment. Integrating physical, chemical, and/or bioremedial measures with phytoremediation as depicted in Fig. 8 could enhance a higher uptake of As by plants, can more effectively minimize biotoxicity through microbial and chemical immobilization, and can potentially eliminate As through the inducement of biomethylation and subsequent volatilization from the system.

VII. SUMMARY AND FUTURE RESEARCH NEEDS

Arsenic is an extremely toxic and carcinogenic metalloid contaminant that adversely affects the environment and human health. Widespread As contamination of terrestrial and aquatic environments from both geogenic and anthropogenic sources has been reported in many countries. Although not anthropogenic, drinking of As-contaminated water has already affected millions of people, particularly in developing countries with the biggest known As calamity occurring in Bangladesh and West Bengal in India. Arsenic in soil and water exists in a different valence state, but predominantly as toxic As(III) and less toxic As(V). The biogeochemistry of As in soil and water is complex and is mostly determined by its chemical speciation resulting from chemical and biological transformations. The chemistry of soil and water (i.e., pH and Eh) and predominantly microbial assemblages play a major role in As dynamics. Although bioaccumulation of As in plants and organisms has been reported, its biochemical transformations within the plant and other biota are still largely unknown.

Risk management of As-contaminated soil and aquatic ecosystems is an important issue and a great challenge; its success is necessary to promote sustainable environmental health and also to minimize the adverse impact on humans. A number of physical, chemical, and biological technologies involving simple filtration, precipitation, biosorption, and rhizofiltration have been developed to remediate As-contaminated soil and water. Conventional physical and chemical remedial measures usually are quite expensive but may prove highly effective. However, most of these technologies have been tested only at the laboratory and pilot scale levels. Large-scale application of such technologies requires trained personnel for the operation of equipment to treat soils and waters. However, phytoremediation, which is relatively inexpensive, has been proven effective in the remediation of metal (loid)-contaminated sites. Certain As-hyperaccumulating plants offer a wide scope for the phytoremediation of As-contaminated soil and water. Nonedible crops, such as ornamental and fuel crops, may be suitable for phytoremediation through which the entry of As into the food chain could largely be avoided. Bioremediation, using biological wastes and/or microbial strains, offers another avenue for remediation. However, as in the case of physical and chemical technologies, most of the research involving bioremediation has been demonstrated in the laboratory only. As such, its feasibility should be tested under diverse field conditions.

Remediation of As-contaminated soils and As stripping from potable and irrigation waters require a multiscalar approach. This involves an "end-use" specific (i.e., drinking vs irrigation and agricultural vs recreational sites) integrated approach, involving a combination of physical, chemical, and biological technologies for the successful and effective management of As-contaminated environments. Future research is, therefore, needed for the following:

- Biogeochemical mechanisms governing As dynamics in different media using advanced spectroscopic-based techniques.

- Elucidation of soil and water environmental factors (e.g., pH and Eh) that govern chemical and biological transformations of As.
- Examination of solid-phase and solution-phase speciation of As in soil and water.
- Identification of biochemical mechanisms involved in the accumulation of As in specific tissues or organs in plants, animals, and humans. This includes the interactive effects of As(V) and $H_2PO_4^-$ on hyperaccumulators such as Chinese brake and water cress.
- Evaluation of As phytotoxicity under field conditions.
- Rhizosphere processes underpinning effective phytoremediation technologies.
- Mycorrhizal role in the bioremediation of As regarding biomethylation, biooxidation, and immobilization of As.
- Developing genetically engineered microorganisms and genetically modified plants to detoxify As in contaminated soil and water.
- *In situ* immobilization techniques in contaminated soils/sediments using inexpensive industrial by-products high in metallic oxides; effect of aging on the release of As from the immobilized media.
- Biomonitors of As as a tool in the risk assessment of As-contaminated sites.
- Highly effective and expensive stripping methods for the removal of As in domestic water supplies destined for irrigation and human consumption.

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