Chapter 10
Arsenic in Paddy Soils and Potential Health Risk

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10.1 Introduction

Arsenic a metalloid has a serious threat to both environment and human health. It has been reported in 70 countries worldwide (Zhao et al. 2010). Especially, in South and Southeast Asia, effects of arsenic toxicity on humans through drinking water and staple food rice have become a serious concern (Smedley et al. 2005). Natural and anthropogenic sources are responsible for arsenic contamination in groundwater and paddy soils (Meharg et al. 2009). In the region, arsenic is mostly reported in rural areas. In groundwater, arsenic is present both in inorganic and organic form. Rice grown on contaminated paddy soil accumulates considerable arsenic and makes it a part of food chain (Meharg et al. 2009).

Paddy rice, a staple food, is mostly irrigated with arsenic-contaminated water in arsenic-affected countries. Arsenic accumulated rice has become a health disaster because rice has a special ability to uptake the arsenic (Meharg and Rahman 2003). So rice has become a potential source of arsenic exposure to humans. Recently, the Joint Food and Agriculture Organization and the World Health Organization (FAO/WHO) Expert Committee on Food Additives suggested a maximum limit of inorganic As of 0.2 mg/kg for polished rice. Environmental Protection Agency (EPA) has classified arsenic as a carcinogenic (Abernathy 1993; Tchounwou et al. 2003) because it can cause serious health effects, including cancers of the skin, lung, bladder, liver, and kidney. Similarly it can disrupt human systems like cardiovascular, neurological, hematological, renal, respiratory, etc. (Ng et al. 2003; Halim et al. 2009; Johnson et al. 2010; Martinez et al. 2011).

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10.2 Arsenic in Paddy Soils: A Threat to Sustainable Rice Cultivation in South and Southeast Asia

Groundwater arsenic-contaminated water within a range of 0.5–5000 µg/l is present in more than 70 countries of the world (Ravenscroft et al. 2009). Arsenic contamination of groundwater in several regions of South and Southeast Asia has become a serious threat. This contaminated groundwater is used for the irrigation of the main cereal crop, i.e., rice, of this region especially in Bangladesh and West Bengal (India). The studies on arsenic-contaminated water is reported in Bangladesh and West Bengal (McArthur et al. 2001), Nepal (Gurung et al. 2005), the Ganga Plains (Acharyya and Shah 2007), Vietnam (Postma et al. 2007), and Taiwan (Liu et al. 2005a, b). Other than these areas, GIS-based geological–geochemical–hydrological models also predict widespread pollution of groundwater in Indonesia, Malaysia, the Philippines, and other regions where still arsenic-related research has not been done (Ravenscroft 2007). Arsenic-contaminated water has created a threat to sustainable rice cultivation in these areas because it is accumulating the arsenic in topsoil and rice of these areas (Brammer and Ravenscroft 2009; Khan et al. 2009, 2010a, b; Dittmar et al. 2010; Meharg and Rahman 2003).

As the agroecological and hydrogeological conditions of the South and Southeast Asian countries are broadly similar, it can be supposed that irrigation of arsenic-contaminated groundwater can affect paddy rice of this entire region. Besides, paddy rice is a major contributor of arsenic exposure to human due to its higher deposition in topsoil from irrigated water and subsequent uptake in rice grain (Dittmar et al. 2010). Rice cultivation in this region through arsenic-contaminated water has been affected in terms of its production as well as its quality. The first reason of this issue is the use of arsenic-contaminated groundwater in South and Southeast Asia during dry season. The second one is that rice is susceptible to arsenic toxicity (Brammer and Ravenscroft 2009). The dependency on groundwater for rice irrigation in this region has increased due to low precipitation level even in monsoon seasons. However, the demand of rice production is expected to increase in near future to meet the needs of increasing population. This trend will increase higher arsenic deposition in topsoil of this region.

10.3 Sources of Arsenic in Paddy Soils

Paddy fields are contaminated with arsenic through various sources (Fig. 10.1), including metal mining (Liao et al. 2005; Liu et al. 2006; Zhu et al. 2008), pesticides, fertilizer application (Bhattacharya et al. 2003; Williams et al. 2007), and irrigation with As-rich groundwater (Mehrag and Rahman 2003; Williams et al. 2006). Among these, the most common one is the irrigation with As-rich groundwater which has increased the As levels in the soil (Heikens et al. 2007; Hossain et al. 2008; Baig et al. 2011) and uptake by rice (Duxbury et al. 2003; Williams et al. 2006; Rahman

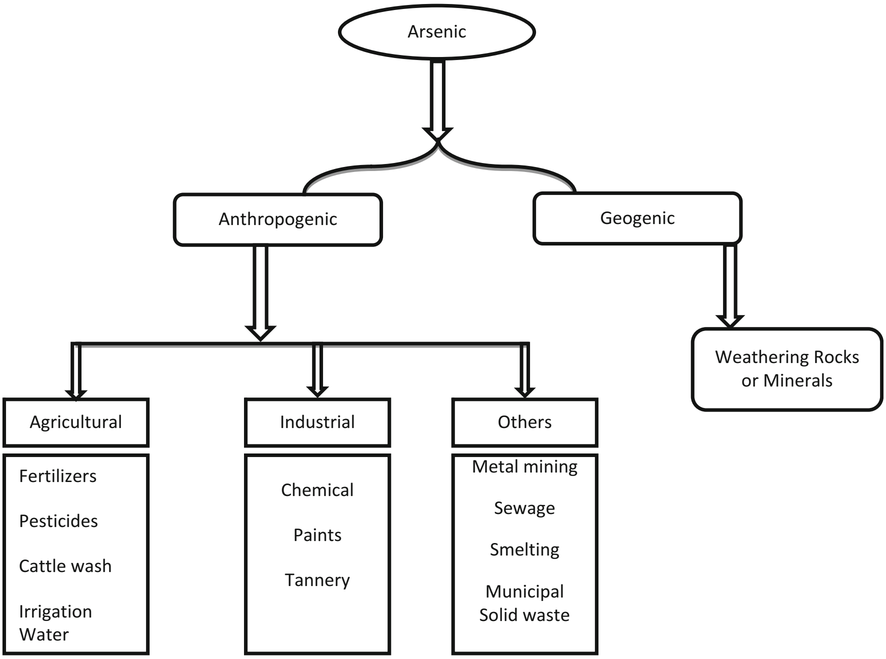

Fig. 10.1 Sources of arsenic contamination

et al. 2007; Rahman and Hasegawa 2011). In a survey from Bangladesh, Meharg and Rahman (2003) showed the positive correlation between As in irrigation water and arsenic in irrigated soil and rice.

Ravenscroft et al. (2009) have pointed out four geochemical mechanisms of natural As pollution: reductive dissolution, alkali desorption, sulfide oxidation, and geothermal activity. In South and Southeast Asia, reductive dissolution is the most common source of arsenic contamination. It occurs where As adsorbed to iron oxy-hydroxides in sediments is liberated into groundwater when microbial degradation of organic matter (e.g., in buried peat beds) reduces ferric iron to the soluble ferrous form (Nickson et al. 2000; McArthur et al. 2001). The As is contained in relatively unweathered alluvial sediments derived from igneous and metamorphic rocks in the Himalayas and related young mountain chains (McArthur et al. 2004; Ravenscropt et al. 2005). Arsenic is not present in large amounts in these sediments: its importance lies in the toxicity of the element at very low concentrations to humans and many plants that absorb it.

10.4 Factors Affecting Arsenic Mobility in Paddy Soils and Uptake by Plant

Several factors like pH, adsorption, desorption process, redox conditions, and biological activity are responsible for mobility of As in water and soil. The presence of high concentration of As in soil depends on the aforesaid factors; organic content; oxides of Al, Fe, and Mn; and soil fractions. Many studies reported As mobilization in coarse and fine soil (Sadiq 1997; Bhattacharya et al. 2010; Cai et al. 2009). Coarser texture of sediments has less As as compared with finer texture. Fine texture contains immobile As but released in the subsurface, while coarse texture is relatively high fraction due to mobile As. Mobility of As is affected by geomorphic characteristic, rainfall infiltration rate, and groundwater level (Bhattacharya et al. 2010).

Arsenic speciation and mobility in soil is highly dependent on redox conditions. In oxidized condition, arsenic prevails as arsenate [As (V)]. Arsenate has affinity for Fe-oxy-hydroxide, and it reduces mobility and uptake by plant in oxidizing environment (Smedly and Kinniburgh 2002). However, in reducing conditions arsenic is present in arsenite [As (III)] form and readily available for uptake of plant due to higher mobility (Takahashi et al. 2004; Xu et al. 2008).

Microorganisms can facilitate the redox processes exclusively bacteria which assist as catalyst in speeding up the reactions. Movement of As in natural system also mainly depends on adsorption and desorption processes. Together arsenate and arsenite adsorb to surfaces of several different solids including iron, aluminum, and manganese oxides, as well as clay minerals. As compared to arsenite, arsenate is much more strongly adsorbed because of its greater negative charge at the same pH. With increasing pH, AsV adsorption decreases in particular above pH 8.5, while the reverse happens for AsIII. The degree to which pH effects As sorption fluctuates between soils. The adsorption maximum for AsV on FeOOH lies around pH 4, whereas for AsIII the maximum is found at approximately pH 7–8.5 (Mahimairaja et al. 2005). AsV and AsIII adsorb mostly to iron (hydr)oxides (FeOOH) existing in the soil, and AsV association is the strongest. The behavior of FeOOH is extremely dependent on redox conditions, creating Fe redox chemistry the most chief factor in regulating As behavior (Fitz and Wenzel 2002; Takahashi et al. 2004). In anaerobic environments, FeOOH readily dissolves, and As is released into the soil solution, where As will be present mostly as AsIII (Takahashi et al. 2004). Microbial action is strictly involved in this procedure (Islam et al. 2004). In aerobic environments FeOOH is fairly insoluble and serves as a sink for As. Fe and As behavior is therefore active and closely related in lowland paddy fields. The As concentrations in the irrigation water frequently differ from those in the soil water. For example, a study reported that As concentrations in irrigation water were higher compared to the soil water concentrations during the non-flooded period because of sorption to FeOOH. In flooded conditions, soil water concentrations increased because of remobilization and, important to note, became higher than the irrigation water concentrations. In flooded conditions, plants can therefore be exposed to much higher concentrations in the soil water than would be expected based on the concentrations in the applied irrigation water (Takahashi et al. 2004).

The presence of FeOOH is mainly occurring in the clay-size soil fraction (<2 μm) and clayey soils; therefore generally they have a higher As content as compared to more sandy soils (Mahimairaja et al. 2005). Under specific soil conditions, such as carbonate minerals and manganese oxides (MnO), sorption substrates can also be relevant (Mahimairaja et al. 2005).

Fe oxides/hydroxides represent as the major sink for As adsorption in soils, whereas the Al- and Ca-bound fractions and their importance are variable. Phosphate (PO_4) has similarity with AsV, making it an important factor in the behavior of As in aerobic soils (Mahimairaja et al. 2005). Both ions act as competing sites for FeOOH and for uptake by plants. The effect of PO_4 additions to aerobic soils on the uptake of As will consequently depend on the existing balance between competition for sorption sites and competition for uptake mechanism.

As III an analogue of PO_4, making the presence of PO_4 possibly less relevant to As behavior in the presence of flooded soil conditions (Takahashi et al. 2004). Role of PO_4 in the rhizosphere is not known (the microenvironment around the roots), where aerobic conditions are dominant under flooded conditions. Other ions are also responsible for As behavior, but their impact seems to be less as compared to PO_4 (Mahimairaja et al. 2005).

Binding of As with iron oxide surfaces is considered as an important reaction in the subsurface soil because iron oxides are present in large number in the environment in the form of coatings on other solids. Arsenate adsorbs strongly to iron oxide surfaces in condition of acidic and near-neutral pH. Organic matter of soil has no contribution in significant quantities of As sorption in soils, especially when the effective sorbents such as hydrous Fe oxides are present.

10.5 Toxicity of Arsenic

The chemical forms and oxidation states of arsenic are more important as regards toxicity. Toxicity also depends on other factors such as the physical state, gas, solution, or powder particle size, the rate of absorption into cells, the rate of elimination, the nature of chemical substituents in the toxic compound, and, of course, the preexisting state of the patient. The toxicity of arsenicals decreases in this order, arsines > iAsIII > arsenoxides (org AsIII) > iAsV > arsonium compounds > As (Whitacre and Pearse 1972). High methylation capacity did not protect the cells from the acute toxicity of trivalent arsenicals as that MMAIII is more cytotoxic to human cells (hepatocytes, epidermal keratinocytes, and bronchial epithelial cells), compared to iAsIII and iAsV (Styblo et al. 2000).

Arsenic specie inactivates the enzyme system (Dhar et al. 1997). The inhibitory action starts with the binding of trivalent arsenic with the SH and OH groups of enzymes when two adjacent HS-groups are present in the enzyme. The iAsV has no ability to react directly with the active sites of enzymes. It first reduces to iAsIII in vivo before producing its toxic effect (Pauwels et al. 1965). The citric acid cycle is mostly affected because of its enzyme inactivation by iAsIII, so these enzymes are unable to produce cellular energy in this cycle. In this inhibitory action, iAsIII makes complexations with pyruvate dehydrogenase, and the generation of adenosine-5-triphosphate (ATP) is prevented. It reduces productions of energy, and cell damages slowly (Belton et al. 1985; Wolochow et al. 1949).

Although iAsIII is a mostly considered hazardous form of the element, however, iAsV as arsenate can also create toxic effects. It causes arsenolysis in which arsenate disturbs the process of oxidative phosphorylation (In this process ATP is produced). Arsenate produces arsenate ester of ADP which is not stable and undergone hydrolysis nonenzymatically. Hence the energy metabolism is inhibited, and glucose-6-arsenate is produced instead of glucose-6-phosphate. Arsenate also causes toxicity by inhabiting mechanism of DNA repairing mechanism as it has the ability to replace the phosphorous in DNA.

10.6 Potential Health Risk

Due to toxicity, chronic exposure of arsenic causes severe health impacts by creating disturbances in all body systems. Since the nineteenth century, several skin diseases (including pigmentation changes, hyperkeratosis, and skin cancers) related to arsenic contamination have been studied (WHO 2001). Several health effects due to arsenic exposure are given below.

10.6.1 Respiratory Effects

Arsenic exposure to human through different ways can lead to several respiratory effects like laryngitis, tracheae bronchitis, rhinitis, pharyngitis, shortness of breath, chest sounds (crepitations and/or rhonchi), nasal congestion, and perforation of the nasal septum (Gerhardsson et al. 1988).

10.6.2 Pulmonary Effects

Pulmonary diseases due to chronic arsenic exposure are mostly occurred by drinking arsenic-contaminated water. Among these the common ones are abnormal skin pigmentation, chronic cough, and lung disease.

10.6.3 Cardiovascular Effect

Arsenic toxicity hinders cardiovascular functions. It causes cardiovascular abnormalities, Raynaud's disease, myocardial infarction, myocardial depolarization, cardiac arrhythmias, thickening of blood vessels, and their occlusion and BFD.

10.6.4 Gastrointestinal Effect

Ingestion of heavy inorganic arsenicals affects gastrointestinal tract. These arsenicals are absorbed on gastrointestinal tract according to their solubility level. Lesser-dose arsenic poisoning attacks in the form of dry mouth and throat, heartburn, nausea, abdominal pains, cramps, and moderate diarrhea. Chronic low-dose arsenic ingestion manifests without symptomatic gastrointestinal irritation, or it can produce mild esophagitis, gastritis, or colitis with respective upper and lower abdominal discomfort. Anorexia, malabsorption, and weight loss are also associated with arsenic contamination (Goebel et al. 1990).

10.6.5 Hematological Effect

The hematopoietic system is also affected by arsenic toxicity. Hemoglobin has affinity for arsenic, which decreases oxygen uptake by cells. Acute, intermediate, and chronic exposure of arsenic causes anemia (normochromic normocytic, aplastic, and megaloblastic) and leukopenia (granulocytopenia, thrombocytopenia, myeloid, myelodysplasia). The direct hemolytic or cytotoxic reactions occur in blood cells, and erythropoiesis is suppressed. High-dose arsenic can result in bone marrow depression in human (Saha et al. 1999).

10.6.6 Hepatic Effect

Arsenic chronic exposure can lead to hepatic effect. Chronic arsenic causes hepatic disturbances including cirrhosis, portal hypertension without cirrhosis, fatty degeneration, and primary hepatic neoplasia. Patients may experience bleeding esophageal varices, ascites, jaundice, or simply an enlarged tender liver, mitochondrial damage, impaired mitochondrial functions, and porphyrin metabolism.

10.6.7 Renal Effects

Kidneys are not so sensitive to arsenic because of their excretion mechanism of arsenic. Only repeated exposure of arsenic can harm the kidneys. The sites of the kidney which are damaged by arsenic are the capillaries, tubules, and glomeruli, which lead to hematuria and proteinuria, oliguria, shock, and dehydration with a real risk of renal failure, cortical necrosis, and cancer (Hopenhayn et al. 1998).

10.6.8 Dermal Effects

Arsenic exposure may also produce a variety of skin issues like diffused and spotted melanosis, leucomelanosis, keratosis, hyperkeratosis, dorsum, Bowen's disease, cancer, etc. Hyperpigmentation may occur on darker parts of the skin (Shannon and Strayer 1989).

10.6.9 Neurological Effect

Ingestion of arsenic can cause neural injury. Neurological effects due to arsenic contamination can be classified on the basis of acute and chronic exposure. In result of acute high exposure (1 mg As/kg/day or more), encephalopathy can occur, and its symptoms are headache, lethargy, mental confusion, hallucination, seizures, and coma. Intermediate and chronic exposures (0.05–0.5 mg As/kg/day) lead to symmetrical peripheral neuropathy, which starts as numbness in the hands and feet but later may develop into a painful "pins-and-needles" sensation, wrist or ankle drop, asymmetric bilateral phrenic nerve, and peripheral neuropathy of both sensory and motor neurons causing numbness, loss of reflexes, and muscle weakness.

10.6.10 Developmental Effects

Impacts on development due to arsenic toxicity are not well studied. However, some studies found that arsenic exposure through dust during pregnancy has a high rate of congenital malformations, below average birth weight. Similarly, a couple of studies reported an increased number of miscarriages among women due to arsenic exposure (Aschengran et al. 1989).

10.6.11 Reproductive Effects

About arsenic effect on reproductive system, it is known since long time that inorganic arsenic crosses the placental barriers and effects the fetal development, but organic arsenic does not. Commonly studies have reported the reproductive issues like an increase in the prevalence of low birth weight infants, higher rates of spontaneous abortions, elevations in congenital malformations, higher frequency of pregnancy complications, mortality rates at birth, and low birth weights due to arsenic contamination (Tabacova et al. 1994).

10.6.12 Immunological Effects

Relationship between human immune system and arsenic toxicity is not well studied. However, a few studies have developed a link and stated that arsenic toxicity attacks on lymphocytes and decreases immunity power of a man (Gonsebatt et al. 1994).

10.6.13 Genotoxic Effects

Arsenic exposure causes genotoxic effects. Several species of arsenic generate these effects according to their potential toxicity. The comutagenecity and cocarcinogenicity of arsenic depend on the mechanism of repair inhibition. Trivalent arsenic induces more potent and genotoxic chromosome aberration frequencies than pentavalent. Organo arsenicals cause greater disturbing effects on the microtubular organization of the cell. So, they have higher mitotic toxicity. Among DMA and MMA, the former one is more toxic. Similarly, TMAO has more potential for inducing both mitotic arrest and tetraploids (Eguchi et al. 1997).

10.6.14 Mutagenetic Effects

Health impacts due to arsenic toxicity in humans also appear in the form of mutagenetic effects. Arsenic damages the DNA structure and induces genetic alteration (like gene mutation) in a man, and these problems transfer genetically in subsequent generation. Arsenic causes genetic damage by inhibiting DNA repair (Bencko et al. 1988).

10.6.15 Carcinogenic Effects

Since a century arsenic carcinogenic effects are known. In different parts of the world, including Japan; Bangladesh; West Bengal, India; Chile; and Argentina, several studies have reported lung, skin, bladder, kidney, and liver cancer due to exposure of arsenic contamination through drinking water. Risk of cancer due to arsenic contamination in humans depends on the level of dose.

10.6.16 Diabetes Mellitus

Drinking water arsenic contamination and prevalence of diabetes mellitus have positive relation. Several studies conducted in Bangladesh (Rahman et al. 1998) and in Taiwan (Lai et al. 1994) have reported that the number of diabetes mellitus patients was higher in those population where drinking water was contaminated with arsenic.

10.7 Conclusions

This chapter has focused on arsenic contamination in paddy rice and its heath impact on humans. Rice as a major staple food of South and Southeast Asia has become an important source of arsenic exposure to human. Arsenic in paddy soil and in rice has a threat to sustainable rice cultivation in the region as well as serious health problems for the people of this region. Arsenic species have different levels of toxicity and make direct attacks on human body functions. It has potential to disrupt all body systems. To protect the people from arsenic toxicity, there is a need to take several mitigations measures. Modification in agricultural practices like by avoiding anoxic soil conditions can decrease the arsenic uptake by rice. Another option is to reduce the rice ability of uptaking arsenic by genetic modification. Public awareness about arsenicosis should be enhanced through proper education and guidance.

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