

ARSENIC CONTAMINATION: SOURCES, EXTENT AND IMPACT ON THE ENVIRONMENT

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ABSTRACT

Arsenic (As) is a heavy metalloid with emanating concern of its environmental toxicology worldwide. Arsenic is released into the living environment via natural and anthropogenic sources. Natural phenomena include dust storms, forest fires, volcanic eruptions, hydrothermal activities, pedogenesis and geothermal activities. Agricultural inputs like chemical fertilizers and pesticides, dumping of municipal wastes, addition of untreated effluents resulting from industrial activities into the surroundings, smelting, mining, cement manufacturing, coal burning and disarmament of the chemical weapons are considered as human activities. The potential threat of Arsenic is extended over 105 nations and 226 million populations on a global scale. As contamination in soil and groundwater is the major route for human exposure. Many parts of the world have been reported As levels exceeding the threshold limits for soil as well as groundwater. The chemical similarity of arsenate and phosphate facilitate the entry of As into plants and disrupt the metabolic and physiological pathways. Apart from its carcinogenic risk, chronic exposure leads to arsenicosis and other disorders. Phytoremediation and microbial remediation are environmental friendly and cost effective technique for As removal and nanotechnology is an emerging technology with wide application in removal of metal pollutants from the contaminated site.

KEY WORDS : Arsenic, Bioaccumulation, Contamination, Geologic, Phytoremediation

INTRODUCTION

Heavy metal pollution has been an emanating concern with serious risk to the living world (Gong *et al.*, 2020). Developing industries liberate naturally degradable and non – degradable materials to the surroundings which ultimately challenge the health of the ecosystem. Among those substances, the consistency of heavy metals and metalloids in the environmental matrices is noticeable because natural phenomena seldom degrade metallic elements unlike organic pollutants (Kabir *et al.*, 2012). Apart from the industrial release of toxic elements, geogenic origin can also be the reason for the heavy metal or metalloid contamination.

Arsenic (As) belongs to the group V of the periodic table, which exhibits intermediate chemical nature between metals and non metals (Ranjan *et al.*, 2020). Oxidation state of an element determines the

nature of chemical reaction they perform. Arsenic rarely exists in 0 and -3 oxidation states (arsenides) while the common oxidation states are +3 (arsenite) and +5 (arsenate). Among these, arsenides are characterized as alloy – like intermetallic compounds (Garelick *et al.*, 2009; Shrivastava *et al.*, 2015). Arsenic, being an element ubiquitous in the environment, ranks 12th inside the human body, 14th in the ocean and 20th among the elements in earth crust (Ranjan *et al.*, 2020; Golfopoulos *et al.*, 2021).

Organic and inorganic forms of As are present in the soil where toxicity of inorganic form is comparatively higher as much as 100 times than organic forms (Jain and Ali, 2000). Immobile forms of arsenic are arsenate, As (V) which are less toxic relative to the mobile and more toxic form of arsenic, i.e., arsenite, As (III) where the speciation of arsenic in soil is regulated by pH and redox potential (Shrivastava *et al.*, 2015; Pigna *et al.*, 2015).

Inhalation, ingestion or dermal contact of the arsenic and related compounds may be the ways of exposure in animals.

Intentional and unintentional release of As contaminate the soil and groundwater which ultimately reach the diet as millions of people around the world rely upon contaminated ground water as the source of potable water (Shankar *et al.*, 2014). Arsenic contamination is a global issue as some studies reported that more than 200 million people residing over 70 countries were exposed to this toxic metalloid (Sodhi *et al.*, 2019). Prolonged exposure for 5 – 10 years towards As, can cause serious health issues from dermal to internal cancers and arsenicosis (Shankar *et al.*, 2014; Das and Sengupta, 2008). Studies regarding the arsenic contamination are advancing at different dimensions as demand for healthy ecosystem and safe food is escalating day by day. But the ubiquitous nature, background release by human activities and diverse chemical forms of As may create perplexing situation to the researchers for abating their levels within permissible limits prescribed by World Health Organization (Shankar *et al.*, 2014). This review paper focuses on the sources, extent of the As contamination in various parts of the world, impact of the As contamination on soil, water resources, human health and food chain, remediation techniques like phytoremediation, bioremediation and nanotechnology with the latest studies in particular area.

Sources of Arsenic Contamination

Sources of arsenic in the environment can be natural or anthropogenic activities. Natural phenomena include dust storms, forest fires, volcanic eruptions, hydrothermal activities, pedogenesis and geothermal activities (Garelick *et al.*, 2009). Within a global view point, natural phenomena have paramount responsibility for the increased concentrations of arsenic while human activities like mining can be the supreme reason under local scale (Amini *et al.*, 2008). Agricultural inputs like chemical fertilizers and pesticides, effluents from industries, dumping of municipal wastes and addition of effluents without any proper treatments into the water resources and soil, lead to accumulation of heavy metals or metalloids in urban areas (Islam *et al.*, 2018). For the river basin of Ganga – Brahmaputra – Meghna (GBM), As contamination is due to geological origin and this created a great

challenge to the population for drinking water (Gupta *et al.*, 2021). Bengal basin, a sedimentary basin constituted by GBM river system serves as the chief source of arsenic contamination in Bangladesh as they are resulted from the deposition of sediments containing arsenic derived from Himalayas, through which As leaches into the groundwater aquifers (Shaji *et al.*, 2021).

Both solid and fluid wastes liberated by the industries as untreated substances enhances metal/metalloid level in nearby land and the composition differs with type of industries like textile, petrochemical, chemical, mining, metal extraction, cement, leather, ceramic etc (Kabir *et al.*, 2012). Arsenic can be a toxic byproduct of the industries dealing with smelting, agro chemicals and glasses and considered to be the major reason for As contamination in Kolkata cities (Chakraborty *et al.*, 2017). Soil profiles of an abandoned as well as active gold mine spoils were compared for their As contamination and observed that abandoned sites have more contamination along with the presence of minerals like scorodite and arsenopyrite (Mensah *et al.*, 2020). Contamination of arsenic spreads over vast areas through wind and rainfall as they can diffuse from the dumped wastes (Gowd *et al.*, 2010).

Natural occurrence of arsenic is prominent as it is present in more than 200 minerals which include arsenides, elemental As, arsenates, oxides and sulphides. Arsenopyrite (FeAsS), which is the dominant mineral form of As in soil along with other As sulphides like orpiment and realgar are developed in earth's crust under high temperature (Smedley and Kinniburgh, 2002). Some of the mineral forms are evolved from weathering and arsenate minerals like beudantite, scorodite, yukonite as well as sulphide As minerals like realgar, pyrite, arsenopyrite, loellingite etc. are generally occurring soil - bound minerals (Shrivastava *et al.*, 2015). Arsenic enters the groundwater by leaching from respective sediments and host rocks. Mobilization of arsenic into groundwater is upregulated by some geochemical conditions like reducing environment, high pH areas of arid and oxidizing environments, oxidative weathering of minerals (sulphide), geothermal activities etc. (Podgorski *et al.*, 2017). A study conducted by Lee *et al.*, 2019 near a copper smelter identified that As contamination is significantly contributed by mineralization of regional ore, i.e., geologic origin despite of nearby anthropogenic source. An analysis showed that, due to coal burning, India produced an average

atmospheric As concentration of 4.57 ng m^{-3} in the year 2015 which exceeded than that of eastern China (Zhang *et al.*, 2020b).

Around 54 nations reported the As contamination derived from anthropogenic activities. For most of the reported As contamination in all continents, major source is sedimentary formations, especially Holocene sediments. In Asia, 45% arsenic contamination is due to sedimentary formation, 10% each due to petroleum and coal, 30% by mining and 5% contributed by volcanic rocks. But the contribution of each source varies with continents (Shaji *et al.*, 2021).

Eventhough intensified studies regarding arsenic contamination is contributed by recent decades, the reasons behind the contamination claim more than a century old. During the 18th and 19th century, arsenic based drugs (e.g. Salvarsan, Fowler's solution) were developed to treat serious illness but declined with time and arsenic based pigments, semiconductors, glass industries, pesticides (e.g. Paris Green, lead arsenate), rat poisons, long term phosphatic fertilizer application, herbicides, wood preservatives and copper smelting industries are the other sources of arsenic exposure (Hughes *et al.*, 2011; Hartley *et al.*, 2013; Golfinopoulos *et al.*, 2021). As a chemical warfare tool, certain arsenic based compounds were used during World War I and World War II like Lewisite, Arsenic trioxide, Clark I, Clark II etc. (Li *et al.*, 2016). As part of the disarmament, these compounds were buried under ground or dumped to sea in China, Europe and Japan but this activity served as a source of arsenic contamination to marine ecosystem and ground water (Hisatomi *et al.*, 2013; Niemikoski *et al.*, 2020).

Extent of Arsenic Toxicity in the world

Arsenic contamination and resultant impacts regarding health hazards have been reported world wide. Studies are conducted in different parts of the world to assess the degree of As contamination around the world which assist in carrying out remedial measures. According to European Union, atmospheric arsenic content should not exceed the limit of 6 ngm^{-3} and WHO prescribed that the permissible limit of As in drinking water should not exceed $10 \text{ } \mu\text{gl}^{-1}$ (Zhang *et al.*, 2020b). But, many parts of the world reported values exceeding far from this limit frequently which need to be considered.

Around the world, arsenic contamination has its potential threat in approximately 105 countries with exposure to 226 million population and particularly

in India, it was estimated around 50 million population and an area of $90,000 \text{ km}^2$ are critically impacted by As (Gupta *et al.*, 2021). China, Argentina, Hungary, Chile, Vietnam, Bangladesh, India (West Bengal) and Mexico were determined as groundwater regions with high As content (Smedley and Kinniburgh, 2002). Bangladesh was threatened in 1996 by massive poisoning of As in nearly half population (Golfinopoulos *et al.*, 2021).

It was observed in some areas where the major contribution of As contamination is from geological origin, surface waters come in contact with the As rich geothermal fluids like Taupo volcanic Zone in New Zealand, Yellowstone National Park in United States etc (Garelick *et al.*, 2009). In the surface soils of agricultural lands in China, As ranged from 0.4 to 175.8 mgkg^{-1} and quantitatively estimated as 3.71×10^6 tonnes (Gong *et al.*, 2020). This study also revealed that South, Southwest and Central China confined with high As concentration as well as certain indices (Geoaccumulation index, Ecological Risk Index) showed that these As have low risk towards the ecosystem. In the sediments, water and soil of two European countries, Cyprus and Greece which entitled to be the 'hotspot' of As contamination, ore deposits, lithology and geology have a major contribution in As contamination (Golfinopoulos *et al.*, 2021).

More than 60,000 people residing in Pannonian Basin, which includes Serbia, Hungary and Romania are posing the risk of drinking water contaminated with arsenic along with Greece, Spain, Italy, Croatia, Turkey, Finland and Czech Republic (Meduniae *et al.*, 2020). As per the permissible limits fixed by BIS (2012), As in groundwater should not exceed $50 \text{ } \mu\text{gl}^{-1}$ (in the deprivation of alternate source for water use) but 86 districts belonging to 10 states, which are, Haryana, Punjab, Karnataka, Jharkhand, Bihar, Chhattisgarh, Manipur, Uttar Pradesh, Assam and West Bengal were reported to have excess values than permissible limit in a survey by Central Ground Water Board Authority of India (Dhillon, 2020). The current scenario of As contamination of groundwater around the globe shows that permissible concentration has been surpassed by nearly 107 nations, most of which belongs to Asia (32 countries) followed by Europe (31), Africa (20), Australia (4), South America (9) and North America (11) while the data regarding population revealed that more than 230 million are prone to high risk of As toxicity whose major portion belongs to Asia (Shaji *et al.*, 2021). It was also reported that most

affected region belongs to South East Asian countries, Burma, China, India, Nepal, Vietnam, Bangladesh and Pakistan in which 4 Union Territories and 20 states of India were also included.

Impact of Arsenic toxicity

Effect of Arsenic Toxicity on Soil and Water resources

Uncontaminated soil have an As concentration below 10 mgkg⁻¹ but regardless of the sources, contaminated soils have a range of <1 to 250000 mg arsenic kg⁻¹ and it varies from country to country as parent material is different in those soils (Ranjan *et al.*, 2020). In agricultural soil, As level is recommended to be below 20 mgkg⁻¹ soil but the sensitive crops have toxic effect at a level of 5 mgkg⁻¹ soil. Microbes are essential component of the soil ecosystem as they have multiple functions and any changes in the soil chemistry may fluctuate the microbial diversity as well as composition. The degree of arsenic contamination in the soil affects the microbial composition preferably over microbial diversity. Arsenite, As (III) is oxidized by NO₃⁻ produced by the microbe *Nitrospirae* while

Acidiobacteria are capable for oxidation of sulfide minerals along with adsorption of arsenate, As (V) through which soil pH is enhanced, thus migration and transformation of soil As is made possible by these microbes (Yu *et al.*, 2020). In coarse soil particles, arsenic has lower mobilization potential than that in fine particles (Mensah *et al.*, 2020). Analysis of the catalytic properties of four soil enzymes namely, dehydrogenase, acid phosphatase, α- glucosidase and alkaline phosphatase in the soil which is under long term As contamination due to realgar mining activities and inferred that kinetic parameters like catalytic efficiency, enzyme – substrate affinity and maximum reaction velocity are sensitive indicators of the changes in soil biochemical behavior under long term As ecotoxicity (Wang *et al.*, 2020).

As per USEPA (United States Environmental Protection Agency) recommendations, arsenic in soil should be within the limit of 24 mgkg⁻¹ (Ranjan *et al.*, 2020). From the lowland paddy soils contaminated with arsenic, arsine gas was released and it was quantitatively measured by chemotrapping and estimated 240 mgha⁻¹yr⁻¹ (Mestrot *et al.*, 2011). Many processes influence arsenic mobility and

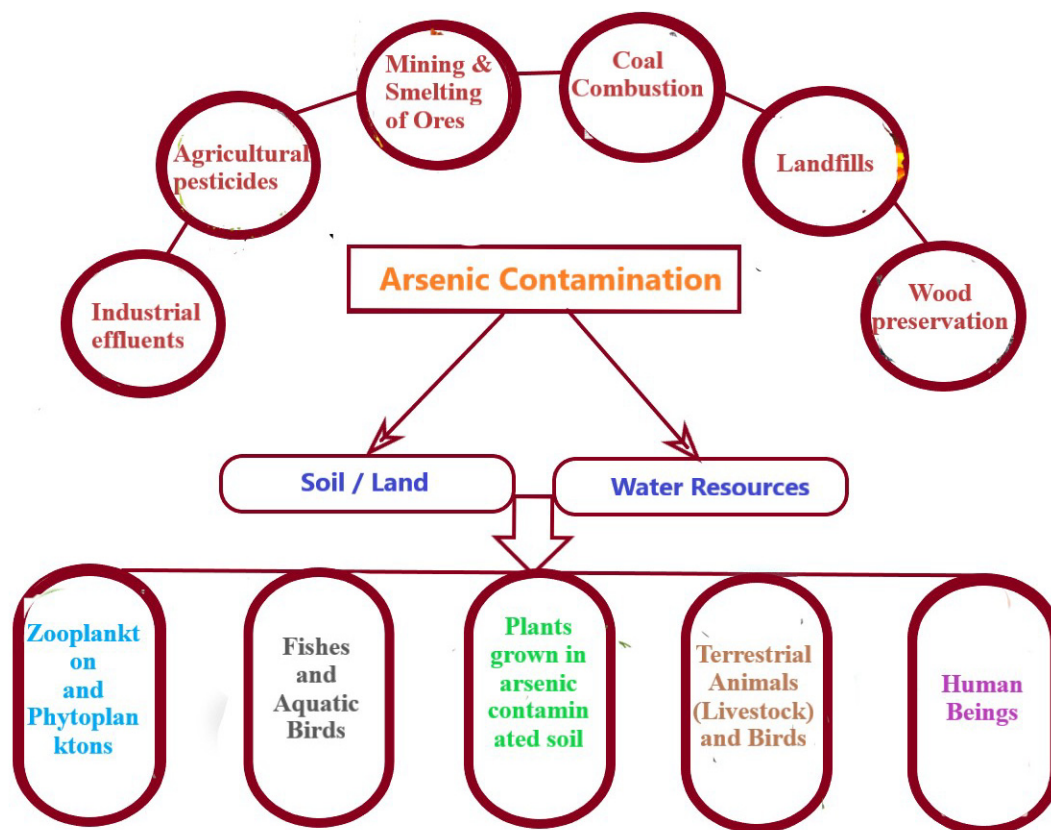


Fig. 1. Anthropogenic Sources of As contamination and the affected living organisms

bioavailability in soils like sorption, precipitation, oxidation, desorption, reduction and surface complexation wherein arsenate and arsenite are adsorbed on edges of phyllosilicates or on other minerals like imogolite, Al, Mn and Fe oxides, allophonic materials etc (Pigna *et al.*, 2015).

Around 150 million populations in the world are affected from water resources contaminated by As (Podgorski *et al.*, 2017). In about 6 hours, As (III) pollution enhances the Antibiotic Resistance Genes in bacteria and the development of this resistance will be maintained even in the absence of any selective pressure upto 7 days which indicates that they can enter drinking water treatment plants. This type of co-selection enriches *Elizabethkingia* sp., *Empedobacter* sp. and *Escherichia – Shigella* (Zhang *et al.*, 2020a).

Effect of Arsenic Toxicity on Plants

As (V) and As (III) have different mechanisms inside the plant body, both of which has been easily absorbed by plant roots. Inside the cell, arsenate turns to arsenite, which is more toxic form. Since, arsenate and phosphate have a similar chemical structure, metabolic reactions depended on the phosphate are likely to be disrupted (Farooq *et al.*, 2016). An important disrupted function is the photophosphorylation and oxidative phosphorylation where ATP is produced (Finnegan and Chen, 2012). Plants allow the uptake and movement of arsenite through major intrinsic proteins like NIPs (plant nodulin 26 – like intrinsic proteins), methylated As through aquaglyceroporins/ major intrinsic proteins and arsenate via phosphate transporters (Bienert and Jahn, 2010; Farooq *et al.*, 2016; Gupta *et al.*, 2021). Proliferation and extension of roots are hindered by the As exposure whereas plant growth is inhibited by arrested biomass accumulation. Yield can be reduced by As toxicity because it can induce fertility loss and abnormal growth of reproductive organs (Hasanuzzaman *et al.*, 2015).

Bioaccumulation of arsenic in plant parts has a relation with transpiration rate which again related to the shoot biomass of the plant (Rahman *et al.*, 2007). In the xylem sap of plants such as rice, *Pteris vittata* and tomato grown with As (V) supplementation, predominant species found was As (III) which indicates that within the root tissues, As (V) reduces to As (III) and then transported to other parts (Kumar *et al.*, 2015). Most of the plants retains As within the root tissues as observed in rice

that As concentration in roots is 75 times more than that in grain and 28 times higher as compared to that of shoots (Rahman *et al.*, 2007). The empty panicles in rice called 'straight head' and misshaped grains namely 'parrot beak' were the reported diseases in USA and Australia during the past centuries which resulted in yield reduction (Bakhat *et al.*, 2019).

Effect of Arsenic Toxicity on Food Chain

Consumption of arsenic containing food or water is responsible for the arsenic toxicity. Various fodders and food crops accumulates arsenic in different parts as they are cultivated by irrigating with As contaminated groundwater and the subsequent consumption by living organism enhances its transport to higher trophic levels. Around 94 – 220 million population have potential risk from highly As contaminated groundwater, with a greater percentage belonging to Asia (Podgorski and Berg, 2020). In an year, irrigation given to the paddy with groundwater containing 0.55 mg l^{-1} adds $5.5 \text{ kg As ha}^{-1}$ to the soil while peeled root samples of the vegetable arum, were found to have highest arsenic concentration ranging from $<10 - >100 \text{ mg kg}^{-1}$ among all other vegetables analyzed (Huq *et al.*, 2006). Among all the food stuffs consumed, cereals and vegetables contributed the highest percentage of arsenic in daily dietary intake in Bangladesh which surpassed the safe limits for target hazard quotients and target carcinogenic risk whereas Tilapia fish had highest average concentration of As, 0.94 mg kg^{-1} (Islam *et al.*, 2017). In Bihar, it was estimated that the arsenic exposure from food is nearly equal to that of drinking water and cooked rice has a greater contribution as compared to wheat flour and potato (Mondal *et al.*, 2021).

Aquatic as well as terrestrial birds were studied for As transfer and accumulation in the food chain and found that aquatic birds are more prone to As toxicity as they belong to higher trophic levels because As has the potential for bioaccumulation and trophic transfer through the food chain (Tasneem *et al.*, 2020). It can be a serious threat to the avian population. It cannot be concluded that all crops grown in As contaminated soil are unsafe to consume because it depends on the type of crop, root system, type of soil, crop duration and concentration of As in soil (Haque *et al.*, 2020). This study was done in Alampur, Bangladesh where the soil has a good retention of arsenic suggesting that As is not transported to the plants. Rice, being the staple food of Bangladesh have been analyzed in

many studies for its accumulative tendency for As. Rice cultivated in Faridpur, Bangladesh where arsenic concentration is high in soils and irrigated groundwater, has accumulated As in its straw and husk which is the edible parts for poultry and livestock that indicates the entry of As into the food chain while the grains have a mean As concentration of 0.08 – 0.45 mgkg⁻¹ (Kabir *et al.*, 2016).

After entering the food chain, inorganic As, which is more toxic form converts to less toxic, organic forms as they undergo methylation that gives mono-, di- or tri- methyl arsine (Shrivastava *et al.*, 2015). In marine organisms or sea food like crustaceans, fish, gastropods and Phaeophyceae, organic arsenic form, mainly arsenobetain is found which is less toxic (Kaise and Fukuli, 1992).

Effect of Arsenic Toxicity on Humans

Humans are exposed to the released toxic substances either through consumption of contaminated food or through inhalation or through dermal contact and these are more possible under occupational environments like mining and smelting (Xue *et al.*, 2017). Arsenic poisoning at a chronic level leads to arsenicosis whose intensity depends on duration of the exposure and quantity of

accumulated metalloid in the body. Keratosis, pigmentation on skin, cancers on skin as well as internal organs, problems in cardiovascular and nervous system are the stages of arsenicosis (Berg *et al.*, 2007). This can also lead to retarded mental growth in children (Amini *et al.*, 2008). In 2005, largest population under the cancer risk by inhalation of As from the atmosphere was in China, but in 2015, India surpassed the China (Zhang *et al.*, 2020). To determine the As toxicity in the population, nail, hair, faeces, skin, urine and lungs are used as indicators because As is excreted by these body parts (Jain and Ali, 2000). In Argentina, As content in the urine and hair of child population exceeded from the reference value (Urine: 50 µg/g creatinine and Hair: 1 mg/kg) as well as it created alterations in the metabolites in urine like increase in inorganic As and monomethylarsonic acid while decrease in dimethylarsinic acid (Calatayud *et al.*, 2019). Also, at the intense As exposed area, the presence of an oxidative DNA marker, namely 8 – OhdG, was found at high values (3.7–37.8 µgg⁻¹ creatinine). Viability of a cell decreases with increasing concentration of arsenic (Xue *et al.*, 2017).

Trivalent arsenic compounds generate oxidative stress in the tissues and disturbs the metabolic

Table 1. Permissible limits of As exposure fixed by the guidelines of various Agencies

Sl. No.	Particulars	Permissible Limits	Agency/ References
1	Drinking Water	10 µgl ⁻¹	WHO, 2018 (Zhang <i>et al.</i> , 2020b); BIS, 2012; EPA, 2018
2	Bottled Water	10 µgl ⁻¹	FDA, 2020
3	Infant Rice Cereal	100 ppb	FDA, 2020
4	Exposure limit in air workplace for 8 hours: for < 15 min:	10 µgm ⁻³ 2 µgm ⁻³	(Gehle, 2009) OSHA NIOSH
5	Byproducts of animals treated with As containing drugs:- Eggs, uncooked edible chicken: Swine:	0.5 ppm 2 ppm	(Gehle, 2009) FDA
6	Irrigation water	0.10 mgl ⁻¹	FDA
7	Uncontaminated Soil	0.1 to 10 mgkg ⁻¹	FAO (Kabir <i>et al.</i> , 2016) Ranjan <i>et al.</i> , 2020
8	Bangladesh Drinking Water Standard	50 µgl ⁻¹	Huq <i>et al.</i> , 2006
9	Dietary Exposure of inorganic As Children: Adult:	(lg kg-bw ⁻¹ day ⁻¹) 0.20 to 0.36 0.11 to 0.17	EFSA, 2014 (Islam <i>et al.</i> , 2017)
10	Agricultural Soil	20 ppm	Kabir <i>et al.</i> , 2016
11	Rice Grain	1 ppm	WHO (Rahman <i>et al.</i> , 2007)
12	Tolerable weekly intake of inorganic As	15 µgkg ⁻¹ body weight	WHO/FAO (Bakhat <i>et al.</i> , 2019)
13	Soil	24 mgkg ⁻¹	USEPA
14	Atmospheric As content	< 6 ng m ⁻³	European Union (Zhang <i>et al.</i> , 2020b)

activity by interactions with sulfur in proteins (Hughes *et al.*, 2011). Inorganic As has a greater affinity to the tissues which can be reduced by methylation that is a detoxification process. Other after effects of As exposure from contaminated water is hepatomegaly, arsenism, splenomegaly, black foot disease, gangrene, non pitting swelling, conjunctivitis and leucomelanism (Jain and Ali, 2000).

Remediation of Arsenic Contamination

Heavy metal/metalloid pollution is an outspreading issue and there exists various remediation techniques to dissolve the issue. For the As removal from the environment, physico- chemical techniques like ultrafiltration, adsorption by activated carbon and activated alumina, reverse osmosis, coagulation preceded by metal ion complexation and ion exchange were found to be applied (Alka *et al.*, 2021). But, it is found to be expensive under high As concentration due to large requirement of chemical reagents. Also, the sludge after the treatment will be polluted with the chemical reagents used in the process that may end up with secondary pollution (Jain and Jha, 2020). Some of the measures proposed by the National Policy for Arsenic Mitigation like rainwater collectors, dug wells, piped water system, As removal units and pond sand filters were found ineffective in Bangladesh (Ahmed *et al.*, 2006). Therefore, techniques with minimum costs, highly efficient and low environmental risks have to be adopted.

Phytoremediation

Phytoremediation is a promising technique by which green plants are used to accumulate metals or organic chemicals from the contaminated groundwater and soil. Plants used in this context are referred to 'hyperaccumulators' as they are capable to accumulate $> 1000 \mu\text{g metal g}^{-1}$ of dry weight (Brooks *et al.*, 1977). The plants selected for the phytoremediation must have following features: high tolerance to As, short life cycle, high rate of propagation, wide range of distribution, increased bioaccumulation factor and high biomass (Visoottiviseth *et al.*, 2002). These types of plants can extract the metal by means of osmoregulation, exclusion, aggregation, distribution and translocation. In Thailand, remediation of the arsenic contaminated land was found more suitable with *Melastoma malabathricum*, *Mimosa pudica* and fern species namely *Pteris vittata* and *Pityrogramma*

calomelanos among which the efficiency of As accumulation was profoundly observed with ferns as they accumulate around $8350 \mu\text{g g}^{-1}$ dry mass in its frond. Some external factors can supplement the capability of plant in taking up the arsenic, such as rhizospheric factors, As speciation, phosphorus fertilization, root exudations, chelating agents and microbial population in the rhizosphere (Cao *et al.*, 2003; Jankong *et al.*, 2007). Other plants designated to be the hyperaccumulators of As are *Pteris umbrosa*, *Pteris criteca*, *I. cappadocica*, *Pteris longifolia* and aquatic macrophytes like *Ceratophyllum demersum*, *Hydrilla verticillata*, *Egeriadensa*, *Eichhornia crassipes*, *Potamogeton pectinatus* and *Lepidium sativum* (Kumar *et al.*, 2015).

Microbial remediation

From the contaminated sites, As can be accumulated by certain microbes through several mechanisms like precipitation, biosorption either to cell wall or to extracellular polysaccharides, transportation across the plasma membrane, redox reactions and entrapment in extracellular capsule (Jain and Jha, 2020). Engineered microbes can also be used as an effective and low cost remediation technique of the present time (Gupta *et al.*, 2021). In rice seedlings grown under As (V) stress, a consortium of the *Pseudomonas putida* (plant growth promoting rhizobacterium) and *Chlorella vulgaris* (green algae) declined the arsenic levels in shoots and roots, reduced the oxidative stress and enhanced the plant growth (Awasthi *et al.*, 2018). *Piriformospora indica* is an endophytic fungus that colonizes in the roots of the host to assist them in biotic and abiotic stress responses (Johri *et al.*, 2015). Arsenic toxicity induced the hyper colonization of *P. indica* around the roots of paddy which enhanced the recovery of root damage, chlorophyll, biomass accumulation along with effective antioxidative system, immobilization of available form of As in the soil and restricting the movement of As towards the plant root (Mohd *et al.*, 2017). In a rice field with As pollution, *Aspergillus flavus* biotransform the available As into As particles which have a reduced toxicity that their presence will not cause any disturbances to the membrane integrity of the nitrogen fixing bacteria, mycelial growth and root colonization of *P. indica*, survival of the *Dictyostelium discoideum* (slime mould) and growth of the plants (Mohd *et al.*, 2019).

Many microbes are potentially capable to transform inorganic As species through successive methylation or reduction reaction into arsine gases

like AsH₃, mono-, di-, and tri-methyl arsines which are volatile and highly toxic (Mestrot *et al.*, 2011). Methylation of inorganic arsenic can be performed by some fungi species like *Penicillium*, *Candida*, *Scopulariopsis*, *Aspergillus*, *Trichoderma* and *Fusarium* (Upadhyay *et al.*, 2018).

Nanotechnology

Application of nanoparticles is an emerging broad spectrum study as they have the advantageous feature of high specific surface area than macro particles. Nanotechnology deals with the science and applications of those materials in between the size range of 1 – 100 nm (Rabbani *et al.*, 2016). This is a cost effective environmental remediation technology (Karn *et al.*, 2009). The adsorptive capacity is directly related to the specific surface area of the nanoparticles which enables them to bind with As with 5 – 7 times efficiency than microparticles (Rajan, 2011). Arsenic remediation from groundwater is effectively done by the Magnetite nanocrystals (Yavuz *et al.*, 2010). Arsenic can be removed from the wastewater with the adsorption mechanism of carbon nanosphere encapsulated by iron oxide nanocomposites, which is an efficient and low cost technology (Su *et al.*, 2017). A fast adsorption of arsenic was also observed in nanocomposite prepared by coating iron oxide on single walled carbon nanotube and performs well at low metalloid concentration (Ma *et al.*, 2018). As compared to the nanoparticles of hydrated zirconium oxides, nanocomposite of carbon nanotubes coated with the ZrO(OH)₂ can much efficiently remove arsenite and arsenate from the drinking water (Liu *et al.*, 2018). Within a short span of time, nanoscale zero valent iron can strongly adsorb As (III) and efficiently removes from the site even under a broad range of pH (Kanel *et al.*, 2005). Palladium bio-nanoparticles are derived from green algae named *Chlorella vulgaris*, which removes As effectively from the aqueous solution by adsorption (Arsiya *et al.*, 2017). When hydroponically grown rice seedlings were amended with 1000 mg l⁻¹ of nano- TiO₂ having rutile crystalline structure, controlled the uptake of As, reduced the bio-accumulation of As in the rice seedlings by 40 – 90% and alleviated the oxidative stress through the strong sorptive capacity of TiO₂ nanoparticles (Wu *et al.*, 2021).

CONCLUSION

Arsenic contamination is a serious concern to be

addressed with suitable solution having long term impact. Many of the recent studies have established the sources, spread and effects of As in the living world. The prescribed guidelines by various agencies mentioned certain threshold limits for As levels in environment, but majority of the reported studies show that as compared to anthropogenic activities, geological sources release arsenic in excess to threshold limits. So, there exist limitations for its remediation. Arsenic exposure in human could be through ingestion of contaminated food and water, inhalation of arsine gas and dermal contact which creates health hazards like arsenicosis, dermal cancer, internal cancer, neurological and cardiovascular disorders. Apart from the legal limits and restrictions, there is need for economical, environment friendly and effective technologies to tackle As contamination. Phytoremediation is environment friendly and efficient natural mechanism for this purpose. Researches should be widened to more plant species that can hyperaccumulate the arsenic in correlation to changing climatic parameters along with economic benefit also.

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