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Arsenic pollution and its impact on agricultural production, including the ecosystem services delivered by biodiversity

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ABSTRACT

Arsenic (As), a noxious metal(loid) widely available in the biosphere, originates mainly from geogenic and anthropogenic origin. Massive global development and industrialization, using pesticides carrying arsenic, arsenical animal feeds, medicine, mining, aquifer sediments, coal burning, and microbial and natural processes continuously release this obnoxious bane to the natural environment and pollute soil and water. Inorganic (iAs) species, mainly arsenate and arsenite, are comparatively more lethal than methylated species. However, pentavalent [As (V)] organic species are nearly non-toxic. An elevated level of arsenic has been found in various crops and feeds consumed by humans and animals. This notable carcinogen threatens human health by drinking arsenic-polluted freshwater and/or ingesting arsenic-adulterated food like cereals, fruits and vegetables grown in arsenic-polluted soil or grown using arsenic-rich irrigation water. Arsenic pollution exerts an irreversible harmful effect on the aquatic and terrestrial ecosystem as well. Much research has been carried out in the last couple of centuries on arsenic pollution and reported its ability to influence the agro-ecosystem to a great extent, including plant accumulation, phytotoxicity, and land degradation. However, underground water is considered the principal source of arsenic pollution, Iron plaque, sulphur oxides, organic matter, microbiome activities and many other factors responsible for speciation, bioavailability and toxicity of As to the environment. This review attempts to comprehend the global arsenic pollution occurrence, its forms, bioavailability and toxicity to humans and microbiota, translocation and accumulation in plants and impact on crop yield. Besides providing the insights, the ultimate targets of this desktop study are to ascertain probable knowledge gaps linked to crop productivity and ecosystem benefit losses that need further investigation.

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I. Introduction

Arsenic (As) is a toxic chemical that is naturally found in the environment, holding the 20th position among the metal (loid)s (NAP.edu, 1977) and is a proven carcinogen for humans when exposed through oral, dermal, and inhalation pathways (IARC.FR, 2019). From the era of the Roman Emperor towards the Renaissance, arsenic was considered the king of all poisons. Because of its silent nature of poisoning, arsenic has a heartless history of use with human food as a secret weapon in the ancient period. This superfluous metalline is deadly toxic to flora, fauna and biosphere irrespectively and equally hazardous to crops, humans and animals (Zhao et al., 2009; Panda et al., 2010; Mirza et al., 2014). It exists in various chemical forms, each with different mobility levels, accounting for their toxicity. In the context of global human health and environmental pollution, it is crucial to understand arsenic speciation, bioavailability, and uptake mechanisms by plants and their species-specific toxicity to plants, animals, and the biosphere. This review intends to present relevant information on how arsenic interacts with ecosystem services, more likely provisioning, regulatory and habitat services, influencing yield potentials and affecting human health and biota. Finally, it summarises the suggestions for mitigation and amelioration of As pollution. This review could add research insights for reducing arsenic pollution.

II. Materials and Methods

This desktop study used the Web of Science from January 2020 to July 2020. Search keywords were arsenic pollution, arsenic toxicity, arsenic and yield, arsenic and ecosystem. Using Google Scholar, a systematic search was conducted and 106 peer-reviewed articles, books and reports were downloaded from a high-impact database using institutional access permission, among which the most relevant 53 were synthesized in this review.

III. Arsenic pollution: Global scenario

Earth's crust is the foremost ecosystem component exposed to arsenic pollution. Regional variation of arsenic concentration in soil ranges between 0.1 mg and 100 gkg^{-1} soil (Mirza et al., 2014). A part of Bangladesh, India, Nepal, and China, jointly known as the Ganges Basin, is a remarkable hotspot of Arsenic pollution. The magnitude of arsenic pollution in irrigation water, food grain and groundwater in the Ganges Basin is 1000 µgL^{-1}, 3947 µgkg^{-1} and 4730 µgl^{-1} respectively, where the admissible arsenic ceiling for drinking water is 10 µgl^{-1} (WHO), and in irrigation water is 100 µgl^{-1} (FAO) (Chakraborti et al., 2018). Many countries experiencing elevated arsenic pollution in their soil, food system and underground water, especially the Indian sub-continent, China, Taiwan, South Africa, Australia, Chile, Argentina, Mexico, USA and Italy (Brammer and Ravenscroft, 2009; Ravenscroft et al., 2009; Panda et al., 2010; Chakraborti et al., 2018 and Ahmad and Bhattacharya, 2019).

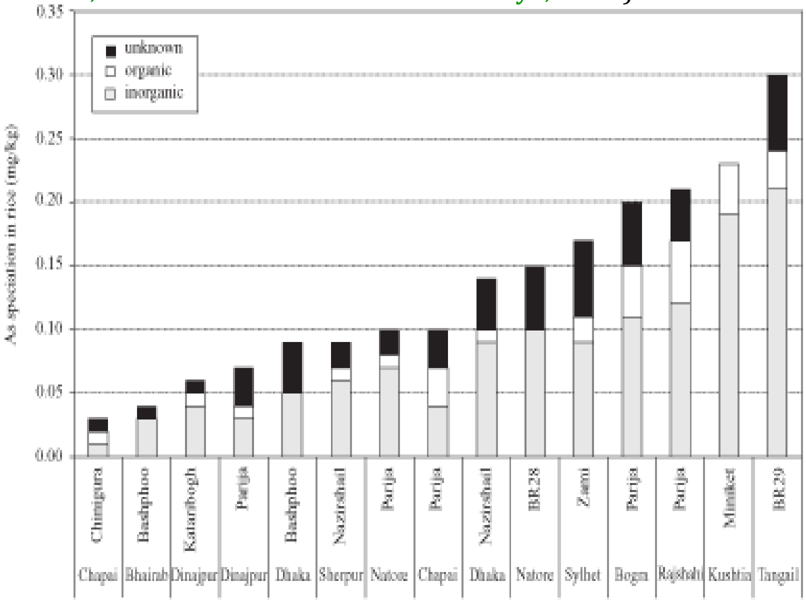

Figure 01. Organic and inorganic arsenic contamination in rice grain (Williams et al., 2005).

Arsenic is mainly a geogenic-originated pollutant and is profusely available in nature. Over 70 countries have documented high arsenic pollution in their drinkable water, bringing considerable health risks to the millions (Ravenscroft et al., 2009; Chakraborti et al., 2018). Soil arsenic content widely varies depending on parent material, soil properties, and anthropogenic activities in a particular ecosystem (Zhou et al., 2018). Normally, virgin soil comprises arsenic ranges from 0.1 to 40 parts per million, whereas average soil arsenic concentration is 5-6 parts per million, considering the geographic location. High sulphide ores containing soil or soil near excessive As-containing minerals have reported arsenic concentrations as high as 8000 ppm (NAP.edu, 1977; Mirza et al., 2014).

Nearly 150 million people throughout the globe have been exposed to this lethal toxicant through the intake of polluted drinkable water and diet. At the same time, soil and ecosystem are degrading due to using contaminated irrigation water in crop fields (Figure 01) (Heikens, 2006; Zhao et al., 2009; Ravenscroft et al., 2009 and Zhao et al., 2010). Irrigated rice has been reported as the super accumulator of inorganic arsenic (iAs). As rice paddy is the staple diet of many people, it is creating a weighty threat to the health and well-being of humans (Williams et al., 2005; Zhu et al., 2008; Zhao et al., 2010).

The principal sources of arsenic in nature are igneous and sedimentary rocks, aquifer sediments and varieties of other minerals. Ores containing sulphides and salt of sulphur are the prime sources of As. In nature, arsenic is commonly associated with Cu, Ag, Pb, Se, Fe, etc and Pt metals (Boyle and Jonasson, 1973; NAP.edu, 1977 and Cullen and Reimer, 1989). These metals (loids) are released to the atmosphere by the weathering and geochemical changes of As-containing minerals, as well as activities of As oxidizing and reducing the microbial community. Besides volcanic eruptions, anthropogenic activities like industrial wastes, urban sludges, mining, agricultural use of arsenical pesticides, coal combustion and lifting aquifer water are adding As in nature (Cullen and Reimer, 1989; Mirza et al., 2014; Kabata-Pendias, 2017).

IV. Arsenic speciation

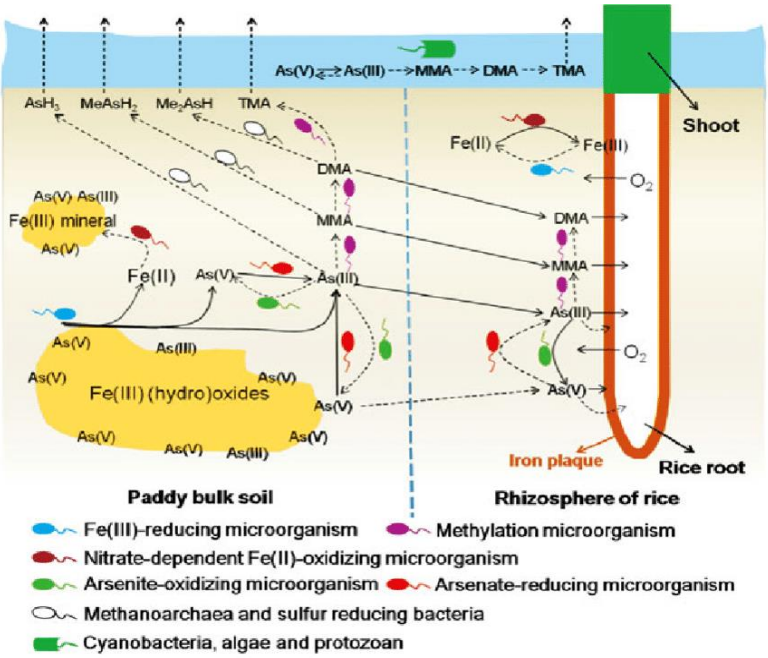

Figure 02. Arsenic cycles in paddy soil. Microbiota in the rhizosphere soil are responsible for methylation and mobilization of arsenic. As species generated via microbial process either uptake and translocate by rice root or volatilize to the environment. Solid lines are dominant speciation and movement process (Zheng, 2012).

The environmental toxicity of As relies on its valence state and mobilization in nature. Several factors like soil and irrigation water As concentration and available As species in the specific environment affect the rate of accumulation and toxicity of flora and fauna to a great extent (Marin et al., 1993 and

Carbonell-Barrachina et al., 1997). Geographic distribution of As pollution is closely linked to geology, groundwater cycle, agricultural practices and land use patterns. Several biotic, geospatial and geochemical factors influence sediment release to groundwater. Repeated irrigation with arsenic-contaminated water escalates the chance of arsenic deposition in rhizospheric soil, particularly flood-irrigated rice cultivation practice in South Asian countries, aggravates pollution (Williams et al., 2005 and Christopher and Haque, 2012).

Ecotoxicity and phytotoxicity of As greatly vary depending on the As species available in the ecosystem. In biosphere III and V are the ordinary valence states, and get-at-able oxidation states are As^{-3}, As^{0}, As^{+3} and As^{+5}. The most abundant and phytoavailable As species are As(III) and As(V) in the terrestrial ecosystem, where As(III) demonstrates 100 times higher toxicity than As(V) (Cullen and Reimer, 1989; Panda et al., 2010 and Chandrakar, et al., 2016). Chemical forms of oxidation states of trivalent (III) arsenic are AsH^3, $As(OH)^3$, and $As(CH_3)^3$ and pentavalent (V) arsenic are $(CH_3)^2AsO(OH)$, $(CH_3)^3AsO$ in the biosphere (Cullen and Reimer, 1989).

The phyto-availability of arsenic in terrestrial ecosystems principally depends on speciation. Generally, the interchange between oxidised and reduced forms is catalysed by the soil properties. Methylation and speciation of As eventuate with the aid of the microbial community (Figure 02). A range of microbes (Bacteria, Fungi, Algae and protozoa) is accountable for methylation and conversion of iAs species to organic compounds and vice-versa. Some microbes convey genes can convert to volatile species that produce garlic smell ((Cullen and Reimer, 1989 and Bentley and Chasteen, 2002). Species of arsenic like arsenals acids, arsenic acids, arsenites, arsenates, monomethylarsonic acids (MMAA), dimethylarsinic acids (DMAA) and trimethylarsine oxide (TMAO) are available in the environment based on their physicochemical properties (Cullen and Reimer, 1989 and Pantsar-Kallio and Korpela, 2000).

Arsenic accumulations are greatly influenced by As species. Depending on arsenic hoarding abilities, plant species are divided into three categories- excluder, intermediate accumulator and hyperaccumulator. Excluder restricts arsenic plant uptake from nature and prohibits arsenic transportation from root to apical part. On the contrary, hyperaccumulators, especially some fern species, can uptake and assimilate arsenic in their aboveground part, nearly 2% of their total dry weight (Zhao et al., 2010). Arsenic-induced toxicity primarily depends on the arsenic species and crops available in the environment. However, speciation may occur in the biosphere or in crop plants, animals and microbes. Decreasing trends of arsenic concentration in different parts of crops are evident. Gradual diminishing order of As deposition: root>stem>foliage>grain has been reported in many studies (Allevato et al., 2019). Primary species found in plants were arsenate, whereas arsenite and dimethyl arsenic acids (DMA) were at trace levels in high substrate concentration, alternatively in low-affinity translocation. Dimethylarsinic acid proved safe in respect of toxicity. However, its mere presence in the rice cannot subside toxicity (Abedin et al., 2002 and Williams et al., 2005).

V. Arsenic mobilization and water pollution

In many geographic locations of the globe, arsenic pollution in drinking and irrigation water is a burning issue. Both oxidized and reduced forms of arsenic are found in seawater, and the most prevalent species is arsenate [As(V)], which comprises 81% of total arsenic. Arsenite, methane sulphonic acid, and cacodylic acid are also present in seawater, and the arsenate to arsenite ratio between 0.1:1 and 10:1 is unexpectedly high at seawater pH 8.1. In the precipitation of iron-rich spring water (pH 5.1), around 80% arsenic was found. Hot spring water has reported 0.7 ppm arsenic content. High arsenic content has been documented in groundwater because of higher thermal activities and arsenic prolific rocks nearby. The uplifted concentration of arsenic is found in rivers, lakes, and other surface and sub-surface water due to the disposal of wastes and use of arsenical pesticides and fertilizer (NAP.edu, 1977). Arsenic mobilization largely depends on the pH of the groundwater (6.5-8.5) and oxidation-reduction potential. Soil arsenic pool is influenced mainly by the pH, and at higher pH, the mobility of arsenic increases (Zhou et al., 2018). Normally, it is thought that As(III), the reduced form, is mostly found in underground water in anaerobic conditions and As(V), the oxidized form, is prevalent in aerobic conditions in surface water. Though all the forms were found in ground and surface water and acidic or basic pH, some water reported the sole presence of arsenite (Howe et al., 2001). Total arsenic in groundwater ranges from 1.7 μgl^{-1} to 404 μgl^{-1} among which dominant species were As(III) (79 to 99.9%). Arsenic concentration in groundwater is much higher than that of WHO recommendation for drinkable water (10 μgl^{-1}) and FAO prescription for irrigation water (100 μgl^{-1}) (Bhattacharya, 2002).

VI. Arsenic pollution in soil

Two oxidized states, arsenate and arsenite, are frequently based on oxidizing and reducing the capacity and pH of the terrestrial environment. In aerobic soil, arsenate is predominant, whereas As(III) is abundant in anaerobic or submerged soil. In their study, Smith et al. found arsenite to be the uppermost available species in irrigated rice, and the aerial part of the plants accumulated and stored in a high concentration (Smith et al., 2009). Depending on mobility and toxicity, trivalent [As(III)] species are a broad environmental concern, though at lower pH and higher redox potential, predominant species are arsenate [As(V)] (Masscheleyn et al., 1991). The abundance of clay minerals and organic matter (OM) greatly influences As mobility in soil systems. Soil containment of Fe, Mn, oxides of Al, clay and OM enhances both absorption and adsorption of As in soil, reducing mobility and toxicity to plant communities and nature (Lin and Puls, 2000 and Balasoiu et al., 2001).

VII. Arsenic translocation in plants

Crops cultivated in highly arsenic-polluted soil or crops irrigated with contaminated groundwater have a higher possibility of pick-up and transportation from the below-ground part to the apical part and storage in leaves, fruits, and grain. Arsenic concentrations found in different plant parts decreased, leaning from root to foliage or grain. The rate of arsenic uptake varied depending on the arsenic species present in the biosphere and cropping season. Accumulation of both oxidized and reduced forms was higher in Aman rice (rainfed) than Boro (irrigated) rice varieties, and this variation was due to plant physicochemical features like the presence of arsenic transporter and varietal tolerance. Phosphate availability also influences the arsenate uptake. Arsenate transportation fluctuated in the presence or absence of phosphate because both As and P use the same transporter, whereas arsenite transportation was reported as usual (Abedin et al., 2002).

Arsenic translocates within the plant system using different types of transporters. As(V) is the analogue of phosphate, an essential compound of plant organelle and in a phosphate fertilizer deficit environment, As(V) efficiently can utilise phosphate co-transporter for its locomotion, whereas [As(III)] utilises the separate mechanism in O_2 deficit condition. In anoxic conditions, arsenite absorbs and transports from rhizospheric soil to the above-ground plant part using OsNIP2.1, a member of the plant aquaporin family (Panda et al., 2010). Phosphate ions (Pi) have proved a significant facilitator of arsenic transportation in the plant-soil system. In a hydroponic culture system, Pi effectively slowed down arsenic uptake, whereas in the soil-plant system, the effectivity of Pi was found to depend on soil properties. Increased Pi in soil influences the phyto availability of arsenate, and in the presence of increased Pi in the plant system, upward transportation of arsenite also increases (Anawar et al., 2018).

Irrigated paddy rice cultivation mobilizes and facilitates arsenite accumulation in anaerobic conditions. Soil reacts with other elements, namely, phosphorus, sulphur and silicon, during its journey from the soil to the uppermost plant part. In flooded conditions, plants draw Arsenite and methylated species from soil solution using a Silicon (Si) transporter and NIP (nodulin 26-like protein, an aquaporin family member), whereas arsenate uses a phosphate transporter to draw arsenate from phosphate deficit soils (Zhao et al., 2010).

VIII. Phytotoxicity of arsenic

Arsenic, the ubiquitous metal(loid), is entirely non-essential. In the agriculture sector, there has been little historical use of arsenic pesticides, and only at trace level was it found beneficial to animals. Arsenic has no records as a plant nutrient. Hence, any concentration is toxic to the living organism, including crops (Panda et al., 2010). Biota in terrestrial and aquatic systems respond differently to arsenic toxicity. Generally, organoarsenic evinced more toxic than methylated derivatives. Arsenic, mainly arsenite (AsIII), is highly necrotic to root membrane. It reacts with thiol or thiol derivatives (sulfhydryl group) and affects the ordinary root functions. Even an uplifted arsenic level in the soil is responsible for cell death of plants. Chemically, arsenic is similar to phosphorus and can easily share the transporter and cell mechanism used by the phosphorus. Its facultative participation in various biochemical reactions exposes the plant to phytotoxicity. However, bacterial cells could use arsenic as a phosphorus substitute (Knodle et al., 2012).

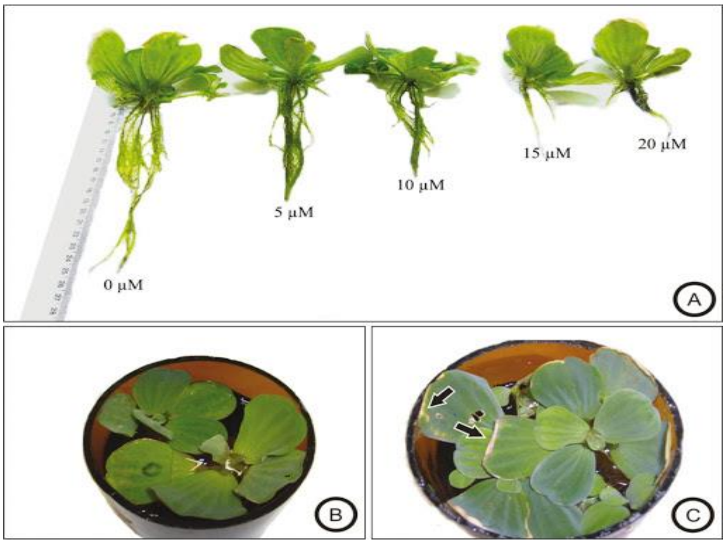

Figure 03. Root and foliar growth retarded at high As (a). Normal growth at control (B). As induced necrotic lesion and toxicity symptoms at higher arsenic concentration (C) (Franese et al., 2014)

Different studies have shown that arsenic hoarding by plant systems is positively influenced by ROS (Reactive Oxygen Species), like superoxide dismutase and peroxidase. It lowered the concentration of chlorophyll and carotenoids and produced physiological stress (Figure 03) (Mascher et al., 2002). It induces ROS directly during the exchange of arsenate to arsenite or it inactivates antioxidants (Chandrakar et al., 2016). In paddy rice, a higher Dimethylarsenic acid (DMAA) uptake rate, translocation and aggregation in root-to-shoot was observed. At the same time, irrigation water arsenic was increased, and DMAA-induced stress reduced rice plant photosynthesis and dry-matter production (Marin et al., 1993). A pot experiment with fenugreek (*Trigonella foenum-graecum* L. cv. Azad) confirmed the tolerance to a certain level of phytotoxicity. Yield and yield attributing feature of this crop increased in control (0 mgk^{-1}) to 20 mgk^{-1} arsenic application, where 30 mgk^{-1} resulted in a sudden decrease. H_2O_2 production increases in both 20 mgk^{-1} and 30 mgk^{-1} arsenic application, while 30 mgk^{-1} generates oxidative stress (Talukdar, 2013).

IX. Arsenic pollution and crop yield

Plant biomass and grain yield performance are directly linked with nutrient uptake and assimilation. Arsenic, the well-known toxicant, impacts plant nutritive uptake and accumulation positively and negatively. Research with arsenic hyperaccumulator [*Pteris vittata* (PV)] and non-hyperaccumulator [*Pteris ensiformis* (PE)] manifest nearly opposite directional observations concerning biomass production. Hyperaccumulator (PV) grown arsenic adulterated soil had gained 5-9 folds vegetative growth than usual, and arsenic promoted growth positively, whereas biomass production retarded and dry-matter gain reduced to 63% in the case of non-hyperaccumulator (PE) (Liu et al., 2018).

In in-vitro hydroponic tomato cultivation, the nutrient solution was manipulated with arsenic, and acknowledgeable impacts were observed with increased arsenic concentrations. Arsenic phytotoxicity disrupts physiological activities and lowers vegetative growth following the reduction of dry-weight, fresh-weight and fruit production (Carbonell-arrachina et al., 1998). Arsenic present in water distracts essential plant nutrient absorption by the root system. Even after uptake, arsenic disrupts different plant metabolic processes, defends the formation of ATPs inactivates essential enzymes, and finally, it derives substantial yield reduction (Figure 03) (Bakhat et al., 2019). Paddy rice has proved a super-feeder of arsenic in both inorganic and organic forms. Arsenic sensitivity and uptake vary significantly depending on rice variety, soil and irrigation water arsenic concentration and cultivation practice. In the greenhouse, rice irrigated with As-rich water imparted notable yield reduction. The yield of local rice variety was impacted by the increase of irrigation water arsenic concentration ranges between 0.2 mg^{-1} and 8.0 mg^{-1} (Abedin et al., 2002; Panaullah et al., 2008).

X. Arsenic influence on plant nutrients

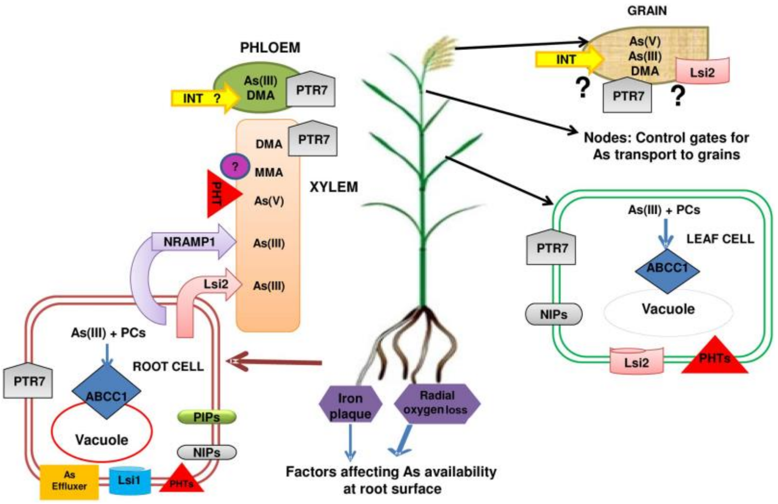

Figure 04. Complex pathway of arsenic Phyto availability, uptake and transportation from soil to grain in plant soil system. Illustration demonstrates the factors responsible for uptake and metabolism of inorganic As within rice plat (Awasthi et al., 2017).

As part of the arsenic-polluted ecosystems, plant communities, especially crops, are the prioritized entities impacted. Roots exposed to arsenic toxicity exhibit reduced expansion and growth carrying the noxious element to shoot, and leaves show physiological and morphological stress in uppermost plant parts (Figure 03). Due to oxidative stress of arsenic, important cell organelle become dysfunctional, membrane structure disorganised results in an imbalance in nutrient uptake using plant-mechanism (Chandrakar et al., 2018).

Plant nutritional availability and uptake depend upon several factors. Groundwater in different parts of the world that are severely contaminated with arsenic is one of the prime sources of soil and surface-water contamination. Crops irrigated with highly arsenic-contaminated ground or surface water influence the uptake and assimilation. But, its presence at low concentration in irrigation water has no countable effect on plant nutrient absorption (Marin et al., 1993).

Production of rice, a staple diet, is highly constrained by the noxious element Arsenic either by competing for essential plant nutrients or by exerting toxicity. Arsenic presence in the soil at a higher concentration competes with and constrains the nutrient uptake by the plant system because arsenic shares a similar route used by the essential plant nutrients. However, the multifactor influences uptake from rhizosphere soil by the root hairs. Iron plaque, radial oxygen loss, phosphate ions and aquaporins influences assimilation and the movement of arsenic species (Figure 04) (Awasthi et al., 2017). Being the analogue of phosphate, the soil at high arsenate [As(V)] concentration, mainly in acidic upland soil, the plant suffers from phosphate ions (Pi) deficiency impacted yield attributes seriously. However, in wetlands, paddy is impacted due to arsenite-induced toxicity (Singh et al., 2015). Availability of sulphur in soils retarded arsenic uptake and vascular transportation in plant systems. Glutathione and Phytochelatins, a short peptide of thiol, trapped the arsenic. These short-chain peptides sequestrate As to vacuoles and stop translocation.

Vegetative growth and dry matter production are directly linked with bioaccumulating essential plant nutrients. Liu et al. in their study found an increased absorption of Arsenic, Iron, Phosphorus, Potassium and Zinc, whereas Calcium (Ca), Magnesium (Mg) and Manganese (Mn) uptake and transportation decreased or remained the same with high arsenic concentrations. *P. vittata* accumulates up to 3.6 and 4.4 folds more iron and phosphorus in the presence of arsenic in soil than normal, where non-hyperaccumulator are affected by arsenic toxicity and retarded growth of up to 63% due to a deficit of essential plant nutrients (Liu et al., 2018). As uptake and translocation studies in tomato plants exhibit the variation in assimilation and storing of the plant macronutrients (Ca, K, Mg, N and P) at different concentrations. In the case of tomato plants, all the macronutrients did not accumulate and stored at the same rate. Root uptake of P, Ca and Na was hindered where N and K uptake increased with an increase in As concentrations (Carbonell-arrachina et al., 1998).

XI. Arsenic-induced plant diseases

A range of arsenic-mediated physiological disorders has been reported in different studies, but little information has been found on assisted plant diseases, except straight head symptoms of rice (Rahman et al., 2008). Franese et al. observed physiogenic disease in water lettuce at a high arsenic concentration (Franese et al., 2014).

XII. Arsenic toxicity to microbiota

The microbial community has a salient role in any ecosystem. The presence or absence of microbial populations widely influences energy transport, nutrient cycling and environmental balance. Different studies have evinced the wider negative impact of As contamination on plants, animals and microbiota. Microbiome exposed to high arsenic toxicity may gradually develop their tolerance. Through the metabolic process, many fungi and bacteria detoxify and minimize arsenic within their cells by exporting arsenic molecules using an efflux pump ((Cullen and Reimer, 1989 and Cervantes et al., 1994). A range of bacteria and fungi resistant to arsenite and arsenate toxicity have been found in arsenic-polluted dip-site root zone soil in Australia. Mycorrhizal fungi genus Acaulospora, Gigaspora and five bacterial strains of Artrobacter, Ochrobactrum, Bacillus and Serrati showed arsenic species-specific tolerance. Endomycorrhizal fungi reduce toxicity and facilitate arsenic uptake by plants. Orchrobatrum sp. showed higher resistance to arsenate, whereas Bacillus and Serratia sp. exhibited higher tolerance to arsenite, but Arthrobacter sp. showed sensitivity to it (Chopra et al., 2007).

XIII. Arsenic toxicity amelioration

Arsenic is linked to various human diseases and environmental pollution as well. Considering the hazardous effects on humans and the environment, there is a burning need to find an appropriate remediation mechanism. Microbial amelioration of arsenic toxicity is mediated by various enzymes encoded by arsenic resistance genes. Some bacterial plasmids consist of arsenic-resistant genes that encode enzymes and activate an efflux pump, which regulates the outflow of arsenic from bacterial cells. Both gram(-ve) and gram(+ve) bacteria have ArsB and ArsC genes, whereas ArsA, a subunit of ATPase, is only found in gram(+vet) bacteria. Cytoplasmic ArsC reduces As(V) to arsenite, a substrate of ArsB and an activator of ArsA, which subside arsenate toxicity (Cervantes et al., 1994). Microbes are an important mediator of arsenic tolerance in the plant-soil system. Several mycorrhizal fungi and rhizosphere bacteria exhibit exceptional resistance to soil arsenate and facilitate the accumulation of arsenic by grass species without any negative impact but rather a positive influence on growth and development. Microbial association with plant species utilizes arsenic-toxic soil (Chopra et al., 2007).

Endophytic bacteria (EB) extracted from hyper-arsenic feeder plants displayed exceptional resistance and tolerance to arsenic pollution. EB found in *P. vittata* evinced more tolerance to arsenate [As(V)], and genera found in *P. multifida* demonstrated resistance to arsenite [As(III)] (Zhu et al., 2014). Their tolerance largely depended on reducing arsenate, oxidising arsenite and holding it in biomass. Endophytic bacteria having the ability to speciation and hold arsenic in plant systems are effectively utilised in microbial remediation of arsenic phytotoxicity. Inter-exchange of two arsenic species (arsenate to arsenite) and detoxification governed by the range of physicochemical and microbial processes. The conversion process is accelerated by pH and oxidation-reduction potential. In the soil system, both oxidizing and reducing microbes are present. Via dissimilatory reduction by microbial community, arsenate is reduced to arsenite, detoxified and pumped out, whereas in anaerobic respiration, arsenate functions as a terminal electron receptor (Bentley and Chasteen, 2002).

The elevated level of Arsenic presence in soil induces the superoxide dismutase (SOD) activities resulting in a decrease of chlorophyll and carotenoid concentrations in clover shoots. The combined application of Zn and Cd was found effective in decreasing the SOD activity and hindered the accumulation of antioxidative polyamines (Pas), and finally reduced the arsenic stress to the clover plant (Mascher et al., 2002). Polyphenol and proline assimilation, nitric oxides (NO), Potassium, salicylic acid and phosphate application in arsenic-rich soil proved useful to subside As-mediated stress in plants. Phosphate and potassium fertilizer effectively prohibited the plant uptake of As. Proline and salicylic acid disrupt plant assimilation of As by activating enzymes and finally mitigate As phytotoxicity (Chandrakar, et al., 2016). Elevated arsenic application in soybean (*Glycine max* L) produces significantly hampered oxidative stress and growth properties. The combined application of As with proline, diphenyleneiodonium (DPI), and 24-epibrassinolide has successfully restricted arsenic accumulation and subsided the oxidative stress (Chandrakar et al., 2018).

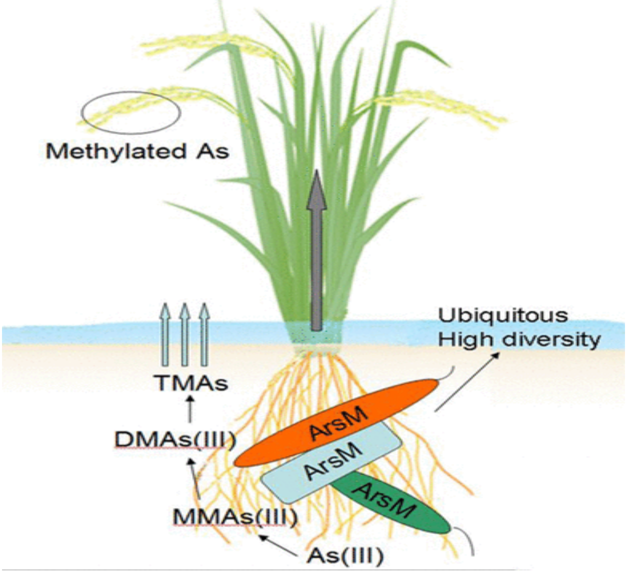

Figure 05. Microbes encoded genes (ArsM) available in rice rhizosphere responsible for methylation and detoxification of inorganic As species (Jia et al., 2013).

Phosphatic fertilizer can ameliorate oxidative stress in the plant. The pot cultivation of fenugreek (*Trigonella foenum-graecum L*. cv. Azad) conforms arsenic tolerance to a certain level (20 mgk^{-1}). But, in 30 mgk^{-1} soil applications, arsenic produces oxidative stress on the plant, which was successfully amended using phosphate (P) fertilizer. P fertilizer can successfully ameliorate arsenic-induced oxidative stress by hindering H_2O_2 production and increasing enzyme activity (Talukdar, 2013).

Aromatic Arsenicals (AAs) were once used as a blistering agent. Methylphenylarsinic acid (MPAA), a highly prevalent species in soybean and paddy, is one of the important family members of AAs. Considering the risk of organic pollutants, remediation is a burning need. AC (Activated charcoal) has proved to be an effective immobilizer of organic soil pollutants. Soil amended with 0.2% AC successfully minimised the grain MPAA concentration. Consecutive AC application in years one and two has effectively reduced the grain MPAA concentration by 3% and 15%, respectively. Soil treated with 0.2% AC was reported to have accelerated (44%) reduction of MPAA in soybean seed (Arao et al., 2011). Rice soils irrigated with groundwater are naturally high in iron content, fostering plaque formation in rice roots that help to sequestrate arsenic and prohibit uptake (Awasthi et al., 2017).

Rice paddy is a predominant source of iAs. Different investigation suggests methylated species are comparatively safer, especially pentavalent methylated species, which is found in grain at a certain level. However, there is no evidence of whether rice plants can methylate inorganic As. Axenic rice cultivation unveiled the fact- that methylation only happened outside the plant. Grain obtained from axenic culture found no methylated species, whereas organic species were prevalent in soil-cultured rice (Lomax et al., 2012 & Bentley and Chasteen, 2002). Hence, the microbial community proved to be responsible for methylation. A study reported that arsenic-methylating prokaryotic bacteria are phylogenetically diverse in rice rhizospheric soil. Prokaryotic soil bacterium encoded genes: arsenite S-adenosyl methionine methyltransferase (ArsM) responsible for methylation of inorganic As, especially arsenite [As(III)], was present in a high concentration at the rice rhizosphere. With rice straw containing the ArsM gene, soil ArsM concentration also increases and fosters the speciation process. Due to the presence of the ArsM gene, irrigated rice was found to have a higher level of methylated species (Figure 05) (Jia et al., 2013). Microbial amelioration of arsenic can be a safer, cheaper and handy option for mitigating arsenic pollution and reducing oxidative stress on plants and microbiota.

XIV. Conclusion

Over several centuries, much research has been conducted on arsenic, the potent toxicant. This essay has reviewed the information regarding arsenic pollution and its impact on the agriculture sector, ecosystem services and probable mitigation approach. Crop yield and phytotoxicity varied depending on culture conditions, species and crop varieties. Inorganic As species reported much toxicity to crops and humans. Most of the research has been conducted either in-vitro or axenically, which may differ with field conditions. Ecosystem services like soil and water quality and nutrient cycling are greatly affected. An intensive study is needed on how As interacts and impacts the total ecosystem. Agronomic practices and microbial remediation have proved effective. Further research must investigate the microbiome and the development of field-oriented and handy methods.

Declaration

This review has been carried out as part of the partial fulfilment of course and had no personal benefits or any financial interest that could bias the work reported in this review.

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