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Mitigation of arsenic toxicity in rice grain through the soil-water-plant continuum

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Abstract: Increased levels of the non-essential hazardous metalloid arsenic (As) in rice grains pose a threat to human health and the sustainability of the rice industry. In several counties, the average As contamination in polished rice has been detected to range from 0.002 to 0.39 mg/kg, which is above the safe limit of 1 mg/kg as recommended by the World Health Organisation. Beyond this limit, the digestive tract, circulatory system, skin, liver, kidney, nervous system and heart can be affected. Humans can develop cancer from consuming or inhaling As. In addition, long-term exposure to drinking water contaminated with arsenic has also been linked to a dose-response relationship with an increased risk of hypertension and diabetes mellitus. Rice has been shown to be an indirect source of arsenic accumulation in human bodies. Under flooded paddy soil, trivalent arsenate (As^{III}) occupies 87–94% of the total As, while under non-flooded soil, pentavalent arsenate (As^{V}) predominates (73–96% of the total As). This review aims to provide a thorough and interdisciplinary understanding of the behaviour of As in the paddy soil and transportation to rice grain and further investigate efficient ways to limit arsenic contamination. Supplementation of soil with specific mineral nutrients such as iron (Fe), sulphur (S) and silicon (Si) can significantly decrease the arsenic accumulation in rice grain by minimising its uptake and translocation. The hydrogen bonding potentials of uronic acids, proteins and amino sugars on the extracellular surface of soil microorganisms facilitate the detoxification of arsenic species. Further, rice is absorbed less when exposed to aerobic water management practices than anaerobic ones since it reduces the build-up of As in rice, and the solution is immobilised as in the soil.

Keywords: sustainable; paddy field; pollution; carcinogen

Millions of people across the globe are facing the potential threat of arsenic (As) contamination through groundwater-soil-crop systems, especially in rice agroecosystems (Wang et al. 2015). With a daily average intake of 0.5 kg per person, rice substantially threatens human health, especially in South and South East Asian countries, where it is the staple crop for approximately half of the world's population. Due to agricultural practices and groundwater contamination, rice is more susceptible to arsenic uptake than

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other crops like wheat and maize. Over 75% of the world's 93 million hectares of rice fields are irrigated with constant floods (Rao et al. 2017). Increased levels of the non-essential hazardous metalloid arsenic in rice grains pose a threat to human health and the sustainability of the rice industry. According to IARC (2004) and Bhattacharya et al. (2020), it is classified as a Group 1 carcinogen. There are two types of As present in rice: inorganic and organic species. Groundwater contamination by arsenic is a major new issue. Approximately 200 million people in 70 nations are severely affected by this metalloid. Srivastava et al. (2016) found that the degree of As pollution was greatest in Southeast Asia, particularly in Bangladesh and some states of India (Table 1). Arsenic levels in paddy soils and plants are quite

Table 1. Arsenic (As) content (including speciation) in raw and polished rice by country of origin

Sl. No.	Country	Rice cultivar	Organic As (mg/kg)	Inorganic As (As^{III} + As^{V}) (mg/kg)	Total As in raw rice (mg/kg)	Reference
1	Bangladesh	Chinigura	0.01	0.01	0.03	Williams et al. (2005)
		Kataribogh	0.01	0.04	0.06	
		Parija	0.01	0.03	0.07	
		Bashphool	< LOD	0.05	0.09	
		Nazirshai	0.02	0.06	0.09	
		BRRI DHAN 28	0.01	0.10	0.15	
		Zami	0.02	0.09	0.17	
		Miniket	0.04	0.19	0.22	
		Nazirshail	0.01	0.09	0.14	
		Bangladeshi Rice	0.005	0.39	0.39	Ohno et al. (2007)
2	India	Market basket	–	0.03	0.07	Meharg et al. (2009)
		Red Rice	0.01	0.05	0.06	Halder et al. (2014)
		Household	–	–	0.13	
		Parijat	–	–	0.25	Mandal et al. (2019)
		Ratna	–	–	0.03	
		Pratik	–	–	0.19	
		Satabdi	–	–	0.15	
		Atab rice	–	–	0.002	
		Ranjit	–	–	0.26	
		Swarna	–	–	0.36	Signes et al. (2008)
		Boiled rice	–	–	0.004	
3	Italy	Risotto	0.08	0.14	0.22	Williams et al. (2005)
4	China		0.05	0.16	0.22	Zhu et al. (2008)
5	Thailand	Jasmine	0.03	0.08	0.11	Williams et al. (2005)
6	Spain	paella	0.05	0.08	0.13	Williams et al. (2005)
7	Taiwan	White rice	0.014	0.07	0.12	Chen et al. (2016)
		Brown rice	0.012	0.11	0.22	
8	Europe	–	0.04	0.08	0.15	Ohno et al. (2007)
9	Brazil	White Rice	0.10	0.11	0.22	Batista et al. (2011)
		Parboiled White Rice	0.075	0.13	0.21	
		Brown Rice	0.14	0.19	0.35	
		Parboiled Brown Rice	0.088	0.17	0.26	
10	Canada	–	0.01	0.08	0.11	Heitkemper et al. (2001)

LOD – limit of detection

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high due to the continuous monoculture irrigated with arsenic-filled groundwater. Hence, pernicious consequences on human health are obvious across rice growing belts in the region due to arsenic poisoning in irrigation water, which is then transported to the food chain *via* rice consumption (Singh and Singh 2020). Many Indian states, such as Assam, West Bengal, Uttar Pradesh, Jharkhand, Bihar, Haryana, Punjab, Andhra Pradesh, Chhattisgarh, etc., have been found to have arsenic contamination (Shukla et al. 2020). It is considered that the Himalayas and the Shillong Plateau are the primary sources of arsenic contamination in the Gangetic River basin and delta sediments. In addition, the Gondwana coal region in the Rajmahal basin of eastern India, the Bihar mica belt of eastern India, the pyrite-bearing region in the Vindhya Range of central India, the Son River Valley gold belt of the eastern area, and the sulphides regions of the eastern Himalayas have all been proposed as possible sources of arsenic. Mishra et al. (2016) revealed concerning data regarding the groundwater As load in the Indo-Gangetic plains, encompassing 14 out of 22 districts in Haryana and 3 out of 33 districts in Punjab districts of Rajasthan, one of Delhi's eleven districts, 25 of Uttar Pradesh's 75 districts, two of Chhattisgarh's 27 districts, 22 of 38 districts of Bihar, 3 of 24 districts of Jharkhand, and most importantly 14 of the 19 districts in West Bengal overall where the total As level significantly exceeded the WHO permissible limit of 10 μg/L. The European Union recommends that soil suitable for agricultural use should have a total arsenic content of less than 20 000 μg/kg (Shrivastava et al. 2017). The research conducted in the Indian states of Uttar Pradesh and Balia showed that agricultural soils contained an excessive level of As ranging from 5 400 to 15 430 μg/kg (Srivastava and Sharma 2013). In addition, according to WHO (World Health Organisation 1989) recommendations, rice grain can have up to 1 mg/kg of As. Beyond this safe limit, the digestive tract, circulatory system, skin, liver, kidney, nervous system, and heart can be affected. Humans can develop cancer from consuming or inhaling As. In addition, long-term exposure to drinking water contaminated with arsenic has also been linked to a dose-response relationship with an increased risk of hypertension and diabetes mellitus. There is no doubt that the As accumulation in rice grains and their subsequent transmission throughout the food chain has made people increasingly reliant on rice and rice-based goods. Therefore, it is desirable to investigate efficient ways to limit arsenic contamination in rice plants to ensure food safety and a healthy environment. Adopting adequate intervention(s) that are technologically practical, economically possible, and acceptable to poor and needy farmers is necessary to reduce arsenic contamination in the food chain *via* the water-soil-plant route.

Status of arsenic contamination in India

Seventeen Indian states and one union territory have been found to have As concentrations above the BIS (2012) threshold of 50 ppb (Figure 1). Almost 25.46 million people, or about 19% of India's population, are in danger of As poisoning. Recent Lok Sabha reports have shown that over 65% of the population of Assam, 60% of the population of Bihar, and 44% of the population of West Bengal are at severe risk of As poisoning (Jadhav 2017). There are two main types of topography in India, both of which contribute to the presence of As in groundwater: the alluvial terrains of West Bengal, Uttar Pradesh, Bihar, Jharkhand, Assam, Manipur, Punjab, and Haryana, and the hard-rock terrains of Karnataka and Chhattisgarh. Rajasthan, Andhra Pradesh, Telangana, Tamil Nadu, and Gujarat

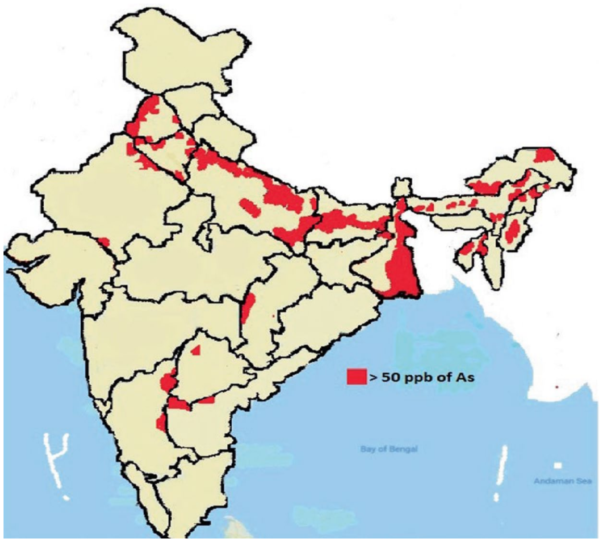

Figure 1. Indian states with groundwater or surface water are affected by arsenic (As) contamination above 50 μg/L. Sixteen states have an As level above the BIS permissible limit. (1) Punjab; (2) Haryana; (3) Rajasthan; (4) Uttar Pradesh; (5) Chhattisgarh; (6) Telangana; (7) Karnataka; (8) Andhra Pradesh; (9) Bihar; (10) Jharkhand; (11) West Bengal; (12) Assam; (13) Arunachal Pradesh; (14) Nagaland; (15) Manipur; (16) Tripura

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are regions where As pollution has been documented in recent years (Bhattarcharya and Lodh 2018).

Arsenic levels above 50 parts per billion were initially observed in 2004 in Karimganj, Dhemaji, and Dhubri districts in Assam (IMGAM 2015). Approximately 2 571 homes are badly affected by the high As levels in 18 out of the 23 districts (Bhattacharya and Lodh 2018). The districts having more than 50 ppb As are Nagaon (48.1–112 ppb), Jorhat (195–657 ppb), Lakhimpur (50–550 ppb), Nalbari (100–422 ppb), Golaghat (100–200 ppb), Dhubri (100–200 ppb), Darrang (200 ppb), Barpeta (100–200 ppb), Dhemaji (100–200 ppb), Cachar (50–350 ppb), and Karimganj (293 ppb) (Bhattacharya et al. 2015). The low-lying parts of the Barak Valley, which are made up of Holocene sediments, may be to blame for the contamination of south Assam. The tertiary Barail hill range and the area's aquifers are the primary sources of groundwater pollution. Holocene deposits form active aquifers in other Assam regions located along the Brahmaputra basin. The adsorbed arsenic in these aquifers is released through the reductive breakdown of the present Fe hydroxides.

Arsenic's behaviour in the soil in paddy fields

Regarding soil natural risk assessment and contamination control, arsenic is regarded as the primary cause for concern within the soil biological system. Numerous authors declared that As had been widely defiled in paddy soil. The weathering of rocks and alluvial deposits is responsible for the regular sources of arsenic in paddy fields. The persistent As-bearing minerals claudetite (As_2O_3), bearsite ($Be_2(AsO_4{\cdot}OH{\cdot}8H_2O)$), and wallisite [(Cu, Ag) $TlPbAs_2S_5$] are the sources of arsenic in paddy soil. In a similar vein, the dissolution of minerals or changes in surrounding conditions releases arsenic into the soil. Arsenic associated with the redox-delicate and bioavailable division is efficiently administered. Arsenic poisoning in the floodplain paddy field is explained by the stable alluvial statement and the transfer of silt by waterway streams. The development of rice is contaminated by As due to pesticides, composts, groundwater rich in As, and mining activities (Liu et al. 2005). The climate in the soil can be found in both natural and inorganic constructions. The two most common natural forms of As are dimethylarsinic corrosive (DMA^V) and monomethylarsonic corrosive (MMA^V), whereas the inorganic forms found in soil are As^V and As^{III}. The poisonousness of As given by Baig et al. (2010) as follows in the accompanying sequence: As^{III} > As^V > MMA > DMA. Through the biomethylation process in soil, inorganic forms of As can be transformed into their natural structure (Jia et al. 2013). Regarding the particular circumstance of the plants' bioavailability, the following species can be distinguished as As^V < MMA < As^{III} < DMA (Marin et al. 1992). Although rice roots are capable of assimilating all forms of arsenic, the rate at which inorganic forms of As are absorbed is significantly higher than that of natural structures (Abedin et al. 2002a, b). While As^{III} and methylated-As species are captivated by aquaporin channels, As^V is transported by roots through phosphate transport channels. In paddy soil that has been flooded, As^{III} occupies 87–94% of the total As, while under non-flooded soil, As^V predominates (73–96% of the total As) (Das et al. 2016). Natural carbon content, pH, oxide-mineral content and earth content are examples of soil chemical qualities that significantly impact the biological system's bioavailability, harmfulness, and solvency (Romero-Freire et al. 2014, Ding et al. 2015). Zhang et al. (2020) observed that the As bioavailability in soil was affected by all of the soil parameters, including dirt, AlOx, FeOx, effective cation exchange capacity (eCEC), pH, and organic carbon (OC). Due to agronomic techniques and rhizospheric conditions contributing to As uptake and accumulation in rice grains, rice development is substantially less resistant to arsenic tainting (Yuan et al. 2021). Pentavalent arsenate (As^V) and trivalent arsenate (As^{III}) are the two inorganic arsenic forms accessible in soil pore water. The two most prominent naturally occurring forms of arsenic detected in paddy soil pore water are DMA^V and MMA^V. When paddy soil overflows, the amount of As that can be adsorbed on the available Fe oxide surface increases. According to Takahashi et al. (2004), flooded soil reduces Fe oxide levels. This is followed by a breakdown in the presence of microorganisms that reduce Fe levels and help absorb As into soil pore water. The accessibility of arsenic in soil pore water is positively correlated with iron and arsenic, a relationship known as the "coupling of Fe and As" (Weber et al. 2010). In both normal soil and residue, Arsic et al. (2018) monitored areas of strength for lowering correspondingly with Mn correspondingly. However, Yuan et al. (2021) observed a decoupling of As and Mn in topsoil and hypothesised that this could be due to the high concentration of Fe in the soil and the oxidation of As^{III} by Mn crystals.

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They also mentioned three important processes that regulate the activation of As from the Fe-oxide surface: (a) the distribution of adsorbed As between the fluid and strong stages and the subsequent desorption; (b) the reduction of $Fe^{(II)}$ to $Fe^{(III)}$; and (c) the reduction of As^V on the Fe oxide-As complex to As^{III}. This immobilisation cycle is initiated by inorganic As trading ligand with OH_2 and in coordination with Fe species. The accompanying condition shows the impact of Fe on the As species' mobility in soil. Fe-oxide structure also affects the process of immobilisation. Additionally, Tufano and Fendorf (2008) showed that Fe oxide can hold onto more As, which is bio-degrade by bacteria that reduce Fe. According to Khan et al. (2010), even dirt has a lot of Fe. If the dirt has formed compounds with iron oxide, it can reduce the amount of As activation. As can be seen in the subsequent response, manganese oxide minerals found in paddy soil function as electron acceptors by oxidising $As^{(III)}$ to $As^{(V)}$ and then adsorbing $As^{(V)}$. Paddy soil that has been flooded reduces the redox potential in the soil's arrangement, which results in the reduction of sulphate (SO_4^{2-}) in sulfate-bearing minerals into sulphide (S^{2-}). As a result of the sulphate cycle's acceleration of As^{III} as arsenic sulphide, less As is formed (Burton et al. 2014). Similarly, As^{III} can react with the sulphide to generate thioarsenite, which accelerates in an overflowing state as AsS or As_2S_3. Phosphate (PO_4^{3-}) competes with As^V for adsorption on the soil mineral surface thus $As^{(V)}$ desorbs. As^{III} is desirable at the adsorption site by the relatively silicic corrosive $Si(OH)_4$, which also makes it available in soil water (Kumarathilaka et al. 2018a,b). As^{III} and $Si(OH)_4$ actually employ the same carrier in rice plants, as demonstrated by Li et al. (2009a,b), which lowers As^{III} uptake in rice. Elevated soil pH seems to favour As accessibility in soil composition. Adsorption sites of As experience a negative charge in an acid soil, which aids in the desorption of As^V and As^{III}. A consistent redox gradient is established between surface water that is rich in oxygen and the subsurface soil in the flooded rhizosphere of rice. The availability of organic matter, which completely regulates the spatial dispersion of redox-sensitive components like As, also causes the soil to decrease in this situation (Arsic et al. 2018). In the rhizosphere, reductive preparation of arsenic in conjunction with other metals, including Fe, Mn, and P, has a negative link with redox potential of the soil-water climate (Yuan et al. 2021). The insoluble combination that organic matter in the soil forms with As reduces the mineral's bioavailability. High levels of organic matter accumulated in paddy soil might, in fact, enhance the biological reduction of Fe oxide, which can assemble the As. As bioavailability can be increased by adsorbing broken-down natural carbon with As^{III} and As^V on the adsorption site of Fe oxide. As-bearing minerals such as bearsite ($Be_2(AsO_4)(OH)·8H_2O$), claudetite (As_2O_3), and wallisite (Cu, Ag)$TlPbAs_2S_5$) are responsible for the geogenic source of As in paddy soil. Because arsenic remains linked to the bioavailable and redox-sensitive stages of the soil, it is effectively accessible in soil water. As a result, the majority of the Fe-oxide is linked to earth minerals. Even though surface runoff during precipitation may remove the majority of the mud minerals in paddy soil, furrowing is a method that might negatively impact the construction of dirt during paddy development. As a result, paddy soil can no longer immobilise As. Like the soil water framework, root plaque in the rhizosphere of paddy growth regulates mobility and bioavailability. Under flooded conditions, the radial oxygen loss mechanism releases oxygen from the root aerenchyma and promotes the formation of Fe plaque. Minerals such as goethite, lepidocrocite, and hydrite are commonly found in Fe plaque, limiting As's mobility by sequestration. Further in-depth research is required to fully understand the geogenic or regular source of arsenic in paddy soil. Basically, very little research has been done on the role that sulphide plays in arsenic activation in paddy soil. A small number of nanoparticles, particularly nanominerals, alter the geochemistry and soil-metal complex science to affect the fate of metals in soil. Future research should take into account how nanoparticles affect the bioavailability of As in paddy soil. The behaviour is similar to paddy fields; the soil is said to be influenced by several unique soil characteristics, which makes the entire process extremely complex and needs to be attended to. The most important test in determining how the soil would behave in such a multifactorial cooperation model is the identification of a certain ingredient.

Pathways of arsenic contamination in rice

The most common and hazardous inorganic forms of arsenic are arsenate [$As^{(V)}$] and arsenite [$As^{(III)}$], both of which are found naturally in the environment. As^{III} accounts for 63% of total arsenic in soil in flooded paddy fields followed by As^V at 36% and methylated

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arsenic species. Specific transporter proteins allow all of these arsenic types to enter plant cells.

Uptake and transport of inorganic arsenic species

There are two pathways *via* which arsenic from inorganic species is taken in by rice roots. $As^{(V)}$ is taken up by plants from the soil solution by means of a high-affinity phosphate transporter (PT). There is a total of 13 OsPT genes (OsPT1–OsPT13) in the rice genome that codes for different phosphate transporters. Whereas OsPT8 is a crucial arsenate transporter protein in rice roots, and arsenate absorption mediated by OsPT8 exerted a significant detrimental effect on root elongation. Aquaporin channels are the second mechanism through which As^{III} is absorbed by root cells. Mitra et al. (2017) found that Lsi2, a silicon efflux transporter, mediates As^{III} efflux to the xylem in rice plants. Lsi1, a nodulin 26-like intrinsic protein (OsNIP2;1), is the primary influx transporter for silicic acid into rice root cells. The Lsi1 protein channel has a bidirectional function, so after root cells take up As^{III}, some of it is immediately released into the rhizosphere. Since rice cannot perform this methylation itself, any arsenic methylated by microorganisms in the rhizosphere must have originated there. Proteins' structural integrity and/or catalytic activity may be altered by $As^{(III)}$ binding to sulfhydryl groups.

Uptake and transport of organic arsenic species

Microbial transformation of inorganic species to organic form yields significant quantities of methylated arsenic species dimethylarsinic acid and fewer amounts of monomethylarsonic acid in the paddy soil, where As^{III} is the dominating species; thus, methylated arsenic species are produced as a result of this organic reaction. Methylated species' absorption mechanisms have been explored far less than those of inorganic arsenic species. The nodulin 26-like intrinsic protein is responsible for both MMA and DMA uptake. Figure 2 shows that inorganic arsenic species (As^{III} and As^{V}) are taken up by roots more efficiently than methylated arsenic species (DMA and MMA); their translocation rate in plant shoots is substantially lower. One possible explanation for the enhanced translocation of methylated-arsenic species is the decreased complex formation of these species with the ligands (glutathione/phytochelatin). Bioaccumulation of As in rice follows the order of roots > shoots > leaves, roots > leaves > shoots and roots > leaves > shoots > husks > grains at 40, 80 and 120 days after transplanting, respectively (Chou et al. 2014).

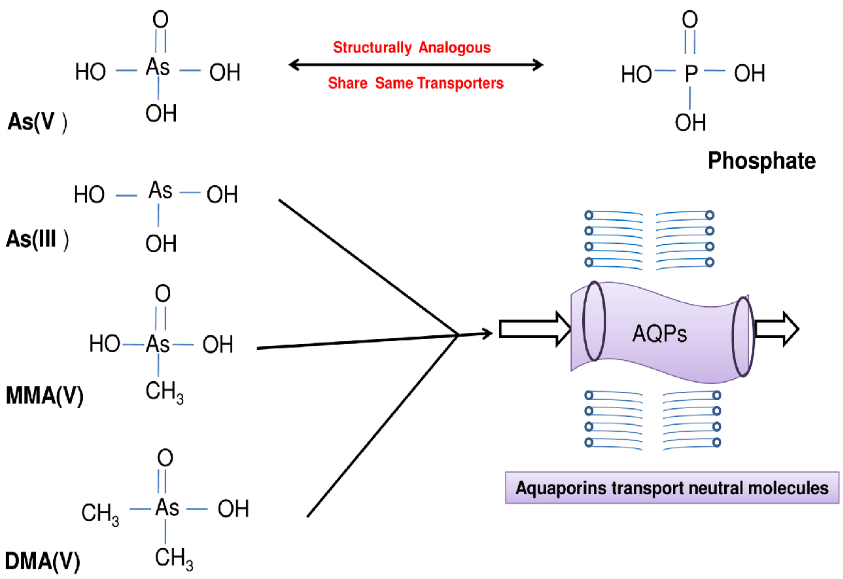

Figure 2. A diagrammatic presentation of different inorganic and organic arsenic (As) species in the environment. The uptake and transport of arsenate $[As^{(V)}]$ occurs through phosphate transporters due to structural analogy, while that of arsenite $[As^{(III)}]$, monomethylarsonic acid $[MMA^{(V)}]$ and dimethylarsinic acid $[DMA^{(V)}]$ *via* aquaglyceroporins (AQPs) transporting neutral molecules

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Loading of arsenic into rice grain

The extent to which As permeates into the endosperm of a rice grain impacts the efficacy of As removal by polishing and, hence, human exposure to As *via* rice. The sub-aleurone layer is another possible source of arsenic that is difficult to eradicate with polishing. Interactions between As and sulphur further complicate arsenic speciation in rice grain. Sulphur is contained in rice grain at quite high amounts (0.1%), predominantly as glutathione among the S-rich amino acids methionine and cysteine and their derivatives. Because of its strong attraction to thiols, arsenite readily combines with glutathione to form stable complexes. As a result, as illustrated in Figure 3 (left) by purple tones in the bicolour plots, the $As^{(III)}$ is highly localised to the bran and OVT (ovular vascular trace) (arrow). Reduced arsenic transfer into rice grains is facilitated by the presence of a tonoplast transporter (OsABCC1) in phloem companion cells, which increases arsenic storage in vacuoles. Seed setting rate, spikelet sterility, and yield reductions may be caused by methylated arsenic species, particularly DMA, which is mobilised at a higher rate than inorganic species and whose redemption in aleurone, endosperm, and embryo permeates into the endosperm and is notably low near the OVT (arrow) (Figure 3 right). The amount of arsenic in rice grain varies from one cultivar to another.

Risk of arsenic from rice diet to human health

Human genotoxicity can be triggered by eating 500 g of cooked rice daily if it contains arsenic at or above 200 mg/kg. Arsenic is absorbed into the bloodstream and undergoes speciation in the intestines (Bastias and Beldarrain 2016). Biotransformations such as oxidation, reduction, methylation, and thiolation occur in the digestive system when arsenic is ingested. When compared to the intestine, arsenic is more bioavailable in the stomach due to its acidic pH (Alava et al. 2015). The thiol-containing amino acid in rice seed endosperm is a preferred binding site for inorganic arsenic species.

Strategies to mitigate arsenic toxicity

Aerating the soil through water management to prevent arsenic reduction, creating conditions that promote the formation and precipitation of insoluble arsenic in soil, and reducing arsenic uptake and translocation in rice plants by increasing mineral nutrients in the soil that compete with arsenic absorption are all viable agronomic methods for mitigating the negative effects of arsenic accumulation in rice. Arsenic in plants is a health danger, but mitigating strategies may help reduce it. Some of the effective strategies are as follows:

1. Fertilisation of soil with minerals;
2. Water management and irrigation practices;
3. Bioremediation strategy;
4. Seed priming.

Fertilisation of soil with minerals

Supplementing soil with specific mineral nutrients like Fe, S, and Si can significantly decrease the arsenic accumulation in edible plant parts by minimising its uptake and translocation in food crops (Bakhat et al. 2017).

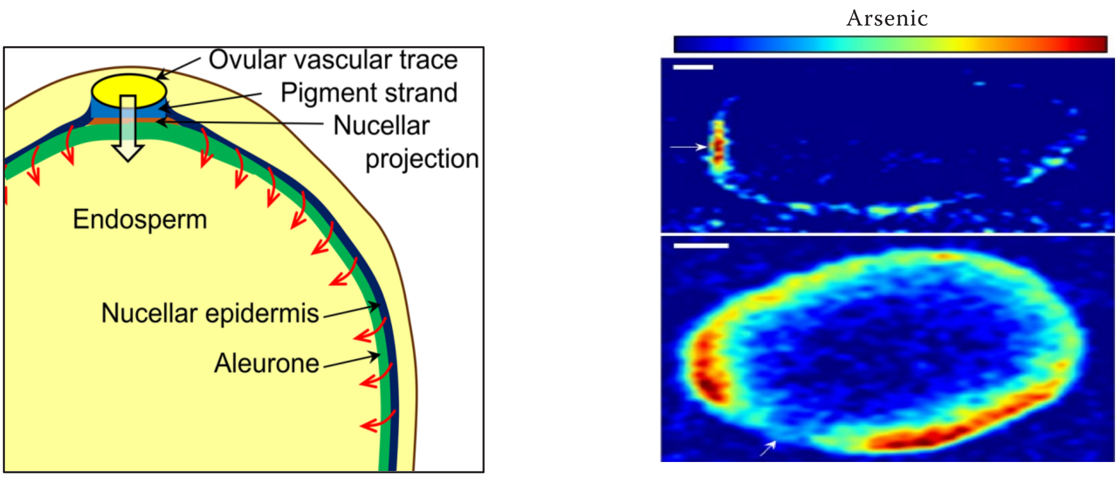

Figure 3. Pathways of arsenic loading into a developing rice grain (left) and distribution of arsenic in rice grain (right)

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Role of iron in alleviating arsenic toxicity

Fe is a crucial plant mineral supplement to reduce arsenic absorption in rice. Rice, unlike many plants native to wetter environments, contains a large number of air-filled cells (aerenchyma) in its root system. This aerenchyma transports oxygen from the shoots to the roots, where it is used for respiration. Because of the lack of oxygen in wet soil, rice plants release part of oxygen through their aerenchyma into the rhizosphere. This phenomenon, known as radial oxygen loss, is sensitive to waterlogging and/or soil O_2 availability (Figure 4), and it varies from genotype to genotype. The release of oxygen causes ferrous iron to become ferric iron, which in turn causes a precipitate of iron oxides/hydroxides to form on the root surface. This orange material, made of iron, is known as a plaque. Iron plaque contains more As than roots and is a primary sink of As because Fe oxides and hydroxides are strong sorbents for As. Consequently, the concentration of Fe oxides in the rhizosphere decreases arsenic uptake in rice plants (Awasthi et al. 2017). This is because Fe-plaque has a high affinity towards As^V and is able to sequester the arsenic, thereby decreasing the translocation of arsenic from roots to shoots.

Role of sulphur in alleviating iron toxicity

Sulphur is a vital nutrient for plant development, and it also prevents arsenic from being taken up by and translocated throughout the plant (Figure 5). Sulphur application greatly diminishes rice arsenic buildup, with three possible causes. The arsenic content in soil is lowered because (1) sulphur causes Fe plaques to grow on the surface of roots and in the rhizosphere; (2) sulphate (SO_4) may improve the desorption of arsenate (As^V) from Fe-plaques, and (3) the transport site for arsenic is the cell membrane. In the same way, phosphate competes with arsenate for transport and metabolism, and SO_4 can limit arsenate transport into cells. Plants' ability to detoxify arsenic through sulphate metabolism is crucial to their survival in arsenic-contaminated soil. Arsenic is removed from the plant body by binding to the sulfhydryl groups of glutathione (GSH) and polychelatin (PC) and then transported to vacuoles. Mobility is significantly influenced by As-thiol complexation, which inhibits either As translocation from root to shoot or arsenic efflux from root to growth media. SO_4 has a considerable affinity towards arsenic under reducing circumstances, leading to its precipitation as insoluble arsenic-sulphide (Mitra et al. 2017); therefore, its application in paddy soils has an additional benefit to mitigate As toxicity.

Role of silica in mitigating arsenic

Rice and other tropical grasses benefit significantly from adding silicon. Only mono silicic acid, one of several soluble Si forms found in soil, is used by plants. By increasing the number of spikelets per

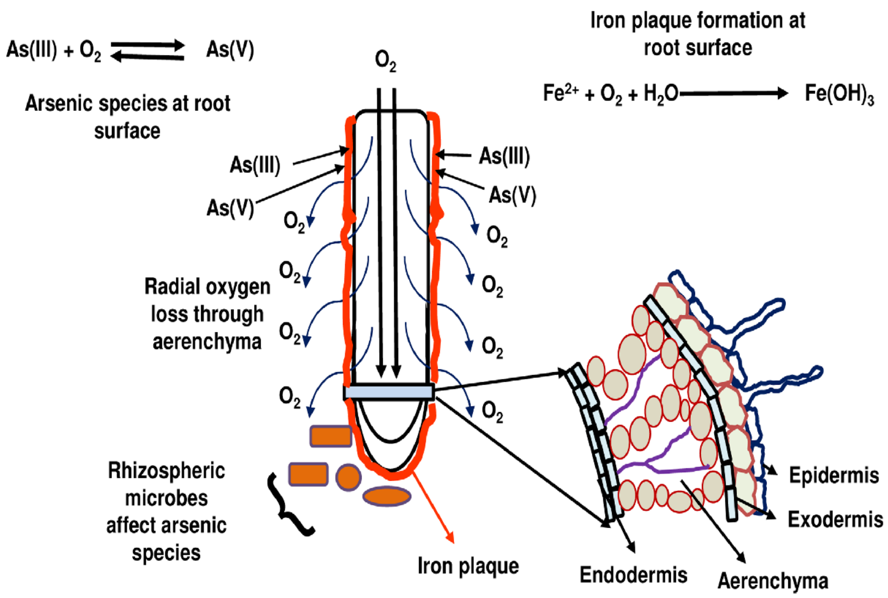

Figure 4. The influence of radial oxygen loss and iron plaque formation on rice root surface on arsenic species availability to rice and consequently arsenic uptake by roots

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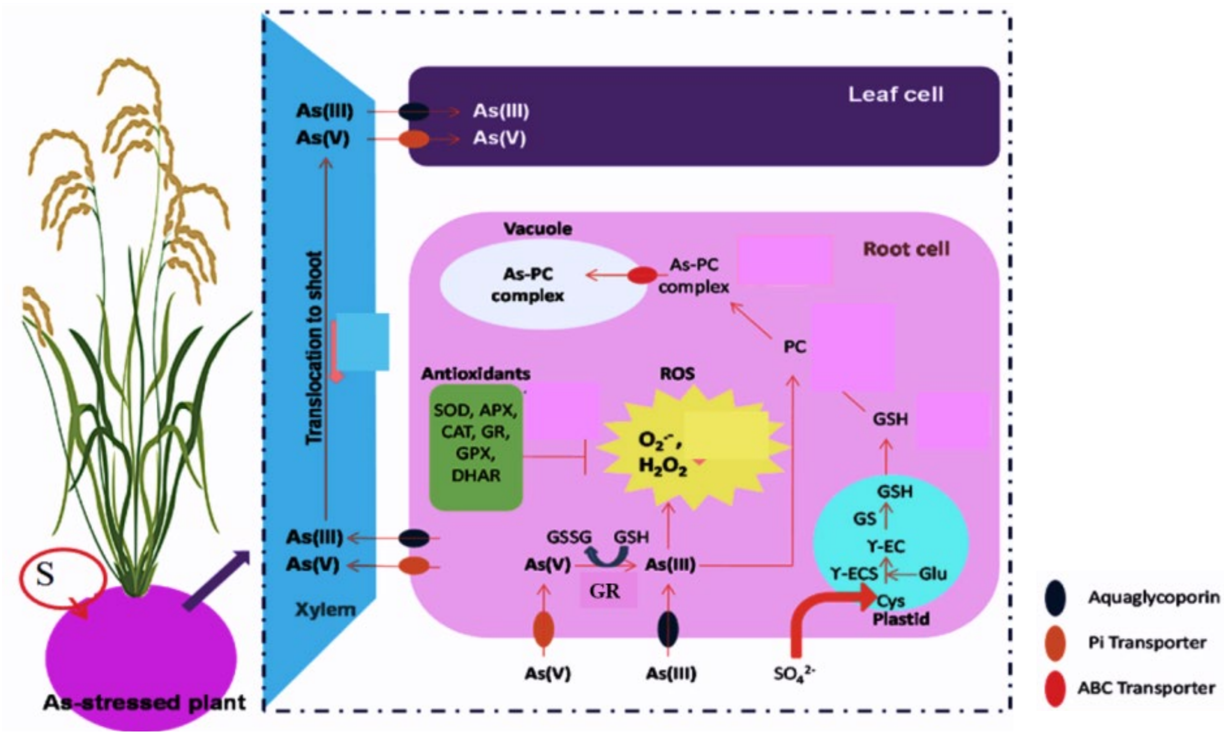

Figure 5. Sulphur-mediated amelioration of arsenic-induced reactive oxygen species (ROS) damage and promotion of vacuolar sequestration of As. As-PC – arsenic polychelatin; SOD – superoxide dismutase; CAT – catalase; GSH – glutathione; ɣ-EC – ɣ-glutamylcysteine; PC – polychelatin; H_2O_2 – hydrogen peroxide; GPX – glutathione peroxidase; GR – glutathione reductase; APX – ascorbate peroxidase; DHAR – dehydroascorbate reductase; glu – glutathione; O_2^- – superoxide radicals; GSSG – oxidised glutathione disulfide; Cys plastid – cytoplasmic plastid; GR – glutathione reductase

panicle and, more importantly, the percentage of filled spikelets, Si supplementation increases crop production. Si supplementation causes modifications to rice's primary metabolism and promotes amino acid remobilisation. The same transporter responsible for the uptake and translocation of Si is also responsible for arsenite uptake. Rice is less likely to absorb arsenite from the soil when there is a significant concentration of silicon there. Si treatments in rice led to a reduction in soil arsenic levels (Mitra et al. 2017).

Bioremediation with soil microorganisms

Microorganisms in the soil regulate mineral concentrations through processes like mineralisation and immobilisation, which in turn affect arsenic's environmental fate and movement. The hydrogen bonding potentials of uronic acids, proteins, and amino sugars on the extracellular surface of soil microorganisms facilitate the detoxification of arsenic species. The development of amorphous Fe hydroxides on the cell surface through creating inner-sphere complexes is another pathway of arsenic detoxification in soil microorganisms. By reducing the mRNA expression of OsLsi1 and OsLsi2, the mediators of As^{III} transport, arbuscular mycorrhizal fungi (AMF) perform a protective function in arsenic translocation (Figure 6).

Water management and irrigation practices

One of the most effective methods of reducing arsenic's bioavailability in the soil-plant system is improved water management in paddy fields. The conversion of As^V to As^{III}, the deadliest arsenic species, with significantly higher solubility, plant availability, and toxicity, is hindered by the oxidising situation brought forth by water management efforts. Arsenic's affinity for soil minerals increases in oxygenated or oxidised soil, and Fe is oxidised, leading to the production of Fe plaques surrounding the root surface'. The

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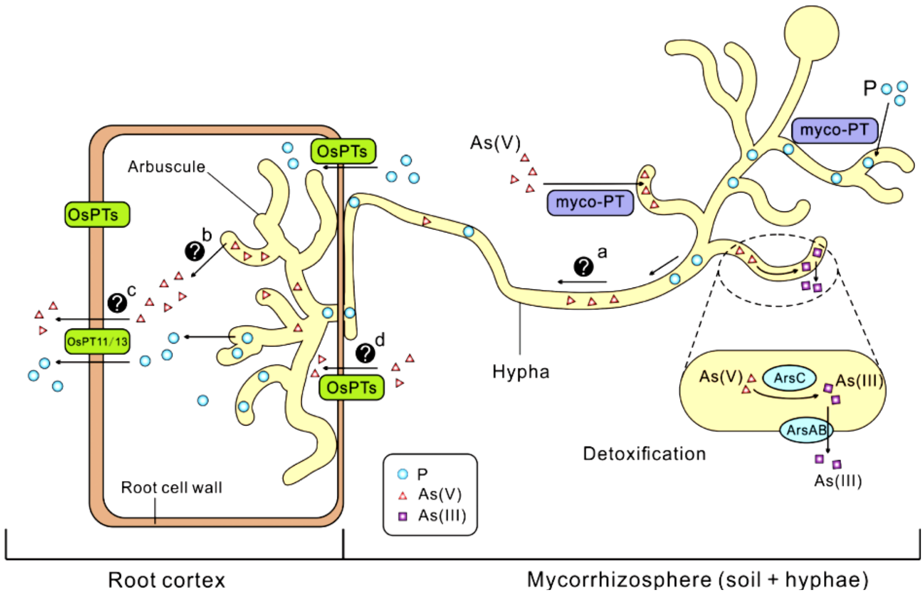

Figure 6. Schematic diagram of rice root-arbuscular mycorrhizal fungi (AMF) interaction in influencing the uptake and transportation of arsenic and phosphorus. The possibility and efficiency of $As^{(V)}$ migration within hyphae remains unclear (question mark a). If As^{V} migration within hyphae is possible, releasing As^{V} in fungus-containing cells through arbuscules of AMF merits further investigation (question mark b). Furthermore, the questions on whether OsPTs (e.g. OsPT1) can mediate As^{V} uptake from soil or apoplastic space into the cytosol and how other OsPTs mediate As^{V} migration (how efficient) from cell to cell need to be answered (question marks c and d). P – phosphorous; OsPTs – rice P transporters; myco-PT – mycorrhizal PTs; ars A, arsB, arsC – arsenic resistance genes. (source: adapted from Li et al. (2022))

net result is less accessible arsenic for plant uptake, as the mobility of arsenic is reduced. Sengupta et al. (2021) found that rice absorbed less arsenic when exposed to aerobic water management practices than anaerobic ones. It has been demonstrated that using aerobic water management techniques with alternative irrigation reduces the build-up of As in rice grains (Minamikawa et al. 2015). In contrast to rice grown under traditional flooded conditions, rice grown under aerobic conditions during its various growth stages reduces As accumulation in the vegetative and grain parts of the plant because As in the soil solution is immobilised.

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