

Arsenic Concentration/Toxicity in Rice

Subjects: Agriculture, Dairy & Animal Science

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Rice is one of the most important routes for arsenic to enter the human food chain and threatens more than half of the world's population. In addition, arsenic-contaminated soils and waters increase the concentration of this element in various tissues of rice plants.

Keywords: rice ; arsenic ; silicon ; phosphorus ; selenium ; calcium

1. Introduction

Agriculture is currently facing the challenge of providing adequate food for a growing population ^[1]. Rice is a staple food worldwide ^[2], and it provides two-thirds of the calories needed for two billion people in Asia; while also being the primary protein source for those people ^{[3][4]}. Different types of rice provide essential elements, vitamins, nutrients, and fibre for the human body ^[5]. However, rice is one of the most widely consumed plants globally and requires a constant water source through irrigation, and plants consume about 60% of the irrigation water. Soil texture affects the uptake and growth of plant nutrients because it alters access to water in the soil ^{[1][6][7]}. One of the most important threats to natural and human ecosystems is the pollution of water and soil resources by heavy metals and metals, which causes fundamental changes in ecosystems while their entry into the biological cycle can have devastating environmental effects ^{[8][9]}. Recently, contamination of soils and groundwater with heavy metals has become a serious problem. They harm crop production worldwide ^{[10][11]}, and also, contaminated soil harms economic growth and development due to the negative effects on agricultural products ^{[12][13]}.

2. Arsenic (As) and Rice

Arsenic is a carcinogenic metalloid, and humans are contaminated mainly through diet and drinking water., increasing health problems ^[14]. The National Toxicology Program and International Agency for Research on Cancer categorized arsenic as the first carcinogenic agent ^{[15][16]}. There are various species of As in nature, and they are listed in **Table 1**. More than other grains, rice accumulates arsenic in its tissues ^[17]. The kinds of As in rice are mainly inorganic (iAs, including arsenate and arsenite), monomethylarsonic acid (MMA), and dimethylarsinic acid (DMA) ^[18]. According to research, inorganic kinds of As are more toxic than DMA and MMA ^[19], and under anaerobic situations, As (III) is the prevailing type in soil solutions ^[20].

Table 1. The list of various species of arsenic.

Arsenic Compounds	Acronyms	Chemical Formula
Arsenate	As (V)	$\text{As}(\text{O}^-)_3$
Arsenite	As (III)	$\text{O}=\text{As}(\text{O}^-)_3$
Methylarsonate	MMA	$\text{CH}_3\text{AsO}(\text{O}^-)_2$
Dimethylarsinate	DMA	$(\text{CH}_3)_2\text{AsO}(\text{O}^-)$
Trimethylarsin oxide	TMAO	$(\text{CH}_3)_3\text{AsO}$
Tetramethylarsonium ion	TETRA	$(\text{CH}_3)_4\text{As}^+$
Arsenobetain	AB	$(\text{CH}_3)_3\text{As}^+\text{CH}_2\text{COO}^-$
Trimethylarsoniopropionate	TMAP	$(\text{CH}_3)_3\text{As}^+\text{CH}_2\text{CH}_2\text{COO}^-$
Arsenocholine	AC	$(\text{CH}_3)_3\text{As}^+\text{CH}_2\text{CH}_2\text{O}^-$
Dimethylarsinoylacetate	DMAA	$(\text{CH}_3)_2(\text{O})\text{As}^+\text{CH}_2\text{COO}^-$

Arsenic Compounds	Acronyms	Chemical Formula
Dimethylarsinoylpropionate	DMAP	$(\text{CH}_3)_2(\text{O})\text{As}^+\text{CH}_2\text{CH}_2\text{COO}^-$

Nomenclature is as proposed by Francesconi and Kuehnelt [21].

Increased arsenic release from soil particles by rice occurs through competition with soil mineral adsorption sites [22]. In anaerobic environments, arsenic motility and viability are significantly increased [20]. Paddy fields are an excellent environment for increasing arsenic bioavailability—the amount of arsenic absorption is such that it can enter the rice and affect rice growth—because the rice plants are grown in flooded conditions [23]. Therefore, since arsenic has a high solubility in water, this element is the most critical pollutant [24]. Arsenic contamination has become the reason for significant health difficulties in humans and animals [25], and in India, China, Sri Lanka, Pakistan, Nepal, Bangladesh, Chile, Mexico, and Argentina, pollution of drinking water sources with arsenic is now a public health emergency [26]. In some mines in southern China's Guangdong, the soil is heavily polluted with arsenic and some other heavy metals, and according to some studies, pollution in agricultural lands around these mines has reached 344.11 mg/kg, which indicates an excessive concentration of arsenic (1 to 40 mg/kg) in the soil [27].

There are two main ways to absorb arsenic in rice: (1) As (V) as a chemical analogue of phosphate is absorbed in rice roots by the phosphate transport protein system. (2) As (III) is an analogue of silicic acid and can be absorbed via the roots of rice with the delivery systems of silicic acid (*Lsi1* and *Lsi2*) (Figure 1) [28][29]. As mentioned, there are two main pathways for arsenic uptake by rice, so because we wanted to investigate the role of microelements and macroelements in reducing toxicity and uptake of arsenic, we looked at elements that have a common uptake pathway with arsenic. Among them, we examined two macroelements (P, Ca) and two microelements (Si, Se) that effectively reduce the toxicity and absorption of arsenic in rice.

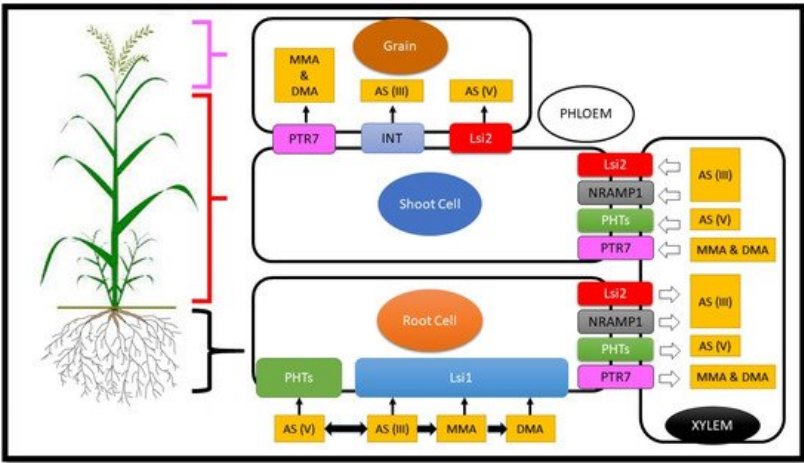


Figure 1. Mechanisms of arsenic uptake, transport, accumulation, and distribution in rice. Nomenclature is as proposed by Shinde and Kumar [30] with some modifications.

Several methods are used to determine the bioavailability and concentration of arsenic in rice, including the in vitro digestion process to determine the bioavailability of arsenic [31] and the Meharg and Jardine [32] method to determine the concentration of arsenic in rice.

3. Silicon (Si) and As

Si is an essential element in the soil and crust of the earth, and soil Si content makes up 1 to 45% of soil's dry weight, but only 0.1 to 0.6% is soluble [33][34]. Si is a motionless element in plants, and rice is absorbed as ionized $\text{Si}(\text{OH})_3\text{O}$ and silicic acid (H_4SiO_4). Si content of rice's dry weight can reach up to 10% [35][36], and rice is a stacked Si plant, often used as a sample plant for Si uptake, transport, and accumulation [3]. According to research, silicon is a practical and valuable element for plant growth, especially in various stress conditions such as plant diseases, plant pests, drought, salinity [37], while one of the significant effects of Si is in reducing the toxicity of metal by decreasing absorption and transport of metals in plants. [38].

Studies have shown that rice roots absorb arsenite via two Si carriers, *Lsi1* (the aquaporin NIP2; 1) and *Lsi2* (an efflux carrier) [39]. *Lsi1* is an invasive transporter responsible for transporting silicon and arsenic (III) from culture solutions to rice root cells [40]. As (III) is absorbed within cells in *Escherichia coli*, the yeast (*Saccharomyces cerevisiae*) via

aquaglyceroporins and several aquaporin channels of plants are dependent on the Nodulin 26 subfamily, the same as the intrinsic protein (NIP) is permeable to As (III) in the case of heterogeneity in yeast [44][42]. The Si rice carrier *Lsi1* (OsNIP2; 1) is also penetrable to As (III) expressed in *Xenopus laevis* and yeast oocytes [39]. The second silicon transporter (*Lsi2*) in rice roots transfers silicon efflux from epidermal and endodermal cells to stele to load xylem, and this transporter also mediates the efflux of As (III) [39][43].

However, adding Si to soil and water significantly decreases the concentration of arsenic in rice. In addition, some studies have shown that Si can help increase methylation in rice tissue and affect the concentration of different As types in rice [44]. Therefore, adding silicon to the soil can reduce As uptake and accumulation in rice, and Si foliar application may also be an alternative route to reduce arsenic accumulation in rice [22].

Different studies have been performed on the efficacy of Si in reducing the uptake and transport of arsenic in rice. For instance, Seyfferth and Fendorf [44] detected that the concentration of As in the grain was significantly reduced by adding Si to the pore water. Si application has also been reported to decrease concentrations of different types of arsenic in stem, leaf, husk, and brown rice (Figure 2) [45].

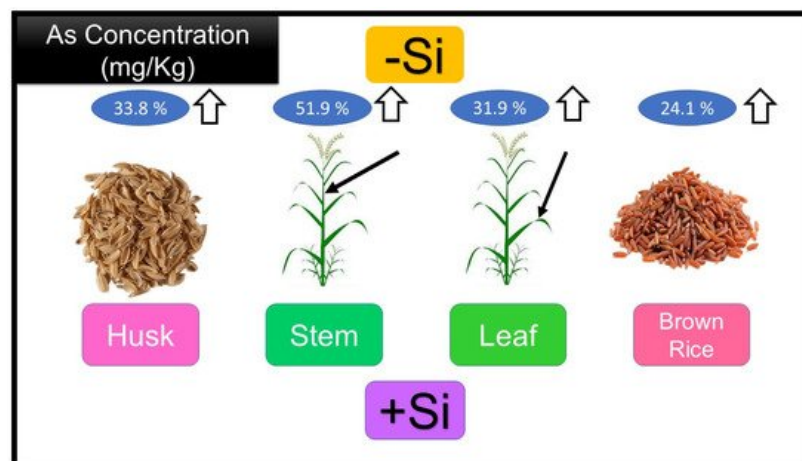


Figure 2. The effect of Adding silicon (+Si) and without silicon (-Si) treatments on arsenic concentration on different rice tissue. Nomenclature is as proposed by Gang, ZHENG [46].

It has also been observed that Si usage significantly decreases the concentration of iAs, while the DMA concentration increases in rice plant tissues [45]. It was found that silicic acid can also dislocate arsenite, arsenate, and Dimethylarsinate from the surface of soil particles, which increases the aggregate concentration of arsenic in the soil solution [47]. Hence, the effects of adding silicon to soil on arsenic bioavailability depend on the interactions between As and Si in pore water, particles of soil, and the absorption of rice roots [48]. According to research, to control the adverse efficacy of silicon usage in paddy soil, Si foliar usage can be a more impressive way to affect the arsenic accumulation rate in rice [22].

4. Phosphorus (P) and As

Phosphorus is a vital element required for growing plants, and plants absorb it mainly as inorganic phosphate (Pi) [49]. Phosphorus plays an essential role in the biochemistry and physiology of plants, and almost all phospholipids, nucleic acids, and ATPs contain P, which is involved in regulating significant metabolic pathways and enzymatic reactions, making phosphorus essential for the worldwide production of sustainable food [50][51]. Agricultural products consume 90% of the extracted non-renewable phosphate reserves annually. As the population of the world increases and phosphate resources are depleted, it is necessary to improve the phosphorus use efficiency (PUE) at the plant and farm-wide scale [50][52]. Due to the high stabilization of phosphorus in the soil and its slow release to the root surface, plants have different strategies to enable phosphorus accessibility from the ground [53].

Arsenic and phosphorus are chemical analogues. However, some of the chemical properties of P and As, including redox reactions, are distinct and cause the biochemical behaviour of the two elements to be different. As mentioned, P is an essential plant growth element, while arsenic is toxic and prevents plant growth [54][55]. In the environment, arsenic occurs as arsenate or arsenite (e.g., AsO_4^{-3} or AsO_3^{-3}); in contrast, phosphorus exists mainly as orthophosphate ions (PO_4^{-3}). Phosphates usually have many physicochemical properties similar to arsenates, like symmetry, acid decomposition constants, and ion size, but P is more susceptible to transport sites than As (V) [55][56][57]. In aqueous conditions, As (V) and P (V) are present as arsenates (AsO_4^{-3}) and phosphate (PO_4^{-3}), which are surrounded by four oxygen atoms in quadrilateral coordination. Arsenate and phosphate are assumed as chemical analogues due to their being similar

chemical species, which can replace each other in chemical reactions. Biogeochemical reactions often are seen as precipitation/dissolution, adsorption/excretion, and competitive/adsorption reactions in plant and microbial systems [58][59][60][61].

Competitive processes of biogeochemical reaction between arsenate and phosphate control the arsenic bioavailability in the environment. However, arsenic oxidation reactions in the atmosphere produce various biogeochemical responses which do not occur for P. For instance, in anaerobic conditions like rice paddies, arsenate is transformed to arsenite because it is not absorbed as much as arsenate on soil particles (especially at low or neutral pH), so, it is more mobile and soluble. Redox mobility creates arsenic distribution in sediments and soils that decreases under fluctuations of oxidation, but P is not changed by redox variation [62]. An experiment on disposal of arsenate showed after using phosphate solutions, only 35% of the adsorbed arsenate was absorbed from goethite, which indicates that the arsenate bonds were more substantial than the phosphate bonds on iron oxide. The toxicity mechanism in organisms is maybe metabolic substitution of arsenate for phosphate [63].

Under aerobic conditions, As (V) and phosphorus (Pi) due to similar chemical properties, stable quadrilateral oxidants form the oxidation state p5. However, there is less correlation between the behaviour of phosphate and arsenite under aqueous conditions because phosphate is not an analogue of As (III), and arsenite transport is not affected by phosphate [64][65]. However, arsenite oxidation to arsenate is distinct in the rice root region [66]. Thus, the effect of phosphate on the behaviour of arsenite in the rhizosphere cannot be completely ignored, and actual cognition of this feature is needed. Unlike hydroponics, P usage in the soil increases arsenic uptake by the plants because of arsenic excretion [67].

Due to the essential role of phosphate in controlling the solubility of arsenic in the soil and its uptake through plants, special attention to P in paddy fields should be given [68]; in addition, the simultaneous usage of calcium and phosphorus forms the Ca-P-As complex and reduces mobility in enriched soils, [69]. Because As and P interactions in the soil-plant system are complicated, most studies have failed, while the variability competition between P and As depends on substrate conditions and soil type [70][71][72].

The much higher application of P may help compete for arsenic uptake in plants. In contrast, increasing the concentration of arsenic with increasing P in the soil solution may also increase arsenic toxicity because of As excretion in the soil solution. On the other hand, excessive P usage for the plants may also enhance the environmental risks [73]. For example, triple superphosphate (TSP) is vital among the phosphorus fertilizers, and the raw material of TSP, phosphate rock, may contain arsenic and release arsenic from solid soils into the soil solution [65].

At similar concentrations of P and As, arsenic is more available for uptake by the plants because of the smaller size of arsenic, and the charge of P ions binds to the soil with a higher intensity than As (V) [64][74]. In addition, P competes with As (V) over time because of the lower soil uptake of P, and according to the stock charge hypothesis, ligand exchange theory, and Steindorf–Rehbon–Shinto equation, Pi is more likely to be replaced by As (V) in soil [64][75].

Soil properties, soil texture, soil mineralogy, and environmental factors may have a significant impact on soil availability, mobility, and interaction of As-Pi [76], and uptake through plants, including mineral components, the presence of anions (e.g., microbial activity, organic matter (OM), redox potential, citrate, phosphate, pH, phytates/phytic acid, and in particular, iron oxide and Al oxide/hydroxides) [77][78]. Amid these factors, pH and goethite firmly control the behaviour of P and As. Iron and magnesium-rich minerals such as phronesis smectites, nontronite, goethite, bronchitis, and pyrolusite absorb more As (V) than Pi when prepared in molar ratio. However, Pi absorbs more than As (V) in non-crystalline allergens containing allophane, boehmite, gibbsite, and clay sections (e.g., vermiculite, illite, and kaolinite) [79][80]. Goethite's high levels in the soil can decrease P and As uptake by plants. Adding Fe and P to high arsenic soils using a sequential combination method can reduce arsenic toxicity to plant roots by providing a food source [81][82].

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