Arsenic speciation in soil-water system and their uptake by rice (*Oryza sativa*)

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ABSTRACT: Rice is the main staple food for billions people worldwide. Geogenic and anthropogenic sources lead to concentration of As, in particular, above the plow pan of paddy soils. Flooded conditions increase the As concentrations in paddy soil-water system above those of non-flooded conditions. Formation of rice root plaque, availability of metal (hydr)oxides (i.e., Fe and Mn), dissolved organic carbon (DOC), competing ions (i.e., P and Si), and microorganisms play an important role in As speciation and distribution in rice rhizosphere and subsequent uptake by rice plant. Arsenic species are acquired by rice roots through the pathways for nutrients and metabolized via a variety of mechanisms. A number of metabolic pathways including As(III) efflux, and As-thiol complexation and sequestration may decrease As burden in rice tissues.

1 INTRODUCTION

Arsenic (As) is a carcinogen and related to human health concern more than any other toxic element or compound. Arsenic mainly associates with sulfur (S) rich minerals such as arsenopyrites (FeAsS), realgar (As₄S₄), and orpiment (As₂S₃). Over the past few decades, millions of people all over the world have been suffering from chronic diseases and deaths, primarily in response to the As-contaminated drinking water. Groundwater As contamination in Bangladesh is recognized as the most drastic mass poisoning in history. Therefore, recommended and regulatory limits established by various authorities have been revised. World Health Organization (WHO) guideline value for total As in drinking water was reduced in 1993 from 50 to 10 µg L⁻¹.

Another important concern regarding source of As exposure is rice (*Oryza sativa*) (Adeyemi *et al.*, 2017; Chen *et al.*, 2016). Rice is cultivated in over 100 countries in the world with distinctive cropping seasons. Rice cultivation is managed in a special way to ensure wet cultivation of rice and the management practices consist: (a) plowing to homogenize of waterlogged top soils (b) submerging (flooding) the top soil during the cropping period (c) soil is drained and dried before the harvest. Natural and anthropogenic activities lead to concentrate and distribution of As in paddy environment. More importantly, rice grains can contain approximately 10 times as much as baseline total As as other cereals (Halder *et al.*, 2014; Ma *et al.*, 2016; Tenni *et al.*, 2017).

2 DISCUSSION

2.1 Arsenic bioavailability in rhizosphere

Paddy management practices (flooding and draining) mainly alter the redox chemistry of paddy soils. Iron and Mn co-exist in rice root plaques under flooded conditions. However, Fe is the main element followed by Mn as secondary in the plaques since Fe(III)-hydro(oxides) precipitate at lower redox potentials than Mn oxides. Radial oxygen loss (ROL) via the root aerenchyma oxidizes the As(III) in rhizosphere and resulted As(V) is sequestered in Fe plaque. Therefore, As(V)/As(III) ratio is high in Fe plaque whereas the As in the soil solution is mainly present as As(III) which is highly mobile.

Dissolved organic carbon (DOC) derived from decomposed plant and animal products plays an important role in As dynamics. Dissolved organic carbon can promote the reduction of Fe(III) (hydr)oxides to release As. The presence of the competing anions such as phosphorus (P) and silicon (Si) influence the As mobility in paddy soil. Phosphate (PO₄³⁻) is an analog to As(V) and can influence on As(V) distribution in soil and subsequent uptake. Similarly, Si competes with As(III) for retention sites on soil mineral surfaces.

Aerobic and anaerobic microorganisms in rhizosphere greatly mediate As speciation through assimilatory and dissimilatory pathways. Phylogenetically diverse *aioA* genes mediate As(III) oxidation to the As(V) whereas *arsC* and *arrA* genes reduce As(V) to As(III) in the detoxification and respiratory pathways,

respectively. Microbial transformation of inorganic As species by *arsM* genes produces methylated arsenicals such as dimethylarsinic acid (DMA(V)), monomethylarsonic acid (MMA(V)). Therefore, methylated As species present in rice plants are the product of rhizosphere microorganisms.

2.2 Arsenic species uptake and translocation

Arsenic species such as As(III), As(V), MMA(V), and DMA(V) in rice rhizosphere are taken up and translocated up into the stalks and grains. Key transporters including nodulin 26-like intrinsic proteins (NIPs) and PO_4^{3-} transporter genes (OsPHTs) mainly involve the uptake of inorganic and methylated As species. In rice roots, Lsi1 can mediate influx of silicic acid $[\text{Si}(\text{OH})_4]$ and as well as As(III). Following the uptake, As(III) efflux is a key mechanism and release portion of As(III) into the external environment minimizing cellular As burden. In addition, the formation of As(III)-thiol complexes and sequestration in vacuoles decrease the As(III) translocation.

Phosphate transporter, OsPHT1;8 (OsPT8), is found to have a high affinity for PO_4^{3-} and As(V) uptake in rice. Following the uptake, As(V) readily reduces into the As(III) and the reduction process is stimulated by As(V) reductase enzymes. It has been suggested that Lsi1 mediates the uptake of undissociated MMA(V) and DMA(V) in rice plants. In rice roots, MMA(V) reduces into MMA(III) which is then bind with thiols. So far, there have been no reports of volatile As species released by rice plant under typical growing conditions unless rice plants are treated with trimethylarsines (TMAs(V)O).

Natural Resistance-Associated Macrophage Protein (NRAMP) transporter, OsNRAMP1, and Lsi2 mediate As(III) efflux in the direction of xylem. Putative peptide transporter in rice, OsPTR7, involves in the long-distance (root to grain) translocation of methylated As species in rice. Interestingly, the phloem transportation acts as the primary route of transport to rice grains for both inorganic and methylated As species.

Despite the rice genotypes, location, and season, total As concentrations in rice tissues decrease in the order of root $\gg$ shoot $>$ straw $>$ husk $>$ grain. The highest translocation efficiency (caryopsis-to-root) in rice is gained by DMA(V) followed by MMA(V) and inorganic As species. The lack of DMA(V)-PC complexation enhances the DMA(V) to be readily moved between root and shoots. Table 1 summarizes the concentration of different As species in rice grains in various localities. The pattern of inorganic and methylated As loading into the grain is time-dependent.

Table 1. Arsenic speciation in market-base rice in different localities (Adeyemi *et al.*, 2017; Chen *et al.*, 2016; Halder *et al.*, 2014; Ma *et al.*, 2016; Tenni *et al.*, 2017). Food and Agricultural Organization (FAO) recommended level for inorganic As in rice is $200 \mu\text{g kg}^{-1}$.

Country	Concentration ($\mu\text{g kg}^{-1}$)			
	As(III)	As(V)	DMA(V)	MMA(V)
Bangladesh	129	66	14	2
China	107.1	4.7	9.6	0.3
Taiwan	61.6	4.3	12.1	2.7
Italy	91	8.2	55	–
Thailand	81.4	3.7	29	<2
South Korea	80	5	30	2
Australia	178*		68	–
USA	98*		157	–
India	50*		10	–
Nigeria	47*		11.5	0.3

*Sum of As(III) and As(V).

3 CONCLUSIONS

Physico-chemical properties together with biological processes contribute to the speciation and bioavailability of As in the rice rhizosphere. Number of transporters and enzymes is associated with As uptake, translocation and transform in rice tissues. Various metabolic pathways may decrease the total As concentration in rice grains. Application of agronomical, physico-chemical, and breeding approaches would further be needed to produce rice for human consumption, particularly in As prone areas.

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