Arsenic accumulation in rice (Oryza sativa L.) is influenced by environment and genetic factors

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1   **Arsenic accumulation in rice (*Oryza sativa* L.) is influenced by environment and genetic**

2   **factors**

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ABSTRACT

Arsenic (As) elevation in soil will have a negative impact on both the yield and grain quality of rice (*Oryza sativa* L.). The mechanistic understanding of As uptake, translocation, and grain filling is an important aspect to produce rice grains with low As concentrations through agronomical, physico-chemical, and breeding approaches. In the paddy soil-water system, a range of physico-chemical, biological, and environmental factors governs the speciation of As and their concentrations. Major As transporters such as phosphate and aquaglyceroporins assimilate both inorganic (As(III) and As(V)) and organic As (DMA(V) and MMA(V)) species from the soil solution. A number of metabolic pathways (i.e., As (V) reduction, As(III) efflux, and As(III)-thiol complexation and sequestration) are likely to play a key role in determining the translocation and substantial accumulation of As species. The order of translocation efficiency (caryopsis-to-root) for As species in rice plants is as follows: DMA(V) > MMA(V) > inorganic As species. The pattern of inorganic and organic As species loading into the grain is largely determined by the genetic makeup of the rice plants, maturity stage, and its environmental interaction. Therefore, the knowledge of As metabolism in rice plants and how it is affected by plant genetics, the environment, and its interactions would pave the way to developing adaptive strategies to mitigate the accumulation of As in rice grains.

Keywords: Arsenic speciation, Arsenic transporters, Arsenic metabolism, Detoxification, Grain filling, Arsenic toxicity

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1. Introduction

Rice (*Oryza sativa*) is the dominant dietary exposure route to arsenic (As), a non-threshold carcinogen. Rice grains can contain approximately 10-times as much as the baseline total of As when compared to other cereal grains (Williams et al., 2007). Rice and rice-based products can lead to an intake of excessive amount of inorganic As, particularly, in the populations in South and South-East Asia (Kile et al., 2007; Meharg et al., 2009). Rice is the primary source of As in a non-seafood diet in Europe and the United States (Fu et al., 2011). Ohno et al. (2007) have demonstrated that rice contributed 56% of the total As intake; the corresponding figure for drinking water, solid food, liquid food, and cereals were 13, 11, 4.4, and 16%, respectively. Contrasting results have also been reported elsewhere suggesting that drinking water has contributed to 93.5% of total As uptake, and rice and vegetables have only contributed to 6.2% and 0.3% of total As intake, respectively, in a groundwater contaminated Bangladeshi setting (Rahman et al., 2013).

Arsenic in the geological environment is mainly associated with sulfur (S) in minerals such as arsenopyrites (FeAsS), realgar (As_4S_4), and orpiment (As_2S_3) (Majzlan et al., 2014). Natural processes such as rock weathering, alluvial deposits may contribute As release into the paddy environment (Bundschuh and Maity, 2015; Herath et al., 2016). Anthropogenic activities (i.e., mining and use of As-contaminated groundwater in the form of irrigation water) promote the accumulation of natural As in paddy ecosystems. Moreover, As-containing insecticides, herbicides, feed additives, and wood preservatives are the potential anthropogenic sources of As in rice ecosystems (Chen et al., 2016b; Zhao et al., 2009).

Natural soils typically contain 0.1 to 10 mg kg^{-1} of total As (Zhao et al., 2010a). European Community (EU) recommends that soils to be used for agricultural purposes should be

100   contained less than 20 mg kg^{-1} of total As (Bhattacharya et al., 2009; Shrivastava et al.,

101   2017). Arsenite (As(III)) and arsenate (As(V)) are the most commonly found inorganic As

102   species whereas monomethylarsonoic acid (MMA(V)) and dimethylarsinic acid (DMA(V))

103   are the frequently reported organic As species in paddy soil-water systems (Honma et al.,

104   2016; Jia et al., 2012). Both inorganic and organic As species are acquired by rice roots

105   through various nutrient assimilatory pathways and they are translocated via a variety of

106   mechanisms (Ma et al., 2008; Wang et al., 2016b).

107

108   Attention is required to understand how rice plants take up and metabolize As species so

109   as to develop mitigation measures against this global contamination in the food chain. Taking

110   these demands into account, this review presents recent progress in As dynamics in the rice

111   ecosystem, and its uptake by rice roots and translocation to the rice grains. Further,

112   mechanisms (i.e., metabolism/detoxification) that have evolved to mitigate the accumulation

113   of As in rice tissues are discussed highlighting the major knowledge gaps that need to be

114   addressed in future research.

115

116   **2. Arsenic phytoavailability in paddy soil-water system**

117   Paddy soils under conventional paddy management practices are subjected to flooded and

118   non-flooded conditions, during initial and final stages of the growth of rice, respectively. The

119   changes in water management regimes may alter redox potential (Eh) of the paddy soil-water

120   systems (Pan et al., 2014). During flooded conditions, water replaces the gaseous phase in the

121   soil matrix. A number of redox reactions (from high Eh ($\sim$ +700 mV) to low Eh ($\sim$ -300 mV):

122   reduction of Mn(IV), Fe(III), and SO$_4^{2-}$, and methanogenesis) take place either sequentially

123   or simultaneously during this phase (Sahrawat, 2015). Arsenate in the soil matrix is converted

124   to As(III), which is highly mobile than As(V), when Eh turns more negative. The

125   As(III)/As(V) ratio is high in the soil solution during the flooded conditions and reverses for

126   non-flooded conditions (Yamaguchi et al., 2014).

127

128   Iron (III) plaque, consisting of amorphous or crystalline Fe hydro(oxides) (FeOOH), has

129   found to have a significant effect on the sequestration of both As(V) and As(III) (Eq. 1 and

130   Eq. 2) (Liu et al., 2004). A higher ratio of As/Fe in Fe(III) plaque around rice roots compared

131   to that of Fe minerals in soil matrix indicates the high capacity of Fe(III) plaque for the

132   retention of As in the rhizosphere (Yamaguchi et al., 2014). Radial oxygen loss (ROL), the

133   process that diffuses O_2 into the rhizosphere through root aerenchyma, promotes the

134   formation of Fe(III) plaque under flooded conditions (Mei et al., 2009). Root anatomy (i.e.,

135   root porosity) in rice genotypes strongly correlates with ROL and substantial formation of

136   Fe(III) plaque (Mei et al., 2009; Wu et al., 2011a). In addition, growth stage of rice plants and

137   background Fe concentration in paddy soils have an effect on the quantity of Fe(III) plaque in

138   rice roots (Li et al., 2015). Therefore, As retention by Fe(III) plaque and subsequent

139   accumulation of As in plant tissues (i.e., root, shoot, husk, and grain) of different rice

140   genotypes are remarkably varied (Lee et al., 2013; Liu et al., 2006).

141

142   $$\equiv FeOH_{(s)} + AsO_{4(aq)}^{3-} + 3H_{(aq)}^{+} \rightarrow FeH_2AsO_{4(s)} + H_2O_{(l)}$$ (Eq. 1)

143   $$\equiv FeOH_{(s)} + AsO_{3(aq)}^{3-} + 3H_{(aq)}^{+} \rightarrow FeH_2AsO_{3(s)} + H_2O_{(l)}$$ (Eq. 2)
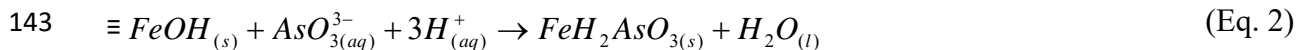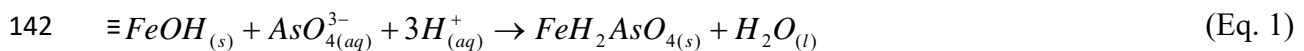
144

145   Paddy soil consists of indigenous FeOOH including: ferrihydrite ($Fe_5HO_8.4H_2O$), goethite

146   (α-FeOOH), lepidocrocite (γ-FeOOH), and hematite (α-F_2O_3). Iron redox cycling (Fe(II)

147   oxidation and Fe(III) reduction) has a significant impact on the mobility and bioavailability

148   of As in paddy ecosystems (Yu et al., 2016b). Iron-reducing bacteria can convert Fe(III) to

149   Fe(II) (Eq. 3) through two different pathways; dissimilatory reduction and assimilation

150   reduction (Das et al., 2016; Qiao et al., 2017).

151

152   $$FeOAs(OH)_{2(s)} \rightarrow Fe^{2+}_{(aq)} + AsO^{3-}_{3(aq)} + 2H^{+}_{(aq)}$$ (Eq. 3)
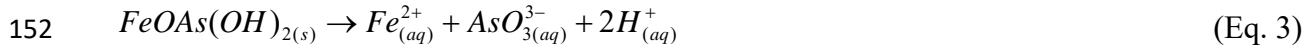
153

154   In contrast, Fe(II)-oxidizing bacteria may re-oxidize Fe(II) to Fe(III), particularly, under

155   non-flooded conditions. Since FeOOH has a strong affinity with both As(V) and As(III), it

156   significantly reduces the mobility and bioavailability of As in paddy soil-water, and the

157   subsequent uptake and accumulation of As in rice tissues (Yu et al., 2016b).

158

159   Recent studies have demonstrated that amorphous Fe oxide-bound As has played an

160   important role in the sinking of As (Liu et al., 2015; Yu et al., 2016a). The conversion of

161   poorly crystalline ferrihydrite (surface area: 100 - 700 m^2 g^{-1}) to other crystalline Fe oxides

162   phases such as goethite (surface area: 8 - 200 m^2 g^{-1}) and hematite (2 - 115 m^2 g^{-1}) may

163   decrease the sorption of As due to the reduction of adsorption sites. External supplementation

164   of Fe (i.e., Fe oxides, mixed Fe sources, and Fe-rich industrial byproducts) can lead to

165   reducing As burden in rice ecosystems for different reasons (Farrow et al., 2015; Yu et al.,

166   2017). Firstly, Fe amendments may increase the percentage of amorphous Fe fraction in

167   paddy soil. Secondly, Fe supplementation could increase the quantity of Fe(III) plaque

168   deposited on root apoplast. Yu et al. (2017) have assessed the effect of Fe compound

169   supplementation on As accumulation in rice tissues throughout the whole growth stages of

170   rice plant and have found that Fe amendments significantly reduced the accumulation of As

171   in rice tissues at the grain-filling stage.

172

Nitrogen is one of the key nutrients, enhancing the growth of rice, and is supplied to paddy fields as N fertilizers (Ata-Ul-Karim et al., 2017). The process of Fe-redox cycling could be affected by nitrogen (N) cycling (i.e., nitrification, denitrification, and ammonification) (Yu et al., 2016b). The coupled NO_3^- reduction and Fe (II) oxidation may reduce the fate of As in the paddy environment (Li et al., 2012). Nitrate (NO_3^-)-dependent Fe(II)-oxidizing bacteria can promote the oxidation of Fe(II) under flooded conditions as shown in Eq. 4 (Sun et al., 2009b). As described above, the higher the level of Fe(III), the lower the concentration of bioavailable As in paddy soil-water. The reduction of Fe(III) could be inhibited by NO_3^- reduction because of their competition for electrons (Yu et al., 2016b). Therefore, high level of NO_3^- in paddy soil may decrease Fe(III) reduction and subsequent uptake and accumulation of As in rice tissues.

$$Fe_{(s)}^{2+} + 5H_2O_{(l)} + NO_{3(aq)}^- \rightarrow 2Fe(OH)_{3(s)} + 4H_{(aq)}^+ + NO_{2(aq)}^- \qquad \text{(Eq. 4)}$$
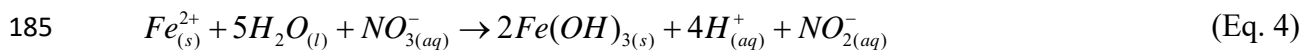
Anammox-bacteria can drive the process of ammonia (NH_3) oxidation under anaerobic conditions. Ammonia oxidation is coupled with Fe(III) reduction as shown in Eq. 5 (Shrestha et al., 2009). However, the impact of NH_3 oxidation on Fe-redox cycling in paddy ecosystem remains unclear.

$$NH_{4(aq)}^+ + 6FeOOH_{(s)} + 10H_{(aq)}^+ \rightarrow NO_{2(aq)}^- + 6Fe_{(s)}^{2+} + 10H_2O_{(l)} \qquad \text{(Eq. 5)}$$
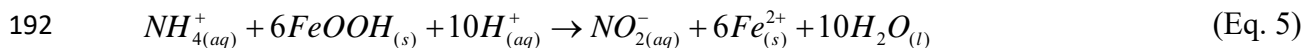
Organic fertilizer, added to keep paddy soil fertility, may influence As dynamics. Humic substances (i.e., humin, humic acid, and fulvic acid), which are key components of organic matter, have a positive and negative effect on the mobility and bioavailability of As (Jiang et al., 2009; Yu et al., 2016b). Arsenic species can be adsorbed to humic substances through

198   organo-As complexes (Williams et al., 2011). In contrast, the process of adsorption of humic

199   substances to sorption sites in soil matrix may increase the bioavailability of As in soil

200   solution due to the site and electrostatic competitions (Mladenov et al., 2015). Humic

201   substances could stimulate microbes-driven Fe(III) reduction by facilitating electron shuttling

202   (Newman and Kolter, 2000). As a result, As(V), sequestrated in FeOOH, may reduce to

203   highly mobile As(III).

204

205   Sulfate (SO_4^{2-}) in soil matrix is reduced to sulfide (S^{2-}) when decreasing redox potential

206   from -120 to -180 mV (Sahrawat, 2015). Sulfate-reducing bacteria can promote the reduction

207   of SO_4^{2-} in paddy environment (Das et al., 2016). The reduction of SO_4^{2-} to S^{2-}, particularly,

208   under flooded conditions, leads to immobilization of As(III) due to precipitation of As(III), as

209   arsenic sulfide, and iron sulfide minerals (Burton et al., 2014). External sulfur (S)

210   supplementation may promote the formation of low molecular weight thiol-rich peptides in

211   rice tissues, which have a high affinity with As(III), and therefore, may reduce As

212   translocation from root to grain (Zhang et al., 2011).

213

214   Manganese oxides (MnOH) play an important role in immobilizing As through oxidation

215   of As(III) to As(V) and substantial complexation of As(V) (Eq. 6 and Eq. 7) (Lafferty et al.,

216   2011). Xu et al. (2017b) have demonstrated that MnOH, as an amendment (1200 mg kg^{-1}),

217   has decreased the accumulation of As in rice straw and grains by 30 - 40%.

218

219     $MnO_{2(s)} + H_3AsO_{3(aq)} + 2H_{(aq)}^+ \rightarrow Mn_{(aq)}^{2+} + H_3AsO_{4(aq)} + H_2O_{(l)}$ (Eq. 6)

220     $2Mn-OH_{(s)} + H_3AsO_{4(aq)} \rightarrow (MnO)_2AsOOH_{(s)} + 2H_2O_{(l)}$ (Eq. 7)

221
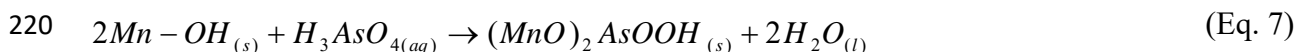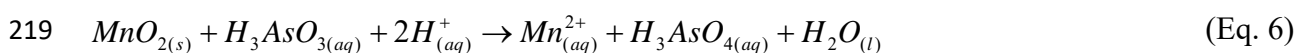
Bacteria, fungi, eukaryotic algae, and archaea, inhabiting in the rhizosphere, can influence on the speciation of As through different biotransformation pathways: oxidation, reduction, methylation, and volatilization (Jia et al., 2012). A variety of genes in microorganisms encode for As-transformation enzymes and transporters. The process of microbial oxidation of As(III), coded for by *aioA* gene, can lead to producing As(V) (Zhang et al., 2015). In contrast, microbial As(V) reduction, coded for by *arsC* and *arrA* genes, may increase the mobility of As, particularly, under flooded conditions (Malasarn et al., 2004; Qiao et al., 2017; Villegas-Torres et al., 2011). Inorganic As species present in paddy ecosystems can be transformed into organic As species such as MMA(V), monomethylarsonous acid (MMA(III)), DMA(V), and dimethylarsinous acid (DMA(III)), and the process is coded for by *arsM* gene. For this reason, organic As species found in paddy soil-water are likely to be microbe-mediated products. Microorganisms can volatilize organic As to arsines, primarily as trimethylarsines ($(CH_3)_3As$), with a smaller quantity of arsine (AsH_3), monomethylarsine (CH_3AsH_2) and dimethylarsine ($(CH_3)_2AsH$) (Hayat et al., 2017; Jia et al., 2012). As a result, microbes-driven As transformation may decrease the phytoavailability of As in paddy soil-water systems. Moreover, microorganisms can indirectly impact on the speciation and mobility of As by influencing Fe, N, and S cycling, as discussed above. Recent findings have further revealed that soil amendments such as biochar may significantly affect the abundance and diversity of microorganisms, and the consequent transformation of As (Qiao et al., 2017; Qiao et al., 2018).

3. Arsenic metabolism in rice plants

Arsenic metabolism in different rice tissues is crucial for understanding uptake of inorganic and organic As species, their translocation, and grain filling. There are different genes involving in As metabolism including reduction, efflux, transformation, complexation

247 and sequestration (Table 1). Fig. 1 illustrates genes associated with the uptake, translocation,

248 and grain filling of inorganic and organic As species in the rice plant.

249

250 3.1. Uptake of inorganic Arsenic species

251 3.1.1. Arsenite

252   Arsenite, the main As species under flooded conditions, is acquired dominantly through

253 nodulin 26-like intrinsic proteins (NIPs), collectively termed as aquaporin channels. In rice

254 roots, OsNIP2;1, also called Lsi1, highly expressed in the distal side of the plasma

255 membranes of the exodermis and endodermis cells where Casparian strips exist, is the major

256 pathway for the influx of silicic acid ($Si(OH)_4$) as well as As(III) (as arsenous acid, $As(OH)_3$)

257 into rice roots (Fleck et al., 2013; Ma et al., 2008). This could be attributed to the similar

258 sizes of both $Si(OH)_4$ and $As(OH)_3$ with tetrahedral orientation along with more or less

259 similar dissociation constants (pK_a) (9.2 and 9.3, respectively). Ma et al. (2008) demonstrated

260 that NIP genes (OsNIP1;1 and OsNIP3;1) in oocytes mediate As(III) uptake but the $Si(OH)_4$

261 pathway was unaffected. Rice OsNIP3;3 and OsNIP3;2 are highly expressed in the lateral

262 roots and stele region of the primary roots suggesting that As(III) is taken up by the highly

263 active part of the root system (Chen et al., 2017b; Katsuhara et al., 2014). In addition, plasma

264 membrane intrinsic proteins (PIPs) such as OsPIP2;4, OsPIP2;6 and OsPIP2;7 are associated

265 with the uptake of As(III) (Mosa et al., 2012) but their functional role is not well studied.

266

267   Aquaporin channel, OsNIP2;2 (Lsi2) being a $Si(OH)_4$ efflux transporter, localized on the

268 plasma membrane of cells in both the exodermis and endodermis of rice roots; however,

269 contrary to Lsi1, Lsi2 is localized on the proximal side of the same cells. Preloading of the

270 *Xenopus oocytes* with Si resulted in a release of Si back into the external environment,

271 demonstrating that Lsi2 is a Si efflux transporter (Ma et al., 2007). Having an influx

272   transporter on one side and an efflux transporter on the other side of the cell, As(III) cannot

273   pass freely towards the stele (Zhao et al., 2010b). In addition to the Lsi2, As(III) efflux

274   transporters are found in other organisms. For instance, Arsenic Compounds Resistance

275   protein 3 (ACR3) in yeast extrudes As(III), however, ACR3 does not exist in flowering plants

276   like rice. Meng et al. (2011) found that the introduction of ACR3 (ScACR3) into rice

277   decreased total As concentration in rice grains by nearly 20% suggesting that the transgenic

278   rice plant extruded As(III) back into the external environment. In this aspect, As(III) efflux is

279   a key mechanism which releases a portion of As(III) into the external environment

280   minimizing cellular As accumulation.

281

282   In some plant species, uptake of As(III) is a bi-directional process; the direction is

283   determined by the concentration gradient. For instance, aquaporins from different plant

284   species such as *Pteris vittata* (PvTIP4;1), *Lotus japonicas* (LjNIP5;1 and LjNIP6;1), and

285   *Arabidopsis thaliana* (AtNIP1;1, AtNIP1;2, AtNIP3;1, AtNIP5;1, AtNIP6;1, and AtNIP7;1)

286   are known to be associated with As(III) efflux into the external environment (Bienert et al.,

287   2008; He et al., 2016; Kamiya and Fujiwara, 2009; Xu et al., 2015). In this sense, a transgenic

288   approach, overexpressing As(III) efflux transporters is likely to mitigate the accumulation of

289   As in rice tissues.

290

291   Following the uptake, besides the As(III) efflux, As(III) has a high affinity for thiol-rich

292   peptides such as glutathione (GSH) and phytochelatins (PCs) that are derived from GSH with

293   the general structure (γ-Glu-Cys)n-Gly (n=2 - 11) in the rice roots. Overexpression of the PCs

294   leads to As resistance in transgenic plants, increasing the level of As in roots, but a

295   remarkably low level of As in rice grains (Shri et al., 2014). After being formed, As(III)-PC

296   complexes are transported into vacuoles for the sequestration by C-type ATP-binding cassette

transporter (OsABCC1) which is expressed in the exodermis and pericle. Similarly, it has been reported that AtABCC1 and AtABCC2 in *Arabidopsis thaliana* mediate the transportation of As(III)-PC complexes into the vacuole (Song et al., 2010). The favorable pH (approximately 5.5) in vacuoles may provide an ideal condition for the stability of As(III)-PC complexes (Zhao et al., 2009). Therefore, vacuole sequestration of As(III)-PC complexes plays an important role in alleviating the translocation of As(III) into the rice grain.

Gene expressions associated with As(III) assimilation (As(III) influx and efflux) are largely varied with the developmental stages of the rice plant and cultivar type. A recent study by Wu et al. (2017) demonstrated that expression of Lsi1 and Lsi2 genes were significantly down-regulated in non-flooded conditions compared to flooded conditions. These genes are strongly associated with As assimilation and it might be one of the major factors that suppress the accumulation of As under non-flooded conditions. It has been found that a mutation in Lsi1 remarkably reduced the uptake and accumulation of As(III) in rice shoots and grains (Ma et al., 2008). Similarly, Guo et al. (2009) demonstrated that a Si-defective mutant in rice plant showed a decrease in As(III) uptake (Guo et al., 2009). Therefore, understanding the temporal distribution of As species and expression of genes across As efficient and inefficient cultivars are paramount for developing mitigation measures of As in rice.

Rice plants are an efficient Si accumulator and can contain Si in shoots about 10% of shoot dry weight (Meharg and Meharg, 2015). In this regard, supplementation of Si fertilizers to As-contaminated paddy soils may provide an effective strategy to minimize As(III) uptake (Guo et al., 2007; Seyfferth and Fendorf, 2012). It has been reported that Si application to the paddy soil, decreased the total As concentration by 33% in rice grains (Fleck et al., 2013). A

322 similar study by Wang et al. (2016a) showed that high Si application rates (9000 kg ha^{-1})

323 decreased the total As concentration in rice grains by 20%. Thus, Si application to As-

324 contaminated paddy soils is beneficial for rice plants, partly because of the decreased uptake

325 of As(III) by rice roots, and partly because of the increased plant resistance to biotic and

326 abiotic stresses.

327

328 3.1.2. Arsenate

329   Arsenate is the most prevalent As species under non-flooded paddy soils. Physiological

330 and electrophysiological studies have revealed that As(V) and PO_4^{3-} share the same uptake

331 pathway (Muehe et al., 2014). In the rice genome, 13 PO_4^{3-} transporter genes (OsPHTs) have

332 been identified; however, their response to As(V) and contribution to As(V) uptake in rice

333 have not been studied in detail yet.

334

335   Phosphate transporter, OsPHT1;8 (OsPT8), was found to have a high affinity for both

336 PO_4^{3-} and As(V) uptake in rice. The overexpression of the OsPT8 has increased the

337 maximum influx of As(V) by 3 - 5 times in rice plants (Wang et al., 2016b; Wu et al., 2011b).

338 The PO_4^{3-} transporter gene, OsPHT1;1, also mediates the uptake of As(V) into the rice roots

339 (Kamiya et al., 2013). It has been found that other plant species may contain PO_4^{3-}

340 transporters which are mediating As(V) uptake. For example, PO_4^{3-} transporters, such as

341 PvPht1;3 in *Pteris vittata* and AtPHT1;1, AtPHT1;4, AtPHT1;5, AtPHT1;7, AtPHT1;8, and

342 AtPHT1;9 from *Arabidopsis thaliana* acquire As(V) from the rhizosphere (DiTusa et al.,

343 2016; Fontenot et al., 2015; Shin et al., 2004).

344

345   Following uptake, As(V) is readily reduced to As(III) in rice roots. As(V) reductase

346 enzymes play a key role in controlling the conversion of As(V) to As(III) (Xu et al., 2007).

347 Efficient As(V) reduction takes place in all tissues of the root apex which was supported by

348 fluorescence-X-ray absorption near-edge spectroscopy (XANES) analysis (Batista et al.,

349 2014). Recently, Shi et al. (2016b) identified two As(V) reductases, OsHAC1;1 (abundant in

350 the epidermis, root hairs, and pericycle cells) and OsHAC1;2 (abundant in the epidermis,

351 outer layers of cortex, and endodermis cells) which play an important role in the reduction of

352 As(V) to As(III) in rice roots.

353

354 Interestingly, As(III) is found in considerable concentrations in plant roots exposed to

355 As(V). However, after the reduction of As(V), As(III) can be released into the external

356 environment via As(III) efflux system or complexed with thiol compounds as mentioned

357 earlier. A new As(V) reductase, OsHAC4, has been identified and it is highly expressed in

358 the epidermis and exodermis of roots, the location which is ideal for the efflux of As(III) to

359 the external environment (Xu et al., 2017a). Similar As(V) reductases, namely As(V)

360 tolerance QTL1 (ATQ1) and High Arsenic Content 1 (HAC1) were identified in *Arabidopsis*

361 *thaliana* (Chao et al., 2014). Therefore, the reduction of As(V) to As(III) and subsequent

362 As(III) efflux or As(III)-thiol complexation in rice roots are likely to play a major role in

363 determining the level of total As in rice grains.

364

365 Since As(V) is an analogue for PO_4^{3-} in plant uptake process, the application of external

366 PO_4^{3-} to the As-contaminated paddy soil could alleviate the accumulation of As(V) in rice

367 tissues (Lihong and Guilan, 2009). Studies have clearly demonstrated that the

368 supplementation of PO_4^{3-} fertilizers to the As-contaminated paddy soils has greatly decreased

369 the concentration of total As in rice grains (Geng et al., 2005). Excess supplementation of

370 PO_4^{3-} fertilizers may lead to eutrophication in surface water bodies. Therefore, a close

371 monitoring must be carried out under excess usage of PO_4^{3-} fertilizers.

372   3.2.   Uptake of organic As species

373   Rice plants are not capable of methylating inorganic As *in vivo*, therefore, organic As

374   species (DMA(V) and MMA(V)) are probably come from the rhizosphere through microbial-

375   mediated methylation processes (Jia et al., 2012; Zhao et al., 2013a). The exact mechanisms

376   that drive the uptake of organic As species in rice are largely unknown. It has been suggested

377   that aquaporin Lsi1 mediates the uptake of undissociated MMA(V) and DMA(V) in rice

378   plants (Li et al., 2009). The pH of the medium has a great effect on the uptake of MMA(V)

379   and DMA(V). More precisely, pH can alter the equilibrium between protonation and

380   dissociation that eventually influence the availability of the MMA(V) and DMA(V) for the

381   membrane transporter, Lsi1 (Li et al., 2009). Therefore, Lsi1 plays a major role in acquiring

382   both inorganic As(III) and organic As species from the rhizosphere.

383

384   There have been not many reports on the metabolism of organic As species in rice roots. A

385   recent study by Mishra et al. (2017) revealed that MMA(V) is readily reduced into MMA(III)

386   which is then bound with thiols in rice roots. In addition, MMA(V) itself can complex with

387   various thiol groups in rice plants. Mishra et al. (2017) found that 16 different MMA(V)-thiol

388   complexes were present in the rice root and shoot. However, DMA(V) is known to neither

389   complex with thiols or convert into the reduced forms. The direct determination of organic

390   As species - thiol complexation in various rice genotypes is an important step for

391   understanding As metabolism in rice plants.

392

393   3.3.   Arsenic species translocation from root to shoot

394   It is likely that both active and passive transporters are associated with the uptake and

395   translocation of As in rice plants. Active transportation is the process of passing materials

396   against a concentration gradient by using the energy of metabolism (Liang et al., 2006).

397   Passive transport is the movement of water and materials without using the energy of

398   metabolism and mainly transport through transpiration flow. For example, a large number of

399   nutrients such as potassium (K), nitrogen (N), Si, is transported through both active and

400   passive processes in rice plants (Bao et al., 2015; Yang et al., 2014). Following the uptake by

401   rice root, various transporters and compounds have involved the translocation of As species

402   from root to shoot.

403

404   The translocation of inorganic As species from root to shoot is determined by various

405   processes. Lsi2 mediates the efflux of uncomplexed As(III) in the direction of xylem. In

406   addition, the Natural Resistance-Associated Macrophage Protein (NRAMP) transporter,

407   OsNRAMP1, may also facilitate the xylem loading of As(III) (Tiwari et al., 2014). Different

408   metabolic activities such as As(III) efflux back into the external environment, and formation

409   of As(III)-thiol complexes and consequent sequestration in vacuoles, limit the translocation

410   of As(III) from root to shoot. Studies have revealed that rice cultivars with low levels of total

411   As in their grains had remarkably higher concentrations of PCs in roots compared to the

412   cultivars with high total As levels in their grains (Duan et al., 2011). In contrast, Batista et al.

413   (2014) found that PCs produced in rice cultivars in response to elevated levels of As exposure

414   did not necessarily reduce the total As concentrations in rice grains.

415

416   The translocation efficiency of organic As species from root to shoot is much higher than

417   that of inorganic As species (Raab et al., 2007). It could be attributed to the favorable

418   dissociation of MMA(V) and DMA(V) at cytoplasmic pH. Since MMA(V) is partly reduced

419   to MMA(III), only untransformed MMA(V) is transported to the shoots (Li et al., 2009). In

420   addition, the lack of DMA(V)-PC complexation enhances the DMA(V) to be readily moved

421   between root and shoots (Zhao et al., 2013b). Putative peptide transporter in rice, OsPTR7,

422 involve in the long-distance (root to grain) translocation of organic As species in rice. The

423 OsPTR7 transcript is more prevalent in the leaves, nodes, and roots at the flowering and grain

424 filling stage; however, during the seedling stage, OsPTR7 is more abundant in the shoots than

425 in the roots (Tang et al., 2017).

426

427 There have been no reports of volatile As species released by rice plants under typical

428 growing conditions. However, a large amount of volatile As is released from paddy soil due

429 to microbial activities. The volatilization of $(CH_3)_3As$ from rice plants grown in an axenic

430 system was detected when rice plants were treated with trimethylarsine oxide $((CH_3)_3AsO)$

431 but not with other inorganic or organic As species (Jia et al., 2012). A soil bacterium,

432 *Rhodopseudomonas palustris*, is found to have a direct influence on As volatilization. When

433 an *arsM* gene from *Rhodopseudomonas palustris* was expressed in rice, transgenic rice

434 produced volatile arsenicals (i.e., $(CH_3)_3As$) which were 10 times greater than that of the

435 control (Meng et al., 2011). Therefore, producing transgenic rice plants with *arsM* gene could

436 be adapted to mitigate the As burden in rice plants by achieving As volatilization out of the

437 rice crop.

438

439 3.4. Phloem and xylem - derived pathways of As species transport

440 A recent study by Ye et al. (2017) revealed that As(III) was the prevalent As species

441 (69%) in the phloem exudates of As(III)-exposed rice, while As(V) dominated (58%) in

442 As(V)-exposed rice and the remainder was As(III). When rice plants were treated with

443 MMA(V) and DMA(V), the major As species in phloem exudates were 55 and 59% of

444 MMA(V) and DMA(V), respectively. Interestingly, a large proportion of As(V) (45 and 41%,

445 respectively) was detected in the phloem exudates when rice was treated with MMA(V) and

446 DMA(V). This observation could correspond to the demethylation process; however, the

447 mechanisms underlying demethylation remain unclear.

448

449   Phloem transportation is likely to be responsible for 54, 56, 100, and 89% of As(III),

450 As(V), MMA(V), and DMA(V) transport into the rice grain, respectively. Organic As species

451 are more mobile than inorganic As species in the phloem as described by Ye et al. (2017).

452 This finding is similar to those of the study reported by Carey et al. (2010). However, Carey

453 et al. (2010) accounted the phloem transport to be responsible for 90 and 55% of

454 transportation of As(III) and DMA(V) to the grain, respectively. The difference in the above

455 two studies could be attributed to the experimental methods used. Stem girding, which blocks

456 phloem transportation, has reduced grain [73]As radioactivity by 97% compared to the

457 ungirdled control (Zhao et al., 2012). Therefore, it can be suggested that phloem acts as the

458 primary route of transport to rice grains for both inorganic and organic As species.

459 Transporters responsible for As species loading into the vascular tissues in rice plant are need

460 to be investigated in detail. Inositol transporters (INT) such as AtINT2 and AtINT4 are

461 associated with phloem loading of As(III) in *Arabidopsis thaliana* (Duan et al., 2016) and

462 similar transporters might responsible for phloem loading of As(III) transport in rice.

463

464   Synchrotron μX-ray fluorescence (μ-XRF) mapping has indicated that As(III) was

465 sequestrated in the phloem, top node, and internode, limiting As(III) loading into the rice

466 grain. The OsABCC transporter, which is expressed in the tonoplast of phloem in nodes,

467 enhances the transportation of As(III)-PC complexes to vacuoles (Song et al., 2014). The

468 knockout mutant of OsABCC has decreased the level of total As in nodes but has increased

469 the level of total As in grains. Therefore, it is likely that rice plants have evolved a

470 mechanism to minimize As loading into their grains.

There are only few reports discussing the transportation of As species through xylem in rice plants. Arsenic(III) is the prevalent form of As present in the xylem of *Pteris vittata* and *Cucumis sativus* (Mihucz et al., 2005; Su et al., 2008). The predominant As species in the xylem sap of rice is vary with water management practices. Ye et al. (2015) found that As(V), accounting for 64 - 88%, was the dominant form of As in the xylem sap of rice under aerobic treatment. In contrast, in the flooded treatment, the prevalent species in the xylem sap in rice was As(III), accounting for 26 - 77%, followed by As(V) (12 - 54 %) and DMA(V) (11 - 20 %) (Ye et al., 2015). Highly expressed Si pathway may load more As(III) into the xylem, in particular, in the flooded cultivation of rice.

3.5. Arsenic species loading into the grain

Arsenic species loading into rice grain is particularly important since it leads to the primary pathway of As exposure in human beings. From the available data, it is clear that there are significant site and genotype interactions on the distribution and concentration of As species in rice grains (Norton et al., 2009; Sommella et al., 2013). DMA(V) translocates from root to rice grain more efficiently (approximately 10-fold greater) compared to inorganic As species (Carey et al., 2010). As mentioned earlier, lack of complexation of DMA(V) may promote the efficient movement of DMA(V) in rice plants. The re-translocation of DMA(V) and MMA(V) from the flag leaf into the filling grain is more efficient than that of As(V) and As(III) which are not detectable even leaves were fed with As(III). The formation and subsequent sequestration of As(III)-PC complexes in rice leaves may restrict the As(III) from loading into the phloem and subsequent translocation to the rice grain (Zheng et al., 2011).

Synchrotron analysis has revealed a marked difference in the pattern of inorganic and organic As species loading into the grain. As(III) is mostly retained in the ovular vascular

496 trace (OVT) region, the vascular entry point into the rice grain and comprises of phloem and

497 xylem cells, whereas DMA(V) disperses throughout the outer layers and into the endosperm

498 (Carey et al., 2010). It is suggested that DMA(V) in the rice grain is derived from the re-

499 translocation of DMA(V) accumulated before flowering. In contrast, inorganic As species

500 mainly transport to the rice grain during flowering. In this respect, DMA(V) would

501 accumulate at considerable concentrations in the initial stage of grain filling and later is

502 diluted by carbohydrate filling to the grain (Zheng et al., 2011). This is exemplified by Carey

503 et al. (2012) that the direct shoot-to-grain translocation is during grain filling and not from

504 vegetative stores that is responsible for inorganic As in rice grains. Relatively higher As

505 concentrations in bran than in polished grain could be due to following reasons: firstly, the

506 bran acts as a physiological barrier for As translocation into the rice grain, secondly, As is

507 likely to be concentrated in the protein-rich tissues including embryo and aleurone layer. So

508 far, none of the studies has shown any effort towards the quantitative determination of As

509 species in different layers of the rice grain under different growing stages, water management

510 regimes, and with supplementation of nutrients and amendments in As-contaminated paddy

511 environment.

512

513 3.6. Translocation efficiency of arsenic species

514 The highest translocation efficiency (caryopsis-to-root) in rice was reported for DMA(V)

515 followed by MMA(V) and inorganic As species (Geng et al., 2017; Jia et al., 2012). The

516 order of translocation efficiency differs in various parts of the rice tissues. Dittmar et al.

517 (2010) showed that the straw to grain transfer factor declined exponentially with increasing

518 the concentration of total As in straw and eventually reached a constant value (~ 0.04). The

519 high yielding rice cultivars tend to have a high efficiency of translocation than the rice

520 cultivars with low yielding capacity (Bhattacharya et al., 2010; Zheng et al., 2011).

521   Regardless of the location and season, total As concentrations in rice tissues decreased in the

522   order: root >> shoot > straw > husk > grain (Table 2 and 3).

523

524   Agronomic practices greatly influence the speciation and accumulation and speciation of

525   As in rice grains. The dynamics of total As in rice grain under both flooded and non-flooded

526   conditions revealed that total As concentrations in rice grains were 10 - 15 times greater in

527   rice grown under flooded conditions than in rice grown under non-flooded conditions (Xu et

528   al., 2008). This is consistent with the study by Spanu et al. (2012) who showed that

529   intermittent irrigation has produced rice grains with 2.8 µg kg^{-1} of total As whereas the

530   corresponding figure for continuous flooding irrigation was 163 µg kg^{-1}. Correlation analysis

531   revealed that a significant positive correlation existed in total As concentrations between soil

532   pore water and rice grains. Similarly, studies have indicated that an increased level of soil As

533   lead to high level of total As in rice straw and grains (Dittmar et al., 2010; Hossain et al.,

534   2008). However, contradicting results have also been reported and these could be due to

535   various factors including irrigation intensity, underlying geology, weather conditions,

536   fertilizer applications, and diseases.

537

538   **4. Arsenic risk to rice plant and humans**

539   4.1. Impact on yield

540   Straighthead disease, in which the panicles remain upright due to lack of grain filling and

541   sterility, is most common in rice due to a high level of As exposure (Li et al., 2016). Both

542   chlorophyll a and b levels in rice leaves tend to decrease under As exposure and this may

543   adversely affect the photosynthesis (Rahman et al., 2007a). Increased level of As(V) in paddy

544   soil pore water negatively affects plant growth parameters including plant height, grain yield,

545   number of filled grains, and root biomass. Further, accumulation of As(V) and As(III)

546 enhances the production of reactive oxygen species (ROS) which damage macromolecules

547 and cell membranes (Finnegan and Chen, 2012). A recent study by Xu et al. (2017a)

548 demonstrated that As(III) binds with reduced cysteine residues in proteins, hence, influence

549 the catalytic functions. Moreover, the preferential translocation of DMA(V) into filial tissues

550 such as embryo, endosperm, and aleurone causes marked reduction in seed setting rate (i.e.,

551 spikelet sterility) and loss of yield (Wang et al., 2015). Rice cultivation in an environment

552 with minimal As level or As-tolerance rice cultivars are, therefore, an important aspect of

553 achieving the goal of sustainable production of rice in terms of quality and quantity.

554

555 4.2. Contribution of rice to arsenic intake in humans

556 Rice and rice-based products with high As concentrations may increase health risk for the

557 humans (Sandhi et al., 2017; Signes-Pastor et al., 2016). The level of total As and As species

558 in rice grains are depended on the rice genotype, physico-chemical, and environmental

559 interactions as summarized in Table 4. Arsenic-containing rice husks are used as cattle feed

560 in several countries (i.e., Bangladesh and China) and may act as an indirect pathway of As

561 exposure to humans through the food chain (Abedin et al., 2002). In addition, As in rice

562 grains leads to the loss of trace mineral nutrition such as Zn, Se, and Ni and amino acid

563 content (Dwivedi et al., 2010; Williams et al., 2009a). High levels of As in rice bran increases

564 the risk, particularly for children, and people on gluten-free products (Abedin et al., 2002).

565 Removing the bran layer during rice processing is an effective way to elimination of

566 inorganic As. However, from a nutritional point of view, removal of the bran results in a

567 substantial loss of nutrients in rice grains.

568

569 There have been many studies focusing on the risk assessment of human exposure to As.

570 For example, the lifetime cancer risk in West Bengal, India was found to be 7.62×10^{-4} which

571 exceed the United States Environmental Protection Agency (USEPA) threshold value of 10^{-4}

572 - 10^{-6} (Mondal and Polya, 2008). Dittmar et al. (2010) predicted that under current irrigation

573 practices in Bangladesh, total As concentration in rice grains would increase from ~ 0.15 to

574 0.25 - 0.58 mg kg^{-1} by 2050. This figure increases the human As intake by 1.5 - 3.8 fold

575 through rice. Therefore, precautionary measures must be undertaken to control the intake of

576 As from rice considering special attention to regions prone to As contamination.

577

578   5. Concluding remarks

579   Arsenic dynamics in paddy soil-water and rice grains are a function of geochemical,

580 microbial and plant genetic factors. The knowledge gained with respect to speciation,

581 mobility, and bioavailability of As in paddy soil-water, and subsequent uptake, efflux,

582 translocation, and sequestration of As is important to develop mitigation measures. Rice

583 production is required to be increased to meet the demand for ever-growing populations.

584 Therefore, there is an urgent need to adapt As mitigation measures in As-prone areas in the

585 world to reduce As burden. Firstly, the mobility and bioavailability of As in paddy-soil water

586 system could be decreased by using agronomical, physico-chemical, and biological

587 approaches. Alternative water management practices may play an important role in reducing

588 As mobility and bioavailability in paddy environment due to changes in redox chemistry.

589 Supplementation of fertilizer and soil amendments can lead to reducing the bioavailability of

590 As for rice plants. Optimum supplementation rates of fertilizer and soil amendments are

591 required to be investigated before introducing them to As-contaminated paddy lands.

592 Microorganisms are a key factor influencing As mobility and bioavailability in paddy soil-

593 water system through direct and indirect pathways. The kinetics of microbes-driven As

594 biotransformation and related rate limiting factors are needed be examined with respect to

595 different As-contaminated localities. Secondly, uptake and translocation of As species in rice

596   plant could be decreased by altering the expression of transporters associated with the uptake,

597   efflux, translocation, and sequestration of As. It is important to study in detail whether

598   changes in expression of transporters related to As metabolism are impact on the uptake and

599   translocation of other essential elements and compounds in rice plants.

600

601   Questions regarding the uptake and translocation of As species in rice plants remain

602   unanswered and must be the aim of future studies. These include the following: (1) the extent

603   of active and passive As uptake and translocation in rice, (2) a detailed survey of possible As

604   demethylation and volatilization mechanisms and identify related genes involving in As

605   demethylation and volatilization rice tissues, (3) the spatial distribution of As species and

606   temporal variations of their concentrations in rice grain at development stages in various rice

607   genotypes under different water management regimes and soil amendments, and (4)

608   determination of As-thiol complexes qualitatively and quantitatively in different rice cultivars

609   at different growing stages.

610

611   As-containing rice grains are a major source of As, particularly, for those consuming a

612   large amount of rice and rice-based products. The development of advanced technologies to

613   an in-situ measurement of As species and associated elements and genes at cellular and sub-

614   cellular levels in rice plants is significantly important to identify rice grains for safe

615   consumption. Therefore, scientific-based studies in As dynamics safeguard the paddy rice

616   ecosystems and human from the As burden.

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Table captions

Table 1

Key representative genes involved in As uptake, transport, and metabolism in rice plants.

Table 2

Arsenic concentration in irrigation water, soil and different plant tissues worldwide from field experiments.

Table 3

Arsenic speciation in different rice tissues from glasshouse experiments.

Table 4

Arsenic speciation in market-based rice in different countries.

Table 1

Key representative genes involved in As uptake, transport, and metabolism in rice plants.

Function	Gene category	Gene name	Reference
As(V) uptake by root, loading into the xylem, phloem, and grain	Phosphate transporters	OsPHT1;8 (OsPT8)	Wang et al. (2016b)
		OsPHT1;1	Kamiya et al. (2013)
As(III) uptake by root	Nodulin 26-like intrinsic proteins (NIPs)	OsNIP2;1 (Lsi1)	Ma et al. (2008)
		OsNIP2;2 (Lsi2)	
		OsNIP1;1	
		OsNIP3;1	
		OsNIP3;2	
		OsNIP3;3	
	Plasma membrane intrinsic proteins (PIPs)	OsPIP2;4	Chen et al. (2017a)
		OsPIP2;6	Katsuhara et al. (2014)

		OsPIP2;7	Mosa et al. (2012)
DMA(V) and MMA(V) uptake by root	Nodulin 26-like intrinsic proteins (NIPs)	OsNIP2;1 (Lsi1)	Li et al. (2009)
As(V) reduction to As(III) in root	As(V) reductase	OsHAC1;1	Shi et al. (2016a)
		OsHAC1;2	
		OsHAC4	Xu et al. (2017a)
As(III) efflux from root to the external environment	Nodulin 26-like intrinsic proteins (NIPs)	OsNIP2;2 (Lsi2)	Xu et al. (2017a)
As(III) complexation in root and phloem	ATP-binding cassette transporter	OsABCC1	Song et al. (2014)
DMA(V) loading into the xylem, phloem, leaves, and grain	Putative peptide transporter	OsPTR7	Tang et al. (2017)
As(III) loading into the xylem	Natural Resistance-Associated Macrophage Protein (NRAMP) transporter	OsNRAMP1	Tiwari et al. (2014)

Table 2

Arsenic concentration in irrigation water, soil and different plant tissues worldwide from field experiments.

Country	Rice variety	Irrigation water (μg L^{-1})	Total As (mg kg^{-1})					References
			Soil	Root	Straw	Husk	Grain	
Bangladesh	BR29	-	~15	-	1.7 (0.3 - 8.5)	-	0.17 (0.08 - 0.43)	Dittmar et al. (2010)
	-	68 - 136	11.41 - 61.04	-	0.571 - 1.916	0.380 - 0.995	0.182 - 0.436	Hossain et al. (2008)
	Boro and Aman	-	-	-	2.64 - 12.52	1.20 - 2.48	0.22 - 0.81	Khan et al. (2010a)
	-	5.1 - 77.4	9.8 - 13	-	2.1	-	0.23	Rahman et al. (2010)
	BRRI dhan28	70	14.5	46.3	1.7	-	0.6	Rahman et al. (2007b)
	BRRI hybrid dhan 1			51.9	1.9	-	0.7	

Country	Cultivar							Reference
Cambodia	-	-	0.8 - 18	-	-	-	0.2 (0.1 - 0.37)	Seyfferth et al. (2014)
China	Bollyou15	-	3 (0.1 - 45.9)	-	-	-	0.092 (0.005 - 0.309)	Fu et al. (2011)
	-	-	6 - 253	-	-	4.07	0.22	Williams et al. (2009b)
	-	-		-	-	-	0.62	Zhu et al. (2008)
	-	-	7.32 (2.5 - 19.2)	-	-	-	0.09 (0.02 - 0.18)	Jiang et al. (2014)
	-	110	17.9	98.9	3.9	1.2	0.7	Chou et al. (2014)
	F299	-	64.44 (52.49 -	196.27	10.08	2.01	0.43	Lei et al. (2013)

83.86)

Country	Variety							Reference
India	Red Minikit	50 - 70	1.34 - 14.09	9.10 - 22.71	1.35 - 2.08	0.49 - 1.11	0.17 - 0.57	Bhattacharya et al. (2010)
	Megi	-	-	6.18 - 19.44	0.55 - 1.73	0.27 - 0.87	0.11 - 0.43	
	-	-	19.4 - 41.24				1.6	Shrivastava et al. (2017)
	CNI1643-3	-	12.43	155	-	-	-	Dwivedi et al. (2010)
	IR68144-127						1.7	
	-	5.33 - 17.27	1.09 - 2.48	-	0.004 - 0.015	-	0.001 - 0.006	Vicky-Singh et al. (2010)
France	-	-	5 - 10	-	10.2 (1.5 - 20.6)	-	0.32 (0.12 - 0.61)	Williams et al. (2007)
Japan	Kirara 397	-	3[a]	-	-	-	0.121	Kuramata et al. (2011)
	Koshihikari						0.166	

Span	-	-	4 - 11	-	3.3 (0.8 - 9.8)	-	0.16 (0.06 - 0.29)	Williams et al. (2007)
Taiwan	Taigon 2	25 - 67	11.8 - 112	20.3 - 188	0.70 - 5.79	1.05 - 4.31	0.29 - 0.66	Hsu et al. (2012)
USA	-	-	2 - 4	-	0.7 (0.4 - 1.3)	-	0.13 (0.08 - 0.18)	Williams et al. (2007)

[a] - As concentration in soil solution

The range of total As concentrations is shown in parenthesis

Table 3

Arsenic speciation in different rice tissues from glasshouse experiments.

Rice genotype	Type of plant tissue	Total As (mg kg^{-1})	As species (mg kg^{-1})				Reference
			As(III)	As(V)	DMA(V)	MMA(V)	
Jiahua	Root	-	83.9	105.2	2.6	0.22	Jia et al. (2012)
	Shoot		4.39	1.29	0.42	0.008	
29 Japonica subspecies and 8 indica subspecies	Grain	0.163	-	-	-	-	Spanu et al. (2012)
-	Straw	0.7 - 13.4	-	-	-	-	Bogdan and Schenk (2008)
C039	Straw	25.77	-	-	-	-	Mei et al. (2009)

							Reference
	Grain	2.72					
Guanglua	Straw	25.13	-	-	-	-	
	Grain	2.28	-	-	-	-	
Azucena	Root	-	-	13	4.6	7.1	Raab et al. (2007)
	Shoot	-	-	2.5	4.0	1.1	
Bala	Root	-	-	26	8.9	18	
	Shoot			0.2	1.0	1.1	
BR11	Root	107.5	-	-	-	-	Abedin et al. (2002)
	Straw	91.5	-	-	-	-	
T116	Root	-	4.25	0.55	0.16	1.95	Geng et al. (2017)
	Stem	-	0.70	0.56	1.08	1.30	
	Grain	-	0.83	-	0.98	0.42	
Y2	Root	-	1.34	0.09	0.16	1.96	
	Stem	-	0.75	0.23	0.85	0.30	

	Grain	-	0.83	2.18	-	-	
Quest	Root	-	57 - 78[a]	16 - 27[a]	-	-	Smith et al. (2008)
	Shoot	-	32 - 63[a]	14 - 28[a]	-	-	
	Grain	-	1 - 6[a]	-	85 - 94[a]	-	
6 different genotypes	Grain	-	19.8 - 54.4[a]	-	45.6 - 80.2[a]	-	Syu et al. (2015)
Shatabdi	Grain	-	33 - 77[a,b]		23 - 67[a]	-	Khan et al. (2010b)
M-206	Bran	-		69 - 88[a]	12 - 3[a]	-	Seyfferth et al. (2011)
	Germ	-	20[a]	80[a]	-	-	

[a] - values are as percentages

[b] - sum of the As(III) and As(V)

Table 4

Arsenic speciation in market-based rice in different countries.

Country	Rice product	Number of samples	As species (µg kg^{-1})				Total As (µg kg^{-1})	Reference
			As(III)	As(V)	DMA(V)	MMA(V)		
Bangladesh	-	29	129	66	14	2	283	Halder et al. (2014)
			(3 - 402)	(7 - 570)	(0 - 53)	(0 - 3)	(28 -961)	
China	-	43	107.1	4.7	9.6	0.3	129.4	Ma et al. (2016)
			(44.5 - 197.7)	(0.0 - 23.8)	(1.4 - 30.6)	(0.0 - 2.8)	(50.2 - 253.0)	
Italy	-	61	91	8.2	55	-	162	Tenni et al. (2017)
Taiwan	White rice	51	61.6	4.3	12.1	2.7	116.6	Chen et al. (2016a)

Country	Rice type	N						Reference
Australia	Brown rice (whole, medium grain)	3		178[a] (156 - 200)	68 (65 - 71)	<dl	287 (290 - 284)	Rahman et al. (2014)
USA	White long grain	7		98[a] (62 - 134)	157 (85 - 229)	<dl	264 (85 - 344)	Heitkemper et al. (2009)
South Korea	Brown rice	30	80	5	30	2	-	Kim et al. (2013)
Nigeria	-	23		47[a]	11.5	0.33	58.8	Adeyemi et al. (2017)
Thailand	White rice	79	81.44 (14.29 - 153.73)	3.74 (<2.0 - 7.85)	29 (2.42 - 85.95)	<2 (<2.0 - 6.40)	139.48 (22.51 - 304.32)	Nookabkaew et al. (2013)
India	Red rice	-		50[a]	10	<dl	80	Williams et al. (2005)
Japan	Rice noodles	6		120[a]		20[b]	190	Sun et al. (2009a)
Japan	Rice	11		210[a]		70[b]	390	Sun et al. (2009a)

crackers

Country	Food type							Reference
UK	Rice cereals	30		75[a] (8 - 188)		45 (13 - 82)	1 (1 - 4)	-	Signes-Pastor et al. (2016)
UK	Baby rice	-		60[a]		30	-	120	Meharg et al. (2008)
Spain	Gluten-free infant rice	13		29 - 121[a]		10 - 198	-	46 - 315	Carbonell-Barrachina et al. (2012)
USA	Rice cereals	-	66		72	100	-	230	Juskelis et al. (2013)

a - sum of As(III) and As(V)

b - sum of DMA(V) and MMA(V)

dl - below the detection limit

The range of concentration for respective As species is shown in parenthesis
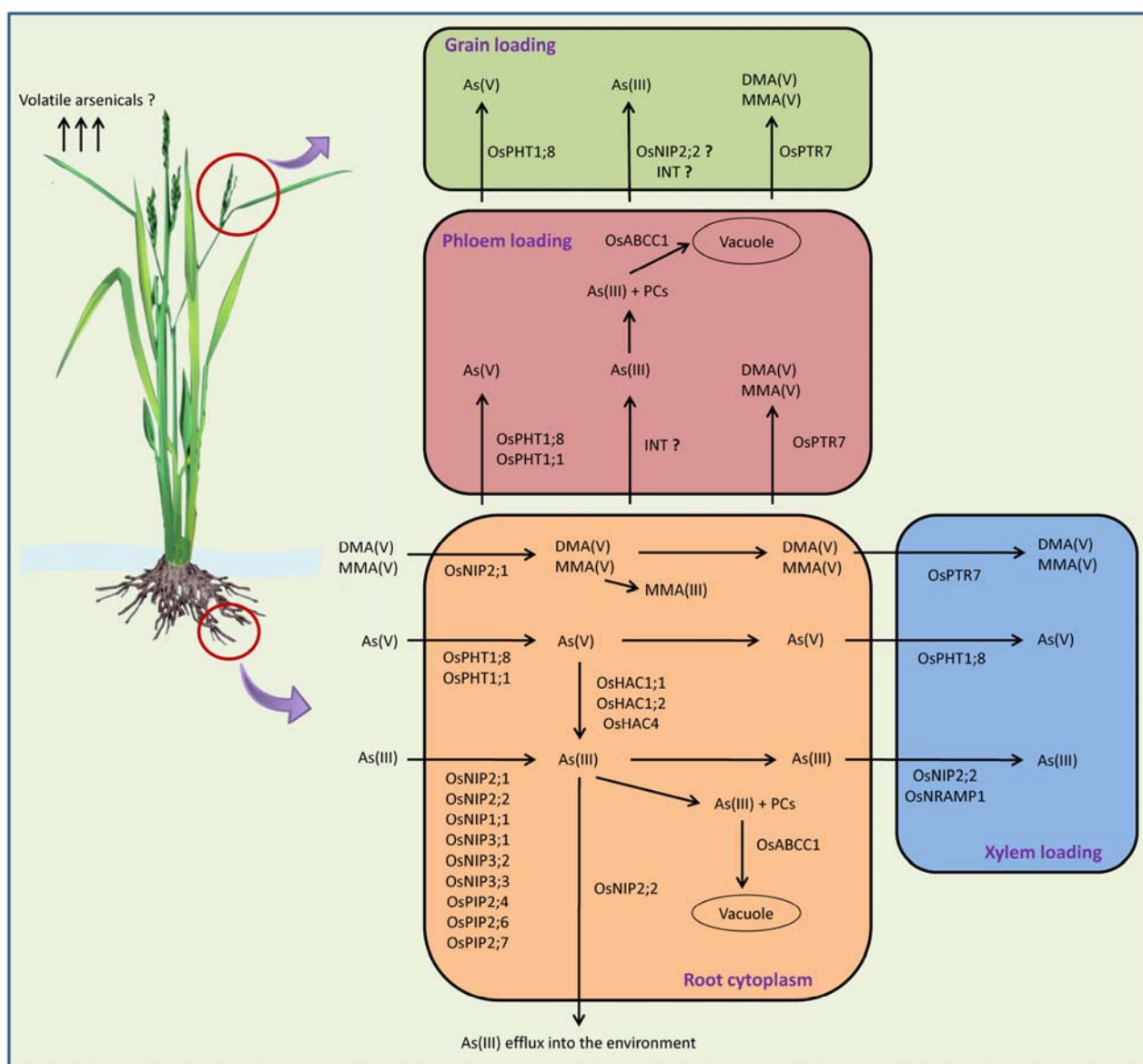
Figure captions

Fig. 1. Genes involving in inorganic and methylated As species uptake, transformation, and

localization in rice plant.

Fig. 1. Genes involving in inorganic and methylated As species uptake, transformation, and localization in rice plant.