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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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26 **ABSTRACT**

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

44

45 **Keywords:** Arsenic speciation, Arsenic transporters, Arsenic metabolism, Detoxification,
46 Grain filling, Arsenic toxicity

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49

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75 **1. Introduction**

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

88

89 Arsenic in the geological environment is mainly associated with sulfur (S) in minerals
90 such as arsenopyrites (FeAsS), realgar (As₄S₄), and orpiment (As₂S₃) (Majzlan et al., 2014).
91 Natural processes such as rock weathering, alluvial deposits may contribute As release into
92 the paddy environment (Bundschuh and Maity, 2015; Herath et al., 2016). Anthropogenic
93 activities (i.e., mining and use of As-contaminated groundwater in the form of irrigation
94 water) promote the accumulation of natural As in paddy ecosystems. Moreover, As-
95 containing insecticides, herbicides, feed additives, and wood preservatives are the potential
96 anthropogenic sources of As in rice ecosystems (Chen et al., 2016b; Zhao et al., 2009).

97

98 Natural soils typically contain 0.1 to 10 mg kg⁻¹ of total As (Zhao et al., 2010a). European
99 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 monomethylarsonic 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**

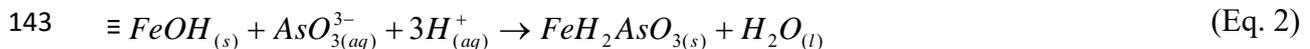
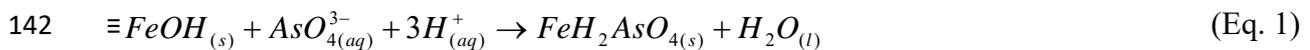
117 Paddy soils under conventional paddy management practices are subjected to flooded and
118 non-flooded conditions, during initial and final stages of the growth of rice, respectively. The
119 changes in water management regimes may alter redox potential (Eh) of the paddy soil-water
120 systems (Pan et al., 2014). During flooded conditions, water replaces the gaseous phase in the
121 soil matrix. A number of redox reactions (from high Eh (~ +700 mV) to low Eh (~ -300 mV):
122 reduction of Mn(IV), Fe(III), and SO₄²⁻, 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 O₂ 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

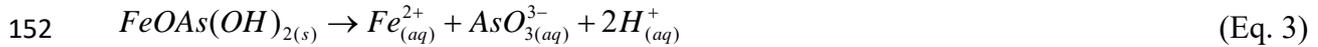


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145 Paddy soil consists of indigenous FeOOH including: ferrihydrite (Fe₅HO₈.4H₂O), goethite
146 (α -FeOOH), lepidocrocite (γ -FeOOH), and hematite (α -Fe₂O₃). Iron redox cycling (Fe(II)
147 oxidation and Fe(III) reduction) has a significant impact 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



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).

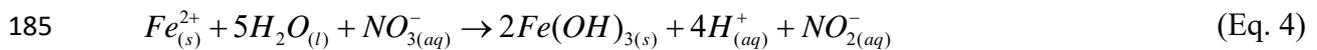
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159 Recent studies have demonstrated that amorphous Fe oxide-bound As has played an
160 important role in the sinking of As (Liu et al., 2015; Yu et al., 2016a). The conversion of
161 poorly crystalline ferrihydrite (surface area: 100 - 700 m² g⁻¹) to other crystalline Fe oxides
162 phases such as goethite (surface area: 8 - 200 m² g⁻¹) and hematite (2 - 115 m² 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

173 Nitrogen is one of the key nutrients, enhancing the growth of rice, and is supplied to paddy
 174 fields as N fertilizers (Ata-Ul-Karim et al., 2017). The process of Fe-redox cycling could be
 175 affected by nitrogen (N) cycling (i.e., nitrification, denitrification, and ammonification) (Yu
 176 et al., 2016b). The coupled NO_3^- reduction and Fe (II) oxidation may reduce the fate of As in
 177 the paddy environment (Li et al., 2012). Nitrate (NO_3^-)-dependent Fe(II)-oxidizing bacteria
 178 can promote the oxidation of Fe(II) under flooded conditions as shown in Eq. 4 (Sun et al.,
 179 2009b). As described above, the higher the level of Fe(III), the lower the concentration of
 180 bioavailable As in paddy soil-water. The reduction of Fe(III) could be inhibited by NO_3^-
 181 reduction because of their competition for electrons (Yu et al., 2016b). Therefore, high level
 182 of NO_3^- in paddy soil may decrease Fe(III) reduction and subsequent uptake and
 183 accumulation of As in rice tissues.

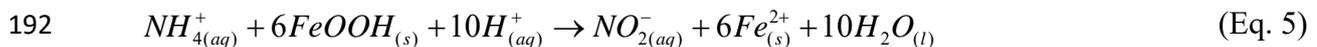
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186

187 Anammox-bacteria can drive the process of ammonia (NH_3) oxidation under anaerobic
 188 conditions. Ammonia oxidation is coupled with Fe(III) reduction as shown in Eq. 5 (Shrestha
 189 et al., 2009). However, the impact of NH_3 oxidation on Fe-redox cycling in paddy ecosystem
 190 remains unclear.

191



193

194 Organic fertilizer, added to keep paddy soil fertility, may influence As dynamics. Humic
 195 substances (i.e., humin, humic acid, and fulvic acid), which are key components of organic
 196 matter, have a positive and negative effect on the mobility and bioavailability of As (Jiang et
 197 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), sequestered in FeOOH, may reduce to
 203 highly mobile As(III).

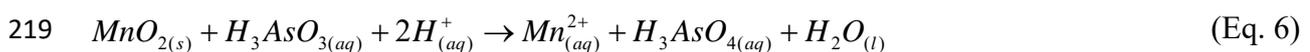
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205 Sulfate (SO_4^{2-}) in soil matrix is reduced to sulfide (S^{2-}) when decreasing redox potential
 206 from -120 to -180 mV (Sahrawat, 2015). Sulfate-reducing bacteria can promote the reduction
 207 of SO_4^{2-} in paddy environment (Das et al., 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



221

222 Bacteria, fungi, eukaryotic algae, and archaea, inhabiting in the rhizosphere, can influence
223 on the speciation of As through different biotransformation pathways: oxidation, reduction,
224 methylation, and volatilization (Jia et al., 2012). A variety of genes in microorganisms
225 encode for As-transformation enzymes and transporters. The process of microbial oxidation
226 of As(III), coded for by *aioA* gene, can lead to producing As(V) (Zhang et al., 2015). In
227 contrast, microbial As(V) reduction, coded for by *arsC* and *arrA* genes, may increase the
228 mobility of As, particularly, under flooded conditions (Malasarn et al., 2004; Qiao et al.,
229 2017; Villegas-Torres et al., 2011). Inorganic As species present in paddy ecosystems can be
230 transformed into organic As species such as MMA(V), monomethylarsonous acid
231 (MMA(III)), DMA(V), and dimethylarsinous acid (DMA(III)), and the process is coded for
232 by *arsM* gene. For this reason, organic As species found in paddy soil-water are likely to be
233 microbe-mediated products. Microorganisms can volatilize organic As to arsines, primarily as
234 trimethylarsines ((CH₃)₃As), with a smaller quantity of arsine (AsH₃), monomethylarsine
235 (CH₃AsH₂) and dimethylarsine ((CH₃)₂AsH) (Hayat et al., 2017; Jia et al., 2012). As a result,
236 microbes-driven As transformation may decrease the phytoavailability of As in paddy soil-
237 water systems. Moreover, microorganisms can indirectly impact on the speciation and
238 mobility of As by influencing Fe, N, and S cycling, as discussed above. Recent findings have
239 further revealed that soil amendments such as biochar may significantly affect the abundance
240 and diversity of microorganisms, and the consequent transformation of As (Qiao et al., 2017;
241 Qiao et al., 2018).

242

243 **3. Arsenic metabolism in rice plants**

244 Arsenic metabolism in different rice tissues is crucial for understanding uptake of
245 inorganic and organic As species, their translocation, and grain filling. There are different
246 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

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

303

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

316

317 Rice plants are an efficient Si accumulator and can contain Si in shoots about 10% of
318 shoot dry weight (Meharg and Meharg, 2015). In this regard, supplementation of Si fertilizers
319 to As-contaminated paddy soils may provide an effective strategy to minimize As(III) uptake
320 (Guo et al., 2007; Seyfferth and Fendorf, 2012). It has been reported that Si application to the
321 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 PO₄³⁻ share the same uptake
331 pathway (Muehe et al., 2014). In the rice genome, 13 PO₄³⁻ 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 PO₄³⁻ 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 PO₄³⁻ 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 PO₄³⁻
340 transporters which are mediating As(V) uptake. For example, PO₄³⁻ 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 $(\text{CH}_3)_3\text{As}$ from rice plants grown in an axenic
430 system was detected when rice plants were treated with trimethylarsine oxide ($(\text{CH}_3)_3\text{AsO}$)
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., $(\text{CH}_3)_3\text{As}$) 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 girdling, which blocks
456 phloem transportation, has reduced grain ⁷³As 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 μ X-ray fluorescence (μ -XRF) mapping has indicated that As(III) was
465 sequestered 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.

471 There are only few reports discussing the transportation of As species through xylem in
472 rice plants. Arsenic(III) is the prevalent form of As present in the xylem of *Pteris vittata* and
473 *Cucumis sativus* (Mihucz et al., 2005; Su et al., 2008). The predominant As species in the
474 xylem sap of rice is vary with water management practices. Ye et al. (2015) found that
475 As(V), accounting for 64 - 88%, was the dominant form of As in the xylem sap of rice under
476 aerobic treatment. In contrast, in the flooded treatment, the prevalent species in the xylem sap
477 in rice was As(III), accounting for 26 - 77%, followed by As(V) (12 - 54 %) and DMA(V)
478 (11 - 20 %) (Ye et al., 2015). Highly expressed Si pathway may load more As(III) into the
479 xylem, in particular, in the flooded cultivation of rice.

480

481 3.5. Arsenic species loading into the grain

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

493

494 Synchrotron analysis has revealed a marked difference in the pattern of inorganic and
495 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 $2.8 \mu\text{g kg}^{-1}$ of total As whereas the
530 corresponding figure for continuous flooding irrigation was $163 \mu\text{g kg}^{-1}$. 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 $0.25 - 0.58 \text{ mg kg}^{-1}$ 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 ($\mu\text{g L}^{-1}$)	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)
-	BRR1 dhan28	70	14.5	46.3	1.7	-	0.6	Rahman et al. (2007b)
-	BRR1 hybrid dhan	-	-	51.9	1.9	-	0.7	-

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

83.86)

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	- Vicky-Singh et al. (2010)
							0.006	
France	-	-	5 - 10	-	10.2	-	0.32	Williams et al. (2007)
					(1.5 - 20.6)		(0.12 - 0.61)	
Japan	Kirara 397	-	3 ^a	-	-	-	0.121	Kuramata et al. (2011)
	Koshihikari						0.166	

Spain	-	-	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)

	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 ($\mu\text{g kg}^{-1}$)				Total As ($\mu\text{g kg}^{-1}$)	Reference
			As(III)	As(V)	DMA(V)	MMA(V)		
Bangladesh	-	29	129 (3 - 402)	66 (7 - 570)	14 (0 - 53)	2 (0 - 3)	283 (28 - 961)	Halder et al. (2014)
China	-	43	107.1 (44.5 - 197.7)	4.7 (0.0 - 23.8)	9.6 (1.4 - 30.6)	0.3 (0.0 - 2.8)	129.4 (50.2 - 253.0)	Ma et al. (2016)
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)

Australia	Brown rice	3		178 ^a	68	<dl	287	Rahman et al. (2014)
	(whole, medium grain)			(156 - 200)	(65 - 71)		(290 - 284)	
USA	White long grain	7		98 ^a	157	<dl	264	Heitkemper et al. (2009)
				(62 - 134)	(85 - 229)		(85 - 344)	
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	3.74	29	<2	139.48	Nookabkaew et al. (2013)
			(14.29 - 153.73)	(<2.0 - 7.85)	(2.42 - 85.95)	(<2.0 - 6.40)	(22.51 - 304.32)	
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							
UK	Rice cereals	30	75 ^a		45	1	-	Signes-Pastor et al. (2016)
			(8 - 188)		(13 - 82)	(1 - 4)		
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.

