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# Aquatic Arsenic: Phytoremediation Using Floating Macrophytes

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23 **Abstract:**

24 Phytoremediation, a plant based green technology, has received increasing attention after the  
25 discovery of hyperaccumulating plants which are able to accumulate, translocate, and  
26 concentrate high amount of certain toxic elements in their above-ground/harvestable parts.  
27 Phytoremediation includes several processes namely, phytoextraction, phytodegradation,  
28 rhizofiltration, phytostabilization and phytovolatilization. Both terrestrial and aquatic plants have  
29 been tested to remediate contaminated soils and waters, respectively. A number of aquatic plant  
30 species have been investigated for the remediation of toxic contaminants such as As, Zn, Cd, Cu,  
31 Pb, Cr, Hg, etc. Arsenic, one of the deadly toxic elements, is widely distributed in the aquatic  
32 systems as a result of mineral dissolution from volcanic or sedimentary rocks as well as from the  
33 dilution of geothermal waters. In addition, the agricultural and industrial effluent discharges are  
34 also considered for arsenic contamination in natural waters. Some aquatic plants have been  
35 reported to accumulate high level of arsenic from contaminated water. Water hyacinth  
36 (*Eichhornia crassipes*), duckweeds (*Lemna gibba*, *L. minor*, *Spirodela polyrhiza*), water spinach  
37 (*Ipomoea aquatica*), water ferns (*Azolla caroliniana*, *Azolla filiculoides*, and *Azolla pinnata*),  
38 water cabbage (*Pistia stratiotes*), hydrilla (*Hydrilla verticillata*) and watercress (*Lepidium*  
39 *sativum*) have been studied to investigate their arsenic uptake ability and mechanisms, and to  
40 evaluate their potential in phytoremediation technology. It has been suggested that the aquatic  
41 macrophytes would be potential for arsenic phytoremediation, and this paper reviews up to date  
42 knowledge on arsenic phytoremediation by common aquatic macrophytes.

43

44 **Keywords:** Arsenic, Aquatic macrophyte, Phytoremediation

45

## 46 **1. Introduction:**

47 Arsenic is a member of the nitrogen family with both metallic and nonmetallic properties,  
48 and is ubiquitous in the environment (soil, water, air and also in living matters) (Tamaki and  
49 Frankenberger, 1992). It is the 20<sup>th</sup> abundant element in earth crust (Woolson, 1975), 22<sup>nd</sup> in  
50 seawater (Brown et al., 1991) and 12<sup>th</sup> in the human body (Mandal and Suzuki, 2002). It has  
51 been used in various fields such as medicine, electronics, agriculture (pesticides, herbicide,  
52 insecticides, fertilizer, etc.), livestock (cattle and sheep dips), and as wood preservatives since its  
53 isolation in 1250 A.D. (Mandal and Suzuki, 2002; Sharma and Sohn, 2009). It is now well  
54 recognized that consumption of arsenic, even at low levels, leads to carcinogenesis (Mandal and  
55 Suzuki, 2002). The toxicity and redistribution of arsenic in the environment make it evoking  
56 public concern.

57 Although the occurrence of arsenic in the environment is mainly from minerals and  
58 geogenic sources, human activities such as mining, burning of fossil fuels, use of arsenic  
59 containing chemicals in agriculture also cause arsenic distribution in the environment (Bissen  
60 and Frimmel, 2003). Indiscriminate use of arsenical pesticides during the early to mid-1900s led  
61 to an extensive contamination of soil (Smith et al., 1998).

62 Arsenic is rarely found as its native form because of its bonding affinity with other  
63 elements. In the environment, arsenic exists in four oxidation states- arsenate (As(V)), arsenite  
64 (As(III)), arsenic (As(0)), and arsine (As(-III)) (Sharma and Sohn, 2009). As(V) is the  
65 thermodynamically stable state of arsenic in oxic waters, while As(III) predominates in reduced  
66 redox conditions (Cullen and Reimer, 1989). In natural waters, the dominant inorganic arsenicals  
67 are incorporated into microorganisms such as phytoplankton, and are converted to  
68 methylarsenicals and/or more high order organoarsenicals such as arsenosugar (Maher, 1984). In

69 addition, the organoarsenicals are mineralized to inorganic- and methylarsenicals by bacteria  
70 ([Hanaoka et al., 1995](#); [Francesconi and Edmonds, 1996](#)). Arsenic compounds found in the  
71 aquatic and terrestrial environments are listed in [Table 1](#).

72 A large number of sites worldwide have been contaminated by arsenic from natural and  
73 anthropogenic sources ([Mandal and Suzuki, 2002](#)). Many countries, especially Taiwan,  
74 Argentina, India, Bangladesh, Mexico, Hungary, and Chile, have reported extensive arsenic  
75 contamination of their groundwater supplies ([Smedley et al., 2002](#); [Nikolaidis et al., 2004](#)). The  
76 range of arsenic in uncontaminated soil ranges from  $< 1$  to  $95 \text{ mg kg}^{-1}$ . The grand mean of soil  
77 arsenic is calculated to be  $8.7 \text{ mg kg}^{-1}$ . Elevated levels of arsenic in agricultural soil could pose a  
78 serious threat to plants and human health and the environment through the food chain pathways  
79 ([Bruce et al., 2003](#); [Duxbury et al., 2003](#)). Arsenic is toxic to living organisms at high  
80 concentration, and inorganic arsenicals are proven carcinogens to human ([Ng, 2005](#)). Arsenic  
81 toxicity depends on its speciation, and generally inorganic arsenic species are more toxic than  
82 those of organic species ([Meharg and Hartley-Whitaker, 2002](#); [Ng, 2005](#)). As(III) is more toxic  
83 than As(V), and dimethylarsinic acid (DMAA) and monomethylarsonic acid (MMAA) are more  
84 toxic than their parent compounds ([Petrick et al., 2000](#)).

85 Remediation of arsenic-contaminated soil and water is important concern. Various  
86 technologies are in place to clean up arsenic or to reduce arsenic exposure from contact with  
87 arsenic-contaminated soil and water. Technologies for remediation of arsenic-contaminated soil  
88 include excavation, immobilization, vetrification, soil washing/flushing and phytoremediation.  
89 Phytoremediation process includes phytoextraction, phytostabilization, phytovolatilization,  
90 phytotransformation, and rhizofiltration ([Table 2](#)). Treatment technologies, applicable for  
91 arsenic-contaminated water, consist of precipitation, membrane filtration, adsorption, ion

92 exchange, permeable reactive barriers and biological treatment. Researchers working with  
93 phytoremediation have come to realize that the development of this technology needs a thorough  
94 understanding of the underlying processes at the genetic, molecular, biochemical, physiological  
95 and agronomic levels. Therefore, some intensive researches have been done on arsenic uptake  
96 mechanisms in plants. Plants initially accumulate arsenic into their roots through phosphate  
97 uptake pathway, i.e., active apoplastic or symplastic mechanisms and translocate to the above  
98 ground parts (shoots and leaves). The amount of arsenic translocated from roots to shoots  
99 indicates the phytoremediation efficiency of that plant. However, more than 90% of total arsenic  
100 accumulated into the plant is stored in roots. Few plants have the ability to translocate high  
101 amount of arsenic from roots to shoots. Chinese brake fern (*Pteris vittata* L.) has shown the  
102 highest ability to accumulate and translocate arsenic from roots to shoots (Ma et al., 2001). The  
103 discovery of *P. vittata* L. was a milestone in arsenic phytoremediation research.

104

## 105 **2. Phytoremediation of toxic elements by aquatic macrophytes**

106 Freshwater as well as seawater resources are being contaminated by various toxic  
107 elements through anthropogenic activities and from natural sources. Therefore, remediation of  
108 contaminated aquatic environment is important as it is for terrestrial environment.  
109 Phytoremediation of the toxic contaminants can be readily achieved by aquatic macrophytes or  
110 by other floating plants since the process involves biosorption and bioaccumulation of the  
111 soluble and bioavailable contaminants from water (Brooks and Robinson, 1998). In aquatic  
112 phytoremediation systems, aquatic plants can be either floating on the water surface or  
113 submerged into the water. The floating aquatic hyperaccumulating plants absorb or accumulate  
114 contaminants by its roots while the submerged plants accumulate metals by their whole body.

115 Many years ago, Hutchinson (1975) reviewed the ability of aquatic macrophytes to  
116 concentrate elements from the aquatic environment and reported that the levels of potentially  
117 toxic elements in the plants were at least an order of magnitude higher than in the supporting  
118 aqueous medium. Later on, Outridge and Noller (1991) reviewed the hyperaccumulation of toxic  
119 trace elements by aquatic vascular plants and discussed about the pathways and rates of  
120 elemental uptake and excretion, environmental factors that control uptake of elements, and the  
121 significance of trace elements uptake for the field of wastewater treatment and biomonitoring of  
122 pollutants, which is of great interest for bioremediation of aquatic systems. By this time,  
123 considerable number of literatures have been published which described different aspects of  
124 biogeochemistry, mechanisms and uptake of toxic elements by a large number of aquatic  
125 macrophytes (Table 3) to develop effective phytoremediation technology. Several aquatic  
126 macrophytes and some other small aquatic floating plants have been investigated for the  
127 remediation of natural and wastewater contaminated with Cu(II), Cd(II) and Hg(II) (Sen and  
128 Mondal, 1987; Selvapathy and Sreedhar, 1991; Alam et al., 1995). *Microspora* and *Lemna minor*  
129 were studied for Pb and Ni remediation (Axtell et al., 2003). Five common aquatic plant species  
130 (*Typha latifolia*, *Myriophyllum exalbescens*, *Potamogeton epihydrus*, *Sparganium angustifolium*  
131 and *Sparganium multipedunculatum*) were tested for Al phytoremediation (Gallon et al., 2004).  
132 Parrot feather (*Myriophyllum aquaticum*), creeping primrose (*Ludwigina palustris*), and water  
133 mint (*Mentha aquatic*) have been reported to remove Fe, Zn, Cu, and Hg from contaminated  
134 water effectively (Kamal et al., 2004). The *L. minor* was reported to accumulate Cu and Cd from  
135 contaminated wastewater (Kara, 2004; Hou et al., 2007). The submerged aquatic plant  
136 *Myriophyllum spicatum* L. has been reported as an efficient plant species for the metal-  
137 contaminated industrial wastewater treatment (Lesage et al., 2007). The aquatic plants *Rorippa*

138 *nasturtium-aquaticum* (L.) and *Mentha* spp. accumulate arsenic from contaminated freshwater  
139 (Robinson et al., 2006). The encouraging results of previous studies regarding phytoremediation  
140 using aquatic plants gained the attention of researchers and scientists to continue studies in this  
141 field. In this review, previous works on phytoremediation of arsenic, one of the major and  
142 widespread contaminants, using aquatic macrophytes has been discussed.

143

### 144 **3. Phytoremediation of arsenic using aquatic macrophytes**

145 As(V) is the predominant species in the oxic water, and As(V) and As(III) are  
146 bioavailable forms for the aquatic plants (Sizova et al., 2002). The dynamics of As(V) exchange  
147 between water and adsorbing colloids are analogous to those of phosphate, though the  
148 competition for exchange sites favors phosphate over As(V) (Mkandawire et al., 2004a). Thus,  
149 aquatic macrophytes can be a good tool for the remediation of arsenic-contaminated aquatic  
150 systems, and some species of aquatic macrophytes have already been reported to accumulate a  
151 formidable amount of arsenic from water (Lee et al., 1991; Elayan, 1999; Robinson et al., 2003;  
152 Mkandawire et al., 2004a; Mkandawire et al., 2004b; Mkandawire and Dudel, 2005; Robinson et  
153 al., 2006; Rahman et al., 2007; Alvarado et al., 2008; Mishra et al., 2008; Tripathi et al., 2008;  
154 Zhang et al., 2008; Mirza et al., 2010). *Lemna gibba* L. and *L. minor* L. are the most studied  
155 species of Lemnaceae family in phytoremediation and ecotoxicology (Mkandawire et al., 2004a;  
156 Mkandawire et al., 2004b; Mkandawire and Dudel, 2005). Some other aquatic macrophytes, such  
157 as water hyacinth (*Eichhornia crassipes*) (Alvarado et al., 2008; Mishra et al., 2008), butterfly fern  
158 (*Salvinia natans* and *Salvinia minima*) (Hoffmann et al., 2004; Rahman et al., 2008c), lesser duckweed (*L.*  
159 *minor* L.) (Robinson et al., 2005; Alvarado et al., 2008; Mishra et al., 2008), greater duckweed (*Spirodela*  
160 *polyrhiza* L. and *Spirodela intermedia*) (Rahman et al., 2007; Mishra et al., 2008; Rahman et al., 2008b;



161 Rahman et al., 2008d), water spinach (*Ipomoea aquatica*) (Lee et al., 1991), esthwaite waterweed/hydrilla  
162 (*Hydrilla verticillata*) (Lee et al., 1991), mosquito fern/water velvet (*Azolla caroliniana*) (Zhang et al.,  
163 2008), water fern (*A. filiculoides* and *A. pinnata*) (Rahman et al., 2008a; Zhang et al., 2008), alligator  
164 weed (*Althernanthera philoxeroides*) (Elayan, 1999), water cabbage/water lettuce (*Pistia stratiotes*) (Lee  
165 et al., 1991; Odjegba and Fasidi, 2004), needle spikerush (*Eleocharis acicularis*) (Ha et al., 2009a),  
166 watercress (*Nasturtium officinale* (formerly *Rorippa nasturtium-aquaticum*), *Lepidium sativum* L.)  
167 (Robinson et al., 2003; Robinson et al., 2005), rigid hornwort (*Ceratophyllum demersum*) (Robinson et al.,  
168 2005), petries starwort (*Callitriche petriei*) (Robinson et al., 2005), waterweed/pondweed (*Elodea*  
169 *canadensis*) (Robinson et al., 2005), miriophyllum (*Myriophyllum propinquum*), Brazilian waterweed  
170 (*Veronica aquatica*) (Robinson et al., 2005), curly waterweed (*Lagarosiphon major*) (Robinson et al.,  
171 2005), water pepper (*Polygonum hydropiper*), have also been reported to uptake arsenic from water.

172

## 173 **4. Potential aquatic macrophytes for arsenic phytoremediation**

### 174 **4.1. Water hyacinth**

175 Water hyacinth is a free-floating perennial aquatic plant native to tropical and sub-  
176 tropical South America, and is now widespread in all tropic climates. The genus *Eichhornia*  
177 comprises seven species of water hyacinth among which *E. crassipes* is the most common and  
178 have been reported to grow very first. However, its enormous biomass production rate, high  
179 tolerance to pollution (Ebel et al., 2007), and absorption capacity of heavy-metal and nutrient  
180 qualify it for use in wastewater treatment (Ebel et al., 2007; Fang et al., 2007).

181 A comprehensive study on the arsenic removal from water by *E. crassipes* was performed  
182 by Alvarado et al. (2008), and the results showed that it had a removal rate of 600 mg arsenic ha<sup>-1</sup>  
183 d<sup>-1</sup> under field condition and a removal recovery of 18% under laboratory conditions. The

184 removal efficiency of water hyacinth was higher due to its high biomass production and  
185 favorable climatic conditions. [Mishra et al. \(2008\)](#) compared arsenic removal efficiency of *E.*  
186 *crassipes*, *L. minor* and *S. polyrhiza* from tropical opencast coalmine effluent and observed that  
187 *E. crassipes* had the highest removal efficiency (80%) compared to other aquatic macrophytes  
188 over a 25 d course. This was supposed to be due to faster growth rate ([Muramoto and Oki, 1983](#);  
189 [Kelley et al., 1999](#)), greater biomass production, and higher uptake ability of arsenic. Water  
190 hyacinth represents a reliable alternative for arsenic bioremediation in aquatic system even  
191 though the plant may cause severe water management problems because of its huge vegetative  
192 reproduction and high growth rate ([Giraldo and Garzon, 2002](#)). So, the use of water hyacinth in  
193 phytoremediation technology should be considered carefully.

194

## 195 **4.2. Duckweed**

196 Duckweeds are small free floating aquatic angiosperm plants which do not have distinct  
197 stems and leaves. The whole plant body is reduced to form a flat small leaf-like structure called  
198 frond. Duckweed family comprises of 4 genera, *Lemna*, *Spirodela*, *Wolffia*, and *Wolffiella*, and of  
199 34 species. Among these 4 genera, *Lemna*, *Spirodela*, and *Wolffia* have been reported to  
200 accumulate arsenic from water ([Mkandawire et al., 2004a](#); [Mkandawire et al., 2004b](#);  
201 [Mkandawire and Dudel, 2005](#); [Rahman et al., 2007](#); [Alvarado et al., 2008](#); [Rahman et al., 2008b](#);  
202 [Zhang et al., 2009](#)). [Mkandawire and Dudel \(2005\)](#) studied the bioaccumulation of arsenic in *L.*  
203 *gibba* L. both in field (tailing water) and at laboratory conditions. Results showed that samples  
204 from tailing water were approximately two-fold less than similar arsenic concentrations in  
205 laboratory solutions. This was because *L. gibba* in the surface mine water was exposed to arsenic  
206 for an undefined period, whereas samples used in laboratory trials were certified to contain a

207 below-detection amount of arsenic and were exposed to arsenic only for 21 d. However, the  
208 mean bioaccumulation coefficients for *L. gibba* were two-folds higher in the laboratory than in  
209 the field. In an arsenic removal efficiency study with *L. minor* L., [Alvarado et al. \(2008\)](#) found  
210 that the removal rate for *L. minor* was 140 mg arsenic ha<sup>-1</sup> d<sup>-1</sup> with a removal recovery of 5%.  
211 Mkandawire and Dudel ([2005](#)) also reported that arsenic accumulation in *L. gibba* L. was  
212 correlated negatively with phosphate concentrations ([Fig. 1](#)) because of the fact that As(V) is the  
213 dominant form of arsenic under oxic conditions and is an analogue of phosphate; they compete  
214 for the same uptake carriers in the plasmalemma.

215 Greater duckweed (*S. polyrhiza* L.) was tested for arsenic accumulation under laboratory  
216 conditions by Rahman et al. ([2007](#); [2008b](#)) to investigate arsenic uptake efficiency and  
217 mechanisms. Results showed that when *S. polyrhiza* L. accumulated higher amount of arsenic  
218 from As(V) solution compared to that from DMAA solution ([Fig. 2](#)). They also observed that  
219 As(V) uptake into *S. polyrhiza* L. was negatively correlated with phosphate uptake and positively  
220 correlated with iron uptake. The facts were explained by the competitive uptake inhibition of  
221 As(V) by phosphate and adsorptive affinity of As(V) on iron oxides of root surfaces. In contrast,  
222 DMAA uptake in *S. polyrhiza* L. was neither affected by phosphate nor correlated with iron  
223 ([Rahman et al., 2007](#)). Thus, it has been proposed that *S. polyrhiza* L. might use different  
224 mechanisms for As(V) and DMAA uptake. However, arsenic uptake ability of *S. polyrhiza* L.  
225 suggests that this macrophyte would be a good option for phytoremediation of contaminated  
226 water.

227 Arsenic accumulation, speciation and tolerance of the rootless duckweed *Wolffia globosa*  
228 and its potential for arsenic phytofiltration was investigated by Zhang et al. ([2009](#)). It was  
229 reported that the frond of *W. globosa* can accumulate >1000 mg arsenic kg<sup>-1</sup> dry weight (dw),

230 and can tolerate up to 400 mg arsenic  $\text{kg}^{-1}$  dw (Zhang et al., 2009). The higher uptake efficiency  
231 (2 to 10 times higher than other duckweed or *Azolla* species) (Fig. 3) and higher tolerance  
232 competence of *W. globosa* would place this aquatic plant potential for arsenic phytoremediation.

233

### 234 **4.3. Water fern (*Azolla*)**

235 Species of mosquito/water fern (*Azolla*) is a small, free-floating fern, and is widely  
236 distributed in paddy fields, rivers, ponds and lakes. It can fix nitrogen by its symbiotic  
237 partnership with *Anabaena* which resides in the dorsal cavity of *Azolla* fronds; for this reason  
238 *Azolla* has been used as a green manure to improve soil fertility and rice production (Wagner,  
239 1997). It has been reported that *Azolla* has a high capacity to accumulate toxic elements such as  
240 mercury, cadmium, chromium, copper, nickel and zinc (Sela et al., 1989; Rai, 2008; Rai and  
241 Tripathi, 2009), and can be used to remove contaminants from wastewater (Bennicelli et al.,  
242 2004; Arora and Saxena, 2005; Rakhshae et al., 2006).

243 Three species of water fern (*A. caroliniana*, *A. filiculoides* and *A. pinnata*) have been  
244 studied for arsenic uptake from water. Zhang et al. (2008) investigated arsenic uptake and  
245 tolerance of fifty strains of *Azolla* and found that arsenic concentrations in the fronds varied by  
246 13.5-fold (ranged between 29 and 397  $\text{mg kg}^{-1}$  dw) upon exposure to 50 mM As(V) solution for  
247 10 d. *A. caroliniana* showed the highest arsenic uptake potential in the frond (284  $\text{mg kg}^{-1}$  dw)  
248 followed by *A. microphylla*, *A. pinnata*, *A. maxicana*, and *A. filiculoides* (Fig. 3). Upon exposure  
249 to As(V), As(III), DMAA and MMAA, methylated species uptake was accounted for only 1–5%,  
250 while As(V) and As(III) were for about 50–60 and 25–40% of the total arsenic, respectively  
251 (Zhang et al., 2008). Rahman et al. (2008a) also reported higher arsenic concentrations in fronds  
252 of *A. pinnata* when As(V) and As(III) were the sources of arsenic in the culture solution. Results

253 revealed that the trends of arsenic uptake in *A. pinnata* was  $\text{As(V)} > \text{As(III)} > \text{DMAA} > \text{MMAA}$   
254 ([Rahman et al., 2008a](#); [Zhang et al., 2008](#)), which is consistent with uptake behavior of arsenic  
255 species by other aquatic macrophytes.

256

#### 257 **4.4. Butterfly fern (*Salvinia*)**

258 *Salvinia* is a free-floating aquatic macrophyte of Salviniaceae. Its wide distribution, faster  
259 growth rate and close relation with other water ferns, including *Azolla* and *Lemna*, make it  
260 potential for phytoremediation. A number of species of this aquatic plant have been studied for  
261 phytoremediation of toxic elements ([Banerjee and Sarker, 1997](#); [Espinoza-Quinones et al., 2005](#);  
262 [Sanchez-Galvan et al., 2008](#); [Dhir, 2009](#); [Wolff et al., 2009](#)). Only two species, *S. natans* and *S.*  
263 *minima*, have been investigated for arsenic remediation ([Hoffmann et al., 2004](#); [Rahman et al.,](#)  
264 [2008c](#)). Arsenic uptake kinetics of *S. minima* reveal that arsenic uptake was increased with  
265 increasing exposure time and arsenic concentration in the growth solution ([Hoffmann et al.,](#)  
266 [2004](#)). The increasing phosphate concentration decreased arsenic uptake in *S. minima* ([Hoffmann](#)  
267 [et al., 2004](#)), which is similar to that of other aquatic floating macrophytes.

268 Influence of phosphate and iron ions in selective uptake of arsenic species by *S. natans* L.  
269 was studied by [Rahman et al. \(2008c\)](#). Results showed that increasing phosphate concentration in  
270 culture solution decreased the arsenic uptake into the plant significantly, when the source of  
271 arsenic was As(V). On the other hand, arsenic uptake was not influenced by phosphate when the  
272 source was DMAA. Significant correlation was reported between arsenic and iron content in  
273 tissues of *S. natans* L. when the source was As(V), while the correlation was not significant  
274 when the source was DMAA ([Rahman et al., 2008c](#)). The results indicate that DMAA uptake

275 mechanisms into *S. natans* L. are deferent from those of As(V), which is also same for *S.*  
276 *polyrhiza* (Rahman et al., 2007).

277

#### 278 **4.5. Water lettuce (*P. stratiotes*)**

279 *Pistia* is a genus of aquatic plant in the family Araceae, comprising a single species, *P.*  
280 *stratiotes*, often called water cabbage or water lettuce. It floats on the surface of the water, and its  
281 roots hanging submersed beneath floating leaves. It is a common aquatic weed in the United  
282 States, particularly in Florida where it may clog waterways.

283 Although *P. stratiotes* mats degrade water quality by blocking the air-water interface,  
284 reducing oxygen levels in the water, and thus threatening aquatic life, it has been tested for metal  
285 remediation (Odjegba and Fasidi, 2004; Skinner et al., 2007), metal detoxification (Tewari et al.,  
286 2008), and treatment of urban sewage (Zimmels et al., 2006). Arsenic uptake by *P. stratiotes* has  
287 not been studied extensively. A field study carried out by Lee et al. (1991) reported that the  
288 average arsenic enrichment (bioaccumulation) factor of *P. stratiotes* was 8632 in roots and 2342  
289 in leaf. It appears that arsenic translocation in *P. stratiotes* was slow and most of the arsenic was  
290 strongly adsorbed onto root surfaces from solution. This agrees with the earlier findings that  
291 arsenic compounds are less readily translocated through the root system of aquatic plants.

292

#### 293 **4.6. Watercress**

294 Watercresses (*N. officinale*, *Nasturtium microphyllum* (formerly *R. nasturtium-aquaticum*,  
295 *R. microphylla*)) are fast-growing, aquatic/semi-aquatic, perennial plants native from Europe to  
296 central Asia, and one of the oldest known leaf vegetables consumed by human. Even though

297 watercresses are popular vegetable in many countries, they have been reported to accumulate  
298 toxic elements from water and soil.

299 Geothermal activity in the Taupo Volcanic Zone (TVZ), New Zealand, has resulted  
300 increase of arsenic levels in soil, and lake and river water of the regions. Some aquatic plants in  
301 the TVZ have been reported to accumulate inordinate amounts of arsenic (Robinson et al., 2003;  
302 Robinson et al., 2006). One of the species of watercress *L. sativum* is consumed as a vegetable,  
303 especially by the indigenous community in New Zealand, (Robinson et al., 2003). An average of  
304 29 and 16 mg kg<sup>-1</sup> of arsenic have been found in leaf and stem of *L. sativum* grown in the  
305 Waikato river, New Zealand, respectively (Robinson et al., 2003). High concentrations of arsenic  
306 have also been reported in *N. microphyllum* (up to 138 mg kg<sup>-1</sup> fresh wt) grown in TVZ, New  
307 Zealand (Robinson et al., 2006). Because of these higher levels arsenic in naturally grown *L.*  
308 *sativum* and *N. microphyllum* of Waikato River, New Zealand, it has been recommended that  
309 watercress from the Waikato River or other areas with elevated water arsenic concentrations  
310 might pose human health risk and should not consume (Robinson et al., 2003).

311 Greenhouse experiments also revealed that watercress reduced arsenic concentration in  
312 the solutions by 7.3% on average (Robinson et al., 2003). High arsenic uptake ability of *L.*  
313 *sativum* and *N. microphyllum* from water containing relatively low concentration of this element  
314 indicated their high bioaccumulation ability and therefore these plants may have potential for  
315 arsenic phytoremediation. Since watercresses are consumed as vegetable, these aquatic plants  
316 should carefully be used in arsenic phytoremediation.

317

#### 318 **4.7. Waterweed (*E. canadensis*) and Needle spikerush (*E. acicularis*)**

319 *E. canadensis* is a perennial aquatic submerge macrophyte native to North America. It  
320 grows rapidly in favorable conditions and can choke shallow ponds, canals, and the margins of  
321 some slow-flowing rivers. *E. canadensis* is also known as Canadian waterweed and have been  
322 studied for toxic element uptake. Another aquatic macrophyte, *E. acicularis* have been tested in  
323 laboratory and field conditions to assess its accumulation capability of antimony, arsenic, copper,  
324 and zinc, and thereby it's potential in phytoremediation (Ha et al., 2009a; Ha et al., 2009b; Ha et  
325 al., 2011). Results show that *E. acicularis* accumulates 6.4 mg arsenic kg<sup>-1</sup> dw after 10 d  
326 exposure to arsenic solution in laboratory conditions, and the removal rate of arsenic was 2.8 µg  
327 L<sup>-1</sup> d<sup>-1</sup> (Ha et al., 2009a). Ha et al. (2009b) also investigated the uptake ability of multiple heavy  
328 metals by aquatic macrophyte *E. acicularis* and its potential application for phytoremediation at  
329 an abandoned mining area in Hokkaido, Japan. The results indicated that *E. acicularis* showed  
330 great potential for the phytoremediation of mine tailing and drainage rich in heavy metals.

331

#### 332 **4.8. Esthwaite waterweed (*H. verticillata*)**

333 *Hydrilla* (esthwaite waterweed or hydrilla), which was first discovered in the United  
334 States in 1960, is an aquatic plant genus which consist of one species; *H. verticillata*, however,  
335 some botanists divide it into several species. It is native to the cool and warm waters in Asia,  
336 Europe, Africa and Australia, with a sparse, scattered distribution; in Europe, it is reported from  
337 Ireland, Great Britain, Germany, and the Baltic States, and in Australia from Northern Territory,  
338 Queensland, and New South Wales (Langeland, 1996; Thorne and Reveal, 2007). A highly  
339 specialized growth habit, physiological characteristics, and reproduction make this plant well  
340 adapted to life in submersed freshwater environments (Langeland, 1996).



341 *H. verticillata* has been tested for the uptake and remediation of arsenic, copper, lead,  
342 zinc and chromium from water (Lee et al., 1991; Elankumaran et al., 2003; Dixit and Dhote,  
343 2010). Elankumaran et al. (2003) reported bioabsorption of copper from wastewater by *H.*  
344 *verticillata*. Dixit and Dhote (2010) studied chromium, lead and zinc uptake in and  
345 morphological changes of *H. verticillata* and observed that this macrophyte uptake the metals on  
346 a dose response basis. They also showed that *H. verticillata* decreased chromium, lead and zinc  
347 concentrations by 72-80, 68-86 and 60-80% after 4 wk, respectively. But the plants die at higher  
348 concentrations ( $> 20 \text{ mg kg}^{-1}$ ) and longer period of exposure. Srivastava et al. (2006) investigated  
349 the responses of *H. verticillata* (L.f.) Royle to different concentrations of copper (0.1–25 M)  
350 upon a 1–7 d exposure. Results showed that the plant accumulated high amount of copper with a  
351 maximum of  $770 \text{ mg kg}^{-1} \text{ dw}$  when exposed to 25 M copper for 7 d. Thus, *H. verticillata* is  
352 would be a promising candidate for the phytoremediation of contaminated water. Lee et al.  
353 (1991) performed a systematic study on arsenic uptake by *H. verticillata* at laboratory condition.  
354 They also measured arsenic concentrations in field samples and found enrichment factor (EF)  
355 (also know as bioaccumulation factor) of 7106 (ranging between 1286 and 11141) for *H.*  
356 *verticillata*. The relatively high EF, reasonable size, ease identification and sampling, hardiness,  
357 relative abundance and common occurrence in the aquatic systems fulfill the criteria for *H.*  
358 *verticillata* to be an bioindicator of arsenic pollution in the aqueous ecosystem (Lee et al., 1991).  
359 Recently, Srivastava et al. (2010) investigated arsenic uptake and metabolism in *H. verticillata*  
360 and the results revealed that the accumulation of arsenic by the plant was dependant on both  
361 concentration of the metalloid in water and duration of exposure. It is evident that *H. verticillata*  
362 accumulates higher arsenic upon exposure to As(III) than to As(V) (Srivastava et al., 2010).  
363 Maximum arsenic accumulation of  $231 \text{ mg kg}^{-1} \text{ dw}$  was observed when the plants were exposed

364 to 10  $\mu\text{M}$  As(III) for 7 d and the accumulation was 121  $\text{mg kg}^{-1}$  dw when exposed to same  
365 concentration of As(V) for the same duration. Because of high arsenic uptake capability  
366 Srivastava et al. (2010) proposed *H. verticillata* as a promising aquatic plant for the  
367 phytoremediation of arsenic-contaminated water.

368 Laboratory studies reveal that arsenic uptake by *H. verticillata* is a function of the initial  
369 concentration of the element, and is inhibited at high phosphate concentration (Lee et al., 1991).  
370 Results showed that upon exposure to 0.4  $\text{mg kg}^{-1}$  As(V), 12 to 160  $\text{mg kg}^{-1}$  phosphate inhibited  
371 arsenic uptake in *H. verticillata* whereas 5  $\text{mg kg}^{-1}$  phosphate did not influence the uptake  
372 significantly. Arsenic uptake was almost completely inhibited by 160  $\text{mg kg}^{-1}$  phosphate. This  
373 might be due to the competitive uptake of phosphate and its chemical analogue As(V) in *H.*  
374 *verticillata*, and the same phenomenon has also been observed for other aquatic plants (Robinson  
375 et al., 2003; Mkandawire et al., 2004a; Rahman et al., 2008c, b). Arsenic accumulation in *H.*  
376 *verticillata* and the response of this plant to different concentrations of As(V) and As(III) were  
377 investigated by Srivastava et al. (2007; 2010). Results showed that arsenic accumulation was  
378 higher in plants exposed to As(III) compared to those plants exposed to As(V). *H. verticillata*  
379 was able to tolerate low concentrations of As(III) and As(V) by detoxifying the metalloid. In  
380 another study, Srivastava and D'Souza (2009) investigated the effect of sulfur (S) on arsenic  
381 accumulation in *H. verticillata*. Results showed that arsenic accumulation was about 2-fold  
382 higher upon exposure to either As(V) or As(III) in S-excess plants compared to that in S-  
383 sufficient and S-deficient plants.

384

## 385 **5. Mechanisms of arsenic uptake in aquatic macrophytes**

386 The inorganic forms (As(V) and As(III)) and the methylated forms (MMAA(V)) and  
387 DMAA(V)) are the main species of arsenic in natural water (Cullen and Reimer, 1989). Aquatic  
388 organisms, such as algae, reduce As(V) to As(III) and further biotransform to methylated  
389 arsenicals which results in the occurrence of thermodynamically unstable As(III) and  
390 methylarsenic compounds in natural water (Meharg and Hartley-Whitaker, 2002; Hellweger et  
391 al., 2003; Hellweger and Lall, 2004). The bulk of the total dissolved arsenic is inorganic arsenic  
392 in seawater (Peterson and Carpenter, 1983) and in freshwater (Seyler and Martin, 1989; Kuhn  
393 and Sigg, 1993). Although the predominant form of methylarsenicals is consistently DMAA(V)  
394 followed by MMAA(V), the existence of trivalent methylarsenic species in the environment has  
395 also been reported (Hasegawa et al., 1994; Hasegawa, 1996; Sohrin et al., 1997).

396 Arsenic uptake mechanisms in terrestrial hyperaccumulating plants have been studied and  
397 reported in a number of literatures (Asher and Reay, 1979; Meharg and Hartley-Whitaker, 2002;  
398 Tripathi et al., 2007; Zhang et al., 2009; Zhao et al., 2009). However, three mechanisms have  
399 been proposed for the uptake of arsenic species in aquatic macrophytes- i) active uptake through  
400 phosphate uptake transporters, ii) passive uptake through aquaglyceroporins, and iii)  
401 physicochemical adsorption on root surfaces. Plants mainly uptake As(V) through phosphate  
402 uptake transporters (Tripathi et al., 2007; Zhao et al., 2009), however, physicochemical  
403 adsorption on root surfaces has also been supposed to be an alternative uptake pathway for this  
404 arsenic species (Robinson et al., 2006; Rahman et al., 2008b). As(III), DMAA and MMAA gets  
405 into the plants by passive mechanism through the aquaglyceroporin channels (Zhao et al., 2009;  
406 Rahman et al., 2011).

407

## 408 **5.1. Active uptake through phosphate uptake transporters**

409 As(V) and phosphate are chemical analogs, and compete for uptake carriers in the  
410 plasmalemma (Mkandawire et al., 2004a). Therefore, more As(V) is expected to be desorbed in  
411 the solution with the increase phosphate concentration (Smith and Read, 2008). Plants uptake  
412 As(V) through phosphate transporters (Tripathi et al., 2007; Zhao et al., 2009) (Fig. 4). The  
413 aquatic plants also use the same mechanisms for the uptake of arsenic species. Mkandawire and  
414 Dudel (2005) and Rahman et al. (2007) showed that *L. gibba* L. and *S. polyrhiza* L. uptake As(V)  
415 through the phosphate uptake pathway.

416

## 417 **5.2. Passive uptake through aquaporins/aquaglyceroporins**

418 Although the exact uptake mechanisms for As(III) and organoarsenicals (DMAA and  
419 MMAA) in higher plants have not been identified, physiological studies suggest that these  
420 arsenic species are transported in rice by passive uptake mechanisms through  
421 aquaporins/aquaglyceroporins (Abedin et al., 2002; Meharg and Jardine, 2003; Rahman et al.,  
422 2011). A recent molecular study explained more clearly that As(III) is transported into rice roots  
423 by nodulin26-like intrinsic membrane proteins (NIPs), one of the major subfamilies of  
424 aquaporins transporter that facilitates the transport of neutral molecules such as water, glycerol,  
425 and urea (Ma et al., 2008). Aquaporins and aquaglyceroporins are two of three subfamilies of  
426 water channel proteins (WCPs), the transmembrane proteins that have a specific three-  
427 dimensional structure with a pore that permeates water molecules (Benga, 2009), which are  
428 permeable to water, glycerol, and/or other small, neutral molecules. The competition between  
429 glycerol and As(III) for uptake into rice (*Oryza sativa* L.) reveal that this arsenic species is  
430 transported across the plasma membrane through aquaporins/ aquaglyceroporins (Meharg and  
431 Jardine, 2003). A recent study also showed that glycerol inhibited DMAA and MMAA uptake in

432 rice roots significantly ( $p \leq 0.0001$  and  $0.0077$  for DMAA and MMAA, respectively) in a  
433 concentration-dependant manner (Rahman et al., 2011). Since rice is an aquatic/wetland plant, it  
434 can be elucidated from the above discussion that aquatic macrophytes may also uptake As(III),  
435 DMAA, and MMAA by passive uptake mechanisms through aquaporins/aquaglyceroporins (Fig.  
436 4).

437

### 438 **5.3. Physicochemical adsorption on root surfaces**

439 Physicochemical adsorption, an alternative mechanism for As(V) accumulation into  
440 aquatic plants, has been proposed by Robinson et al. (2006). In this mechanism, suspended  
441 oxides of iron (Fe-plaque) on the aquatic plant surfaces adsorb and accumulate arsenic. Robinson  
442 et al. (2006) observed positive correlation between arsenic and iron concentrations in aquatic  
443 plants, which is supposed to be for the adsorption of arsenic on iron oxides on plant surfaces. But,  
444 which species of arsenic was mostly adsorbed by iron oxides was not clear from their studies.  
445 Rahman et al. (2008b) studied the adsorption of arsenic species on precipitated iron oxides on  
446 roots/fronds of *S. polyrhiza* L. and found significant correlation between arsenic and iron  
447 concentrations in tissues when the plant was exposed to As(V). There was no correlation  
448 between arsenic and iron in plant tissue when *S. polyrhiza* L. was exposed to As(III), DMAA,  
449 and MMAA. Results reveal that As(V) is predominantly adsorbed on precipitated iron oxides on  
450 the roots of aquatic plants and accumulated by physicochemical adsorption mechanism. Rahman  
451 et al. (2008b) also observed that upon exposure to As(V), arsenic and iron concentrations in *S.*  
452 *polyrhiza* L. were highly correlated in phosphate-deficient condition, while they were not  
453 significantly correlated in phosphate-sufficient condition. This can be attributed to the high

454 adsorption of arsenic on iron plaque of the plant surfaces in phosphate-deficient solution, which  
455 was blocked by phosphate in phosphate-sufficient solution.

456

## 457 **6. Arsenic metabolism and detoxification in aquatic macrophytes**

458 Arsenic exists predominantly as As(V) in oxic condition and as As(III) in reduced  
459 condition (Zhao et al., 2009). As(V) shares the same transporter with phosphate in plants while  
460 As(III) gets into the plant cells through aquaporins of NIPs (Zhao et al., 2009; Srivastava et al.,  
461 2010). These two forms of arsenic induce differential biochemical responses in aquatic plants  
462 because of their dissimilar chemical properties (Srivastava et al., 2007). As(V) does not bind to  
463 thiol ligands whereas As(III) has high binding affinity to sulphhydryl (-SH) groups of peptides  
464 such as glutathione (GSH) and phytochelatins (PCs) (Raab et al., 2007; Zhao et al., 2009).  
465 Arsenic speciation in plant tissues shows that arsenic is predominantly present in the As(III)  
466 oxidation state, even though plants had been exposed to As(V). This means that, following  
467 uptake, As(V) is reduced to As(III) in plant cells efficiently, and that most plants have high  
468 competence for As(V) reduction (Zhao et al., 2009). The reduction of As(V) to As(III) is  
469 mediated by GSH (Delnomdedieu et al., 1994) and by enzyme (Bleeker et al., 2006), which is  
470 thought to be a detoxification mechanism of the plants. Upon uptake, As(V) and As(III) have  
471 been reported to produce reactive oxygen species (ROS) inside the cells (Meharg and Hartley-  
472 Whitaker, 2002), and plants control the production of ROS by various enzymes and cellular  
473 compounds (Mittler, 2002). The GSH can act as an antioxidant and is required for the synthesis  
474 of metalloid chelating ligands, the PCs (Srivastava et al., 2007). Schmoeger et al. (2000) reported  
475 rapid induction of PCs biosynthesis in cell suspension cultures of *Rauvolfia serpentina*, in  
476 seedlings of *Arabidopsis*, and in enzyme preparations of *Silene vulgaris* upon exposure to As(III)

477 and As(V). Others (Raab et al., 2005; Raab et al., 2007) also identified a number of As(III)-GSH  
478 and As(III)-PCs complexes in sunflower (*Helianthus annuus*), which are subsequently  
479 sequestered in the vacuoles and excreted from the cell.

480 Recently, arsenic accumulation and detoxification in aquatic plant *H. verticillata* have  
481 been investigated by Srivastava and D'Souza (2009) and by others (Srivastava et al., 2007;  
482 Srivastava et al., 2010). Arsenic detoxification mechanisms in aquatic plants seems to be as same  
483 as in the terrestrial plants. Upon exposure to either As(III) or As(V), *H. verticillata* increased the  
484 synthesis of thiols such as PCs, and increased antioxidant enzyme activity (Srivastava et al.,  
485 2007). Although the levels of thiolic compounds (such as NP-SH, cysteine, GSH, and oxidized  
486 glutathione (GSSG)) in *H. verticillata* were increased significantly upon exposure to both As(III)  
487 and As(V) (Srivastava et al., 2007), As(III) was found to induce the activities of cysteine  
488 synthase and  $\gamma$ -glutamylcysteine synthetase and the amount of cysteine and GSH to higher levels  
489 than that of As(V) (Srivastava et al., 2010). The analysis of PCs revealed that the accumulation  
490 of PC<sub>1</sub> and PC<sub>2</sub> in *H. verticillata* was increased with the increase of both As(III) and As(V)  
491 concentrations (Srivastava et al., 2007). Thus, phytochelatins and antioxidant systems in *H.*  
492 *verticillata* respond differentially during As(III) and As(V) stress which is thought to be the  
493 detoxification mechanism of the plant.

494

## 495 **7. Management and treatment of phytoremediating aquatic macrophytes**

496 With increasing interest about the phytoremediation of arsenic contaminated water by  
497 hyperaccumulating aquatic plants and the promising economic and environmental prospects of  
498 this technology, the eventual fate of those plants with high arsenic burden will be a vital issue in  
499 the future. Although a number of field studies as well as laboratory experiments have shown that

500 some aquatic plants are potential for arsenic accumulation and would be used for  
501 phytoremediation of arsenic contaminated water, large scale implementation of this technology  
502 has not been reported yet. With large scale implementation of this technology, management and  
503 disposal of the huge amount of phytoremediating plants with high arsenic content will be an  
504 important concern. If the phytoremediating plants will not be disposed properly, those plants  
505 might be another source of arsenic contamination in the environment. Up to date, studies about  
506 the management and disposal of arsenic phytoremediating aquatic plants are inadequate. Without  
507 proper management and disposal of the phytoremediating plants with high arsenic content, only  
508 the accumulation and removal of the metalloid from water by aquatic plants would not be  
509 enough for the successful implementation of this emerging technology. There may be some  
510 processes for the disposal of high arsenic burden aquatic plants, but it is difficult to elucidate if  
511 this would be economically and environmentally feasible or not.

512

### 513 **7.1. Carbonization and incineration**

514 The high arsenic content aquatic plants may be used for the making charcoal and the by-  
515 product gas can be used as fuel. Previously water hyacinth has been used in this purpose  
516 ([Thomas and Eden, 1990](#)). There are two problems in using the aquatic phytoremediating plants  
517 for making charcoal. First, there is a need to reduce the water content, and second the ash content  
518 of air-dried water is too high (for example, 40% for water hyacinth ([Thomas and Eden, 1990](#))) to  
519 get a good fuel as an end product. The high investments and technological level necessary also  
520 make carbonization.

521 Incineration of the hyperaccumulating plants would be one option. Sun drying and direct  
522 burning of water hyacinth is used on a small scale in certain parts of the world to use the ash as



523 fertilizer (Gunnarsson and Petersen, 2007). Fresh aquatic plants have high moisture content and  
524 therefore, it may take longer time for drying. In addition, there is no evidence whether arsenic is  
525 completely vanished after burning the plants. Incineration of the plants with high arsenic content  
526 may also be a source of arsenic emission in the air. It has been reported that burning high  
527 arsenic-containing coal is one of the major sources of arsenic exposure (10-20% of the total  
528 arsenic exposure) for the population of Guizhou, China (Liu et al., 2002). Another study also  
529 revealed that burning coal with high arsenic content increased arsenic content in hair, urine, and  
530 blood in children residing in polluted area (Bencko and Symon, 1977). So, burning arsenic  
531 hyperaccumulating aquatic plants would not be environmentally safe, and would be hazardous  
532 for human health.

533

## 534 **7.2. Hydrolysis and fermentation**

535 Liquid fuel, such as ethanol, may be produced from phytoremediating aquatic plants by  
536 hydrolysis together with fermentation which would make aquatic plants a good substrate.  
537 Hydrolysis and fermentation also require yeast fermentable sugars that may available only to a  
538 very low extent in aquatic phytoremediating plants. Some kind of pre-treatment is, therefore,  
539 needed to make the sugar more easily available for chemical hydrolysis (Gunnarsson and  
540 Petersen, 2007). The pre-treatment requires a relatively high temperature, strong acids and  
541 pressurized reactors. Thomas and Eden (1990) conclude that hydrolysis of water hyacinths to  
542 produce fuel is only feasible in situations where there is a high need for ethanol as a liquid fuel  
543 because of the negative energy balance. Even it is economically feasible to produce fuel from  
544 phytoremediating aquatic plants, arsenic content in bye-product sludge and its recontamination  
545 possibility should be tested.

546

### 547 **7.3. Briquetting**

548 Briquettes have been widely sold commercially for cooking food. Briquetting would be a  
549 good option for the treatment of the phytoremediating aquatic plants. Thomas and Eden (1990)  
550 reported briquetting as a possible treatment of water hyacinth. The briquettes are made by sun-  
551 drying the water hyacinth for a few days, disintegrating, screening and chopping the dried water  
552 hyacinths to pieces about 6 mm long. The shredded water hyacinth can then be compressed into  
553 briquettes or pellets. The material resulting after briquetting water hyacinth has an energy density  
554 of 8.3 GJ m<sup>-3</sup>, which is comparable to charcoal which has 9.6 GJ/m<sup>3</sup> (Thomas and Eden, 1990;  
555 Gunnarsson and Petersen, 2007).

556

### 557 **7.4. Anaerobic digestion and production of biogas**

558 Anaerobic digestion is a biological process by which organic matter is degraded in the  
559 absence of oxygen and biogas is produced as a by-product. The gas can be used directly for  
560 cooking, heating or production of electricity. Biogas has very useful by-products and positive  
561 impacts on public health and pollution. This, together with the growing shortage of firewood and  
562 rising cost of fossil fuels, has made anaerobic digestion increasingly demanding. These  
563 advantages of the process might make it well suited for use in developing countries (Gunnarsson  
564 and Petersen, 2007). Aquatic plants, such as water hyacinths, can be degraded easily, and give  
565 quite a high gas yield (Gunnerson and Stuckey, 1986).

566 Biogas production from phytoremediation biomass would be a viable, interesting and  
567 environmentally sound idea for phytoremediating aquatic plant management. Chanakya et al.  
568 (1993) found that water hyacinth has a high content of fermentable matter and therefore a high

569 potential for biogas production. However, there are some limitations in biogas production from  
570 water hyacinth. The high lignin content can reduce the actual production and the low bulk  
571 density could result in large voids with poor compaction and low feed rates (Chanakya et al.,  
572 1993). The use of crop residue and aquatic weeds has been tested for biogas production by El-  
573 Shinnawi et al. (1989). They mixed rice straw, maize stalks, cotton stalks and water hyacinths  
574 with cow dung and were digested in different containers. The mixture of water hyacinth and cow  
575 dung was found to produce more biogas per kg organic matter than that of maize and cotton  
576 stalks, but the total biogas production per kilogram dry matter added was lower for the water  
577 hyacinths. The low values for total gas production was probably mostly due to the high lignin  
578 content and low percentage of volatile solids in the water hyacinths (Chanakya et al., 1993;  
579 Gunnarsson and Petersen, 2007). Gunnarsson and Petersen (2007) showed that water hyacinths  
580 can compete well with any kind of animal manure as a substrate for biogas production.

581 Singhal and Rai (2003) studied the use of water hyacinth and channel grass, used for  
582 phytoremediation of industrial effluents, in biogas production. Although extensive studies have  
583 not been done on this subject, there is a good possibility to use phytoremediation plants in biogas  
584 production. But arsenic content and speciation in sludge from the anaerobic digestion should be  
585 investigated to prevent its redistribution in the environment.

586

## 587 **8. Conclusions:**

588 Increasing use of arsenic-contaminated underground water for agricultural purposes  
589 (irrigation in rice and other crop fields) in the arsenic affected areas, especially in Bangladesh  
590 and West Bengal (India), results in the increased concentration of arsenic in freshwater systems.  
591 Arsenic contamination in freshwater systems poses health threat not only to the aquatic

592 organisms but also to the humans. High level of arsenic have been reported in a number of  
593 aquatic plants grown in contaminated water bodies (rivers and lakes) which are consumed as  
594 vegetable in many countries (Robinson et al., 2006). A number of studies revealed that humans  
595 are exposed to arsenic poisoning not only from contaminated drinking water but also from food  
596 items grown in and collected from arsenic contaminated sites. Therefore, remediation of arsenic  
597 contaminated aquatic systems is important for human health.

598         Phytoremediation of contaminated water by aquatic macrophytes would be a good option  
599 in long term. A large number of aquatic plant species have been tested for the remediation of  
600 toxic elements from fresh water systems. Few aquatic plants (mostly macrophytes) have shown  
601 the ability to accumulate high level of arsenic from water. Among those aquatic plants, water  
602 hyacinth (*E. crassipes*), duckweed (*Lemna*, *Spirodela*, and *Wolffia*), water fern (*Azolla* spp.),  
603 Hydrilla (*H. verticillata*), and watercresses (*N. officinale*, *N. microphyllum*) have been proposed  
604 to be potential for phytoremediation due to their arsenic hyperaccumulation ability and growth  
605 habit. A number of studies revealed that phytoremediation of arsenic using aquatic macrophytes  
606 would be a good option to clean polluted water. Even though a number of aquatic plants have  
607 been shown high arsenic uptake and suggested to be effective for arsenic phytoremediation, the  
608 management and disposal of those phytoremediating aquatic macrophytes is a major concern for  
609 the successful implementation of phytoremediation technology.

610

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614

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1049 **Table 1:** Important inorganic, organic, and biological forms of arsenic in the environments

Name	Abbreviation	Formula/Structure	Reference
<b>Inorganic arsenicals</b>			
Arsine	As(-III)	AsH <sub>3</sub>	*
Arsenious acid or arsenite	As(III)	As <sup>3+</sup> (OH) <sub>3</sub>	*, **
Arsenic acid or arsenate	As(V)	H <sub>3</sub> As <sup>5+</sup> O <sub>4</sub>	*, **
<b>Methylarsenicals</b>			
Methylarsine	-	AsH <sub>2</sub> CH <sub>3</sub>	*, **
Dimethylarsine	-	AsH(CH <sub>3</sub> ) <sub>2</sub>	*, **
Trimethylarsine	-	As(CH <sub>3</sub> ) <sub>3</sub>	*, **
Monomethylarsonous acid	MMAA(III)	As(OH) <sub>2</sub> CH <sub>3</sub>	*, **
Dimethylarsinous acid	DMAA(III)	As(OH)(CH <sub>3</sub> ) <sub>2</sub>	*, **
Monomethylarsonic acid	MMAA(V)	AsO(OH) <sub>2</sub> CH <sub>3</sub>	*, **
Dimethylarsinic acid	DMAA(V)	AsO(OH)(CH <sub>3</sub> ) <sub>2</sub>	*, **
Trimethylarsine oxide	TMAO	AsO(CH <sub>3</sub> ) <sub>3</sub>	*, **
Tetramethylarsonium ion	TMA <sup>+</sup>	As <sup>+</sup> (CH <sub>3</sub> ) <sub>4</sub>	***
<b>Organoarsenicals</b>			
Arsenocholine	AsC	(CH <sub>3</sub> ) <sub>3</sub> As <sup>+</sup> CH <sub>2</sub> CH <sub>2</sub> O	**
Arsenobetaine	AsB	(CH <sub>3</sub> ) <sub>3</sub> As <sup>+</sup> CH <sub>2</sub> COO <sup>-</sup>	**
Rosarsone	-	C <sub>6</sub> H <sub>6</sub> AsNO <sub>6</sub>	**
<b>Arsenosugars</b>			
Dimethylarsinoylribosides	AsS		****
Triaklylarsonioribosides	AsS		****

<b>Others</b>		
Dimethylarsinoylethanol	DMAE	*****
Glycerophospho(arsenocholine)	GPAC	
Glycerophosphatidylarsenocholine	-	***

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- 1051 \* [Maher, 1984](#); [Kaise et al., 1988](#); [Francesconi and Edmonds, 1996](#); [Craig, 2003](#); [Sharma and Sohn, 2009](#).
- 1052 \*\* [Craig, 2003](#); [O'Day, 2006](#).
- 1053 \*\*\* [O'Day, 2006](#); [Sharma and Sohn, 2009](#).
- 1054 \*\*\*\* [Francesconi and Edmonds, 1996](#); [Sharma and Sohn, 2009](#).
- 1055 \*\*\*\*\* [Francesconi and Edmonds, 1996](#).
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1064 **Table 2:** Different phytoremediation processes (Vamerali et al., 2010)

Phytoextraction	In this process, plants uptake pollutants from soil and water, and translocate to and store in the harvestable biomass of the plants. Phytoextraction aims to remove pollutants from the contaminated sites. This process is usually observed in hyperaccumulating plants resistant to the pollutants.
Phytostabilization	Plants reduce mobility and phytoavailability of contaminants in the environment. This process does not remove pollutants from contaminated sites but reduces mobility and excludes metals from plant uptake.
Phytovolatilization	Hyperaccumulating plants uptake pollutants from soil and water, and translocate to the aerial parts of the plants, and volatilize the pollutants in the air.
Phytotransformation	This process is one kind of plant's defense mechanism to the environmental pollutants. The hyperaccumulating plants modify, inactivate, degrade (phytodegradation), or immobilize (phytostabilization) the pollutants through their metabolism.
Rhizofiltration	Usually aquatic plants perform this process. The hyperaccumulating aquatic plants adsorb and absorb pollutants from aquatic environments (water and wastewater).

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1073 **Table 3:** A number of aquatic plants have been tested for the remediation of trace elements from water. This table summarizes the aquatic plants  
 1074 which have been studied for phytoremediation of trace elements.

Common Name	Scientific Name	Trace Elements	References
Duckweed	<i>Lemna gibba</i> L.	As, U, Zn	Fritioff and Greger, 2003; Mkandawire et al., 2004a; Mkandawire et al., 2004b; Mkandawire and Dudel, 2005
Lesser duckweed	<i>Lemna minor</i> L.	As, Zn, Cu, Hg	Fritioff and Greger, 2003; Kara, 2004; Miretzky et al., 2004; Robinson et al., 2005; Alvarado et al., 2008; Mishra et al., 2008
Star duckweed	<i>Lemna trisulca</i> L.	Zn	Huebert and Shay, 1992
Water hyacinth	<i>Eichhornia crassipes</i>	As, Fe, Cu, Zn, Pb, Cd, Cr, Ni, Hg	Wolverton and McDonald, 1978; Muramoto and Oki, 1983; Delgado et al., 1993; Vesk et al., 1999; Cordes et al., 2000; Chandra and Kulshreshtha, 2004; Odjegba and Fasidi, 2007; Alvarado et al., 2008; Espinoza-Quiñones et al., 2008; Junior et al., 2008; Mishra et al., 2008; Dixit and Dhote, 2010
Water-starwort	<i>Callitriche cophocarpa</i>	Cr(V)	Augustynowicz et al., 2010
Petries starwort	<i>Callitriche petriei</i>	As	Robinson et al., 2005
Common reed	<i>Phragmites australis</i>	Cr, Cu, Ni, Pb, S, V, Zn, Cd	Deng et al., 2004; Ghassemzadeh et al., 2008; Baldantoni et al., 2009
Butterfly fern	<i>Salvinia rotundifolia</i>	Pb(II)	Banerjee and Sarker, 1997; Dhir, 2009
	<i>Salvinia natans</i>	As, Ni, Cu, Hg(II)	Sen and Mondal, 1987, 1990; Sen and Bhattacharyya, 1993; Rahman et al., 2008c
	<i>Salvinia minima</i>	As, Pb, Cd, Cr	Olguin et al., 2003; Hoffmann et al., 2004; Sanchez-Galvan et al., 2008

	<i>Salvinia herzogii</i>	Cd, Cr	<a href="#">Maine et al., 2004</a> ; <a href="#">Suñe et al., 2007</a>
Eared watermoss	<i>Salvinia auriculata</i>	Zn, Hg, Cr	<a href="#">Molisani et al., 2006</a> ; <a href="#">Espinoza-Quiñones et al., 2008</a> ; <a href="#">Wolff et al., 2009</a>
Greater duckweed	<i>Spirodela intermedia</i>	Cu, Zn, Mn, Cr, Pb	<a href="#">Miretzky et al., 2004</a>
	<i>Spirodela polyrhiza</i> L.	As, Hg	<a href="#">Rahman et al., 2007</a> ; <a href="#">Mishra et al., 2008</a> ; <a href="#">Rahman et al., 2008b</a>
Indian/Sacred lotus	<i>Nelymbium speciosum</i>	Cr, Cu, Ba, Ti, Co, Pb	<a href="#">Vardanyan and Ingole, 2006</a>
	<i>Ludwigia perennis</i> L.		
Arrowhead	<i>Sagittaria sagittifolia</i> L.		
-	<i>Nymphoides cristatum</i>		
Shoreline seapurslane	<i>Sasuvium portulacastrum</i> L.		
-	<i>Nymphae stellata</i>		
Water spinach	<i>Ipomoea aquatica</i>	As, Cd, Pb, Hg, Cu, Zn	<a href="#">Lee et al., 1991</a> ; <a href="#">Göthberg et al., 2002</a> ; <a href="#">Gothberg et al., 2004</a> ; <a href="#">Hu et al., 2008</a> ; <a href="#">Wang et al., 2008</a>
Eelgrass/Eelweed	<i>Vallisneria spiralis</i> L.	Cu, Cd, Hg	<a href="#">Rai and Tripathi, 2009</a> ; <a href="#">Wang et al., 2010</a>
Esthwaite waterweed	<i>Hydrilla verticillata</i>	As, Pb, Zn, Cr	<a href="#">Lee et al., 1991</a> ; <a href="#">Dixit and Dhote, 2010</a>
Mosquito fern	<i>Azolla caroliniana</i>	As	<a href="#">Zhang et al., 2008</a>
Water fern	<i>Azolla filiculoides</i>	As, Hg, Cd	<a href="#">Rahman et al., 2008a</a> ; <a href="#">Rai, 2008</a> ; <a href="#">Zhang et al., 2008</a> ; <a href="#">Rai and Tripathi, 2009</a>
	<i>Azolla pinnata</i>		
Elephant's ear	<i>Colocasia esculenta</i>	Cd, Cu, Pb, Zn	<a href="#">Cardwell et al., 2002</a>
Umbrella sedge	<i>Cyperus eragrostis</i>		
Spike rush	<i>Eleocharis equisetina</i>		
Parrot's feather	<i>Myriophyllum aquaticum</i>		



Miriophyllum	<i>Myriophyllum propinquum</i>	As	<a href="#">Robinson et al., 2005</a>
Water lily	<i>Nymphaea violacea</i>	Cd, Cu, Pb, Zn	<a href="#">Cardwell et al., 2002</a>
	<i>Nymphaea aurora</i>	Cd	<a href="#">Schor-Fumbarov et al., 2003</a>
Marshwort	<i>Nymphoides germinata</i>	Cd, Cu, Pb, Zn	<a href="#">Cardwell et al., 2002</a>
Knotweeds	<i>Persicaria attenuatum</i>		
-	<i>Persicaria orientalis</i>		
-	<i>Persicaria subsessilis</i>		
-	<i>Potamogeton orchreatus</i>	As	<a href="#">Robinson et al., 2005</a>
Willow smartweed	<i>Persicaria lapathifolium</i>	Cd, Cu, Pb, Zn	<a href="#">Cardwell et al., 2002</a>
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Fennel pondweed	<i>Potamogeton pectinatus</i>	Cd, Pb, Cr, Ni, Zn, Cu	<a href="#">Demirezen and Aksoy, 2004</a>
Curled dock	<i>Rumex crispus</i>	Cd, Cu, Pb, Zn	<a href="#">Cardwell et al., 2002</a>
River clubrush	<i>Schoenoplectus validus</i>		
Cumbungi	<i>Typha domingensis</i>		
Cumbung	<i>Typha orientalis</i>		
Lesser Bulrush	<i>Typha angustifolia</i>	Cd, Pb, Cr, Ni, Zn, Cu	<a href="#">Chandra and Kulshreshtha, 2004</a> ; <a href="#">Demirezen and Aksoy, 2004</a>
Bulrush	<i>Typha latifolia</i>	Cr, As, Zn, Pb, Cd, Cu, Ni	<a href="#">Ye et al., 1997</a> ; <a href="#">Ye et al., 1998</a> ; <a href="#">Hozhina et al., 2001</a> ; <a href="#">Blute et al., 2004</a> ; <a href="#">Chandra and Kulshreshtha, 2004</a> ; <a href="#">Deng et al., 2004</a> ; <a href="#">Pratas et al., 2007</a> ; <a href="#">Sasmaz et al., 2008</a>
Waterweed/Pondweed	<i>Elodea canadensis</i>	As, Pb, Cr, Zn, Cu, Cd	<a href="#">Mayes et al., 1977</a> ; <a href="#">Mal et al., 2002</a> ; <a href="#">Fritioff and Greger, 2003</a> ; <a href="#">Chandra and Kulshreshtha, 2004</a> ; <a href="#">Robinson et al., 2005</a> ; <a href="#">Dogan et al., 2009</a>

Brazilian Waterweed	<i>Veronica aquatica</i>	As	<a href="#">Robinson et al., 2005</a>
Water-milfoil	<i>Myriophyllum spicatum</i>	Co, Cr, Cu, Pb, Zn, Ni	<a href="#">Keskinan et al., 2003</a> ; <a href="#">Chandra and Kulshreshtha, 2004</a> ; <a href="#">Lesage et al., 2007</a>
Fragrant water lily	<i>Nymphaea odorata</i>	Cr	<a href="#">Chandra and Kulshreshtha, 2004</a>
Pickerelweed	<i>Pontederia cordata</i>		
Tape grass/Eel grass	<i>Vallisneria spiralis</i>	Hg	<a href="#">Gupta and Chandra, 1998</a>
Wild celery	<i>Vallisneria americana</i>	Cr	<a href="#">Chandra and Kulshreshtha, 2004</a>
-	<i>Nymphaea spontanea</i>	Cr(VI)	<a href="#">Choo et al., 2006</a>
Shichito matgrass	<i>Cyperus malaccensis</i> Lam.	Pb, Zn, Cu, Cd	<a href="#">Deng et al., 2004</a>
Swamp rice grass	<i>Leersia hexandra</i> Swartz.		
Burma reed	<i>Neyraudia reynaudiana</i>		
Flagroot	<i>Acorus calamus</i> L.		
-	<i>Eleocharis valleculosa</i>		
Water pepper	<i>Polygonum hydropiper</i>	As	<a href="#">Robinson et al., 2005</a>
Reed canary grass	<i>Phalaris arundinacea</i> L.	Pb, Zn, Cu, Cd	<a href="#">Deng et al., 2004</a>
-	<i>Equisetum ramosisti</i> Desf.		
Soft rush	<i>Juncus effusus</i> L.		
-	<i>Polypogon fugax</i> Steud.		
-	<i>Egeria densa</i>	As	<a href="#">Robinson et al., 2005</a>
Alligatorweed	<i>Althernanthera philoxeroides</i>	As, Pb	<a href="#">Elayan, 1999</a>
Water lettuce	<i>Pistia stratiotes</i>	As, Cr, Pb, Ag, Cd, Cu, Hg,	<a href="#">Lee et al., 1991</a> ; <a href="#">Maine et al., 2004</a> ; <a href="#">Miretzky et al., 2004</a> ; <a href="#">Espinoza-</a>

		Ni, Zn	<a href="#">Quiñones et al., 2008; Espinoza-Quiñones et al., 2009</a>
Floating pondweed	<i>Potamogeton natans</i>	Zn, Cu, Cd, Pb	<a href="#">Fritioff and Greger, 2003, 2006</a>
Willow moss	<i>Fontinalis antipyretica</i>	Cu, Zn	<a href="#">Goncalves and Boaventura, 1998</a> ) ( <a href="#">Martins and Boaventura, 2002</a>
Needle spikerush	<i>Eleocharis acicularis</i>	As, In, Ag, Pb, Cu, Cd, Zn, Sb, Ni, Mg	<a href="#">Ha et al., 2009a; Ha et al., 2009b; Ha et al., 2011</a>
Rigid hornwort	<i>Ceratophyllum demersum</i>	As, Pb, Zn, Cu	<a href="#">Keskinkan et al., 2004; Robinson et al., 2005</a>
Watercress	<i>Lepidium sativum</i> L.	As	<a href="#">Robinson et al., 2003</a>
-	<i>Najas indica</i>	Pb	<a href="#">Singh et al., 2010</a>
Watercresses	<i>Nasturtium officinale</i>	Cu, Zn, Ni	<a href="#">Kara, 2005</a>
Curly waterweed	<i>Lagarosiphon major</i>	As	<a href="#">Robinson et al., 2005</a>

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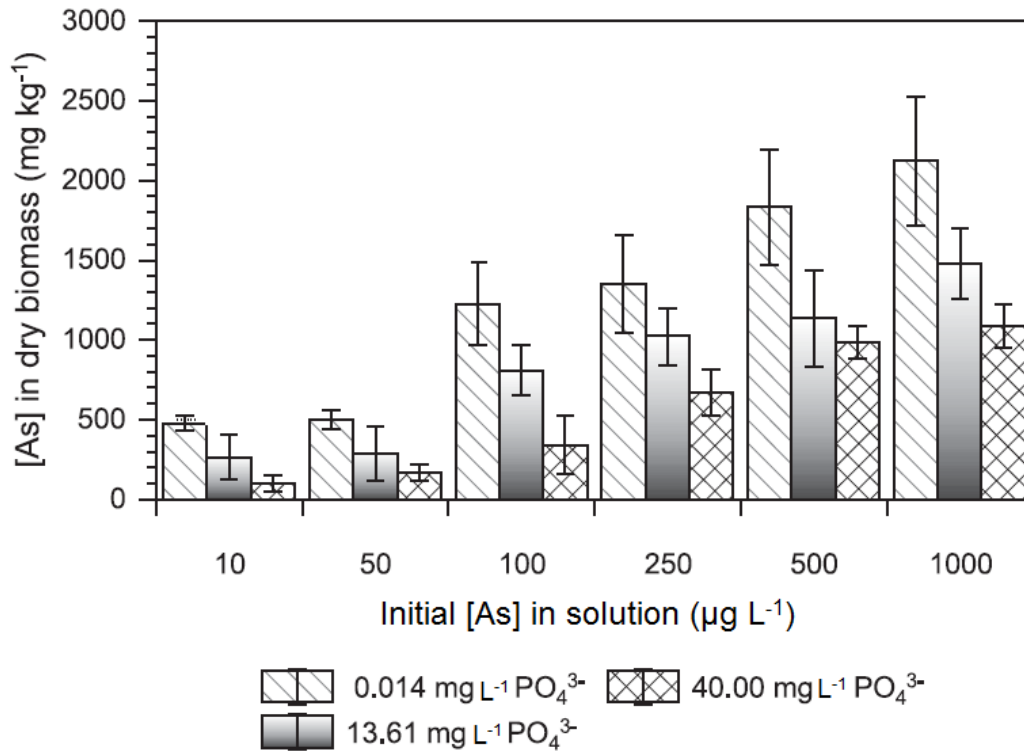
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1088 **Fig. 1:** Influence of phosphate concentrations on arsenic uptake in *L. gibba* L. (Mkandawire and  
 1089 [Dudel, 2005](#)).

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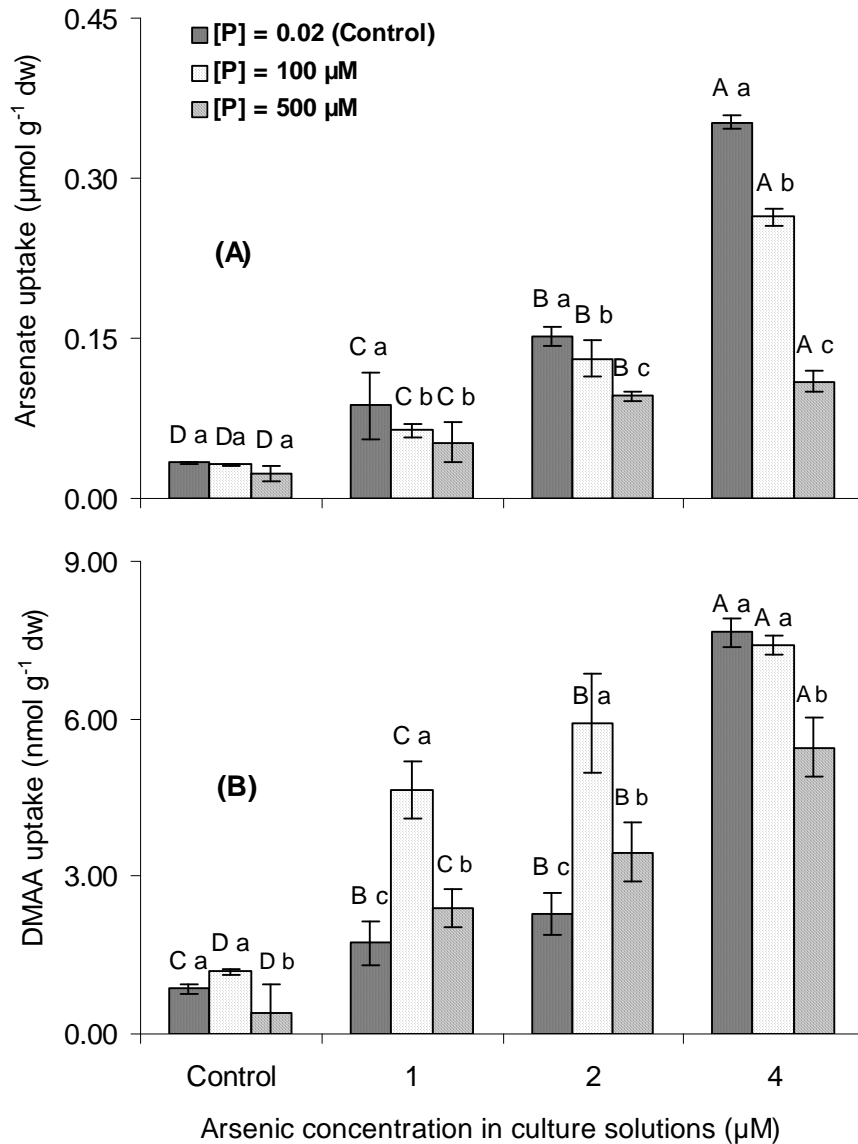
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1102 **Fig. 2:** Arsenic uptake in *S. polyrhiza* L. exposed to the different concentrations of As(V) (a) and

1103 DMAA (b). Error bars represent  $\pm$ SD ( $n = 3$ ). Different capital letters indicate significant

1104 differences between arsenic treatments and small letters indicate significant differences

1105 between phosphate treatments at 5% level (Rahman et al., 2007).

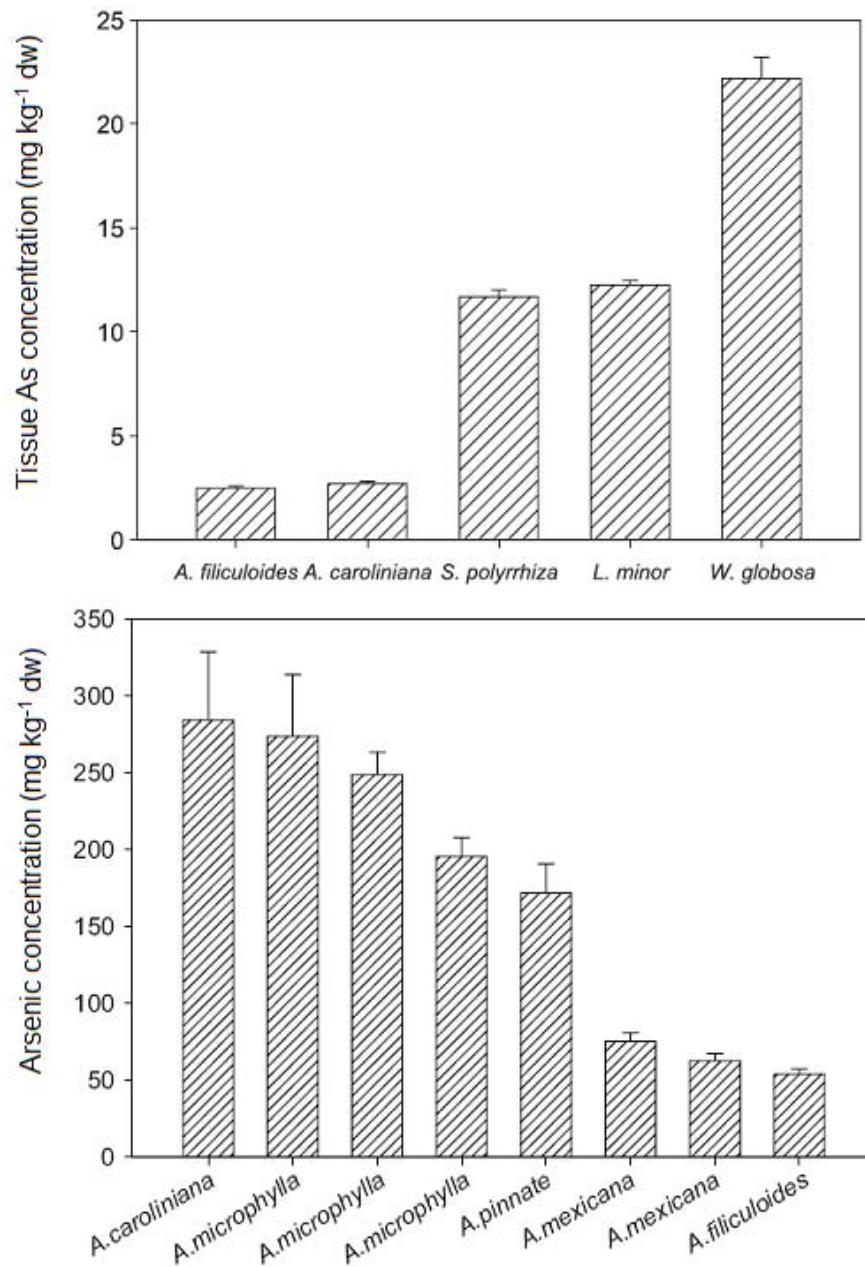
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1112 **Fig. 3:** Arsenic concentration in duckweed (*S. polyrrhiza*, *L. minor* and *W. globosa*) and *Azolla* grown

1113 in nutrient solutions with 1  $\mu$ M and 50  $\mu$ M As(V) for 5 and 10 d, respectively. Data are

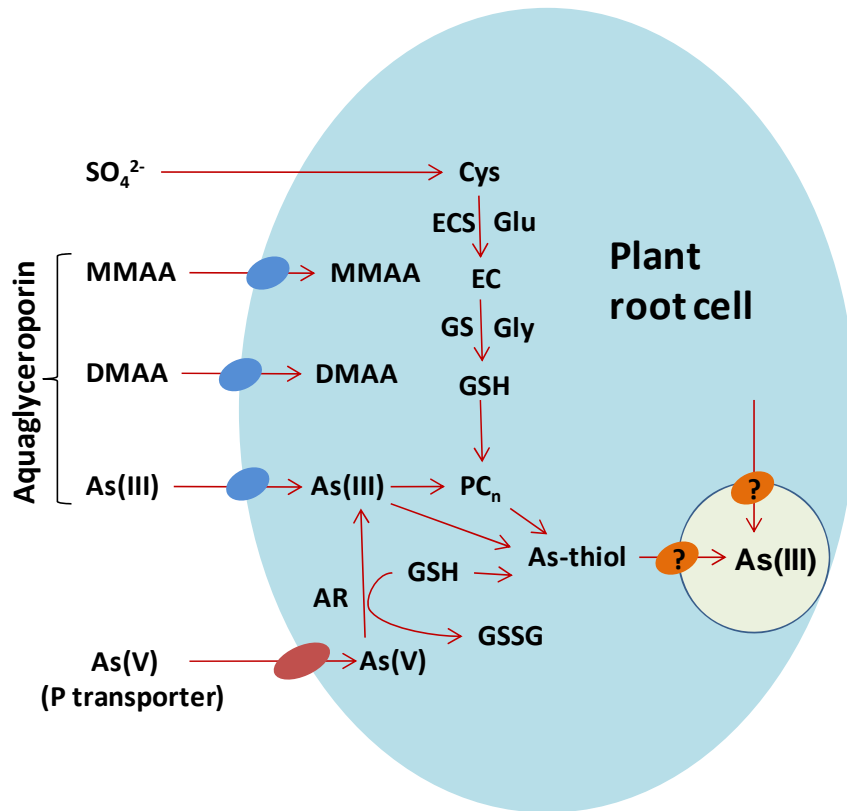
1114 means  $\pm$  SE ( $n = 3$ ) (Zhang et al., 2008; Zhang et al., 2009).

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1120 **Fig. 4:** Mechanisms of arsenic uptake into plant cells (Tripathi et al., 2007). As(V) is transported  
 1121 through phosphate transporters, and As(III) through aquaglyceroporins (Tripathi et al., 2007;  
 1122 Rahman et al., 2008b; Zhao et al., 2009). The organoarsenic species (MMAA and DMAA)  
 1123 might be taken up by aquaglyceroporins (Rahman et al., 2011).