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The Fate of Arsenic in Soil-Plant Systems

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1 **1 Introduction**

2 ***1.1 The Properties of Arsenic***

3 Arsenic (As) is an element belonging to the group V-A, and demonstrates
4 characteristics of a metalloid. Because arsenic more easily forms anions, its non-metal
5 properties dominate. When arsenic is in an oxidation state of +5, it acts similarly to
6 phosphorus, a fact that has many implications for the way in which it reacts in soil, as
7 well as its potential toxicity in plants. The most common oxidation states of As are -3,
8 0, +3, and +5. Arsines and metal arsines are those in which As has an oxidation state of
9 -3, and these forms, are very unstable under oxidizing conditions. Under aerobic
10 conditions, the oxidation state of As tends to be +5, and, when this occurs at a pH of
11 between 2 and 3 the arsenic acid (H_3AsO_4) is formed. When the pH rises to values
12 between 3 and 11, this compound disassociates to H_2AsO_4^- and HAsO_4^{2-} (Smedley and
13 Kinniburgh 2002). Under anaerobic conditions, the predominant As species is H_3AsO_3 .
14 Arsenic also biomethylates easily (Barán 1995).

15 Arsenic is widely distributed throughout the environment, and can be detected in
16 the lithosphere in concentrations between 1.5 and 2 mg kg^{-1} , making it the 52nd most
17 abundant element (Adriano 2001). Arsenic forms a part of more than 245 minerals that
18 include arsenates (60%), sulfides and sulfosals (20%), as well as other compounds such
19 as arseniurates, arsenites, oxides and silicates (20%) (Mandal and Suzuki 2002). The
20 majority of arsenic deposits in the earth's surface are found as sulfurous minerals
21 (arsenopyrite).

22 ***1.2 The Presence of and Exposure to Arsenic in the Environment***

23 Inorganic arsenic is present in soil, water, air and food such that humans are
24 constantly exposed to this contaminant (Mandal and Suzuki 2002). The range at which
25 arsenic is present in soils varies normally between 0.2 and 40 mg kg^{-1} , while in urban
26 areas the concentration in atmospheric air is approximately 0.02 $\mu\text{g m}^{-3}$. On a global
27 level, drinking contaminated water is the major source of exposure to this contaminant
28 (Smedley and Kinniburgh 2002). It is estimated that some thirty million people are
29 exposed to waters contaminated with arsenic, a quarter of them showing symptoms
30 associated with long term exposure in at least five South Asian countries: Bangladesh,
31 India, Nepal, Thailand and Myanmar (Caussy 2003). The World Health Organization
32 (WHO) recommends a maximum level of arsenic in waters of 10 $\mu\text{g L}^{-1}$ (Bissen and
33 Frimmel 2003); however, the concentration of arsenic in surface waters is greater than

34 2000 $\mu\text{g L}^{-1}$ in certain regions of Bangladesh and India (Tripathi et al. 2007). Soil and
35 water are the main sources of human exposure to arsenic at any given location, either by
36 consumption (greatest in children; Rodríguez et al. 2003), inhalation or direct skin
37 contact (DEFRA 2002). Because arsenic accumulates in vegetables, fruits, and other
38 plants that grow in contaminated soils, another important pathway of exposure is the
39 transfer of arsenic within the food chain (Meharg and Hartley-Whitaker 2002).

40 In terms of anthropogenic sources, annual global production of arsenic is
41 estimated to be between 75 and $100 \cdot 10^3$ t (Adriano 2001). Natural sources (those in
42 which human intervention does not play an important role) will depend, in many cases,
43 on the geochemistry of each site, principally of the site's lithology and dispersion
44 pathways. The major human activities that produce As are mining, metallurgy,
45 agriculture, forestry, fossil fuel treatment plants, urban waste and cattle farming
46 (Adriano 2001; Fitz and Wenzel 2002). In both mining and metallurgy, arsenic is
47 produced as a by-product of little value, making it an unwanted waste. There are
48 important arsenic deposits in some components of the earth's surface, which gives way
49 to an elevated concentration of arsenic in the adjacent environment (up to 3% As in the
50 soil) that rapidly decreases with distance from the contaminated sites (Zhang and Selim
51 2008). Also, some industrial activities may be a source of As; for example, when old
52 glass manufacturing industries disposed of rich As wastes in the early 20th century
53 (Madejón and Lepp 2007). Many biocides, used to control diseases in agriculture and
54 forestry, are composed of As (Lepp 1981). Similarly, the use of fertilizers is also a
55 source of arsenic in soils (Matschullat 2000). Urban wastes derived from treatment
56 plants and compost, often used as organic amendments, may contain arsenic in varying
57 quantities (Beesley and Dickinson 2010). Lastly, fossil fuel combustion also produces
58 quantities of arsenic that may lead to long term accumulation from the gases emitted to
59 the surrounding areas (Matschullat 2000). All of these factors release arsenic into the
60 environment and can result in its accumulation in soils. When present in soils, As is
61 generally observed to be more abundant in its inorganic form, with As(V) as the
62 predominant species found under aerobic conditions (Akter and Naidu 2006). In soils,
63 organic As species are usually found as monomethylarsonic acid (MMA) and
64 dimethylarsinic acid (DMA) (Takamatsu et al. 1982; Mestrot et al. 2011).

65

66 **2 The Dynamics of Arsenic in Soil**

67 Some authors believe that base concentrations of 10-40 mg kg⁻¹ of arsenic exist
68 in areas where the lithology has no known unnatural sources of contamination (Fitz and
69 Wenzel 2002; Mandal and Suzuki 2002); however, estimates of the average
70 concentration that exists in the pedosphere are only 5-8 mg kg⁻¹ (Matschullat 2000). In
71 the Andalusia region of Spain, values of 33 mg kg⁻¹ of As have been documented to
72 occur in soil, although amounts are highly dependent on the soil horizon, the type of soil
73 and the lithology (Martín et al. 2007). In rare instances, either because of natural or
74 anthropogenic sources, some soils are known to contain extraordinarily high levels of
75 arsenic, i.e., values of 0.1 and 2% arsenic (Chang et al. 2005; Ongley et al. 2007; King
76 et al. 2008). Such places pose a risk to human health as well as to ecosystem health, and
77 if deemed necessary, these areas must be managed to reduce probable exposure risks.

78 An important variable in the study of As in soils is the heterogeneity in which it
79 can appear, such that regions displaying high concentrations may be adjacent to regions
80 that have much lower levels. In such cases, contaminant hot spots must be identified,
81 because they will pose the hardest-to-manage threats (Dickinson et al. 2009). Several
82 authors have described events in which As levels are greater in surface soil horizons
83 (Adriano 2001; Clemente et al. 2008). When this occurs, it would indicate that
84 contamination took place after the genesis of the soil in which it appears. However, this
85 phenomenon depends on the source and method by which arsenic made its way into the
86 soil. In one review (Fitz and Wenzel 2002), the authors described how, in the European
87 Union, there may be up to 1.4 million soil sites that are contaminated with metals,
88 metalloids, and/or organic compounds. These authors also estimated that, in the United
89 States, approximately 41% of the soil sites catalogued as being contaminated were
90 catalogued as such because of arsenic. Similarly, in Australia, there are more than
91 10,000 soil sites contaminated by As. Some of these Australian sites are extensive in
92 area and constitute large-scale events of As contamination.

93 When setting safe levels, environmental legislation or regulation tends to rely on
94 values that reflect total arsenic levels, but the total content of a trace element, as
95 determined by acid digestion, is rarely a good indicator of the element's mobility or
96 potential risk (Allen 2001).

97

98 ***2.1 The Mobility and Solubility of Arsenic in Soils***

99 The solubility of soil contaminants is a key parameter to understanding their
100 probable mobility. The soluble fraction in which contaminants exist is in equilibrium
101 with others that exist in the soil environment. Once dissolved in soil water, elements are
102 often present as different species that have different ionic activities (Sauvé 2001).
103 Typical concentrations of arsenic in the soil solution, under aerobic conditions are <50
104 nM in non-contaminated soils, while they can reach values of up to 2 μM in
105 contaminated soils (Wenzel et al. 2002; Moreno- Jiménez et al. 2011a); however, an
106 exception was one sample from a semi-flooded mine soil that had up to 40 μM As. In
107 flooded soils (where the predominate species is arsenite), typical concentrations of As in
108 solution vary between 0.01 and 3 μM (Zhao et al. 2009). In one As study, using lupine
109 plants as indicators of As availability, the behavior of the in-soil crop was compared
110 with that same crop grown hydroponically. In this study, an exposure of less than 10
111 μM of As in soil solution was established, wherein the total concentration of As was
112 more than 2000 mg kg^{-1} (Moreno-Jiménez et al. 2010b). In comparison to other trace
113 elements, arsenic shows a low solubility in well-aerated soils (Beesley et al. 2010a;
114 Moreno-Jiménez et al. 2010a).

115 Traditionally, sequential extraction has been used to fractionate trace elements
116 that appear in soil. For arsenic, which is usually present in its anionic form in soils,
117 specific protocols for arsenic extraction have been developed from these methods
118 (Onken and Adriano 1997; Shiowatana et al. 2001; Wenzel et al. 2001). These
119 extraction protocols have enabled researchers to determine that arsenic is often
120 associated with oxides and hydroxides in soil (McLaren et al. 2006). The exchange
121 surfaces of silicates and organic matter tend to be negatively charged, and therefore
122 have a greater tendency to retain cations. In soils that have a low pH (where positive
123 charges predominate), conditions may favor the retention of As in exchange positions.
124 In soils affected by pyritic materials or one that are associated with pyritic mining,
125 arsenic may be found in large proportions within the residual fraction, indicating that it
126 is bound in its mineral form (i.e., associated with sulfides; Conesa et al. 2008)

127 The study of how arsenic is fractionated within soils can provide useful
128 information about its mobility, migration, and potential toxicity. The As fraction
129 retained in a labile form, within the soil matrix (soil and water) will be the most
130 biologically active (bioavailable fraction) and the most mobile (soluble fraction) one.
131 Fig. 1 is an illustration that depicts the equilibrium achieved by As among several soil

132 phases. From an ecological and toxicological point of view, the fraction that contains
133 the contaminants in the soil matrix is the most important one, and should be used as an
134 indicator, when analyzing soil contaminant risks (Mench et al. 2009). Therefore, the
135 soil's solid phase is less important than the liquid phase or the equilibrium established
136 between the solid and liquid phases (Sauvé 2001). To date, there is neither a clear
137 consensus surrounding the concept of bioavailability, nor is there an exact way of
138 defining it, in the context of As. In plants, the bioavailable As fraction would be *the*
139 *amount of As a plant takes up from the soil*, although this concept has yet to be
140 measured and cannot be predicted (Fitz and Wenzel 2006). The available and
141 unavailable fractions of contaminants tend to be in equilibrium within the soil, but any
142 change in environmental factors (pH, Eh, climate, biology, hydrology, organic matter,
143 etc.), or alterations in mineral content (e.g., from dissolution-precipitation; oxidation-
144 reduction; formation of complexes-disassociation; adsorption-desorption) can alter the
145 availability of an element (Mench et al. 2009). This dynamic behavior notwithstanding,
146 the analysis of soils by many methods have produced interesting results when
147 estimating a contaminant's potential plant bioavailability. The available fraction has
148 generally been measured by correlating amounts of the element found in the soil vs.
149 amounts found within the plants grown in the soil (Feng et al. 2005; Vázquez et al.
150 2008a). When this approach is used, some neutral salt extraction methods (Vázquez et
151 al 2008a), or those utilizing organic acid mixtures (Feng et al. 2005) have produced
152 satisfactory results. Moreover, monitoring programs that rely on rhizosphere suction
153 cups have been employed, and these are designed to measure the available fraction of
154 interstitial water that occurs within samples (Clemente et al. 2010). One factor that is
155 insufficiently understood is the rate of exchange that takes place between unavailable
156 and available fractions, although that rate appears to be rather slow (Cattani et al. 2009).

157 **2.2 Factors Determining Arsenic Availability in Soils**

158 **2.2.1 The Effect of pH and Eh**

159 In contrast to what happens with other trace elements, a rise in pH often results
160 in mobilization of arsenic in the soil. In general, a rise in soil pH causes a release of
161 anions from within their exchange positions, such that arsenate and arsenite are released
162 (Smith et al. 1999; Fitz and Wenzel 2002; Beesley et al. 2010b; Moreno-Jiménez et al.
163 2010a). However, several experiments (mainly with mine soils) have shown that high
164 pH values, in the presence of sulfates and carbonates, can produce either a co-

165 precipitation of arsenic in the subsequently formed oxyhydroxides and sulfates (García
166 et al. 2009), or a precipitate such as calcium arsenate (which is slightly less insoluble
167 than calcium phosphate) (Burriel et al. 1999). For this reason, some soils probably
168 demonstrate their maximum As(V) retention at a pH near 10.5 (Goldberg and Glaubig
169 1988). In well aerated alkaline soils, the solubility of As is limited by its precipitation as
170 Ca or Fe arsenates (Xie and Naidu 2006). In soils with a high pH, carbonates can play
171 an important role in the retention of arsenate (Zhang and Selim 2008). When the pH
172 drops below 2.5, As(V) becomes completely protonated (Zhang and Selim 2008),
173 rendering it less likely to be retained by soil particles.

174 As(V) is the predominant form that exists in soils, in which the $pH+pe > 10$; in
175 contrast, As(III) is the dominant form found in soils, in which the $pH+pe$ is less than 6
176 (Sadiq 1997). Under aerobic conditions, sulfides are easily oxidized, and as a
177 consequence arsenic is released into the environment (Adriano 2001); when soil pH is
178 between 3 and 13, the major species found are $H_2AsO_4^-$ and $HAsO_4^{2-}$ (Smedley and
179 Kinniburgh 2002). In reducing environments, arsenic is found as arsenite the
180 predominant species of which is H_3AsO_3 . Poor adsorption of As(III) results from its
181 neutral character in soils (Lakshmipathiraj et al. 2006). Arsenite is more mobile and
182 more toxic than is arsenate. Poor adsorption occurs when the redox potential of the soil
183 is negative (Fitz and Wenzel 2002), and changes in the handling or conditions of soils
184 results in speciation changes of As (Carbonell-Barrachina et al. 2004). Highly reducing
185 conditions can cause As co-precipitation with iron-sulfurs, such as arsenopyrite, or the
186 formation of arsenic sulfides (AsS , As_2S_3). During the oxidation of pyrite, Fe is
187 oxidized from valence II to III, and arsenic is oxidized to arsenate. In contrast, under
188 reducing conditions, Fe and Mn oxides are dissolved, releasing arsenate that is rapidly
189 reduced to arsenite (Gräfe and Sparks 2006).

190 **2.2.2 The Role of Fe, Al and Mn Oxides and Oxyhydroxides**

191 Soils frequently retain important quantities of Fe, Al and Mn oxides and
192 oxyhydroxides. The distribution of these solids in the soil depends on both the pH and
193 Eh of the soils involved. Under reducing conditions, the structure of Fe and Mn
194 hydroxides is broken, and arsenic that was fixed to the interior or to the surface of these
195 compounds is released. The activity of arsenic in the soil solution is controlled by
196 reactions of retention and release along the surfaces of Fe, Mn, and Al oxides and
197 hydroxides (Livesey and Huang 1981; Fitz and Wenzel 2002; de Brouwere et al. 2004),

198 and soils with a large quantity of iron had a greater retention capacity of both arsenate
199 and arsenite (Manning and Goldberg 1997), arsenite being retained in lower quantities
200 than arsenate (Fitz and Wenzel 2002). As (V) has a high affinity for the surfaces of iron
201 oxides, where it forms inner-sphere complexes; however, As (V) can also be retained in
202 external-sphere complexes (Waychaunas et al. 1993; Cheng et al. 2008). The results of
203 several studies have shown that As(III) can be adsorbed and oxidized along the surfaces
204 of some Fe-oxyhydroxides, such as goethite and ferrihydrite, or those of Mn (such as
205 birnesite; Lin and Puls 2000). In other studies, it was demonstrated that the adsorption
206 of As(V) on goethite, magnetite, and hematite is reduced when the pH is raised
207 (Manning et al. 1997; Giménez et al. 2007). Giménez et al. (2007) found that hematite
208 had the largest sorption capacity, followed by goethite and then magnetite. Arsenate has
209 a high affinity for the surfaces of iron oxides, as phosphate; however, arsenate has a
210 lower affinity for aluminum oxides than phosphate (Adriano 2001). Under reducing
211 conditions, when a large portion of the Fe and Mn oxides have been reduced, gibbsite
212 (which is more thermodynamically stable in anaerobic conditions) is able to absorb
213 some of the As released by other oxides (Mello et al. 2006). The adsorption of arsenic
214 onto oxides depends on the duration of the interaction between As and the oxide, the
215 release of arsenic being more difficult as the interaction time increases (Gräfe and
216 Sparks 2006).

217 The addition of Fe to the soil in several forms immobilizes As. For example,
218 additions of Fe oxides, iron-rich soils (those reddish in color), inorganic Fe salts or
219 industrial byproducts, rich in Fe, together with CaCO₃, have all been used to raise the
220 quantity of soil oxides, which, in turn, immobilizes As (Hartley et al. 2004; Hartley and
221 Lepp 2008; Vithanage et al. 2007).

222 **2.2.3 Concentration of P and other Elements in the Soil**

223 The phosphate anion, the major species of P present in soils (Marschner 1995),
224 is an analog to arsenate. The application of P to soil results in a release of retained As
225 (Fitz and Wenzel 2002; Cao et al. 2003). This release results from competition between
226 the retention of both anions. Such ions not only compete non-specifically for anionic
227 exchange positions, but they also compete in complexation reactions or in the retention
228 by oxides. When exchange positions are involved, there are competitor ions that are less
229 efficient than phosphorus in displacing arsenic. Phosphate and arsenate are more
230 effectively retained than are other anions, such as Cl⁻ and NO₃⁻, which are rapidly

231 mobilized. This could result from the fact that chlorides and nitrates are adsorbed with
232 little specificity along the colloidal surface, whereas phosphates and arsenates are
233 specifically adsorbed in soils components. Roy et al. (1986) were able to show that the
234 retention capacity of As(V) was lowered in the presence of phosphate ions. In a similar
235 study, the presence of anions other than phosphate had no effect on As(V) retention
236 (Livesey and Huang 1981). Woolson (1973) demonstrated how the application of
237 phosphorous fertilizers in soils, contaminated by arsenic, mobilized up to 77% of the
238 total arsenic found in the soil, and increased the availability of arsenic. It has been
239 shown in numerous other studies that the application of P in soils causes an increase in
240 the extractable fraction of As. This increase, however, is not necessarily reflected by a
241 greater absorption of As by plants, because arsenate and phosphate are competitors also
242 for absorption by plants (Esteban et al. 2003).

243 In addition to phosphate, As interacts with other anions. Increasing ionic
244 strength of a soil solution is therefore one method used to reduce the quantity of As
245 retained, and provoke competition between anions for exchange positions (Gräfe and
246 Sparks 2006). The action of anions, other than phosphate, appears to be significant only
247 in the absence of phosphate. Therefore, Stachowicz et al. (2008) observed that, in the
248 absence of phosphate, carbonates moderately compete with arsenate for exchange
249 positions, but when phosphorus is present, the effects of carbonates were not significant.
250 Alternatively, cations can alter the retention/mobilization of As in soils. Smith et al.
251 (2002) determined that the presence of Ca^{2+} and Na^+ causes an increase in the retention
252 of As. Similarly, Stachowicz et al. (2008) described how Ca^{2+} and Mg^{2+} can induce the
253 adsorption of phosphate and arsenate in soils.

254 **2.2.4 The Effect of Clay Minerals**

255 In general, the availability of arsenic is greater in sandy than in clay soils
256 (Adriano 2001), although the retention of As in clays is less efficient than with oxides
257 (Gräfe and Sparks 2006). Again, As(III) adsorbs to clay minerals less intensely than
258 does As(V). There are many factors involved in the soil adsorption and desorption
259 processes that affect As mobility. Among these factors is the structure of primary and
260 secondary minerals to which As comes into contact. Another factor is the duration of
261 interaction that exists between the clays of a soil and arsenic; the adsorption of As(V)
262 and As(III) by clay minerals increases with time (Lin and Puls 2000). Zhang and Selim
263 (2008) suggest that isomorphic substitutions of Fe by Al in clays contribute to the

264 adsorption of As. The anionic character of arsenic suggests that the mechanism of clay
265 adsorption of this metalloid may be similar to that of P, through calcium-bridging
266 mechanisms (Fixen and Grove 1990). Frost and Griffin (1977) reported that
267 montmorillonite can adsorb more As(V) and As(III) than does kaolonite, and the
268 difference is derived from the increased surface charge of montmorillonite. Lin and
269 Puls (2000) found that halosite and chlorite clays had a greater capacity to adsorb As(V)
270 than did other clay minerals, and that kaolonite and illite/montmorillonite, adsorb As
271 (V) to a moderate degree. Arsenic is initially adsorbed on the clay surface, but with
272 time, it is incorporated into the structure of the mineral. It was demonstrated that
273 Californian soils having a greater percent of clay and appreciable quantities of Fe oxides
274 had a greater As retention capacity (Manning and Goldberg 1997).

275 **2.2.5 Interactions with Organic Matter**

276 Organic matter is of a heterogeneous chemical nature, and constitutes a series of
277 organic compounds of variable molecular weights that are differentially polymerized.
278 This soil fraction is dominated elementally by carbon, oxygen, hydrogen, nitrogen and
279 phosphorus (in this order), and commonly has the following functional groups:
280 carboxyls, carbonyls, alcohols and amines (Stevenson 1982). The level of
281 polymerization of humic compounds and their molecular weights influence their
282 solubility: as these compounds diminish in size, they have a greater proportion of
283 functional groups (organic, fulvic and humic acids), and display higher solubility. If
284 more highly polymerized, humic compounds have fewer functional groups, e.g.,
285 humines, and will display lower water solubility. The effect organic matter has on trace
286 elements depends on the qualitative composition of the organic matter. An organic
287 fraction that has a large molecular weight will more effectively retain trace elements,
288 whereas a more soluble and lighter fraction tends to dissolve elements, either by
289 chelating (metals) or by displacing (anions) them. Depending on what the predominant
290 compound in the soil is, either of these effects will be observed in the soil.

291 How soil organic matter affects arsenic is inconsistent: in some studies, the
292 application of organic matter reduced the mobility of arsenic (Gadepalle et al. 2007),
293 whereas, in others As is released after the application of compost (or there is a higher
294 correlation between soluble carbon and soluble arsenic in soils; Mench et al. 2003;
295 Clemente et al. 2008). Weng et al. (2009) have recently studied how fulvic and humic
296 acids in solution are able to reduce the capacity for arsenate retention in goethite

297 through electrostatic competition. Therefore, dissolved organic matter can compete with
298 arsenate and arsenite for soil retention positions (Bernal et al. 2009). Alternatively,
299 some humic acids may form humic-clay complexes that have the capacity to retain As
300 (Saada et al. 2003). Therefore, the relationship between soil arsenic and organic matter
301 is complex and depends on multiple factors that include: the ratio of soluble organic
302 carbon present, and the fractions of insoluble and stable humus, and the concentrations
303 of Fe, Al, and Mn present in the organic matter (Gräfe and Sparks 2006). One important
304 consideration, when adding organic amendments to a soil, is that the bioavailable
305 fraction of As may be high (Beesley and Dickinson 2010), despite the fact that the total
306 concentration of As is usually $<30 \text{ mg kg}^{-1}$ (Adriano 2001).

307 **2.2.6 Other Factors**

308 Large differences in various soil parameters may exist during the year, and
309 hence, the availability of trace elements in soil may also be variable (Vanderlinden et al.
310 2006). These variations result from changes in soil physical properties (humidity,
311 aeration, porosity, temperature, etc.), chemical changes (pH, appearance of precipitates,
312 E, etc.), and biological changes (microbial activity, vegetation cover, etc.). Depending
313 on the concentration of As present and the humidity regime in the soil, precipitates of
314 insoluble salts (e.g., Fe and Ca arsenates, or co-precipitates with jarosite, gypsum or
315 calcite) can form (de Brouwere et al. 2004; Zhang and Selim 2008; Cheng et al. 2008;
316 Kreidie et al. 2011). Such precipitates are frequent in mining sites, where high
317 concentrations of As exist in the soil; if As concentrations are high and rainfall takes
318 place the risk that As will leach from soil will increase. The duration of the interaction
319 between arsenic contamination and the soil is another factor that must be considered,
320 since the bioavailability of As decreases as it ages in soil (favoring its retention in less
321 available fractions; Lombi et al. 1999).

322 **3 Arsenic in Plants**

323 ***3.1 Absorption and Transport***

324 Different arsenic species simultaneously exist in soils (e.g., As(III), As(V),
325 MMA, DMA; Takamatsu et al. 1982). Where the inorganic form of As predominate, the
326 arsenic is primarily taken up into plants via root absorption, in a process analogous to
327 how nutrients and other trace elements are absorbed.

328 **3.1.1 Changes to As Mobility**

329 Plant roots use fairly efficient mechanisms to modify the solubility and
330 availability of mineral elements in the soil (Marschner 1995). Hence, a plant has a direct
331 influence over the biogeochemical conditions in the area of the root or rhizosphere
332 (Mengel and Kirkby 2001). For example, organic exudates, organic molecules of low
333 molecular weight, are able to mobilize nutrients that are available only in low quantities
334 in the soil, thus rendering anions (phosphates) and cations (Fe, Cu) more available.
335 Alternatively, mechanisms by which plants immobilize toxic soil elements, as is the
336 case of aluminum, have also been described (Mariano and Keljten 2003). It is also
337 known that plants are capable of altering the pH of the rhizosphere (Marschner 1995),
338 thanks to the release of organic acids that serve as soil solution buffers. Moreover, most
339 plants establish relationships with microorganisms (fungus and bacteria) at the root
340 level that also influence the biogeochemical cycle in the rhizosphere. If bacterial
341 activity in the rhizosphere is particularly high, methylation, reduction, or other forms of
342 bacteria-based biochemical activity is favored (Renella et al. 2007). Little is known
343 about the mechanisms by which the availability of toxic soil elements are altered (Kidd
344 et al. 2009), but it is known that the characteristics of the rhizosphere intrinsically
345 depend on the plant species involved.

346 Although little information exists on the mechanisms by which plants mobilize
347 or immobilize As (Fitz and Wenzel 2002), the analogy drawn between phosphate and
348 arsenate allows us to establish certain parallels between the rhizospheric dynamics of P
349 and As. Many plant species have an active mechanism for pumping organic acids from
350 roots into the rhizosphere, rendering P more mobile (Smith and Read 1997). The
351 mobilization of P induced by organic acids has been attributed to root-influenced pH
352 changes (Raghothama 1999). These organic acids have a low molecular weight
353 (carboxylic acids such as citric and malic acids), and are able to displace phosphate
354 from positions of retention within the soil; they then act to chelate metals that
355 immobilize P, and form metal-chelate complexes with P (Fitz and Wenzel 2002). The
356 soil solubilization of P and its absorption by plants has additionally been attributed to
357 the secretion of flavonoids from roots (Tomasi et al. 2008). Because arsenate and
358 phosphate are chemically analogous, all of these processes are likely to mobilize As; for
359 example, organic acids are capable of displacing arsenate from exchange positions in
360 soils (Redman et al. 2002; Wenzel 2009). Additionally, plant strategies to attack oxides-

361 hydroxides of Fe will also alter the surfaces on which As is retained, and this can
362 potentially solubilize As (Fitz and Wenzel 2002).

363 Mycorrhizae are associations between plant roots and fungi, wherein the fungi
364 are able to colonize roots, either intra- or extra-cellularly (depending on the type of
365 mycorrhiza formed). Hence, mycorrhizae play an important role in the mineral nutrition
366 and absorption of elements by plants (Marschner 1995; Azcón-Aguilar and Barea 1997;
367 Fitz and Wenzel 2002). Mycorrhizal interactions are produced in approximately 80% of
368 angiosperms and in all gymnosperms (Fitz and Wenzel 2006), and in many cases
369 provide plants with increased resistance to biotic and abiotic stresses (Latch 1993;
370 Schützendubel and Polle 2002). Phosphorus is particularly important: many
371 mycorrhizae play a fundamental role in P nutrition in the plant (Mengel and Kirkby
372 2001), and act to increase, by 2-3 times, the amount of P accumulated in plants (Fitz and
373 Wenzel 2006). Therefore, the study of mycorrhizae is relevant to an understanding of
374 how As/P interact in plants. As absorption is reduced in the presence of mycorrhizae in
375 several plant species, including *Pteris vittata*, lentils, alfalfa, tomatoes, sunflowers and
376 corn (Trotta et al. 2006; Ahmed et al. 2006; Chen et al. 2007; Liu et al. 2005; Ultra et al.
377 2007a; Yu et al. 2009). Corn mycorrhizae were able to significantly reduce the amount
378 of arsenate, but not arsenite, absorbed by roots (Yu et al. 2009). In this same
379 experiment, a reduction in arsenate reductase activity also occurred in the root from a
380 fungal infection. Some authors attributed the lower concentrations of As in the plants
381 infected with mycorrhizae to a blockage of absorption (Yu et al. 2009), whereas others
382 attributed it to a dilution effect observed from the increase in overall plant mass (Chen
383 et al. 2007).

384 **3.1.2 Absorption of Arsenic**

385 Root absorption of elements first occurs by diffusion from the soil solution
386 within the root apoplast, followed by the symplast, effecting penetration to the interior
387 of plant cells (Mengel and Kirkby 2001). At the cellular membrane, ions enter via
388 transport proteins that are often specific for one or several elements of similar chemical
389 characteristics. Aquaporins and phosphate transporters both are involved in the
390 transmembrane transport and absorption of arsenic.

391 Aquaporins are water channels; however, other non-charged molecules, like
392 arsenious acid, also enter through them. Various authors have addressed aquaporins in
393 relation to the absorption of As(III) (Isayenkov and Maathuis 2008; Ma et al. 2008).

394 Interestingly, it has been experimentally determined that As(III) and Si both share the
395 same methods of entrance into and transport in rice (Ma et al. 2008). Hence, there is a
396 group of aquaporins (NIPs) that play a fundamental role in the absorption of non
397 charged molecules, such as glycerol, ammonia, and the boric, arsenious and silic acids
398 (Zhao et al. 2009).

399 Physiological studies in plants have illustrated the important role that phosphate
400 carriers play in the absorption of arsenate, and the interaction that occurs between both
401 P and As(V) at the root uptake level (Meharg and Macnair 1992; Esteban et al. 2003).
402 The phosphate/arsenate mechanism of absorption involves the co-transport of the anion
403 with protons, in a stoichiometry of 2H^+ for each anion (Zhao et al. 2009).

404 Organic forms of As are absorbed less effectively than are inorganic As forms
405 (Marín et al. 1992; Raab et al. 2007; Zhao et al. 2009), and Si transporters may also be
406 involved (Li et al. 2009a).

407 **3.1.3 Accumulation and Transport**

408 Once inside the cell, arsenate is reduced to arsenite, which consumes reduced
409 glutathione: $\text{AsO}_4^{-3} + 2 \text{GSH} \rightarrow \text{AsO}_3^{-3} + \text{GSSG}$, a reaction that is catalyzed by arsenate
410 reductase (Verbruggen et al. 2009). It has therefore been shown that the majority of
411 arsenic that exists in plant tissue is present as arsenite (Tripanthi et al. 2007), regardless
412 of what was in the solution at the time of plant growth. Arsenite has a high affinity for
413 SH groups and tends to be complexed and stored in vacuoles, although it can also be
414 transported via the xylem to other plant tissues. Movement through the xylem is
415 controlled by the flow of the transpiration stream, but is also influenced by membrane
416 transport proteins. Recently, two transporters (Lsi1 and Lsi2) were described between
417 plant endodermis and exodermis, and these mediate the entrance of arsenite into the
418 xylem or its efflux to the external medium (Zhao et al. 2009). These Lsi transporters are
419 principally involved in Si nutrition (Ma et al. 2008).

420 The transport of As, in most plant species, is generally not very effective and,
421 hence, As tends to remain in roots. An exception exists for those plants that are
422 unusually effective at accumulating As in aerial plant parts. Accumulation of arsenite in
423 the vacuole may be one reason for why As transport into the xylem is reduced (Zhao et
424 al. 2009). Xylem transport of As has been intensely studied over the past years, giving
425 interesting, although somewhat contradictory results. In many plant species, the
426 reduction of As(V) in roots appears to be a key factor that results in blocking the xylem

427 transport of As. Since phosphate is an anion that is completely mobile within plants, one
428 would expect As(V) to act similarly (given the analogy between both anions), but this is
429 not the case in any plant species. The influence of reduced As to block its transport was
430 tested in plants (*Arabidopsis thaliana*) mutated to silence arsenate reductase. These
431 plants demonstrated a ratio of $[As]_{\text{Aerial tissue}}:[As]_{\text{Root}}$ that was 25 times greater than the
432 wild type (Dhankher et al. 2006). These authors suggest that this change results from a
433 greater proportion of As(V) being available for transport through the xylem in roots,
434 presumably through the same pathways that handles phosphate.

435 The majority of As that does not accumulate in aerial tissue exists as As(III)
436 (Pickering et al. 2000; Dhankher et al. 2002; Castillo-Michel et al. 2007; Xu et al.
437 2007). The reducing process in roots may constitute a physiological mechanism by
438 which plants limit the flow of As into aerial tissues, thus protecting them from the
439 effects of this metalloid. Additionally, the majority of As in the root is found as
440 complexes (Vázquez et al. 2005), and there is a negative correlation between the percent
441 of As complexed by –SH groups in roots vs. the amounts translocated to aerial tissue
442 (Huang et al. 2008). In this respect, Raab et al. (2005) proposed that complexed As is
443 not transported through the xylem. In hyper-accumulator plants, some authors have
444 utilized synchrotron and liquid chromatography, coupled to ICP-MS techniques, to
445 determine how As is transported from roots to aerial tissues as As(V), and how As is
446 later stored in leaves as As(III) (Zhao et al. 2003; Pickering et al. 2006; Hokura et al.
447 2006; Tripathi et al. 2007). Duan et al. (2005), however, reported that arsenate reductase
448 has greater activity in the roots of *P. vittata*, postulating that As transported through the
449 xylem in this fern is primarily in the form of arsenite. Notwithstanding, in both plants
450 that accumulate arsenic and in those that do not, it appears that once inside the
451 cytoplasm, As is stored in vacuoles, thus avoiding interference with normal cellular
452 function (Verbruggen et al. 2009). Other trace elements are generally stored in tissues
453 that are less metabolically active, like epidermic (Vázquez et al. 1992), or senescing
454 tissues (Ernst et al. 2000).

455 Baker (1981) established a classification that grouped plants into three
456 categories, based on how much element they accumulated in shoots. The three classes
457 are called excluders, indicators and accumulators, and these terms will be used
458 henceforth below. Some species are able to hyper-accumulate As: *Pteris vittata* (up to
459 22,000 mg As kg⁻¹), *Jasione montana* (6640), *Calluna vulgaris* (4130), *Agrostis tenuis*

460 and *stolonifera* (10000), *Pityrogramma calomelanos*, *Mimosa pudica*, *Melastoma*
461 *malabratricum* (8350) (Wang and Mulligan 2006). Except for these particular plants,
462 most plants accumulate arsenic in their roots. This, however, does not exclude the fact
463 that many plants are adapted to grow in soils that have high As concentrations, without
464 accumulating it. Among such plants are the tolerant excluder ecotypes. The
465 concentration of arsenic in non-accumulator plants rarely exceeds 2 mg As kg⁻¹ in aerial
466 parts (Horswell and Speir 2006). From an agricultural perspective, areas flooded with
467 waters rich in As may pose a problem, because these crops may contain sufficient As
468 levels to render them dangerous for human consumption (Bhattacharya et al. 2007). In
469 Fig. 2, links between physiological traits in plants and As-phytoaccumulation strategies
470 are presented.

471 **3.2 Arsenic Toxicity in Plants**

472 When present within plant cells, As has various negative physiological effects,
473 many of which have recently been the subject of intense study. Arsenic has no known
474 biological function, although positive effects have been described at low concentrations
475 of arsenate. The reason behind these positive effects has yet to be determined. Although
476 these effects may be attributed to As itself, they may also result from an increase in the
477 absorption of P when As concentrations remain below toxic thresholds (Carbonell-
478 Barrachina et al. 1998). Arsenite is generally more toxic than arsenate, partially because
479 of its greater solubility and mobility. The sensing and signaling of an excess of As in
480 plants and the complex biochemical changes it induces are still unknown, although they
481 have been extensively studied in the recent years (Verbruggen et al. 2009). When the
482 toxicity of trace elements is studied in plants, herbaceous plants and/or crops are
483 generally the target species used. Woody species are uncommonly used in As plant
484 toxicity testing, despite the fact that they are favored when attempts are made to
485 revegetate degraded soils.

486 The toxicity of organoarsenics has been scarcely studied in plants; however, they
487 appear to block meristematic tissues, and also affect protein synthesis (Horswell and
488 Speir 2006).

489 **3.2.1 Visual Effects**

490 Impairment of plant development is one of the observed symptoms from arsenic
491 toxicity. Arsenate and arsenite both reduce the growth of plant species, such as *Holcus*
492 *lanatus*, *Lupinus albus* and *Triticum aestivum*, when grown under hydroponic

493 conditions (Hartley-Whitaker et al. 2001; Vázquez et al. 2005; Geng et al. 2006).
494 Among the symptoms induced by As exposure in plants are reduced root elongation,
495 loss of root branching, chlorosis in leaves, and shrinking or necrosis in aerial plant parts
496 (Carbonell-Barrachina et al. 1998).

497 **3.2.2 Oxidative Stress**

498 Elements that have several oxidation states often serve as good reaction catalysts
499 in which oxidation-reduction is involved (As, Cu, Hg, etc.). In aqueous solutions of near
500 neutral pH, such as in the cytoplasm, radicals can produce H₂O₂, which later produce
501 hydroxyl radical. All reactive oxygen species (ROS) can directly damage biomolecules
502 and cause peroxidation of membrane lipids. Arsenic can also induce oxidative stress in
503 plant cells, a fact reflected as an increase in the concentration of malondialdehyde
504 (MDA) in vegetable tissues; MDA is a metabolic product of the peroxidation of lipids
505 in biological membranes. The stimulation of oxidative stress, associated with the
506 accumulation of arsenic in plants, has been shown to occur in both cultivated plants, and
507 in wild bushes (Hartley-Whitaker et al. 2001; Mascher et al. 2002; Moreno-Jiménez et
508 al. 2008, 2009a). Arsenic also modifies the gene expression involved in cellular
509 homeostasis for redox perturbation (Requejo and Tena 2005) and activates some
510 antioxidant enzymes (Srivastava et al. 2005).

511 **3.2.3 Nutritional Disorders**

512 Plant mineral nutrition is affected in a non-specific manner by many toxic
513 elements. Effects result either from an alteration in transport processes of the cellular
514 membrane, or effects on transpiration. The most notable effect produced by As results
515 from the similarities that exist between arsenate and phosphate. Addition of arsenate
516 causes a decrease in the levels of P in plants, because the entry of both ions is mediated
517 through the same membrane transporter (Meharg and Macnair 1992; Vázquez et al.
518 2005). Among other changes to nutritional patterns caused by the presence of As in the
519 environment in which plants are grown, is a decrease in the concentrations of Mn, Fe,
520 Cu, N, Zn and Mg (Mascher et al. 2002; Vázquez et al. 2008b).

521 **3.2.4 Photosynthetic Inhibition**

522 Arsenic causes chlorosis in plant leaves because of the induced decrease in
523 chlorophyll levels (Mascher et al. 2002). There may be other reasons for As-induced
524 chlorosis (such as iron deficiency), but the primary cause is directly attributed to the
525 inhibition of pigment synthesis (Jain and Gadre 1997). The effects produced result

526 from limited availability of δ -aminolevulinic acid (a precursor to chlorophyll) and from
527 alterations in proteins rich in thiol groups.

528 **3.2.5 Metabolic and Genetic Alterations**

529 Theoretically, arsenate can substitute for phosphate in some metabolic processes.
530 Within the cytoplasm, arsenate competes with phosphate in phosphorylation reactions,
531 such as the synthesis of ATP. Herein, ADP-As is formed, altering the energetics of the
532 cell cycle because of its instability (Verbruggen et al. 2009). Arsenite demonstrates a
533 high affinity for –SH groups of biomolecules (enzymes and proteins), inhibiting their
534 function (Meharg and Hartley-Whitaker 2002). As(III) and (AsV) are mutagenic
535 compounds that can alter the genome (Lin et al. 2008). For this reason, the presence of
536 repair biomolecules in the chromatin may be able to increase a plant's tolerance to
537 arsenic (Verbruggen et al. 2009).

538 **3.3 Mechanisms of Arsenic Resistance in Plants**

539 There is a difference between plant resistance and plant tolerance to toxic
540 elements. Resistance to toxic elements is generally defined by a plant's capacity to
541 support an excess of a toxic element present in the environment. By comparison,
542 tolerance is the exceptional capacity of a plant to survive in a soil that is toxic to other
543 plants, demonstrated by the interaction between genotype-environment (Hall 2002).
544 Ernst et al. (2008) have established another classification, based on the
545 tolerance/sensitivity a plant has to trace elements: (i) hypotolerant, sensitive, or
546 hypersensitive plants are those with genetically modified phenotypes that are extremely
547 vulnerable to one or many metals or metalloids; (ii) basal tolerant --would be equivalent
548 to resistance, meaning genetic resistance of one species (also called non-metallic
549 populations or populations with constitutive tolerance); (iii) hypertolerants are
550 populations that show a low sensitivity to one or more elements due to adaptive
551 mechanisms (also called metalophytes). Plants resist the effects of toxicity by using
552 several biological mechanisms, all of which are known to be detoxification
553 mechanisms. There is still insufficient research information available to explain what
554 cellular mechanisms plants use to detect the presence of As. Moreover, what signals are
555 triggered after As is detected and detoxification mechanisms initiated is also not known,
556 other than those cellular signals derived from the tissue damage produced (Verbruggen
557 et al. 2009).

558 **3.3.1 Mycorrhization**

559 Mycorrhizae are able to modify tolerance patterns in host plants (Sharples et al.
560 2000; González-Chávez et al. 2002; Leung et al. 2006). In regard to the effects that
561 mycorrhizae cause in their hosts, plants can be categorized as follows: (i) plants that
562 respond positively to mycorrhization, with increases in biomass and improvements in
563 mineral nutrition (AM-r plants), and (ii) plants in which mycorrhization has no effect
564 (n-AM-r plants). Smith et al. (2010) discussed how mycorrhization effectively
565 alleviated the toxic effects of As on AM-r plants, whereas literature references on those
566 same effects on n-AM-r plants are variable. In wild rye, for example, some plants
567 infected with mycorrhizae (n-AM-r) showed no improved tolerance to As (Knudson et
568 al. 2003), while in other cases, many plants infected with mycorrhizae did show
569 tolerance improvement. When tolerance was improved in plants infected with
570 mycorrhizae, there were several different reasons for the improvement. Xu et al. (2009),
571 for example, attributed improvement to greater absorption of P and a reduced
572 concentration of As in *Medicago truncatula* plants, while Yu et al. (2009) explained this
573 same effect as an inhibition in the absorption and speciation of As in plants infected
574 with mycorrhizae.

575 **3.3.2 Immobilization Within the Rhizosphere**

576 It has been shown that, in flooded soils, iron plaques are formed in areas
577 surrounding the roots. These plaques are able to retain high concentrations of As, and
578 act as the first filter at the root level. This mechanism is especially efficient in rice
579 paddies or where plants grown in liquid media (Hansel et al. 2002; Liu et al. 2004,
580 2006). In the rhizosphere of aerated soils, redox reactions favor the formation of iron
581 plaques that retain As in the areas directly surrounding roots. Fe, retained in the
582 apoplastic area surrounding roots of plants grown in well aerated soils, could act in a
583 similar manner as that of flooded soils (Douceff and Terry 2002).

584 **3.3.3 Exclusion**

585 Exclusion reduces the entrance of As via changes in the mechanisms of root
586 absorption. Tolerant populations of the plant *Holcus lanatus* lack the high affinity
587 uptake system for phosphate absorption (Meharg and Macnair 1992). For this reason,
588 these plants had reduced absorption of both phosphate and arsenate, and were better
589 adapted to environments having high concentrations of As (Meharg and Hartley-
590 Whitaker 2002). *Arabidopsis thaliana* plants, in the presence of As(V), slowed gene
591 expression associated with phosphate absorption; simultaneously, the plant induced

592 transcriptional gene expression that was stimulated by As, suggesting that there are
593 distinct transcriptional pathways that regulate the deficiency of P and that the responses
594 to As are interconnected (Catarcha et al. 2007).

595 **3.3.4 Active Efflux**

596 Arsenic can be pumped out of plant cells (Xu et al. 2007), mainly in the form of
597 arsenite. Although this mechanism has yet to be clearly established, the status of the
598 information that exists on the subject was recently summarized by Zhao et al. (2009).
599 Active efflux of arsenite has been observed to occur in various plant species grown
600 under hydroponic conditions: wheat, barley, corn, tomato, *Holcus lanatus* and
601 *Arabidopsis thaliana*. Physiological evidence indicates that the expulsion process is
602 active and depends on a proton gradient created by cellular metabolism. It has yet to be
603 demonstrated that increased expulsion correlates directly with improved plant tolerance
604 within a given plant population; however, this relationship has been demonstrated in
605 microorganisms (Bhattacharjee and Rosen 2007). Studies performed in soil have
606 provided evidence that arsenite accumulates in areas directly surrounding the roots of
607 sunflower and corn (Ultra et al. 2007a,b; Vetterlein et al. 2007). It is estimated that up
608 to 50-80% of the As absorbed by roots may be secreted via active efflux in non-
609 accumulating plants (Verbruggen et al. 2009). In contrast, it has been demonstrated that
610 hyper-accumulating plants do not show As efflux to the environment via roots (Zhao et
611 al. 2009).

612 **3.3.5 Complexation**

613 Plants take advantage of the high affinity arsenite has for –SH groups to
614 deactivate the toxic effects of As. Therefore, there are many ligands in the cytosol for
615 which trace elements have a high affinity. In certain plant species, As(III) complexes
616 exist that have different biomolecules rich in thiol groups such as glutathione and
617 phytochelatines (Meharg and Hartley-Whitaker 2002). For example, it has been shown
618 that the presence of some trace elements, such as Ag, As, Cd, Cu, Hg, Se or Pb in
619 plants, provoke the synthesis of phytochelatines. Phytochelatines (PCs) are small
620 peptides, rich in cysteine, that have the general structure (γ-Glu-Cys)_n-Gly, where n=2-
621 11. PCs are bound to trace elements via thiolate bonds that are synthesized from
622 glutathione (GSH) and catalyzed by the enzyme PCsynthase. PCs are able to effectively
623 complex inorganic arsenic that accumulates in plants, and GS₃-As(III) complexes have
624 been identified to exist in certain plants (Pickering et al. 2000). Many plant species have

625 responded to the presence of As in the environment, such as lupin, *Holcus lanatus*,
626 sunflower or *Silene vulgaris* (Sneller et al. 2000; Hartley-Whitaker et al. 2001; Vázquez
627 et al. 2005; Raab et al. 2005; Aldrich et al. 2007; Moreno-Jiménez et al. 2008, 2009a).
628 *Arabidopsis* plants that have a greater capacity to synthesize PCs were more tolerant
629 than were the wild types (Dhanker et al. 2002); moreover, resistant clones of *H. lanatus*
630 showed a greater production of PCs in response to As than sensitive plants (Hartley-
631 Whitaker et al. 2001). The foregoing points indicate that PCs, and probably GSH play a
632 role in the detoxification of As. However, this mechanism requires great metabolic
633 effort and, in some instances, greater tolerance has not been correlated to greater levels
634 of phytochelatinates or thiols. Therefore, in hyper-accumulating plants, this detoxification
635 method appears to be limited in comparison to the high levels of As that accumulate
636 (Zhao et al. 2003). And, there is some evidence that the proportion of As complexed by
637 SH in the root is negatively correlated with the translocation of As to the aerial portion
638 of the plant (Huang et al. 2008).

639 **3.3.6 Compartmentalization**

640 Once arsenite is complexed, it is most probably stored in the vacuoles of root
641 cells, which reduces its mobility in the cytoplasm and its translocation through the
642 xylem. It is believed, however, that vacuolar compartmentalization, and thereby,
643 detoxification of As, is important in all plant organs (Pickering et al. 2006). Once inside
644 the vacuole, where the pH is approximately 8, the rupture of the complex could take
645 place, and the ligand could then be used to complex more arsenite. Although there is no
646 experimental data to show that the entrance of PC-As or GSH-As through the tonoplast
647 takes place under in vivo conditions (Tripanthi et al. 2007), it is known to occur under
648 *in vitro* conditions (Dhanker et al. 2006). The entrance of such arsenite forms that are
649 complexed to thiol groups is most likely facilitated via ABC-(ATP binding cassette
650 superfamily) type transporters (Verbruggen et al. 2009).

651 Some authors have suggested that As is retained in cell walls (Douceff and
652 Terry 2002; Vázquez et al. 2007), although this has not clearly been established. Cell
653 wall retention has been demonstrated to be an effective detoxification mechanism for
654 other trace elements, such as Cd and Hg (Zornoza et al. 2002; Moreno-Jiménez et al.
655 2007).

656

657 **4 Practical Applications for Mitigating Arsenic's Effects**

658 **4.1 Phytoremediation**

659 Phytoremediation is the use of plants to remediate organic or inorganic
660 contaminates of soils and water (Salt et al. 1995). Chaney et al. (1997) defined soil
661 phytoremediation as the use of plants, amendments, or agricultural techniques to
662 eliminate, retain or reduce the toxicity of soil contaminants. From the onset,
663 phytoremediation was seen as a competitive technology for recuperating soils. It has
664 promised and has produced positive results, which makes it attractive to both the
665 commercial and scientific communities (Peuke and Rennenberg 2005). The benefits that
666 phytoremediation has shown over competitive techniques (physico-chemical site-
667 cleaning methods) are as follows: (i) it is inexpensive, (ii) it is less invasive, and (iii) it
668 is well received both environmentally and socially. Phytoremediation has been
669 successfully used to clean arsenic-contaminated soils and water.

670 **4.1.1 Phytoextraction**

671 Phytoextraction is the technique plants use to accumulate significant quantities
672 of a contaminant in their tissues, and these plants can later be harvested or collected for
673 appropriate disposal or management (McGrath and Zhao 2003). This technology has
674 been studied and applied to events connected with Cd, Zn, Pb, Ni and As
675 contamination. Except for Ni, which has economic value (the technique with Ni clean-
676 up is called phyto-mining; Chaney et al. 2007), the other forms of contaminated plant
677 biomass pose a disposal problem (Robinson et al. 2006). In some cases, phytoextraction
678 has been assisted by mobilizing agents, although the experiments have shown that one
679 must be careful to control leaching, because there is high risk that the contaminant could
680 disperse into water sources (Nowack et al. 2006). McGrath and Zhao (2003) estimated
681 that, if one plant produced 10 t of biomass ha⁻¹, it would need to accumulate a
682 contaminant (soil/plant concentration ratio) by 20 fold to reduce it to 50% of the
683 original soil level, after 10 plant cycles. Phytoextraction of As (Fig. 3) has been tested
684 using in-container studies that utilize the hyper-accumulating plant species *Pteris*
685 *vittata*, although other hyper-accumulating plants are available (Meharg 2005). A recent
686 and cogent review was published that was specific to As accumulation in *P. vittata* (Xie
687 et al. 2009).

688 *P. vittata* has root-level transporters that have high affinity and capacity for As
689 absorption (Poyton et al. 2004). In addition, this species shows a limited root
690 complexing of As (Zhao et al. 2003), and elevated concentrations of As in sap (Su et al.

691 2008). Together, these characteristics trigger an extraordinary level of translocation of
692 As towards the aerial portion of the plant (Tu and Ma 2002). Although As is usually not
693 that bioavailable from soils, the rhizosphere of *P. vittata* appears to be uniquely capable
694 of mobilizing As, even from soil fractions that are barely available (Fitz et al. 2003). A
695 reduction in redox potential, and an increase in the amount of organic carbon released in
696 the rhizosphere of ferns may be what enhances As uptake by the plant. Moreover,
697 following phytoextraction with this plant, the available As fraction was reduced.
698 Unfortunately, the distribution and ecological niche of *Pteris vittata* is restricted, which
699 confines its application to specific zones. In addition, there is the problem of having to
700 dispose of the harvested (contaminated) plant tissue. Recently, two reviews have been
701 authored, in which the necessity of improving the genetics of phytoextracting plants
702 through molecular plant biology was described (Tripathi et al. 2007; Zhu and Rosen
703 2009).

704 It has recently been determined that the As fraction retained in labile form is
705 recharged at a slow rate, which impedes phytoextraction (Cattani et al. 2009). With
706 respect to assisted phytoextraction of As, results have revealed that As absorption by
707 plants increased after application of phosphate (Tassi et al. 2004) or biodegradable
708 chelating agents such as HIDS (Hydroxyiminodisuccinic Acid) and EDDS
709 (Ethylenediamine-N,N'-disuccinic Acid) (Azizur-Rahman et al. 2009). In this case, it is
710 necessary to carefully evaluate the consequence of diffuse contamination, when As
711 becomes more soil mobile (Peñalosa et al. 2007).

712 **4.1.2 Phytostabilization**

713 Phytostabilization is the mixed use of plants and agricultural practices to reduce
714 mobilization and transfer of contaminants (Chaney et al. 1997). When plants are present
715 in the soil, contaminants are stabilized, making them less susceptible to erosion and
716 wind dispersion. Plants accumulate contaminants in the root, which further impedes
717 their transfer and mobility. When this occurs, auto-sustainable plant species that have a
718 prolonged life cycle and are adapted to such environmental conditions are especially
719 interesting. The concept of natural attenuation consists of an ecosystem's and soil's
720 capacity to auto-regulate and react slowly to chemical attacks, which can potentially
721 reduce the risks associated with the presence of the contaminating element (Adriano et
722 al. 2004). Assisted natural attenuation refers to the use of techniques such as replanting
723 or the application of amendments to accelerate the process of natural attenuation

724 (Madejón et al. 2006). For As, it has been demonstrated that both natural attenuation as
725 well as phytostabilization could be useful field techniques (Vázquez et al. 2006;
726 Madejón and Lepp 2007; Domínguez et al. 2008; Moreno-Jiménez et al. 2010a, 2011b).

727 The authors of some studies, however, have described plants that have little
728 influence on the available As fraction, particularly when As exists at high soil
729 concentrations (King et al. 2008). Phytostabilization is aided when organic or inorganic
730 amendments are used; these materials improve soil properties by retaining metalloids or
731 preventing their solubilization (de la Fuente et al. 2009). Kumpiene et al. (2008)
732 reviewed different amendments that could immobilize As in soils. They concluded that
733 the amendments could be both useful and effective in managing arsenic contamination.
734 Among useful inorganic amendments are those rich in iron (red sludge, rolling mill
735 scale, etc.), fly ash, clays or liming materials (Kumpiene et al. 2008; de la Fuente et al.
736 2010), whereas organic amendments capable of immobilizing As are those that have
737 high stability of the humus (de la Fuente et al. 2009). In either case, it is necessary to
738 monitor contaminants over time to assure that the phytostabilization process has been a
739 success (Vangronsveld et al. 2009).

740 Recently, phyto-attenuation has been described as the process by which a plant
741 extracts the most available fraction of an element from the soil, which can later be
742 harvested in such a way that it reduces the risks associated with inorganic soil
743 contamination (Meers et al. 2010). Phytostabilization of arsenic in roots has been
744 confirmed as a useful remediation technique, because there is low risk of As being
745 remobilized, even when the roots themselves are mineralized (Vázquez et al. 2008c;
746 Moreno-Jiménez et al. 2009b).

747 **4.1.3 Phytofiltration**

748 The presence of As in water presents one of the greatest of environmental risks
749 to human health; As presents both a direct risk through consumption, as well as through
750 indirect risk from contaminated irrigation waters. Phytofiltration is a technique that uses
751 plants/roots to decontaminate water (Raskin et al. 1997). Aquatic, semi-aquatic, and
752 terrestrial plants, and plant biomass (Haque et al. 2007) have all been used to eliminate
753 or reduce arsenic contaminated water. Ideally, plants used in phytofiltration must be
754 effective in capturing the contaminant from water, and must also grow rapidly. Plants
755 that are not adapted to grow in anoxic conditions or those that are unable to grow
756 rapidly in such conditions, may require the water in which they grow to be artificially

757 aerated. Blastofiltration is the use of plant seedlings instead of plants. Seedling use
758 increases the surface-area ratio of contact/volume of water, allowing better contaminant
759 absorption in plant material (Raskin et al. 1997). Anawar et al. (2008) recently reviewed
760 the use of phytofiltration in water, concluding that this method could be an effective
761 alternative. Two strategies to deal with As contamination by this method have been
762 studied: (i) employing plants that need a support structure and (ii) using species of
763 plants that float on water. The first strategy relies on *P. vittata* to eliminate As from
764 solutions by growing the plants under hydroponic conditions in contaminated water
765 (Malik et al. 2009). Plants can purify solutions that retain up to 200 $\mu\text{g L}^{-1}$ of As, and
766 can lower the concentration present to less than 10 $\mu\text{g L}^{-1}$, in only 24 hours (Huang et al.
767 2004). In other experiments, design parameters were optimized to achieve maximal As
768 uptake by stabilizing the pH below 5.2 (Tu and Ma 2003). In the second strategy, plants
769 of the genus *Lemna* and the macrophyte *Spirodela polyrhiza* were able to reduce the
770 concentration of As in contaminated waters (Azizur-Rahman et al. 2007; Sasmaz and
771 Obek 2009).

772 **4.2 Reducing Arsenic Transfer to Edible Plant Tissues**

773 The main sources of arsenic exposure to humans are through consuming
774 contaminated water (Hurtado-Jiménez and Gardea-Torresdey 2006) or food (Meharg et
775 al. 2008). In some countries, there is a high risk of exposure to arsenic from eating
776 contaminated foods (Meharg et al. 2009).

777 **4.2.1 Presence of Arsenic in Rice**

778 Rice is the principal source of human nutrition in much of the world. It is
779 commonly grown in naturally or artificially flooded soils. When rice is grown under
780 conditions of poor aeration, arsenic is primarily found as As(III), which is highly
781 mobile. In this form, As is easily absorbed by rice plants, whose capacity to accumulate
782 As is greater than most other crops, such as wheat or barley (Williams et al. 2007). As is
783 stored in rice tissues at increasing concentrations in the following parts: external iron
784 plaque>root>straw>husk>grain (Liu et al. 2006). Therefore, formation of an external
785 iron plaque inhibits, in part, the accumulation of As in the rice plant (Liu et al. 2006).

786 Regardless of order, the concentrations of As that appear in edible portions of
787 rice are very high, especially considering the quantities of rice eaten by humans.
788 Meharg et al. (2009) have shown that eating rice is the main source of As exposure in
789 many countries, and increases risks associated with chronic arsenic exposure. Liao et al.

790 (2010) described how consuming contaminated rice is associated with skin disease in
791 children. The average concentrations of As in rice are between 0.05 and 0.95 mg kg⁻¹,
792 although some samples exceed 1 mg As kg⁻¹ (Williams et al. 2005). It has been
793 estimated that the quantity of arsenic consumed per person, per day, in some countries,
794 may be up to 0.9 mg As day⁻¹ (Butcher 2009). According to the WHO, this intake
795 amount approaches the maximum tolerable limit for daily ingestion of As (Williams et
796 al. 2005).

797 Experiments in recent years have shown that the development of agricultural and
798 genetic techniques may help control or reduce such risks (Tripathi et al. 2007; Zhao et
799 al. 2009). One approach to risk reduction involves selecting varieties of rice that
800 accumulate less As in their edible parts (Williams et al. 2005). Alternatively, the same
801 end may be achieved by using genetic techniques (Tripathi et al. 2007). Lemont,
802 Azucena and Te-qing are rice cultivars that apparently accumulate less As in their seeds
803 (Norton et al. 2009). Genetic modification studies are also being conducted to evaluate
804 methods by which As accumulation in edible tissues can be reduced, or As
805 volatilization increased from edible tissues (Tripathi et al. 2007).

806 Work to mitigate As levels in crops through changes in agricultural practices
807 have also been attempted (Fig.3). Using As-contaminated water for crop irrigation has
808 increased As uptake from soils into plants for decades (Williams et al. 2006; Khan et al.
809 2009). Using clean irrigation water, or purifying the water before use in irrigation would
810 obviously reduce food levels of arsenic. Improving aeration of soils would help
811 immobilize any As present, and would reduce its plant availability (Xu et al. 2008).
812 As(III) is absorbed through plant roots via water channels that also are involved in the
813 absorption of boron and silicon (Ma et al. 2008). Competition between these elements
814 and arsenite may therefore exist, which would explain why rice fertilized with Si had
815 lower concentrations of As (Guo et al. 2009; Li et al. 2009b). Finally, consumers can
816 reduce their As exposure risk by boiling rice in abundant water (Raab et al. 2009), or by
817 substituting rice with other grains, such as wheat or corn, if possible (Signes-Pastor et
818 al. 2009).

819 **4.2.2 Selecting Crops for Low As Levels**

820 Reducing the oral intake of As in humans by reducing the amounts consumed in
821 crops would greatly improve food safety. Some crops accumulate higher levels of As
822 than others do. Since As is generally retained in plant roots (Moreno-Jiménez et al.

823 2008; Zhang et al. 2009), tubers and edible roots may accumulate As, and it would be
824 most wise to closely evaluate these where they are heavily consumed. Potatoes plants
825 (Moyano et al. 2009) and other tubers grown in As -contaminated soils, such as radishes
826 (Warren et al. 2003), carrots, garlic and onions (Huang et al. 2006; Zhao et al. 2009),
827 have shown significant levels of As. In contrast to crops showing high As levels, de la
828 Fuente et al. (2010) reported only low or moderate levels of As in potatoes, carrots and
829 sugar beets.

830 Other plant organs are also subjected to As accumulation. Huang et al. (2006)
831 described the following pattern of As concentrations in the edible parts of the following
832 edible crops: celery>mustard>spinach>lettuce>taro>bokchoi >cowpea>cauliflower
833 >eggplant. De la Fuente et al. (2010) reported the following pattern in several crops: red
834 cabbage~curly endive>barley~wheat~sugar beet~leek>cabbage~green pepper. Zhao et
835 al. (2009) found As concentrations to be high in lettuce, eggplant, and green onions,
836 whereas, Gulz et al. (2005) found As concentrations in sunflower and rape to be greater
837 than those of corn. Warren et al. (2003) reported concentrations of As to be greater in
838 lettuce and broccoli than in spinach, but above all, these authors found the greatest
839 concentrations of As to occur in radishes. The percentage of inorganic As in edible
840 crops was reported to be high, although the concentration found posed no serious risk
841 for human consumption (de la Fuente et al. 2010). Gulz et al. (2005) advised against
842 using sunflower and rape seeds to produce cooking oil, because As levels in these crops
843 surpassed the maximum levels permitted in Switzerland of 0.2 mg As kg⁻¹.

844 **4.2.3 Using Soil Amendments and Mycorrhizae**

845 Applying inorganic amendments can affect the mode of uptake and level of
846 available As in soils. Particularly effective are amendments rich in Fe, because iron
847 oxides effectively retain As (Mench et al. 2003; Warren et al. 2003; Hartley and Lepp
848 2008; de la Fuente et al. 2010). Fertilization with P also alters the absorption of As,
849 because phosphate displaces arsenate in the soil and mobilizes it. Gunes et al. (2008)
850 reported an increase in As accumulation when P was applied; however, the application
851 of phosphorus-based fertilizers reduced the As plant levels (Khattak et al. 1991; Pigna
852 et al. 2009).

853 Raising the soil pH increases As plant bioavailability (Smith et al. 1999; Fitz
854 and Wenzel 2002), although some studies indicate that application of CaCO₃ to acidic
855 soils reduced As availability (Simón et al. 2005).

856 The application of organic amendments increases the soil mobility of, and
857 therefore, As plant uptake (Mench et al. 2003; Hartley and Lepp 2008; Renella et al.
858 2007; Clemente et al. 2010), but some studies show that available As is stabilized with
859 the application of organic matter to soil (Gadepalle et al. 2007). The fact that organic
860 matter is both stable and is highly polymerized may help to explain such contradictory
861 results. Combining Fe-enriched amendments with organic materials should be a future
862 focus of research, since these amendments provide a good environment for plant
863 growth, and reduce or

864 prevent the transfer of harmful As or other metal concentrations to edible plant
865 tissues.

866 Ninety percent of higher plants interact with mycorrhizae (González-Chávez et
867 al. 2002; Leung et al. 2006; Chen et al. 2007) and mycorrhizae appear to affect the soil
868 behavior of As. Existing data suggest that plants infected with mycorrhizae have a
869 greater ratio of P/As in their tissues, and this bestows greater As tolerance on them
870 (Smith et al. 2010). In some studies, the reduction of As in plants that were infected by
871 mycorrhizae was attributed to two effects: (i) a slower rate of root absorption of As (Yu
872 et al. 2009), and (ii) a dilution effect from accentuated plant growth (Smith et al. 2010).
873 Further research is needed to find improved plant-microorganism combinations that
874 minimize As accumulation in plant tissues destined for human consumption.

875 **4.3 Alternatives: Using Contaminated Crops for Non-food Purposes**

876 An alternative to consuming As-contaminated food, is to use As-contaminated
877 biomass for non-food purposes (Vangronsveld et al. 2009). Such biomass could be used
878 in energy production or as primary material inputs for industrial products (Thewys
879 2008; Dickinson et al. 2009; Pandey et al. 2009; Mench et al. 2010). In either case, the
880 use of phytotechnologies is viable for managing contaminated soils and as means to
881 return them to economic profitability (Thewys and Koppens 2008). The examples in
882 which such alternative uses were actually put into practice are few, but, when used, the
883 results have proven satisfactory; notwithstanding, improvements to these techniques are
884 required (Thewys and Koppens 2008). Several experiments were conducted in
885 contaminated soils using plant species such as *Salix* spp., corn, sunflower, tobacco,
886 poplar, *Brassica* ssp., *Pteris vittata*, etc. (Vangronsveld et al. 2009). Energy from such
887 biomass could be in the form of biogas generation, direct incineration, pyrolysis,
888 biomass gasification, fermentation into biofuels, etc. (Mench et al. 2010). Degraded

889 sites can be managed to produce energy and at the same time reduce the environmental
890 risk associated with arsenic. For this purpose, contaminated soils may be used to amend
891 wastes (compost, biochar, or iron oxides), thus recycling the materials. Both renewable
892 energy production and human waste recycling are key factors for the future global
893 environmental agenda (Dickinson et al. 2009). Crops grown in contaminated soils could
894 also be used to produce other non-food goods. Examples are: cosmetics, industrial
895 products, essential oils, paper, cardboard, wood, plant fibers, etc. (Mench et al. 2010).
896 Regardless of the end use to which contaminated plant biomass is put, avoiding
897 unacceptable environmental impact is crucial, particularly when arsenic or other
898 contaminants are present in plant biomass.

899

900 **5 Summary**

901 Arsenic is a natural trace element found in the environment. In some cases and
902 places, human activities have increased the soil concentration of As to levels that exceed
903 hazard thresholds. Amongst the main contributing sources of As contamination of soil
904 and water are the following: geologic origin, pyritic mining, agriculture and coal
905 burning. Arsenic speciation in soils occurs and is relatively complex. Soils contain both
906 organic and inorganic arsenic species. Inorganic As species include arsenite and
907 arsenate, which are the most abundant forms found in the environment. The majority of
908 As in aerated soils exists as H_2AsO_4^- (acid soils) or HAsO_4^{2-} (neutral and basic).
909 However, H_3AsO_3 is the predominant species in anaerobic soils, where arsenic
910 availability is higher and As(III) is more weakly retained in the soil matrix than is
911 As(V). The availability of As in soils is usually driven by multiple factors. Among these
912 factors is the presence of Fe-oxides, and/or phosphorus, (co)precipitation in salts, pH,
913 organic matter, clay content, rainfall amount, etc. The available and most labile As
914 fraction can potentially be taken up by plant roots, although the concentration of this
915 fraction is usually low.

916 Arsenic has no known biological function in plants. Once inside root cells,
917 As(V) is quickly reduced to As(III), and, in many plant species, becomes complexed.
918 Phosphorus nutrition influences As(V) uptake and toxicity in plants, whilst silicon has
919 similar influences on As(III). Plants cope with As contamination in their tissues by
920 possessing detoxification mechanisms. Such mechanisms include complexation, and
921 compartmentalization. However, once these mechanisms are saturated, symptoms of

922 phytotoxicity appear. Phytotoxic effects commonly observed from As exposure includes
923 growth inhibition, chlorophyll degradation, nutrient depletion and oxidative stress.
924 Plants vary in their ability to accumulate and tolerate As (from tolerant
925 hyperaccumulators to sensitive excluders), and some plants are useful for soil
926 reclamation and in sustainable agriculture.

927 The status of current scientific knowledge allows us to manage As
928 contamination in the soil-plant system and to mitigate arsenic's effects.
929 Phytoremediation is an emerging technology suitable for reclaiming As-contaminated
930 soils and waters. Phytoextraction has been used to clean As-contaminated soils,
931 although its applicability has not yet reached maturity. Phytostabilization has been
932 employed to reduce environmental risk by confining As as an inert form in soils, and
933 has shown success in both laboratory experiments and in field trials. Phytofiltration has
934 been used to treat As-enriched waters. Such treatment removes As when it is
935 accumulated in plants grown in or on water. In agricultural food production, appropriate
936 soil management and plant variety/species selection can minimize As-associated human
937 diseases and the transfer of As within the food chain. Selecting suitable plants for use
938 on As contaminated soils may also enhance alternative land use, such as for energy or
939 raw material production.

940

941 **Keywords:** arsenate, arsenite, phytoremediation, phytotoxicity, crops, environmental
942 risk

943

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950

951 **References**

952 Adriano DC (2001) Trace elements in terrestrial environments. Biogeochemistry,
953 bioavailability and risks of metals. Springer-Verlag, New York.

- 954 Adriano DC, Wenzel WW, Vangronsveld J, Bolan NS (2004) Role of assisted natural
955 remediation in environmental cleanup. *Geoderma* 122:121-142.
- 956 Ahmed FRS, Killham K, Alexander I (2006) Influences of arbuscular mycorrhizal
957 fungus *Glomus mosseae* on growth and nutrition of lentil irrigated with arsenic
958 contaminated water. *Plant Soil* 283:33–41.
- 959 Aldrich MV, Peralta-Videa JR, Parsons JG, Gardea-Torresdey JL (2007) Examination
960 of arsenic(III) and (V) uptake by the desert plant species mesquite (*Prosopis* spp.)
961 using X-ray absorption spectroscopy. *Sci Tot Environ* 379:249-255.
- 962 Allen HE (2001) Terrestrial ecosystem: an overview. In: Allen HE, (ed) Bioavailability
963 of Metals in Terrestrial Ecosystems: Importance of Partitioning for Availability to
964 Invertebrates, Microbes, and Plants. SETAC Press, pp. 1-6, Pensacola, Florida.
- 965 Anawar HM, Garcia-Sanchez A, Regina IS (2008) Evaluation of various chemical
966 extraction methods to estimate. Plant-available arsenic in mine soils. *Chemosphere*
967 70:1459–1467.
- 968 Atker K, Naidu R (2006) Arsenic speciation in the environment. In: Naidu R. et al. (eds)
969 Managing Arsenic in the Environment. From Soils to Human Health. CSIRO Pub.,
970 Collingwood, Australia, pp. 61-74.
- 971 Azcón-Aguilar C, Barea JM (1997) Applying mycorrhiza biotechnology to horticulture:
972 significance and potentials. *Sci Hortic* 68:1-24.
- 973 Azizur Rahman M, Hasegawa H, Mahfuzur Rahman M, Arifur Rahman M, Miah MAM
974 (2007) Accumulation of arsenic in tissues of rice plant (*Oryza sativa* L.) and its
975 distribution in fractions of rice grain. *Chemosphere* 69:942-948.
- 976 Azizur-Rahman M, Hasegawa H, Kadohashi K, Maki T, Ueda K (2009)
977 Hydroxyaminodisuccinic acid (HIDS): A novel biodegradable chelating ligand for the
978 increase of iron bioavailability and arsenic phytoextraction. *Chemosphere* 77:207-
979 213.
- 980 Baker AJM (1981) Accumulators and excluders: strategies in the response of plants to
981 heavy metals. *J Plant Nutr* 25:369-386.
- 982 Barán EJ (1995) *Química Bioinorgánica*. McGraw-Hill, Madrid.
- 983 Beesley L, Dickinson N (2010) Carbon and trace element mobility in an urban soil
984 amended with green waste compost. *J Soils Sedim* 10:215-222.
- 985 Beesley L, Moreno-Jiménez E, Clemente R, Lepp N, Dickinson N (2010a) Mobility of
986 arsenic, cadmium and zinc in a multi-element contaminated soil profile assessed by
987 in-situ soil pore water sampling, column leaching and sequential extraction. *Environ*
988 *Pollut* 158:155-160.

- 989 Beesley L, Moreno-Jiménez E, Gómez-Eyles JL (2010b) Effects of biochar and
 990 greenwaste compost amendments on mobility, bioavailability and toxicity of
 991 inorganic and organic contaminants in a multi-element polluted soil. *Environ Pollut*
 992 158:2282-2287.
- 993 Bernal MP, Clemente R, Walker DJ (2009) Interaction of heavy metals with soil
 994 organic matter in relation to phytoremediation. In: Navarro-Aviño JP Ed.,
 995 Phytoremediation: The Green Salvation of the World. Research Signpost, Kerala,
 996 India, pp. 109-129.
- 997 Bhattacharjee H, Rosen BP (2007) Arsenic metabolism in prokaryotic and eukaryotic
 998 microbes. In: Nies DH, Silver S Eds., *Molecular microbiology of heavy metals*.
 999 Springer-Verlag, Berlin, pp. 371–406.
- 1000 Bhattacharya P, Welch AH, Stollenwerk KG, McLaughlin MJ, Bundschuh J, Panaullah
 1001 G (2007) Arsenic in the environment: biology and chemistry. *Sci Tot Environ*
 1002 379:109-120.
- 1003 Bissen M, Frimmel FH (2003) Arsenic- a review. Part I; Ocurrence, toxicity, speciation,
 1004 mobility. *Acta Hydrochim Hydrobiol* 31:9-18.
- 1005 Burriel F, Lucena F, Arribas S, Hernández J (1999) *Química Analítica Cualitativa*.
 1006 Paraninfo, Madrid. Apéndice VI.
- 1007 Butcher DJ (2009) Phytoremediation of arsenic: fundamentals studies, practical
 1008 applications, and future prospects. *Appl Spectrom Rev* 44:534-551.
- 1009 Cao X, Ma LQ, Shiralipour A (2003) Effects of compost and phosphate amendments on
 1010 arsenic mobility in soils and arsenic uptake by the hyperaccumulator *Pteris vittata* L.
 1011 *Environ Pollut* 126:157–167.
- 1012 Carbonell-Barrachina AA, Aarabi MA, DeLaune RD, Gambrell RP, Patrick WH Jr
 1013 (1998) The influence of arsenic chemical form and concentration on *Spartina patens*
 1014 and *Spartina alterniflora* growth and tissue arsenic concentration. *Plant Soil* 198:33–
 1015 43.
- 1016 Carbonell-Barrachina AA, Rocamora A, García C (2004) Arsenic and zinc
 1017 biogeochemistry in pyrite mine wate from the Aznalcóllar environmental disaster.
 1018 *Geoderma* 122:195-203.
- 1019 Castillo-Michel H, Parsons JG, Peralta-Videa JR, Martínez-Martínez A, Dokken KM,
 1020 Gardea-Torresdey JL (2007) Use of X-ray absorption spectroscopy and biochemical
 1021 techniques to characterize arsenic uptake and reduction in pea (*Pisum sativum*)
 1022 plants. *Plant Physiol Biochem*. 45:457-463.

- 1023 Catarecha P, Segura MD, Franco-Zorrilla JM, Garcia-Ponce B, Lanza M, Solano R,
1024 Paz-Ares J, Leyva A (2007) A mutant of the Arabidopsis phosphate transporter
1025 PHT1;1 displays enhanced arsenic accumulation. *Plant Cell* 19:1123-1133.
- 1026 Cattani I, Capri E, Boccelli R, del Re AAM (2009) Assessment of arsenic availability to
1027 roots in contaminated Tuscany soils by diffusive gradients in thin films(DGT)
1028 method and uptake by *Pteris vittata* and *Agrostis castellana*. *Eur J Soil Sci* 60:539-
1029 548.
- 1030 Caussy D (2003) Case studies of the impact of understanding bioavailability: arsenic.
1031 *Ecotoxicol Environ Saf* 56:164-173.
- 1032 Chaney RL, Malik KM, Li YM, Brown SL, Brewer EP, Angle JS, Baker AJM (1997)
1033 Phytoremediation of soil metals. *Current Opin. Biotechnol.* 8:279-284.
- 1034 Chaney RL, Angle JS, Broadhurst CL, Peters CA, Tappero RV, Sparks DL (2007)
1035 Improved understanding of hyperaccumulation yields commercial phytoextraction
1036 and phytomining technologies. *J Environ Qual* 36:1429-1443.
- 1037 Chang P, Kim JY, Kim KW (2005) Concentrations of arsenic and heavy metals in
1038 vegetation at two abandoned mine tailings in South Korea. *Environ Geochem Health*
1039 27:109-119.
- 1040 Chen B, Xiao D, Zhu X, Smith G, Xie FA, Smith S E (2007) The arbuscular
1041 mycorrhizal fungus *Glomus mosseae* gives contradictory effects on phosphorus and
1042 arsenic acquisition by *Medicago sativa* Linn. *Sci Tot Environ* 379:226–234.
- 1043 Cheng H, Hu Y, Luo J, Zhao J (2008) Geochemical processes controlling fate and
1044 transport of arsenic in acid mine drainage (AMD) and natural systems. *J Hazar Mater*
1045 165:13-26.
- 1046 Clemente R, Dickinson NM, Lepp NW (2008) Mobility of metals and metalloids in a
1047 multi-element contaminated soil 20 years after cessation of the pollution source
1048 activity. *Environ Pollut* 155:254-261.
- 1049 Clemente R, Hartley W, Riby P, Dickinson NM, Lepp NW (2010) Trace element
1050 mobility in a contaminated soil two years after field-amendment with a greenwaste
1051 compost mulch. *Environ Pollut* 158:1644-1651.
- 1052 Conesa HM, Robinson BH, Schulin B, Nowack B (2008) Metal extractability in acidic
1053 and neutral mine tailings from the Cartagena-La Unión Mining District (SE Spain).
1054 *Appl Geochem.* 23:1232–1240
- 1055 De Brouwere K, Smolders E, Merckx R (2004) Soil properties affecting solid-liquid
1056 distribution of As(V) in soils. *Eur J Soil Sci* 55:165-173.

- 1057 de la Fuente C, Albuquerque JA, Clemente R, Martínez-Alcalá I, Bernal MP (2009)
 1058 Estrategias de Recuperación de Suelos Enriquecidos con Arsénico en la Provincia de
 1059 Segovia. Imprenta Comercial Segoviana, Segovia, España.
- 1060 de la Fuente C, Clemente R, Albuquerque JA, Vélez D, Bernal MP (2010) Implications
 1061 of the use of As-rich groundwater for agricultural purposes and the effects of soil
 1062 amendments on As solubility. *Environ Sci Technol* 44:9463-9469.
- 1063 DEFRA (2002) Soil Guideline Values for Arsenic Contamination. Environmental
 1064 Agency, Bristol, UK.
- 1065 Dhankher OP, Li Y, Rosen BP, Shi J, Salt D, Senecoff JF, Sashti NA, Meagher RB
 1066 (2002) Engineering tolerance and hyperaccumulation of arsenic in plants by
 1067 combining arsenate reductase and γ -glutamylcysteine synthetase expression. *Nat*
 1068 *Biotechnol* 20:1140-1145.
- 1069 Dhankher OP, Rosen BP, McKinney EC, Meagher RB (2006) Hyperaccumulation of
 1070 arsenic in the shoots of *Arabidopsis* silenced for arsenate reductase (ACR2). *Proc*
 1071 *Nat Acad Sci* 103:5413–5418.
- 1072 Dickinson NM, Baker AJM, Doronilla A, Laidlaw S, Reeves RD (2009)
 1073 Phytoremediation of inorganics: realism and synergies. *Int. J. Phytoremediat.* 11:97-
 1074 114.
- 1075 Domínguez MT, Marañón T, Murillo JM, Schulin R, Robinson BH (2008) Trace
 1076 element accumulation in woody plants of the Guadiamar Valley, SW Spain: A large-
 1077 scale phytomanagement case study. *Environ Pollut* 152:150-159.
- 1078 Doucleff M, Terry N (2002) Pumping out the arsenic. *Nat Biotechnol* 20:1094–1095.
- 1079 Duan GL, Zhu YG, Tong YP, Cai C, Kneer R (2005) Characterization of arsenate
 1080 reductase in the extract of roots and fronds of Chinese brake fern, an arsenic
 1081 hyperaccumulator. *Plant Physiol* 138:461–469.
- 1082 Ernst WHO, Nelissen HJM, Ten Bookum WM (2000) Combination toxicology of metal
 1083 enriched soils: physiological responses of a Zn- and Cd-resistant ecotype of *Silene*
 1084 *vulgaris* on polymetallic soils. *Environ Exp Bot* 43:55–71.
- 1085 Ernst WHO, Krauss GJ, Verkleij JA, Wesenberg D (2008) Interaction of heavy metals
 1086 with the sulphur metabolism in angiosperms from an ecological point of view. *Plant*
 1087 *Cell Environ* 31:123-143.
- 1088 Esteban E, Carpena RO, Meharg AA (2003) High-affinity phosphate/arsenate transport
 1089 in white lupin (*Lupinus albus*) is relatively insensitive to phosphate status. *New*
 1090 *Phytol* 158:165-173.

- 1091 Feng MH, Shan XQ, Zhang SZ, Wen B (2005) Comparison of a rhizosphere-based
1092 method with other one-step extraction methods for assessing the bioavailability of
1093 soil metals to wheat. *Chemosphere* 59:939–949.
- 1094 Fixen PE, Grove JH (1990) Testing soils for phosphorus. In: *Soil Testing and Plant*
1095 *Analysis*, 3rd Ed., Westerman RL Ed., Soil Science Society of America, Inc.
1096 Madison, Wisconsin, USA. pp. 141-180.
- 1097 Fitz WJ, Wenzel WW (2002) Arsenic transformations in the soil-rhizosphere-plant
1098 system: fundamentals and potential application to phytoremediation. *J Biotechnol*
1099 99:259-278.
- 1100 Fitz WJ, Wenzel WW, Zhang H, Nurmi J, Stipek K, Fischerova Z, Schweiger P,
1101 Köllensperger G, Ma LQ, Stingeder G (2003) Rhizosphere characteristics of the
1102 arsenic hyperaccumulator *Pteris vittata* L. and monitoring of phytoremoval
1103 efficiency. *Environ Sci Technol* 37:5008-5014.
- 1104 Fitz WJ, Wenzel WW (2006) Sequestration of arsenic by plants. In: Naidu R et al. (eds)
1105 *Managing Arsenic in the Environment. From Soils to Human Health*. CSIRO Pub.,
1106 Collingwood, Australia, pp. 209-222.
- 1107 Frost RR, Griffin RA (1977) Effect of pH on adsorption of arsenic and selenium from
1108 landfill leachate by clay minerals. *Soil Sci Soc A J* 41:53-57.
- 1109 Gadepalle VP, Ouki SK, Van Herwijnen R, Hutchings T (2007) Immobilization of
1110 heavy metals in soil using natural and waste materials for vegetation establishment
1111 on contaminated sites. *Soil Sedim Contam* 16:233-251.
- 1112 García I, Díez M, Martín F, Simón M, Dorronsoro C (2009) Mobility of arsenic and
1113 heavy metals in a Sandy-loam textured and carbonated soil. *Pedosphere* 19:166-175.
- 1114 Geng CN, Zhu YG, Tong YP, Smith SE, Smith FA (2006) Arsenate (As) uptake by and
1115 distribution in two cultivars of winter wheat (*Triticum aestivum* L.). *Chemosphere*
1116 62:608–615.
- 1117 Giménez J, Martínez M, de Pablo J, Rovira M, Duro L (2007) Arsenic sorption onto
1118 natural hematite, magnetite, and goethite. *J Hazard Mater* 141:575-580.
- 1119 Goldberg S, Glaubig RA (1988) Anion sorption on a calcareous, montmorillonitic soil –
1120 arsenic. *Soil Sci Soc A J* 52:1154-1157.
- 1121 González-Chávez C, Harris PJ, Dood J, Meharg AA (2002) Arbuscular mycorrhizal
1122 fungi confer enhanced arsenic resistance on *Holcus lanatus*. *New Phytol* 155:163-
1123 171.

- 1124 Gräfe M, Sparks DL (2006) Solid phase speciation of arsenic. In: Naidu R, et al. Eds.
 1125 Managing Arsenic in the Environment. From Soils to Human Health. CSIRO Pub.,
 1126 Collingwood, Australia, pp. 75-92.
- 1127 Gulz PA, Gupta SK, Schulin R (2005) Arsenic accumulation of common plants from
 1128 contaminated soils. *Plant Soil* 272:337-347.
- 1129 Gunes A, Pilbeam DJ, Inal A (2008) Effect of arsenic–phosphorus interaction on
 1130 arsenic-induced oxidative stress in chickpea plants. *Plant Soil* 314:211-220.
- 1131 Guo W, Zhang J, Teng M, Li LH (2009) Arsenic uptake is suppressed in a rice mutant
 1132 defective in silicon uptake. *J Plant Nutr Soil Sci* 172:867-874.
- 1133 Hall JL (2002) Cellular mechanisms for heavy metal detoxification and tolerance. *J Exp*
 1134 *Bot* 53:1–11.
- 1135 Haque MN, Morrison GM, Perrusquíz G, Gutiérrez M, Aguilera AF, Cano-Aguilera I,
 1136 Gardea Torresdey JL (2007) Characteristics of arsenic adsorption to sorghum
 1137 biomass. *J Hazard Mater* 145:30-35.
- 1138 Hansel CM, La Force MJ, Fendorf S, Sutton S (2002) Spatial and temporal association
 1139 of As and Fe species on aquatic plant roots. *Environ Sci Technol* 36:1988–1994.
- 1140 Hartley-Whitaker J, Ainsworth G, Meharg AA (2001) Copper- and arsenate-induced
 1141 oxidative stress in *Holcus lanatus* L. clones with differential sensitivity. *Plant Cell*
 1142 *Environ* 24:713–722.
- 1143 Hartley W, Edwards R, Lepp NW (2004) Arsenic and heavy metal mobility in iron
 1144 oxide-amended contaminated soils as evaluated by short- and long-term leaching
 1145 tests. *Environ Pollut* 131:495–504.
- 1146 Hartley W, Lepp NW (2008) Remediation of arsenic contaminated soils by iron-oxide
 1147 application, evaluated in terms of plant productivity, arsenic and phytotoxic metal
 1148 uptake. *Sci Tot Environ* 390:35-44.
- 1149 Horswell J, Speir T (2006) Arsenic phytotoxicity. In: Naidu R, et al. Eds. Managing
 1150 Arsenic in the Environment. From Soils to Human Health. CSIRO Pub.,
 1151 Collingwood, Australia, pp. 183-208.
- 1152 Hokura A, Omuma R, Tereda Y, Kitajima N, Abe T, Saito H, Yoshida S, Nakai I (2006)
 1153 Arsenic distribution and speciation in an arsenic hyperaccumulator fern by X-ray
 1154 spectroscopy utilizing a synchrotron radiation source. *J Anal Atom Spectrom* 21:321-
 1155 328.
- 1156 Huang JW, Poynton CY, Kochian LV, Elless MP (2004) Phytofiltration of arsenic from
 1157 drinking water using arsenic-hyperaccumulating ferns. *Environ Sci Technol* 38:3412-
 1158 3417.

- 1159 Huang R, Gao S, Wang W, Staunton S, Wang G (2006) Soil arsenic availability and the
1160 transfer of soil arsenic to crops in suburban areas in Fujian Province, southeast
1161 China. *Sci Tot Environ* 368:531-541.
- 1162 Huang ZC, Chen TB, Lei M, Liu YR, Hu TD (2008) Difference of toxicity and
1163 accumulation of methylated and inorganic arsenic in arsenic-hyperaccumulating and
1164 -hypertolerant plants. *Environ Sci Technol* 42:5106–5111.
- 1165 Hurtado-Jiménez R, Gardea-Torredey JL (2006) Arsenic in drinking water in the Los
1166 Altos de Jalisco region of Mexico. *Revista Panamericana de Salud Pública* 20:236-
1167 246.
- 1168 Isayenkov SV, Maathuis FJM (2008) The *Arabidopsis thaliana* aquaglyceroporin
1169 AtNIP7;1 is a pathway for arsenite uptake. *FEBS Let* 582:1625–1628.
- 1170 Jain M, Gadre RP (1997) Effect of As on chlorophyll and protein contents and enzymic
1171 activities in greening maize tissues. *Water Air Soil Pollut* 93:109–115.
- 1172 Kahn MA, Islam MR, Panaullah GM, Duxbury JM, Jahiruddin M, Loeppert RH (2009)
1173 Fate of irrigation-water arsenic in rice soils of Bangladesh. *Plant Soil* 322:263-277.
- 1174 Khattak RA, Page AL, Parker DR, Bakhtar D (1991) Accumulation and interactions of
1175 arsenic, selenium, molybdenum and phosphorus in alfalfa. *J Environ Qual* 20:165-
1176 168.
- 1177 Kidd P, Barceló J, Bernal MP, Navari-Izzo F, Poschenrieder C, Shilev S, Clemente R,
1178 Monterroso C (2009) Trace element behaviour at the root-soil interface: implications
1179 on phytoremediation. *Environ Exp Bot* 67:243-259.
- 1180 King DJ, Doronila AI, Feenstra C, Baker AJM, Woodrow IE (2008) Phytostabilisation
1181 of arsenical gold mine tailings using four Eucalyptus species: Growth, arsenic uptake
1182 and availability after five years. *Sci Tot Environ* 406:35-42.
- 1183 Knudson JA, Meikle T, DeLuca TH (2003) Role of mycorrhizal fungi and phosphorus
1184 in the arsenic tolerance of the basin wildrye. *J Environ Qual* 32:200-2006.
- 1185 Kreidie N, Armiento G, Cibin G, Cinque G, Crovato C, Nardi E, Pacifico R, Cremisini
1186 C, Mottana A (2011) An integrated geochemical and mineralogical approach for the
1187 evaluation of arsenic mobility in mining soils. *J Soil Sedim* 11:35-52.
- 1188 Kumpiene J, Lagerkvist A, Maurice C (2008) Stabilization of As, Cr, Cu, Pb and Zn in
1189 soil using amendments-A review. *Waste Manag* 28:215-225.
- 1190 Lakshminathiraj BRV, Narasimhan S, Prabhakar S (2006) Absorption of arsenate on
1191 synthetic goethite from aqueous solutions. *J Hazard Mater* 136:281-287.

- 1192 Latch GCM (1993) Physiological interactions of endophytic fungi and their hosts. Biotic
1193 stress tolerance imparted to grasses by endophytes. *Agric Ecosys Environ* 44:143-
1194 156.
- 1195 Lepp NW (1981) Effect of heavy metals pollution on plants. Vol. 1. Effects of trace
1196 metal on plant function. Applied Science Publishers, London & New Jersey.
- 1197 Leung HM, Ye ZH, Wong MH (2006) Interactions of mycorrhizal fungi with *Pteris*
1198 *vittata* (As hyperaccumulator) in As-contaminated soils. *Environ Pollut* 139:1–8.
- 1199 Li RY, Ago Y, Liu WJ, Mitani N, Feldmann J, McGrath SP, Ma JF, Zhao FJ (2009a)
1200 The rice aquaporin Lsi1 mediates uptake of methylated arsenic species. *Plant Physiol*
1201 150:2071-2080.
- 1202 Li RY, Stroud JL, Ma JF, McGrath SP, Zhao FJ (2009b) Mitigation of arsenic
1203 accumulation in rice with water management and silicon fertilization. *Environ Sci*
1204 *Technol* 43:3778-3783.
- 1205 Liao CM, Li TM, Hsieh NH, Chen WY (2010) Assessing the arsenic-contaminated rice
1206 (*Oryza sativa*) associated children skin lesions. *J Hazard Mater* 176:239-251.
- 1207 Lin Z, Puls RW (2000) Adsorption, desorption and oxidation of arsenic affected by clay
1208 minerals and aging processes. *Environ Geol* 39:753-759.
- 1209 Lin A, Zhang X, Zhu YG, Zhao FJ (2008) Arsenate-induced toxicity: effects on
1210 antioxidative enzymes and DNA damage in *Vicia faba*. *Environ Toxicol Chem*
1211 27:413-419.
- 1212 Liu WJ, Zhu YG, Hu Y, Williams PN, Gault AG, Meharg AA, Charnock JM, Smith FA
1213 (2006) Arsenic sequestration in iron plaque, its accumulation and speciation in
1214 mature rice plants (*Oryza sativa* L.). *Environ Sci Technol* 40:5730–5736.
- 1215 Liu WJ, Zhu YG, Smith FA, Smith SE (2004) Do phosphorus nutrition and iron plaque
1216 alter arsenate (As) uptake by rice seedlings in hydroponic culture? *New Phytol*
1217 162:481–488.
- 1218 Liu Y, Zhu YG, Chen BD, Christie P, Li XL (2005) Yield and arsenate uptake of
1219 arbuscular mycorrhizal tomato colonized by *Glomus mosseae* BEG167 in As spiked
1220 soil under glasshouse conditions. *Environ Int* 31:867–873.
- 1221 Livesey NT, Huang PM (1981) Adsorption of arsenate by soils and its relation to
1222 selected properties and anions. *Soil Sci* 131:88-94.
- 1223 Lombi E, Wenzel WW, Sletten RS (1999) Arsenic adsorption by soils and iron-coated
1224 sand: kinetics and reversibility. *J Plant Nutr Soil Sci* 162:451-456.

- 1225 Ma JF, Yamaji N, Mitani N, Xu XY, Su YH, McGrath SP, Zhao FJ (2008) Transporters
1226 of arsenite in rice and their role in arsenic accumulation in rice grain. *Proc Nat Acad*
1227 *Sci* 105:9931-9935.
- 1228 Madejón E, Perez de Mora A, Felipe E, Burgos P, Cabrera F (2006) Soil amendments
1229 reduce trace element solubility in a contaminated soil and allow regrowth of natural
1230 vegetation. *Environ Pollut* 139:40-52.
- 1231 Madejón P, Lepp NW (2007) Arsenic in soils and plants of woodland regenerated on an
1232 arsenic-contaminated substrate: A sustainable natural remediation? *Sci Tot Environ*
1233 379:256-262.
- 1234 Malik AH, Khan ZM, Mehmood Q, Nasreen S, Bhatti ZA (2009) Perspectives of low
1235 cost arsenic remediation of drinking water in Pakistan and other countries. *J Hazar*
1236 *Mater* 168:1-12.
- 1237 Mandal BK, Suzuki KT (2002) Arsenic round the world: a review. *Talanta* 58:201-235.
- 1238 Manning BA, Goldberg S (1997) Arsenic (III) and arsenic (V) adsorption on three
1239 California soils. *Soil Sci* 162:886-895.
- 1240 Marschner H (1995) *Mineral Nutrition of Higher Plants*. Academic Press, San Diego.
- 1241 Marin AR, Masscheleyn PH, Patrick WH (1992) The influence of chemical form and
1242 concentration of arsenic on rice growth and tissue arsenic concentration. *Plant Soil*
1243 139:175-183.
- 1244 Martín F, Díez M, García I, Simón M, Dorronsoro C, Iriarte A, Aguilar J (2007)
1245 Weathering of primary minerals and mobility of major elements in soils affected by
1246 an accidental spill of pyrite tailing. *Sci Tot Environ* 378:49-52.
- 1247 Mascher R, Lippmann B, Holzinger S, Bergmann H (2002) Arsenate toxicity: effects on
1248 oxidative stress response molecules and enzymes in red clover plants. *Plant Sci*
1249 163:961-969.
- 1250 Mariano ED, Keljten WG (2003) Evaluating the root of citrate exudation as mechanism
1251 of aluminium resistance in maize. *Plant Soil* 256:469-479.
- 1252 Matschullat J (2000) Arsenic in the geosphere – a review. *Sci Tot Environ* 249:297-312.
- 1253 McGrath SP, Zhao FJ (2003) Phytoextraction of metals and metalloids from
1254 contaminated soils, *Current Opin Biotechnol* 14:277-282.
- 1255 McLaren RG, Megharaj M, Naidu R (2006) Fate of arsenic in the soil environment. In:
1256 Naidu R et al. Eds. *Managing Arsenic in the Environment. From Soil to Human*
1257 *Health*. CSIRO Publishing, Australia. pp. 157-182.

- 1258 Meers E, Van Slyken S, Adriaensen K, Ruttens A, Vangronsveld J, Du Laing G,
 1259 Thewys T, Tack FMG (2010) The use of bio-energy crops (*Zea mays*) for
 1260 'phytoattenuation' of heavy metals on moderately contaminated soils: A field
 1261 experiment. *Chemosphere* 78:35-41.
- 1262 Meharg AA, Macnair MR (1992) Suppression of the high affinity phosphate uptake
 1263 system: a mechanism of arsenate tolerance in *Holcus lanatus* L. *J Exp Bot* 43:519–
 1264 524.
- 1265 Meharg AA, Hartley-Whitaker J (2002) Arsenic uptake and metabolism in arsenic
 1266 resistant and nonresistant plant species. *New Phytol* 154:29–43.
- 1267 Meharg AA (2005) Mechanisms of plant resistance to metal and metalloid ions and
 1268 potential biotechnological applications. *Plant Soil* 274:163–174.
- 1269 Meharg AA, Lombi E, Williams PN, Scheckel KG, Feldman J, Raab A, Zhu YG, Islam
 1270 R (2008) Speciation and localization of arsenic in white and brown rice grains.
 1271 *Environ Sci Technol*. 42:1051-1057.
- 1272 Meharg AA, Williams PN, Adomako E, Lawgali YL, Campell RCJ, Sun G, Zhu YG,
 1273 Feldman J, Raab A, Zhao FJ, Islam R, Hossain S., Yanai J (2009) Geographical
 1274 variation in total and inorganic arsenic content of polished (white) rice. *Environ Sci*
 1275 *Technol* 43:1612-1617.
- 1276 Mello JWV, Roy WR, Talbott JL, Stucki JW (2006) Mineralogy and Arsenic
 1277 mobilization in arsenic-rich Brazilian soils and sediments. *J Soil Sedim* 6:9–19.
- 1278 Mench M, Bussiere S, Vangronsveld J, Manceau A (2003) Progress in remediation and
 1279 revegetation of the barren Jales gold mine spoil after in-situ treatments. *Plant Soil*
 1280 249:187–202.
- 1281 Mench M, Schwitzguébel JP, Schroeder P, Bert V, Gawronski S, Gupta S (2009)
 1282 Assessment of successful experiments and limitations of phytotechnologies:
 1283 contaminant uptake, detoxification, and sequestration, and consequences to food
 1284 safety. *Environ Sci Pollut Res* 16:876-900.
- 1285 Mench M, Lepp N, Bert V, Schwitzguébel JP, Gawronski SW, Schöder P,
 1286 Vangronsveld J (2010) Successes and limitations of phytotechnologies at field scale:
 1287 outcomes, assessment and outlook from COST action 859. *J Soil Sedim* 10:1039-
 1288 1070.
- 1289 Mengel K, Kirkby EA (2001) *Principles of Plant Nutrition*. Kluwer Ac. Publ.
 1290 Dordrecht, The Netherlands.
- 1291 Mestrot A, Feldmann J, Krupp EM, Hossain MS, Roman-Ross G, Meharg AA (2011)
 1292 Field fluxes and speciation of arsines emanating from soils. *Environ Sci Technol*
 1293 45:1798-1804.

- 1294 Moreno-Jiménez E, Peñalosa JM, Esteban E, Carpena RO (2007) Mercury
1295 accumulation and resistance to mercury stress in *Rumex induratus* and *Marrubium*
1296 *vulgare* grown on perlite. J Plant Nutr Soil Sci 170:485–494.
- 1297 Moreno-Jiménez E, Peñalosa JM, Carpena-Ruiz RO, Esteban E (2008) Comparison of
1298 arsenic resistance in Mediterranean woody shrubs used in restoration activities.
1299 Chemosphere 71:466-473.
- 1300 Moreno-Jiménez E, Esteban E, Carpena-Ruiz RO, Peñalosa JM (2009a) Induced
1301 phytotoxicity in mediterranean shrubs *P. lentiscus* and *T. gallica* after arsenic or
1302 mercury accumulation. Ecotoxicol Environ Saf 72:1781-1789.
- 1303 Moreno-Jiménez E, Peñalosa JM, Esteban E, Bernal MP (2009b). Feasibility of arsenic
1304 phytostabilisation using Mediterranean shrubs: impact of root mineralization on As
1305 availability in soils. J Environ Monitor 11:1375-1380.
- 1306 Moreno-Jiménez E, Manzano R, Esteban E, Peñalosa JM (2010a) The fate of arsenic in
1307 soils adjacent to an old-mine site (Bustarviejo, Spain): mobility and transfer to native
1308 flora. J Soil Sedim 10:301-312.
- 1309 Moreno-Jiménez, E., Esteban, E., Fresno, T, López de Egea, C., and Peñalosa, J.M.
1310 (2010b) Hydroponics as a valid tool to assess arsenic availability in mine soils.
1311 Chemosphere 79:513-517.
- 1312 Moreno-Jiménez E, Beesley L, Lepp NW, Dickinson NM, Hartley W, Clemente R
1313 (2011a) Field sampling of soil pore water to evaluate trace element mobility and
1314 associated environmental risk. Environ Pollut *in press*,
1315 doi:10.1016/j.envpol.2011.04.004.
- 1316 Moreno-Jiménez E, Vázquez S, Carpena-Ruiz RO, Esteban E, Peñalosa JM (2011b)
1317 Using Mediterranean shrubs for the phytoremediation of a soil impacted by pyritic
1318 wastes in Southern Spain: A field experiment. J Environ Manag 92:1584-1590.
- 1319 Moyano A, García-Sánchez A, Mayoraga P, Anawar HM, Álvarez-Ayuso E (2009)
1320 Impact of irrigation with arsenic-rich groundwater on soils and crops. J Environ
1321 Monitor 11:498-502.
- 1322 Norton GJ, Duan GL, Dasgupta T, Islam MR, Lei M, Zhu YG, Deacon CM, Moran AC,
1323 Islam S, Zhao FJ, Stroud JL, McGrath SP, Feldman J, Price AH, Meharg AA (2009)
1324 Environmental and genetic control of arsenic accumulation and speciation in rice
1325 grain: comparing a range of common cultivars grown in contaminated sites across
1326 Bangladesh, China, and India. Environ Sci Technol 43:8381-8386.
- 1327 Nowack B, Schulin R, Robinson BH (2006) Critical assessment of chelant-enhanced
1328 metal phytoextraction. Environ Sci Technol 40:5225-5232.

- 1329 Ongley LK, Sherman L, Armienta A, Concilio A, Ferguson Salina C (2007) Arsenic in
1330 the soils of Zimapán, México. *Environ Pollut* 145:793-799.
- 1331 Onken BM, Adriano DC (1997) Arsenic availability in soil with time under saturated
1332 and subsaturated conditions. *Soil Sci Soc A J* 61:746-752.
- 1333 Padey VC, Abhilash PC, Singh N (2009) The Indian perspective of utilizing fly ash in
1334 phytoremediation, phytomanagement and biomass production. *J Environ Manag*
1335 90:2943-2958.
- 1336 Peñalosa JM, Carpena RO, Vázquez S, Agha R, Granado A, Sarro MJ, Esteban E
1337 (2007) Chelate-assisted phytoextraction of heavy metals in a soil contaminated with
1338 a pyritic sludge. *Sci Tot Environ* 378:199-204.
- 1339 Peuke AD, Rennenberg H (2005) Phytoremediation. *EMBO Rep* 6:497-501.
- 1340 Pickering IJ, Prince RC, George MJ, Smith RD, George GN, Salt DE (2000) Reduction
1341 and coordination of arsenic in Indian mustard. *Plant Physiol* 122:1171–1178.
- 1342 Pickering IJ, Gumaelius L, Harris HH, Prince RC, Hirsch G, Banks JA, Salt DE, George
1343 GN (2006) Localizing the biochemical transformations of arsenate in a
1344 hyperaccumulating fern. *Environ Sci Technol* 40:5010–5014
- 1345 Pigna M, Cozzolino V, Violante A, Meharg AA (2009) Influence of phosphate on the
1346 arsenic uptake by wheat (*Triticum durum* L.) irrigated with arsenic solutions at three
1347 different concentrations. *Water Air Soil Pollut* 197:371-380.
- 1348 Poynton CY, Huang JW, Blaylock MJ, Kochian LV, Elless MP (2004) Mechanisms of
1349 arsenic hyperaccumulation in *Pteris* species: root As influx and translocation. *Planta*
1350 219:1080-1088.
- 1351 Raab A, Schat H, Meharg AA, Feldmann J (2005) Uptake, translocation and
1352 transformation of arsenate and arsenite in sunflower (*Helianthus annuus*): formation
1353 of arsenic–phytochelatin complexes during exposure to high arsenic concentrations.
1354 *New Phytol* 168:551–558.
- 1355 Raab A, Williams PN, Meharg A, Feldmann J (2007) Uptake and translocation of
1356 inorganic and methylated arsenic species by plants. *Environ Chem* 4:197–203.
- 1357 Raab A, Baskaran C, Feldman J, Meharg AA (2009) Cooking rice in a high water to
1358 rice ratio reduces inorganic arsenic content. *J Environ Monitor* 11:41-44.
- 1359 Raskin I, Smith RD, Salt DE (1997) Phytoremediation of metals: using plants to remove
1360 pollutants from the environment. *Current Opin Biotechnol* 8:221-226.
- 1361 Raghothama KG (1999) Phosphate acquisition. *Ann Rev Plant Physiol Plant Mol Biol*
1362 50:665-693.

- 1363 Redman AD, Macalady DL, Ahmann D (2002) Natural organic matter affects arsenic
1364 speciation and sorption onto hematite. *Environ Sci Technol* 36:2889-2896.
- 1365 Requejo R, Tena M (2005) Proteome analysis of maize roots reveals that oxidative
1366 stress is a main contributing factor to plant arsenic toxicity. *Phytochem* 66 :1519-
1367 1528.
- 1368 Renella G, Landi L, Valori F, Nannipieri P (2007) Microbial and hydrolase activity
1369 after release of low molecular weight organic compounds by a model root surface in
1370 a clayey and sandy soil. *Appl Soil Ecol* 36:124-129.
- 1371 Robinson B, Schulin R, Nowack B, Roulier S, Menon M, Clothier B, Green S, Mills T
1372 (2006) Phytoremediation for the management of metal flux in contaminated sites.
1373 *Forest Snow Landsc Res* 80:221–234.
- 1374 Rodríguez RR, Basta NT, Casteel SW, Armstrong FP, Ward DC (2003) Chemical
1375 extraction methods to assess bioavailable arsenic in soil and solid media. *J Environ*
1376 *Qual* 32:876–884.
- 1377 Roy WR, Hassett JJ, Griffin RA (1986) Competitive interactions of phosphate and
1378 molybdate on arsenate adsorption. *Soil Sci* 142 :203-210.
- 1379 Saada A, Breeze D, Crouzet C, Cornu S, Baranger P (2003) Adsorption of arsenic (V)
1380 on kaolinite and on kaolinite–humic acid complexes: Role of humic acid nitrogen
1381 groups. *Chemosphere* 51:757-763.
- 1382 Sadiq M (1997) Arsenic chemistry in soils: an overview of thermodynamic prediction
1383 and field observations. *Water Air Soil Pollut* 93:117-136.
- 1384 Salt DE, Blaylock M, Kumar NPBA, Dushenkov V, Ensley BD, Chet I, Raskin I (1995)
1385 Phytoremediation: a novel strategy for the removal of toxic metals from the
1386 environment using plants. *Biotechnol* 13:468-474.
- 1387 Sasmaz A, Obek E (2009) The accumulation of arsenic, uranium, and boron in *Lemna*
1388 *gibba* L. exposed to secondary effluents. *Ecol Eng* 35:1564-1567.
- 1389 Sauv  S (2001) Speciation of metals in soils. In: Allen HE Ed., *Bioavailability of*
1390 *Metals in Terrestrial Ecosystems: Importance of Partitioning for Bioavailability to*
1391 *Invertebrates, Microbes, and Plants*. SETAC Press, Pensacola, Florida, pp. 7-38.
- 1392 Schutzenhubel A, Polle A (2002) Plant responses to abiotic stresses: heavy metal-
1393 induced oxidative stress and protection by mycorrhization. *J Exp Bot* 53:1351-1365.
- 1394 Sharples JM, Meharg AA, Chambers SM, Cairney JWG (2000) Evolution: symbiotic
1395 solution to arsenic contamination. *Nature* 404:951-952.

- 1396 Shiowatana J, McLaren RG, Chanmekha N, Samphao A (2001) Fractionation of arsenic
1397 in soil by a continuous-flow sequential extraction method. *J Environ Qual* 30:1940-
1398 1949.
- 1399 Signes-Pastor AJ, Deacon C, Jenkins RO, Haris PI, Carbonell-Barrachina AA, Meharg
1400 AA (2009) Arsenic speciation in Japanese rice drinks and condiments. *J Environ*
1401 *Monitor* 11:1930-1934.
- 1402 Simón M, Martín F, García I, Bouza P, Dorronsoro C, Aguilar J (2005) Interaction of
1403 limostone grains and acidic solutions from the oxidation of pyrite tailings. *Environ*
1404 *Pollut* 135:65–72.
- 1405 Smedley PL, Kinniburgh DG (2002) A review of the source, behavior and distribution
1406 of arsenic in natural waters. *Appl Geochem* 17:517-568.
- 1407 Smith SE, Read DJ (1997) *Mycorrhizal Symbiosis*. Academic Press, San Diego,
1408 California.
- 1409 Smith E, Naidu R, Alston AM (1999) Chemistry of arsenic in soils. I. Sorption of
1410 arsenate and arsenite by four Australian soils. *J Environ Qual* 28:1719-1726.
- 1411 Smith E, Naidu R, Alston AM (2002) Chemistry of inorganic arsenic in soils. II. Effect
1412 of phosphorous, sodium, and calcium on arsenic sorption. *J Environ Qual* 31:557–
1413 563.
- 1414 Smith SE, Christophersen HM, Pope S, Smith A (2010) Arsenic uptake and toxicity in
1415 plants: integrating mycorrhizal influences. *Plant Soil* 327:1-21.
- 1416 Sneller FEC, Van Heerwaarden LM, Kraaijeveld-Smit FJL, Koevoets PLM, Schat H,
1417 Verkleij JAC (2000) Derivatization of phytochelatins from *Silene vulgaris*, induced
1418 upon exposure to arsenate and cadmium: comparison of derivatization with Ellman's
1419 reagent and monobromobimane. *J Agric Food Chem* 48:4014–4019.
- 1420 Srivastava M, Ma LQ, Singh N, Singh S (2005) Antioxidant responses of hyper-
1421 accumulator and sensitive fern species to arsenic. *J Exp Bot* 56:1335-1342.
- 1422 Stachowicz M, Hiemstra T, van Riemsdijk WH (2008) Multi-competitive interaction of
1423 As(III) and As(V) oxyanions with Ca^{2+} , Mg^{2+} , PO_4^{3-} , and CO_3^{2-} ions on goethite. *J*
1424 *Colloid Interf Sci* 320:400-414.
- 1425 Stevenson FJ (1982) *Humus Chemistry. Genesis, Composition, Reactions*. John Wiley
1426 & Sons, Nueva York.
- 1427 Su YH, McGrath SP, Zhu YG, Zhao FJ (2008) Highly efficient xylem transport of
1428 arsenite in the arsenic hyperaccumulator *Pteris vittata*. *New Phytol* 180:434-444.

- 1429 Takamatsu T, Aoki H, Yoshida T (1982) Determination of arsenate, arsenite,
1430 monomethylarsonate, dimethylarsinate in soil polluted with arsenic. *Soil Science*
1431 133:239-246.
- 1432 Tassi E, Barbafieri M, Petruzzelli G (2004) Phosphate-Assisted Phytoextraction in As-
1433 Contaminated Soil. *Eng Life Sci* 4:341-346.
- 1434 Thewys T (2008) Economic opportunities of phytoremediation. In: Bert V Ed,
1435 Phytotechnologies in practice: biomass production, agricultural methods, legacy,
1436 legal and economic aspects. COST Action 859, Verneuil-en-Halatte, France, pp 45–
1437 46.
- 1438 Thewys T, Kuppens T (2008) Economics of willow pyrolysis after phytoextraction. *Int*
1439 *J Phytoremediat* 10:561–583
- 1440 Tomasi N, Weisskopf L, Renella G, Landi L, Pinton R, Varani Z, Nannipieri P, Torrent
1441 J, Martinoia E, Cesco S (2008) Flavonoids of white lupin roots participate in
1442 phosphorus mobilization from soil. *Soil Biol Biochem* 40:1971-1974.
- 1443 Trotta A, Falaschi P, Cornara L, Minganti V, Fusconi A, Drava G, Berta G (2006)
1444 Arbuscular mycorrhizae increase the arsenic translocation factor in the As
1445 hyperaccumulating fern *Pteris vittata* L. *Chemosphere* 65:74–81.
- 1446 Tripathi RD, Srivastava S, Mishra S, Singh N, Tuli R, Gupta DK, Maathuis FJM (2007)
1447 Arsenic hazards: strategies for tolerance and remediation by plants. *Trends*
1448 *Biotechnol* 25:158–165.
- 1449 Tu C, Ma LQ (2002) Effects of arsenic concentrations and forms on arsenic uptake by
1450 the hyperaccumulator ladder brake. *J. Environ. Qual.* 31:641-647.
- 1451 Tu C, Ma LQ (2003) Interactive effects of pH, arsenic and phosphorus on uptake of As
1452 and P and growth of the arsenic hyperaccumulator *Pteris vittata* L. under
1453 hydroponic conditions. *Environ. Exp. Bot.* 50:243-251.
- 1454 Ultra VU, Tanaka S, Sakurai K, Iwasaki K (2007a) Effects of arbuscular mycorrhiza
1455 and phosphorus application on arsenic toxicity in sunflower (*Helianthus annuus* L.)
1456 and on the transformation of arsenic in the rhizosphere. *Plant Soil* 290:29–41.
- 1457 Ultra VUY, Tanaka S, Sakurai K, Iwasaki K (2007b) Arbuscular mycorrhizal fungus
1458 (*Glomus aggregatum*) influences biotransformation of arsenic in the rhizosphere of
1459 sunflower (*Helianthus annuus* L.). *Soil Sci Plant Nutr* 53:499–508.
- 1460 Vanderlinden K, Polo MJ, Ordoñez R, Giráldez R (2006) Spatiotemporal evolution of
1461 soil pH and zinc after the Aznalcóllar mine spill. *J. Environ. Qual.* 35:37-49.
- 1462 Vangronsveld J, Herzig R, Weyens N, Boulet J, Adriaensen K, Ruttens A, Thewys T,
1463 Vassilev A, Meers E, Nehnevajova E, van der Lie D, Mench M (2009)

- 1464 Phytoremediation of contaminated soils and groundwater: lessons from the field.
1465 Environ. Sci. Pollut. Res. 16:765-794.
- 1466 Vazquez MD, Barcelo J, Poschenrieder C, Madico J, Hatton P, Baker AJM, Cope GH
1467 (1992) Localization of zinc and cadmium in *Thlaspi caerulescens* (Brassicaceae) a
1468 metallophyte that can hyperaccumulate both metals. J Plant Physiol 140:350–355.
- 1469 Vázquez S, Esteban E, Goldsbrough P (2005) Arsenate-induced phytochelatins in white
1470 lupin: influence of phosphate status. Physiol Plantarum 124:41-49.
- 1471 Vázquez S, Agha R, Granado A, Sarro MJ, Esteban E, Peñalosa JM, Carpena RO
1472 (2006) Use of white lupin plant for phytostabilization of Cd and As polluted acid
1473 soil. Water Air Soil Pollut 177:349–365.
- 1474 Vázquez S, Moreno E, Carpena R (2007) Role of iron in the retention of As by cell
1475 walls of lupin roots. COST meeting, Vilnius, Lithuania.
- 1476 Vázquez S, Moreno E, Carpena RO (2008a) Bioavailability of metals and As from
1477 acidified multicontaminated soils: use of white lupin to validate several extraction
1478 methods. Environ Geochem Health 30:193-198.
- 1479 Vázquez S, Esteban E, Carpena RO (2008b) Evolution of arsenate toxicity in nodulated
1480 white lupine in a long-term culture. J Agric Food Chem 56:8580-8587.
- 1481 Vázquez S, Carpena RO, Bernal MP (2008c) Contribution of heavy metals and As-
1482 loaded lupin root mineralization to the availability of the pollutants in multi-
1483 contaminated soils. Environ Pollut 152:373-379.
- 1484 Verbruggen N, Hermans C, Schat H (2009) Mechanisms to cope with arsenic or
1485 cadmium excess in plants. Current Opin Plant Biol 12:364-12372.
- 1486 Vetterlein D, Szegedi K, Neackermann J, Mattusch J, Neue HU, Tanneberg H, Jahn R
1487 (2007) Competitive mobilization of phosphate and arsenate associated with goethite
1488 by root activity. J Environ Qual 36:1811–1820.
- 1489 Vithanage M, Senevirathna W, Chandrajith R, Weerasooriya R (2007) Arsenic binding
1490 mechanisms on natural red earth. A potential substrate for pollution control. Sci Tot
1491 Environ 379:244-248.
- 1492 Wang S, Mulligan C (2006) Natural attenuation processes for remediation of arsenic
1493 contaminated soils and groundwater. J Hazard Mater 138:459-470.
- 1494 Warren GP, Alloway BJ, Lepp NW, Singh B, Bochereau FJM, Penny C (2003) Field
1495 trials to assess the uptake of arsenic by vegetables from contaminated soils and soil
1496 remediation with iron oxides. Sci Tot Environ 311:19-33.

- 1497 Waychunas GA, Fuller CC, Rea BA, Davis JA (1993) Surface chemistry of ferrihydrite:
1498 1. EXAFS studies on the geometry of coprecipitated and adsorbed arsenate. *Geochim*
1499 *Cosmochim Ac* 57:2251-2269.
- 1500 Weng L, Van Riemsdijk WH, Hiemstra T (2009) Effects of fulvic acids on arsenate
1501 adsorption to goethite: experiments and modelling. *Environ Sci Technol* 43:7198-
1502 7204.
- 1503 Wenzel WW, Kirchbaumer N, Prohaska T, Stingeder G, Lombi E, Adriano DC (2001)
1504 Arsenic fractionation in soils using an improved sequential extraction procedure.
1505 *Anal Chim Acta* 436:309-323.
- 1506 Wenzel WW, Brandstetter A, Lombi E, Prohaska T, Stingeder G, Adriano DC (2002)
1507 Arsenic in field-collected soil solutions and extracts of contaminated soils and its
1508 implication to soil standards. *J Plant Nutr Soil Sci* 165:221-228.
- 1509 Wenzel WW (2009) Rhizosphere processes and management in plant-assisted
1510 bioremediation (phytoremediation) of soils. *Plant Soil* 321:385-408.
- 1511 Williams PN, Price AH, Raab A, Hossain SA, Feldman J, Meharg AA (2005) Variation
1512 in arsenic speciation and concentration in paddy rice related to dietary exposure.
1513 *Environ Sci Technol* 39:5631-5540.
- 1514 Williams PN, Islam MR, Adomako EE, Raab A, Hossain SA, Zhu YG, Feldmann J,
1515 Meharg AA (2006) Increase in rice grain arsenic for regions of Bangladesh irrigating
1516 paddies with elevated arsenic in groundwaters. *Environ Sci Technol* 40:4903-4908.
- 1517 Williams PN, Villada A, Deacon C, Raab A, Figuerola J, Green AJ, Feldman J, Meharg
1518 AA (2007) Greatly enhanced arsenic shoot assimilation in rice leads to elevated grain
1519 levels compare to wheat and barley. *Environ Sci Technol* 41:6854-6859.
- 1520 Woolson EA (1973) Arsenic phytotoxicity and uptake in six vegetable crops. *Weed Sci*
1521 21:524-527.
- 1522 Xie ZM, Naidu R (2006) Factors influencing bioavailability of arsenic to crops. In:
1523 Naidu R, et al. Eds. *Managing Arsenic in the Environment. From Soils to Human*
1524 *Health*. CSIRO Pub., Collingwood, Australia, pp. 223-234.
- 1525 Xie QE, Yan XL, Liao XY, Li X (2009) The arsenic hyperaccumulator fern *Pteris*
1526 *vittata* L. *Environ Sci Technol* 43:8488-8495.
- 1527 Xu XY, McGrath SP, Zhao FJ (2007) Rapid reduction of arsenate in the medium
1528 mediated by plant roots. *New Phytol* 176:590-599.
- 1529 Xu XY, McGrath SP, Meharg AA, Zhao FJ (2008) Growing rice aerobically markedly
1530 decreases arsenic accumulation. *Environ Sci Technol* 42:5574-5579.

- 1531 Xu P, Christie P, Liu Y, Zhang J, Li X (2009) The arbuscular mycorrhizal fungus
1532 *Glomus mosseae* can enhance arsenic tolerance in *Medicago truncatula* by increasing
1533 plant phosphorus status and restricting arsenate uptake. Environ Pollut 156:215-220.
- 1534 Yu Y, Zhang S, Huang H, Luo L, Wen B (2009) Arsenic accumulation and speciation in
1535 maize as affected by inoculation with arbuscular mycorrhizal fungus *Glomus*
1536 *mossaeae*. J Agric Food Chem 57:3695-3701.
- 1537 Zhang H, Selim HM (2008) Reaction and transport of arsenic in soils: equilibrium and
1538 kinetic modeling. Adv Agron 98:45-115.
- 1539 Zhang WD, Liu DS, Tian JC, He (2009) Toxicity and accumulation of arsenic in wheat
1540 (*Triticum aestivum* L.) varieties of China. Phyton-Int J Exp Bot 78:147-154.
- 1541 Zhao FJ, Wang JR, Barker JHA, Schat H, Bleeker PM, McGrath SP (2003) The role of
1542 phytochelatins in arsenic tolerance in the hyperaccumulator *Pteris vittata*. New
1543 Phytol 159:403–410.
- 1544 Zhao FJ, Ma F, Meharg AA, McGrath SP (2009) Arsenic uptake and metabolism in
1545 plants. New Phytol 181:777-794.
- 1546 Zhu YG, Rosen BP (2009) Perspectives for genetic engineering for the
1547 phytoremediation of arsenic-contaminated environments: from imagination to
1548 reality? Current Opin Biotechnol 20:220-224.
- 1549 Zornoza P, Vázquez S, Esteban E, Fernández-Pascual M, Carpena RO (2002)
1550 Cadmium stress in nodulated white lupin: strategies to avoid toxicity. Plant Physiol
1551 Biochem 4:1003–1009.
- 1552

1553 **Fig. 1** Soil-As interactions and strategies to manage As availability and mobility in soils

1554 * denotes liming and organic matter application, which may cause either As fixation or
1555 release depending on the case

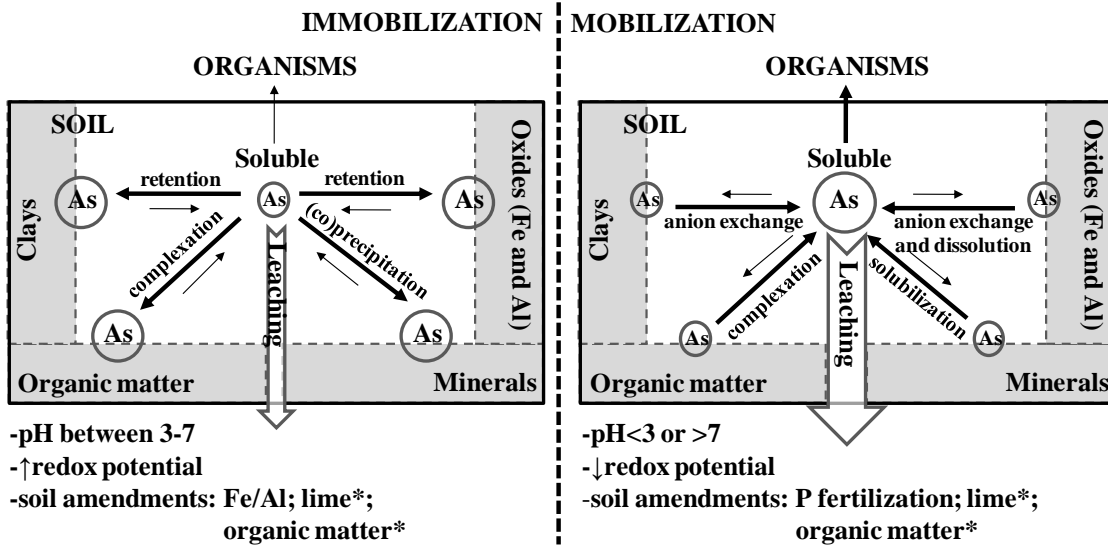
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1557 **Fig. 2** Plant's traits and physiological mechanisms recognized to be associated with
1558 contrasting patterns of As phytoaccumulation: accumulator plants (left) vs. excludory
1559 plants (right). (Blank boxes denote lack of information)

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1561 **Fig. 3** Optimizing arsenic management in soil-plant systems. (The size of circles and of
1562 "As" symbols represent the concentration magnitude of the metalloid. The
1563 discontinuous polygons represent the flux of As, with the broadest, being the most
1564 intense flux. The white discontinuous squares represent the endpoint of the biomass. In
1565 grain, As in organic form ensures the lower ecotoxicological risk)

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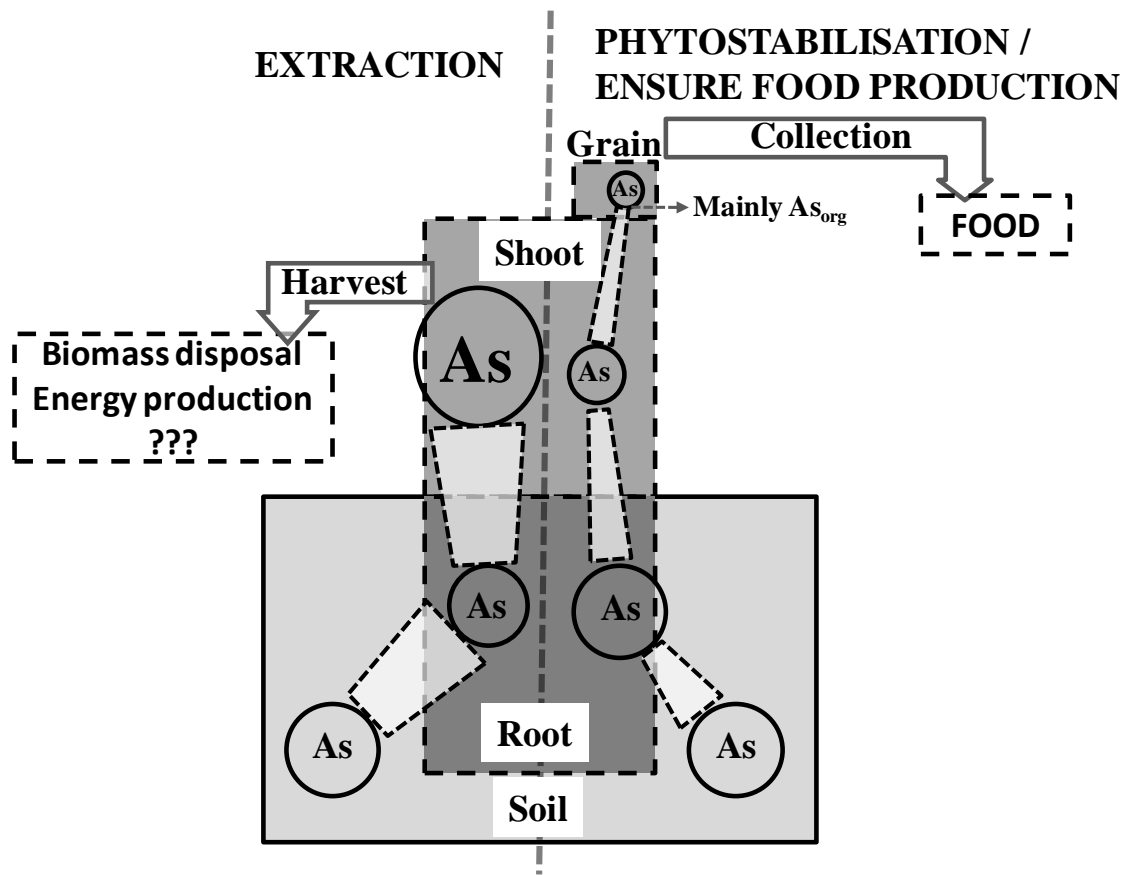
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PLANT ACCUMULATION	PROCESSES	PLANT EXCLUSION
	Phloem transport	Low phloem As concentration and poor uptake by grains
In shoots	Vacuole storage	In roots
Free As III or V are highly translocated	Xylem transport	Low xylem As concentration, in As-SH complex forms
Low rates of complexation	Complexation	High rates of complexation and accumulation in roots
Very low	Root efflux	Intense
High numbers of membrane transporters, with high affinity for As Low levels of Si or P in the growing media	Uptake	Transporters having higher affinity for P or Si than for As High levels of Si or P in the growing media
As-mobilizing populations	Microbial activity in the rhizosphere	As-immobilizing populations

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