REVIEW

# Arsenic uptake by plants and possible phytoremediation applications: a brief overview

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**Abstract** This review focuses the behaviour of arsenic in plant-soil and plant-water systems, arsenic-plant cell interactions, phytoremediation, and biosorption. Arsenate and arsenite uptake by plants varies in different environment conditions. An eco-friendly and low-cost method for arsenic removal from soil-water system is phytoremediation, in which living plants are used to remove arsenic from the environment or to render it less toxic. Several factors such as soil redox conditions, arsenic speciation in soils, and the presence of phosphates play a major role. Translocation factor is the important feature for categorising plants for their remediation ability. Phytoremediation techniques often do not take into account the biosorption processes of living plants and plant litter. In biosorption techniques, contaminants can be removed by a biological substrate, as a sorbent, bacteria, fungi, algae, or vascular plants surfaces based on passive binding of arsenic or other contaminants on cell wall surfaces containing special active functional groups. Evaluation of the current

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Department of Land and Water Resources Engineering, KTH-International Groundwater Arsenic Research Group, Royal Institute of Technology, 100 44 Stockholm, Sweden literature suggests that understanding molecular level processes, and kinetic aspects in phytoremediation using advanced analytical techniques are essential for designing phytoremediation technologies with improved, predictable remedial success. Hence, more efforts are needed on addressing the molecular level behaviour of arsenic in plants, kinetics of uptake, and transfer of arsenic in plants with flowing waters, remobilisation through decay, possible methylation, and volatilisation.

**Keywords** Arsenic toxicity · Bioremediation · Biosorption · Translocation · Bioconcentration · Bioaccumulation

## Introduction

This minireview is an abridged version of our book chapter published in the book Environmental for a Sustainable World (Dabrowska et al. 2012). Although arsenic occurs as the 20th most abundant element in the geosphere, arsenic is highly toxic to the biota. In many areas, arsenic levels in the environment have exceeded the safe threshold for human health, 10  $\mu$ g/l (WHO 1993). During the last three decades, high concentrations of arsenic in groundwater have been reported in different regions of the world such as the Bengal Delta (West Bengal-India and Bangladesh (Mandal et al. 1996; Bhattacharya et al. 1997, Chowdhury et al. 2000), Madhya Pradesh (Pandey et al. 1999, 2009), and many countries such as China, Mexico, Chile, USA, Argentina, Vietnam, and Taiwan (Bhattacharya et al. 2002; Smedley and Kinniburgh 2002; Bundschuh et al. 2009; Polya and Charlet 2009). Conventional remediation technologies have been used to clean up metal-contaminated sites because they are relatively insensitive to the heterogeneity in contaminated matrix and can function over a wide range of oxygen, pH, pressure, temperature, and osmotic potentials (Cunningham and Berti 1993; Mohan et al. 2007). However, they are expensive and time-consuming, often hazardous to workers, and produce secondary wastes that may not be environmental friendly. Among the disadvantages of conventional remediation methods, cost is the primary driving force behind the search for alternative remediation technologies, such as phytoremediation (Bhattacharya et al. 2002; Naidu et al. 2006).

In this study, we present an overview of: (1) behaviour of arsenic in relation to plant–soil and plant–water systems, (2) arsenic species in plant cell interactions, (3) phytoremediation as a bioremediation technique for arsenic removal, and (4) research carried out on plant and fungi materials useful as biosorbents. Phytoremediation techniques usually do not consider the biosorption processes of living plants and their dead and decaying parts. Combining bioaccumulation and biosorption may improve the effectiveness of arsenic remediation techniques and may reduce the disposal problem of arsenic-adsorbed material. However, further studies are needed for the development of the methodology and to enhance its cost-effectiveness.

#### Soil-water and plant interaction

Inorganic arsenic detaches phosphorylation and inhibits phosphate uptake, and hence, the presence of inorganic arsenic in soils and water is highly toxic to plants since it interferes with plant metabolic processes and reduces their growth. Similarly, the two most common inorganic arsenic species, arsenate and arsenite, act differently in different systems. Under certain conditions, it may lead to plant death (Geng et al. 2006). Arsenate, the dominant inorganic species of arsenic in aerobic/oxic environments, is taken up by plants via phosphate transport system since phosphate ion is similar to arsenate ion (Dixon 1997). The arsenic toxicity threshold limit for most plants is 40 and 200 mg kg<sup>-1</sup> in sandy and clay soils, respectively (Tu and Ma 2002). Plants can be classified into three basic groups based on the growth in contaminated soil: excluders, indicators, and accumulators (Baker 1981; Prasad 2008). Details on their phyto-processes and examples are given in Table 1.

# **Phytoremediation processes**

Transfer of arsenic species from bulk soil to the root surface: the plant factor

Arsenic transport from soil to plant roots depends on the oxygen level at the rhizosphere of the plant species. The speciation of arsenic greatly depends on the redox condition in the soil (Massechelyn and Patrick 1994; Heikens et al. 2007; Tripathi et al. 2007). For example, arsenate is more available in aerobic condition where arsenite found more in anaerobic condition (Zhao et al. 2003). A previous study suggested some physiological features (enhanced root uptake, high root-to-shoot translocation rate, and tolerance to metalloid contamination) (Wang et al. 2002; Ma et al. 2001). The physiological role of hyperaccumulators in the rhizosphere has been described in recent literature (Lasat 2002; Wenzel et al. 2003; Rajkumar and Freitas 2008). Also, some certain micro-organisms may enhance the transformation of trace elements by means of various mechanisms including methylation, demethylation, complex formation, and oxidation (Alexander 1999; Adriano et al. 2004). However, at present, the mechanisms of monomethyl arsenic acid and dimethylarsinic acid uptake by plant roots are unknown.

Three separate systems are being used by plants to take up arsenic: (1) passive uptake through the apoplast, (2) direct transcellular transport from the environment to the plant vascular system, and (3) active uptake through the symplast (Ross and Kaye 1994; Marschner 1995; Siedlecka et al. 2001; Greger 2005. There are a number of root factors controlling trace element uptake from soils that are soil acidification by root exudates, activity and selectivity of the translocators, root membrane activity, strategy

Table 1 Different plant groups in contaminated soils, phyto-processes, examples, and references

Plant groups	Principal phyto-process	Typical examples	References
Excluders	Restrict metalloid uptake and translocation of arsenic to the shoots	Bidens pilosa	Sun et al. (2009)
Indicators	Actively accumulate trace elements in their aerial tissues and generally reflect metal levels in the soil	Deparia sp., Pteris sp.	Chang et al. (2009) and reference therein
Accumulators	Uptake and translocate arsenic to shoots without toxic symptoms	Carex rostrata, Eriophorum angustifolium, Phragmites australis, Salix sp., P. vittata, Talinum sp.	Ross and Kaye (1994) Prasad (2008), Del Rio et al. (2002), Porter and Peterson (1975), Ma et al. (2001), Lombi et al. (2002), Sekhar et al. (2007)

mechanisms of avoidance, and release of redactors and/or oxidants, root excretion of chelators, phytosiderophores, acids, and hydrogen ions (Ross and Kaye 1994; Marschner 1995; Siedlecka et al. 2001; Greger 2005). Besides root factors, a number of elements (e.g. Fe, S, P, and Si) play an important role for inorganic arsenic species uptake mechanism in the plant (Zhao et al. 2003). Generally, accumulated arsenate species functions as phosphorus analogy; on the other hand, arsenite reacts with sulfydryl groups of enzymes and tissue proteins in the plant (Lombi et al. 2002).

#### Translocation mechanisms from the root to the shoot

Translocation ability is considered one of the important factor for plant species as it determines the phytoremediation capability of the particular plant species for arsenic (Xie et al. 2009). The change between inorganic arsenic species inside of the plant body has reported, where As(V) converted to As(III) with the help of arsenic reductases (Ali et al. 2009; Hokura et al. 2006). The AF (accumulation factor – As content in plant part/As content in the medium) value of plant species helps to classify into arsenic hyperaccumulator, accumulators, and excluders. Unlike phosphorus, arsenic shows low mobility with respect to translocation from roots to shoots, except for hyperaccumulators (Zhao et al. 2003). Several previous studies have suggested that arsenic transferred from root to shoot as arsenite (Zhu and Rosen 2009). Meanwhile, the uptake of arsenic by plant roots varies for different plants or their parts (Stoltz and Greger 2002, 2005, 2006). The translocation of arsenic ions from root to shoot depends on root pressure and leaf transpiration (Raskin et al. 1997; Caille et al. 2004; Ghosh and Singh 2005). Arsenate translocation happens by reducing it to arsenite by glutathione (GSH) (Sattelmacher 2001; Caille et al. 2004). In vascular plants, dicotyledons are more responsible for arsenic transportation than in monocots (Bondada and Ma 2003). In the case of hyperaccumulators, arsenic is localised in epidermal cells, mesophyll cells, and xylem tissues (Bondada et al. 2007).

The translocation factor (TF) (Baker and Whiting 2002) is an important feature for characterising plant capacity in phytoremediation techniques (Tu et al. 2002; Sekhar et al. 2007). Various studies have reported different TF values (Stoltz and Greger 2002; Fitz and Wenzel 2002; Raab et al. 2007). Hyperaccumulators demonstrated high TF values (Ma et al. 2001; Franseconi et al. 2002). TF values lower than 1 for plants indicate that arsenic transportation to the shoots is limited (Gonzaga et al. 2006) and that could be due to high phosphate concentrations (Knudson et al. 2003; Rahman et al. 2008). However, still there is a knowledge gap on the extent and mechanisms of As transport in the

phloem, particularly in rice (*Oryza sativa*), as concentrations decrease distinctly from roots to grain (roots > stems and leaves > husks > grain) (Abedin et al. 2002; Xu et al. 1991). Zhao et al. (2003) pointed out therefore that the contributions of xylem- versus phloem-derived As to the grain need more attention.

#### Bioconcentration and bioaccumulation

The trace element concentrations in plant tissues could be expressed as a bioconcentration factor (BCF, BF, or CF) (Tu and Ma 2002; Sekhar et al. 2007). The shoot or root AF (AF<sub>bio</sub>) is calculated as the ratio of the NH<sub>4</sub>OAc-extractable concentration from the arsenic in plant (Stoltz and Greger 2002). Arsenic concentrations in ranges  $5-20 \text{ mg kg}^{-1}$  DM are critical for most of the non-accumulating plants (Kabata-Pendias and Pendias 2001, Lombi et al. 2002). Del Rio et al. (2002) described wild plants occurring on uncontaminated sites, after arsenic-contaminated sludge was spilled in that area values ranged from 0.1 to 0.6 mgAs  $kg^{-1}$  DM. Luongo and Ma (2005) reported that Pteris vittata was able to translocate arsenic from roots to fronds, reducing arsenate to arsenite, and maintaining high concentrations of phosphate in the roots that can be contributed to arsenic tolerance and hyperaccumulation. Arsenic uptake showed an increase in the presence of acetate, carbonate, and phosphate ions, as well as NPK combination, whereas nitrate, chloride, and sulphate significantly decreased arsenic uptake Chandra et al. (2007). Therefore, it is important to pay attention to the other ions in the solution in this field of research.

#### **Phytoremediation methods**

In the end of last century, phytoremediation has got more exposure due to its cost-effectiveness, in situ application, environment friendliness, and less negative affect towards surrounding biodiversity (Salt et al. 1995; Watanbe 1997; Kabata-Pendias and Pendias 2001). The term phytoremediation covers a range of plant-based remediation techniques such as phytoextraction, phytostabilisation, phytoimmobilisation, rhizofiltration, and phytovolatilisation. Among all the techniques, phytoextraction got prioritised due its economic and scientific value (Peuke and Rennenberg 2005). The main process used in phytoextraction techniques is bioconcentration in the above-ground parts of the plant species.

Arsenic-tolerant plants that may be potentially used for phytostabilisation purposes have been known for a long time (Rocovich and West 1975; Benson et al. 1981). As phytostabilisation is a long-term process, native plant species will be prioritised for reducing ecological conflict with local ecosystem (Moreno-Jiménez et al. 2010). Phytoimmobilisation is an area where data are scarce (Doyle and Otte 1997) in soil science which focuses to decrease the availability of contaminants to water and plants by altering soil factors by formation of precipitates and insoluble compounds and by sorption onto the roots.

The rhizofiltration method has been used for filtration of contaminated water including groundwater, storm water, and other effluents using aquatic macrophytes and macroalgae (Salt et al. 1995; Mazej and Germ 2009). In the phytovolatilisation process, plants transpire or diffuse volatile arsenic out of their roots, leaves, or stems. In this mechanism, the plants absorb organic and inorganic pollutants from soil or water in the transpiration stream and volatilise them into the atmosphere in a modified or unmodified form at comparatively low concentrations. Both methylated and volatile arsenic compounds are involved in this process (Frankenberger and Arshad 2002; Adriano et al. 2004). However, literature on phytovolatilised arsenic is sparse. It has been observed that the presence of sulphate and salinity in soils hinder the volatilisation process (Terry and Zayed 1994). Data are scarce for the kinetics of arsenic release from soils and uptake kinetics of different plants (Abedin et al. 2002; Irtelli and Navari-Izzo 2008; Sarkar et al. 2007; Tyrovola and Nikolaidis 2009; Li et al. 2011) as well. Hence, it will be important to focus the future research on arsenic release kinetics in contaminated soils and kinetics of plant uptake in the presence of different ligands and chelating agents in addition.

#### Bioremediation

Bioremediation technology is another group of process based on degradation, stabilisation, or volatilisation of contaminants from sites using micro-organism (fungi and bacteria) (Andrews et al. 2000; Bhattacharya et al. 2002). The main mechanisms of arsenic bioremediation are biooxidation and biomethylation. Bio-oxidation has been tested in arsenic-contaminated water under aerobic conditions (Osborne and Ehrlich 1976; Ahmann et al. 1997).

Biomethylation of arsenic was studied both under aerobic and anaerobic conditions with the help of fungi (Cox and Alexander 1973; Andrews et al. 2000). The rate of biomethylation depends on environmental conditions such as temperature, potential redox, and pH (Fergusson 1990; Wallschläger and London 2008). Arsenic methylation typically occurs under phosphate- or nitrogen-deficient environments (Luongo and Ma 2005); however, concentration of nitrates and sulphates can be moderately reduced by bacterial processes (Bhattacharya et al. 2002). Potential of biomethylation has been studied by different filamentous fungi (Huysmans and Frankenberger 1991; Andrews et al. 2000).

#### Biosorption

Arsenic biosorbents were taken from inactive, dead biological biomass, such as algae (Hansen et al. 2006; Vilar et al. 2006), vascular plants (e.g. Pandey et al. 2009), fungi (Dambies et al. 2002; Say et al. 2003; Loukidou et al. 2003; Mohan et al. 2007), and bacterial materials (e.g. Kuvucak and Volesky 1988). A plant-based biosorbent mainly consists of cellulose and lignins. Primary plant cell walls consist of micelles of cellulose, hemicellulose (including pectins), and glucoproteins. Different models have been used to describe arsenic solutions-biosorbent equilibrium, the most common being Languimir, Freundlich, Hill, and Dubinin-Radushkevich isotherms (Mohan and Pittman 2007; Febrianto et al. 2009). Most of the biosorbent capacities reported in literature are low in relation to the capacity of activated carbon (Dabrowska et al. 2012). The recent attention is now given to different biochars for arsenic immobilisation from soils and adsorptive removal in aqueous media (Namgay et al. 2009; Hartley et al. 2009).

Biosorption mechanisms can be divided into two main categories: metabolism dependent (transport across cell membrane and intracellular precipitation and accumulation) and metabolism independent (precipitation, physical and chemical adsorption, ion exchange, and complexation) (e.g. Veglio and Beolchini 1997). Biosorption mechanisms that are independent of cell metabolism are relatively rapid and are reversible (Kuyucak and Volesky 1988; Hoffman et al. 2004; Mukherjee and Kumar 2005). Dead biomass has higher metal uptake capacity, and the process is nutrient independent (Aksu et al. 1991).

Adsorption by plant material consists of three steps: surface adsorption (physical and chemical), diffusion into particles, and adsorption and fixation within the mineral particles. However, not many studies have been conducted to observe the actual arsenic binding mechanism to the biosorbents. Kuyucak and Volesky (1988) hypothesised that some metal ion biosorption by dead biomass of algae, fungi, and yeasts takes place through electrostatic interactions between ions in solution and cell walls. Few studies by Ghimire et al. (2003) showed that the phosphorylation of biosorbent leads to higher binding of arsenates to the cell wall. Arsenic removal from solution could also take place through formation of complexes on the cell surface (e.g. Mcafee et al. 2001). Metal ions can bind on to single ligand or through chelation. However, no other records were found on biosorption through arsenic complexation. Advanced synchrotron and other spectroscopic techniques will be able to reveal the mechanisms and speciation behind.

# Plants as biosorbents

#### Vascular plants

Plant materials such as living plants (Hoffman et al. 2004), their parts or their dried, seized, and chemically treated seeds (Kumari et al. 2006; Koivula et al. 2009; Pandey et al. 2009), and also the residue of vascular plants from industry or agriculture, such as rice polish and orange wastes (Ranjan et al. 2009; Ghimire et al. 2003), were tested as biosorbent material for arsenic removal. Maximum biosorption capacity for living plants was sometimes observed to be a two-stage process, that is, rapid first phase, and a slow second phase. Pandey et al. (2009) reported chelation of As(III) with the -OH groups for fresh different parts of the biomass of Momordicacharantia. Most of these experimental results were in good agreement with the Langmuir and Freundlich sorption models. However, the Dubinin-Radushkevich (D-R) sorption isotherms were applied to evaluate the nature of sorption and were used to explain the heterogeneity of surface energies (Ranjan et al. 2009).

## Plant litter as biosorbent

Fibres, lignins, cellulose, and other substances bind to cell walls, such as phenols, cutin, suberins, waxes, and others (e.g. Berg et al. 2003). Certain cell wall components, specially lignin and pectin, are assumed to be connected with the sorption of metal ions (Bailey et al. 1999; Quek et al. 1998; Randall et al. 1974; Senthilkumaar et al. 2000; Volesky and Holan 1995). Plant fibres are capacious for sorption of metal ions and have been tested for water cleaning (e.g. Bailey et al. 1999).

#### Other plant groups

Alginate, a component of the outer cell wall of brown algae, *Prokaryotes* cell walls, is composed of polysaccharides, proteins, and lipids (offers particularly abundant metal-binding functional groups, such as carboxylate, hydroxyl, sulphate, phosphate, and amino groups), and mushrooms, filamentous fungi, chitin, chitosan, and other fungi have been studied for arsenic retention (Hansen et al. 2006; Loukidou et al. 2003; Mcafee et al. 2001; Say et al. 2003; Murugesan et al. 2006). However, not much attention has been given to understand the mechanisms behind these biosorption processes.

## Conclusion

Phytoremediation and bioremediation techniques are good and inexpensive tool for removing and/or stabilising arsenic and to clean up of water-soil systems. However, its success depends on both plant and soil factors such as soil suitability for plant growth, depth of contamination, depth of the plant root system, level of contamination, and urgency in cleaning up. About 450 plant species have been recorded as phytoremediation; however, a few number of arsenic hyperaccumulator plants have been found. The crucial factor in using hyperaccumulators for phytoremediation of arsenic is their climate limitations and postharvest management of the arsenic-containing biomass. However, the gaps in knowledge regarding the molecular level mechanism and kinetics behind arsenic and plants, microbes etc. are still limiting the use of phytoremediation for arsenic removal. In situ techniques will be more useful in such developments in view of the fact that the sequential extraction techniques or other common methods are not reliable in understanding speciation. The advanced synchrotron techniques and nano-Secondary Ion Mass Spectroscopy will be very useful in this regard to investigate and understand the mechanisms behind the arsenic interactions with plants. Further investigations are required to clarify whether active exclusion and the phosphate pathway uptake mechanism are simultaneously employed in different species. Transfer of accumulated arsenic in plants carried with flowing waters, remobilisation through decay, possible methylation, and volatilisation are needed to be considered. Hence, further studies are important to ascertain the extent of arsenic remobilisation through decay and other microbial process and influence of geochemical changes following physical and metabolic gaseous exchanges, and exudates in the total aquatic system are necessary. Since the retention of arsenic from soils and plants is very complex, it is difficult to quantify by experimentation since there are several variables such as plant species, soil physicochemical processes, climatic conditions, and soil arsenic bioavailability. Hence, a need exists to develop a mathematical model for predicting dynamic uptake, translocation, accumulation, and mobilisation of arsenic in the soil-plant system.

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