



REVIEW ARTICLE

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## Arsenic: behavior in the environment, plant uptake mechanisms and human health risks

### *Arsênio: comportamento no ambiente, mecanismos de absorção pelas plantas e riscos à saúde humana*

**ABSTRACT:** Negative impacts caused by arsenic (As) in soils and waters have attracted public interest due to contamination of ecosystems and human populations dwelling in the vicinity of its generating sources. The main anthropogenic sources of such contamination result from the oxidation of sulfide residues containing arsenopyrite in piles of mining tailings and the leaching of soils with high background of As. This contamination presents serious consequences to the functional components of ecosystems. Through plant uptake, this element can enter the food chain and cause several health problems, even at low exposure ( $<10 \text{ mg L}^{-1}$ ). Therefore, to reduce the environmental impacts caused by contamination of soil, watercourses, and groundwater, the use of phytotechnologies applicable to the remediation of contaminated environments have been highlighted. The objective was to describe the current state of research on As, focusing on plant behavior and risks to health and the environment. Phytoremediation is a promising technique to recover local sites contaminated by trace elements such as As. Unfortunately, few plant species have presented phytoremediation potential so far. In the relation between soil-plant-behavior of As and human health risk, studies should be directed to the discovery of species with remediation potential and to analysis on the interactions of As with Pb, Zn and Cd, naturally associated with secondary minerals. To this end, the mineralogy and stability of these minerals should be studied via X-ray diffraction and X-ray absorption spectroscopy, combined with bioaccessibility analyses.

**RESUMO:** O impacto negativo causado pelo arsênio (As) aos solos e águas tem preocupado a sociedade, devido à contaminação humana de populações vizinhas às fontes geradoras de dos ecossistemas. As principais fontes antropogênicas de contaminação são a oxidação de resíduos de sulfetos, contendo arsenopirita, em pilhas de rejeitos de mineração, e a lixiviação de solos com background de As elevado. A contaminação acarreta sérias consequências sobre os componentes funcionais dos ecossistemas. A partir da absorção pelas plantas, o elemento pode entrar na cadeia trófica e causar problemas diversos à saúde, mesmo em baixa exposição ( $<10 \text{ mg L}^{-1}$ ). Portanto, para reduzir os impactos ambientais gerados pela contaminação do solo, dos cursos de água e do lençol freático, o uso de fitotecnologias aplicáveis à remediação de ambientes contaminados tem se destacado. O objetivo foi descrever o estado atual das pesquisas sobre o As, com foco no comportamento das plantas, e os riscos à saúde e ao ambiente. A fitorremediação tem se constituído em uma técnica promissora para recuperar locais contaminados por elementos-traço, como o As. Infelizmente, ainda são poucas as espécies de plantas com potencial fitorremediador. Na relação solo-planta-comportamento do As e risco à saúde humana, os estudos devem ser direcionados para a descoberta de espécies com potencial remediador e para as análises sobre as interações do As com Pb, Zn e Cd, naturalmente associados aos minerais secundários. Faz-se importante estudar a mineralogia e a estabilidade desses minerais via difração de raios X e espectroscopia de absorção de raios X, aliadas a análises de bioacessibilidade.

## 1 Introduction

Arsenic (As) is a toxic metalloid from natural sources widely distributed in the environment. It is released through weathering, anthropogenic actions, and human activity. Arsenic is ranked by the United States Environmental Protection Agency (USEPA, 2002) as the most toxic and harmful substance to human health. Its most abundant inorganic forms in terrestrial and aquatic environments are arsenate (AsV) and arsenite (AsIII) (Bundschuh et al., 2013). The high toxicity of As to the human, plant and animal populations has caused increasing concern of society, because several cases of contamination have been reported in different parts of the world. In India, millions of people are at risk of As poisoning by contaminated drinking water. In Australia, Vietnam, Cambodia and Nepal, contamination by As from groundwater has also been reported (Da Sacco et al., 2013). Exposure of humans to As polluted environments can cause several types of cancer, such as skin, lung and pancreas, as well as injuries to the nervous system, neurological malformations, and miscarriages. Children are the main risk group because of their low body weight, and death caused by chronic exposure to low As doses (0.05-0.1 mg kg<sup>-1</sup> d<sup>-1</sup>) in drinking water has been reported (ATSDR, 2014).

One of the most common chronic effects owing to ingestion of inorganic As are skin lesions (hyperpigmentation in the form of dots or diffuse on the palms and soles), which have been observed even in individuals with low levels of exposure (0.005-0.01 mg L<sup>-1</sup>). The following effects of As ingestion are highlighted: neurological condition, systemic arterial hypertension (SAH), peripheral vascular disease, respiratory and cardiovascular problems, and diabetes mellitus (Chakraborti et al., 2013).

The source of As present in terrestrial and aqueous environments occurs because of its release from geological sources (natural) owing to the weathering of mineral phases containing As or to human action (anthropogenic). The main anthropogenic sources are industrial activities such as mining (extraction of gold and metals associated with sulfides, such as pyrite and arsenopyrite) (Toujaguez et al., 2013), wood preservation, and production and application of agricultural pesticides (Cheng et al., 2009).

Remediation of soils polluted with metals, including As, has occurred through the utilization of various techniques, such as excavation and backfill - avoiding soil loss through erosion and leaching, and immobilization with the use of ameliorative chemicals - making metals less available in the soil. Although these techniques present good results as protection tools to human life and the environment, they are costly.

Phytoremediation (or the use of phytotechnologies) as an emerging, simple and inexpensive technique that generates minimal disturbance to the soil and landscape, constitutes a promising alternative compared with techniques of physical and chemical treatment. It uses plants, or plants and associated microorganisms, to remove pollutants from the environment or reduce their toxicity (De Oliveira et al., 2014). It mitigates the environmental impact and improves the physical structure, fertility and biodiversity of soils within the concept of sustainable development.

The discovery of plants capable of accumulating large amounts of trace elements (hyperaccumulators) resulted in advancements to the adoption of this technique for the remediation of contaminated environments. In order to be As hyperaccumulators, plants must have the ability to absorb and retain, in their aerial parts, at least 1.000 mg kg<sup>-1</sup> of As. Few plants are able to translocate large amounts of As from roots to shoots (De Oliveira et al., 2014).

The fern (*Pteris vittata* L.) (Ma et al., 2001) is the first plant species described as hyperaccumulator of As; it presents great phytoextraction potential, accumulating a high amount of As in the fronds and showing good biomass production. Some other types of ferns have also been described as hyperaccumulators of As, such as *Pteris biaurita*, *Pteris cretica*, *Pityrogramma calomelanos* and *Pteris logifolia* (Srivastava et al., 2006). However, most of the species studied are of temperate climate, and information about tropical species is scarce and necessary. Knowledge about the behavior of As in water, sediments, soil and plants, as well as about tolerant and hyperaccumulating species, including those of tropical regions; the understanding of the physiological mechanisms related to As accumulation; and interactions of As with other factors, may contribute to the reduction and remediation of contaminated areas, reducing the risk to human health. The purpose was to describe the current state of research on As, focusing on plant behavior and risks to human health and the environment.

## 2 Development

### 2.1 Arsenic in the environment

Arsenic is found in rocks, soil, water and organisms with different mobility and geochemical stability, comprising over 245 minerals (Mandal; Suzuki, 2002). It is a chalcophile element with high affinity with sulfides, where it appears together with copper, nickel, lead, cobalt and other trace elements. It presents a diverse dynamics, being able to vary in toxicity and reactivity according to the oxidation state. Arsenic oxidation states are -III, 0, +III and V and its predominant forms are As (III) and As(V) (Toujaguez et al., 2013). The amount and chemical species of As depend mainly on the concentration of the oxides of Fe, Al and Mn, redox potential, clay content, and pH. In oxic conditions, As is present in the environment as arsenate (AsV), while arsenite (AsIII) is found in anoxic conditions and consists of the reduced form (Kabata-Pendias, 2011).

The mean concentration of As in the earth's crust is 2 mg kg<sup>-1</sup> (Kabata-Pendias, 2011). The content of As in the environment depends mainly on the composition of the geological material. However, anthropic activities increase the levels of As in soil and water. According to the Agency for Toxic Substances and Disease Registry - ATSDR (2014), weathering of rocks, volcanic activity, aerosols of seawater, and microbial volatilization are the natural sources that contribute to As enrichment. Furthermore, pesticides, herbicides, wood preservatives, burning of fossil fuels, fertilizers, smelting of gold, lead, copper and nickel, and production of iron and steel are the main anthropogenic sources of As (Mandal; Suzuki, 2002).

Anthropogenic contamination contributes to the dispersion of As, even to areas with no influence of contaminating activities. Under these conditions, As can be transported over long distances as suspended particles through the air and water. As is considered toxic even at low levels regardless of its sources in the environment, which may present a risk to human health (ATSDR, 2014; Kabata-Pendias, 2011).

Arsenic content in the soil varies according to the parent material. Soils derived from magmatic rocks can present 0.5-2.6 mg kg<sup>-1</sup> of As, while sedimentary rocks can contain 1.0-13 mg kg<sup>-1</sup> of this element (Kabata-Pendias, 2011). Pedogenesis also influences the behavior of As in the soil; sandy soils generally show lower levels of As compared with organic soils. In acidic soils, As is usually found bound to oxides of Fe and Al as AlAsO<sub>4</sub> and FeAsO<sub>4</sub>, while in alkaline soils there is predominance of arsenate - Ca Ca<sub>3</sub> (AsO<sub>4</sub>)<sub>2</sub> (Da Sacco et al., 2013; Kabata-Pendias, 2011). In non-altered rocks, during weathering, As is concentrated in the hydrated phases of oxy-hydroxides, mainly associated with sulfide such as arsenopyrite (FeAsS), where As sulfide is converted to As trioxide (Mandal; Suzuki, 2002).

Arsenic tends to concentrate in the surface horizons because of atmospheric deposition, vegetation recycling, and the presence of oxides and organic matter, which reduce mobility. The concentration of As in the so-called non-contaminated soils can range from 1 to 20 mg kg<sup>-1</sup>, but in contaminated agricultural soils this value can reach 600 mg kg<sup>-1</sup> (Kabata-Pendias, 2011).

The total concentration of As in the soil does not necessarily determine its availability to plant uptake (Kabata-Pendias, 2011). Several soil properties affect the bioavailability of As, such as chemical, biological and physical attributes, and texture, in addition to the type of As source: inorganic or organic (Toujaguez et al., 2013). The behavior of arsenate in the soil also resembles that of phosphate and vanadate (Kabata-Pendias, 2011). Arsenate is adsorbed on oxides of aluminum and iron, non-crystalline aluminosilicates and, to a lesser extent, on silicate clays. Arsenate is the anion of the H<sub>3</sub>AsO<sub>4</sub> acid, which shows pKa values of 2.24, 6.94 and 11.5, and it is effectively adsorbed at pH values between 4 and 7. The anions AsO<sub>2</sub><sup>-</sup>, AsO<sub>4</sub><sup>-3</sup>, HAsO<sub>4</sub><sup>-2</sup> and H<sub>2</sub>AsO<sub>3</sub><sup>-</sup> are mobile forms of As adsorbed at pH values between 7 and 10 (Kabata-Pendias, 2011).

In natural waters, As occurs mainly in the form of arsenite As (III) and arsenate As (V), and arsenite is more toxic than arsenate (Toujaguez et al., 2013). The depth of water bodies and the redox potential influence the speciation and toxicity of As. In surface water bodies, oxidation of arsenite to arsenate occurs because of the contact with oxygen from the atmosphere, with arsenate prevailing in the surface layer. Arsenite predominates under conditions of low redox potential, while arsenate predominates under high redox potential (Bundschuh et al., 2013).

Acceptable concentrations of As in drinking water are between 10 and 50 µg L<sup>-1</sup> (USEPA, 2002). In Latin America, As levels higher than 10 µg L<sup>-1</sup> have been reported in Argentina, Bolivia, Chile, Colombia, Cuba, Ecuador, El Salvador, Guatemala, Honduras, Mexico, Nicaragua, Peru and Uruguay (Bundschuh et al., 2013; Toujaguez et al., 2013). In Brazil,

surface water bodies with values higher than 10 µg L<sup>-1</sup> have been verified by studies of human exposure in the Quadrilátero Ferrífero area, Minas Gerais state (Figueiredo, 2006) and in the municipality of Santana, Amapá state (Figueiredo et al., 2007). The main source of contamination at these sites is the mining of metals, mainly gold, iron and manganese.

The occurrence of As in hydrothermal waters has been reported in different parts of the world, including the USA, Mexico, Chile, Japan, the Philippines, China, India and Brazil (Bundschuh et al., 2013). The high levels of As in these countries are related to both anthropogenic and geogenic sources. In some regions of India, China, Turkey and Bangladesh, high concentrations of As are related to volcanic and sedimentary formations, which are rich in this metalloid. Concentration of As in groundwater depends on geology and tectonic activities, combined with conditions of temperature, pH, redox potential, biological activity, and pressure, which favor the reduction of As of primary and secondary minerals (Bundschuh et al., 2013). The use of water with high contents of As is a threat to human health and the ecosystem, because of consumption and use in irrigation.

In Brazil, occurrence of contamination with As has been reported in water (until 0.36 mg L<sup>-1</sup>), soils (until 860 mg kg<sup>-1</sup>), and sediments (until 3.200 mg kg<sup>-1</sup>) in the vicinity of industrial or mining areas (Cantoni, 2010). The earliest analysis records of As concentration in Brazilian soils were carried out by Curi and Franzmeier (1987). In Minas Gerais state, these authors found contents of As ranging from 10 to 36 mg kg<sup>-1</sup> in Ferriferous Latosol.

## 2.2 Arsenic and human health

Every two years, the United States Environmental Protection Agency (ATSDR, 2014) ranks the most dangerous substances to human health; As has been at the top of the list since 1997. This naturally occurring metalloid is found generally at low concentrations (<1 g kg<sup>-1</sup>) in soils and rocks, and it does not represent a risk to human beings under natural conditions.

The risk to human health due to As poisoning is associated with chronic exposure over several years. Consumption of contaminated food and water is more worrying when regarding children, because of the exposure time that they will have to endure (ATSDR, 2014).

In Southern Asia, mainly India and Bangladesh present the most serious problems of As contamination worldwide. In these regions, exposure to geogenic sources (sediments rich in pyrite with As) and reducing conditions favor the release of As to groundwater at concentrations greater than 50 µg L<sup>-1</sup>. The result of oral exposure to these waters has caused the poisoning of thousands of people, with the presence of hyperkeratosis and the development of cancer (ATSDR, 2014).

High levels of As in nail and hair have been related to high levels of As in soil and water in northeastern India. In this region, the exposure of humans to As has caused dermal diseases, miscarriages, skin pigmentation, premature birth, and various types of cancer (Chakraborti et al., 2012). The consumption of water, fish, grains, cereals, fruits and milk is the main source of contamination to humans. The cultivation of agricultural crops in contaminated soils, combined with

irrigation water rich in As, presents a high risk to human health in different parts of the world (Chakraborti et al., 2012; Da Sacco et al., 2013).

As in the case of water, soil contamination by As and its translocation to plants also represents a risk to ecology and human health through the consumption of vegetables, and it can also compromise agricultural productivity and the sustainability of ecosystems (Lessl; Ma, 2013).

### 2.3 Phytoremediation of soils contaminated with arsenic

Different techniques based on chemical, physical and biological remediation have been adopted for soils contaminated by As. These remediation techniques can be assessed in two categories: *ex situ* and *in situ*. Remediation *ex situ* is based on the removal of contaminated material through excavation and the removal and subsequent disposal of material in an appropriate landfill, with incineration in the case of contaminated plants. On the other hand, *in situ* techniques are based on the recovery of the area where contamination occurred through heat treatment, acid leaching, and phytoremediation (Rahimi et al., 2012).

Phytoremediation is a technique that uses plants and their associated microbiota to remove, immobilize or make contaminants less harmful to the ecosystem. It has been recognized as an emerging technique for environmental decontamination (De Oliveira et al., 2014). Thus, the development of strategies for phytoremediation of As-contaminated soils has become an important alternative, because it is less costly and causes less soil mobility and impact on the ecosystem when compared with other techniques (Danh et al., 2014).

Phytoremediation species show different tolerance mechanisms to accumulate and transport As with no damage to metabolism. The physiological and biochemical behavior of species with potential for phytoremediation is complex and little known for As. Several strategies are adopted by the different plants, which depend on the plant species and on the total content, speciation, and bioavailability of the element in the soil. Characteristics intrinsic to the soil also influence the ability of plants to uptake As. Soil attributes such as pH, and contents of clay and oxides of Fe, Al and Mn influence the uptake of As by plants (Kabata-Pendias, 2011), because of their influence on the availability and mobility of the element in the soil.

Phytoremediation provides several mechanisms to reduce contamination, and phytostabilization and phytoextraction are highlighted for areas contaminated with As. Phytostabilization is the branch of phytoremediation in which plants are used to reduce the mobility and availability of the contaminant in the soil. This mechanism is applied in situations where the soil presents high contamination, and only tolerant plants are able to endure. Tolerant species usually have roots with large biomass, which are able to adsorb, precipitate, and accumulate the element in their root system, without translocating it to their shoot system. Although the contaminants are not removed from the site, phytostabilization allows reducing the risk of erosion and the leaching of pollutants, preventing groundwater

contamination and reducing the risk of As entry in the food chain, thus avoiding possible contamination to human beings and the environment (De Oliveira et al., 2014).

Phytoextraction consists of the uptake, translocation, and accumulation of the element in the aerial part of plants. The ideal plant for As phytoextraction should be tolerant to high concentrations in the aerial part and present high growth rate, good biomass production, and extensive root system (De Oliveira et al., 2014). Finding plants with capacity to hyperaccumulate metals and metalloids is probably the greatest challenge to be overcome by the phytoremediation technique.

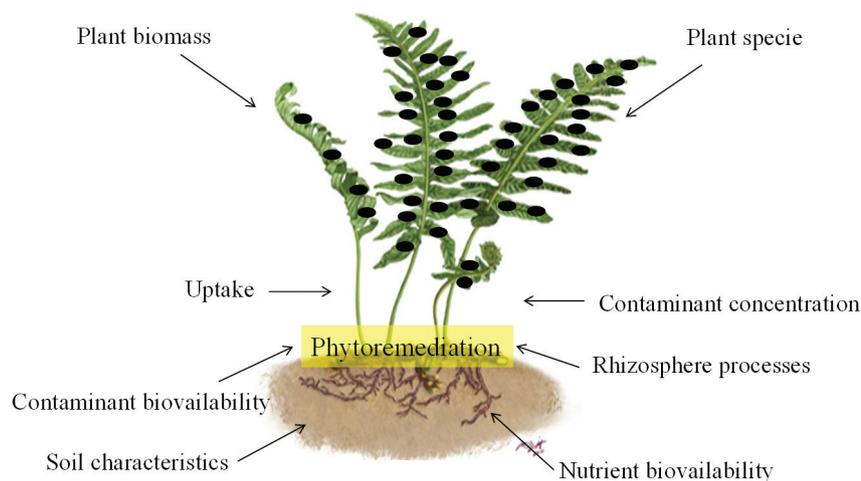
### 2.4 Arsenic hyperaccumulator plants

Hyperaccumulation of metals and metalloids is a rare phenomenon in terrestrial higher plants (angiosperms and gymnosperms). Hyperaccumulators are plants that can take up and concentrate in their aboveground biomass at least 1.0 g kg<sup>-1</sup> of As compared with non-accumulating plants, and present high rates of accumulation, growth and biomass production. They must have the ability to absorb As even at low available levels and, concurrently, with many elements, and present high levels of resistance and tolerance to pests and diseases (Ma et al., 2001).

The factors used to characterize the hyperaccumulation of metals and metalloids by plants are the translocation factor (TF) and the bioaccumulation factor (BF) (Rahimi et al., 2012; De Oliveira et al., 2014). The TF demonstrates the efficiency of a plant in transporting an element from the roots to the aerial part, while the BF evaluates the efficiency of a plant to accumulate the element, taking into account its concentration in the environment. The higher the BF, the higher the transfer of the element from the soil or water to the plant and, consequently, the greater the ability of the plant to remove it from the environment. Both factors, when greater than 1, confirm the hyperaccumulation trait of the plant (Ma et al., 2001). Most plants tolerate As concentrations in soil in the range between 1 and 50 mg kg<sup>-1</sup> (Kabata-Pendias, 2011), whereas hyperaccumulators grow in soil with up to 1.000 mg kg<sup>-1</sup> of As (Ma et al., 2001).

The fern, *P. vittata* L. (Ma et al., 2001) was the first plant described as hyperaccumulator. It has great potential as phytoextractor, accumulating high quantity of As in its fronds and presenting good biomass production (De Oliveira et al., 2014). Srivastava et al. (2006) observed that a new species of fern, *Pteris biaurita* L., accumulated an amount of As similar to that of *P. vittata*, when the two species were cultivated in nutrient solution with 50 µg L<sup>-1</sup> of As. In *Pteris fauriei* fern, Wang et al. (2007) found As accumulation greater than 1.000 mg kg<sup>-1</sup> in the fronds, characterizing it as hyperaccumulator. Most of the species studied are of temperate climate, and further studies on tropical species are needed.

The capacity of plants to uptake As varies as a function of concentration, availability, and speciation of this element in the soil, as well as the presence of other elements, such as phosphate (Figure 1). In the soil solution, As uptake occurs through plant roots by mass flow, where it tends to concentrate, with little translocation to the aerial part (Kabata-Pendias, 2011). In the shoots, As concentration decreases from older



**Figure 1.** Factors influencing the uptake of As by plants. Adapted from Gonzaga et al. (2006).

to younger leaves, stems, seeds, and finally, to fruits, where contents are even lower. Higher levels of As in the root system compared with the aerial part is a characteristic of species with phytoremediation potential. As accumulation in the roots is a strategy to mitigate the toxic effects of the element in organs where physiological processes prevail, such as the leaves (Lessl; Ma, 2013).

The uptake and translocation of arsenate occur similarly to that of phosphate, which is movable in the plant and easily spread from one storage organ to another. Phosphate can provide As to be absorbed by hyperaccumulator plants or compete for adsorption and absorption sites. Hyperaccumulator plants accumulate more phosphorus (P) in the roots and more As in the shoots, given the competitive absorption. This mechanism is adopted to reduce the toxic effects of As and mitigate its metabolic interference in the plant (Lessl; Ma, 2013).

In studies with *P. vittata* L. for remediation of soils contaminated with As, addition of low solubility P increased arsenate absorption without causing P deficiency in the plant (Lessl; Ma, 2013). Low contents of labile P in the soil can induce increased root biomass. The higher the growth of the root system, the greater the contact of roots with the metalloid, and the greater the absorption (Lessl; Ma, 2013).

Hyperaccumulator and tolerant species preferentially absorb As in its dominant form in aerobic soils - arsenate (AsV) (Tu et al., 2004). Because of its similarity to phosphate ( $\text{PO}_4^{3-}$ ), arsenate is absorbed by the plasmalemma of roots; while arsenite (AsIII) occurs passively via aquaglyceroporins, or channels that allow water movement and neutral solutes in the roots (Wang et al., 2002). However, phosphorus does not compete with arsenite uptake; therefore, arsenite does not share the same transport system as phosphate. Even when exposed to high concentrations, arsenic-tolerant plants have mechanisms that reduce its absorption. When the plant necessities to phosphorus are satisfied, the operation of this mechanism is reduced, preventing the uptake of As. Once absorbed, plants are able to metabolize it to less toxic forms, promoting its sequestration, which reduces the symptoms of

phytotoxicity (Lessl; Ma, 2013; De Oliveira et al., 2014). On the other hand, species unable to tolerate or hyperaccumulate As, such as *Acácia mangium* and *Mimosa caesalpiniaefolia* (Cipriani et al., 2013), may experience phytotoxicity, affecting their development and causing death. In rice, As uptake occurs in the form of arsenite as well as arsenate, depending on the cultivation conditions: arsenite prevails in rice crops grown in flooded areas, while arsenate prevails under aerobic conditions. Under anaerobic conditions, the amount of As absorbed can be 15 times higher than under aerobic conditions. The reduction conditions increase the availability of As and, consequently, its absorption by the rice plant. In rice, As absorption occurs via aquaporins, which are permeable to arsenite and non-permeable to arsenate (Da Sacco et al., 2013).

Continuous phytoextraction of As is a viable alternative in environmental recovery programs, especially for the fraction of available As. The remediation of the total fraction of As through phytoextraction is a mechanism that can last decades. However, phytoextraction of the labile fraction can be reduced according to the species employed in the recovery program (Danh et al., 2014). In a study with *P. vittata*, Lessl and Ma (2013) reported a 42% reduction in the phytoavailability and bioaccessibility of As after 30 months of cultivation. As removal in the second year of cultivation was higher than in the first year, which emphasizes the potential of *P. vittata* for phytoextraction of As in the long term.

Just as phosphate, sulfate also influences the absorption and translocation of As in plants. The effect of sulfate on the absorption of As in *P. vittata* was investigated by Fanrong et al. (2011). They observed that the enrichment of sulfate promoted the uptake and translocation of As from roots to fronds. The reason for this occurrence is that sulfate acts in the reduction of arsenate to arsenite because sulfur groups form complexes with As. In addition, sulfur is a good oxygen donor and acts on redox reactions, particularly in anaerobic conditions where arsenite is the predominant species. In microorganisms, the reduction of arsenate to arsenite is catalyzed by glutathione, but in *P. vittata* this mechanism has not been proven.

## 2.5 Phytotoxicity of arsenic

Phytotoxicity of As occurs due to the interference of this element in the inhibition of plant metabolism. Arsenate can impair oxidative phosphorylation and ATP production, as well as compete with phosphorus in various reactions (Gonzaga et al., 2006). Under high concentrations of available As in soil, most plants show symptoms of phytotoxicity such as wilting and necrosis of leaves, slow growth of roots and shoots, purplish color, and death (Kabata-Pendias, 2011).

In As-tolerant plant species, absorption of this element can be reduced even when exposed to high concentrations. Reduction in As uptake can be related to changes in the transport mechanisms of phosphate (Tu et al., 2004). When the plant necessity for phosphorus is satisfied, it reduces the uptake of both P and As (Shaw, 1989). Even after uptake, the plant can complex, compartmentalize, and biotransform As. Complexation of As by lipids in the vacuole and cell wall is a strategy of hyperaccumulator plants to reduce the toxic effect of As (Shaw, 1989; Tu et al., 2004).

The reduction of arsenate to arsenite inside the plant is a strategy of hyperaccumulators to accumulate As without developing symptoms of toxicity (Tu et al., 2004). When investigating the relation between As(V) and Cr(VI) in *P. vittata*, De Oliveira et al. (2014) reported that 72% of the As translocated to the fronds was in the form of arsenite. In an experiment of As speciation conducted by Tu et al. (2004), 90% of the As was present as arsenate in the biomass of the root system of *P. vittata* L., while arsenite was predominant in the fronds (94%), and no organic compound containing As was detected. Although arsenite is more toxic than arsenate, once reduction has occurred arsenite becomes less toxic owing to complexation in metabolic compounds such as phytochelatin and sequestration in vacuoles.

## 2.6 Mechanisms of arsenic tolerance in plants

Plant resistance to As may occur through mechanisms that prevent the absorption of metals or by tolerance itself (Shaw, 1989). The following mechanisms of As tolerance should be highlighted: i) selective exclusion; ii) change in absorption capacity, where impediment can occur in absorption as a result of change in membrane permeability; iii) increased exudation of chelating substances that reduce the bioavailability of the metal to the plant; iv) transport restriction; v) metal retention in the root and/or conduction pathways; vi) immobilization in the cell wall; vii) associations with mycorrhizae; viii) biochemical mechanisms - changes in the forms of compartmentalization of the metal, immobilization in the vacuole, alterations in cellular metabolism, and production of intercellular binding compounds with formation of sequestering and inactivating compounds of the metals; and ix) tolerance of the enzyme system to the metal (Shaw, 1989).

The biochemical mechanisms of tolerance can present different mechanisms in response to excessive trace elements, which include production of intracellular compounds that bind with metals; formation of thiol-rich peptides (phytochelatin and metallothioneins); chelation by organic acids and amino acids; and compartmentalization of the metal in subcellular structures (Shaw, 1989).

The role of citric and malic acids as mitigating substances of metals is still not clear. Accumulation of these acids as a function of metal exposure may merely reflect metabolic disorders. Chelators contribute to metal detoxification by reducing the concentration of free metal in the cytosol, limiting reactivity and solubility. In plants, the major known classes of trace elements chelators include phytochelatin, metallothioneins, organic acids, and amino acids (Shaw, 1989).

Phytochelatin is formed from three amino acids: glutamate (Glu), cysteine (Cys) and glycine (Gly), with Glu and Cys bound through an  $\alpha$ -carboxyl amide. Phytochelatin present the general structure ( $\gamma$ -glutamyl-cysteine) glycine n-(n-2-11), as well as variants with repeated units of  $\gamma$ -glutamyl cyteinil, which are formed in plants and yeast. Phytochelatin are able to bind to As and to the metals Cd, Cu or Zn via the sulfhydryl and carboxyl residues, but their synthesis is controlled preferentially by the metalloid As (Inouhe et al., 2005).

Two common characteristics of species known as As hyperaccumulator are the massive transport of As to the aerial parts and the formation of phytochelatin in the root system. These characteristics suggest that the detoxification of metals by phytochelatin can be a type of evolutionarily ancient defense mechanism, established in microalgae and microfungi, and the independent additional mechanism of phytochelatin via vascular transport system was established later in plants (Inouhe et al., 2005).

Hyperaccumulation is regulated by the physiological, biochemical, and genetic processes of the plant. Species or varieties of the same plant exposed to a similar concentration of trace elements may differ in the absorption and/or internal distribution of these metals in the plant. This may result in differences in the capacity to retain the element in the roots and/or in variations of xylem loading (Shaw, 1989). Other factors such as stage of development, time of exposure to the metal, and the different chemical species of the elements, can also interfere with these aspects, reflecting the levels of metals in different plant parts (De Oliveira et al., 2014). This diversity of actions against trace elements demonstrates the responsiveness of these plants using different strategies of defense, resistance and tolerance, with varying mechanisms.

## 3 Concluding remarks

Arsenic behavior in the soil varies according to parent material and anthropogenic activities. Under natural conditions, the levels of As are usually low, causing no risk to human health and the ecosystem. Oxides of Fe and Al, redox potential, and pH influence the availability, mobility and chemical speciation of the element in soil and water. Phytoextraction of As by hyperaccumulator plants and phytostabilization are the main mechanisms used by a limited group of plant species in the remediation of contaminated soil. The most effective species for this purpose so far are *P. vittata* and *Pityrogramma calomelanos*; both of temperate regions. In tropical regions, genetic studies and field tests suggest species of the Leguminosae family as tolerant; however, no plant species under tropical conditions was classified as As hyperaccumulator.

In the relation between soil-plant-behavior of As and human health risk, researches show the necessity to assess not only the behavior of As in the soil, but also the interactions between As, Pb, Zn and Cd, considering that these elements are combined to form primary mineral phases in the rock and subsequently, after weathering, form new supergene minerals as arsenates also present in the soil.

The risk of As to human health can be estimated based on detailed mineralogical studies by X-ray diffraction (XRD) and X-ray absorption spectroscopy (XANES, EXAFS) of tailings exposed in soil, combined with analysis of gastric and gastro intestinal bioaccessibility *in vitro*.

Future research should focus on molecular genetic technologies with plants that are more resistant and present high uptake of trace elements. The discovery of molecular mechanisms of tolerance and accumulation in hyperaccumulator species can facilitate the identification of genes that rule the hyperaccumulation of toxic elements in plants. The discovery of plants capable of performing the phytoremediation of more than one species of trace elements is a perspective of biotechnology, because toxic elements are in synergy with other elements under natural conditions. The future of plant biomass after the remediation program should be carefully studied so that contamination of new areas with improper disposal of plant material could be avoided.

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