

Methods to Remediate Arsenic-Contaminated Soils

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Arsenic is a metalloid widely distributed in the environment and of global concern for human health. In a promising breakthrough for sustainable arsenic soil remediation, a fern, *Pteris vittata* L., was discovered to take up arsenic from the soil and accumulate it in its fronds at up to ~100 times soil concentrations. Successively harvesting the fronds removes, or phytoextracts, arsenic from the soil with potential environmental and economic benefits including low site disturbance and low cost.

Keywords: arsenic ; soil ; rhizosphere

1. Introduction

Arsenic is a metalloid widely distributed in the environment and of global concern for human health. Arsenic can cause acute and chronic poisoning through exposure routes including inhalation and ingestion of water, food, and soil material. Arsenic causes numerous adverse health effects to humans ^[1]. Globally, the major concern comes from the contamination of drinking water from natural geological sources ^{[2][3]}. However, health risks from arsenic-contaminated soil should not be underestimated. In the USA, arsenic tops the Substance Priority List (SPL) created by the Agency for Toxic Substances and Disease Registry/US EPA, which ranks pollutants at Superfund sites based on toxicity and potential for exposure ^[4].

Conventional arsenic remediation methods are too expensive to clean up large, moderately contaminated areas, where the risk of negative environmental and health impacts is still unacceptably high ^[5]. In a promising breakthrough for large-scale, sustainable arsenic soil remediation, *Pteris vittata* L., a fern distributed globally in tropical and subtropical climates ^[6], was discovered to take up arsenic from the soil and accumulate it in its fronds at up to ~100 times soil concentrations ^[7]. Successively harvesting the fronds removes, or phytoextracts, arsenic from the soil with limited disturbance. Although there are costs associated with phytoextraction, for example, treating arsenic-enriched fronds, phytoextraction could be less expensive than other methods ^[8].

Many challenges still lie ahead for arsenic phytoextraction with *P. vittata* ^[9]. These challenges largely stem from the complex nature of the soil, especially spatial and temporal variation in soil characteristics. Remediation time estimates derived from rates measured under field conditions are long, about 40 years to remove 180 kg As/ha (100 mg As/kg) from soil (0 to 15 cm depth) ^{[10][11][12][13]}. The application of soil amendments has been investigated in efforts to increase arsenic uptake rates and shorten remediation times, but results are inconsistent. Frond arsenic concentrations and biomass were higher in *P. vittata* supplied with sparingly soluble compared to soluble phosphorus ^{[14][15]}, though in other cases phosphorus application did not affect arsenic uptake in *P. vittata* regardless of solubility ^{[16][17][18][19]}, and soluble phosphorus increased arsenic concentrations in porewater but not in *P. vittata* fronds ^[20]. Furthermore, some studies have shown that the presence of other soil contaminants will negatively affect arsenic uptake by *P. vittata* ^{[20][21]}. Finally, it is not well understood how arsenic depletion from soil correlates to arsenic accumulation in *P. vittata* fronds, for example, if all arsenic depleted from soil is accumulated in the fern or lost to other processes ^{[11][13][22]}, especially under field conditions where fern roots have access to a larger volume of soil than in pot experiments ^{[23][24]}.

2. Chemical Stabilization

Chemical stabilization, which involves applying a sorptive amendment to the soil to lower the soluble fraction of contaminants and decrease plant uptake ^[25], could be a less destructive alternative to conventional remediation approaches ^[26]. Chemical stabilization of arsenic typically involves applying precursors of iron (Fe) oxides (ferrous (FeSO₄) or ferric sulfates (Fe₂(SO₄)₃)) and zerovalent iron (Fe(0)), or directly applying poorly crystalline (ferrihydrite (Fe(OH)₃) or crystalline iron oxides goethite α-FeOOH). Other materials, including aluminum-based industrial by-product compounds, have also been shown to be effective ^[27].

Amending soil with iron compounds decreases arsenic mobility and therefore soil and porewater toxicity in ex situ studies. Amendment with iron sulfates, together with lime to avoid soil acidification, decreased the concentration of water-soluble arsenic [28] and of arsenic in leachates [29][30], as well as arsenic uptake by crops [25][31]. The addition of zerovalent iron decreased the concentration of arsenic in soil porewater, leachates, and plant tissues, as well as of extractable and bioaccessible arsenic [29][30][32][33][34][35][36]. Goethite and ferrihydrite amendments decreased arsenic concentrations in porewater [37][38][39], in leachates [29][30][36], and arsenic uptake by plants and phytoavailability [40].

However, there are limitations to using these methods in more complex field conditions [26][35][41][42]. For example, amendments with iron sulfates plus lime or zerovalent iron led to increased concentrations of metals such as cadmium, copper, zinc, and lead in leachates or in plant tissues compared to untreated soils [29][30][34]. Additionally, when used in situ, arsenic stabilization methods were much less efficient than when used in batch or pot experiments [31][32]. Finally, even if amendments effectively decrease arsenic mobility under current geochemical conditions, changing conditions, especially changing redox potential due to microbial activity [43] could lead to arsenic release. On-going site monitoring is required to ensure effective remediation over timescales of years, akin to monitored natural attenuation [44].

3. Phytoextraction Using *Pteris vittata* and Other Arsenic-Hyperaccumulating Plants

3.1. Phytoextraction with Hyperaccumulators

Phytoextraction is a soil remediation method where plants extract contaminants from the soil and concentrate them in their aboveground biomass, which is then harvested to remove the contaminants while leaving the soil in place. Phytoextraction of metal(loid)s has been investigated using naturally occurring metal(loid) hyperaccumulators and non-hyperaccumulators including genetically modified plants [45]. Here, researchers focus on phytoextraction with non-genetically modified hyperaccumulators to explore the relationships between natural hyperaccumulator ecology and soil geochemistry.

Brooks et al. [46] established the term hyperaccumulator in a study focusing on nickel to describe plants able to accumulate nickel at concentrations >1000 mg/kg (ppm) in dry leaf tissue. Since then, the term hyperaccumulator has been extended to other metals and metalloids with element-specific thresholds. Other criteria include extreme metal tolerance [47], a shoot-to-root metal(loid) concentration ratio (or translocation factor) typically >1 [48], and a ratio of metal(loid) concentrations in plant biomass to those in soils (or bioconcentration factor) typically >1. Hyperaccumulators tolerate high concentrations of metal in soils, but hyperaccumulation is a genetically distinct trait from tolerance [49]. Natural hyperaccumulation depends on both constitutive up-regulation of transporters to move metal(loid)s across membranes [50], and mechanisms that confer tolerance of the high concentrations of metal(loid)s thus taken up [51].

Several theories have been proposed to explain hyperaccumulation, including the defense theory, where high metal(loid) concentrations kill or deter pests [52][53]; allelopathy, where litterfall locally increases soil metal(loid) concentrations above those tolerable to other species [54]; and the phosphorus starvation theory, where metal(loid) uptake is a byproduct of nutrient acquisition [55].

3.2. Arsenic-Hyperaccumulators

As early as 1975, many plants accumulating >1000 mg/kg arsenic in their leaves and with a translocation ratio >1 were found growing in soils enriched in arsenic, mainly around mining sites. Among them *Jasione montana* L., *Calluna vulgaris* (L.) Hull, *Agrostis tenuis* Sibth. and *Agrostis stolonifera* L. were found in the UK [56], *Agrostis castellana* in Portugal [57] and *Paspalum racemosum* and *Bidens cynapiifolia* in Peru [58]. However, since those plants grew on soils extremely enriched in arsenic, the bioconcentration factor was <1, despite high concentrations in plant tissues, and those plants are consequently not hyperaccumulators, according to the bioconcentration criterion presented earlier.

The first plant to be labeled an arsenic hyperaccumulator was the fern *Pteris vittata* L. *P. vittata*, an invasive species in Florida, USA [59], was identified in 1998 as an arsenic hyperaccumulator during a survey of plants growing on a Florida site contaminated with chromated copper arsenate (CCA) [60][61]. There, *P. vittata* accumulated between 1442 and 7526 mg/kg arsenic in its fronds with no observed toxicity effects [7]. In addition, in a pot experiment with a soil spiked with 1500 mg/kg arsenic, *P. vittata* was able to accumulate as high as 22,630 mg/kg arsenic [7]. The ratio of arsenic concentrations in fronds to roots in *P. vittata* was >20 and the bioconcentration factor ranged between 5 and >100 [7]. Simultaneously, arsenic hyperaccumulation in *P. vittata* was discovered separately in populations growing in an arsenic sulfide mine in Hunan Province, China [62].

Since then, other arsenic-hyperaccumulating plants have been identified, most of them belonging to the fern family, and more specifically to the *Pteris* genus [9]. However, not all *Pteris* species hyperaccumulate arsenic [63][64]. Known arsenic-hyperaccumulating ferns include many varieties of *Pteris cretica* [63][64][65][66][67][68][69], *Pityrogramma calomelanos* [70][71], *Pteris longifolia* [67], *Pteris umbrosa* [63][67][72], many varieties of *Pteris multifida* [64][65], *Pteris biaurita* L., *Pteris quadriaurita* Retz and *Pteris ryukyuensis* Tagawa [68], *Pteris aspericaulis*, *Pteris fauriei*, and *Pteris oshimensis* [64]. Zhao et al. [67] suggested that arsenic hyperaccumulation is a constitutive property in *P. vittata* (i.e., it is expressed in all members of the species regardless of the presence of arsenic in the soil), similarly to what was proposed for hyperaccumulation of metals generally [73], and for zinc and cadmium in *Arabidopsis halleri* and *Thlaspi caerulescens* specifically [74]. The constitutive property of arsenic hyperaccumulation was later revealed in populations of *P. multifida*, *P. oshimensis* and *P. cretica* var. *nervosa* and confirmed in *P. vittata* [64]. *P. vittata* is the most studied of the above ferns and is considered a model arsenic-hyperaccumulating plant [75][76].

3.3. Arsenic Hyperaccumulation in *P. vittata*

The mechanisms of arsenic tolerance, translocation and transformation in *P. vittata* have been extensively reviewed [9][77][78] and will be discussed here briefly in regard to implications for arsenic cycling in the whole soil-water-plant system. *P. vittata* absorbs arsenic from soil through its roots, which are primarily found in the 0–10 cm soil depth interval [79]. *P. vittata* primarily takes up arsenate and only limited arsenite, with the rate of arsenate uptake being 10 times that of arsenite uptake [80]. Like many plants, *P. vittata* takes up arsenate, a chemical analogue of phosphate, through the phosphate intake pathway, specifically through phosphate transporters in the root plasmalemma [55][80]. Arsenite uptake is also efficient and occurs through an active transport process [81]. *P. vittata* translocates and sequesters most accumulated arsenic in its pinnae [82], though arsenic translocation decreases under metal stress [83] and the rhizome can be a secondary storage organ when soil arsenic is highly available [79]. In pinnae, arsenic is compartmentalized in the vacuoles of pinnae epidermal cells [82], located on pinnae surfaces as crystalline deposits [84], and in trichomes on pinnae surfaces [85]. Between 47 and 94% of the arsenic in *P. vittata* fronds is present as arsenite and the rest as arsenate [7][82][86][87]. Indeed, during arsenic translocation in the fern, arsenate is reduced to arsenite [7], although there is disagreement about whether reduction occurs in roots [88], stipes [89] and/or pinnae [90]. Arsenite reoxidation was found in older fronds 18 weeks of age [87] and in senesced fronds [76].

3.4. Mechanisms for Arsenic Release from Soil

Arsenic uptake, and therefore hyperaccumulation, is likely linked to nutrient uptake in *P. vittata*. According to the phosphorus starvation theory, arsenic could be released from soil and taken up into the fern as a byproduct of rhizosphere-based nutrient scavenging processes [55][91]. In response to nutrient deficits [92], *P. vittata* likely releases root exudates [14][93][94][95] that mobilize phosphorus, iron, and arsenic from soil through ligand-enhanced dissolution of iron minerals [93][96][97].

P. vittata exudates include oxalic ($C_2H_2O_4$), malic ($C_4H_6O_5$), and phytic ($C_6H_{18}O_{24}P_6$) acids [14][94][98]. Oxalic and malic acids are common root exudates across plant communities [99], and oxalic acid is a well-known effective metal complexer [100][101]. Phytic acid, also a metal complexer [102] is less well-known as a root exudate but is released by fern roots [94][98]. Iron-oxalate and -phytate complexes lead to dissolution of iron oxides [103].

Both oxalic and phytic acid supplied hydroponically to *P. vittata* lead to release of arsenic from iron oxides and to higher *P. vittata* frond arsenic concentrations [98][103], but phytic acid could be more important to arsenic uptake in the fern [103]. *P. vittata* produced 4 to 7 times more phytic acid than oxalic acid [94], phytic acid released 1.2 to 50 times more arsenic from $FeAsO_4$ than oxalic acid [94][98], and *P. vittata* frond arsenic concentrations were 3–10 times higher when phytate compared to oxalate was supplied [103]. The ability to sustain phytic acid production in the presence of arsenic could be a characteristic of arsenic tolerance in *P. vittata*, as phytic acid release from non-hyperaccumulating ferns decreased in the presence of arsenic [94][98].

The importance of root exudates to *P. vittata* arsenic uptake suggests the rhizosphere is a key zone for arsenic phytoextraction. Indeed, 66–95% of arsenic accumulated in *P. vittata* was shown to be extracted from rhizosphere soils, depending on soil texture, based on calculations of the mass of arsenic taken up in the fern through transpiration of bulk soil porewater [104]. The importance of rhizosphere processes suggests that is primarily rhizosphere, not bulk, soils that are effectively phytoextracted.

Even if arsenic uptake in the fern is closely associated with root exudate activity, the link between exudate compounds and nutrient budgets, especially phosphorus and iron, in *P. vittata* needs further elucidation. *P. vittata* frond phosphorus concentrations increased when ferns were supplied with higher (500–1000 μM) [98][105] but not lower (50 μM) [103][105]

concentrations of phytic acid. It remains unclear how phytic acid release relates to *P. vittata* phosphorus budgets. *P. vittata* could use externally supplied phytic acid as a phosphorus source [98]. Phytase present in *P. vittata* root exudates [14][98] could help the fern recover released phytic acid [106]. Iron and arsenic cycling in *P. vittata* are likely related, given that arsenic in oxic soils is usually associated with iron minerals. Frond iron concentrations increased when ferns were supplied with phytic or oxalic acid in some cases [98] but not in others [103][105].

In addition to acting through ligand-exchange mechanisms, root exudates could affect rhizosphere pH and therefore arsenic availability. *P. vittata* rhizosphere pH, a key factor in arsenic release from iron oxides, is not well understood. Compared to bulk soil, *P. vittata* rhizosphere pH has been found to be lower [107], similar [93], or higher [95][108]. Counterintuitively, decreasing pH below neutral would increase iron oxyhydroxide solubility [109] but also increase the amount of arsenic sorbed [110]. pH also affects root exudate behavior. Oxalate has a higher affinity for iron at lower pH [111], so decreasing pH could increase ligand-enhanced dissolution of iron oxides, increasing arsenic release. Alternately, oxalic and acetic acid release was shown to increase soil pH adjacent to artificial roots, possibly due to mineral dissolution or dissimilatory metal reduction [100], which would also increase arsenic release.

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