

Localization and Speciation of Arsenic in Soil and Desert Plant *Parkinsonia florida* Using μ XRF and μ XANES

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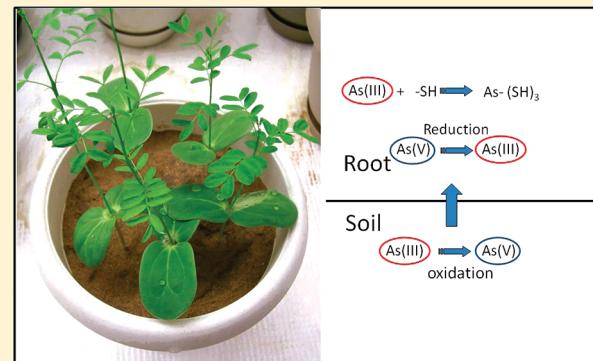
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 Supporting Information

ABSTRACT: *Parkinsonia florida* is a plant species native to the semidesert regions of North America. The cultivation characteristics of this shrub/tree suggest that it could be used for phytoremediation purposes in semiarid regions. This work describes, through the use of synchrotron μ XRF and μ XANES techniques and ICP-OES, the arsenic (As) accumulation and distribution in *P. florida* plants grown in two soils spiked with As at 20 mg kg⁻¹. Plants grown in a sandy soil accumulated at least twice more As in the roots compared to plants grown in a loamy soil. The lower As accumulation in plants grown in the loamy soil corresponded to a lower concentration of As in the water-soluble fraction (WSF) of this soil. LC-ICP-MS speciation analysis showed only As(V) in the WSF from all treatments. In contrast, linear combination XANES speciation analysis from the root tissues showed As mainly present in the reduced As(III) form. Moreover, a fraction of the reduced As was found coordinating to S in a form consistent with As—Cys₃. The percentage of As coordinated to sulfur was smaller for plants grown in the loamy soil when compared to the sandy soil.



INTRODUCTION

Arsenic (As) is an element widely distributed in the earth's crust. Despite the low abundance of As (0.0001%), it is easily found in nature with ores of lead, copper, and gold.¹ Arsenic can exist in four oxidation states: As(-III), As(0), As(III), and As(V), of which inorganic As(III) and As(V) are the most toxic and predominant forms. The toxicity of inorganic As depends on its chemical form. Arsenate [As(V)] enters plant cells as a molecular analog of phosphate,² whereas arsenite [As(III)] does it via aqua-glyceroporins and is even more broadly toxic³ than As(V).

Accumulation of As in plants has been extensively studied in hyperaccumulator plants and rice cultivars.^{4–10} A few of these studies have relied on synchrotron micro X-ray fluorescence (μ XRF) and micro X-ray absorption near edge structure (μ XANES).^{7–10} The formation of Fe plaques in the root surface is considered to be a limiting factor in As uptake, since it mainly consists of Fe(III) amorphous oxides to which As species have great affinity (especially As(V)). Seyfferth et al.⁹ investigated the formation of Fe plaque around the rice roots using synchrotron μ XRF. They reported that the formation of Fe plaque was not homogeneous in the root surface; moreover young roots did not show any Fe plaque formation. It was concluded that Fe plaque

formation was not the main limiting factor for As concentration in the roots. Frommer et al.¹⁰ studied the influence of rice roots in the surrounding soil (rhizosphere) geochemistry in paddy fields. μ XRF studies demonstrated the root influence in soil distribution of Fe, Mn, and As up to 1 mm away from the root–soil interface. μ XANES identified Fe present mainly in the form of a two-line ferrihydrite-like phase with the associated As in the form of mostly As(V).

The concept of phytoremediation for As became feasible after the identification of As hyperaccumulator plants. The most studied As hyperaccumulator plant species belong to the *Pteris* genus (brake ferns)^{5,6,8} which grows well in tropical and subtropical environments, but are not adapted to the harsh conditions of the Southwestern U.S. To our knowledge no desert plant species has been identified as As hyperaccumulator. For this reason, *Parkinsonia* shrubs/tree species native to semiarid regions of the U.S. are being studied for their As accumulation potential.¹¹ In a previous study, *P. florida* was identified as the

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best As accumulator *Parkinsonia* species out of the three studied species.¹¹ In this research, the objective was to study the effect of soil composition in the accumulation, distribution, and speciation of As in the tissues of *P. florida*. A sandy soil and a loamy soil serve as good proxies for low and high As sorption capacity soils, respectively. The localization and speciation of As in the *P. florida* plants was studied by synchrotron based μ XRF and μ XANES and by liquid chromatography—inductively coupled plasma—mass spectrometry (LC-ICP-MS).

MATERIALS AND METHODS

Soil Preparation. Two types of soil were used for this study: a sandy soil and a loamy soil. Samples of top soil (0–30 cm) were collected from a region in El Paso, TX free of arsenic contamination (<5 mg As kg⁻¹). The soil was dried for 2 days at 60 °C in a Fisher Scientific Isotemp oven (Pittsburgh, PA) and passed through a 2-mm-mesh stainless steel sieve to obtain homogeneous grain size. The properties of both types of soils are shown in the Supporting Information (Table 1 SI).¹² Three sets of 2.5 kg of soil were placed in plastic pots and watered with deionized (DI) water (control), or a solution containing either As(V) (from Na₂HAsO₄·7H₂O) or As(III) (from As₂O₃) to obtain a final concentration of 20 mg As per kg of soil. The As solutions were adjusted to pH 5.8 ± 0.1 and the water-holding capacity of the soil was determined by adding enough water to saturate the soil without leaching (Table 1 SI). The soil was left in the pots for one month to allow adsorption and equilibration of As. Then the soil from each replicate was removed from the pots and homogenized by crushing the aggregates and mixing the soil.

Plant Sowing. Seeds of *P. florida* from Granite seed company (Lehi, UT, USA) were first immersed in concentrated sulfuric acid for 2.5 h for scarification (a process to crack the hard coating of seeds to allow water and gases to penetrate into the seed), triple rinsed with DI water, and finally soaked for 24 h in DI water to speed up germination. Five seeds were sown in each pot and watered with 150 mL of DI water. After that, plants were watered daily with 20–30 mL of DI water to maintain soil moisture. All treatments were arranged in a completely random design with three replicates per treatment. The pots were set at 25 ± 2 °C, a light–dark cycle of 12/12 h, and illumination of 53 μmol m⁻² s⁻¹. The plants were harvested eight weeks after sowing and washed with 0.01 M HNO₃ twice and twice with DI to remove any soil particles or metal bound to the root surface. Plant material was separated into roots, stems, and leaves for inductively coupled plasma—optical emission spectroscopy (ICP-OES) analysis. One set of plants was transported alive to the Advanced Light Source (ALS, Berkeley National Laboratories, Berkeley, CA) for μ XAS studies.

ICP-OES Elemental Analysis. For the ICP analysis, the plant samples were digested in a CEM MarsX microwave oven (CEM, Mathews, NC) with 5 mL of trace-pure HNO₃ (SCP Science, NY) and diluted to 25 mL using double-DI water. The total As concentration in the tissues was determined using ICP-OES (Perkin-Elmer Optima 4300 DV). For QC/QA of the ICP readings, every 10 samples, the blank and a spiked sample containing As at 0.1 mg L⁻¹ were read. The average reading for As in the spiked sample was 0.106 ± 0.003 mg L⁻¹ (*n* = 5). The ICP-OES parameters used were as follows: nebulizer flow, 0.80 L min⁻¹; power, 1450 W; peristaltic pump rate, 1.5 mL min⁻¹; flush time, 15 s; delay time, 20 s; read time, 10 s; wash time, 60 s; and every sample was read in triplicate. Soil samples were analyzed

for Mn, Al, Fe, P, and S using the above-mentioned ICP-OES parameters after digestion with concentrated HNO₃ following EPA method 3051.¹³ The Mn average recovery from San Joaquin soil certified reference material (SRM 2709a) treated in the same way as samples was 77% (*n* = 6).

LC-ICP-MS As Speciation. For As speciation in soil, 1 g of a homogenized sample was added to 20 mL of Millipore water in rocking motion for 1 h. After that, the sample was centrifuged at 3000g on a benchtop centrifuge for 5 min. The supernatant was filtered through a 0.22-μm Durapore filter (PVDF, Millipore, Bedford, MA). A Perkin-Elmer 200 LC coupled to an ELAN DRC II (dynamic cell reaction) 6000 ICP-MS axial field technology (PerkinElmer, Shelton, CT) were used for the separation of the arsenic species. The LC-ICP-MS operating parameters used were those previously reported by Lopez-Moreno et al.¹⁴ Blank and standards were analyzed at the beginning and at the end of the analysis. The As species [As(III) and As(V)] were separated using a PRP-X-100 anion exchange column (150 × 4.6 mm, Hamilton). The ICP-MS DRC was operated using oxygen as auxiliary gas to eliminate ⁴⁰Ar³⁵Cl⁺ interference (the As ion was monitored at *m/z* 90.92).¹⁴ Integrated peaks areas from chromatographic peaks were imported into Microsoft Excel and correlation coefficients from calibration curves were between 0.99999 and 1 for As(III) and As(V). Six spiked soil samples (500 ppb) were treated as samples and analyzed using LC-ICP-MS in order to obtain the recovery percentage for arsenic species. The average recovery (for *n* = 4) of the spikes was 91.4%, demonstrating that the total quantification for As species was accurate. The As recovery from San Joaquin soil (SRM 2709a) treated in the same way as samples was 90% (*n* = 4).

μ XAS Data Acquisition. The roots of *P. florida* plants treated with 20 mg L⁻¹ of As were washed with 0.01 M HNO₃ and three times with DI water to eliminate any excess of As on root surface. Roots were then cross sectioned at the beamline with a stainless steel blade and mounted onto a Mo foil sample holder on top of a freeze pack block. The root samples were dissected 2–4 cm from the root–stem intersection. The μ XRF mapping of the distribution of As and relevant elements in the roots was performed at beamline 10.3.2 at the ALS.¹⁵ Root sections were fixed on an *x*–*y* translation stage, cooled to -20 °C to reduce radiation damage, and scanned under a micro focused beam. Maps were recorded using a 5 × 5 μm (H × V) beam at 12 keV with a 10 × 10 μm pixel size and a 100 ms dwell time. The fluorescence yield was measured with a seven-element germanium (Ge) solid-state detector and normalized by *I*₀ and the dwell time. Several spots of interest were selected from the μ XRF maps for As K-edge μ XANES analysis. XANES spectra were processed using a suite of programs available at beamline 10.3.2. Briefly, spectra were energy-calibrated with respect to the white line max feature of Na₂HAsO₄ (11873.7 eV) and the pre-edge background was subtracted and normalized using a linear pre-edge. XANES model compounds were aqueous Na₂HAsO₄ (pH 2, 5.8, 7.5, and 12) and As₂O₃ (pH 3), and solid Na₂HAsO₄, As₂O₃, As₂S₃, and As–Cys₃. The As–Cys₃ model compound was synthesized by reacting L-cysteine hydrochloride and AsCl₃ (Sigma Aldrich, St. Louis, MO) at a 3:1 molar ratio in 50 mL of ethanol at room temperature. The mixture was stirred on a hot plate using low heat. After several minutes, a white precipitate was formed. The precipitate was collected by vacuum filtration and dried overnight. The dried product was then ground using mortar and pestle and stored in microcentrifuge tubes in the dark until analyses were performed. Confirmation of the product was done

Table 1. Concentration of As(V) in the Soil Water-Soluble Fraction As Determined by LC-ICP-MS^a

	$\mu\text{g As(V) L}^{-1}$	mg As(V) kg^{-1} soil	% of total
sandy soil			
control	$1.64 \pm 0.18^{\text{A}}$	0.032 ± 0.003	
As(V)	$417 \pm 14^{\text{B}}$	8.4 ± 0.5	42 ± 1.4
As(III)	$310 \pm 63^{\text{C}}$	6.2 ± 0.15	31 ± 0.7
loamy soil			
control	$12.5 \pm 1.5^{\text{a*}}$	0.25 ± 0.03	
As(V)	$158 \pm 13.5^{\text{b*}}$	3.2 ± 0.3	15.8 ± 1.3
As(III)	$158 \pm 9.6^{\text{b*}}$	3.2 ± 0.2	15.8 ± 1

^aCapital letters stand for mean comparison in the sandy soil and lower case letters stand for mean comparison in the loamy soil (Tukey test $\alpha = 0.05$). *Significantly different for the same As treatment in different type of soil (t -test 0.05).

by extended X-ray absorption fine structure and by comparison of the whiteline max feature energy position to the As_2S_3 .¹⁶

■ RESULTS AND DISCUSSION

Arsenic Speciation in the Soil Water-Soluble Fraction. The most immediately bioavailable As pool in soils is the water-soluble fraction (WSF). Arsenic in this fraction is mobilized by the presence of water in the soil pores and can easily reach the root surface to be further taken up by plants. The As concentrations in the WSF of the sandy soil and loamy soil are shown in Table 1. In the WSF, As was present in the form of As(V), which indicates that As(III) was oxidized to As(V) in the soil. The oxidation of As(III) can be effectively achieved by the action of As-oxidizing bacteria and/or Mn oxides.^{17,18} The sandy soil and loamy soil used in the present study had 65.9 and 185 mg Mn kg^{-1} soil, respectively (Table 1 SI).

The concentration of As in the WSF of the sandy soil was significantly higher compared to the loamy soil (Table 1). This could be explained by higher amount of Fe and Al in the loamy soil (almost twice compared with the sandy soil) (Table 1 SI). The adsorption of As to Fe and Al oxides is an important process that affects As mobility in soils.¹⁹

The concentration of As in the WSF of the sandy soil was similar to those reported in poultry waste samples collected from two locations in Mississippi between 1997 and 2000.²⁰ The percentage of As in the WSF of those soils varied between 36 and 75% from total concentrations ranging between 11 and 36.2 mg As kg^{-1} soil. In contrast, the values in the WSF of the loamy soil were significantly lower at 15% for both As(III) and As(V).

The spatial distribution of As, Fe, and Mn was investigated only in the loamy soil due to limited beam time availability. Samples of soil were collected 2 cm below the surface and 2 cm away from the roots (cylindrical samples) and flattened between layers of polypropylene windows. Fluorescence maps were collected from the As(III) and As(V) contaminated soils in which the fluorescence signals for As, Fe, and Mn were assigned the colors red, green, and blue, respectively. The color-coded fluorescence signals are superimposed and the resulting mixing of colors representative of metal associations. The μXRF maps showed strong spatial correlation between As and Fe in both As(III) (Pearson correlation coefficient of 0.811) and As(V)

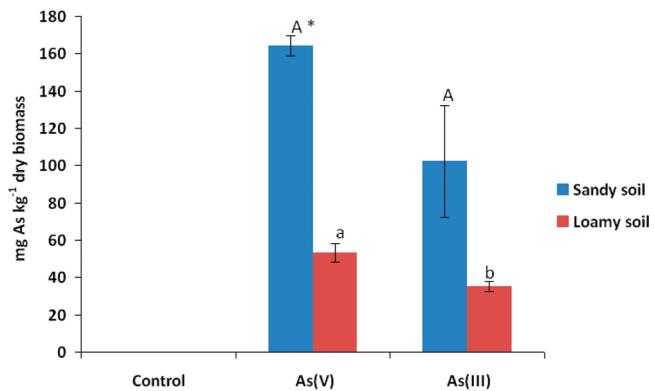


Figure 1. Accumulation of As in the root tissues of *P. florida* plants germinated and grown for eight weeks in As contaminated soil (20 mg As kg^{-1} soil). Error bars are standard errors of $n = 3$. Capital letters stand for mean comparison in the sandy soil and lower case letters stand for mean comparison in the loamy soil (Tukey test $\alpha = 0.05$). *significantly different for the same As treatment in different type of soil (Tukey test $\alpha = 0.05$).

(Pearson correlation coefficient of 0.857) contaminated loamy soil (see Figure 1 SI and Figure 2 SI).

These results suggest that the As adsorption onto Fe oxides is a main geochemical process occurring in the loamy soil. The μXRF maps revealed spots where As and Mn are correlated in the loamy soil (purple color in Figure 1A SI); these are sites where As(III) oxidation by Mn oxides may have occurred. The adsorption of As onto Fe oxides and the oxidation of As(III) by Mn oxides in soils have been previously studied and confirmed by XAS.^{17,19,21,22}

As Accumulation in the Roots of *P. florida*. Arsenic accumulation in the tissues of *P. florida* was determined eight weeks after germination and growth in As contaminated soil. The concentration of As in the stems and leaves of *P. florida* was below the detection limits of the ICP-OES. Similar results were previously reported for *Parkinsonia aculeata* and *Parkinsonia microphylla*.¹¹ The accumulation of As in the roots of *P. florida* plants from the sandy soil was similar to the values reported in another desert plant species *P. juliflora* grown in a similar artificially contaminated sandy soil for 45 days.²³ *P. juliflora* plants accumulated more As from the As(V) treatment (400 mg As kg^{-1} dry biomass) compared to the As(III) treatment (210 mg As kg^{-1} dry biomass).²³ A similar result was observed in the roots of *P. florida* grown in the sandy soil (Figure 1). This was an expected result since the concentration of As in the WSF from the As(III) treated sandy soil was significantly lower compared to the same soil treated with As(V) (Table 1). Accumulation of As from the As(III) treated loamy soil was also significantly lower compared to the same soil treated with As(V).

Two mechanisms have been proposed in the literature for As absorption by roots. One of the mechanisms involves the active absorption of inorganic As(V) via phosphate carriers into the root symplast.^{24,25} The other mechanism involves the passive absorption of neutral species ($\text{pH} < 9.2$) of inorganic As(III) via aquaporin channels.²⁶ These oxidation state specific mechanisms could lead to differential uptake of inorganic As(III) and As(V); however, in the present study, As(V) was the predominant form in the WSF and the most likely predominant form in the soil. The reduced accumulation of As from the As(III) treated sandy soil is then better explained in terms of its decreased availability as indicated by the lower concentration of As in the WSF (Table 1).

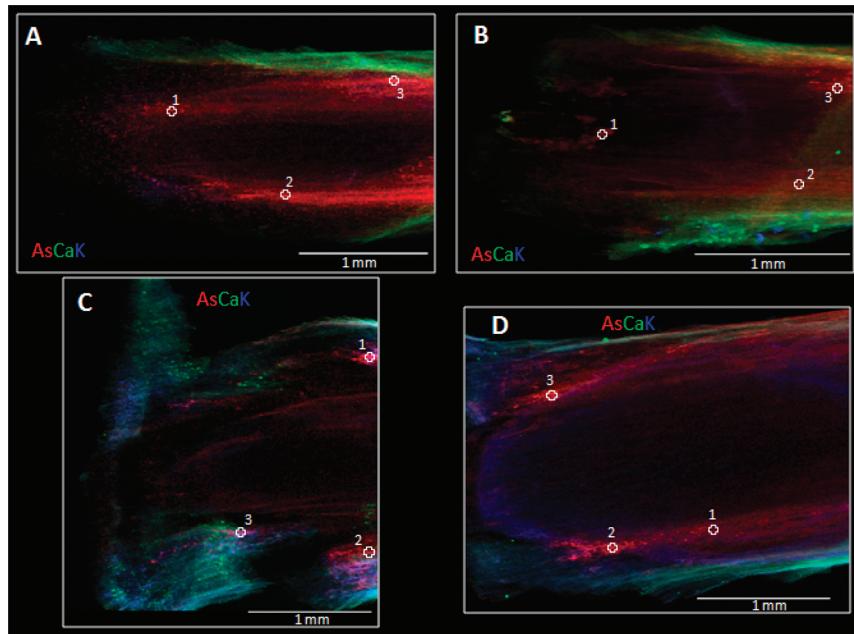


Figure 2. μ XRF maps of *Parkinsonia florida* roots grown in As contaminated soil: (A) sandy soil As(V), (B) sandy soil As(III), (C) loamy soil As(V), (D) loamy soil As(III). Map acquisition performed at 12 KeV with $10\ \mu\text{m}$ pixel size and a 100 ms dwell time. Numbers in the figures correspond to spots where As K-edge XANES data were collected. (As = red, Ca = green, K = blue).

The formation of an insoluble As–Mn solid phase from the oxidation of As(III) by Mn oxides is a possible explanation for the decreased As concentration in the WSF. On the other hand, differential As uptake was also observed for the plants grown in the loamy soil. Accumulation of As from the As(V) treated loamy soil (about $50\ \text{mg As kg}^{-1}$) was significantly higher compared to that of the As(III) treated soil (about $30\ \text{mg kg}^{-1}$) (Figure 1). In general, arsenic accumulation in the roots of *P. florida* was higher in the sandy soil compared to the loamy soil. The higher Fe, Al, Mn, and clay content in the loamy soil can explain the decreased availability of As in this soil.

Sulfur Accumulation in the Roots of *P. florida*. Sulfur, an important element for As detoxification and tolerance, is present in plant molecules such as glutathione (GSH) and phytochelatins. Thiol groups ($-\text{SH}$) are present in the cysteine residues of the antioxidant GSH and in the metal-induced binding peptides phytochelatins (PCs) and metallothioneins. Increased S absorption can lead to enhanced As tolerance and accumulation in plants due to a positive effect on thiol metabolism and antioxidant capacity.^{27–29} The S accumulation in the roots of *P. florida* under the exposure to As is shown in Figure 3 SI. Accumulation of S in the roots of *P. florida* plants grown in all loamy soil treatments was significantly higher compared to the sandy soil treatments. The S content in the loamy soil is significantly higher compared to the sandy soil (Table 1 SI) and agrees with the S accumulation results in the roots (Table 1 SI). Enhanced S accumulation was observed in the plants grown in the As treated sandy soil and corresponded with higher As accumulation in the roots (Figure 1). Experiments performed with *Prosopis* sp. and *Hydrilla verticillata* showed an increase in S accumulation with increasing accumulation of As in the tissues.^{27,28} The increase in S accumulation was correlated with more production of total thiols and a positive effect in the antioxidant status of *H. verticillata*. Also an increased production of low molecular weight thiols and glutathione S-transferase activity was observed. Results

Table 2. LC-XANES Fitting Results of *P. florida* Roots Exposed to As Contaminated Soil^a

	As–Cys ₃ %	As(III) %	As(V) %
Florida As(V) sandy soil			
spot 1	68	22	11
spot 2	74	18	8
spot 3	85	4	11
Florida As(III) sandy soil			
spot 1	64	9	27
spot 2	74	15	11
spot 3	67	15	18
Florida As(V) loamy soil			
spot 1	81	16	4
spot 2	43	30	26
spot 3	50	33	16
Florida As(III) loamy soil			
spot 1	69	15	17
spot 2	52	24	23
spot 3	75	10	16

^a Reference compounds used were aqueous solutions from As_2O_3 ($\text{pH} = 3.0$) and $\text{Na}_2\text{HAsO}_4 \cdot 7\ \text{H}_2\text{O}$ ($\text{pH} = 5.8$) for As(III) and As(V), respectively. As–Cys₃ was analyzed as a dry fine powder

from the present study suggest that *P. florida* plants absorbed more S in response to As accumulation in order to maintain their antioxidant capacity and cope with As toxicity in the sandy soil. The results suggest there is a threshold concentration of As at which S accumulation in the roots is enhanced.

Arsenic Speciation and Distribution in the Roots of *P. florida*. The spatial distribution and speciation of As in the roots of *P. florida* plants was studied using synchrotron μ XRF and μ XANES.

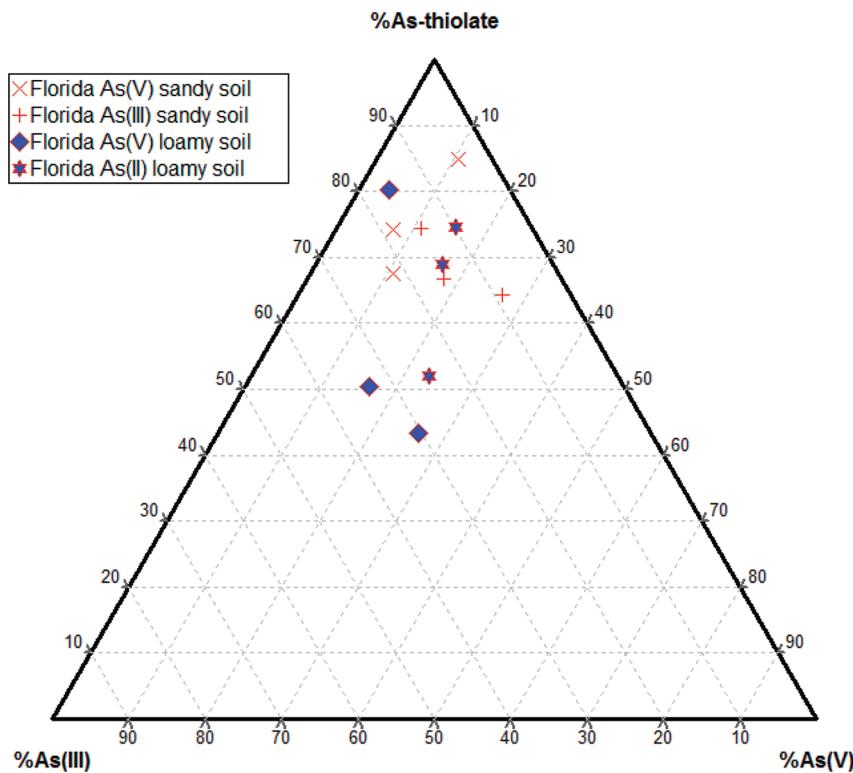


Figure 3. Ternary plot of LC-XANES fitting results from spots where As K-edge XANES data were collected. Reference compounds used were aqueous solutions from As_2O_3 ($\text{pH} = 3.0$) and $\text{Na}_2\text{HAsO}_4 \cdot 7 \text{ H}_2\text{O}$ ($\text{pH} = 5.8$) for As(III) and As(V), respectively. As—Cys₃ was used as proxy for As—thiolate species and analyzed as a dry fine powder.

The distribution of As in root tissues and the spots chosen for XANES data collection are shown in Figure 2. The fluorescence signal from Ca and K was used to provide better contrast for the μ XRF images (Figure 2A–D). From Figure 2 it can be observed that Ca was mainly accumulated in the epidermis of the roots and K in the vascular region. In contrast, As fluorescence signal (Figure 2A–D) was from a region between the epidermis and the vascular tissues, as it is not perfectly colocated with either Ca or K (this could be the procambium region). These results corroborate the absence of As in the aerial tissues of *P. florida* plants, because the vascular tissue is where the transport from roots to shoots of soil solution with elements takes place, and As was not observed in the vascular tissue. The present results demonstrate that *P. florida* retained As in the roots tissues. This makes *P. florida* a good candidate for As phytostabilization (a long-term remediation process where contaminants are accumulated in the roots and rhizosphere reducing their bioavailability and mobility).³⁰

The results from linear combination XANES (LC-XANES) analyses are shown in Table 2. LC-XANES fittings showed that the spectra from all the spots fit to linear combinations of those from inorganic As(V), As(III), and As—Cys₃ model compounds. The predominant form of As within the root tissues of *P. florida* is consistent with As—Cys₃ (used as a proxy for As—thiolate species). This is in contrast with what is reported for rice, in which inorganic As(V) and As(III) are the predominant species in the root tissues.⁹ The reduction of As(V) to As(III) followed by coordination to thiol containing groups such as GSH or phytochelatins is a well reported mechanism for As detoxification in plants and other organisms.^{14,27} This is contradictory because the reduction process can lead to As toxicity since As(III) has a

high affinity for the thiol groups in the amino acid cysteine.²⁷ Some of the As in the roots has an XAS spectrum consistent with As—Cys₃ and may be any As—S organic form, such as As bound to thiolate groups in GSH, phytochelatins, or proteins. The binding of arsenic to cysteine residues from proteins can disrupt the structure and protein–protein interactions affecting key metabolic processes in the cell. Also, the antioxidant status of the cell can be affected by depletion of GSH once it is bound to As(III). Considering no visual symptoms of toxicity such as chlorosis, necrosis, wilting, or stunting were observed in *P. florida* plants, it is hypothesized that GSH and/or phytochelatins play an important role in the detoxification of As in the roots of this plant species. The percentage of As present in plants as an As—thiolate species in the sandy soil (67–85%) was higher compared to the percentage observed in plants grown in the loamy soil (43–81%), as can be seen in Figure 3. These results correspond to the plants where a significant increase in S accumulation compared to control plants was observed (Figure S3). Plants from sandy soil treatments also accumulated more As in the tissues compared to the ones from the loamy soil. A relationship between S and As accumulation and the coordination to thiol groups was confirmed in this work supporting the working hypothesis of this study that thiolates (GSH or phytochelatins) are essential for As tolerance in *P. florida* plants. The role of thiolates in As tolerance and detoxification has been demonstrated in other desert plant species.^{27,31}

The results from the present study have depicted the differential response to As of *P. florida* grown in soils with different physicochemical properties. Furthermore, the results have shown that *P. florida* stores As in the form of a less toxic and more stable species (As—Cys₃),³² which makes this plant a

candidate for phytostabilization of As in arid regions. Further studies in multielement contaminated soils (e.g., mine tailings) with longer periods of exposure can help to confirm the As phytostabilization capacity of *P. florida* in arid regions.

■ ASSOCIATED CONTENT

Supporting Information. Sulfur accumulation data, XRF maps from the loamy soil, and soil properties tables and figures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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