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Speciation and uptake of arsenic accumulated by corn seedlings using XAS and DRC-ICP-MS

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Abstract

ICP-MS was used to investigate the uptake of As(III) and As(V) from hydroponics growth media by corn seedlings. It was found that arsenic uptake by the plant roots for the arsenic(V) and arsenic(III) treatments were 95 and 112 ppm, respectively. However, in the shoots of the arsenic(V) treatments had 18 ppm whereas arsenic(III) treatments had 12 ppm. XANES studies showed that As for both treatments arsenic was present as a mixture of an As(III) sulfur complex and an As(V) oxygen complex. The XANES data was corroborated by the EXAFS studies showing the presence of both oxygen and sulfur ligands coordinated to the arsenic. Iron concentrations were found to increase by 4 fold in the As(V) contaminated growth media and 7 fold in the As(III) treatment compared to the control iron concentration of 500 ppm. Whereas, the total iron concentration in the shoots was found to decrease by approximately the same amount for both treatments from 360 ppm in the control to approximately 125 ppm in both arsenic treatments. Phosphorus concentrations were found to decrease in both the roots and shoots compared to the control plants. The total sulfur in the roots was found to increase in the arsenic(III) and arsenic(V) treatments to 560 ppm and 800 ppm, respectively, compared to the control plants 358 ppm. In addition, the total sulfur in shoots of the plants was found to remain relatively constant at approximately 1080 ppm. The potassium concentrations in the plants were found to increase in the roots and decrease in the shoots.

Keywords

Arsenic; Speciation; XAS; ICP-MS; Corn

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Introduction

There are a number of different sources of arsenic pollution in the environment. However, the most important or largest source of arsenic in the environment is anthropogenic (Fengxiang, *et al.*, 2003). During the 1970's and the 1980's arsenic and other toxic elements such as mercury were commonly used in pesticides. Unlike organic pesticides, inorganic pesticides containing toxic elements such as arsenic are very persistent in the environment. In addition, elements such as arsenic have the tendency to be bio-accumulated by plants, animals and fish (Meador *et al.*, 2004, Pickering *et al.*, 2000, Dushenko *et al.*, 1995, Tompson and Watling 1987, Maeda *et al.*, 1985, Zhang *et al.*, 2001, Carbonell-Barrachina *et al.*, 1999). The toxic effects of both arsenic(III) and arsenic(V) have been shown throughout the literature in many different species of plants (Jain and Ali, 2000).

Although arsenic is a toxic element in either of its oxidized states, many organisms have developed defense systems towards arsenic(V), making arsenic(V) less toxic than arsenic(III) (Pickering *et al.*, 2000). Many plant species use phytochelatins to detoxify arsenic(V), which have the chemical make up of (Glu-Cys-Gly)_n, where n ranges from 2 to 11. Phytochelatins coordinate to arsenic and allow this element to be stored in vesicles within the plant. Also, it has been shown that in some plant species low molecular weight thiols coordinate to arsenic for storage and detoxification. As stated above, arsenic(III) has been found to be more toxic than arsenic(V) in living organisms including plants, however, to our knowledge, this higher toxicity is not well understood.

In this study a plant, corn, which has a known phytochelatins response to arsenic contamination was investigated. The plants were subjected to arsenic(V) and arsenic(III) hydroponics treatments to observe any differences in the chemical response to the different arsenic oxidation states. The coordination and the speciation of the arsenic, after the uptake of arsenic(III) and arsenic(V) was studied using EXAFS (extended x-ray absorption fine structure) and XANES (x-ray absorption near edge structure) spectroscopy. In addition, the total concentration of arsenic accumulated from both treatments of arsenic(III) and arsenic(V) were examined using DRC-ICP-MS. The effects of arsenic(III) and arsenic(V) treatments on the uptake of essential nutrients including Fe, Mn, K, P, and S were also examined. The results of these studies are reported herein.

Experimental

Plant growth

The corn seeds were germinated on sterilized paper towels that were dampened with sterilized nutrient solution containing KNO₃ (2.55×10⁻⁴ M); Mg(NO₃)₂·6H₂O, (9.10×10⁻⁴ M); Fe(NO₃)₃·6H₂O, (1.0×10⁻⁵ M); H₃BO₃, (2.31×10⁻⁵ M); MnCl₂·4H₂O, (4.0×10⁻⁶ M); CuSO₄·5H₂O, (4.4×10⁻⁷ M); Zn(NO₃)₂·6H₂O, (3.70×10⁻⁷ M); Ca(NO₃)₂·4H₂O, (3.57×10⁻⁴ M); KH₂PO₄, (9.68×10⁻⁴ M); MoO₃, (6.95×10⁻⁸ M); CaCl₂·2H₂O, (2.14×10⁻³ M) as published by Peralta *et al.*, (Peralta-Videa *et al.*, 2002). For the arsenic (III) and arsenic(V) treatments the growth media was contaminated with 5.0 ppm of As from As₂O₃ or As₂O₅, respectively. After germination the seedlings were transferred to hydroponics solutions contaminated with either arsenic(III) or arsenic(V). The plants were

grown in the arsenic contaminated hydroponics solution for 1 week, after germination the plants were separated into roots and shoots and were then lyophilized.

XAS sample preparation

The lyophilized corn samples were then ground using a mortar and pestle and packed into 1 mm aluminum sample holders with Kapton® tape windows for XAS analysis at Stanford Synchrotron Radiation Laboratory (SSRL).

Room temperature fluorescence spectra of the samples were taken at the arsenic K edge (E_0 11.868 keV) on beamline 2-3 using a 13-element germanium detector. The beamline set up was as follows: an energy of 3.0 GeV, a current ranging between 80-100 mA, a Si (111) double crystal monochromator with a ϕ 0 orientation, and a 1.0 mm slit. The sample spectra were taken with the use of an internal As(0) foil for calibration purposes.

XAS data analysis

The XAS data analyses were performed using standard methods and the WinXAS software (Ressler, 1998). Briefly, the samples and model compounds were energy calibrated using the energy determined by the second degree derivative of the arsenic(0) foil (E_0 11.868 keV). The samples and model compounds were background corrected using polynomial fittings of the pre and post edge regions using a 1st degree polynomial and a 5th degree polynomial, respectively. The sample and model compound spectra were then normalized to one absorption unit and the XANES spectra were extracted from the sample spectra from 11.8-11.96 keV. The spectra were then converted into k-space on the basis of the energy of the photoelectron ejected from the samples and model compounds spectra. EXAFS spectra were then extracted by taking a spline (four knots) of the k space spectra from 2.0-12.4 Å⁻¹. The EXAFS were then Fourier transformed in a Bessel window, and subsequently back transformed from 0.7-3.0 to extract the first shell of neighboring atoms for fitting purposes. The fittings of the EXAFS were performed using least squared fittings from outputs from the FEFF 8.00 software (Ankudinov *et al.*, 1998). The parameters calculated from the fittings were the interatomic distances, coordination numbers, and the Debye Waller factors. The input files for the FEFF software were created using the ATOMS software and crystallographic data from the literature (Ravel, 2001).

ICP-MS sample preparation

A portion of the lyophilized samples (masses of approximately 0.020g) were acid digested in triplicate using microwave assisted digestion in a CEM (Mars SX) under EPA (U.S. Environmental Protection Agency) method 3051 using 5.0 mL of trace pure nitric acid (U.S. Environmental Protection Agency, 1994). Subsequent to digestion the samples were first diluted to 25 mL (final volume) in 18 MΩ D.I.(deionized) water followed by a dilution of a 1.0 mL aliquot (of the diluted sample) in 10 mL (final volume) of 18 MΩ D.I. water.

ICP-MS sample analysis

The digested samples were analyzed using a Perkin Elmer Elan DRC II ICP-MS spectrometer. The operating conditions of the ICP-MS are summarized in Table 1. In addition, the samples were analyzed using the DRC (dynamic reaction cell) mode under

ammonia gas to reduce the interferences on the As ions and these conditions are also summarized in Table 1. To ensure QA/QC requirements all samples and standards were spiked with 200 μ L of a 10 ppm multi-element internal standard consisting of ^6Li , Sc, Ge, Y, In, Tb, Bi, to check for accuracy of the ICP-MS analysis. Furthermore, blank samples and the mid calibration point were examined for changes in concentrations during and at the end of the sample analysis analysis.

Results

XANES Data

Figure 1 A shows the XANES of the arsenic(III) and arsenic(V) model compounds; whereas, Figure 1 B shows the arsenic found in the roots of the corn plants grown in both arsenic species. Also, Table 2 shows the LC-XANES fittings of the arsenic within the corn plants. As can be observed in Table 2, some of the arsenic in the plants contaminated with the arsenic(V) has been transformed into arsenic(III) coordinated to sulfur by approximately 50% in the roots. However, the root biotransformation is incomplete as the other 50% of the arsenic found in the plant is still present as arsenic(V) coordinated to oxygen ligands. The arsenic within the corn treated with arsenic(III) oxide has a different speciation than the treatment of the samples with arsenic(V). As can be seen in Table 2, in the samples from the arsenic(III) treatment a large portion of the arsenic found, in the roots was an arsenic(V) oxide type of compound at approximately 62 %.

EXAFS Data

Figure 2 A shows the Fourier transformed EXAFS of some arsenic(III) and arsenic(V) model compounds, while Figure 2 B shows the arsenic(III) and arsenic(V) accumulated in the corn roots. In addition, Table 3 shows the FEFF 8.00 fittings of the arsenic accumulated in the corn's roots and the arsenic model compounds. It can be observed, in both Figure 2B and Table 3, that the arsenic in the roots is in a mixed coordination environment consisting of oxygen and sulfur ligands. The root samples treated with arsenic(III) have a coordination environment consisting of 2 sulfur neighbors and 2 oxygen neighbors at 2.24 Å and 1.74 Å, respectively. This type of coordination environment is shown graphically in Figure 3. Additionally, in Table 3 it can be seen that the coordination environment of arsenic(V) treatment consists of 1 oxygen ligand and 3 sulfur ligands at 1.71 Å and 2.26 Å, respectively.

ICP-MS Data

Arsenic—Figure 4 shows the ICP-MS data for the arsenic accumulation in the roots and shoots of the corn plants. As can be seen in Figure 4, the amount of arsenic accumulated in the roots of the corn plants is much larger when compared to the shoot portions of the plants. This is true for both, the arsenic(III) and arsenic(V) treated plants. The concentration observed in the roots of the corn plants treated with arsenic(III) was found to be approximately 112 ppm, whereas in the shoots of the same treatment was observed to be approximately 12 ppm. Similarly, in the arsenic(V) treated plants the observed concentration was approximately 95 ppm in the roots and approximately 18 ppm in the shoots.

Iron—Figure 5 shows the iron concentration in the roots was found to be approximately 500 ppm. However, in the arsenic(V) treated plants the concentration of iron in the roots was found to be approximately 2000 ppm and in the arsenic(III) treated plants the iron concentration was found to be approximately 3800 ppm. In addition, the concentrations of iron in the shoots of the treated plants were found to be approximately 150 ppm and in the control plants the iron concentration was found to have been approximately 450 ppm.

Manganese—The manganese concentrations found within the plants are presented in Figure 6, which shows a decrease in the Mn concentrations in both the roots and shoots of the arsenic treated corn plants compared to the control plants. In the roots of the control plants the Mn concentration was found to be approximately 35 ppm; whereas in the arsenic(III) and arsenic(V) treated plants, the Mn concentration was found to be approximately 30 and 20 ppm, respectively. However, the shoot concentrations of the Mn found were approximately 110 ppm, 40 ppm and 25 ppm for the control, arsenic(V), and arsenic(III) treated plants, respectively.

Sulfur, Phosphorus, and Potassium—Figure 7 shows the concentrations of S, P, and K found within the roots and shoots of the plants treated with arsenic(III) and arsenic(V). In the roots of the plants treated with arsenic(III) and arsenic(V) the sulfur concentrations were approximately 580 and 800 ppm, respectively. However, in the control plants the S concentration was only 360 ppm (Figure 7A). Additionally, the concentration of the S observed in the shoot tissues was not affected as shown in Figure 7B (and are approximately 1000 ppm total Sulfur).

The P concentrations found in the roots of the control plants the plants were approximately 5300 ppm; whereas in the arsenic(III) and arsenic(V) treated plants the P concentrations were found to be approximately 1900 and 2200 ppm, respectively (Figure 7A). On the other hand the P concentrations in the shoots of the control plants were found to be approximately 7000 ppm, which decreased to 4500 ppm and 5100 ppm in the arsenic(III) and arsenic(V) treated plant shoots, respectively (Figure 7B).

K concentrations in the roots of the plants treated with As were found to increase in either the As(V) (5100 ppm) or As(III) (4800 ppm) treatment, compared to the control plants (3700 ppm), (Figure 7A). However, potassium levels in the shoots of the plants treated with both arsenic(V) and arsenic(III) were found to decrease to approximately 8500 ppm (approximately a 60% decrease in concentration) compared to the control plants 21000 ppm (Figure 7B).

Discussion

XANES

The XANES results may be indicating that the corn is first oxidizing the arsenic(III) to arsenic(V) and then biotransforming the arsenic(V) to an arsenic(III) sulfur compound. To our knowledge, this has not been previously shown in the literature. This initial oxidation of the arsenic(III) to arsenic(V) could explain why arsenic(III) is more toxic than arsenic(V). The conversion of arsenic(V) and arsenic(III) oxygen compounds to arsenic(III) sulfur

containing compounds has been shown in the literature for different plant species including the Chinese break fern, honey mesquite, and Indian mustard (Webb *et al.*, 2003, Zhao *et al.*, 2002, Aldrich *et al.*, 2007).

EXAFS

The EXAFS results indicate that the biotransformation of arsenic(III) by the corn plants in the roots is not complete, which corroborates the LC-XANES fittings. Similarly, the roots of the corn plants treated with arsenic(V) show that the majority of the coordination environment is sulfur, with a minor fraction still bound to oxygen ligands as was suggested by the XANES studies. The results of the EXAFS fittings indicate that the oxygen coordinated in both the arsenic(III) and arsenic(V) treated root samples is coordinated to an arsenic(V) center. The arsenic in the roots of the plants contaminated with arsenic(V) is missing the arsenic-arsenic interaction found in arsenic(III) sulfide, an inorganic model compound, at approximately 3.60 Å. The arsenic-sulfur oscillation within the plant samples has a shoulder at approximately 3.10 Å in the Fourier transformed EXFAS. The Shoulder at 3.10 Å may be indicating the presence of carbon atoms, as would be found in a low molecular weight As-thiol compound. In the uptake and biotransformation of arsenic in the Chinese break fern studied by Webb *et al.*, similar results were observed a mixture of the arsenic oxygen and arsenic sulfur ligands present within the plant (Webb *et al.*, 2003). .

ICP-MS

Arsenic—Other investigators have observed similar results in other plant species with high root arsenic concentrations and much lower arsenic concentrations in the shoots (Gultz *et al.*, 2005, Wen-Ju and Yong-Guan 2005). High root and low shoot concentrations indicate that the arsenic is not very mobile within the plants. Low mobility of arsenic species within plants has been linked to the formation of iron or manganese plaques on the root surfaces that sorbs the arsenic and makes it relatively immobile (Wen-Ju and Yong-Guan 2005, Blute *et al.*, 2004, Lui *et al.*, 2005, Lui *et al.*, 2006, Boisson *et al.*, 1999).

Iron—The possible formation of an iron plaque on the root surface of the corn plants is further supported by the iron concentrations found in the roots and shoots of the arsenic treated plants, which are shown in Figure 5. High concentrations of iron in the arsenic treated plants may indicate that the plants are forming an iron oxide plaque to prevent the arsenic uptake and translocation. Furthermore, the higher iron concentration of the arsenic(III) compared to the arsenic(V) treated plants may be related to the higher toxicity of arsenic(III), as compared to arsenic(V). Also it should be noted that the iron concentrations in the shoots of the control plants is much higher than the concentration of iron in the arsenic treated plants (approximately 3 times the concentration).

Manganese—Very little effect on the Mn concentration in the arsenic(III) treated plants, but a large decrease in the arsenic(V) treated plants, was observed. These small effects could be related to the formation/composition of the possible iron plaques formed on the roots of the plants. In the arsenic (V) treated plants more Mn is transported to the upper portion of the plants than the arsenic (III) treated plants. This indicates that in the arsenic(III) treated plants the Mn is stopped at the roots and not transported freely through the plants to the

upper portions. This effect on Mn concentrations has been observed in the literature for Maize plants (Boisson *et al.*, 1999).

Sulfur, Phosphorus, and Potassium—Additionally, the concentrations of S, P and K found within the roots and shoots of the plants treated with arsenic(III) and arsenic(V) were investigated (Figure 7). The S concentrations found within the roots of the arsenic treated plants showed a large increase in the total S present in the plants. It has been shown in the literature that many plant species use glutathione or small molecular weight thiols to reduce arsenic toxicity, to increase arsenic transport, and for arsenic storage (Pickering *et al.*, 2000, Webb *et al.*, 2003, Zhao *et al.*, 2002, Aldrich *et al.*, 2007). This large increase in the total S concentrations in the roots of the arsenic treated plants indicates that the arsenic may be inducing the formation of thiol rich compounds for transport processes. This result concurs with the XAS results and the presence of sulfur coordinated to the arsenic in the roots of the arsenic treated plants. The observed S concentrations in shoots of the treated plants compared to the shoots of the untreated plants show relatively no change in the concentrations. The unchanging S concentrations in the shoot portion of the plants suggests that the arsenic is being stored at the root level in this plant and arsenic has only limited translocation to the shoot portion of the plants.

The concentrations of P within the plant were found to decrease by approximately 50% in the roots of the treated plants, as compared to the control. This decrease may be suggesting that the arsenic is affecting the phosphate mechanisms within the plants by substituting for phosphate in different energy mechanisms within the plant. In the roots of the corn plants the concentrations of P are dramatically affected by the addition of either arsenic(III) or arsenic(V) to the growth media. These results have been suggested by other authors for the effect of As on P concentrations within different plants (Boisson *et al.*, 1999, Tu and Ma 2004). As with the root samples the concentration of P in the shoot samples was found to decrease, but to a much smaller extent. The decreasing P concentrations could be an effect of the lower concentration of both As(III) and As(V), as observed in the shoot portion of the plants.

An increase in the concentration of K in the roots was observed in the roots of the arsenic treated plants. This increase in the K concentrations in the plants may be due to the physical sorption of a positive cation onto the negatively charged arsenic species adsorbed onto the roots surface as would be suggested by the formation of arsenic sorption onto iron root plaques (Lui *et al.*, 2005, Blute *et al.*, 2004, Lui *et al.*, 2005, Lui *et al.*, 2006). Additionally, a decrease in the K concentration was observed in the shoots of the plants; whereas, the potassium concentrations in the shoots of the treated plants decreases by approximately 60% as compared to the control plants. The decrease in the K concentrations could be related to the formation of plaques on the roots which prevent the translocation of elements through out the corn plants.

Conclusions

The XANES and EXAFS studies compliment each other showing the mixed coordination environment of the arsenic in the corn. These data indicate that arsenic(V) is more easily

biotransformed to arsenic sulfide than is arsenic(III). The data also indicate that the possible arsenic(III) toxicity within the plants is due to an extra step within the arsenic biotransformation process. This extra step, when dealing with arsenic(III), is the primary oxidation of arsenic(III) to arsenic(V), which is followed by the reduction of the arsenic(V) to an arsenic(III) thiol compound. The ICP-MS data also suggest that there may be iron plaques present on the roots. The formation of the iron plaques on the roots would explain the high concentrations of elements found on the roots and lower concentrations of the elements found in the shoots in the arsenic treatments as compared to the control plants. In addition, the formation of an iron plaque would also explain the oxygen ligands observed in the XAS data for the roots. Finally, the ICP-MS data also suggest that once inside the plants the arsenic is coordinated to sulfur ligands, which supports the XAS data.

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Figure 1.

A. XANES spectra from 11.8 keV to 11.96 keV of the arsenic(III) and arsenic(V) model compounds arsenic(III) oxide, arsenic(V) oxide, sodium form of arsenous acid, and arsenic(III) sulfide. **B.** XANES spectra from 11.8 keV to 11.96 keV of the arsenic uptaken into the roots of the corn plants from the arsenic(III) and arsenic(V) treatments.

Figure 2.

A. Fourier transformed EXAFS from $2.0 \text{ \AA}^{-1}$ to $12.47 \text{ \AA}^{-1}$ of the arsenic(III) and arsenic(V) model compounds arsenic(III) oxide, arsenic(V) oxide, and arsenic(III) sulfide. **B.** Fourier transformed EXAFS from $2.0 \text{ \AA}^{-1}$ to $12.47 \text{ \AA}^{-1}$ of the arsenic uptaken into the roots of the corn plants from the arsenic(III) and arsenic(V) treatments.

Figure 3.

Diagram of an arsenic atom coordinated to low molecular weight thiol compounds showing the interatomic distances between the arsenic and the sulfur and the arsenic and neighboring carbons atoms.

Figure 4. ICP-MS results of total arsenic accumulated for the arsenic(III), and arsenic(V) treatments in corn roots and shoots.

Figure 5. ICP-MS results of total iron accumulated for the control, arsenic(III), and arsenic(V) treatments in corn roots and shoots.

Figure 6. ICP-MS results of total manganese accumulated for the control, arsenic(III), and arsenic(V) treatments in corn roots and shoots.

Figure 7.

A. ICP-MS results of total phosphorus, sulfur, and potassium accumulated for the control, arsenic(III), and arsenic(V) treatments in corn roots. **B.** ICP-MS data of total iron accumulated for the control, arsenic(III), and arsenic(V) treatments in corn shoots.

Table 1

DRC-ICP-MS conditions used for determination of elemental uptake by corn seedlings under arsenic(III) and arsenic(V) treatments.

Parameter	Setting
RF Power	1100 W
Nebulizer	Meinhard Type A Quartz
Nebulizer Flow	0.95 L/min
Plasma Flow (Ar)	15 L/min
CeO/Ce	<2%
NH ₃	0.5 mL/min

Table 2

LC-XANES fittings of arsenic uptaken by corn from hydroponics media.

Sample	% As_2S_3	% As_2O_5	% As_2O_3	% Na_2HAsO_4
As(V) Roots	49.6	42.5	0.0	7.9
As(III) Roots	35.8	61.6	2.1	0.5

Table 3

FEFF 8.0 fittings of arsenic model compounds and arsenic uptaken by Corn plants.

Sample	Interaction	CN	R($\text{\AA}$)	$\sigma^2(\text{\AA}^2)$
As ₂ O ₅	As-O	3.9	1.67	0.0015
As ₂ O ₃	As-O	3.0	1.79	0.0026
As ₂ S ₃	As-S	3.0	2.27	0.0015
As(V) Roots	As-S	2.8	2.26	0.0040
	As-O	1.0	1.71	0.0038
As(III) Roots	As-S	2.0	2.24	0.0042
	As-O	2.0	1.74	0.0058