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Examination of arsenic(III) and (V) uptake by the desert plant species mesquite (*Prosopis* spp.) using X-ray absorption spectroscopy

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Abstract

This study describes the effects of Arsenic(III) and (V) on the growth and their uptake by the desert plant mesquite (*Prosopis* spp.). Seedlings were sown in agar-based medium containing a modified Hoagland's nutrient solution. After 1 week, the seedlings were transplanted to arsenic (As) treated agar media that contained 5 mgL^{-1} of As either As(III) (As_2O_3) or As(V) (As_2O_5). The plants were harvested after 14 days of growth and sectioned into roots, stems, and leaves. After digestion, As concentrations in the roots, stems, and leaves were determined using inductively coupled plasma–optical emission spectroscopy (ICP–OES). Our results showed that the As concentrations from As(V) were significantly higher than the As concentrations from As(III) in all portions of the plant. Plants exposed to As(V) concentrated (mg As kg^{-1} d wt) about 770±191, 326±94, and 119±18 in roots, stems, and leaves, respectively. X-ray absorption spectroscopy (XAS) showed that As(V) was reduced to As(III) inside the mesquite plant. In addition, greater than 90% of the As(III) found in the mesquite plants was bound to sulfur ligands in the roots, stems and leaves.

Keywords: Mesquite; Arsenic; Phytoremediation

1. Introduction

Arsenic (As) contamination occurs in many areas especially around coal combustion and mining operations (Codling and Wright, 1998; Milton and Johnson, 1999) and in the past it was commonly used in pesticides and herbicides (NRC, 1977). Although many minerals contain As compounds, the anthropogenic contribution to the environment in the past accounted for 82,000 metric tons/year worldwide (Nriagu and Pacyna, 1988). In addition, the mobility of As through the soil profile is minimal, meaning that the As is trapped at the surface. However, when As is concentrated in waste lagoons and stockpiles, it becomes mobile and moves through the sedimentary aquifers contaminating groundwater reserves (Bohn et al., 1985; Bagla and Kaiser, 1996; Anawar et al., 2002, 2003; Bhattacharya et al., 2002; Ahmed et al., 2004). Because of the toxicity of As, the EPA drinking water standard has been reexamined and the previous level of 50 μg L^{-1} was lowered to 10 μg L^{-1} (Eaton et al., 2002). The toxicological effects of ingesting As include skin lesions, gangrene, and cancer (Finkelman et al., 1999; Brown et al., 1989; Tondel et al., 1999).

Conventional remediation of As contaminated soils includes burial and chemical stabilization, which may pose long-term health threats leakage or chemical instability (Allen, 2001; Förstner and Haase, 1998).

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However, the concept of phytoremediation to clean up contaminated sites, which was proposed more than two decades ago, eliminates these possible health threats (Chaney, 1983). The concept of phytoremediation involves monitoring metal uptake through the course of plant growth. Eventually, the maximum amount of metal the plant is able to uptake is reached and physiological changes can occur at which point the plant can be harvested and thus removing a portion of the contaminant from the environment (Nedelkoska and Doran, 2000). Phytoremediation has the potential to become an environmentally friendly and low-cost alternative remediation technique compared to the currently used remediation technologies.

It is well documented that some tropical and subtropical plants species can tolerate and uptake As (Meharg and Hartley-Whitaker, 2002; Tu et al., 2002). However, a significant gap of information exists on the ability of desert plant species that can uptake As or other toxic elements. Desert plants are inherently tolerant of physiologically stressful conditions such as drought, high salt environments, and nutrient poor soils. These characteristics make them more likely to adapt to high concentrations of toxic elements such as As that is a frequent contaminant in areas with mine tailings (Anawar et al., 2006), found in desert areas (Oyarzun et al., 2004; Rampe and Runnells, 1989).

Numerous researchers have experimented with the uptake of As using various plant species. Nie et al. (2002) reported successful remediation of As contaminated soil with a transgenic canola species and a growth promoting bacterium *Enterobacter cloacae* CAL2. Pickering et al. (2000) have reported on As uptake in Indian mustard (*Brassica juncea*). Tu and Ma (2002) reported that Ladder brake fern (*Pteris vittata* L.) could survive in soils contaminated at levels of 500 mg As kg^{-1} and that up to 26% of the As was removed. In addition, Meharg and Hartley-Whitaker (2002) provide a comprehensive review of plant species that are capable of taking up and survive in various inorganic and organic forms of As. Mesquite is a plant that grows well in humid and desert environments. This plant has shown to absorb Cr(VI) and other metals such as lead (Aldrich et al., 2004). In addition, XAS (X-ray absorption spectroscopy) studies have shown that mesquite is able to bioreduce Cr(VI) to the less toxic Cr(III) (Aldrich et al., 2003). Thus, it is hypothesized that mesquite could be a good candidate for the uptake of As in contaminated soils in arid regions (Rampe and Runnells, 1989).

In this study, this hypothesis is tested and taken forward within the science by an examination of the within-plant As speciation. For this, mesquite seeds were germinated in growth media contaminated with either As(III) or As(V) at concentrations of 5 mg L^{-1} and the total amount and speciation of the As within the plants was determined.

2. Materials and methods

2.1. Plant germination and cultivation

The seeds used in this experiment were supplied by the Wild Seeds Company (Tempe, AZ). The seeds were soaked overnight in distilled water, washed, and then treated with Captan® to deter fungal growth. A modified Hoagland's nutrient solution was used for these experiments half strength, which consisted of the following: $Ca(NO_3)_2 \cdot 4H_2O$, (3.57×10^{-4} M); H_3BO_3, (2.31×10^{-5} M); $CaCl_2 \cdot 2H_2O$, (2.14×10^{-3} M); KH_2PO_4, (9.68×10^{-6} M); KNO_3, (2.55×10^{-4} M); $MgClO_4$, (1.04×10^{-3} M); $FeCl_3$, (6.83×10^{-5} M); and MoO_3, (1×10^{-5} M), as previously published (Peralta et al., 2001). Arsenic was added as AsO_3 or As_2O_5 for a final concentration of 5 mg L^{-1}.

For the agar experiments, Bacto-Agar™ was added at 0.5% w/v. All treatments were set in quadruplicate for statistical purposes. Mesquite seeds were placed on a growing medium without the As addition under a laminar flow hood and set under a 14/10-h light and dark cycle. The temperatures were set to 25 °C during the day and 18 °C at night. One week after germination, the seedlings were transplanted to As treated growth media. Controls for both studies were the plants grown with the mineral solution without As present treatment. After 2 weeks of growth in the As contaminated media, the plants were harvested and washed in 0.01 M HCl and then rinsed with deionized water.

2.2. Sample preparation for Inductively Coupled Plasma–Optical Emission Spectroscopy (ICP–OES)

Seedlings from all treatments were then separated into root, stem, and leaf portions and oven dried at 70 °C for 2 days. The dried samples were prepared for ICP–OES analysis by using 10 mL of trace pure nitric acid and then placing in a PerkinElmer Multiwave® microwave oven. EPA method 3051 (Link et al., 1998) was used to digest the samples, after which the digested samples were diluted to a 1:9 (sample: deionized water) ratio.

2.3. ICP–OES analysis

A Perkin Elmer Optima model 4300 DV ICP–OES was used for the determination of As. The ICP–OES