

## **Absorption and distribution of Arsenic by plants & role of soil conditions**

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## Absorption and distribution of Arsenic by plants & role of soil conditions

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### **Abstract:**

Arsenic poisoning is a major health hazard affecting millions of people worldwide. Major contribution to arsenic contamination of soil is due to repeated use of fertilizers and pesticides. This results in higher amounts of arsenic in plants. We explored arsenic absorption by several different types of plants under different soil conditions such as presence of  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  ions in the soil. X-ray fluorescence spectroscopy (XFS) utilized to determine distribution of arsenic within a plant in different areas such as leaves, stem, and trunk. Chemical nature and association and possible association with iron ions were studied X-ray Absorption Near Edge Structure (XANES). at arsenic K edge employed to study microstructure such as bonding properties and number of near neighbour atoms of iron and arsenic within plants. Results indicate that presence of more  $\text{Fe}^{3+}$  in the soil facilitate arsenic absorption by plants.

**Keywords:** Arsenic, Absorption, X ray, XANES, soil conditions,  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ .

### **Introduction:**

Arsenic is a naturally occurring substance in the Earth's crust. The average Arsenic concentration of the Earth's crust is approximately 1.5 ppm. The amount present varies depending on the geographic location and type of soil and rock. In some areas it can go up to 35,000 ppm<sup>1</sup>. Arsenic and its compounds are known toxics. According to Environmental Protection Agency (EPA) and the World Health Organization (WHO) Arsenic is a well-known carcinogen<sup>2</sup>. The level of toxicity depends on the type of compound. For example, Arsenic in organic compounds is less toxic but Arsenic in inorganic compounds is more toxic. Arsine ( $\text{AsH}_3$ ), Arsenite, and Arsenate in particular are highly toxic compounds. Humans unknowingly consume Arsenic through drinking water and plants. In addition to naturally occurring Arsenic, the Arsenic concentration of soil increases due to human activity. Arsenic compounds are used in the industry sector in the manufacturing of semi-conductors, glass production, papers, metal adhesives, ceramics, wood preservatives, and explosives<sup>3</sup>. Inorganic Arsenic compounds were used as pesticides in the United States of America (USA) before the 1950's. Naturally occurring Arsenic and Arsenic from industrial waste products are becoming a growing concern to human health as the use of material containing Arsenic and expansion of human settlements to former agricultural and industrial lands widens. Small doses of Arsenic in the body are considered harmless. Once Arsenic enters the body it circulates within the blood stream and exits the body through urine. But high doses of Arsenic can be very toxic. It can cause cancer, bladder, liver, and kidney problems. Much of the worldwide concern surrounding food safety is centered on toxic chemicals present in foods consumed. Consumers are more aware of the danger to food crops due to absorption of toxic elements, whether it is those that are naturally occurring in the soil or added to the soil by means of fertilizer or pesticides. This has resulted in a very high demand for organic food in the USA and worldwide. For example, organic food and beverage sales in the USA rose from \$1 billion in 1990 to \$26.7 billion in 2010<sup>4</sup>. There are numerous studies concerning the amount of Arsenic found in food crops. But most of those studies do not take into consideration the identity or chemical nature of

Arsenic compounds in plants<sup>5-10</sup>. Arsenic occurs with several stable oxidation states such as -3, -1, 0, 3, and 5. Toxicity level and the amount of absorbed by plants is dependent on the oxidation state of Arsenic. For example, As (III) bearing species are considered to be more toxic and mobile than others<sup>11</sup>. Arsenic forms strong bonds with Iron via bonding with hydroxyl groups and Iron oxide or intermetallic bonds with Fe (0). The uptake of Arsenic in plants occurs mainly through Fe-As bonding. Therefore it is important to obtain information about Arsenic absorption by plants under different soil conditions. X-ray absorption spectroscopy (XAFS), which includes X-ray Absorption Near Edge structure (XANES) and Extended X-ray absorption fine structure (EXAFS), is a very useful tool for the examination of absorption and local environments of specific elements. For example, absorption edge energy is sensitive to the oxidation state of the absorbing atom. The main edge height of the absorption spectrum is proportional to the amount of absorbing atoms present in a sample. Consequently, XANES can be used to identify the oxidation state of Arsenic compounds in samples. EXAFS is a valuable tool to determine parameters such as near neighbor bond length, number, and type of near neighbor atoms.

### **Experimental methods:**

#### **X-ray Absorption Spectroscopy:**

X-ray Absorption Spectroscopy consists of two areas of absorption spectrum, namely X-ray Absorption Near Edge Structure (XANES) and Extended X-ray Absorption Fine Structure (EXAFS). These two experiments yield different types of information regarding the absorbing atom. In X-ray absorption experiments, X-ray absorption by the sample is measured as a function of X-ray energy near the vicinity of an absorption edge of specific atom (for example 11,867 eV Arsenic K edge). XANES studies the absorption spectrum immediately before and after the main edge. During these experiments, absorption coefficients of samples were measured as a function of X-ray energy. In a typical experiment the absorption coefficient is measured in the energy range of about 200 eV below the absorption edge to 1000 eV above the absorption edge. Experimental procedure was explained in detail earlier<sup>12-14</sup>. When the energy of incoming X-rays is below the absorption edge, no absorption occurs. As the energy of X-rays reaches the edge energy, a sharp increase of the absorption occurs due to the ejection of core electrons of the absorbing atom. Beyond the absorption edge, extra energy becomes the kinetic energy of the ejected photo electron. As these ejected photo electrons travel away from the absorbing atom, they encounter neighboring atoms. Some of the photo electrons bounce back due to interaction with these neighboring atoms. These scattered electrons and outgoing electrons can interfere constructively or destructively depending on the phase difference. The total phase difference depends on the type of the central atom, type of the near neighbor atoms, and distance between the absorbing atom and near neighbor atom. This interference causes oscillations, called EXAFS, in the absorption coefficient above the absorption edge. The absorption edge position is sensitive to oxidation state, the shape of the main edge is sensitive to chemical environment of the absorbing atom, and height of the absorption edge is proportional to the amount of absorbing atoms. By analyzing EXAFS oscillations, we can derive information such as nearest neighbor bond length, type of nearest neighbor atom, and co-ordination number of specific central atom. Using these experiments, even a very minute amount of Arsenic can be investigated. These experiments were conducted at synchrotron facilities, National Synchrotron Light Source of Brookhaven National Laboratory, and Cornell High Energy Synchrotron Source (CHESS).

During this study, we investigate the amount of arsenic and its chemical nature in two different plants under variety of soil conditions. Two different plants were used in this study, collard green (*Brassica oleracea*) and parsley (*Petroselinum crispum*). Plants were grown in controlled soil conditions. Two sets of soil with added  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  ions were prepared. Arsenic was added to both soil samples by same amount. Then two sets of pots were prepared using these soil samples. One with Arsenic with  $\text{Fe}^{2+}$ , and the other with Arsenic and  $\text{Fe}^{3+}$ . Plants were grown in pots with soil containing arsenic and either  $\text{Fe}^{2+}$  or  $\text{Fe}^{3+}$ . Leave samples were collected in regular intervals for analysis. Collected samples were dried at 2000F and grounded to fine powder form. Same amount, by weight, of powder samples were mounted on identical sample holders for X ray absorption study. X ray absorption experiments were done using synchrotron radiation laboratories of Brookhaven national lab and Cornell university high energy synchrotron facility.

## Results and Discussion:

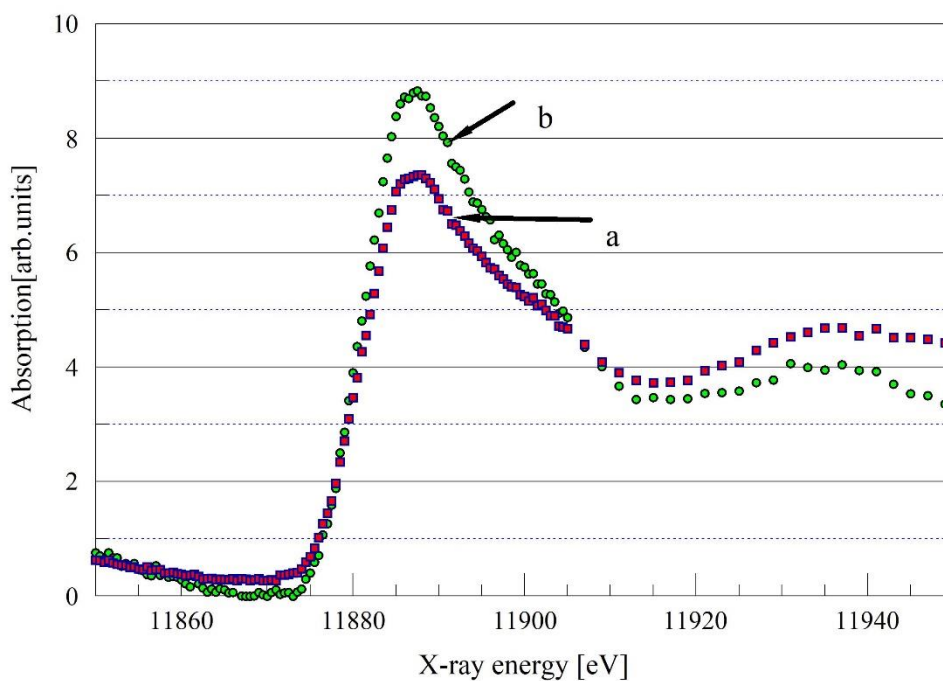


Figure 1: X ray absorption near edge of arsenic in soil containing additional  $\text{Fe}^{3+}$  ions. a- Parsley, b- Collard green

X ray Absorption Near Edge Structure (XANES) can be used to determine relative amounts of certain element presents in a sample, and for the comparison of structural properties of elements present in samples. For example, main edge energy position is sensitive to oxidation state of the

element under investigation. All XANES measurements were done on fluorescence mode with samples oriented 45 degrees to the incoming beam. As shown in figure 1, in both parsley and collard green samples, grown in soil with additional  $\text{Fe}^{3+}$ , XANES appears to be identical except peak height. In both samples onset of absorption occurs at X ray energy of 11,875 eV and peak energy position at 11,885 eV. This indicates that in both types of plants local structure around As atoms similar. But amount of As in collard green appears slightly greater than that of parsley plants.

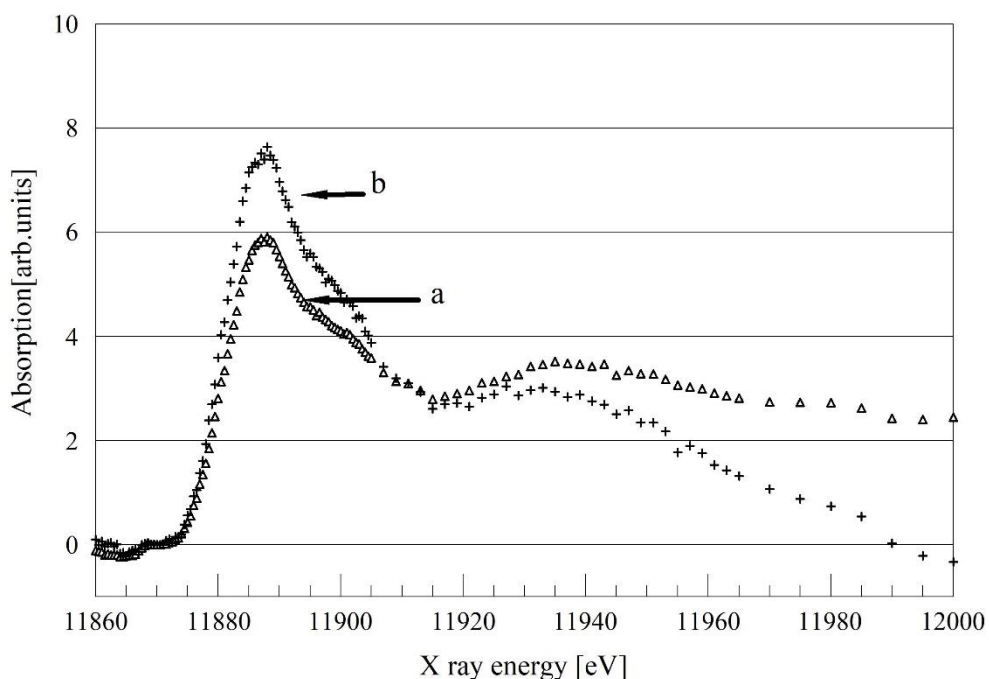


Figure 2: X ray absorption near edge of arsenic in soil containing additional  $\text{Fe}^{2+}$  ions. a- Parsley, b- Collard green

Figure 2 shows the XANES of parsley and collard green samples collected from plants grown in soil containing additional  $\text{Fe}^{2+}$  ions. Similar to the case of As in plants grown in soil with additional  $\text{Fe}^{3+}$ , plants in soil with added  $\text{Fe}^{2+}$  also showing similar properties. Onset of absorption and peak energy position is identical in both samples. But peak height in both samples little less compared to figure 1. This indicates that presence of  $\text{Fe}^{3+}$  ions enhance arsenic absorption more than  $\text{Fe}^{2+}$ . Also in figure 2 a shoulder appears in both spectra near the energy of 11,900 eV. This feature is absence in figure 1. This may be due to slight change in bonding of Arsenic in the figure 2. Further analysis is required for better clarification. Perhaps analysis of Extended X ray Absorption Fine Structure (EXAFS), small oscillations appear beyond the main edge will shed light on this structural difference.

## **Conclusion:**

This work studied XANES of collard green and parsley tissue samples collected from plants grown in controlled soil with added Arsenic and either  $\text{Fe}^{2+}$ , or  $\text{Fe}^{3+}$  ions. There is no significant change in the arsenic compounds of plants regardless of presence of  $\text{Fe}^{2+}$ , or  $\text{Fe}^{3+}$  ions. But absorption of Arsenic by plants grown with  $\text{Fe}^{3+}$  ions in soil is greater compared to soil with  $\text{Fe}^{2+}$  ions. Further analysis of EXAFS region of X ray absorption spectra in future will clarify differences in more structural information of arsenic in plants.

## **Broader Impact of the project:**

This X-ray absorption project supports skill development, consistent with several targeted topics in the ASEE Conference.

(1) The Innovations in Engineering Education targeted area could use a problem based project via synchrotron data from National Lab, and students going to Brookhaven need to be trained in the related safety protocols. The synchrotron data are not simulations but real time data acquisition to engage students in the understanding of electronics, physics, math, and data analysis. The skill development in terms of experiential learning is invaluable to the students.

(2) The Equity, and inclusion in Engineering targeted area would be fulfilled since we have been engaging CSTEP students in the data analysis. The CSTEP students are part of a NYS program. The students are usually African American students as first-generation students. Some CSTEP students may not have the patience to pass the safety protocol, but data analysis skill development for the CSTEP students are unique application experience.

(3) The Multi-Disciplinary Engineering targeted area could use this synchrotron based project example to illustrate atomic techniques crucial to nano-scale technique with applications to electrical engineering, mechanical engineering, material engineering, etc.

(4) The Research Experience for Undergraduates (REU) target area is fulfilled with our REU students doing synchrotron based projects, supported by NSF REU Grant “ A Community College REU Site for Physics Applications”Award Number:1359310, PI: Lieberman. Previous student projects included Fe, Mo, Co,... in bio-battery-cell projects, soil nutrient projects, Vycor substrate based projects, etc.

(5) The improving critical thinking targeted area is fulfilled for those students collecting data on site and also for students doing the data analysis in the modeling the data noise, fitting the data to a specific model, alternative hypothesis, etc.

In general, instructors engage students in active learning with X. The X is a tool which could be participation credit in terms of discussion threads on Blackboard or responsibility credit in terms of the reading of theory in a flipped classroom. The synchrotron-based project offers another X tool accepted by NSF REU in terms of skill development and research experience in a college curriculum.

## **Acknowledgement:**

This work is based upon research conducted at the Materials Solutions Network at CHESS (MSN-C) which is supported by the Air Force Research Laboratory under award FA8650-19-2-5220 and use of the National Synchrotron Light source, Brookhaven National Laboratory, was supported by the U.S. Department of Energy, office of science, office of basic energy sciences, under contract No. DE-AC02-98CH10886. The was supported by several PSC-CUNY grants. Breeya Skye thanks NSF funded REU program of Queensborough Community College for the support.

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