7 Uptake Behaviour and Interdependence Study of Arsenic and Selenium in Mung Bean by Inductively Coupled Plasma Optical Emission Spectrometry

The quality of human life depends on the chemical composition of food and of the surroundings. Trace element plays an important role in chemical, biological metabolic and enzymatic reactions in plants, animals and human being [Hashmi et al., 2007]. Uptake of metals by plants depends on the physicochemical makeup of the plant species and soil [Dudka and Miller, 1999; Albering et al., 1999; Samøe-Petersen et al., 2002; Combs, 2001]. Arsenic and selenium have high impact in environmental and biological studies. Arsenic contamination has a negative impact on the environment, as it can generate severe toxicological effects to both vegetation and animal organisms. Similarly, trace amount of selenium is found to be essential for both humans and animals which plays an important role in immune defense but the same is toxic at higher concentrations.

Inorganic arsenics are known to be 70 times more toxic than monomethylarsonic acid (MMA) and dimethylarsonic acid (DMA) [Squibb and Fowler, 1983; Van Herreweghe et al., 2003] Thus it is an important species rather than the total amount.

There are around 25 selenoproteins in humans and many of these are enzymes that act to protect the body against oxidative damage. Without selenium, the function of the selenium-requiring proteins can be compromised that results in the signs and symptoms of deficiency. Insufficient selenium intake tends to cause several health problems including cardiac failure. Further, the number of cancer patients is also increasing consequent upon the selenium deficiency in everyday diet [Flores-Mateo et al., 2006]. So, either insufficient or excess selenium intake can have dramatic consequences. Selenium is often described as a “two-edged sword”. The intoxication depends on selenium concentration and chemical forms of this element [Barceloux, 1999]. It is also well known that As and Se act as metabolic antagonists [Gailer, 2007]. The Se deficiency may induce the accumulation of As in liver and decrease excretion of inorganic and organic As in animal models [Kenyon et al., 1997]. But Se sufficiency may accelerate the rate of excretion [Miyazaki et al., 2005]. Therefore it is very important to detect As and Se accurately in a sample.

Determination of total arsenic by differential pulse cathode stripping voltammetry (DPCSV) has been described by a few researchers [Eguiarte et al., 1996; Henze et al., 1997; Ferri et al., 1989]. The limits of detection achieved were 0.05 ng/mL [Eguiarte et al., 1996], 0.52 ng/mL [Henze et al., 1997] and 121 ng/mL [Ferri et al., 1989] depending on the time and way of the analyte concentration on the electrode, and the results were in good agreement with those obtained by hydride generation atomic absorption spectrometry (HGAAS) [Eguiarte et al., 1996]. Li and Smart, 1996 have discussed different electroanalytical methods for determination of arsenic proposed in literature and developed by them. Total As in sea water, measured by direct current stripping voltamperometry with the gold electrode, have been reported by Hua et al., 1987. Neutron activation analysis (NAA) is a very powerful technique for As detection and in this method detection limit of arsenic is 0.02 ng/mL [Van elteren et al., 1989; Mok and Wai, 1988; Sims and Gladney, 1991]. An important advantage of the NAA method is that the sample analyzed is not destroyed and can be used repetitively. The limits of detection of As and other elements are different and depends on techniques such as total reflection X-ray fluorescence, continuous-flow hydride generation atomic fluorescence spectrometry, inductively coupled plasma, etc. [Messerschmidt et al., 1997; Moreda-Pineiro et al., 1997; Simeonsson et al., 1997; Bulska et al., 1993]. The hydride generation method before the introduction of analyte to the plasma enables a separation of the elements under determination from the interfering matrix. The results obtained by ICP-AES are comparable to those in HGAAS determinations with the detection limit of 0.2 ng/mL [Fernandez et al., 1992]. The critical toxic threshold level [Broeck et al., 1997] and speciation study have been performed by liquid chromatography inductively coupled plasma-mass spectrometry of arsenic in Mung bean seedlings used as a bio-indicator for the arsenic contamination [Broeck et al., 1998]. The most popular and widely applied method for determination of arsenic in ore is spectrophotometry of arsenomolybdic acid in presence of molybdenum blue [Rao et al., 1993]. The silver diethyldithiocarbamate spectrophotornetry procedure for the determination of arsenic has been modified to perform the differential determination of inorganic arsenic(III) and arsenic(V) species [Howard and Arbab-Zavar, 1980]. Authors shown that the use of hydride generation in a continuous mode, coupled to retention in liquid nitrogen, permits the use of gas phase

molecular absorption spectrometry (GPMAS) for the simultaneous determination of As, Sb and Se down to trace levels [Pinilos et al., 1995]. Selenium and arsenic are normally found in low concentrations in environmental samples. Therefore, their direct determination by spectrometric techniques using pneumatic nebulization is not a proper way to detect because the limits of detection are relatively high for both elements. Sensitivity can be improved by one or two orders of magnitude by applying special sample introduction and hydride generation (HG) systems coupled with the instrument, irrespective of the methodology namely, atomic emission spectrometry (AES) [Fernandez et al., 1992; Bulska et al., 1993; Hueber et al., 1993; Pena-Vazquez et al., 2005; Suarez and Gine, 2005; Grotti et al., 2005; da Luz Lopes et al., 2009; Gil et al., 2007; Koh et al., 2005; Karthikeyan and Hirata, 2003; Vuchkova and Arpadjan, 1996; Ochenkuhn-Petropulu and Schramel, 1995; Vassileva and Hoenig, 2001; Matos-Reyes et al., 2010; Masson et al., 2006; Nakahara and Kikui, 1985; Narasaki and Cao, 1996; Stripeikisa et al., 2001; Carrio´na et al., 2003; Ilander and Väisänen, 2011], mass spectrometry (MS) [Bowman et al., 1997; Chen and Jiang, 2006; Hu et al., 2005; Layton-Matthews et al., 2006; Yang and Husain, 2006; Hall and Pelchat, 1997; Stroh and Volkopf, 1993; Ribeiro et al., 2004], atomic absorption spectrometry (AAS) [Welz et al., 1993; Le et al., 1993; Ritsema and van Heerde, 1997; Erdem and Henden, 2004; Coelho et al., 2002; Anthemidis and Martavaltzoglou, 2006; Karadjova et al., 2006; Loska and Wiechula, 2006; Zhang et al., 2006; Pechová et al., 2005; Guo et al., 1997] and atomic florescence spectrometry (AFS) [Liu et al., 2005; Barra et al., 2000; Coelho et al., 2003, Shi et al., 2003; Leal et al., 2004; Tang et al., 2005]. Soil samples were analyzed and the concentrations of 15 elements including selenium and arsenic were reported by instrumental neutron activation analysis (INAA) using reactor neutrons and high resolution g-ray spectrometry [Srivastava et al., 2011].

The catalytic-spectrophotometric methylene blue method for Se determination has been modified by the cationic surfactant Cetyltrimethylammonium bromide (CTAB) to increase its analytical sensitivity in the lower range of Se concentrations while maintaining its precision at acceptable levels [Arikan et al., 1996]. The spectrophotometric method for the determination of Se in water, soil, cereal and cattle feed samples using 2,3-diaminenaphthalene was established and the detection limit of the

method is 0.5 - 12 mg/L [Ramachandran and Kumar, 1996], but using 6-amino-1-naphthol-3-sulphonic acid (J-acid) allows to enhance the detection limit in the range of 0.08–0.8 mg/L [Ramachaandran et al., 1993]. Although the former method is less sensitive than J-acid methods, the modification is significant in view of its wide application and makes the reaction faster and enhances the reproducibility. In acidic medium Se(IV) reacts with 3,3'-diaminobenzidine (DAB) and form the yellow piazselenol, which is sparingly soluble in water and used for spectrophotometric determination of Se [Marczenko and Balcerzak, 1998]. An analytical method, based on differential pulse polarography, has been described for determination of trace levels of selenium in solid matrices [Ferri et al., 1989], in nitric acid medium [Trivedi and Thakkar, 1989] and in Chinese herbal drugs [Taijun et al., 1992]. The catalytic polarographic determination of total selenium in tea leaves by using the $SeSO_3^{2-}$-KIO_3 system was described [Xunjian et al., 1992]. This method is sensitive, accurate, rapid and requires only small quantities of sample. The detection limit for selenium was 0.04 ng/mL in the final solution. Direct milk sample analysis by ICP-MS was proposed but despite the better results, the accuracy attained for Se was not suitable due to the occurrence of isobaric interferences [No´brega et al., 1997]. Later on, authors developed a procedure [Aleixo and No´brega, 2003] by which Se was determined in bovine milk using conventional heating programmes without any modifier or with Pd modifier, respectively. Se in mushrooms [Kula et al., 2011] and in human blood [Massadeh et al., 2010] was determined by ICP-OES after microwave digestion with a detection limit of 0.2 mg/L and 0.332 mg/L, respectively. Without total sample digestion, slurry sampling hydride generation (SS-HG) method for the determination of Se in biological and environmentally standard reference materials has been developed using batch mode generation system coupled with microwave induced plasma optical emission spectrometry (MIP-OES). The detection limit in this method was 0.15 µg/g [Matusiewicz and S´lachcin˜ski, 2006]. A new, simple and sensitive method by combining headspace Pd(II)-coated graphite bar microextraction (GBME) with electrothermal vaporization–inductively coupled plasma mass spectrometry (ETV-ICP-MS) was developed for the determination of trace Se in seawater and human hair [Xiong and Hu, 2010]. To generate

hydrides of Se, the graphite bar was coated with Pd(II) and the limit of detection was 8.6 ng/L.

An uptake study of environmentally hazardous ^{51}Cr in Mung beans has been shown by Banerjee et al., 2008. The metabolism and biokinetics of trace metals in humans can be successfully studied employing stable isotopes of the investigated elements as tracers in mung beans (*Vigna radiate*) [Giussani et al., 1998]. Further seed of the Mung bean plant is used as a common food grain use in everyday diet and is widely cultivated in Indian subcontinent. Mung bean plants are known for the high sensitivity towards different sources of pollutants. They grow very rapidly, so that the effect of pollution can be evaluated in a short period of time (6 days). In this work, we have studied the uptake of As and Se in the different part in a common plant, Mung (*V. radiate)* by ICP-OES to have an insight on the migration and bio-magnification behaviour of As and Se. We have also compared the effect of simultaneous addition of As and Se in the growth medium and change in uptake behaviour of As and Se in presence of each other.

7.1 Experimental

7.1.1 Reagents and samples

Sodium selenite pentahydrate, Na_2SeO_3. $5H_2O$, (Sigma-Aldrich), Sodium-m-Arsenite, $NaAsO_2$, (Spectrochem, India), Suprapure nitric acid (65%) and Hydrogen peroxide (30%) were procured from E. Merck, Germany. The deionized water with a maximum resistivity of 18.2 MΩ-cm was obtained from Bransted NANO pure Diamond, Thermo Scientific, Germany and was used throughout the experiment. All chemical reagents were used without further purification.

7.1.2 Plantation of Mung bean (V. radiata) seeds and growth

Mung beans were procured from local shops, Kolkata, India. Procured Mung beans were rinsed thoroughly water and finally with deionized water and allowed to soak in sufficient amount of deionized water for 4 h at room temperature (28 ^oC). The excess

water was drained out and the seeds were rinsed 5 times to make them clean. The rest amount of water was soaked in tissue paper. Fine grain of sieved sand was rinsed with water and air dried. Sand (50 g) was taken in a 50 mL borosil glass beaker for each set of study. Hoagland's nutrient solution (see composition in **Table 7.1**) was prepared and used this nutrient solution to prepare various concentrations of arsenic and selenium solutions [Broeck et al., 1997]. The seeds were then sowed in the sand. Sand is a good substrate for plant culture as it is devoid of any toxic element causing harmful effects to the plant [Davies et al., 2001]. The Hoagland solution mixture was added to the 50 g sand placed in 50 mL borosil beaker. Healthy seeds were planted in the sand. Each beaker contained six seeds.

Table 7.1 Composition of the Hoagland solution.

Component	Composition (mg/L)
H_3BO_3	3.1
$MnSO_4.H_2O$	1520
$CuSO_4.5H_2O$	75
$Na_2MoO_4.2H_2O$	24
$ZnSO_4.7H_2O$	222
KNO_3	505
$Ca(NO_3)_2.4H_2O$	1180
KH_2PO_4	136
$MgSO_4.7H_2O$	492
$FeSO_4.7H_2O$	0.43
Na_2EDTA	0.30

Growth rates were studied with four replicas for each concentration of As (III), Se (IV) and As (III) + Se (IV) separately. Plant growth was observed in light and dark cycle for 6 days. In order to study the growth rate of the Mung bean, the root and shoot length of the plant at the end of the experiment (6^{th} day) was compared with that of the control plant (grown in the absence of As (III) and Se (IV). The seedlings were removed and washed with deionized water to make it free from sand as well as the growth medium. Then the plants were divided into two parts, namely the root and shoot (hypocotyls+ epicotyls).

7.1.3 Chemical procedure: Microwave digestion

Finally dried samples were transferred to 100 mL Teflon vessel. Samples were digested by 3 mL conc. HNO_3 acid and 0.5 ml H_2O_2 in a Mars Xpress microwave digester (maximum power 1600 W, hold time 60 min and temperature 80 ^oC). The digested solution was filtered with 42 Whatman paper and diluted to 10 mL with deionised water. SRM (Orchard leaves, NIST, 1571) were taken as standers for ICP-OES analysis and the same chemical treatment was done with standard and the samples. The resulting solution was cooled and the final volume was 20 mL. Reagent blank was prepared in the same way.

7.1.4 ICP-OES analysis

The total amounts of As and Se absorbed under different conditions by root and shoot were measured by inductively coupled plasma optical emission spectrometry (ICP-OES). SRM, Orchard leaves, 1571 solutions were diluted to various strengths to measure the As content in root and shoot of Mung bean. For calibration of Se, the standard solutions were prepared by diluting stock solutions of 100 mg L^{-1} multielemental (Prod. 1.09494.0100, E Merck, Germany) solution with 2% HNO_3. A blank solution of 2% HNO_3 was also prepared. The measurements were carried out using an ICP-OES (Model no. iCAP 6500 duo, Thermo Fisher Scientific) with 7 pm resolution at 200 nm. The operating conditions are listed in **Table 3.2**, page 37 and the selected emission line for As was 189.042 nm and for Se it was 196.090 nm.

7.2 Results and discussion

To see the uptake behaviour and interdependence study of arsenic and selenium in Mung bean, various strength of As(III) and Se(IV) solutions were added to the medium. It was observed that seedlings were not germinated at all by addition of 15 ppm As solution (volume 15 mL) to the sand bed. Even addition of 1.5 ppm As solution resulted in slight wrinkling of the leaves. Whereas normal growth of seedlings was observed up to 9 ppm of Se, and only nominal hindrance in growth was observed up to 15 ppm

concentration of Se. Therefore, we took solutions of As from 15 ppb to 1.5 ppm; while 1 ppm to 15 ppm Se solutions were taken. The physical observations of seeds at various concentration of As and Se are given in **Table 7.3**.

Table 7.3 Physical observations of seeds at various concentration of As and Se.

Concentration	Growth observation
1 ppm As	Normal
9 ppm Se	Normal
1.5 ppm As	Growth hindered, leaves wrinkled
12 ppm Se	Growth hindered, leaves wrinkled
5 ppm As	No growth at all
25 ppm Se	No growth at all

The results of this experiment are given in **Figure 7.1 and Figure 7.2**. No As uptake was observed at 15 ppb As solution in the sand bed. However addition of 150 ppb to 1.5 ppm solution shows uptake of As in Mung beans and the concentration of As was magnified up to the level of 0.15 to 2.6 ppm. Similarly a direct relation between uptake of Se and concentration of Se solution added to the sand was observed. The relative uptake of Se in shoot was less than that in root. Maximum Se concentration in root was ~ 250 ppm. Further, Se accumulation was reduced in presence of minute amount of As while As uptake was higher in presence of Se.

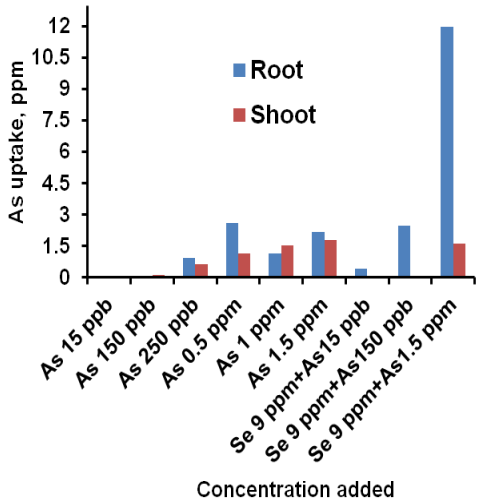

Figure 7.1 Uptake behaviour of As in presence and absence of Se in Mung bean.

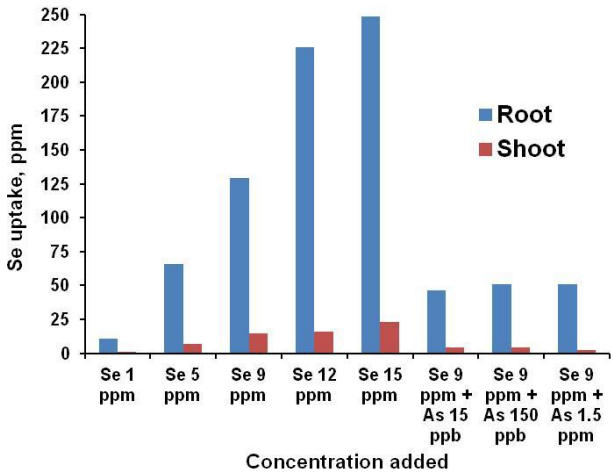

Figure 7.2 Uptake behaviour of Se in presence and absence of As in Mung bean.

7.3 Conclusion

In this work we have shown that the concentration of As and Se in root and shoot parts in a common plant, Mung (*V. radiate)* affects the migration and bio-magnification behaviour of As and Se to human body. The data indicate that the addition of 150 ppb to 1.5 ppm solution shows uptake of As in Mung beans and the concentration of As was magnified up to the level of 0.15 to 2.6 ppm and relative uptake of Se in shoot was less than that in root. Maximum Se concentration in root was ~ 250 ppm. Further, Se accumulation was reduced in presence of minute amount of As while As uptake was higher in presence of Se.

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