

The arsenic speciation transformation in artificially arsenic-contaminated fluvo-aquic soil (Beijing, China)

X. Zeng, Q. He, L. Bai, L. Li, S. Su

Key Laboratory of Agro-Environment and Climate Change, Institute of Environment and Sustainable Development in Agriculture, Chinese Academy of Agricultural Sciences, Beijing, P.R. China

ABSTRACT

Arsenic (As) speciation transformation often accompanies adsorption-desorption when exogenous arsenide is poured into soil. Disregarding the speciation transformation when evaluating adsorption-desorption of As can greatly influence the experimental results. In this study, batch experiments were conducted, and the results indicated that exogenous monomethylarsonic acid (MMA) or dimethylarsinic acid (DMA) added to fluvo-aquic soil collected from agricultural area in Beijing of China, was completely converted into As(V) after cultivated for 60 or 90 days. However, when exogenous As(V) was added to the soil, no speciation transformation of As(V) was observed. Furthermore, although the total As concentration, which was 6.55 or 11.55 mg/kg in aqueous extracts of the soil to which MMA or DMA had been added, respectively, remained stable after cultivated for 30 or 60 days, the As speciation transformation of MMA or DMA into As(V) in soil still occurred. Differences in As speciation can result in different fates and behaviors of As in soil, and As speciation transformation should be taken into account when evaluating the adsorption-desorption of As.

Keywords: As(V); MMA; DMA; conversion; adsorption-desorption

Arsenic (As) is ubiquitous in the Earth's crust, but non-essential for plant and animal life. As can be accumulated in soil through various approaches, such as weathering of rocks, volcanic activity, and anthropogenic input (Cullen and Reimer 1989, Ochiai 1995). Both inorganic and organic arsenide can also be poured into soil, and subsequently undergo speciation transformation and adsorption-desorption between As and soil colloidal particles, these processes largely affect the As toxicity in soil (Figure 1) (Kumaresan and Riyazuddin 2001, Turpeinen et al. 2002). As-enriched soils are considered major sources of contamination in the food chain and water supplies, and this is of great environmental concern because As is known to be a carcinogen and a mutagen (Fayiga and Ma 2006). Thus, there is currently growing concern regarding human exposure to As through soil-plant-human transfer besides of

water supplies. However, the soil-plant uptake of As depends on the nature of the interaction between soluble As and soil colloidal particles (Naidu et al. 2009). Although research on the sorption of As in soils has been reported from a number of countries (Simth et al. 1998, 2002, Álvarez-Benedí et al. 2005), As speciation transformation was less taken into account when evaluating the adsorption-desorption of As in soil. Speciation transformation often accompanies adsorption-desorption when exogenous arsenide is poured into soil, and less insight into the speciation transformation when evaluating the adsorption-desorption of As can greatly influence the experimental results. Furthermore, artificially As-contaminated soils were used as experimental soils in many studies (Tokunaga and Hakuta 2002, Tang et al. 2007), however, the processes of speciation transformation and adsorption-desorption of As in soil were

Supported by the Natural Science Foundation of China, Project No. 40871102, and by the National Exploration Project of Science and Technology in the Eleventh Five-Year Plan, Projects No. 2006BAD05B01 and 2007BAD89B03.

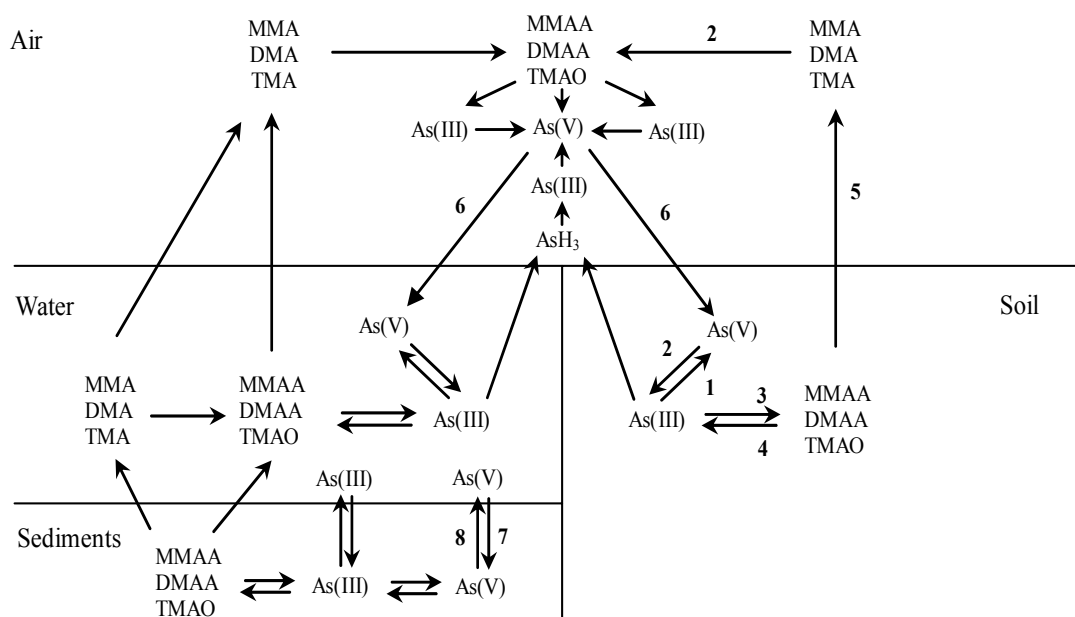


Figure 1. Geochemical cycle of arsenic. 1. oxidation; 2. reduction; 3. biomethylation; 4. demethylation; 5. rain or dry deposit; 6. biovolatilization; 7. precipitation; 8. dissolution

often ignored when artificially As-contaminated soil was prepared. Insufficient cultivation and preparation of artificially As-contaminated soil will directly affect the research results. Hence, to better understand the geochemical activity of As in soil and fully characterise artificially As-contaminated soil as an experimental soil, in this study exogenous arsenate [As(V)], monomethylarsonic acid (MMA), and dimethylarsinic acid (DMA) were added individually to fluvo-aquic soil collected from Beijing, China. After cultivated for different time, the As speciation present in aqueous extracts of the soil was assayed using high performance liquid chromatography-hydride generation-atomic fluorescence spectrometry (HPLC-HG-AFS), and consequently, the interaction between the adsorption-desorption and the speciation transformation of As were highlighted.

MATERIALS AND METHODS

Experimental soil. The fluvo-aquic soil, collected from an agricultural field belonging to the Chinese Academy of Agricultural Sciences (CAAS) in Beijing, China, was adopted as the experimental soil. After the soil was dried naturally, mixed and sieved using a 2 mm nylon mesh, the following physical and chemical properties were determined:

organic matter, 15.69 g/kg; total nitrogen, 1.21 g/kg; total phosphate, 1.72 g/kg; total potassium, 4.99 g/kg; total arsenic, 9.42 mg/kg; water-extracted arsenic, 0.41 mg/kg; and pH, 8.28.

Experimental design. In this experiment, the solutions of As(V) ($\text{Na}_3\text{AsO}_4 \cdot 12 \text{H}_2\text{O}$), MMA ($\text{CH}_3\text{AsNa}_2\text{O}_3 \cdot 6 \text{H}_2\text{O}$), and DMA [$(\text{CH}_3)_2\text{AsO}_2\text{Na} \cdot 3 \text{H}_2\text{O}$] were spiked into experimental soil of 200 g to make the added As concentration in soil reach 30 mg/kg. Subsequent to sufficiently mixed, the soil culture systems were randomly arranged in an incubation chamber with the constant temperature of 25°C. During the entire cultivation period, the soil moisture content was maintained at 70% of the largest field water-holding capacity using the constant weight method. This soil moisture level was chosen to mimic the water level in natural soils. Soil samples were sampled at the cultivation intervals of 1, 2, 7, 21, 30, 60, and 90 days. The concentrations of different As speciation and total As in aqueous extracts of soil were assayed. Soil without added exogenous As was used as a control. Four duplicates were done for each sampling time.

Analytical methods. 0.5000 g sampled fresh soil and 10 ml ultra pure water were transferred into a 50 ml centrifuge tube. After extracted for 30-min by ultrasonic assistance, the soil-water mixtures were centrifuged for 15 min at 3500 rpm. The extracted aqueous solution was filtered through

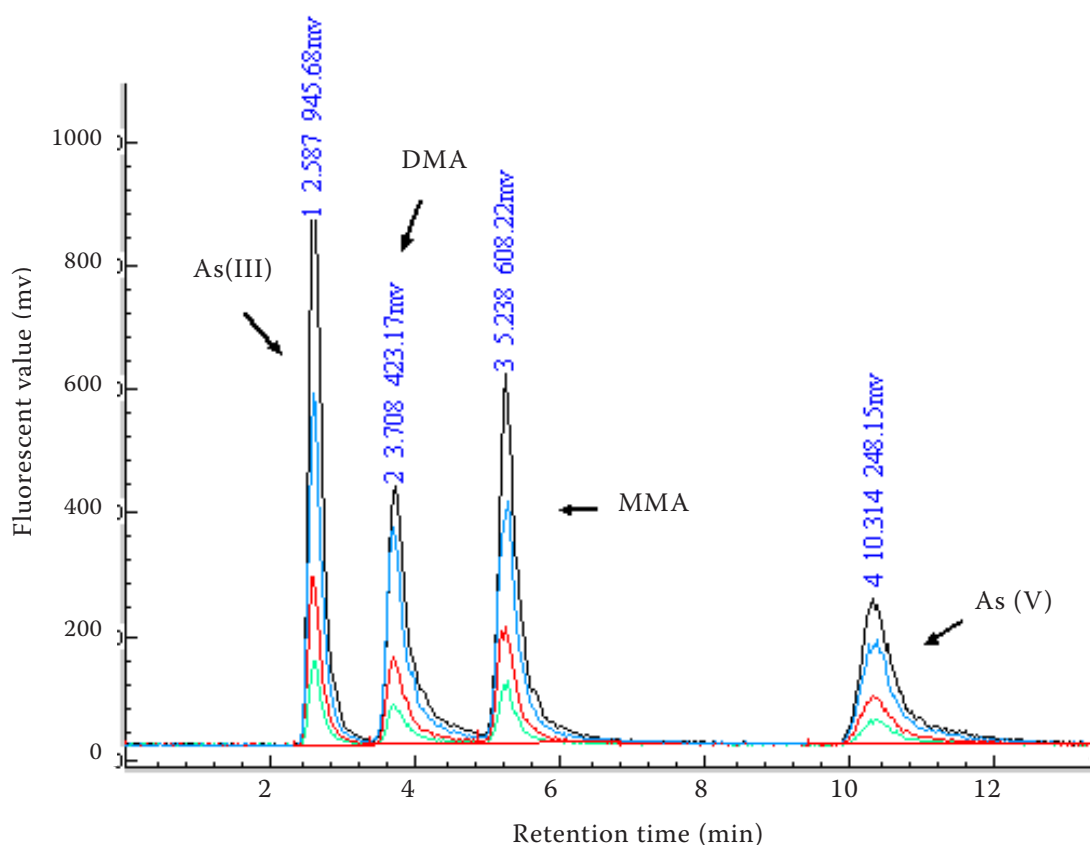


Figure 2. The spectra of standard arsenic solutions containing As(V), As(III), monomethylarsonic (MMA), and dimethylarsinic (DMA) analyzed using high performance liquid chromatography-hydride generation-atomic fluorescence spectrometry (HPLC-HG-AFS)

a 0.22 μm filter (JinLon, Membrana Company, Germany) and stored at 4°C. The extraction process was repeated. The As speciation in extract was detected using HPLC-HG-AFS (SA-10, Titan Instruments Co., Ltd, Beijing, China). Figure 2 shows the spectra of standard As speciation. The

main operating conditions are given in Table 1. The total As concentration in soil extract also was determined using hydride generation atomic fluorescence spectrometry (HG-AFS 9120, Titan instrument Co., Ltd, Beijing, China; detection limit < 0.02 μg As/L).

Table 1. The primary operating conditions for HPLC-HG-AFS detection and concentration determination for As species

High performance liquid chromatography conditions	
Chromatographic column	PXP-X100 (Reno, NV, USA)
Mobile phase	15 mmol/L $(\text{NH}_4)_2\text{HPO}_4$ with pH 6.0
Mobile phase flow	1 ml/min
Spectrometer conditions	
Total current	90 mA
Auxiliary cathode current	40 mA
Negative high voltage	295 V
Hydride generation conditions	
HCl	7% (v/v)
NaOH + KBH_4	5 g/L + 15 g/L
Peristaltic pump speed	80 rpm
Air flow	400 ml/min

The total arsenic, As(V), DMA, and MMA standards were prepared using As stock solutions (GBW08611, GBW08667, GBW08668, and GBW08669), respectively; Chinese Metrology Institute of Science and Technology, Beijing). All glassware used in the experiment was cleaned by soaking in 10% HNO₃ for 12 h and then rinsed with ultra pure water from a Milli-Q water purification system (France). All reagents were of analytical grade.

RESULTS AND DISCUSSION

Transformation of exogenous As(V), MMA, or DMA in soil. When exogenous As(V) was added to soil and cultivated for 1 day, the As(V) concentration in the soil extract was decreased to about 10 mg/kg, which accounted for approximately 30% of original concentration of 30 mg/kg (Figure 3a). After cultivated for 30–90 days, the As(V) concentration with 7.41 mg/kg, which accounted for about 24.7% of the original As concentration, was kept stable. It is possible that As(V) added to the soil was rapidly adsorbed by soil colloidal particles. Then, after cultivated for a certain time, the adsorption-desorption equilibrium between free As(V) and the soil colloidal particles was achieved,

with only a small amount of the added As(V) available for extraction. Our results are consistent with those of a study by Zhang and Selim (2006), who suggested that the rate of As(V) retention in soils is high initially, followed by reduced retention with increasing time. Álvarez-Benedí et al. (2005) found that when exogenous As(V) is added into three Spanish soils, a relatively rapid first adsorption process is completed within a few hours. Furthermore, in this case, there was no other As speciation observed in the soil extract other than As(V). The speciation transformation of As(V) does not occur readily in fluvo-aquic soil under some environmental circumstance.

The results of speciation transformations of exogenously added MMA and DMA in soil are showed in Figures 3b and 3c, respectively. When exogenous MMA or DMA was spiked into soil, similar variety trends for As species were found with increasing cultivation time. Briefly, the concentration of MMA or DMA gradually decreased, and the concentration of As(V) gradually increased in soil extract simultaneously. After cultivated for 90 days, only 0.32 mg/kg of MMA in soil extract was detected, while the As(V) concentration increased to 12.97 mg/kg (Figure 3b). When exogenous DMA was added to soil for 60 days, the DMA in soil extract was difficult to assay,

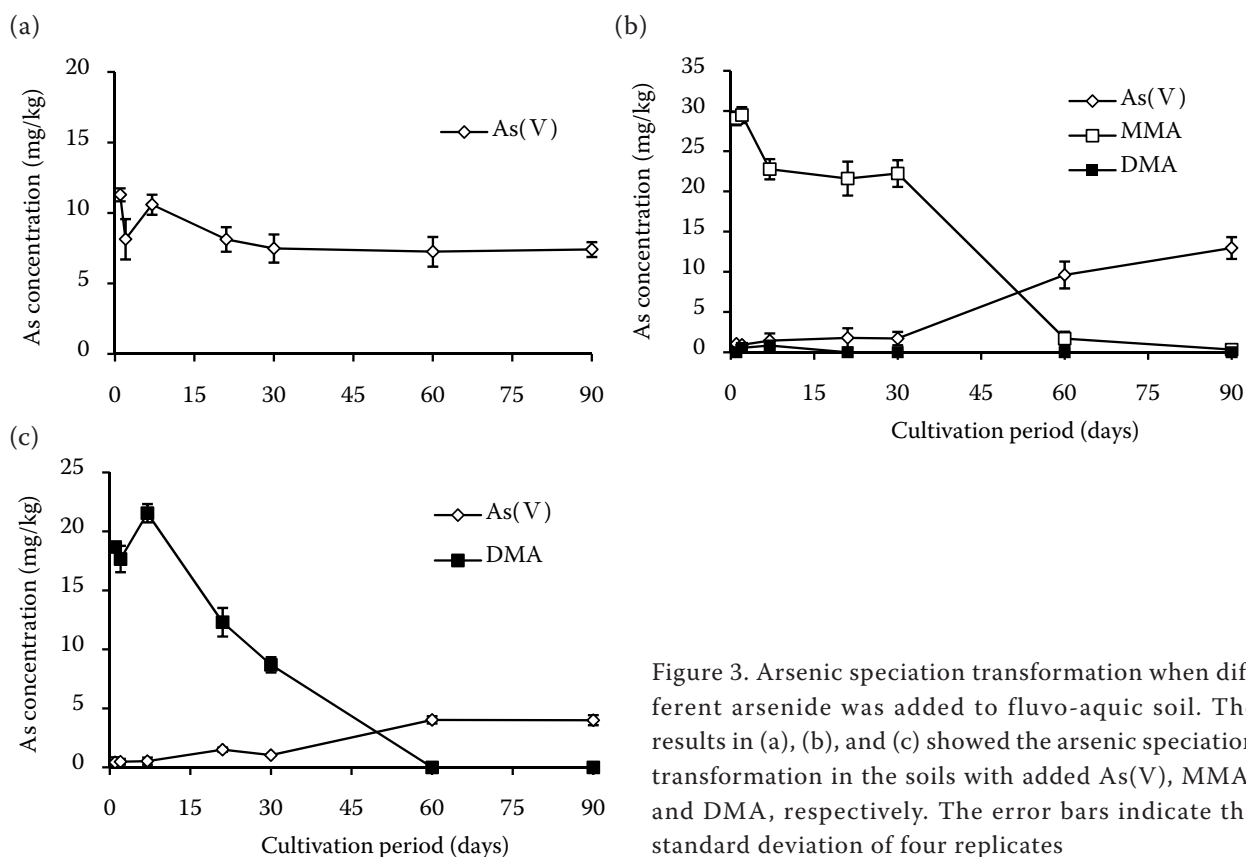


Figure 3. Arsenic speciation transformation when different arsenide was added to fluvo-aquic soil. The results in (a), (b), and (c) showed the arsenic speciation transformation in the soils with added As(V), MMA, and DMA, respectively. The error bars indicate the standard deviation of four replicates

while the As(V) concentration was 4.03 mg/kg (Figure 3c). It was very likely that the demethylation of added MMA or DMA yielded As(V), and the experimental conditions adopted in this study may promote the demethylation of MMA or DMA in soil. Gong et al. (2002) suggested that As(V) and As(III) are the major As species found in most soil samples. As is commonly present as As(V) under oxic soil condition (Marin et al. 1993). Huang et al. (2007) demonstrated that when DMA is added to soil that was collected from the forest floor and fen materials at the 'Coulissenhieb' site, DMA could be converted into MMA, and then further demethylated with inorganic arsenic as the final product. In this case, the presence of the MMA intermediate in soil samples spiked with exogenous DMA was not found. It is possible that the MMA intermediate was promptly demethylated to yield As(V), and the physical and chemical characteristics of fluvo-aquic soil might influence the transformation process. Furthermore, when the cultivation time ranged 1–20 days, there was a small amount of DMA detected in the soil sample to which exogenous MMA was added (Figure 3b). This result indicates that the methylation of MMA yielded DMA in the soil can occur under some circumstance. However, with the extending cultivation time, the DMA disappeared, therefore, it can be concluded that the demethylation of MMA yielding As(V) was the dominate reaction during the entire process.

Arsenide added to soil undergoes adsorption-desorption with soil colloidal particles and speciation transformation, both of which occur simultaneously and interactively (Lin and Puls 2000, Ko et al. 2004). The dynamic of As adsorption-desorption in the

soil environment varies with the nature of the As species (Naidu et al. 2009). For example, As(V) and As(III) present different absorption abilities due to differences in the arsenic oxidation state. The results from Ladeira and Ciminelli (2004) show that As(V) is a more efficient adsorbent with goethite and gibbsite than As(III), and further studies indicated that As(V) is mainly adsorbed as an inner sphere complex, while As(III) may be adsorbed as an inner or an outer neutral complex. Lafferty and Loeppert (2005) found that MMA and As(V) exhibit high adsorption affinities on both goethite and ferrihydrite from pH 3 to 10, whereas DMA is adsorbed only at pH values below 8 by ferrihydrite and below 7 by goethite. Furthermore, the soil characteristics also largely influence the geochemistry, concentrations, and mobility of As in soil. In this study, exogenous MMA and DMA were easily converted into As(V) (Figures 3b, 3c). Therefore, the adsorption-desorption in the soil was very complicated, and the changes in the MMA, DMA, and As(V) concentrations in the soil extracts were the combined effects of speciation transformation and adsorption-desorption. Although no speciation transformation of exogenously added As(V) in soil was found (Figure 3a), it could occur when the environmental conditions are correct (Yan et al. 2000, Balasoju et al. 2001). Therefore, it is necessary to take As speciation transformation into account when studying the adsorption-desorption of As in the future.

Additionally, the As speciation transformation in soil also largely influenced the environmental toxicity of As, which varies depending upon its chemical state. In general, inorganic forms as As(V) and As(III) are more toxic than organic

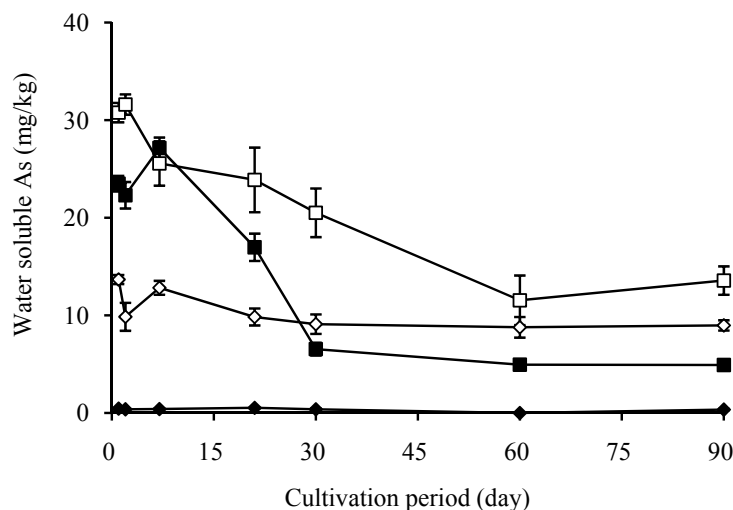


Figure 4. The changes in the total arsenic concentrations in soil extracts with increasing cultivation time. The line with the hollow squares, solid squares, hollow diamonds, and solid diamonds represent the soils with added MMA, DMA, and As(V) and the control soil, respectively. The error bars indicate the standard deviation of four replicates

complexes such as MMA and DMA (Alvarez et al. 2006). However, differences in As speciations can result in different fates and behaviors of As in soils (Huang and Matzner 2007a,b). High mobility of As in soil might indicate a risk of plant uptake and transfer to surface water by superficial flow under heavy rain events. In this study, the transformation of exogenously added MMA and DMA into As(V) might increase the toxicity of As in soil to some extent, and the subsequent effect on soil-plant transfer will be summarized in a further study.

Total arsenic concentration varies in soil extracts. The results from Figure 4 showed that with the cultivation time extending, the total As concentrations in all soil extracts first decreased and then remained constant after a cultivation period of 30–60 days. This result can be explained by the fact that when different speciation of As was added to soil, speciation transformation and adsorption-desorption occurred, which ultimately lead to the decrease in the concentration of soluble total As. Furthermore, the As concentrations were kept constant with 6.55 and 11.55 mg/kg in the aqueous extracts of soil to which DMA and MMA had been added after cultivated for 30 and 60 days, respectively. However, combining the results from As speciation transformation outlined above, we could find that, although the total As concentrations remained constant in these treatments, the As speciation transformation of MMA or DMA into As(V) in soil still occurred. Therefore, to achieve equilibrium a longer cultivation time is needed. Our results provide insight into the preparation and use of artificially As-contaminated soil in research. When exogenous As is added to soil to mimic artificially As-contaminated soil, attention should be focused on the variations in the total As concentration in soil extracts and on the possible changes in As speciation present, and the latter might need a longer time to reach equilibrium. Insufficient cultivation and preparation of artificially As-contaminated soil may influence the research results. In addition, when exogenous As(V) or DMA was added to soil and cultivated for 1 day, the total As concentrations were 13.679 or 23.493 mg/kg, respectively, which accounted for 45.6% or 78.3% of the original As concentration of 30 mg/kg. It is very likely that exogenous As(V) and DMA might be promptly adsorbed by the soil. This result is inconsistent with the results from Takamatsu et al. (1982). However, the total As concentration in the treatment of added MMA was 30.778 mg/kg, which was still equivalent to

the original As concentration. It is possible that the adsorption of MMA was more difficult than that of As(V) or DMA in fluvo-aquic soils and the details need to be further studied.

In conclusion, when exogenous As(V), MMA, or DMA was added to soil, speciation transformation and adsorption-desorption of As occurred simultaneously. Both processes interacted and cooperated until the final equilibrium was reached. In further studies, additional attention should be paid to speciation transformation when evaluating the adsorption-desorption of As. Sufficient cultivation time is also needed for experiments involving artificially As-contaminated soil.

REFERENCES

- Alvarez R., Ordóñez A., Loredó J. (2006): Geochemical assessment of an arsenic mine adjacent to a water reservoir (León, Spain). *Environmental Geology*, 50: 873–884.
- Álvarez-Benedí J., Bolado S., Cancillo I., Calvo C., García-Sinovas D. (2005): Adsorption-desorption of arsenate in three Spanish soils. *Vadose Zone Journal*, 4: 282–290.
- Balasoju C.F., Zagury G.J., Deschênes L. (2001): Partitioning and speciation of chromium, copper, and arsenic in CCA-contaminated soils: influence of soil composition. *Science of the Total Environment*, 280: 239–255.
- Cullen W.R., Reimer K.J. (1989): Arsenic speciation in the environment. *Chemical Reviews*, 89: 713–764.
- Fayiga A.O., Ma L.Q. (2006): Using phosphate rock to immobilize metals in soil and increase arsenic uptake by hyperaccumulator *Pteris vitata*. *The Science of the Total Environment*, 359: 17–25.
- Gong Z.L., Lu X.F., Ma M.S., Watt C., Le X.C. (2002): Arsenic speciation analysis. *Talanta*, 58: 7–96.
- Huang J.H., Matzner E. (2007a): Mobile arsenic species in unpolluted and polluted soils. *Science of the Total Environment*, 377: 308–318.
- Huang J.H., Matzner E. (2007b): Biogeochemistry of organic and inorganic arsenic species in a forested catchment in Germany. *Environmental Science and Technology*, 41: 1564–1569.
- Huang J.H., Scherr F., Matzner E. (2007): Demethylation of dimethylarsinic acid and arsenobetaine in different organic soils. *Water, Air and Soil Pollution*, 182: 31–41.
- Ko I., Kim J.Y., Kim K.W. (2004): Arsenic speciation and sorption kinetics in the As-humic acid system. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 234: 43–50.
- Kumaresan M., Riyazuddin P. (2001): Overview of speciation chemistry of arsenic. *Current Science*, 80: 837–846.
- Ladeira A.C.Q., Ciminelli V.S.T. (2004): Adsorption and desorption of arsenic on an Oxisol and its constituents. *Water Research*, 38: 2087–2094.
- Lafferty B.J., Loeppert R.H. (2005): Methyl arsenic adsorption and desorption behavior on iron oxides. *Environmental Science and Technology*, 39: 2120–2127.
- Lin Z., Puls R.W. (2000): Adsorption, desorption and oxidation of arsenic affected by clay minerals and aging process. *Environmental Geology*, 39: 753–759.

- Marin A.R., Masscheleyn P.H., Patrick W.H. (1993): Soil redox-pH stability of arsenic species and its influence on arsenic uptake by rice. *Plant and Soil*, 52: 245–253.
- Naidu R., Smith E., Huq S.M., Owens G. (2009): Sorption and bioavailability of arsenic in selected Bangladesh soils. *Environmental Geochemistry and Health*, 31: 61–68.
- Ochiai E.I. (1995): Toxicity of heavy metals and biological defense. *Journal of Chemical Education*, 72: 479–484.
- Simth E., Naidu R., Alston A.M. (2002): Chemistry of inorganic arsenic in soils: II. Effect of phosphorus, sodium, and calcium on arsenic sorption. *Journal of Environmental Quality*, 31: 557–563.
- Simth E., Naidu R., Alston A.M. (1998): Arsenic in the soil environment: A review. *Advances in Agronomy*, 64: 149–195.
- Takamatsu T., Aoki H., Yoshida T. (1982): Determination of arsenate, arsenite, monomethylarsenate and dimethylarsinate in soil polluted with arsenic. *Soil Science*, 133: 239–246.
- Tang X.Y., Zhu Y.G., Shan X.Q., McLaren R., Duan J. (2007): The ageing effect on the bioaccessibility and fraction of arsenic in soils from China. *Chemosphere*, 66: 1183–1190.
- Tokunaga S., Hakuta T. (2002): Acid washing and stabilization of an artificial arsenic-contaminated soil. *Chemosphere*, 46: 31–38.
- Turpeinen R., Kallio M.P., Kairesalo T. (2002): Role of microbes in controlling the speciation of arsenic and production of arsines in contaminated soils. *The Science of the Total Environment*, 285: 133–145.
- Yan X.P., Kerrich R., Hendry M.J. (2000): Distribution of arsenic (III), arsenic (V), and total inorganic arsenic in porewaters from a thick till and clay-rich aquitard sequence, Saskatchewan, Canada. *Geochimica et Cosmochimica Acta*, 62: 2637–3648.
- Zhang H., Selim H.M. (2006): Modeling the transport and retention of arsenic (V) in soils. *Soil Science Society of America Journal*, 70: 1677–1687.

Received on July 27, 2010

Corresponding author:

Prof. Xibai Zeng, Ph.D, Institute of Environment and Sustainable Development in Agriculture, Chinese Academy of Agricultural Sciences, Beijing, 100081, P.R. China
phone/fax: + 86 10 82105612, e-mail: zengxb@ieda.org.cn
