Arsenic compounds in the leaves and roots of radish grown in three soils treated by dimethylarsinic acid

P. Tlustoš[1], W. Gössler[2], J. Száková[1], D. Pavlíková[1], J. Balík[1]

[1]*Czech University of Agriculture in Prague, Czech Republic*
[2]*Institute for Analytical Chemistry, Karl-Franzens-University in Graz, Austria*

ABSTRACT

The effect of dimethylarsinic acid (DMA) on the growth of radish and the content of As compounds in roots and leaves of the radish were investigated. Radish was grown in pots in three soils (Fluvisols, Chernozems and Luvisols) amended with 20 mg As/kg of soil in form of DMA. Behavior and transformations of DMA in the soils differed depending on the individual soil type. In the first season, plants grew up at Luvisols only. In the second season the plants were able to grow at Luvisols and Chernozems, too. The roots and leaves of radish from Luvisols had DMA as the dominant arsenic compound present (~ 90% in the extract) in the first season. In the roots of the subsequently growing radish DMA accounted for 20% and arsenite for most of the total arsenic in the extract. In the leaves of the second-crop of radish DMA remained the dominant arsenic compound (~ 60% in the extract) with arsenate and arsenite for the remaining 40%. Roots and leaves of radish grown in Chernozems and Luvisols had a similar pattern of arsenic compounds. Soil properties significantly affected transformation of As species in the soils. At Fluvisols was the lowest As immobilization and about 98% was found as DMA after two years of experiments in the other two soils was higher As immobilization and DMA was recovered to inorganic As (V) – 31% in Luvisols and 78% in Chernozems.

Keywords: arsenate; arsenite; dimethylarsinic acid; HPLC-ICP-MS; plant-availability; radish; soil properties; extraction

Behavior and transformation of arsenic in soil and their dependence on different physical-chemical soil properties were widely investigated (O'Neill 1990). The influence of soil texture, pH, redox-potential, content of organic matter, inter-element interactions on arsenic sorption/desorption and plant-availability was already discussed (O'Neill 1990, Masscheleyn et al. 1991, McGeehan and Naylor 1994). The mobile portions of arsenic in soils are relatively low compared to most mobile elements such as cadmium and zinc. The concentration of isotopically exchangeable arsenic in 27 contaminated soils ranged between 1.2 and 19% of its total content (Brouwere et al. 2003). The range of extractable arsenic content from the set of 35 soil samples differing in physicochemical parameters and/or total arsenic content represented 0.06–1.45% for water extracts and 0.017–1.22% for 0.01 mol/l $CaCl_2$ extract (Száková et al. 2001). Water extractable contents in soils containing 5.3–1226 mg/kg of total arsenic ranged between 10 and 40 μg/kg and at highly contaminated pasture soil (2035 mg/kg) reached to 8.48 mg/kg (Baroni et al. 2004). However, only limited information can be found if detailed information concerning individual arsenic compounds in soil is needed. Only arsenate was found to be present in soil, which can be easily converted to arsenite under reducing soil (Masscheleyn et al. 1991, Marin et al. 1993, Bowell 1994). Small percentages of methylated arsenic compounds in soils were also reported (Bowell 1994). Soil amendment by arsenite, arsenate, dimethylarsinic acid (DMA) and methylarsonic acid (MA) before cultivation of Chinese brake (*Pteris vittata* L.) resulted in complete conversion of almost all the arsenic compounds to arsenate after harvest of fern plants (18 weeks). However, very small amounts of arsenite, MMA and DMA were detected in the soil solution treated with arsenite, MMA, and DMA (Tu et al. 2003). Fitz et al. (2003) cultivated *Pteris vittata* plants in rhizoboxes filled with soil containing 2270 mg As/kg. Dissolved organic carbon (DOC) concentrations in rhizosphere soil solution were increased by 86% and appeared to enhance total Fe solubility due to complexation reactions. Despite substantial removal of As by the fern, As was not significantly decreased in the rhizsophere soil solution after one cropping, apparently due to the large buffer capacity of the soil and possibly because of ion competition with DOC. However, the difference between 0.05 mol/l $(NH_4)_2SO_4$-extractable labile As in bulk and rhizosphere soil accounted for 8.9% of total As accumulated in the fern, indicating that As was mainly acquired from less available pools.

Supported by COST, Project OC 631.002, and AKTION Österreich-Tschechische Republik, Project 5w 12.

Assessment of As compounds revealed that only arsenate was present in bulk and rhizosphere soil solution. 80% of arsenate and small percentages of arsenite, MA and DMA in water and methanol-water extracts of soil containing 632 mg/kg of total arsenic was reported by Pizarro et al. (2003). In this case, extractability of arsenic by both water and methanol-water extracting agents reached up to 50% of total arsenic. However, freeze-dried soil sample kept frozen until extraction was analyzed instead of usually used air-dried soil sample. Moreover, soil physicochemical characteristics of soil studied by Pizarro et al. (2003) are not mentioned.

Phytoavailability and phytotoxicity of individual arsenic compounds in soils were summarized by Sheppard (1992). The dominant role of the soil properties and the source of arsenic are evident. Inorganic As was 5-fold more toxic in sandy and loamy soils than in clay soils. Inorganic and waste forms of As were less toxic as compared to organic sources. In the opposite, if rice was planted in liquid soil suspensions amended by dimethylarsinic acid (DMA), this compound was less plant – available then inorganic ones (Marin et al. 1992). Methylarsonic acid (MA) was in this case two times more phytoavailable for rice then the inorganic As forms and increased with decreasing pH and redox-potential (Marin et al. 1992, 1993).

Concerning plant-availability of As, the influence of arsenic compounds on plant yield and/or total arsenic contents are usually evaluated (O'Neill 1990, Marin et al. 1992, 1993, Jiang and Singh 1994) and very rarely the individual arsenic species. In tissue culture of periwinkle grown in medium containing arsenate the presence of arsenate, arsenite and low levels of MA and DMA was determined in cell extracts (Cullen and Reimer 1989). These results suggested that higher plants are able to methylate inorganic arsenic compounds. More detailed evaluation of arsenic compounds in soils and plants could elucidate the biological processes in soil-plant system and describe the toxic effects of arsenic in soil.

In this study the behavior of DMA added to three soils different in their physical-chemical properties, its phytoavailability for radish (*Raphanus sativus* L.) and distribution of arsenic compounds in radish were evaluated.

MATERIAL AND METHODS

Pot experiment

Three types of soil (Luvisols, Fluvisols, Chernozems) with the properties summarized in Table 1 were applied. Aliquots (5.0 kg) of these soils were placed into plastic pots. To each aliquot was added an aqueous solution (10.0 mg As/ml) dimethylarsinic acid in the rate representing 20 mg As/kg of soil. The mixture was shaken thoroughly. Radish seeds (cv. Duo) were sowed into the three soils immediately after amendment with dimethylarsinic acid. The soils were watered with deionized water to keep soil moisture at 60% of its maximal water holding capacity. The radishes were harvested 43 days after sowing. The radish roots were freed from adhering soil by washing with deionized water. The leaves were separated from the roots with a stainless steel knife. Leaves and roots were dried at 60°C to constant mass and then separately ground to a fine powder in a mixer. The dry powders were sieved (< 0.1 mm). Soil samples were taken immediately after the harvest of the radishes from the bulk, and then air dried at 20°C ground in a mortar and passed through a 2-mm plastic sieve. The bulk of the soil was dried in the air at room temperature and stored in plastic bags until another batch of radishes was grown subsequently in these soils one year later under conditions identical to the first growth experiment. The second batch of radishes was harvested 49 days after sowing of the seeds.

Sample decomposition

Dry ashing. An aliquot (~ 1 g) of the dried and powdered leaves or roots were weighed to 1 mg into a borosilicate glass test-tube and decomposed in a mixture of oxidizing gases ($O_2 + O_3 + NO_x$) at 400°C for 10 hours in Apion Dry Mode Mineralizer

Table 1. The main characteristics of the experimental soils

Soil	pH (KCl)	C_{ox} (%)	CEC (mmol/kg)	Texture (%)			As_{total} (mg/kg)	
				clay	silt	sand	mean	*SD*
Luvisols	6.70	1.37	151	26	35	39	15.1	2.5
Fluvisols	6.40	0.70	95	12	6	82	4.6	1.0
Chernozems	7.06	1.82	214	34	32	34	21.4	2.0

SD – standard deviation

(Tessek, Czech Republic) (Miholová et al. 1993). The ash was dissolved in 25 ml of 1.5% HNO_3 (electronic grade purity, Analytika Ltd., Czech Republic), and kept in glass tubes until measurement. Aliquots of the certified reference material RM 12-02-03 Lucerne was mineralized under the same conditions for quality assurance of the analytical data. In this material containing 0.263 ± 0.007 mg As/kg was found 0.257 ± 0.056 mg As/kg. In the case of soil, total arsenic contents were determined in digests obtained by two-step decomposition as follows: 0.5 of sample was decomposed by dry ashing in a mixture of oxidizing gases ($O_2 + O_3 + NO_x$) in an Apion Dry Mode Mineralizer (Tessek, CZ) at 400°C for 10 h; the ash was then decomposed in a mixture of HNO_3 + HF, evaporated to dryness at 160°C and dissolved in diluted *aqua regia* (Száková et al. 2000). Certified reference material RM 7003 Silty Clay Loam (Analytika, CZ) was used for quality assurance of the analytical data. In this material containing 16.7 ± 3.1 mg As/kg was found 19.0 ± 4.0 mg As/kg.

Pressurized wet ashing. An aliquot (~ 250 mg) of the dried and powdered leaves or roots were weighed to 0.1 mg into a Teflon® digestion vessel. Concentrated nitric acid (3.0 ml) (Merck p.a. Nr. 100456), purified in an all-quartz subboiling distillation unit, and 30% H_2O_2 (1.0 ml) (Merck Suprapur® Nr. 107298) were added. The mixture was heated in an MLS-1200 Mega (MLS GmbH, Leutkirch, Germany) microwave assisted wet digestion system (Gössler et al. 1997a). After cooling the digest was quantitatively transferred into a 50-ml polypropylene tube. An indium solution (100 µl, 10 mg In/l) was added. The tube was filled to the mark with Milli-Q water. Aliquots of the RM 12-02-02 Green Algae reference material were mineralized under the same conditions. In this material containing 0.076 mg As/kg was found 0.079 ± 0.034 mg As/kg.

Extraction of arsenic compounds from plant material

Aliquots (~ 500 mg) of the dried and powdered leaves or roots weighed to 0.1 mg were placed into 50-ml screw-capped polyethylene tubes. A methanol/water mixture (20 ml, 8 + 2 v/v) was added. The closed tubes were fastened to the arms of a cross-shaped rotor and turned top over bottom at 45 rpm for 14 hours. The mixtures were then centrifuged for 10 min at 3000 rpm the supernatant was transferred to a 250-ml round bottom flask and evaporated to dryness in a Rotavapor at room temperature under an aspirator vacuum. The residue was treated with 10 ml Milli-Q water. The resulting solution was filtered through a 0.22 µm cellulose-nitrate ester filter (Millex-GS, Milipore, Bedford, MA, USA). Aliquots of this solution (100 µl) were chromatographed.

Extraction of arsenic compounds from soils

Aliquots (~ 1000 mg) of the dried soil samples were extracted with (i) methanol/water (20 ml, 8 + 2 v/v); (ii) Milli-Q water (1 + 19, w/v); (iii) 0.1 mol/l aqueous $NH_4H_2PO_4$ solution at pH 6.0 (1 + 19, w/v) for 14 hours as described for the plant material. The methanol/water mixture was evaporated to dryness, redissolved in water and filtered as described above. The water and aqueous $NH_4H_2PO_4$ solution extractants were centrifuged for 10 min at 3000 rpm, filtered through 0.22 µm cellulose-nitrate ester filters and chromatographed.

Determination of total arsenic content in the digests

Atomic absorption spectrometry: total arsenic in the roots and leaves decomposed by dry ashing procedure was determined by hydride generation atomic absorption spectrometry (Varian SpectrAA 300, Australia, equipped with continuous hydride generator VGA-76).

Inductively coupled plasma mass spectrometry: total arsenic was determined in the diluted wet digests of leaves and roots as well as in the methanol/water, water and aqueous $NH_4H_2PO_4$ solution extracts of soil and plant biomass with an inductively coupled plasma mass spectrometer VG Plasma Quad 2 Turbo Plus, VG Elemental, UK, equipped with a Fassel-type torch, a Gilson Minipuls-3 peristaltic pump and a Meinhard TR-30-A3 nebulizer (Gössler et al. 1997a).

Chromatographic system

The high-performance liquid chromatography system for the separation of the arsenic compounds consisted of a Hewlett Packard 1050 solvent delivery unit (Germany) and a Rheodyne 9125 six-port injection valve (USA) equipped with a 100 µl loop. The arsenic compounds were separated on a Hamilton PRP-X100 (USA) anion-exchange column (250 mm × 4.1 mm i.d., spherical 10-µm particles of a styrene-divinylbenzene copolymer with trimethylammonium exchange sites). An aqueous 0.020 mol/l $NH_4H_2PO_4$ solution at pH 6.0 served as mobile phase at a flow rate of 1.5 ml/min. The column effluent was routed to a hydraulic high-pressure nebulizer (HHPN) through a 700 mm PEEK (poly-ether-ether-ketone) capillary (0.13 mm i.d.).

The aerosol produced by the HHPN was introduced into the plasma of the ICP-MS (Gössler et al. 1997b) for arsenic – specific detection.

RESULTS AND DISCUSSION

Soils

The proportion of arsenic compounds in the soil extracts was dependent on both soil properties and the extracting medium used (Table 2). Total concentrations in extracts decreased in order phosphate buffer > water > methanol/water. On the contrary, Pizarro et al. (2003) reported comparable extractability of arsenic from soil by both water and methanol-water (1:1) extracting agents reaching up to 50% of total arsenic. As mentioned above, they analysed highly contaminated soil after different sample pre-treatment without detailed information concerning physico-chemical properties of the soil. The ability of organic solvents to remove small quantities of organically bound soil elements was already described by Beckett (1989). Phosphate solutions are effective for extraction of specifically sorbed As from mineral surfaces. At equal concentrations, phosphates in soil can release arsenates from the adsorption sites because of their smaller size and higher charge density of phosphates (Wenzel et al. 2001). Smith et al. (2002) observed that the presence of P (0.16 mmol/l) greatly decreased arsenate sorption by soils containing low amounts of Fe oxides, indicating competitive adsorption between P and As (V) for sorption sites. In contrast, the presence of a similar amount of P had little effect on the amount of As (V) adsorbed by soils with high Fe content (> 800 mmol/kg). These authors already demonstrated that As (V) sorption substantially decreased from 0.63 to 0.37 mmol/kg as P concentration was increased from 0.16 to 3.2 mmol/l. This suggests an increased competition between P and As (V) for soil sorption sites, through neither the higher affinity nor the effect of mass action of the increasing concentration of P in solution. Thus, a higher efficiency of phosphate buffer on arsenic release from the soil compared to water and methanol/water was expectable. Pure water belongs to the extractants representing approximately the element fraction present in soil solution and the most readily plant available, comparable to mild soil extractants based on unbuffered salt solutions (Száková et al. 2001).

The type of soil dominantly influenced the behavior of DMA in soil and the proportions of individual As compounds in soil were approximately confirmed by all three extractants used (Table 2). The transformations of DMA in experimental soils can be characterized as follows: (i) Luvisols: In this soil, the lowest total extractable As contents in both seasons were determined and a fall of As extractability in 2nd season was observed. The ratio of arsenic species was stable for all the growing periods and DMA remained mostly as the dominant As compound in both growing seasons. In untreated soil containing 15.1 ± 2.5 mg/kg of total arsenic, arsenate was the dominant arsenic compound in water extract (91%) and arsenite (6%) and DMA (3%) were also present (Tlustoš et al. 2002). (ii) Chernozems: In this soil, decreasing As extractability in 2nd season was observed as in the case of Luvisols. However, DMA was decomposed and replaced by As (V) and in lesser extent by MA after 2nd growing season. The removal of arsenic from the soil can be also a result of soil microbial activity, as well. Soil bacteria are able to reduce arsenate to arsenite followed by methylation to dimethylarsine. Fungi are also able to convert both organic and inorganic arsenic compounds into volatile methylarsines (Baker et al. 1983, Frankenberger and Losi 1995). The effect of soil

Table 2. The total extractable soil As contents (As_{tot}) by three different extractants (mg/kg) and distribution of As species in the extracts (%) of DMA amended soils

Soil/season	Water					Methanol/water					Phosphate buffer				
	As_{tot}	As (III)	As (V)	MA	DMA	As_{tot}	As (III)	As (V)	MA	DMA	As_{tot}	As (III)	As (V)	MA	DMA
Fluvisols/1st	12.5	0.5	1.1	a	98	4.23	0.6	0.3	a	99	16.5	0.3	2.2	a	97
Fluvisols/2nd	12.2	0.7	0.9	a	98	3.66	0.9	0.4	a	99	15.4	0.5	2.5	a	98
Chernozems/1st	10.2	0.9	14	3.1	82	0.26	7.0	5.9	a	87	20.6	0.2	51	a	49
Chernozems/2nd	4.0	0.3	78	6.2	15	0.05	13	60	a	26	16.9	0.2	91	3.5	5.7
Luvisols/1st	4.9	0.5	22	4.4	73	0.19	6.9	9.4	a	84	14.6	a	53	4.0	43
Luvisols/2nd	3.6	0.7	31	4.5	63	0.09	17	6.6	a	76	10.7	0.4	68	3.8	28

a – compound not detected

Table 3. Average yield of dry biomass of radish per pot (g) and total arsenic contents (mg/kg) determined in individual treatments

Soil/season	Roots						Leaves					
	control			DMA amended			control			DMA amended		
	yield	As_{total}		yield	As_{total}		yield	As_{total}		yield	As_{total}	
		mean	*SD*		mean	*SD*		mean	*SD*		mean	*SD*
Fluvisols/1st	254	0.821	0.046	b	b	b	93	0.986	0.217	b	b	b
Fluvisols/2nd	180	0.451	0.040	b	b	b	72	0.863	0.106	b	b	b
Chernozems/1st	286	0.522	0.008	b	b	b	88	1.370	0.130	b	b	b
Chernozems/2nd	136	0.414	0.204	86	5.08	0.96	49	0.706	0.023	44	2.01	0.24
Luvisols/1st	290	0.248	0.063	124	4.87	2.20	96	0.604	0.006	43	4.75	0.42
Luvisols/2nd	182	0.628	0.047	212	6.88	1.19	55	0.850	0.022	64	1.76	0.01

b – plants not grown, *SD* – standard deviation

microbial activity can be expected predominantly at the organic matter-rich soils such as Chernozems. (iii) Fluvisols: The highest total extractable As contents in both seasons because of lack of sorption sites and/or low content of organic matter in this soil were observed in this case. In soils with low content of oxide minerals was observed three times lower sorption of arsenate compared to highly oxidic soils (Smith et al. 1999). Almost all the arsenic present in extracts was DMA (98%) without any changes between growing seasons.

Plants

The application of DMA to the soil strongly affected the radish growth. In the first season, the plants grown up in Luvisols had only a reduced yield of both roots and leaves (Table 3). The suppressed growth of radish (Carbonell-Barrachina et al. 1999a) and turnip (Carbonell-Barrachina et al. 1999b) in soil-less culture after the addition of DMA into the growing medium was already described. As confirmed by Tlustoš et al. (1998), in the second growing season, the plants died only in Fluvisols while in Chernozems the growth was reduced and in Luvisols not affected. They reported that the total arsenic contents in plants varied between 5.9–7.6 mg/kg (roots) and 4.0–6.0 mg/kg (leaves) in the case of Luvisols amended by arsenite, arsenate and DMA in the rate of 20 mg/kg of the soil while in control sample at Luvisols the total arsenic content did not exceed 0.5 mg/kg (0.43 mg/kg in leaves and 0.36 mg/kg in roots). Similar values were determined in this experiment as indicated in Table 3. The methanol/water extractant was able to release a max. 77% of total arsenic from roots and 59% from leaves and extractability of As decreased with decreasing DMA concentration in extracts (Table 4).

The results of the determination of arsenic species in plants are summarized in Table 4. The roots and leaves of radish from Luvisols in 1st season had DMA as the dominant arsenic compound present (88% in the extract). In the roots of the radish grown in the 2nd season, DMA accounted for 20% while 64% of extractable As was found as arsenite, but in leaves DMA remained as the dominant arsenic compound (70% in the extract). Our previous results (Tlustoš et al. 2002) suggested that arsenite was the dominant compound in radish roots planted at the untreated soil while in leaves

Table 4. The total extractable (methanol/water) As plant contents (As_{tot}) in roots and leaves of radish (mg/kg) and distribution of As compounds in the extracts of individual plant samples (%)

Soil/season	Roots					Leaves				
	As_{tot}	As (III)	As (V)	MA	DMA	As_{tot}	As (III)	As (V)	MA	DMA
Chernozems/2nd	3.26	59	8	4	29	1.22	27	11	5	57
Luvisols/1st	4.74	5	2	4	89	3.56	3	6	3	88
Luvisols/2nd	4.58	64	14	3	19	1.14	14	11	5	70

most of present arsenic was arsenate. DMA was also detected in both plant tissues, 17% in roots and 18% in leaves. Similarly, Carbonell et al. (1998) determined increased translocation of DMA to shoots of marsh grass while inorganic arsenicals and MA were mainly accumulated in roots. Vela et al. (2001) determined inorganic As (III) and As (V) as the only species in carrot root samples, as well. Roots and leaves of radish grown in Chernozems and Luvisols in 2nd season had a similar pattern of arsenic compounds.

These results suggested the important role of the plant in the transformation of plant-available arsenic compounds from the soil. Because the dominant arsenic compound in soil under aerobic conditions is arsenate (Masscheleyn et al. 1991, Marin et al. 1993, Bowell 1994) the immobilization of a high amount of DMA seems to be a long-term and difficult process. In Fluvisols, the soil with poor sorption capacity and low content of clay particles, DMA remained in plant-available state in phytotoxic contents. Chernozems and Luvisols were able to decrease the phytotoxic levels of DMA via adsorption, volatilization and/or decomposition so that the radish growth was possible. However, the adsorption characteristics of DMA on iron oxide minerals (goethite and ferrihydrite) showed lower adsorption affinity as compared to As (V) and MA (Lafferty and Loeppert 2003).

The results of distribution of arsenic compounds in plants suggested in agreement with Cullen and Reimer (1989) the ability of plants to transform available arsenic compounds. The differences in plant-availability of individual As compounds by individual parts of plants are also evident. After immobilization of toxic concentrations of DMA added to soil, arsenite becomes to be the main compound in roots while DMA remains as the dominant As specie in leaves without respect to the distribution of arsenic compounds in soils.

REFERENCES

Baker M.D., Innis W.E., Mayfield C.I., Wong P.T.S., Chau Y.K. (1983): Effect of pH on the methylation of mercury and arsenic by sediment microorganisms. Environ. Technol. Lett., *4*: 89–100.

Baroni F., Boscagli A., DiLella L.A., Protano G., Riccobono F. (2004): Arsenic in soil and vegetation of contaminated areas in southern Tuscany (Italy). J. Geochem. Explor., *81*: 1–14.

Beckett P.H.R.T. (1989): The use of extractants in studies on trace metals in soils, sewage sludges and sludge-treated soils. Adv. Soil Sci., *9*: 143–176.

Bowell R.J. (1994): Sulphide oxidation and arsenic speciation in tropical soils. Environ. Geochem. Health, *16*: 84.

Brouwere K.D.E., Smolders E., Merckx R. (2003): Soil properties affecting solid-liquid distribution of As (V) in soils. Eur. J. Soil Sci., *55*: 165–173.

Carbonell A.A., Aarabi M.A., DeLaune R.D., Gambrell R.P., Patrick W.H. (1998): Arsenic in wetland vegetation: Availability, phytotoxicity, uptake and effects on plant growth and nutrition. Sci. Tot. Environ., *217*: 189–199.

Carbonell-Barrachina A.A., Burlo F., Lopez E., Martinez-Sanchez F.J. (1999a): Arsenic toxicity and accumulation in radish as affected by arsenic chemical speciation. Environ. Sci. Health, *34*: 661–679.

Carbonell-Barrachina A.A., Burlo F., Valero D., Lopez E., Martinez-Romero D., Martinez-Sanchez F.J. (1999b): Arsenic toxicity and accumulation in turnip as affected by arsenic chemical speciation. Agr. Food Chem., *47*: 2288–2294.

Cullen W.R., Reimer K.J. (1989): Arsenic speciation in the environment. Chem. Rev., *89*: 713–764.

Fitz W.J., Wenzel W.W., Zhang H., Nurmi J., Štípek K., Fischerová Z., Schweiger P., Köllensperger G., Ma L.Q., Stingeder G. (2003): Rhizosphere characteristics of the arsenic hyperaccumulator *Pteris vittata* L. and monitoring of phytoremoval efficiency. Environ. Sci. Technol., *37*: 5008–5014.

Frankenberger W.T., Jr., Losi M.E. (1995): Applications of bioremediation in the cleanup of heavy metals and metalloids. In: Skipper H.D., Turco R.F. (eds.): Bioremediation: Science and applications. Soil Sci. Soc. Am., Madison: 173–210.

Gössler W., Lintschinger J., Száková J., Mader P., Kopecký J., Doucha J., Irgolic K.J. (1997a): Chlorella sp. and arsenic compounds: An attempt to prepare an algal reference material for arsenic compounds. Appl. Organometall. Chem., *11*: 57–66.

Gössler W., Maher W., Irgolic K.J., Kühnelt D., Schlagenhaufen C., Kaise T. (1997b): Arsenic compounds in a marine food chain. Fresen. J. Anal. Chem., *359*: 434–437.

Jiang Q.Q., Singh B.R. (1994): Effect of different forms and sources of arsenic on crop yield and arsenic concentration. Water Air Soil Pollut., *74*: 321–343.

Lafferty B.J., Loeppert R.H. (2003): Mono- and dimethyl arsenic(V) adsorption on iron oxides. Proc. 7th Int. Conf. Biochemistry of trace elements, Vol. 2, Uppsala: 82–83.

Marin A.R., Masscheleyn P.H., Patrick W.H., Jr. (1992): The influence of chemical form and concentration of As on rice growth and tissue arsenic concentration. Plant Soil, *139*: 175–183.

Marin A.R., Masscheleyn P.H., Patrick W.H., Jr. (1993): Soil redox-pH stability of arsenic species and its influence on arsenic uptake by rice. Plant Soil, *152*: 245–253.

Masscheleyn P.H., Delaune R.D., Patrick W.H., Jr. (1991): Effect of redox potential and pH on arsenic speciation and solubility in a contaminated soil. Environ. Sci. Technol., *25*: 1414–1419.

McGeehan S.L., Naylor D.V. (1994): Sorption and redox transformation of arsenite and arsenate in two flooded soils. Soil Sci. Soc. Am. J., *58*: 337–342.

Miholová D., Mader P., Száková J., Slámová A., Svatoš Z. (1993): Czechoslovakian biological reference materials and their use in the analytical quality assurance system in a trace element laboratory. Fresen. J. Anal. Chem., *345*: 256–260.

O'Neill P. (1990): Arsenic. In: Alloway B.J. (ed.): Heavy metals in soils. Blackie, London: 83–99.

Pizarro I., Gómez M., Cámara C., Palacios M.A. (2003): Arsenic speciation in environmental and biological samples. Extraction and stability studies. Anal. Chim. Acta, *495*: 85–98.

Sheppard S.C. (1992): Summary of phytotoxic levels of arsenic. Water Air Soil Pollut., *64*: 539–550.

Smith E., Naidu R., Alston A.M. (1999): Chemistry of arsenic in soils: I. Sorption of arsenate and arsenite by four Australian soils. J. Environ. Qual., *28*: 1719–1726.

Smith E., Naidu R., Alston A.M. (2002): Chemistry of arsenic in soils: II. Effect of phosphorus, sodium, and calcium on arsenic sorption. J. Environ. Qual., *31*: 557–563.

Száková J., Tlustoš P., Balík J., Pavlíková D., Balíková M. (2000): Efficiency of extractants to release As, Cd, and Zn from main soil compartments. Analusis, *28*: 808–812.

Száková J., Tlustoš P., Balík J., Pavlíková D., Balíková M. (2001): Porovnání slabých extrakčních činidel pro stanovení rostlinou přijatelného podílu As, Cd a Zn v půdě. Chem. Listy, *95*: 179–183.

Tlustoš P., Balík J., Száková J., Pavlíková D. (1998): The accumulation of arsenic in radish biomass when different forms of As were applied in the soil. Rostl. Výr., *44*: 7–13.

Tlustoš P., Gössler W., Száková J., Balík J. (2002): Arsenic compounds in leaves and roots of radish grown in soil treated by arsenite, arsenate and dimethylarsinic acid. Appl. Organometall. Chem., *16*: 216–220.

Tu C., Ma L.Q., Zhang W., Cai Y., Harris W.G. (2003): Arsenic species and leachability in the fronds of the hyperaccumulator Chinese brake (*Pteris vittata* L.). Environ. Pollut., *124*: 223–230.

Vela N.P., Heitkemper D.T., Stewart K.R. (2001): Arsenic extraction and speciation in carrots using accelerated solvent extraction, liquid chromatography and plasma mass spectrometry. Analyst, *126*: 1011–1017.

Wenzel W.W., Kirchbaumer N., Prohaska T., Stingeder G., Lombi E., Adriano D.C. (2001): Arsenic fractionation in soils using an improved sequential extraction procedure. Anal. Chim. Acta, *170*: 1–15.

Received on April 29, 2004

ABSTRAKT

Sloučeniny arzenu v listech a kořenech ředkvičky pěstované na třech půdách ošetřených kyselinou dimetylarzeničnou

Byl studován vliv přídavku kyseliny dimetylarzeničné (DMA) do půdy na růst ředkviček a na obsah sloučenin arzenu v kořenech a v listech ředkviček. Ředkvičky byly pěstovány v nádobách na třech půdách (fluvizem, černozem a luvizem), které byly jednorázově kontaminovány DMA v množství reprezentujícím 20 mg As/kg půdy. Chování a přeměna DMA v půdě se významně lišily v závislosti na použitém půdním typu. V prvním kultivačním cyklu rostly rostliny pouze na luvizemi, v druhém kultivačním cyklu pak nejen na luvizemi, ale i na černozemi. V prvním kultivačním cyklu byla v kořenech i listech ředkviček pěstovaných na luvizemi dominantní sloučeninou DMA (~ 90 % v extraktu). V druhém kultivačním cyklu pak obsah DMA v kořenech představoval pouze 20 % celkového extrahovatelného arzenu a dominantní sloučeninou zde byl arzenitan. V listech pak DMA zůstala i v druhém kultivačním cyklu dominantní sloučeninou (~ 60 % v extraktu), zatímco zbývajících 40 % připadlo na arzenitan, arzeničnan a v menší míře také kyselinu monometylarzeničnou (MA). Distribuce sloučenin arzenu v kořenech a listech ředkviček pěstovaných na černozemi byla srovnatelná s luvizemí. Půdní vlastnosti měly významný vliv na transformaci sloučenin arzenu v půdě. Na fluvizemi byla imobilizace a transformace přidané DMA velmi nízká, takže přibližně 98 % extrahovatelného As reprezentovala právě DMA, a to i po skončení druhého kultivačního cyklu. Na ostatních dvou půdách byla zaznamenána vyšší míra imobilizace As a přidaná DMA byla transformována na As (V) – 31% na luvizemi a 78% na černozemi.

Klíčová slova: arzenitan; arzeničnan; kyselina dimetylarzeničná; HPLC-ICP-MS; přijatelnost rostlinami; ředkvičky; půdní vlastnosti; extrakce

Corresponding author:

Prof. Ing. Pavel Tlustoš, CSc., Česká zemědělská univerzita v Praze, 165 21 Praha 6-Suchdol, Česká republika
phone: + 420 224 382 733, fax: + 420 234 381 801, e-mail: tlustos@af.czu.cz