Mercury distribution and mobility in contaminated soils from vicinity of waste incineration plant

A. Šípková[1], J. Száková[1], P. Coufalík[2], O. Zvěřina[2], L. Kacálková[3], P. Tlustoš[1]

[1]Department of Agroenvironmental Chemistry and Plant Nutrition, Faculty of Agrobiology, Food and Natural Resources, Czech University of Life Sciences Prague, Prague, Czech Republic
[2]Department of Chemistry, Faculty of Science, Masaryk University, Brno, Czech Republic
[3]Department of Biology, Faculty of Science, University of Hradec Králové, Hradec Králové, Czech Republic

ABSTRACT

The potential bioavailability of Hg from soil might be estimated by a variety of chemical extraction procedures, differing in the extraction agent, its concentration, the sample weight, and the time of extraction. In this study, a comparative analysis of several extraction methods, commonly used for obtaining the mobile and potentially mobilizable phase of the mercury was carried out. Concentrated HNO_3, 0.01 mol/L $Na_2S_2O_3$, 0.05 mol/L EDTA and 0.11 mol/L CH_3COOH were used as the single extraction agents. Moreover, the sequential extraction was performed. This procedure involved the following fractions: water soluble Hg, Hg extracted in acidic conditions, Hg bound to humic substances, elemental Hg and mercury bound to complexes, and residual Hg. The results showed that even strong acid HNO_3 is unable to release the mercury tightly bound to the soil matrix. This particular method with microwave digestion is commonly used for the estimation of anthropogenic pollution. Conversely, the lowest mercury yield was obtained using the acetic acid as the single extraction agent. In this case, the concentrations were below 0.15% of the total Hg content, which is a proportion generally defined as bioavailable to plants.

Keywords: bioavailability; extraction methods; inductively coupled plasma mass spectroscopy; advanced mercury analyzer AMA-254

Mercury can be released from soil by different extraction procedures. These procedures enable the determination of particular species present, the varying amounts of Hg bound to soil, and also the bioavailability and toxicity. The least tightly bound water-soluble fraction is obtained by the simple extraction using deionised water (Rodrigues et al. 2010). It estimates Hg portion present in soil pore water. This fraction of mercury is usually not in the form of the water-soluble ionic species but as species bound to dissolved organic matter; nevertheless, not directly on carbon (Biester and Scholz 1996). The application of diluted CH_3COOH as an extraction agent belongs to the methods simulating approximately composition of the soil solution similarly as other mild extraction procedures such as $CaCl_2$ solution (Novozamsky et al. 1993). The extraction solutions based on the chelating agents such as EDTA or DTPA represent another more efficient possibility. These agents are able to displace metals from insoluble organic or organometallic complexes in addition to those adsorbed on inorganic soil components (Rao et al. 2008). The other species are mercury fractions bound on iron sulphides, manganese hydroxides and carbonates, and Hg bound to the minerals. This strongly bound mercury species can be obtained by acids, e.g. HCl (Lechler et al. 1997).

Supported by the Czech Science Foundation, Grant No. P503/12/0682 and by the Czech University of Life Science Prague, Project No. 21140/1313/3130.

In soil, mercury can be bound very tightly to sulphur forming the insoluble HgS (Boszke et al. 2008). This phase of mercury can be obtained either by aqua regia extraction in a microwave oven (Fernándes-Martínez and Rucandio 2003), or using the saturated Na_2S solution from the residue remaining after the extraction procedures (Revis et al. 1989). The effect of the concentration of $Na_2S_2O_3$ on the extraction efficiency was in detail studied by Issaro et al. (2010).

The proportion of Hg, which is not firmly bound to the silicate matrix of soil, is often obtained by using HNO_3 as an extraction agent (Reis et al. 2010). The mercury concentration in these extracts enables an estimation of the amount of Hg from anthropogenic sources. In some cases, concentrated nitric acid combined with HCl (Teršič et al. 2011) or H_2SO_4 (Mailman and Bodaly 2005) is employed for total mercury content determination. It might also be used in sequential extraction procedures to obtain elemental Hg (Bloom et al. 2003). Sequential extractions are suitable methods for the mercury speciation analysis of solid samples. However, there is no universal sequential extraction concerning the individual Hg fraction determination. Several approaches were demonstrated by many authors (Renneberg and Dudas 2001, Sánchez et al. 2005, Han et al. 2006, Liu et al. 2006).

In this work, four various extraction agents as well as sequential extraction were applied for the assessment of Hg mobility and fractionation in one anthropogenically contaminated soil.

MATERIAL AND METHODS

Samples. Ten soil samples were collected from the former waste incineration plant in the suburb of Hradec Králové, Czech Republic. The selection of sampling sites was based on the experiment of Kacálková et al. (2009). Samples were collected in the vicinity of points 3 and 5. The plot 3 represented the average values of contamination (our samples 1–5), while extreme Hg content was measured in the plot 5 closer to the plant (our samples 6–10). Samples were taken from the top layer (0–30 cm), air-dried, sieved < 2 mm and kept at 4°C for several weeks. Following characteristics of soil were measured: pH_{CaCl_2} (Novozamsky et al. 1993), organic matter content (Sims and Haby 1971) and cation exchange capacity (ISO 1994). Total content of S was determined by X-ray fluorescence spectrometry (Spectro IQ, Kleve, Germany), mercury analyser AMA-254 (LECO model, Altec, Czech Republic, Plzeň) was used for total Hg determination. All experiments were carried out in three repetitions.

Extractable fractions of mercury. Four extraction agents HNO_3, $Na_2S_2O_3$, EDTA, and CH_3COOH were used to determine the mobile and mobilizable phases of Hg. For determination of potentially mobilizable mercury portions, 0.25 g of each sample was decomposed in 5 mL of concentrated HNO_3. The reaction mixture was digested at 280°C during 75 min by using microwave heating in MLS ultraCLAVE IV system (Milestone, Leutkirch im Allgäu, Germany) and then milli-q water was added to a final volume of 50 mL. The mild extraction procedures were performed as follows: (i) $Na_2S_2O_3$ extraction proceeded overnight in 10 mL of 0.01 mol/L solution, which was added to 1 g of the sample; (ii) 0.05 mol/L EDTA was adjusted with NaOH to pH 7. Subsequently, 1 g of soil was added to 10 mL of extraction solution and shaken for 1 h; (iii) 0.5 g of sample was added to 10 mL of 0.11 mol/L solution of CH_3COOH and shaken overnight. Subsequently, all the samples were centrifuged for 10 min at 3000 rpm.

Hg content in all extracts was measured by inductively coupled plasma mass spectrometry (Agilent 7700x, Agilent Technologies Inc., Santa Clara, USA). The isotope Hg(202) was measured and Pt(195) was used as an internal standard in concentration 10 µg/L. As reference material, San Joaquin Soil (SRM 2709) was utilized (theoretical Hg content is 1.4 ± 0.08 mg/kg; obtained recovery was 98%).

Sequential extraction. The sequential extraction procedure was designed by modifying the existing extraction schemes (Bloom et al. 2003, Boszke et al. 2008). 0.1 g of each sample was leached into 10 mL of chloroform, shaken for 3 h and centrifuged. This step was considered as F0 and residue obtained after the extractions was used in the next procedure. The soil/liquid ratio was the same for all extraction reagents. The extraction procedure was performed on the bulk samples according to the following scheme: F1 with redistilled water – Hg leachable in water, F2 with 0.5 mol/L HCl – Hg leachable under acidic conditions, F3 with 0.2 mol/L KOH – Hg bound to humic substances, F4 with 50% HNO_3 – elemental Hg and complexes, and F5 is solid residue. Experiments were carried out at laboratory temperature on shakers GFL 3006 (Burgwedel, Germany) at 300 rpm and the extraction time was 18 h in all fractionation steps. Subsequently, extracts were separated from a solid phase by centrifugation for 10 min at 4000 rpm. The extraction agents from each single step were used as blank samples and the mercury content in all extracts was determined by using the AMA-254 analyser.

RESULTS AND DISCUSSION

Soil characteristic. The pH_{CaCl_2} of our samples equalled 7.18 ± 0.28 and the cation exchange capacity was 131.7 ± 3.8 $mmol_+$/kg. An oxidizable carbon and sulphur content ranged between 1.2–3.4% and 0.28–0.56%, respectively. The organic matter composition and/or content as well as mercury affinity to the individual fractions were described in the other works (Kacálková et al. 2009, Šípková et al. 2014). The measurements of the total Hg content indicated that in the vicinity of the former waste incineration plant there are places with relatively low Hg concentration; however, the sample with the amount of mercury reached even almost 29 mg/kg (Table 1). Kacálková et al. (2009) reported the same variability of the mercury content present in the same area showing the concentrations ranging from 0.15 to 12 mg/kg. Moreover, the highest organic matter content was observed in the samples representing the highest Hg values.

Single extractions. The extraction yields by individual extraction agents are shown in Table 1 and summarized in Figure 1 as relative Hg portions extractable from the total content. HNO_3 released around 50% of total Hg content in 8 of 10 samples. In the case of the most contaminated sample the concentration was approximately 70% and even 96%. Using $Na_2S_2O_3$ as an extraction agent the mercury yield was also highest in the last two samples. The average yield of these particular samples attains approximately 20% of the total. In other samples, the content of mercury ranged from 1.2% to 3.4%. Thus, it might be inferred that in places with higher anthropogenic contamination, the presence of mercury species bound to sulphur is higher than in less contaminated samples. In the case of the most contaminated site the rate of extractable Hg using $Na_2S_2O_3$ corresponds with the results reported by Issaro et al. (2010). They showed that the extraction yield of $Na_2S_2O_3$ usually reaches 50 ± 5% of Hg obtained by HNO_3 extraction from soils with high Hg levels from agricultural processes near Paris, France. Moreover, they showed that the rate of extractable Hg by $Na_2S_2O_3$ is decreasing with decreasing total Hg content. On the other hand, Subirés-Munoz et al. (2011) obtained by this type of extraction approximately 20% of the total Hg content. Their soils originated from the mining district of Almadén, Spain with high background Hg levels and influence of anthropogenic activities.

Further, using chelating agent EDTA, the values of extractable Hg ranged between 0.5% and 2% of the total Hg content, in all the experimental samples. These results correspond to those reported by Subirés-Munoz et al. (2011) who obtained less than 2% of the total Hg. This small variability suggests that the amount of mercury, which might serve as a source for plant uptake, is similar both in more and less contaminated places. Coinciding results were also obtained by extraction with a solution of CH_3COOH, which simulates natural conditions of soil solution. The yields of CH_3COOH were below 0.15% and confirmed no significant differences. The low availability therefore seems to indicate

Table 1. Total and extractable contents of mercury after single extractions (µg/kg)

Sample	Total	HNO_3	$Na_2S_2O_3$	EDTA	CH_3COOH
1	1070	578	14.3	6.92	0.49
2	236	132	7.04	1.99	0.34
3	415	201	7.82	5.21	0.37
4	419	234	8.03	8.80	0.48
5	550	273	10.4	6.27	0.45
6	2050	1132	52.1	9.37	0.73
7	396	223	13.5	2.95	0.44
8	580	300	6.95	2.94	0.78
9	28 800	20 108	5877	481	11.3
10	10 500	10 040	2094	64.7	8.64

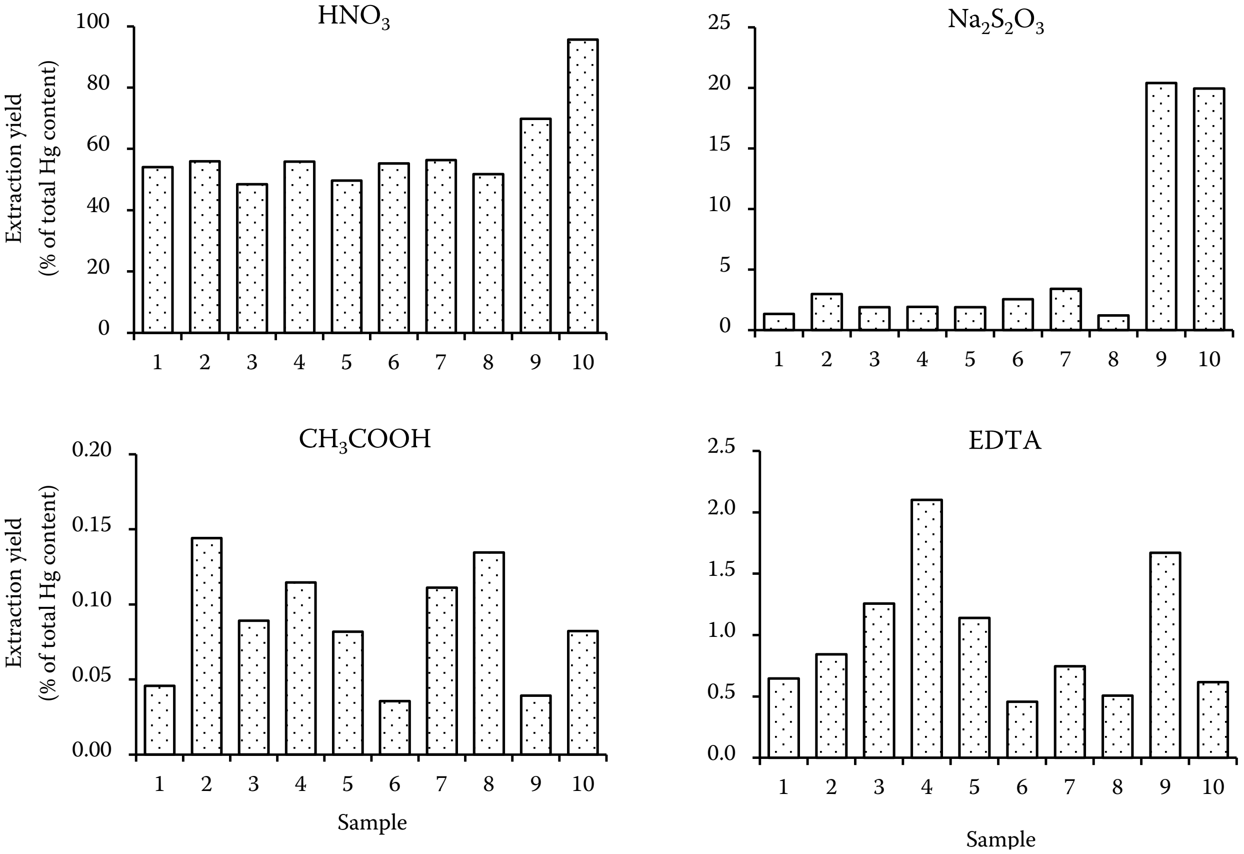

Figure 1. Extraction yield after single extraction using individual chemical agents

that mercury is strongly bound to sulphide phases and/or to insoluble clay minerals and organic matter in the samples (Rodrigues et al. 2010).

Sequential extraction. Mercury contents extracted in each step (F1–F5) are reported in Table 2. The sum of the amount removed by each extraction was in good agreement with the total amounts obtained by AMA-254. Values of recoveries ranged from 93% to 107%.

First fraction representing the total content of organomercury compounds (F0) was below the quantification limit (2 μg/kg) in all samples. Mobile fractions F1 and F2 were also very low for the majority of samples. Hg leachable in water was detectable only in the samples No. 9 and 10, containing the highest level of the total mercury content. Rodrigues et al. (2010) found similar value in samples from vicinity of chlor-alkali plant. The mercury leachable under acid conditions was measured in the aforementioned most contaminated samples and its content was less than 8%. Such high mercury content discovered in soil from the cinnabar refinery and mine by Miller et al. (1995). Low amount of this Hg species was found also in sample 6, which is the third site with high mercury concentration.

In the case of F3, Hg species values obtained were substantially higher. The semi-mobile mercury contents ranged from 18% to 30%. These Hg species bound to organic matter were regarded as stronger complexes and thus have limited mobility (Liu et al. 2006). Almost identical scale of the mercury fractions observed in the study of mercury mobility and bioavailability Boszke et al. (2008). The organic carbon content was also similar in this particular soil. Teršič et al. (2011) described mercury distribution in very contaminated soil from mining district of Idrija, Slovenia and in their study, Hg bound to organic or mineral soil matter reached from 35% to 40% of the total mercury content. These higher values can be connected with acidic pH because mercury is particularly bound to organic matter under the low pH (Schwesig et al. 1999). On the contrary, in our samples 9 and 10 the percentage ratios of this species were approximately 9% and differences among the amounts of mobile and semi-mobile fractions were relatively low.

Table 2. Mercury contents in individual fractions after sequential extraction (μg/kg)

Sample	F1	F2	F3	F4	F5
1	*	*	270	610	150
2	*	*	70	130	20
3	*	*	120	250	50
4	*	*	120	240	50
5	*	*	160	320	30
6	*	30	360	1400	220
7	*	*	80	280	30
8	*	*	130	350	70
9	400	2300	2500	16 200	5300
10	160	620	960	4900	3200

*data below the quantification limit (2 μg/kg). F1 – redistilled water; F2 – 0.5 mol/L HCl; F3 – 0.2 mol/L KOH; F4 – 50% HNO_3; F5 – residue

The highest Hg content was found in the case of non-mobile fraction, i.e. elemental mercury and Hg bound to complexes (F4). Although the sequential extraction by Lechler et al. (1997) was carried out with distinct extraction agent, results of Hg speciation showed the highest proportion of elemental mercury in the soil samples from former amalgamation milling of Ag-Au ores in Nevada, USA. Reis et al. (2010) divided the mercury species in a different way and their semi-mobile fraction included also elemental mercury. Thus, their values obtained from samples from the industrial complex and sulphide mine in Portugal, were similar to the results obtained in this study and the proportion ranged between 63% and 97%.

The content of mercury in solid residues after the extraction was in the majority of samples below 12%. However, in more contaminated samples these values were higher. Obviously, the substantial proportions of residues content are species bound to silica or Hg sulphides. Liu et al. (2006) found around 10% of Hg species bound to sulphur, which corresponds to our hypothesis.

In order to describe the mobility and bioavailability of mercury, several extraction agents and the sequential extraction described above were applied on soil collected near Hradec Králové, Czech Republic. In the area, several samples with high Hg concentration were found and the highest amount reached almost 29 mg/kg. Nevertheless, the total Hg content mostly achieved less than 2 mg/kg.

Based on the results of analyses, only a low amount of a mobile fraction, having the highest toxicity, was determined. In the majority of samples, which originated from the surroundings of the former waste incineration plant, less that 2% of the total Hg content was found. The lowest mercury yield was obtained using the acetic acid as a single extraction agent, which is a proportion generally defined as biologically available to plants (Quevauviller et al. 1993). In all experiments, the concentrations were below 0.15%.

Conversely, elemental Hg and mercury complexes were present in the highest amount and the proportion of this fraction ranged between approximately 50% and 70%. In the case of Hg bound to humic acids representing the semi-mobile species was determined as the second highest. Contrarily, higher Hg amounts were measured in the residuals of the two most contaminated samples. The results of this study concern on specific site and therefore the outcomes should not be taken as general characteristics of all anthropogenically contaminated soils.

REFERENCES

Biester H., Scholz C. (1996): Determination of mercury binding forms in contaminated soils. Mercury pyrolysis versus sequential extractions. Environmental Science and Technology, *31*: 233–239.

Bloom N.S., Preus E., Katon J., Hiltner M. (2003): Selective extractions to assess the biogeochemically relevant fractionation of inorganic mercury in sediments and soils. Analytica Chimica Acta, *479*: 233–248.

Boszke L., Kowalski A., Astel A., Barański A., Gworek B., Siepak J. (2008): Mercury mobility and bioavailability in soil from contaminated area. Environmental Geology, *55*: 1075–1087.

Fernández-Martínez R., Rucandio M.I. (2003): Study of extraction conditions for the quantitative determination of Hg bound to sulfide in soils from Almaden (Spain). Analytical and Bioanalytical Chemistry, *375*: 1089–1096.

Han F.X., Su Y., Monts D.L., Waggoner C.A., Plodinec M.J. (2006): Binding, distribution, and plant uptake of mercury in a soil from Oak Ridge, Tennessee, USA. Science of the Total Environment, *368*: 753–768.

ISO 11260 (1994): Standard of Soil Quality – Determination of Effective cation Exchange Capacity and Base Saturation Level Using Barium Chloride Solution. International Organization for Standardization, Geneva.

Issaro N., Besancon S., Bermond A. (2010): Thermodynamic and kinetic study of the single extraction of mercury from soil using sodium-thiosulfate. Talanta, *82*: 1659–1667.

Kacálková L., Tlustoš P., Száková J. (2009): Phytoextraction of cadmium, copper, zinc and mercury by selected plants. Plant, Soil and Environment, *55*: 295–304.

Lechler P.J., Miller J.R., Hsu L.C., Desilets M.O. (1997): Mercury mobility at the Carson River superfund site, west-central Nevada, USA: Interpretation of mercury speciation data in mill tailings, soils, and sediments. Journal of Geochemical Exploration, *58*: 259–267.

Liu G., Cabrera J., Allen M., Cai Y. (2006): Mercury characterization in a soil sample collected nearby the DOE Oak Ridge Reservation utilizing sequential extraction and thermal desorption method. Science of the Total Environment, *369*: 384–392.

Mailman M., Bodaly R.A. (2005): Total mercury, methyl mercury, and carbon in fresh and burned plants and soil in Northwestern Ontario. Environmental Pollution, *138*: 161–166.

Miller E.L., Dobb D.E., Heithmar E.M. (1995): Speciation of mercury in soils by sequential extraction. In: Proceedings of USEPA Metal Speciation and Contamination of Surface Water Workshop, Jekyll Island.

Novozamsky I., Lexmond Th.M., Houba V.J.G. (1993): A single extraction procedure of soil for evaluation of uptake of some heavy metals in plants. International Journal of Environmental Analytical Chemistry, *51*: 47–58.

Quevauviller Ph., Ure A., Muntau H., Griepink B. (1993): Improvement of analytical measurements within the BCR-programme – Single and sequential extraction procedures applied to soil and sediment analysis. International Journal of Environmental Analytical Chemistry, *51*: 129–134.

Rao C.R.M., Sahuquillo A., Lopez Sanchez J.F. (2008): A review of the different methods applied in environmental geochemistry for single and sequential extraction of trace elements in soils and related materials. Water, Air, and Soil Pollution, *189*: 291–333.

Reis A.T., Rodrigues S.M., Davidson C.M., Pereira E., Duarte A.C. (2010): Extractability and mobility of mercury from agricultural soils surrounding industrial and mining contaminated areas. Chemosphere, *81*: 1369–1377.

Renneberg A.J., Dudas M.J. (2001): Transformations of elemental mercury to inorganic and organic forms in mercury and hydrocarbon co-contaminated soils. Chemosphere, *45*: 1103–1109.

Revis N.W., Osborne T.R., Sedgley D., King A. (1989): Quantitative method for determining the concentration of mercury(II) sulphide in soils and sediments. Analyst, *114*: 823–825.

Rodrigues S.M., Henriques B., Coimbra J., Ferreira da Silva E., Pereira M.E., Duarte A.C. (2010): Water-soluble fraction of mercury, arsenic and other potentially toxic elements in highly contaminated sediments and soils. Chemosphere, *78*: 1301–1312.

Sánchez D.M., Quejido A.J., Fernández M., Hernández C., Schmid T., Millán R., González M., Aldea M., Martín R., Morante R. (2005): Mercury and trace element fractionation in Almaden soils by application of different sequential extraction procedures. Analytical and Bioanalytical Chemistry, *381*: 1507–1513.

Schwesig D., Ilgen G., Matzner E. (1999): Mercury and methylmercury in upland and wetland acid forest soils of a watershed in Ne-Bavaria, Germany. Water, Air, and Soil Pollution, *113*: 141–154.

Sims J.R., Haby V.A. (1971): Simplified colorimetric determination of soil organic matter. Soil Science, *112*: 137–141.

Šípková A., Száková J., Tlustoš P. (2014): Affinity of selected elements to individual fractions of soil organic matter. Water, Air, and Soil Pollution, *225*: 1802.

Subirés-Munoz J.D., García-Rubio A., Vereda-Alonso C., Gómez-Lahoz C., Rodríguez-Maroto J.M., García-Herruzo F., Paz-García J.M. (2011): Feasibility study of the use of different extractant agents in the remediation of a mercury contaminated soil from Almaden. Separation and Purification Technology, *79*: 151–156.

Teršič T., Gosar M., Biester H. (2011): Distribution and speciation of mercury in soil in the area of an ancient mercury ore roasting site, Frbejžene trate (Idrija area, Slovenia). Journal of Geochemical Exploration, *110*: 136–145.

Received on August 29, 2013
Accepted on January 23, 2014

Corresponding author:

Ing. Adéla Šípková, Česká zemědělská univerzita v Praze, Fakulta agrobiologie, potravinových a přírodních zdrojů,
Katedra agroenvironmentální chemie a výživy rostlin, Kamýcká 129, 16521 Praha 6-Suchdol, Česká republika
e-mail: sipkovaa@af.czu.cz