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ORIGINAL PAPER

PREDICTION OF CADMIUM, LEAD AND MERCURY AVAILABILITY TO PLANTS: A COMPARISON BETWEEN DIFFUSIVE GRADIENTS MEASURED IN A THIN FILMS TECHNIQUE AND SOIL GROWN PLANTS

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ABSTRACT

Dandelion plants (Taraxacum officinale) were sampled together with soil from three sites of the city of Brno differentially impacted by soil pollution. The sampling site at Opuštěná Street situated in the city centre represents a heavily polluted industrial location, the sampling site at Vídeňská Street constitutes a medium polluted location and a relatively clean location is represented by Šrámkova Street. Of the soil pollutants, cadmium, mercury and lead were studied. Cadmium and lead concentrations were determined in the eluates of resin gels, in leachates, plant digestates and in soil solutions using an electrothermal atomic absorption spectrometer ContrAA 700, while the total mercury content in soil, dried plant samples and resin gels was measured using one purpose atomic absorption spectrometer Advanced Mercury Analyser, AMA 254. CE represents the concentration of a metal that is effectively available from both the soil solution and solid-phase labile pool. The metal effective concentrations CE, measured by diffusive gradients in the thin films technique (DGT), were correlated with the metal uptake by plants. The DGT measurement can be also interpreted in terms of the ratio R, which was obtained experimentally. Fluxes of cadmium, lead and mercury to the DGT unit during a 15-day exposure were determined. High correlation coefficients demonstrated that DGT results could be used as physical surrogates for plant uptake, thus offering the possibility of a simple test procedure for soils. The DGT measurement of effective concentrations (CE) may provide a major step forward in assessing the hazards posed by metals in contaminated soils.

Keywords: bioavailability, cadmium, mercury, lead, dandelion plant, diffusive gradient in thin film technique (DGT).

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INTRODUCTION

The accumulation of toxic metals in soils is a growing concern due to the negative effects on soil ecosystems and potential health risks. Soil-to-plant transfer of trace metals is one of the major pathways of human exposure to toxic metal contamination. The prediction of metal bioavailability and bioaccessibility in soils is then essential for the assessment of environmental quality and health risks. Hence, there is a great interest in finding efficient environmental monitoring methods for their determination. Analytical testing of chemical pollutants based on various leaching procedures (TESSIER et al. 1979, URE 1996) provides a simple classification of soil metal fractions, but these are based on arbitrary responses to chemical reagents and do not provide information on the potential impact of pollution on resident organisms. Therefore, there is a need for a simple procedure, which reliably estimates metal accessibility and predicts the uptake of toxic metals by plants.

New approaches are still being sought to obtain better characterization of bioavailable forms of metals and their transport from the soil to the plant. An *in situ* technique known as a diffusive gradient in a thin films technique (DGT), capable of quantitative measurement of labile metal species, has been developed (DAVISON, ZHANG 1994). This emerging technique is based on a simple device that accumulates metal ions on a cation-exchange resin, immobilized in a thin layer of hydrogel, after passage through a diffusion layer. Like plants, the DGT technique locally lowers metal concentrations in the soil solution and responds to a metal re-supplied from labile species in solution and the labile metal pool in the soil solid phase. The kinetically labile solid phase pool of metals clearly plays an important role in plant uptake and is included in the DGT measurement. The evaluation of the metal labile pool in soil is therefore a fundamental issue in the assessment of the soil pollution level (LEHTO et al. 2006).

The objectives of this study are to identify the relationship between concentrations of cadmium, mercury and lead fluxes measured by the DGT and their elevated levels in plants grown in differentially contaminated urban soils, and to confirm the capability of the DGT to predict metal uptake by plants.

MATERIALS AND METHODS

Soil and plant sample collection

The soil and plant samples were collected from the topsoil of three sampling sites in the city of Brno, which is the second largest city of the Czech Republic. It has a wide range of industries, including smelting (heating plants, incineration plants, cement and lime processing, a crematorium) and automotive exhaust fumes, which produce emissions with consequent deposits on soil and vegetation surfaces.

The common dandelion (*Taraxacum officinale*) often used as a biomonitor for metal pollution (KABATA-PENDIAS, DUDKA 1991, KROLAK 2003, GWOREK et al. 2011, KLECKEROVÁ, DOČEKALOVÁ 2014) was used in the experiment. Sampling was performed in the middle of April 2012, when the first flowers appeared, as the metal content of plant parts could vary seasonally (DJINGOVA, KULEFF 1993). The sampling site at Opuštěná Street situated in the city centre represents a heavily polluted industrial location with high traffic density. The sampling site at Vídeňská Street constitutes a medium polluted location, which is situated close to major roads. A relatively clean location is represented by Srámkova Street, which is in a residential area situated in a peripheral city district with lower contamination loading. Soil samples were collected in the immediate vicinity of the dandelion plants from a depth horizon of 0-10 cm. Ten samples were taken at each of the three sampling sites, which represented an area of 10 m². Ten plants of common dandelion collected at each sampling site were carefully extracted from the soil, placed in plastic bags, and transported to the laboratory. The dandelion shoots and roots were separated and washed with distilled water and air-dried.

Analyses of soil and plant material

Soil physicochemical properties were determined in the air-dried fraction with the particle size of less than 2 mm in diameter obtained by sieving the air-dried raw sample, from which large components were separated (stones, plant parts). pH/KCl and C_{ox} were determined using conventional methods (ZBÍRAL 1996). Water holding capacity (WHC) was determined gravimetrically, according to the method described by MUHAMMAD et al. (2012).

Single leaching procedure commonly used in the Czech Republic for the measurement of pseudototal metal fractions (ZBÍRAL 1996) was used for Cd and Pb determinations in soil samples.

A 7 g portion of dried and sieved soil was shaken in an extraction bottle at the ambient temperature (25°C) with 70 mL of 2 mol L^{-1} nitric acid for 16 h. The extract was immediately filtered and the filtrate was collected in a polyethylene bottle.

0.2 g of dried and homogenized plant samples was decomposed in a microwave oven (Milestone, MLS 1200, Italy) using 6 mL of concentrated HNO₃ and 1 mL of 30 % H_2O_2 .

DGT experiments

Gel preparation

Polyacrylamide diffusive gel and Chelex resin gels were prepared according to the procedure developed by ZHANG and DAVISON (1995) and ZHANG et al. (1995). Acrylamide (Sigma-Aldrich, Germany), agarose derivative DGT cross-linker (DGT Research Ltd., UK), ammonium persulfate (Sigma-Aldrich, Germany), tramethylethylenediamine (Sigma-Aldrich, Germany) were used for diffusive gel preparation. For measuring cadmium and lead, Chelex-100, Na form, 100 - 200 wet mesh (Bio-Rad Laboratories) as ion-exchange resin was embedded into polyacrylamide gel.

For mercury determinations, Duolit GT73 resin (Sigma-Aldrich, Germany) with thiol groups was used (ZHANG, DAVISON 1999, DIVIŠ et al. 2009, 2010, PELCOVÁ et al. 2014, 2015). Because of the large diameter size of Duolit GT73 resin particles $(0.5 \cdot 0.7 \text{ mm})$, it was impossible to incorporate the resin into polyacrylamide hydrogel (the thickness of plastic spacers determining the diameter size of the resin was 0.25 mm). For this reason, a pretreatment of the resin before use was necessary. The resin was ground in a porcelain mortar and sieved through a teflon sieve ($\leq 150 \mu m$). The sieved fraction was soaked in concentrated hydrochloric acid solution overnight, then washed several times with Milli Q water, dried at 45°C, and used for resin gel preparation. The commonly used polyacrylamide diffusive gel was found to be unsuitable as a diffusive medium for mercury determination because of mercury binding on the amine groups of polyacrylamide. Agarose diffusive gel having a different structure from polyacrylamide gel was therefore used (DOČEKALOVÁ, DIVIŠ 2005). The diffusive gel was prepared by dissolving agarose in an appropriate volume of 80°C warm Milli-Q water.

Soil slurry preparation

The amount of 110 g of soil sample was mixed with Milli Q water (Millipore, Ltd.) to 98-100% WHC. The water/soil mass phase ratio was 0.44 mL g¹ for Opuštěná Street sample, 0.42 mL g¹ for Vídeňská Street sample and 0.45 mL g¹ for Šrámkova Street sample. Soil-water mixtures were shaken for 5 minutes in containers to homogenize the slurries. The mixtures were then equilibrated in closed containers at 21°C for 5 days. Petri dishes with wet cellulose paper were placed into containers to keep moisture of the mixture constant.

Time deployment experiment

Six DGT units (three units with Chelex-100 resin for determination of Cd and Pb, and three with Duolit DT73 and agarose diffusive gel for Hg determination per one container) were applied to the saturated soil slurries prepared from mixed samples from each locality. DGT units were slightly pushed into the surface, thus ensuring complete contact of the membrane with soil solution without any air bubbles. The containers with DGT units were kept at ambient temperature of 21°C. The containers were closed and Petri dishes with wet cellulose were placed into the containers to keep moisture of the soil mixture constant. One container without DGT served as the start blank. After 0.25, 0.5, 1, 1.5, 2, 3, 4, 5, 7, 9, 12 and 15 days the DGT units were removed from the soil, carefully rinsed with Milli Q water and dismantled. The Chelex resin gels were retrieved and immersed into polypropylene vials (Plastibrand, Brand, Germany) with 1 mL of 1 mol L^1 nitric acid and eluted for 24 h for Cd and Pb determination. If necessary, the eluate was diluted with distilled water before analysis. The Duolit GT73 resin gels were analyzed directly in an AMA 254 spectrometer. The whole experiment was performed in two replications.

Determination of C_E

To obtain data for the calculation of an effective concentration, an additional DGT experiment was performed. Soil slurry was prepared from each soil sample by the above mentioned procedure. Three DGT units with Chelex-100 resin gel and three units with Duolit DT73 were applied to each soil slurry sample for 24 h at 21°C.

Simultaneously, the samples of soil solution from soil slurries were extracted by centrifugation for 10 min at 5000 rpm. The supernatant was filtered using 0.45 μ m pore size disposable polysulfone filter assemblies (Pall Corporation, Port Washington, NY, USA) and then acidified using HNO₃.

Determination of metals

Cadmium and lead concentrations were determined in the eluates of the resin gels, in the leachates, plant digestates and in soil solutions. An electrothermal atomic absorption spectrometer (AAS ContrAA 700, Analytik Jena, Germany) was used under the recommended conditions specified by the producer. Calibration was performed using Astasol aqueous metal standard solutions (Analytika Ltd, Czech Republic). The total mercury content in soil, dried plant samples and resin gels was measured using one purpose atomic absorption spectrometer Advanced Mercury Analyser, AMA 254 (Altec, Czech Republic), based on combustion of a sample in oxygen atmosphere and amalgamation preconcentration.

Method validation

The reference materials (CRM 7001 - Light Sandy Soil with normal analyte levels and 7003 – Silty Clay Loam with normal analyte levels, Analytika, Czech Republic and IAEA-V-10 – Hay powder) were used for the validation of the method.

Statistical analysis

The results are presented as means \pm standard deviation (SD). Normal distribution of measured data was tested by the Kolmogorov-Smirnov test. Statistical analyses of metal content in soil and plant parts were made using analysis of variance (ANOVA) and statistical significance was declared when p value was equal to or less than 0.05. The significance of differences among the average values from the individual localities was tested at the level of

significance $\alpha = 0.05$ with the Tukey's HSD (Honestly Significant Difference) test. The *t*-test analysis was carried out with the shoot and root plant samples; analyzed metals showing differences were identified. Relationships between parameters were expressed by the Pearson correlation coefficients. Statistical significance was determined by *p* value equal to or less than 0.05. Software Statistica.12 (Statsoft, Czech Republic) was used for statistical analysis.

RESULTS AND DISCUSSION

All analytical methods used during this study passed the quality control tests. The precision and accuracy of the methods have been verified by analysis of certified reference materials (CRM 7001- Light Sandy Soil with normal analyte levels and 7003 – Silty Clay Loam with normal analyte levels, Analytika, Czech Republic and IAEA-V-10 - Hay powder). The recoveries obtained (96 \pm 5% for soils and 98 \pm 3% for plant material) were in agreement with the certified values. Detection limits were adequate for the metal analysis of selected samples.

Soil and plant analyses

The sampled soils were classified as neutral soil without humus. Basic characteristics of the soil samples are summarized in Table 1.

Table 1

Sampling site	Opuštěná Street	Vídeňská Street	Šrámkova Street
pH	7.100	7.270	7.090
* C _{ox} (%)	1.500	1.200	2.100

General characteristic of soil samples

* $C_{av}(\%)$ – the percentage of the organic matter content in homogenized samples

The concentrations of the investigated metals in the soil and plant tissue were found, as expected, significantly higher in the samples collected in the city centre than in those collected in clean areas situated in the peripheral city district (Table 2).

DGT experiments

The availability of metals in soil is related to the flux of metals from the solid phase to the plant and to a DGT device. Metal *in situ* fluxes (F) to the DGT device were obtained by using the equation (Eq. 1):

Table	2
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Concentra-	Sample	Sampling sites		
(mg kg ⁻¹)		Opuštěná	Vídeňská	Šrámkova
Cd	soil	0.666 ± 0.058^a	0.450 ± 0.099^{b}	$0.104 \pm 0.070^{\circ}$
	shoots	$0.171 \pm 0.041^{a^{***}}$	$0.137 \pm 0.021^{b^{***}}$	$0.047 \pm 0.011^{c^{***}}$
	roots	0.240 ± 0.041^a	0.166 ± 0.024^{b}	$0.092 \pm 0.013^{\circ}$
Pb	soil	63.10 ± 14.70^{a}	29.40 ± 5.680^{b}	$10.60 \pm 3.910^{\circ}$
	shoots	$9.060 \pm 0.960^{a^{***}}$	$3.940 \pm 0.750^{b^{***}}$	$2.130 \pm 0.310^{c^{***}}$
	roots	4.020 ± 1.750^{a}	1.670 ± 0.490^{b}	1.490 ± 0.310^{b}
Hg	soil	0.628 ± 0.207^{a}	0.063 ± 0.015^{b}	0.050 ± 0.040^{b}
	shoots	$0.062 \pm 0.013^{a^{***}}$	$0.038 \pm 0.008^{b^{***}}$	$0.020 \pm 0.002^{c^{***}}$
	roots	0.049 ± 0.008^a	0.012 ± 0.003^{b}	$0.009 \pm 0.001^{\circ}$

Concentrations of cadmium, lead and mercury in soil and plant parts (mg kg-1 dry weight)

Values are means of 10 samples \pm standard deviation.

Different letters in rows indicate significant differences at p < 0.05 (ANOVA) in localities. Significance of differences between plant parts from paired *t*-test is indicated beside letters in the columns (* p < 0.05, ** p < 0.01, *** p < 0.001).

$$F = \frac{DC}{\Delta g} = \frac{M}{AT},\tag{1}$$

where: D – diffusion coefficient of a metal in a diffusion gel,

C – time-average metal concentration at the DGT solution interface,

 Δg – thickness of the diffusive gel,

M – mass of the metal diffused through the diffusion area A

and captured by the resin gel during the time of exposition T.

Fluxes of cadmium, lead and mercury to the DGT unit during a 15-day exposure are summarized in Figures 1, 2, 3.



▲ Opuštěná Street ■ Vídeňská Street ◆ Šrámkova Street

Fig. 1 Time limited Cd soil/pore water fluxes measured by DGT units in urban soils. Error bars are not shown in order to achieve better clarity (n = 6)



▲ Opuštěná Street ■ Vídeňská Street ◆ Šrámkova Street

Fig. 2 Time limited Pb soil/pore water fluxes measured by DGT units in urban soils. Error bars are not shown in order to achieve better clarity (n = 6)



▲ Opuštěná Street ■ Vídeňská Street ◆ Šrámkova Street Fig. 3 Time limited Hg soil/pore water fluxes measured by DGT units in urban soils. Error bars are not shown in order to achieve better clarity (n = 6)

Cadmium showed a sharp decrease in the metal flux during 24 h.; lead fluxes decreased during two days, and mobile mercury species were depleted during seven days.

DGT-measured fluxes characterized the soil system and enabled estimation of the long-term metal resupply fluxes (ng cm⁻²d⁻¹). The long-term resupply fluxes for cadmium, mercury and lead in the Brno urban soil usable by the DGT or plants are summarized in Table 3.

The time-average metal concentration C_{DGT} at the DGT solution interface was calculated by using Eq.2:

Sampling sites	$\mathrm{Cd}-F~(\mathrm{ng}~\mathrm{d}^{\cdot1}~\mathrm{cm}^{\cdot2})$	$\mathrm{Hg}-F~(\mathrm{ng}~\mathrm{d}^{\cdot1}~\mathrm{cm}^{\cdot2})$	$Pb - F (ng d^{\cdot 1} cm^{\cdot 2})$
Opuštěná Street	7.150 ± 0.250	0.257 ± 0.017	32.59 ± 6.030
Vídeňská Street	5.480 ± 0.300	0.178 ± 0.007	13.01 ± 0.300
Šrámkova Street	3.700 ± 0.130	0.130 ± 0.016	4.610 ± 1.400

Long-term resupply fluxes measured over the period of day 7 to 15

$$C_{DGT} = \frac{M\Delta g}{ADT},\tag{2}$$

where is $\Delta g = 0.93$ mm for Cd and Pb, $\Delta g = 0.63$ mm for Hg, A = 3.14 cm², the diffusion coefficient (D) of each metal at 21°C in the diffusive gel $(D_{Cd} = 5.46 \cdot 10^{-6} \text{ cm}^2 \text{ s}^{-1}, D_{Pb} = 7.19 \cdot 10^{-6} \text{ cm}^2 \text{ s}^{-1}, D_{Hg} = 8.12 \cdot 10^{-6} \text{ cm}^2 \text{ s}^{-1})$ and the deployment time (T) (ZHANG, DAVISON 1995, ZHANG et al. 2001, FERNANDEZ-GOMEZ et al. 2015).

Soil solution is a non-mixed system and C_{DGT} decreases gradually after several hours (days). Depleted metals in the vicinity of a DGT devise could be supplied from both the solid phase and solution.

The DGT measurement can be also interpreted in terms of the ratio R, which was obtained experimentally. The value of the ratio R (0 < R < 1) reflects the ability and capacity of the soil solid phase to resupply local metal concentration in soil solution and the kinetics of this transfer (DGT-Research). The DGT-interpreted concentration C_{DGT} will be less than or equal to the total concentration of labile metal species in the soil solution (C_{sol}) measured by an independent analytical method (Eq. 3). The ratio C_{DGT} to C_{sol} expresses R-value:

$$R = \frac{C_{DGT}}{C_{sol}}.$$
(3)

The *R*-value approaching unity means the metal is present in mobile and kinetically labile species in the solid phase and also the metal resupply from the solid phase to pore water is sufficiently fast. The *R*-value approaching 0 is indicative of a limited or even absent metal resupply from the solid phase and the metal concentration decreases in the vicinity of the DGT probe during the deployment period.

The *R*-values are summarized in Table 4. The low values of the *R* ratio indicated that only a very small part of the total metal content is apparently reflected by the DGT technique, especially for mercury and cadmium. The lowest *R*-value for mercury reflected the strong bonding of mercury to the solid phase and its extremely low mobility (Table 4). The highest *R*-value was found for lead in soil samples from Opuštěná Street (0.35) and Vídeňská Street (0.16). These city sites belong to places with high traffic density. The accessible lead levels found in the soil could probably originate from leaded petrol used in the past.

Sampling sites	Cd - <i>R</i>	Hg - R	Pb - <i>R</i>
Opuštěná Street	0.100 ± 0.002	0.057 ± 0.005	0.346 ± 0.011
Vídeňská Street	0.089 ± 0.001	0.074 ± 0.003	0.160 ± 0.013
Šrámkova Street	0.056 ± 0.001	0.056 ± 0.002	0.133 ± 0.010

R – value for Cd, Pb and Hg in deployment time of 24 h

Calculation of C_E from DGT measurement

The concentration directly measured by the DGT (C_{DGT}) can be converted to an effective concentration (C_F) using Eq. 4 (ZHANG et al. 2001):

$$C_E = \frac{C_{DGT}}{R_{diff}}.$$
(4)

 $C_{\scriptscriptstyle E}$ represents the concentration of metal that is effectively available from both the soil solution and solid-phase labile pool. $R_{\rm diff}$ is the ratio of the metal concentration at the DGT surface for the diffusion only case (i.e. no resupply from the solid phase) and the concentration in the soil solution. $R_{\rm diff}$ was calculated using the 2D DIFS (DGT induced fluxes in soils and sediments), which is freely available for general use on the web (http://www.es.lancs. ac.uk/wdgroup/aquach.htm). It is a dynamic, full numerical model of the DGT-soil system - two dimensions of the time dependent interaction of a DGT unit of variable geometry with soils having various properties (HARPER et al. 1998, 2000, SOCHACZEWSKI et al. 2007). Input parameters of the mathematical model such as the particle concentration (P_c), soil porosity (φ) and the diffusion coefficient of a metal in the soil (D_s) were calculated using Eqs 5-7:

$$P_c = \frac{m}{V},\tag{5}$$

$$\varphi = \frac{d_p}{P_c + d_p},\tag{6}$$

$$D_s = \frac{D_0}{1 - \ln\varphi^2}$$
 (7)

where *m* is the total mass of all soil particles, *V* is the pore water volume in a given volume of total soil slurry, D_{o} is the diffusion coefficient of metal in water, and d_{p} is the density of the soil particles, which is commonly assumed to be 2.65 g cm⁻³ in soil (BIELDERS et al. 1990). Input parameters used in this work for 2D DIFS calculation were: particle concentration $P_{c} = 0.119 \cdot 0.129$ g mL⁻¹, porosity $\varphi = 0.953 \cdot 0.957$, effective diffusion coefficient of metals in soils $D_{s}(Cd) = 4.98 \cdot 5.02 \cdot 10^{-6}$; $D_{s}(Pb) = 6.56 \cdot 6.61 \cdot 10^{-6}$; $D_{s}(Hg) = 7.71 \cdot 7.46 \cdot 10^{-6}$, soil response time $T_{c} = 1 \cdot 10^{9}$ and plant available fraction of element bound to the soil $K_{d} = 1 \cdot 10^{-9}$.

The following R_{diff} values calculated using 2D DIFS were found: Street (Cd – 0.079; Pb – 0.072; Hg – 0.048), Opuštěná Street (Cd – 0.079; Pb – 0.072; Hg – 0.057) and Šrámkova Street (Cd – 0.079; Pb – 0.072; Hg – 0.048).

Using equation 4, the effective concentrations of studied metals were calculated and are summarized in Table 5.

Table 5

Sampling sites	Cd - C_E (µg l ⁻¹)	Hg - C_E (µg l ⁻¹)	Pb - C_E (µg l ⁻¹)
Opuštěná Street	25.22 ± 0.720	1.420 ± 0.010	126.3 ± 1.260
Vídeňská Street	16.49 ± 0.790	1.100 ± 0.030	51.48 ± 1.590
Šrámkova Street	8.840 ± 0.410	0.630 ± 0.010	22.56 ± 1.500

Effective concentrations $C_{\rm \scriptscriptstyle E}$ of the studied metals in deployment time of 24 h

The effective concentration of labile metal, C_E (ZHANG et al. 2001, 2004) obtained by DGT measurement represents the supply of metal to any sink, be it DGT or a plant that comes from both diffusion in a solution and release from the solid phase. C_E is the concentration that would have to be present in the soil solution to supply the same mass of metal accumulated by DGT. The DGT mimics plant uptake processes as plant uptake also locally lowers soil concentration, so C_E can be expected to relate directly to plant uptake

The calculated effective concentrations C_E were correlated to the metal concentration in plant tissues (shoots and roots) – Figure 4. Plant concentrations were linearly related and highly correlated with C_E . Correlation coefficients are recorded in Figure 4. The highest correlation coefficient (0.98) was found for cadmium between C_E and roots, the lowest for mercury between C_E and roots (0.84). The large variance in plant tissue metal concentrations was caused by biological differences.

ZHANG et al. (2001) found a linear correlation relationship between a DGT measured log C_E and the logarithm of the copper concentration in Lepidium heterophyllum cultivated in agricultural soils contaminated by smelter emission.

Dandelion plants, which are studied in this work as a monitoring plant, were grown in urban contaminated soils. Linear correlations were found between the root and shoot metal concentrations for cadmium, lead and mercury in plants (KLECKEROVÁ, DOČEKALOVÁ 2014). Correlations between C_E and both plant parts confirmed the conclusions drawn by NOWACK et al. (2004).

Previous experiments have been performed for different metals, plants and soils (FITZ et al. 2003, NOLAN et al. 2003, ZHANG et al. 2004, WANG et al. 2014). The values of the effective concentration C_E for lead (19.2 - 194 µg L⁻¹) and for cadmium (1.84 - 10.5 µg L⁻¹) in unpolluted urban/agricultural soils presented by SENILA et al. (2012, 2014) were very similar to our results. In low contaminated localities, Senila et al. found the pseudototal average content of lead (29.4 mg kg⁻¹) that is identical to our results from Vídeňská



Fig. 4 Relationships of $C_{\scriptscriptstyle E}$ and metal concentration in plants. Values R^2 are regression coefficients and values r are the Pearson correlation coefficients; *** p < 0.001

Street in this work (Table 2). Due to different properties of soil samples, the input parameters for calculating C_E differed and the calculated average C_E of lead in soil from Vídeňská Street was higher – 37.3 µg L^{·1} (SENILA et al. 2014) and 51.48 µg L^{·1} (Vídeňská Street). On the other hand (SORIANO-DISLA et al.

2010) presented the effective concentration for lead and cadmium in one to two orders of magnitude higher in the contaminated areas (for lead $0.082 \pm 0.146 \text{ mg L}^{-1}$ and for cadmium $0.039 \pm 0.048 \text{ mg L}^{-1}$). It is not possible to compare the effective concentration for Hg, calculated in this experiment, with data from the literature, which are abssent.

Consequently, the effective concentration C_E measured by the DGT and calculated in this work and similar results published previously have shown to give very good correlation to plant uptake (DAVISON, ZHANG 2000, ZHANG et al. 2001, 2004). The C_E concept actually predicts the root uptake of metals.

Our work broadens the current knowledge about the feasibility of available metal species of cadmium and lead and brings new results about mercury in urban soils measurement using the DGT technique.

CONCLUSION

The data obtained in this work justify the conclusion that the DGT is an effective technique for the prediction and assessment of metal bioavailability in soils and could be used as a physical surrogate for plant uptake and for assessment of bioavailable metal pools in soils. The calculated C_E of cadmium, mercury and lead in urban soils differentially impacted by pollution has been shown to give very good correlation to the uptake by the common dandelion plants which grow in these soils. Moreover, the DGT-measured fluxes could characterize the soil system, and the long-term metal resupply fluxes can be estimated.

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