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Diffusive gradient in thin films technique for assessment of cadmium and copper bioaccessibility to radish (*Raphanus sativus*)

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ABSTRACT

The aim of this study was to assess cadmium and copper uptake by radish (*Raphanus sativus*) and to test the capability of the diffusive gradient in thin films (DGT) technique to predict bioaccessibility of the metals for this plant. Radish plants were grown in pots filled with uncontaminated control and artificially contaminated soils differing in cadmium and copper contents. Metal concentrations in plants were compared with free ion metal concentrations in soil solution, and concentrations measured by DGT. Significant correlation was found between metal fluxes to plant and metal fluxes into DGT. Pearson correlation coefficient for cadmium was 0.994 and for copper 0.998. The obtained results showed that DGT offers the possibility of simple test procedure for soils and can be used as a physical surrogate for plant uptake.

1. Introduction

Metal contamination on large areas of agricultural soils is gradually increasing due to various processes such as the deposition of industrial and traffic emissions, excessive use of low quality fertilizers, the application of bio-wastes as fertilizers and wastewater irrigation actively practiced in various parts of the world, especially in developing countries. Using contaminated land for the production of food or feed crop plants bears the risk of subsequent translocation of various metal species into the food chain and creates health risks for humans and animals. In addition to serious health hazards toxic metals affect soil microbial interaction and reduce soil fertility leading agro-ecosystems to remain unsustainable in the long term. For this reason, protection of soil fertility along with the quality of agricultural production has become the major concern for sustainable agriculture. Therefore, there is a need for a simple procedure, which reliably estimates metals accessibility and predicts the uptake of toxic metals by plants. Various leaching procedures are applied for this purpose. The extraction procedures provide a simple classification of soil metal fractions, but these are based on arbitrary responses to chemical reagents rather than on a true reflection of metal accessibility [1–4]. Thus, there is an ever-increasing interest in the use of monitoring methods such as analysis of organisms that are bioaccumulators [5–8]. However, it is not generally assumed that different organisms transport metals by the same mechanisms and the soil–plant transport is affected by external environmental conditions [9]. A lack of understanding of the basic physiological, biochemical, and molecular mechanisms prevents the correct evaluation of their influence on metal transport to living organisms. Therefore, new approaches are still being sought to obtain better characterization of bioaccessible forms of metals and their transport from soil to plants. An *in situ* technique known as the diffusive gradient in thin films (DGT) technique capable of quantitative measurement of labile metal species has been developed [10]. This 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 the diffusion layer. Like plants, the DGT unit locally lowers metal concentrations in the soil solution and responds to metals re-supplied from labile species in solution and the labile metal pool in the soil solid phase. The evaluation of the metal labile pool in soil is therefore a fundamental topic in soil pollution level determination.

The aim of the present work was to investigate the relationship between concentrations of metals measured by DGT and their elevated levels in crops and to confirm the capability of DGT to predict cadmium and copper uptake by plants at varying levels of metal supply. The experimental plant (*Raphanus sativus*) was grown in a greenhouse on not-treated control and gradually spiked soils. The amount of cadmium and copper uptake to plant tissue was correlated with the DGT recovered fluxes and compared

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with metals concentrations in soil solution. Quasi-total metal contents in non-treated and spiked soil samples during experiments were controlled by nitric acid leaching procedure.

2. Materials and methods

2.1. Soil samples

The experiment with radish plants was carried out during April–June 2012. Two hundred kilograms of soil was sampled from the Experimental field station of Mendel University in Žabčice, situated 25 km south of Brno, Czech Republic.

A composite sample of topsoil was collected from a depth of 0–20 cm. Larger impurities were taken out and the dry soil was sieved to exclude particles larger than 2 mm. The soil was classified as neutral, slightly acidic soil with lack of humus, and soil texture (65.2% sand, 23.2% clay, 11.6% silt; sandy loam), pH (6.3) and organic matter (1.7%) were determined. Soil properties, including dry matter content, acidity (pH/KCl) and water holding capacity (WHC) were measured using conventional methods [11,12]. Soil organic content was determined gravimetrically after ignition at 550 °C.

An air-dried homogenized soil sample was used for plant cultivation and DGT experiments. The bulk sample was divided into six parts, two non-treated controls and four portions of soil, two of them spiked with cadmium nitrate and two spiked with copper chloride solutions to the final concentrations of 1 mg kg^{-1} Cd (soil A) and 2 mg kg^{-1} Cd (soil B) and 100 mg kg^{-1} Cu (soil C) and 200 mg kg^{-1} Cu (soil D). Moisture content of all soil samples corresponded to 50% of WHC. The WHC of the studied soil was adjusted to 24.9 ± 1.1 wt%. Non-treated and spiked soils were potted (6 kg of each moist soil per pot) and incubated for six months.

A sub-sample of the soil was collected from each pot before sowing and after the last harvest for the conventional leaching procedure with nitric acid in order to assess the individual accessible pools of elements in the experimental soils.

2.2. Leaching procedure

A single leaching procedure commonly used in the Czech Republic for measurement of quasi-total metal fraction [12] was used for cadmium and copper determinations in non-treated and spiked soils samples. A portion of 7 g dried and sieved soil was shaken in an extraction bottle with 70 ml of 2 mol L^{-1} nitric acid at horizontal 60 rpm and at the ambient temperature (25 °C) for 16 h. The extract was immediately filtered through a membrane filter (0.45 μm pore size, 25 mm in diameter, Supor®-450, Pall Corporation, Michigan, USA) and the filtrate was collected in a polyethylene bottle.

2.3. Greenhouse experiment

Five seeds of radish (*R. sativus*) were sown in each pot and grown for 6 weeks under greenhouse conditions. No fertilizer was used. The soil moisture content was restored daily by adding water to 50% of WHC.

Representative specimens of radish plants were taken within two subsequent harvests. Roots were rinsed with deionized water and clean plants were air-dried. Fresh weight of plants was recorded. Dry matter content was determined after drying in an oven at 105 °C. After the first harvest, soil in the pots was mixed.

2.4. Plant tissues analysis

Plant tissues were dry ashed at 380 °C in oxidizing atmosphere of oxygen, nitrogen oxides and ozone, prepared by ashing of ammonia in an ozonizer of Dry mode mineralizator APION (Tessek, CZ). The ash was dissolved in nitric acid. Finally, cadmium and copper concentrations were determined by electrothermal atomic absorption spectrometry (ET-AAS) employing a Perkin-Elmer Model AAnalyst 600 Zeeman effect background corrected atomic absorption spectrometer.

2.5. DGT experiments

Simultaneously, DGT experiments were performed in the laboratory with soil slurries prepared from non-sown pots and from sown pots after the last harvest to characterize the kinetics of metal re-supply from the solid phase to the soil solution. Soil solutions were isolated from these slurries by centrifugation followed by membrane filtration (0.45 μm pore size, Supor®-450, Pall Corporation, Michigan, USA) before and after DGT deployment. Gels and sample units for DGT experiments were prepared according to the conventional procedures [13].

Accumulation of metals from soil slurries in DGT probes was investigated as a function of time. In these experiments, two soil sub-samples from each pot before the first sowing and after the second harvest were sampled and a mixed sample of each type of soil was prepared. Mixed soil portions of 75 g of each soil type were weight in 8 plastic containers, adequate amounts of deionized water (19 ml) were added to the soil until saturation (0.25 ml/g) and the resulting slurries were stored overnight and allowed to equilibrate for 24 h in closed containers at ambient temperature. After equilibration, the DGT units were applied to the saturated soil slurries, slightly pushed into the surface, thus ensuring good contact of the membrane with the soil solution without any air bubbles. The containers were closed and Petri dishes with wet cellulose were placed into the containers to keep moisture of the soil mixture constant. Three replicates per container were kept at ambient temperature 25 °C, one container without DGT served as the start blank. After 6, 12, 24, 30, 48, 72 and 96 h the DGT units were removed from the soil, carefully rinsed with deionized water and dismantled. The resin layer was retrieved and immersed in 1 ml of 1 M HNO_3 for 24 h. After DGT deployment, soil solution was obtained from slurries by centrifugation at 6000 rpm for 10 min and by subsequent filtration. The start blank soil solution was used as 0 h. Cadmium and copper concentrations in 1 M HNO_3 eluates and soil solution were determined by electrothermal atomic absorption spectrometry (ET-AAS) employing the Perkin-Elmer Model AAnalyst 600 Zeeman effect background corrected atomic absorption spectrometer and used for soil characterization and also for calculation of the ratio of DTG-measured c_{DGT} and total c_{sol} concentrations of a metal in soil solution $R = c_{DGT}/c_{sol}$ [14], which can characterize bioaccessibility of a metal.

2.6. Statistical analysis

One-way analysis of variance (ANOVA) (Microsoft Excel 2007) was used to evaluate the results. Statistical significance was declared when *p* Value was equal to or less than 0.05. The results are presented as means ± standard deviation. Relationships between parameters were expressed by correlation coefficients after Pearson.

Table 1
Cadmium content in non-sown soils samples determined by leaching procedure, content of metals in the soil evaluated from soil solution and DGT measurements.

Soil/extracting agent	2 M HNO_3 (μg kg^{-1} Cd)	Soil solution (μg kg^{-1} Cd)	DGT (μg kg^{-1} Cd)
Non-treated soil	49 ± 3	0.9 ± 0.1	0.015 ± 0.003
Soil A	990 ± 28	1.9 ± 0.7	1.5 ± 0.3
Soil B	1998 ± 51	3.8 ± 0.5	3.3 ± 1.0

Table 2
Copper content in non-sown soils samples determined by leaching procedure, content of metals in the soils evaluated from soil solution and DGT measurements.

Soil/extracting agent	2 M HNO_3 (mg kg^{-1} Cu)	Soil solution (mg kg^{-1} Cu)	DGT (mg kg^{-1} Cu)
Non-treated soil	7 ± 1	0.008 ± 0.001	0.003 ± 0.001
Soil C	124 ± 11	0.076 ± 0.019	0.032 ± 0.003
Soil D	225 ± 19	0.100 ± 0.006	0.051 ± 0.003

3. Results and discussion

3.1. Leaching experiments

Nitric acid leachable contents of cadmium and copper related to a dry mass of soil samples are summarized together with their contents calculated from soil solutions and measured by DGT in Tables 1 and 2.

The artificial loading of soil was validated. The quasi-total concentrations of cadmium and copper found in spiked soil samples were in good agreement with the addition of metals salts. Analogously to our previous work [15], the contents of DGT measured labile metals were several orders of magnitude lower than quasi-total metal contents obtained by nitric acid leaching. The concentrations calculated from soil solution were in case of cadmium in spiked soils very similar to those obtained by DGT. This showed high ion exchangeable fraction of cadmium in these soils. In contrast, DGT recorded less than 20% of soluble cadmium in the non-treated control soil. In the case of copper, DGT measured concentrations were only a half of those calculated from soil solution concentration. Some of the soluble copper species were non-DGT measured. It is assumed that soluble free ion metal fraction in soil solution corresponds to the mobile and plant accessible fraction [16–18]. However, the results obtained by DGT showed that some soluble metal species could not be measured and bioaccessible. Therefore, researchers understand a DGT measured metal fraction as the more really bioaccessible one.

The concentration of both metals in sown soil samples did not statistically differ from non-sown soils. It demonstrated that radish plants took up some amounts of metals to their tissues during growing, but this loss did not influence the metals amount and metal speciation in soils.

3.2. DGT experiments

3.2.1. DGT metal accumulation as a function of time

The accessibility of metals in soil is related to the metal flux from the solid phase to the plant and to the DGT. The fluxes of cadmium and copper in spiked soils (both non-sown and sown) were within statistical scope of measurements independent of time exposition (till 96 h) (Figs. 1 and 2). On the other hand, the non-treated control soil had only a small supply of released metals. The mass flux of cadmium in non-treated soil decreased after two days from 3.5 ng cm^{-2} d^{-1} to 1.3 ng cm^{-2} d^{-1} (Fig. 3) and the mass flux of copper into DGT was reduced rapidly, the most mobile and accessible part was depleted in one day from 14 ng cm^{-2} d^{-1} to 4 ng cm^{-2} d^{-1} (Fig. 4). The rapid depletion showed strongly bonded copper on solid soil phase than more mobile cadmium. By contrast,

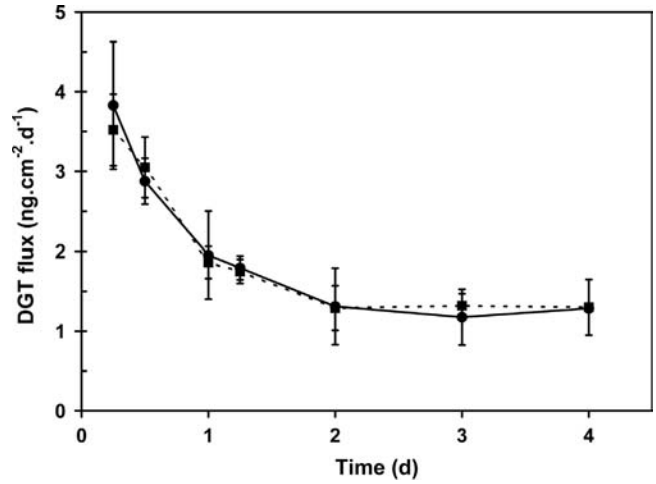

Fig. 1. Dependence of the cadmium flux from the solid phase to the DGT on time exposition for the non-treated control soil. ■ – Non-sown soil, ● – sown soil.

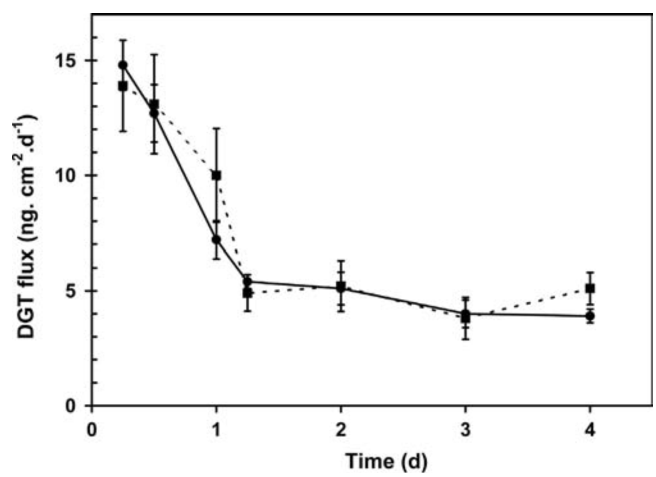

Fig. 2. Dependence of the copper flux from the solid phase to the DGT on time exposition for the non-treated control soil. ■ – Non-sown soil, ● – sown soil.

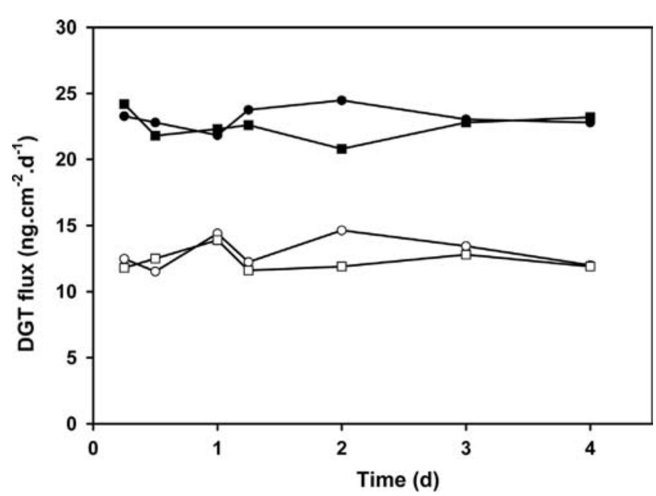

Fig. 3. Dependence of the cadmium flux from the solid phase to the DGT on time exposition for the spiked soils. ■ – 2 mg kg^{-1} non-sown soil, ● – 2 mg kg^{-1} sown soil, □ – 1 mg kg^{-1} non-sown soil, ○ – 1 mg kg^{-1} sown soil. Error bars are not shown in order to achieve better clarity (n=3).

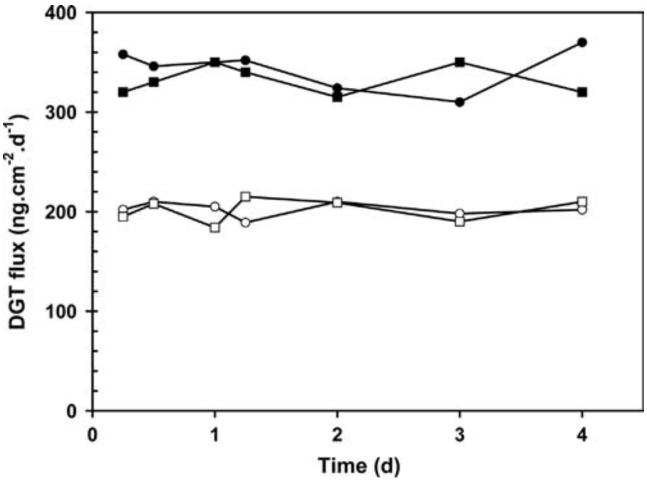

Fig. 4. Dependence of the copper flux from the solid phase to the DGT on time exposition for the spiked soils. ■ – 200 mg kg^{-1} non-sown soil, ● – 200 mg kg^{-1} sown soil, □ – 100 mg kg^{-1} non-sown soil, ○ – 100 mg kg –^{1} sown soil. Error bars are not shown in order to achieve better clarity (n=3).

the released supply of the spiked soils was proportional to the added amount of metal salts. These soils were able to resupply cadmium and copper to soil solution continuously during the experimental period (4 days) under DGT demand. The average fluxes for spike 1 and 2 mg kg^{-1}cadmium in non-sown soil were 13.0 ± 1.3 ng cm^{-2} d^{-1} and 23.1 ± 2.1 ng cm^{-2} d^{-1}, respectively, and in sown soil 12.3 ± 1.5 ng cm^{-2} d^{-1} and 22.5 ± 2.0 ng cm^{-2} d^{-1}, respectively. The average fluxes for spike 100 and 200 mg kg^{-1} copper in non-sown soil were 202 ± 28 ng cm^{-2} d^{-1} and 348 ± 25 ng cm^{-2} d^{-1}, respectively, and in sown soil 201 ± 26 ng cm^{-2} d^{-1} and 332 ± 32 ng cm^{-2} d^{-1}, respectively. These values could be considered as soil long term maximum metals resupply fluxes (ng cm^{-2} d^{-1}).

Both the leaching experiments and experiments with DGT showed that radish growing did not influence the metals amount and speciation in soils.

3.2.2. *Metal concentrations estimated by DGT technique*

Providing the DGT-measured flux remains constant throughout the deployment, *in situ* concentrations of metals in soil solution c_{DGT} can be calculated directly from the DGT measurements of fluxes of metal ions to the DGT unit

$$c_{DGT} = (F\Delta g)/D$$

where F is flux of metal ions diffusing through the gel layer, Δg is the thickness of the gel layer and D is the diffusion coefficient of the metal in the gel.

Comparison of the DTG-estimated c_{DGT} and total concentrations of a metal in soil solution, $c_{sol,}$ expressed by value R ($R = c_{DGT}/c_{sol}$; $0 < R < 1$), can characterize bioaccessibility of a metal in a soil. The R-value approaching 1 means the metal is present in form of mobile and kinetically labile species in the solid phase and also the metal re-supply from the solid phase to pore water is sufficiently fast. The R-value approaching 0 is an indicative of only limited or even no metal re-supply from the solid phase and the metal concentration decreases in the vicinity of the DGT unit during the deployment period [14].

Before and after deployment of the DGT units, the soil solutions were extracted. No significant changes in metal concentrations in equilibrated soil solutions in all the experiments were observed. This suggested that metal losses caused by DGT units were fully re-supplied with respect to the total concentration in the soil solution. However, the ratio of the DGT-measured concentration and the total concentration in soil solution (R) (Tables 3 and 4)

Table 3
R-value ($R = c_{DGT}/c_{sol}$) for cadmium.

Soil	C_{sol} (ng ml^{-1})	C_{DGT} (ng ml^{-1})	Ratio R ($R = c_{DGT}/c_{sol}$)
Non-treated soil	0.9 ± 0.3	0.2 ± 0.1	0.25 ± 0.12
Soil A	13.7 ± 3.2	11.5 ± 2.4	0.84 ± 0.48
Soil B	36.9 ± 8.3	32.5 ± 6.1	0.88 ± 0.56

Table 4
R-value ($R = c_{DGT}/c_{sol}$) for copper.

Soil	C_{sol} (ng ml^{-1})	C_{DGT} (ng ml^{-1})	Ratio R ($R = c_{DGT}/c_{sol}$)
Non-treated soil	13 ± 3	1.4 ± 0.6	0.11 ± 0.04
Soil C	127 ± 12	45 ± 14	0.32 ± 0.11
Soil D	202 ± 13	64 ± 7	0.32 ± 0.04

indicated that in the control non-treated soil only a part of the total metal content was apparently detected by the DGT technique. The higher value of ratio R for cadmium (0.25) than for copper (0.11) confirmed that cadmium was more mobile in the tested non-treated soil. Metals applied as in soil metal salts were in different forms than in the natural non-treated soil even after a six-month equilibration. The added cadmium was very mobile. Copper R-value indicated that only a part of copper species in soil solution was apparently reflected by the DGT technique which confirmed more strongly bonding of copper to soil solid phase. It corresponded with the results reported by Korcak and Fanning [19]. Their results obtained in an experiment study on plant uptake of zinc and cadmium showed differences between artificially and naturally contaminated soils. The use of natural soils is therefore essential for the assessment of hazards posed by metals.

3.3. *Plant experiments*

The mass of radish plants grown on non-treated and spiked soils did not statistically differ. The average mass of one radish plant during the experiment with cadmium was 7.50 ± 2.12 g and with copper 7.30 ± 1.81 g. It indicated that the addition of cadmium and copper salts did not influence plant growth. In average, the weight of leaves reached 20 ± 2% and the weight of bulb reached 78 ± 5% of the total plant mass. Concentration of cadmium and copper in both parts of radish increased with increasing content of metals in soil. Metal uptake by radish bulb was higher than by leafs (about 75%). The metal concentrations in plants were used for calculation of the metal flux of metal to plants expressed as μg of metal intake into the plant per day. The metals fluxes to radish were correlated with the metal fluxes to the DGT units (Figs. 5 and 6).

3.4. *Comparison of the used procedures*

The concentrations of cadmium and copper in all used soils obtained by the DGT technique were compared with those calculated from soil solution. The high values of correlation coefficients ($R^2 > 0.95$) were found between the content of metals in soil solution and content of metals in radish plants. Numerous experiments showed that the biological effects of trace metals are related to the free metal ion activity [16,17]. The accessibility of metals in soil is related to the metal flux from the solid phase to the plant and to the DGT. Zhang et al. [18] reported first that DGT measured fluxes of copper related well to copper uptake by *Lepidium heterophyllum* plant. Similar experiments have been performed for different metals, plants and soils [20,21]. We found high correlation flux to radish plant and flux to DGT, for cadmium R^2=0.994 and for copper R^2=0.998. The relation of DGT flux

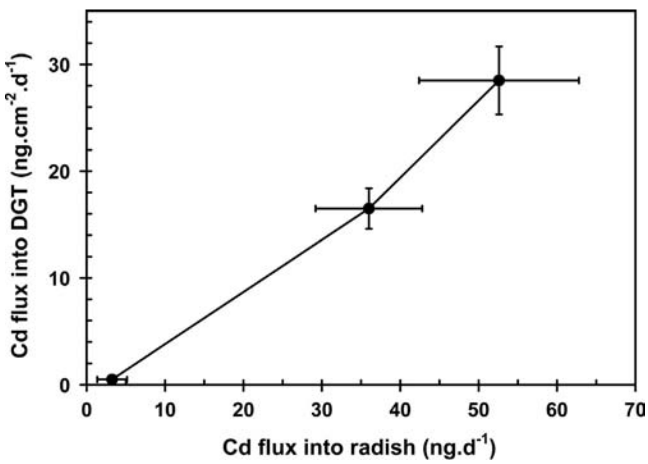

Fig. 5. Relation of Cd flux to DGT (ng cm^{-2} d^{-1}) to the flux into radish plant (ng d^{-1}).

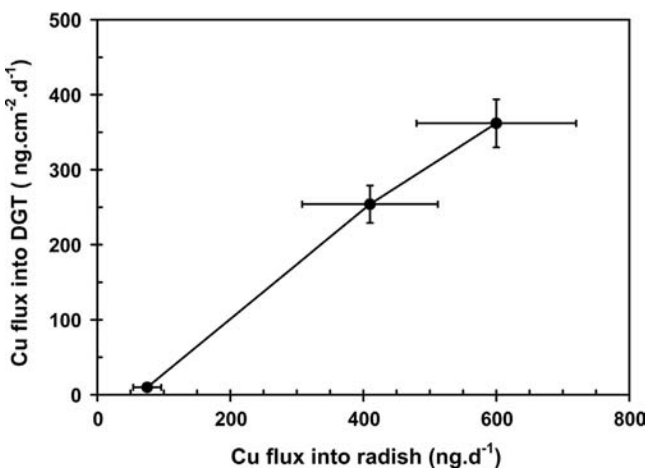

Fig. 6. Relation of Cu flux to DGT (ng cm^{-2} d^{-1}) to the flux into radish plant (ng d^{-1}).

(ng cm^2 d^{-1}) to flux into radish plant (μg d^{-1}) is shown in Figs. 5 and 6. The fluctuation of individual results indicated biological variability among the plants grown in the experimental pots.

4. Conclusion

For assessment of quasi-total contents of cadmium and copper in the studied soils, leaching procedure with nitric acid was used. Complementary the soil slurries were prepared, soil solutions extracted and DGT units applied. The quasi-total contents found in spiked soils were in good agreement with the addition of metal salts that means soil samples were correctly loaded by both studied elements.

Experiments with DGT showed that spiked soils were able to supply metals depletion caused by DGT unit continuously during the time of the experiment (4 days) while the non-treated control soils had only a small pool of accessible metal forms. After one day (copper) and 2 days (cadmium) of DGT deployment the fluxes were reduced to 0.3 (copper) and 0.4 (cadmium) of the initial values. Metals added into the soil in the form of inorganic salts showed different behavior in spite of the six months incubation period. Cadmium showed to be more mobile; *R*-value for non-treated control soil was 0.25, for spiked soils was 0.84–0.88. Copper was relatively strongly fixed to soil particles, *R*-value for the non-treated soil was 0.11 and for spiked soils was 0.32. This fact indicated that only a part of copper species in soil solution was apparently measured by the DGT technique. Concentrations of cadmium and copper were determined in tissues of radish plants grown on the studied soils and metals fluxes to plant were calculated. High values of correlation coefficients ($R^2 > 0.95$) were found between the content of metals in plant tissues and metal contents in soil evaluated from soil solution. Highly significant correlations were found between flux to radish plant and flux to DGT, for cadmium $R^2 = 0.994$ and for copper $R^2 = 0.998$.

It can be supposed that the DGT technique can be used as physical surrogates for plant uptake, thus offering the possibility of a simple test procedure for measurement of bioaccessible metal species in soils.

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