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# PREDICTION OF BIOAVAILABILITY OF METALS TO PLANTS: COMPARISON BETWEEN CHEMICAL ANALYSIS, DGT MEASUREMENT AND SOIL GROWN PLANTS

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**The accumulation of trace metals and metalloids in soils is of increasing concern due to the negative effects on soil ecosystems and potential health risk. Soil to plant transfer of trace metals is one of the major pathways of human contamination. The prediction of bioavailability is then essential for the assessment of environmental quality and health risks. Experiments were performed with the radish *(Raphanus sativus)* grown in a greenhouse in non-treated and gradually spiked soils (100 and 200 mg Cu/kg and 1 and 2 mg Cd/kg). Dandelion plants (*Taraxacum officinale)* were sampled together with soil from three sides of the city of Brno differentially impacted by soil pollution, and Cd and Pb were studied. The metal concentrations in soils calculated from soil solution were correlated with Diffusive Gradient in Thin Films technique (DGT) measurements and metal uptake by plants.**

## Can DGT predict metals accessibilty for plants?

## METHODOLOGY:

**Radish plants were grown in greenhouse on tested not-treated and gradually spiked soils**

### Soil treatment

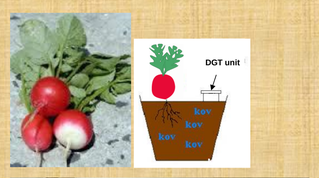
Homogenized and sieved soil sample Žabčice site, South Moravia district, Czech Republic
Soil sample distributed into pots with 6 kg of soil
**Spiking soil sample in pots:**
Soil samples in pots were enriched with $Cd^{2+}$ (1 and 2 mg/kg) and $Cu^{2+}$ (100 and 200 mg/kg) 100 mg/kg and 200 mg/kg
**Control sample:** Non-spiked soil

### Pot experiments

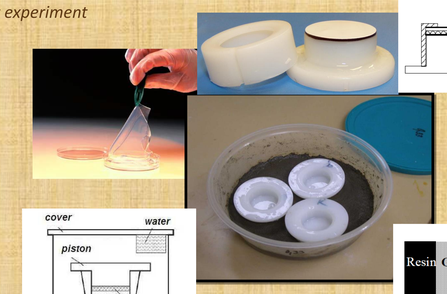
**Sowing of radish plants:**
Both in the control sample and enriched soils
5 radish plants were cultivated in each of 4 pots with the same soil sample
**Harvesting of radish plants:**
2 harvests during April-June 2012
5 weeks after sowing
Plants rinsed with deionized water and air dried mineralized and analysed

### DGT experiments

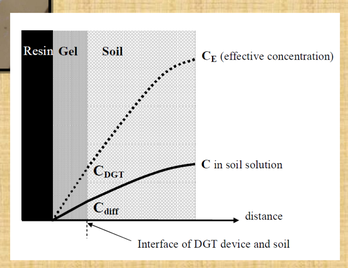
Gels and sampling units for DGT experiments were prepared according to the conventional procedures [1, 2]
**Application of DGT units into the soil:**
DGT sampling units were placed in each soil sample slurry in triplicate with the moisture content of 100% of MWHC at 24°C (Fig. 4)
**Determination of the accumulated mass of Cd and Cu**
Elution of resin gel in 1M $HNO_3$




*Plant experiment*




*DGT experiment*




*Schematic illustration of how measured quantity $C_{DGT}$ relates to the effective concentration in soil solution $C_E$*

### Soil solution analysis

centrifugation followed by membrane filtration (0.45µm)

### Determination of metals

Electrothermal atomic absorption spectrometry , ET AAS employing Perkin-Elmer Model AAnalyst 600 Zeeman -effect background corrected atomic absorption spectrometer was used for determination of Cd, Cu and Pb in soils, plants and DGT eluates

**Dandelion plants were sampled together with soil from three sides in the city of Brno differentially impacted by pollution, Cd and Pb were studied**


*The sampling site at **Opuštěná** Street (**A**) represents an industrial heavily polluted location with high traffic density, situated in the city centre. Sampling site at **Vídeňská** Streets(**B**) belong to medium polluted location situated close to busy roads. Relatively clean location is represented by **Šrámkova** Street (**C**) residential areas, situated in peripheral city district with lower contamination loading.*

### Soil samples

Soil samples were collected in April 2012 in the immediate vicinity of the dandeli on plant from a depth horizon of 0-10 cm, ten samples at every sampling place, which represented an area of 10sq.m.

### Plant samples

Ten plants of the common dandelion grown on the sampling place were carefully extracted from the soil, placed in plastic bags and transported to the laboratory. There dandelion leaves and roots were separated and washed with distilled water, air-dried, mineralized and analysed.

### Effective concentration, $C_E$

$C_E$ represents as a concentration the supply of metal to any sink, be it DGT or a plant, that comes from both diffusion in solution and release from the solid phase.

### Calculation of $C_E$ from DGTmeasurement

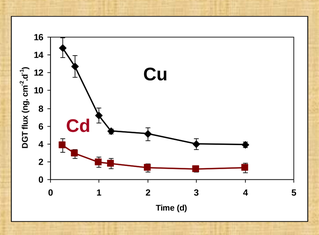
A full numerical model in two dimensions of the tome dependent interaction of a DGT device of variable geometry with soils having various properties – **2D DIFS** was used. *http://www.es.lancs.ac.uk/wdgroup/aquach.htm*

$C_{diff} = ( M . \Delta g ) / ( D . A . t )$ – *the mean interfacial concentration*

$R_{diff} = C_{diff} / C_{sol}$

$C_E = C_{DGT} / R_{diff}$

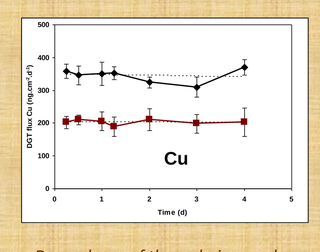
## RESULTS:

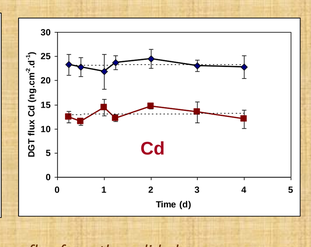



*Time limited copper soil/pore water flux measured by DGT samplers in the non-spiked control soil*

Non-treated soils had only a small pool of accessible metal forms in both experiments.

- **Estimation of long term maximum metal resupply flux (ng cm$^{-2}$ d$^{-1}$) of studied soil**



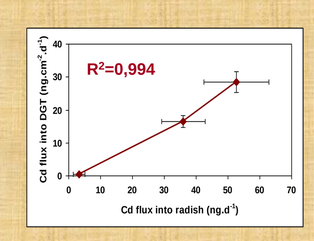



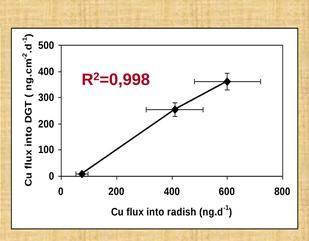

*Dependence of the cadmium and copper flux from the solid phase to the DGT on time exposition for spiked soils*

*Cd: ♦ 2 mg.kg$^{-1}$ ■ 1 mg.kg$^{-1}$, Cu: ♦ 200 mg.kg$^{-1}$ ■ 1 mg.kg$^{-1}$*

Spiked soils were able to supply metals depletion caused by DGT unit continuously during the time of experiment (4 days).

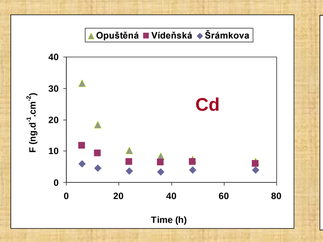
Metals added into the soil in the form of inorganic salts showed different behavior in spite of the six months incubation period.

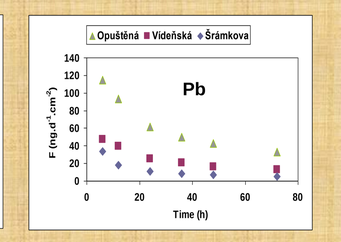


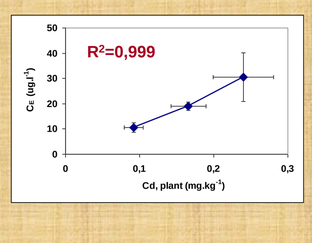

*Relation of DGT Cd and Cu-flux to the flux into radish plants*

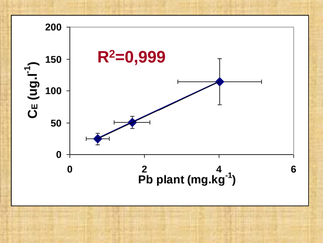
Concentration of Cd and Cu were determined in tissues of radish plants growing on studied soils and metals fluxes to plant were calculated.
High values of correlation coefficients ($R^2 > 0.95$) were found between the content of metals in plant tissues and metal contents in soil evaluated from soil solution.
**The significant high correlations were found between flux to radish plants and flux to DGT.**




*Time limited Pb and Cd soil/pore water flux measured by DGT samplers in the urban soils*




*Relation of $C_E$ and metal concentrations in plants*

**The significant high correlations were found between flux to dandelion plants and flux to DGT**

## CONCLUSION:

**It was shown that DGT can be used as physical surrogate for plant uptake. DGT offers the possibility of simple test procedure for measuring bioaccessible metal species in soils. The DGT measurement of effective concentrations, $C_E$, has been shown to give a better correlation to plant uptake than any other measurement and may provide a major step forward in assessing hazards posed by metals in contaminated soils.**

**DGT can be used as an alternative tool for assessment of bioavailable metal pool in soils.**

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*[1] Davison W., Zhang H.: Nature 367, 545 (1994)*
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*[3] Sachaczewski L, Tych W, Davison W, Zhang H, 2D DGT induced fluxes in sediments and soils (2D DIFS), Environmental Modelling and Softwarwe, 22, 1, 14-23 (2007)*