

Characterization of Czech Soils by Diffusive Gradients in Thin Films Technique*

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In situ measurements were performed by means of the diffusive gradients in thin films (DGT) technique in order to characterize the sewage sludge amended soil from one representative sampling site in the Czech Republic, included in the monitoring investigations. This technique reflects actual metal ion concentrations in soil solution, the rate of metal resupply from soil solids to soil solution, and the transport rate of metal ions through the soil. The DGT technique is likely to provide a good surrogate for a metal pool in contaminated soils, which might be available for a metal uptake by a plant root system.

Recently an *in situ* technique capable of quantitative measuring of labile metal species in waters has been developed [1]. This technique, known as diffusive gradients in thin films (DGT) technique, has been successfully used to measure the *in situ* concentrations of metals in natural waters, metal fluxes in sediments and soils, and also to estimate concentration of metals in pore waters [2–5].

The DGT technique employs a specific ion-exchange resin (typically Chelex 100) embedded in a hydrogel, which is covered by a layer of ion-permeable hydrogel of well-defined thickness (Δg). Both layers of hydrogel are held together in a piston-like assembly so that only ion-permeable gel is exposed to the solution (Fig. 1). Consequently, transport of simple metal ions from the solution to the resin gel is determined by concentration gradient induced in the diffusive gel. Schematic view of the commercially available polypropylene piston probe equipped with a diffusion window of 2 cm in diameter is presented in Fig. 2.

After diffusing through the ion-permeable gel, metal ions are rapidly immobilized by the resin gel. Provided this resin sink is not saturated and the solution concentration remains constant, a linear concentration gradient is established in the ion-permeable gel in a short time period of approximately one minute. In this instance, the solution to sink flux (F) of a given metal ion is based on the Fick's first law of diffusion

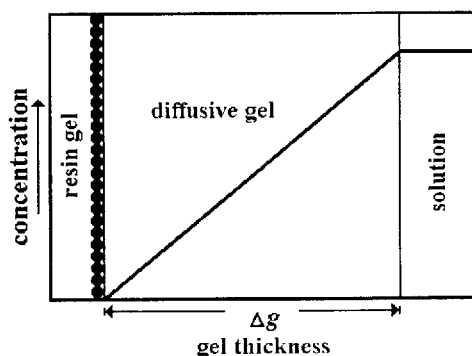


Fig. 1. Scheme of the concentration gradient of metal ion species established in the ion-permeable gel by diffusion processes and metal uptake by resin gel.

$$F = D \cdot c / \Delta g = m / (A \cdot t) \quad (1)$$

where c is the free ion concentration in the solution, D is the diffusion coefficient of an ion in a diffusion gel, typically indistinguishable from the value of the free ion in water (order of $10^{-6} \text{ cm}^2 \text{ s}^{-1}$), m is the mass of metal ion diffused through the diffusion area A after deployment time t . The metal flux and subsequently the *in situ* metal concentration in the bulk solution can be calculated from the mass (m) directly measured by using suitable elution and analytical procedures. This

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EXPERIMENTAL

Soil Samples

A representative sample of arable soil from one site contaminated with heavy metals as a result of the fertilization with sewage sludge in the Czech Republic (Zlín, cadastral No. 7901, longitude 49°12'40", latitude 17°34'48", elevation 195 m) was taken in spring 1999 [6]. The sample represented an average from a mixture of 4 × 8 sub-samples taken with a probe rod method (EDELMAN's probe) of an area of 100 m² (25 m × 40 m) from the depth soil horizon of 0–10 cm. For characterization, a fine soil fraction of particle size below 2 mm was obtained by sieving the air-dried raw sample, from which large components were separated (stones, plant parts).

The main soil characteristics found according to the ordinary test methods [7, 8] are: middle soil type, pH 6.9, content of plant available macroelement 444 mg kg⁻¹ P, 320 mg kg⁻¹ K, 277 mg kg⁻¹ Mg, an 6500 mg kg⁻¹ Ca, content of exchangeable hydrogen 4.1 %, content of organic matter 2.64 % and humic acids 4.55 % [9].

For all laboratory DGT deployment experiment the air-dried soil sample (dry matter content of (98 ± 0.5) %) was weighed into acid-cleaned polypropylene containers and slurried well with high-purity water. The mixture was then equilibrated for 2 days at ambient temperature in closed containers. The water/soil mass phase ratio reflected in fact the moisture content, expressed in percentage as a ratio of a mass of water contained in 1 g of an oven-dried soil sample. It can be interpreted as moisture content in field conditions.

Preparation of DGT Probes

DGT pistons, special tools and reagents were obtained from DGT Research (Lancaster, Great Britain; <http://dgtresearch.com/>), unless otherwise specified. Both resin-embedded and ion-permeable gels were based on a polyacrylamide hydrogel, which was composed of 15 vol. % acrylamide and 0.3 vol. % pattern agarose-derived cross-linker. Freshly prepared ammonium persulfate initiator (70 mm³ of 10 % solution) and TEMED (tetramethylethylenediamine) catalyst (20 mm³) were added to each 10 cm³ of gel solution. In addition, the resin gel solution contained 2 g of Chelex 100 ion-exchanger (Na-saturated, "20 400 mesh", Bio-Rad). The gel solution was cast between two glass plates and set at (42 ± 3)°C for 30 min in an incubator. Thickness of final gels was controlled by using plastic spacers, e.g. for manufacturing gel layers of 0.8 mm thickness, typically the 0.5 mm thick spacer was employed. The gels were then hydrated in high-purity water for at least one day to allow them to swell to a stable thickness. A fully

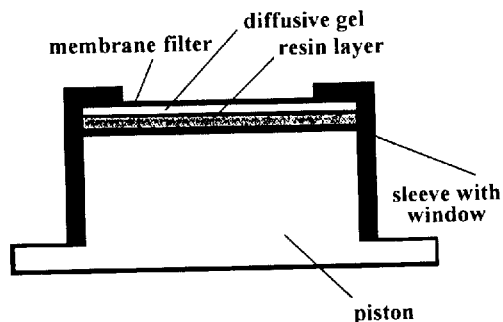


Fig. 2. Schematic view of the commercially available DGT probe (DGT Research, Lancaster, Great Britain; <http://dgtresearch.com/>).

holds for open solutions, where convective processes maintain constant concentration of a metal in the solution.

However, transport in pore waters is by molecular diffusion, which may be further limited by tortuosity of the diffusion pathway. Consequently, concentration within the pore water close to the gel can be progressively depleted with increasing exposure time. The Fick's second law of diffusion, which can be solved numerically for known boundary conditions [5], then defines concentration profiles. The instantaneous flux to the resin layer can be calculated from the actual concentration gradient at the gel surface at any time during deployment of a gel assembly. In this instance, gel assemblies measure the metal mass per unit area in the resin layer, which divided by the time of deployment, gives a mean flux to the resin layer.

If used in soil systems, it is an important feature of the DGT that it perturbs *in situ* the soil–solution system in a known way while simultaneously recording the response. When metal ions are removed from a soil solution by a plant uptake or by the DGT system they may be resupplied by diffusion processes from the outer zones of pore water of the soil or directly from the solid phase near the gel. Thus, DGT can provide information about the kinetics of metal release from the solid phase to the solution in soils when the latter process predominates. Since the mass or flux measured by DGT depends on the concentration gradient between the soil solution and the resin gel, a variable "demand" for metal ions can be created by manipulating the thickness of the ion-permeable gel. Thus, metal uptake by a root system of a plant can be simulated. A linear plot of the measured mass or flux against reciprocal diffusive gel thickness ($1/\Delta g$) implies that the rate of resupply of metal ions from the solid phase is the same as their rate of removal from the solution.

In this work, the DGT technique was applied for characterization of a soil from a monitored field in the Czech Republic amended recently by a contaminated municipal sewage sludge.

drated ion-permeable gel contained about 95 mass % of water. Finally, gel disks of 2.5 cm in diameter were cut from the gel layer by a plastic tool and stored in 0.01 mol dm^{-3} high-purity NaNO_3 solution. The two-part DGT assembly (Fig. 2) was completed with a resin gel, covered with a disk of diffusive gel and membrane filter ($0.45 \mu\text{m}$ pore size Gelman Laboratory Supor®-450 hydrophilic polyethersulfone, Pall Corporation, Michigan, USA) on top of it to prevent soil particles to adhere onto the diffusive gel. Unless otherwise stated, 0.8 mm thick ion-permeable and 0.4 mm thick resin gels were used.

Deployment Procedure

The DGT pistons were placed onto the prepared soil surface with intimate contact between filter and soil to avoid air bubbles in the interface region. Typically, when not specified, DGT devices were deployed in soil samples in triplicate for 24 h. All experiments were conducted at $(25 \pm 2)^\circ\text{C}$. In order to prevent the loss of water from equilibrated soil samples the gas phase was saturated with water vapour.

On retrieval, the DGT unit was rinsed with high-purity water and then disassembled. The resin disk was placed for 24 h into an acid-cleaned plastic vial containing 1 cm^3 of high-purity 1 mol dm^{-3} HNO_3 and metals chemisorbed in the resin were eluted. The DGT-accumulated masses of metals were calculated from their concentrations in the eluate. Total volume of the gel and eluate (1.16 cm^3 for 0.4 mm resin disks) and elution efficiency of 0.8 were taken into account. *In situ* fluxes of metals to DGT device and metals concentration in the soil solution were obtained by using the equation of the Fick's first law of diffusion, where

corresponding values of diffusion coefficients of simple ions were introduced (eqn (1)). Simultaneously, blank experiments, which included gel preparation and elution, were carried out.

In addition, a portion of the equilibrated soil was taken before and after the deployment and the soil solution was obtained by centrifugation at 6000 min^{-1} for 10 min and by subsequent filtration through the membrane filters ($0.45 \mu\text{m}$ pore size, Gelman Laboratory).

Determination of Metals by Atomic Absorption Spectrometry

Metals (Cd, Cu, Cr, Ni, and Pb) were determined in the eluates and filtrates under recommended conditions, specified by the producer, by electrothermal atomic absorption spectrometry employing Perkin—Elmer Model 4110 atomic absorption spectrometer equipped with Zeeman effect background correction system, transversally heated graphite tube with integrated platform and corresponding hollow cathode lamps. Calibration was performed by standard addition method, when using ASTASOL (Analytika, Prague, Czech Republic) metal aqueous standard solutions. In determination of cadmium and lead, recommended palladium and magnesium nitrate chemical modifiers were used.

RESULTS AND DISCUSSION

In field conditions soils may have a range of moisture contents. Therefore, knowledge of the effect of soil moisture content on availability of metal ions in soil solution is essential. To investigate the effect of

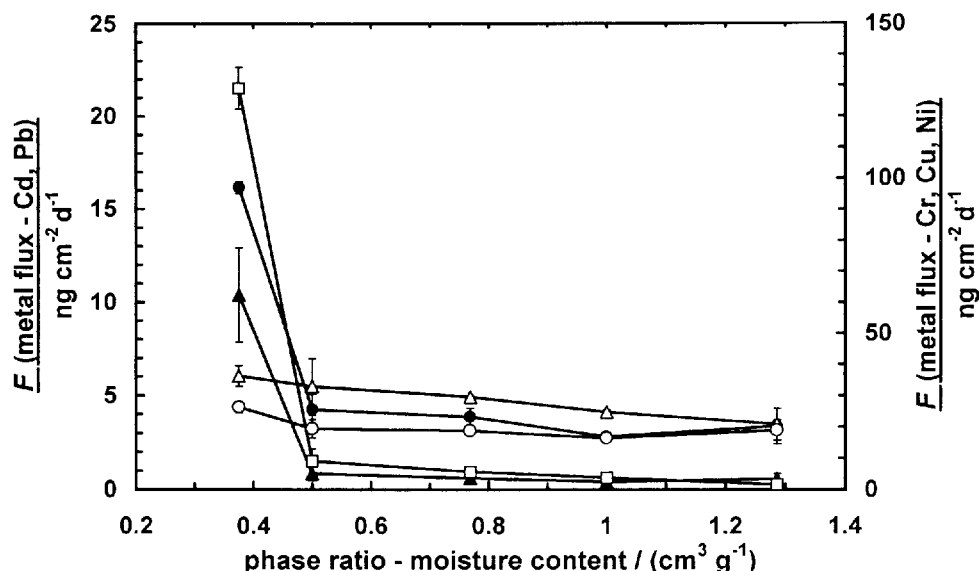


Fig. 3. Influence of moisture content on the metal flux measured by the DGT probe for sampling site Zlín, depth horizon 0–10 cm, deployment time 1 d, temperature 25°C . ● Cd, □ Cr, △ Cu, ○ Ni, ▲ Pb.

varying soil moisture, the DGT devices were deployed in the soil aliquots with various soil moisture contents ($m_{\text{water}}/m_{\text{soil}}$ ratio) from 37 % to 130 %. Devices with 0.82 mm thick gels were deployed for 24 h. The results are graphically summarized in Fig. 3. The metal fluxes were strongly influenced by soil moisture content. Behaviour of Cd, Cr, Pb and Cu, Ni groups of elements significantly differed in the region of low soil moisture content.

These differences can be explained by the influence of various parameters in heterogeneous equilibrium between the soil solution and the solid phase of a soil. Analogously to ion-exchange equilibrium, the heterogeneous equilibrium can be described by the equilibrium distribution coefficient K_d , which is in this instance a ratio of the equilibrium concentration of the respective metal ion in the soil solution (pore water) and the equilibrium concentration of the same metal in the soil

$$K_d = (c_{\text{pore water}}/c_{\text{soil}})_{\text{eq.}} = D_e/r \quad (2)$$

where D_e is the conditional distribution ratio of the metal and r is the soil water/soil solid matrix phase ratio (soil moisture content). Competitive complexation, acid-base, redox, and solubility processes might be incorporated in this equilibrium distribution coefficient K_d , and can be reflected by the value of this coefficient. The equilibrium concentration of the metal ion in the soil solution (leachate, pore water) can be expressed by means of the initial concentration of an extractable component of a metal in the soil $c_{0 \text{ soil}}$

$$c_{\text{pore water}} = c_{0 \text{ soil}} \cdot 1/((1/K_d) + r) \quad (3)$$

Assuming the same initial concentration of a metal in the soil $c_{0 \text{ soil}}$, this equation enables to estimate the influence of the phase ratio and the value of the distribution coefficient on the concentration of a metal ion in the soil solution. It is evident that the concentration of the metal ion in the soil solution increases hyperbolically with decreasing soil moisture content. This concentration effect is enhanced when solubility of the metal species in the solid phase of the soil is high ($K_d \rightarrow \infty$). On the contrary, when competitive processes in the solid phase are very strong, the concentration effect is reduced. Obviously, this effect is responsible for differences observed between elements of the same soil sample. Copper and nickel are probably bound more strongly to the soil components than cadmium, chromium, and lead, so that the effective values of distribution coefficients for copper and nickel are lowered, down to the value of 10^0 g cm^{-3} .

In addition to the heterogeneous equilibrium, an effect of the water regain by solid matrix of a soil can also be expected. Evidently, when mixing dry soil samples of various types in laboratory experiments, water is retained in a soil matrix in a different manner. This

is probably due to specific hydrophilic demand of soil components in each type of a soil. A fraction of water added, which is occupied by these soil components reduces effective volume of the liquid phase introduced, apparently available for the extraction of metals. The phase ratio can then be diminished and the concentration of a metal in the soil solution increased. Of course this effect is more pronounced, if low phase ratios are applied. Consequently, results obtained for the apparently same soil moisture content would be shifted towards the lower phase ratio with different increment. Enhancement in metal concentrations would relate to the maximum water holding capacity (MWHC), typically measured as a water uptake of a defined volume of a nondisturbed soil layer (vol. %), when no suction is applied [10]. For Zlín sampling site relatively high value of MWHC of 43 vol. % was found.

Resupply of metal ions from a soil can be also measured by DGT technique. When accumulating metals by DGT as a function of time and gel thickness, the DGT device can effectively operate as an infinite sink somewhat analogously to the root system, provided the membrane transport is not the limiting process. DGT device can monitor for a long period, comparable to real situations in plant cultivation, the depletion of the available metal adjacent to its surface and also the extent of resupply from the soil's solid phase solution, together with in-soil diffusion processes. The length of time the device can be deployed depends on the capacity of the resin gel. Capability of the soil to balance the demand of the root system can be simulated by the potential DGT demand, when changing the thickness of the diffusive gel.

Devices with different diffusive gel thickness (0.82 mm, 1.14 mm, 1.81 mm, and 3.51 mm) were used to create various diffusion gradients and hence different rates of demand for metal ions. The devices were deployed for 48 h in soils of 0–10 cm horizon, hydrated in phase ratios of $0.600 \text{ cm}^{-3} \text{ g}^{-1}$. This hydration corresponded to approximately 1.5-fold soil moisture content of the MWHC. The measured fluxes of metal ions to the DGT sink are plotted against the reciprocal gel thickness ($1/\Delta g$) in Fig. 4. In the linear range of these plots, *i.e.* for small values of reciprocal thickness corresponding to thicker gel disks of 1.81–3.51 mm, an increase in value of $1/\Delta g$ was followed by a proportional increase in a metal flux. This suggests that the metal concentration in solution is well buffered by rapid resupply from the solid phase. When thinner gel disks (below 1.8 mm) were used, the DGT devices demanded larger fluxes. These fluxes exceeded the maximum that the soil can supply. The DGT measured flux, which is the average value for the whole deployment period, was then smaller than that for the well-buffered case, which is exhibited as a curvature in plots in Fig. 4. The maximum metal resupply flux ($F/(\text{ng cm}^{-2} \text{ d}^{-1})$), which can be assessed from the graphs for Zlín sampling site are 45, 2, 35, 23, and 0.

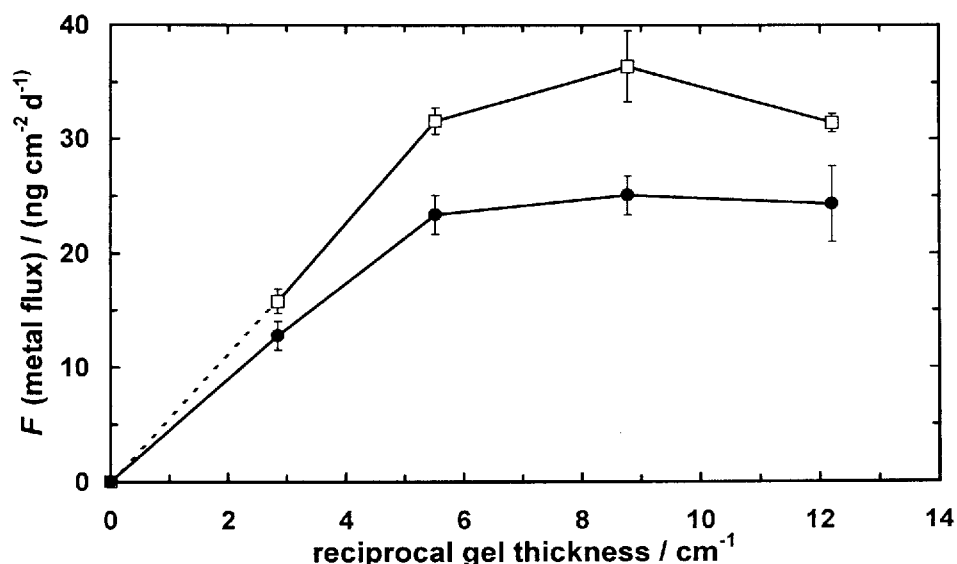


Fig. 4. Influence of a DGT demand (reciprocal diffusive gel layer thickness) on copper and nickel resupply fluxes. Sampling site Zlín, phase ratio $0.6 \text{ cm}^3 \text{ g}^{-1}$, deployment time 2 d, temperature 25°C . \square Cu, \bullet Ni.

for Cd, Cr, Cu, Ni, and Pb, respectively. These fluxes represent the available part of metal pools, which can be supplied potentially to the root system.

Providing the DGT-measured flux remains constant throughout the deployment, *in situ* concentrations of heavy metals in soil solution can be obtained according to eqn (1) directly from the DGT measurements of fluxes of metal ions to the DGT sink.

No significant changes were observed within uncertainty of 5 % in concentrations of metals in equilibrated soil solutions taken before and after deployment of DGT sinks in all the experiments described above. It suggested that metal losses caused by DGT sinks in soil solution were fully resupplied with respect to a total concentration in a soil solution. However, the ratios of the DGT-measured concentration and the total concentration in soil solution, 91 %, 70 %, 27 %, and 39 % found for Cd, Cr, Cu, and Ni, respectively, indicate that only a part of the total concentration is apparently reflected by the DGT technique. Metal concentration at the surface of the DGT device could be insufficiently resupplied due to enhanced DGT demand, thus resulting in lower metal concentration, because local concentration disturbance could not be attained by determination of the metal concentration in a supernatant of the soil slurry. Defined by diffusive gel characteristics, size exclusion or resistance for diffusive transport (decreased values of diffusion coefficients) for large molecules containing a metal could be also responsible for this effect. Lower concentration yields could be also obtained, when DGT-labile and -nonlabile species of a metal are present in a soil solution. Because DGT device accumulates only metal ions from labile species, DGT-estimated concentration might be interpreted as a response of a concentration of available species. In fact,

this part of a metal in a soil solution can really be available to the root system. Therefore, DGT response can become a measure of the bioavailability, in which all the composition of a soil solution, form of metal species, local disturbances, and diffusive transport effects in the soil are included. Thus, DGT-estimated concentration can be considered as a virtual concentration of a bioavailable metal form.

Further systematic speciation studies on real soil solutions, *e.g.* by gel permeation chromatography, ion-exchange chromatography, *etc.* should be made and compared with DGT measurements in order to investigate the fidelity of the DGT response on the real soil systems.

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