In Situ Measurements of Solution Concentrations and Fluxes of Trace Metals in Soils Using DGT

4 AUTHORS, INCLUDING:

Hao Zhang
Lancaster University

191 PUBLICATIONS **6,704** CITATIONS

William Davison
Lancaster University

237 PUBLICATIONS **10,055** CITATIONS

In Situ Measurements of Solution Concentrations and Fluxes of Trace Metals in Soils Using DGT

HAO ZHANG,*,† WILLIAM DAVISON,†
BRUCE KNIGHT,‡ AND STEVE MCGRATH‡

*Division of Environmental Science, Lancaster University,
Lancaster, LA1 4YQ, U.K., and Soil Science Department,
IACR–Rothamsted, Harpenden, Herts, AL5 2JQ, U.K.*

Assessments of the availability of toxic or nutrient metals in soils need to consider solution speciation, mobility, and the kinetics of exchange between solution and solid phase. The newly developed technique of diffusive gradients in thin films (DGT) accumulates metals in a well-defined geometry that allows quantification of their supply from the solid phase. DGT was used to measure potential maximum fluxes of available metals in old arable and ex-woodland soils variously treated with sewage sludge with and without metal amendments. The flux increased with increasing sludge application. The results suggest that for Zn and Cd there are two separate pools of metal associated with the solid phase. In untreated soils or those with 100 m^3 ha^{-1} yr^{-1} sludge treatments, Zn and Cd appear to have higher resupply rate constants from the solid phase than in soils with 300 m^3 ha^{-1} yr^{-1} sludge treatments (assuming the ratio of labile solid-phase metal to soil solution metal does not change). However, the actual rate of resupply is higher in the treated soils due to the much higher concentration associated with the solid phase. For Ni and Cu there appears to be only one pool of metal irrespective of the extent of sludge treatment.

Introduction

Assessment of the impact of potentially toxic metals in soils and the need for bioremediation is hindered by poor understanding of both chemical speciation in soil solution and the kinetics of exchange between solution and solid phase. Different soil properties can alter the toxicity of metals by modifying their bioavailability and hence reducing the impact of the total metal loading (*1*). Variation in solution speciation affects bioavailability, element mobility, and the partition through adsorption/desorption and dissolution/precipitation with the heterogeneous solid phase. To understand the above processes, it is necessary to consider the chemical forms in solution rather than total dissolved concentrations.

Any procedure that separates solution and solid phase inevitably disrupts the physical–chemical equilibrium, which may affect the distribution of species in solution. Furthermore, soil solution obtained by separation cannot represent the 'true' unaltered solution because spatial variability of soil-solution properties on a macro- and microscale are obscured (*2*). Ideally chemical speciation measurements in

soil solution should be made in situ by procedures which either minimize disturbance or perturb the solution in a controlled way.

Metals in the soil matrix are either incorporated within discrete phases or exist as surface-adsorbed complexes. If metal is removed from solution by, for example, biological uptake, it may be rapidly resupplied from the solid phase. Conventional measurements of bioavailability have been unable to measure directly or quantify fully this flux from the solid phase to solution. Several studies have been carried out on the bioavailability of metals and nutrients in soils using either ion-exchange resins directly (batch techniques) or resins encapsulated in, for example, porous materials or embedded in membranes (*3–8*). Results obtained by batch techniques, in which resin and soil are mixed and shaken, are dependent on resin/soil/solution ratios, shaking time, and ionic strength (*9, 10*). Batch techniques cannot provide detailed information on the transportation of ions from soil to the resin sink, which is important for assessing bioavailability. Resin in the form of bags, capsules, and membranes have been used to simulate metal and nutrient movement to plant roots in a more realistic and sensitive manner (*4, 5*). The devices are buried in soil or inserted into a prepared slurry of soil and water. The resin continuously removes species from solution and so provides an in situ measure of their availability to the resin. Although the resin-available fraction correlates with the amount taken up by plants (*5, 11*), these procedures are limited. Due to the poorly defined geometry of the bags and the diffusion layer between solution and resin, the fluxes from soil to solution and from solution to resin cannot be quantified, and so the results obtained by different workers from different laboratories cannot be compared.

Recently an in situ procedure able to measure labile solution species and the flux of available species from solid phase to solution has been developed (*12*). Known as DGT (diffusive gradients in thin films), it has been successfully used to measure the in situ speciation of trace metals in natural waters (*13*) and in situ fluxes from solid phase to pore waters within sediments (*14, 15*). In this paper, we adapt DGT theory for soil applications and present the first set of results of DGT measurements in soils treated with varying amounts of sewage sludge containing heavy metals. To avoid as yet unknown effects associated with unsaturated soils, these initial measurements were made in the laboratory on soils where moisture contents were raised to 120%.

Theory

Concentration Measurement. The DGT technique is based on Fick's first law of diffusion. An ion-exchange resin layer is separated from bulk solution by an ion-permeable hydrogel membrane of thickness Δg (Figure 1). Simple metal ions diffuse through the gel membrane and are rapidly bound by the resin. Providing, as in this work, that the capacity of the resin is not exceeded, the concentration at the resin surface is maintained at effectively zero throughout the deployment, creating a steep concentration gradient in the gel layer. If this concentration gradient remains constant during the deployment time (t) (case i in Figure 1), the flux of ions diffusing through the gel layer (F) is given by eq 1 and the concentration of ions in bulk solution (C) can be calculated using eq 2 (*13*)

$$F = DC/\Delta g \tag{1}$$

$$C = M\Delta g/(DtA) \tag{2}$$

* To whom correspondence should be addressed. E-mail: h.zhang@lancaster.ac.uk; tel: 44-1524-593899; fax: 44-1524-593985.
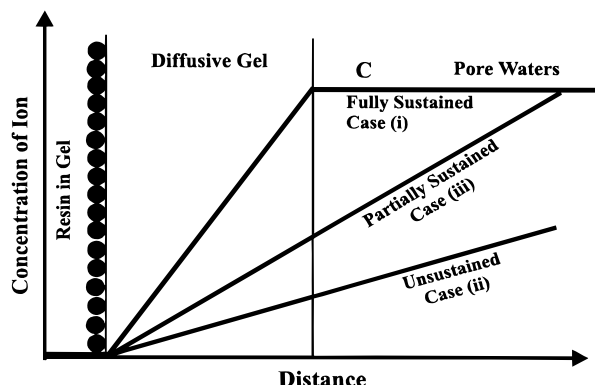† Lancaster University.
‡ IACR–Rothamsted.

FIGURE 1. Schematic representation of the concentration gradient in a DGT assembly in contact with pore waters where the concentration is fully sustained (case i), partially sustained (case iii), or unsustained (case ii) by resupply from the solid phase in soil.

where D is the diffusion coefficient of a given metal ion, A is the area of gel membrane exposed to the bulk solution, and M is the mass of metal accumulated in the resin layer. M can be determined either directly using techniques capable of analyzing solids, such as PIXE or laser ablation ICP−MS, or indirectly using any appropriate analytical tool after elution of metal ions. Diffusion coefficients in hydrogels have been measured using a simple diffusion cell (*16*).

Flux Measurements. DGT is able to measure directly a flux by accumulating a mass of ions (M) over time (t) through a well-defined area (A):

$$F_{DGT} = M/(tA) \qquad (3)$$

When ions are removed from solution by DGT, they may be resupplied from the solid phase of the soil to the solution. There will be a net flux from soil to solution induced by the DGT device. This DGT-induced soil to solution flux, F_{ss}, may not be the same as the potential maximum flux from soil to solution, F_{pm}. Depending on the nature of the DGT device, F_{ss} will be a fraction of F_{pm} and is therefore referred to as a partial flux. The directly measured DGT flux (F_{DGT}) relates to the partial flux (F_{ss}) and potential flux (F_{pm}) of metal ions from soil to solution in one of three possible ways (Figure 1).

(i) Fully Sustained. Ions removed from the soil solution by the DGT device are rapidly resupplied from soil solid phase; the concentration in solution is effectively buffered to a constant value. If the mass of accumulated ions in the resin layer is measured after a known deployment time, the local in situ concentration in the soil solution can be calculated using eq 2. The DGT flux can be obtained using eq 3. It represents the partial flux of ions from soil to solution that is smaller than the local potential flux ($F_{ss} = F_{DGT} < F_{pm}$).

(ii) Unsustained. There is no resupply from the soil to solution ($F_{pm} = 0$). The supply of ions to the DGT device is solely by diffusion from the soil solution, which becomes progressively depleted first in the vicinity of the DGT device and then extending into the soil solution. The DGT flux consequently declines with deployment time. However, the initial concentration in solution can be calculated from the DGT measured mass using a numerical solution of the time-dependent diffusion equations (*14*).

(iii) Partially Sustained. There is some resupply of ions from soil to solution, but it is insufficient to sustain the initial bulk concentration and to satisfy fully the DGT demands. The flux measured by the DGT device can be equated to the in situ local flux from soil to solution induced by DGT and is close to the potential flux of the soil ($F_{ss} = F_{DGT} \sim F_{pm}$).

Case i (fully sustained) and case iii (partially sustained) are conditional. They are related to the DGT demand, which

is determined by the diffusive gel layer thickness and the initial concentration in soil solution. As the diffusive gel layer becomes thinner, the demand becomes greater and the fully sustained case may become partially sustained.

Identifying Different Cases. The above three cases can be simply identified by comparing solution concentrations calculated from the DGT measurement (C_{DGT}) with those obtained directly by conventional analytical methods (C_{soln}). If $C_{DGT} = C_{soln}$, the concentration of metal in soil solution is fully sustained by the soil. If $C_{DGT} < C_{soln}$, the soil solution is partially sustained or unsustained. If C_{DGT} is less than 10% of C_{soln}, the flux can mainly be accounted for by simple diffusion. There is effectively no resupply to the soil solution in this unsustained case (*14*). Deploying DGT devices with different thickness for the same time period may also help to distinguish cases i and iii. The plot of DGT flux (F_{DGT}) vs $1/\Delta g$ will be linear for case i according to eq 1 and nonlinear for case iii (*17*).

Speciation Measurement. The diffusive gel layer used in this work has an open structure that allows free diffusion of inorganic labile species and some metal organic complexes (*16*). The discrimination of the measured species by DGT is also kinetically based according to similar principles to those of anodic stripping voltammetry (*13*). When used in solution, it measures those species that can dissociate within the time it takes for ions to be transported through the diffusion layer (typically minutes). The theory for solution speciation was initially developed solely for the use of DGT in solution. When DGT is applied to soils, it also measures labile species. When there is diffusional supply only (case ii), species less labile than the lability cutoff for the solution-only case will be included in the measurement (effectively a thicker diffusion layer). When there is additionally resupply from the solid phase (cases i and iii), all resupplied species will be measured, unless they are rapidly and effectively irreversibly complexed by excess ligands.

Experimental Section

Gel Preparation and DGT Assembly. A polyacrylamide hydrogel comprising 15 vol % acrylamide (Boehringer) and 0.3 vol % patented agarose-derived cross linker (DGT Research Ltd. U.K.) was used throughout this work as the diffusive gel layer. Freshly prepared ammonium persulfate initiator (70 μL of 10%) and TEMED catalyst (20 μL) were added to each 10 mL of gel solution. The solution was immediately cast between two glass plates separated by plastic spacers and allowed to set at a temperature of 42 $\pm$ 3 °C for about 45 min. The resin gel consisted of 2 g of ion-exchange resin Chelex-100 (Na form, 100−200 wet mesh) in 10 mL of gel solution. Less ammonium persulfate and TEMED were used to prolong the setting process and to allow the resin to settle by gravity to one side of the gel. All gels were hydrated in MilliQ (MQ) water for at least 24 h before use. During this hydration step, the gel expanded to a new stable dimension. The volume of gel increased by a factor of 3.2 such that the water content was about 95%. The diffusive gels were stored in 0.01 M NaNO$_3$ solution (*16*), and the resin gels were stored in MQ water.

The DGT device (Figure 2) was based on a simple tight-fitting piston design. It consisted of a backing cylinder and a front cap with a 2.0 cm diameter window. A layer of resin gel was placed on the base with the side containing the resin facing upward. A layer of diffusive gel was placed directly on top of it. Unless stated, a 0.8 mm thick diffusive gel disk was used along with a 0.4 mm thick resin gel disk. To prevent soil particles adhering to the gel surface, a 100 μm thick, 0.45 μm pore size Millipore cellulose nitrate membrane was placed on top of the diffusive gel. The filter has been shown to behave like an extension of the gel layer (*13*).
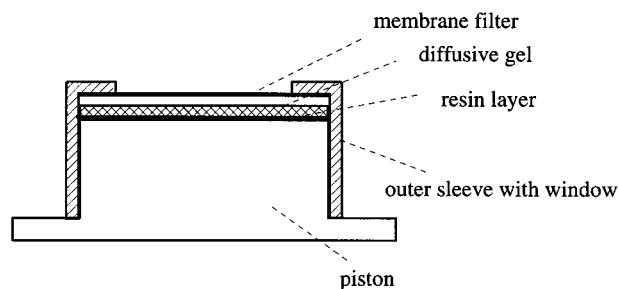
FIGURE 2. Schematic representation of a section through the DGT holder.

Soil History and Soil Treatment. Soils were sampled from the plowed (0–20 cm) layer of two long-term field experiments in Braunschweig, Germany. These were effectively on the same field, with silty loam soils (50% silt, 45% sand, and 5% clay). The 'old arable' section had been cleared from the forest many years ago, and the 'ex-woodland' had been cleared for agriculture over 40 years ago. The main difference between the plots was in soil pH and carbon content, with the old arable and ex-woodland sections having average bulk soil pH values in water on average of 6.7 and 5.7, total soil organic carbon of 1.2% and 1.8%, and original cation exchange capacity (CEC) of 7.3 and 9.6 mequiv 100 g^{-1}, respectively (18). Both soil types received the same treatments using the same materials: (a) no sludge, inorganic fertilizers only; (b) unamended sewage sludge from a local works, two treatments applied at rates of 100 or 300 m^3 ha^{-1} yr^{-1} (equivalent to 4 and 12 t ha^{-1} dry solids) between 1980 and 1990; (c) metal-amended sewage sludge. The same local sludge was incubated anaerobically in large vats on site with chloride salts of Zn, Cu, Ni, Cd, Cr, and Pb for 6 weeks with mixing in order to transform the chlorides to less available organic or sulfide forms prior to application to the field at the same rates for the same period as above.

Sample Treatment. Soils were seived to <3 mm and maintained at field moisture prior to use. A subsample of each soil (30 g) was placed in individual acid-washed plastic containers. Appropriate amounts of MQ water were added to obtain 80% moisture content. The soil samples were then equilibrated at 7 °C for 2 weeks. The water content of the soils was then raised from 80% to 120% to obtain a soil slurry that was mixed using a glass rod and kept at room temperature for 24 h prior to DGT deployment.

DGT Deployment and Retrieval. DGT units were placed on the surface of the soil slurry at an angle and pushed gently into the surface, making sure that there was no air bubble between the soil solution and the DGT device. The DGT units were then pushed slightly into the soil, and the container was loosely covered with a lid. After maintaining at room temperature (20 ± 2 °C) for 16 h, the DGT units were retrieved from the soil and rinsed with MQ water to wash away all the soil particles adhered on the filter membrane. The resin gel was retrieved and placed into a clean plastic sample vial. To elute metals, the resin gel was completely immersed in 0.75 mL of 1 M HNO$_3$ for 24 h.

Sample Analysis. After at least 10-fold dilution, samples were analyzed by inductively coupled plasma–mass spectrometry (ICP–MS, Varian Ultramass) using a direct injection nebulizer (Cetac) requiring only 200 μL of sample (19). The masses of metal in the resin gel (M) were obtained using eq 4, where C_e is the concentration of metals in the elution solution (in μg/L), V_{HNO_3} is the volume of HNO$_3$ added to the resin gel, V_{gel} is the volume of the resin gel, typically 0.15 mL, and f_e is the elution factor for the metals typically 0.8 (13).

$$M = C_e(V_{HNO_3} + V_{gel})/f_e \qquad (4)$$

Soil solutions were extracted from soil samples by centrifugation at 12 500 rpm for 30 min. Solutions were immediately acidified to about pH 2 using HNO$_3$ solution. As attempts to analyze soil solutions by ICP–MS were not successful due to matrix interference with the Rh internal standard, Zeeman furnace atomic absorption spectroscopy (ZFAAS, Perkin-Elmer Zeeman 4100 ZL) was used.

Results and Discussions

Concentration in Soil Solutions. The soil-solution pH decreased from 6.7 to 5.4 on average in old arable soils and from 5.1 to 4.6 in ex-woodland soils with increasing amounts of sludge applied (Table 1). The dissolved organic matter increased with application of sludge for both types of soils to approximately double that of the untreated soil with the 300 m^3 ha^{-1} yr^{-1} treatment. In the old arable soil-dissolved Zn, Cd, Cu, and Ni concentrations increased with increasing quantity of sludge application for both metal-amended and unamended sludge. Similar trends in trace metal concentrations were found for the ex-woodland soil. Total dissolved metal concentrations in the ex-woodland soils were generally greater than in comparable sludge-amended plots of the old arable soils, presumably due to the pH difference, as the total metal concentrations in the soils are similar in comparable treatments (18).

Concentrations Measured by DGT. When the DGT-deduced concentrations, C_{DGT}, were plotted against the directly measured concentrations in solution, C_{soln}, two distinct situations could be observed for Zn and Cd (Figure 3). In old arable and ex-woodland soils, both without sludge treatment and with 100 m^3 ha^{-1} yr^{-1} of either unamended or metal-amended sludge, situation I applied. Zn and Cd concentrations measured by DGT were in good agreement with those measured in soil solutions directly. The regression equations (forced through the origin) were Zn$_{(DGT)}$ = 0.94Zn$_{(soln)}$ ($r^2 = 0.88$) and Cd$_{(DGT)}$ = 1.04Cd$_{(soln)}$ ($r^2 = 0.95$). The good agreement exemplified by the near-unity slopes suggests that (a) the metal concentrations in soil solution are well buffered by resupply of metal from the solid phase (case i in the Theory section) and (b) labile metal species account for all the metal in the soil solution. The resupply of metal from soil to solution is sufficiently rapid to meet the demand of the DGT device as a sink. This well-buffered behavior of Zn and Cd, due to rapid resupply from solid to solution, has also been observed in the sediments of a productive lake (14). Situation II applied to soils treated with 300 m^3 ha^{-1} yr^{-1} of unamended or metal-amended sludge. Metal concentrations measured by DGT were generally lower than the concentrations measured in soil solutions directly by ZFAAS. Although these lower DGT-derived concentrations only applied to Zn and Cd for high sludge treatments, for Cu and Ni it applied to all soils. For all metals the concentrations measured by DGT increased linearly (good correlation) with soil solution concentrations (Figure 3). The regression equations (forced through zero) were Zn$_{(DGT)}$ = 0.32Zn$_{(soln)}$ ($r^2 = 0.86$), Cd$_{(DGT)}$ = 0.32Cd$_{(soln)}$ ($r^2 = 0.94$), Cu$_{(DGT)}$ = 0.29Cu$_{(soln)}$ ($r^2 = 0.95$), and Ni$_{(DGT)}$ = 0.32Ni$_{(soln)}$ ($r^2 = 0.97$).

A lower DGT response can be explained by either a significant fraction of the metal species in solution being present as nonlabile complexes or as colloids or kinetic limitation providing only a partial resupply from solid phase to solution. The speciation explanation appears unlikely because (a) there was no evidence of nonlabile complexation of Zn and Cd in soils with lower sludge treatments, (b) a similar degree of complexation for all metals is unlikely, (c) a high excess of ligands would be required to produce the observed linear response with respect to concentration, and (d) speciation calculations using WHAM (20) predict that

TABLE 1. Trace Metal Concentration (in μg L^{-1} except Zn as mg L^{-1}) in Soil Solutions and Fluxes (in ng cm^{-2} s^{-1}) from Solid Phase to Solution as Negative Logarithms (pF_{ss} = $-$log F_{ss}) in Old Arable and Ex-woodland Soils Treated with Unamended Sludge or Metal-Amended Sludge[a]

	old arable soil					ex-woodland soil				
	A	B	C	D	E	A	B	C	D	E
pH	6.7	6.4	6.7	5.7	5.4	5.1	5.1	5.2	4.8	4.6
DOC	18.3	20.5	25.0	29.6	32.3	17.2	24.5	21.4	32.4	34.0
Ca	249	310	258	282	260	319	305	300	351	317
Mg	27.2	29.8	23.5	31.4	31.2	41.5	36.0	39.2	37.6	39.4
K	105	119	137	130	116	139	137	112	121	102
Concentrations										
Zn	<0.01	0.02	0.04	0.11	2.26	0.06	0.20	1.01	2.69	4.80
Cd	0.1	0.2	0.7	0.6	11.2	1.6	1.9	7.4	11.8	48.9
Ni	3.9	8.1	22.8	25.8	281	13.7	25.9	93.4	180	907
Cu	12.2	26.1	49.3	39.6	140	11.2	19.0	33.9	63.7	189
Fluxes (pF_{ss} = $-$log F_{ss})										
Zn	3.55	2.87	2.42	2.03	1.25	2.41	1.88	1.76	1.31	0.95
Cd	5.08	4.98	4.43	4.52	3.49	3.97	3.94	3.68	3.68	2.96
Ni	3.86	3.73	3.27	3.08	2.14	3.41	3.08	2.76	2.60	1.72
Cu	3.68	3.48	3.12	3.14	2.57	3.66	3.35	3.17	2.95	2.38

[a] The results of pH, DOC (mg L^{-1}), and concentrations of Ca, Mg, and K (mg L^{-1}) in soil solutions are also given. The figures are the means of four individual measurement from replicate soils sample. Treatment A, no sludge applied; B, 100 m^3 ha^{-1} yr^{-1} unamended sludge applied; C, 100 m^3 ha^{-1} yr^{-1} metal-amended sludge applied; D, 300 m^3 ha^{-1} yr^{-1} unamended sludge applied; E, 300 m^3 ha^{-1} yr^{-1} metal-amended sludge applied.
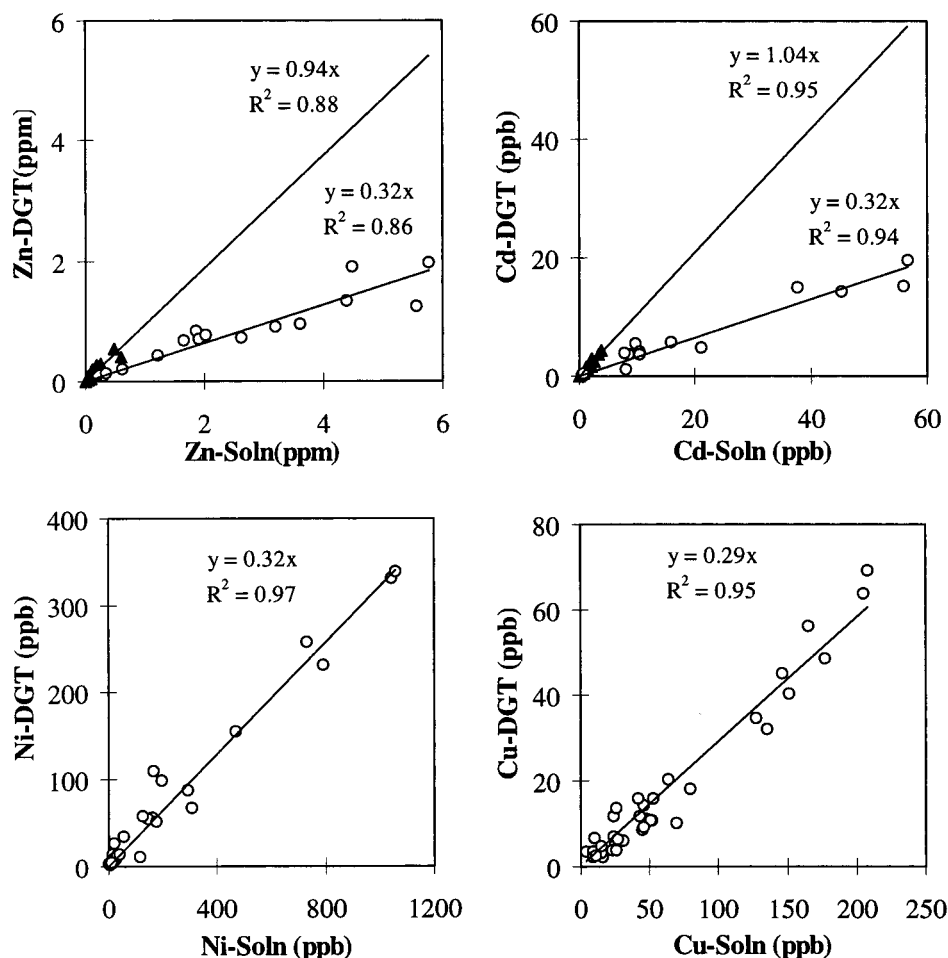

FIGURE 3. Comparison of Zn and Cd concentrations measured by DGT with those measured directly in extracted soil solutions (▲, soils without treatment and treated with 100 m^3 ha^{-1} yr^{-1} of sewage sludge; ○, soils treated with 300 m^3 ha^{-1}yr^{-1} of sewage sludge) and comparison of Cu and Ni concentrations measured by DGT with those measured directly in extracted soil solutions, for all soils. The fitted lines show the two pools of metal for Zn and Cd and the single pools for Cu and Ni.

the proportion of inorganic metal increases with sludge application. As soil solutions were separated from soil by centrifugation, it is possible that the solutions contained fine colloidal material. However, such material would be unlikely to contain a constant proportion of all metals as compared to soil solution concentrations. Furthermore, there is no reason it should be absent in soil solutions from soils with lower treatments, as implied by the Zn and Cd results.

The lower DGT response as compared to soil solutions for most situations indicates that the system is partially sustained. In this case, the concentration of metals in the vicinity of the DGT device decreases after deployment (Figure 1). Consequently, the flux to the DGT device is less than the maximum possible, and the mean concentration measured by DGT is inevitably lower than the initial concentration in the soil solution.

The linear relationship between the DGT response and the concentration measured in the soil solution was a consequence of the application of sludge, which had the effect of increasing the concentration of labile metal species in the solid phase. If the supply of metal from solid phase to solution is assumed to be an irreversible first-order process, it is proportional to a rate constant, k, and the labile solid-phase concentration, C_{ls} (eq 5).

$$F_{DGT} \propto \partial C / \partial t \propto k C_{ls} \qquad (5)$$

Assuming a pseudo-steady-state, the concentration measured by DGT, C_{DGT}, is proportional to the DGT measured flux, F_{DGT}. Therefore the DGT measured concentration is linearly related to the concentration of labile metal species in the solid phase through a proportionality constant, ρ (eq 6). The ratio of the concentration measured by DGT to that in soil solution, (C_{soln})

$$C_{DGT} = \rho k C_{ls} \qquad (6)$$

can be expected to be constant irrespective of the application of sludge if the metal is partitioned between solid phase and solution in a constant ratio (eq 7).

$$C_{DGT} / C_{soln} = \rho k (C_{ls} / C_{soln}) \qquad (7)$$

As C_{ls}/C_{soln} is effectively a distribution coefficient, K_d (expressed in terms of labile metal concentration in the solid phase rather than total concentration), it is not surprising that C_{DGT}/C_{soln} is observed to be constant. When sludge application is increased, the concentration in the solution phase (C_{soln}) increases, and according to eq 1 there is a proportionally greater DGT demand. When K_d is constant, however, the solid-phase concentration (C_{ls}) also increases proportionally, and even though the rate constant for dissociation from the solid phase remains the same (eq 5), the rate of resupply, kC_{ls} increases to keep pace with the DGT demand. Fast resupply kinetics are necessary to ensure that the concentration in solution is fully sustained ($C_{DGT}/C_{soln} \geq 0.95$). This can be achieved by the proportion in solution being high (large K_d) and /or the dissociation rate constant, k, being large.

Equations 5−7 have been introduced to aid the conceptual appreciation of the DGT measurement. Equation 7 should only be used when interpreting the partially sustained case. A numerical time-dependent model simulating the interaction of the DGT device with a sediment or saturated soil has been developed (17). It incorporates a reversible first-order (de)sorption process with two-dimensional diffusional transport in a fashion similar to analytical solutions of Vaidyanathan and Nye (21, 22). For the interpretations attempted here, however, it is sufficient to recognize that the measured ratio of C_{DGT}/C_{soln} is determined by the distribution between solid phase and solution, K_d, and the rate constant of resupply. The DGT measured flux is determined by the rate of resupply that, for a constant K_d, will increase with the concentration in the soil solution.

The ratio of the DGT measured concentration to the soil solution concentration is a constant for Ni and Cu in all soils irrespective of the sludge treatment. According to eq 7, it appears that sludge application in soils had no marked effect on either distribution coefficients or on the rate constants of resupply from solid to solution. However, for Zn and Cd in soils without sludge treatment or with lower doses (100 m³ ha⁻¹ yr⁻¹) of sludge, the ratio is close to 1, indicating that Zn and Cd in solution are well buffered by the rapid resupply from solid phase. When soils were treated with higher doses (300 m³ ha⁻¹ yr⁻¹) of sludge, the flux to the DGT device increased (see the next section), but the ratio of C_{DGT}/C_{soln} was reduced to about 0.3, which represents the partially sustained case. Clearly either K_d, k, or both must have decreased. High organic content introduced by high doses of sludge (Table 1) may modify the availability of Zn and Cd from the solid phase. Consequently the proportion of labile metals in the solid phase (C_{ls}) may be reduced, and therefore the K_d may become smaller (eq 6). Chemical extractions with ammonium nitrate indicated that K_d remained constant for Zn, Cu, and Ni irrespective of treatment, but this extractable fraction may not be a good surrogate for the labile solid-phase metal. An explanation assuming a constant K_d is that the high dose sludge application may modify binding sites, changing the rate constants of Zn and Cd resupply to smaller values.

Such a change in the ability of soils to sustain solution concentrations of metals in the soil solution suggests that there are two pools of labile solid-phase Zn and Cd. In the untreated soils, the resupply rate constant and/or K_d are different from those in the treated soils. There appears to be only one pool of metal for Ni and Cu irrespective of sludge treatment. The ratio of about 0.3 found for Ni and Cu in all soils and for Zn and Cd for high doses of sludge indicates that the distribution coefficients, K_d, and the resupply rate constants for each metal are similar under these conditions.

Fluxes from Soil to Solution. The above comparison of DGT derived concentrations with soil solution concentrations indicated that in many cases the metals in soil solution are partially sustained by resupply from the solid phase. Therefore, the DGT results should be interpreted as fluxes rather than concentrations. Fluxes from solution to the DGT unit (F_{DGT}) were calculated using eq 3 and equated to net fluxes from soil to solution induced by DGT (F_{ss}). The term pF_{ss} ($pF_{ss} = - \log F_{ss}$) was used to allow comparison of a wide range of values. The smaller pF_{ss}, the greater the flux. Measured values of pF_{ss} are given in Table 1. For all metals, fluxes increased (pF_{ss} decreased) with increasing amount of sludge application, either unamended or metal amended, for both old arable soil and ex-woodland soil. At each rate of application, higher fluxes (smaller values of pF_{ss}) were observed in soils with metal-amended sludge treatment. These results suggest that sludge applications to both soils enhance the rate of metal ion transport from soil to solution, with the effect being most marked for metal-amended sludge. The higher rates could simply reflect a larger pool of labile metal due to both metal introduced with the sludge and a lower pH.

To investigate further the detailed characteristics of metal transport from soil to solution, DGT devices with different diffusive layer thickness from 0.13 to 2.13 mm were deployed for 16 h in an old arable soil treated with 100 m³ ha⁻¹ yr⁻¹ metal-amended sludge. Fluxes from soil solution to the DGT units (F_{DGT}) for each different thickness were calculated using eq 3. Example plots of F_{DGT} vs $1/\Delta g$ for Zn, Cd, Ni, and Cu are presented in Figure 4. All the plots show similar trends, with DGT fluxes increasingly deviating from linearity with decreasing gel layer thickness. The initial part of the plot, corresponding to thicker diffusive gel layers (1.3−2.13 mm), approximates to linearity, which according to eq 3 represents the well-buffered case. When relatively thick diffusive gel layers are used, the flux from solution to the DGT device is relatively low, and the flux from soil to solution comes closer to satisfying the DGT demand. With thinner gel layers, the
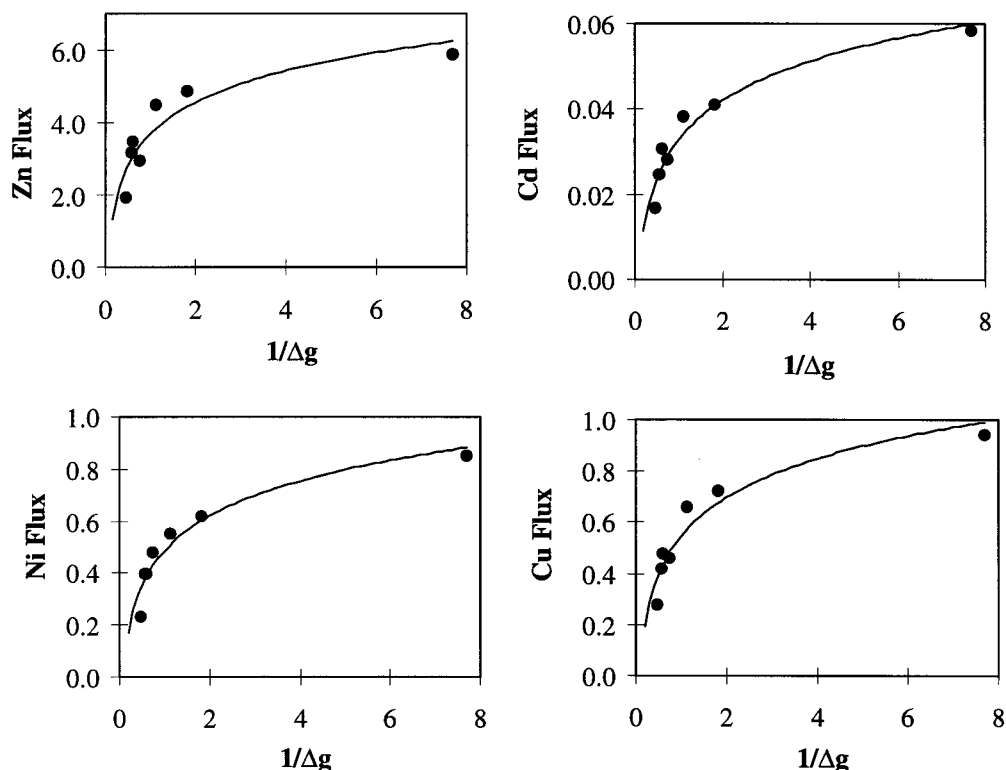
FIGURE 4. DGT fluxes (in pg cm^{-2} s^{-1}) of trace metals plotted against the reciprocal of diffusive gel layer thickness (in mm) for an old arable soil sample treated with 100 m^3 ha^{-1} yr^{-1} of metal-amended sewage sludge.

DGT devices demand higher fluxes. If soil to solution fluxes cannot satisfy this demand, local solution concentrations become depleted as illustrated in Figure 1.

According to eq 1, the slope of the approximately linear region of Figure 4 is equal to DC and therefore can be used to calculate concentration. The diffusion coefficient (D) in hydrogels used in this work is the same as in water (*13, 16*). The resulting concentrations of Zn, Cd, and Ni of 60, 0.8, and 15 μg L^{-1}, respectively, are within the range of values measured directly in soil solution. When gels with thickness smaller than 1.3 mm, such as 0.8, 0.5, and 0.13 mm, were used, the DGT fluxes deviated from linearity, indicating that metal concentrations in the solution are only partially sustained by the soil. This agrees with the observation made by comparing the concentrations measured by DGT using a 0.8 mm thick gel with soil solution concentrations. That is that the Zn and Cd in soils treated with 100 m^3 ha^{-1} yr^{-1} of metal-amended sludge are on the borderline of being fully or partially sustained.

The plots of DGT fluxes vs 1/Δg in Figure 4 also provide information on the potential flux of metal from soil to solution. The DGT device with the thinnest diffusion layer (0.13 mm) provides an approximate estimate of the potential flux of 5.8, 0.06, 0.85, and 0.94 pg cm^{-2} s^{-1} for Zn, Cd, Ni, and Cu, respectively. The fluxes corresponding to a diffusion layer thickness of 0.8 mm are only about 70% of the potential flux. If this finding can be extrapolated to other soils studied in this work, an estimate of their potential flux of metals can be obtained by dividing the partial flux measured using a 0.8 mm gel (Table 1) by 0.7.

General Appraisal

DGT has provided the first fully quantitative in situ measurements of the potential resupply flux of metal from soil to solution. It has shown that Zn and Cd in soil solutions in the two soils used in this study were well buffered by resupply from solid phase to solution, if the soils received either no sludge or a low dose of sludge. For Zn and Cd in soils with higher treatments of sludge and for Cu and Ni in all soils, the resupply from soil to solution was unable to sustain the DGT demand, and the DGT measured flux provided an estimate of the in situ flux from soil to solution. The in situ flux for Zn, Cd, Ni, and Cu increased with increasing sludge application and consequently lower pH.

As DGT is known to work well in saturated sediments, these first measurements of soil to solution fluxes have been made on hydrated soils. They demonstrate the applicability of DGT to soils and its potential usefulness as an in situ technique. Preliminary measurements at lower moisture contents look encouraging, opening up the possibility of using DGT as a simple in situ probe for assessing bio available metals in soils. How well metals in soil solution are sustained by resupply from solid phase depends on the rate of removal and consequently the rate of resupply. In nature the rate of removal may vary (e.g., different plant species and conditions). Similarly, with DGT the rate of removal may vary. It depends on the gel layer thickness and the initial pore water concentration. If these factors are varied, the ability to sustain metal concentrations in soil solution may change even if the rate of resupply is constant. However, if experiments are performed in different laboratories using the same diffusion layer thickness, the assessment of the resupply characteristic of the soil will be quantitatively comparable.

DGT is effectively a simple experimental device that initiates a controlled perturbation in situ and automatically monitors the response. Because the geometry and the diffusion layer thickness are well defined, calibration is not necessary. However, detailed interpretation in terms of fluxes and concentrations is made easier if replicate measurements are made using different diffusion layer thickness. The feature of in situ preconcentration overcomes analytical and contamination problems associated with trace metal measurements. Although this study has focused on trace metals, work in progress is showing that, by appropriate selection of resin, DGT can be used to measure nutrients and radionuclides. It can also be used to make measurements

at high spatial resolution (down to $100 \mu m$) (23), which should greatly aid our understanding of root uptake mechanisms and the role of heterogeneity.

Acknowledgments

Literature Cited

(1) Knight, B.; McGrath, S. P. *Environ. Toxicol. Chem.* **1995**, *14*, 2033−2039.

(2) Sposito, G. *The Chemistry of Soils*; Oxford University Press: New York, 1989.

(3) Yang, J. E.; Skogley, E. O.; Georgitis, S. J.; Schaff, B. E.; Ferguson, A. H. *Soil Sci. Soc. Am. J.* **1991**, 55, 1358.

(4) Skogley, E. O.; Dobermann, A. *J. Environ. Qual.* **1996**, *25*, 13.

(5) Lee, D. Y.; Chiang, P. H.; Houng, K. H. *Plant Soil* **1996**, *181*, 233.

(6) Liang, J.; Schoenau, J. J. *Int. J. Environ. Anal. Chem.* **1995**, *59*, 265.

(7) Lee, D. Y.; Zheng, H. C. *Plant Soil* **1994**, 164, 19.

(8) Jing, J.; Logan, T. J. *Commun. Soil Sci. Plant Anal.* **1991**, *22*, 2029.

(9) Sibbesen, E. *Plant Soil* **1978**, *50*, 305.

(10) Van Raij, B.; Quaggio, J. H.; DeSilva, N. M. *Commun. Soil Sci. Plant Anal.* **1986**, *17*, 547.

(11) Wimaladasa, G. D.; Sinclair, A. H. *Anal. Proc.* **1988**, *25*, 65.

(12) Davison, W.; Zhang, H. *Nature* **1994**, *367*, 546.

(13) Zhang, H.; Davison, W. *Anal. Chem.* **1995**, *67*, 3391.

(14) Zhang, H.; Davison, W.; Miller, S.; Tych, W. *Geochim. Cosmochim. Acta* **1995**, *59*, 4181.

(15) Zhang, H.; Davison, W.; Grime, G. W. *Dredging, Remediation, and Containment of Contaminated Sediments*; Demars, K. R., et al., Eds.; ASTM STP 1293; American Society for Testing and Materials: Philadephia, **1995**; 170 pp.

(16) Zhang, H.; Davison, W. *Diffusion in Hydrogels*. In preparation.

(17) Harper, M.; Davison, W.; Zhang, H.; Tych, W. Submitted to *Geochim. Cosmochim. Acta*.

(18) Chaudri, A. M.; McGrath, S. P.; Giller, K. E.; Rietz, E.; Sauerbeck, D. R. *Soil Biol. Biochem.* **1993**, *25*, 301.

(19) Zhang, H.; Waterhouse, K.; Davison, W. In preparation.

(20) Tipping, E. *Comput. Geosci.* **1994**, *20*, 973.

(21) Vaidyanathan, L. A.; Nye, P. H. *J. Soil Sci.* **1966**, *17*, 175.

(22) Abrams, M. M.; Jarrell, W. M. *Soil Sci. Soc. Am. J.* **1992**, *56*, 1532.

(23) Davison W.; Fones, G.; Grime, G. W. *Nature* **1997**, *387*, 885.