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Desorption Kinetics of Cd, Zn, and Ni Measured in Soils by DGT

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DGT (diffusive gradients in thin films) was used to measure the distribution and rates of exchange of Zn, Cd, and Ni between solid phase and solution in five different soils. Soil texture ranged from sandy loam to clay, pH ranged from 4.9 to 7.1, and organic carbon content ranged from 0.8% to 5.8%. DGT devices continuously remove metal to a Chelex gel layer after passage through a well-defined diffusion layer. The magnitude of the induced remobilization flux from the solid phase is related to the pool size of labile metal and the exchange kinetics between dissolved and sorbed metal. DGT devices were deployed over a series of times (4 h to 3 weeks), and the DIFS model (DGT induced fluxes in soils) was used to derive distribution coefficients for labile metal (K_{dl}) and the rate at which the soil system can supply metal from solid phase to solution, expressed as a response time. Response times for Zn and Cd were short generally (<8 min). They were so short in some soils (<1 min) that no distinction could be made between supply of metal being controlled by diffusion or the rate of release. Generally longer response times for Ni (5−20 min) were consistent with its slow desorption. The major factor influencing K_{dl} for Zn and Cd was pH, but association with humic substances in the solid phase also appeared to be important. The systematic decline, with increasing pH, in both the pool size of Ni available to the DGT device and the rate constant for its release is consistent with a part of the soil Ni pool being unavailable within a time scale of 1−20 min. This kinetic limitation is likely to limit the availability of Ni to plants.

Introduction

Appreciation of the exchange of trace metals between solid phase and solution is an essential prerequisite to understanding trace metal mobility and bioavailability (*1*−*3*). Most studies have focused on the equilibrium partitioning in the soil (*4*, *5*), with less emphasis on the kinetic aspects of trace metal exchange. Measurements of rates of metal exchange are assuming a greater importance with the recognition of potential kinetic controls on metal supply to biota (*6*).

Rates of chemical reactions in soil are frequently assessed in batch or flow-through experiments (*7*). The kinetics of trace metal partitioning in the soil may also be followed by isotopic exchange methods (*8*). An alternative approach, where the soil is minimally disturbed, has recently been proposed (*9*). It uses the technique of DGT (diffusive gradients in thin-films) to obtain information on the kinetics of metal release from solid phase to solution. DGT was initially developed for measuring speciation in waters (*10*). When applied to soils, it can be used to quantify the distribution coefficient of labile metal and exchange kinetics between solid phase and solution (*9*, *11*). DGT consists of a layer of Chelex resin embedded in gel, which is separated from the soil by a diffusion layer (*12*). The strong binding of labile metal species by the Chelex resin induces a flux of trace metals from the soil solids to soil solution. The magnitude of the flux is dependent on diffusion in solution and the rate of exchange of metal between solid and solution. A one-site, first-order, kinetic model that describes exchange of metal between solid phase and solution when a soil is perturbed by a DGT device (DIFS − DGT induced fluxes in soils) (*11*) can be used to obtain kinetic and pool size parameters of the soil from the DGT measurements.

The DGT measurement, which embraces both kinetic and capacity control, has been shown to be a good predictor of the concentration of metals in plants (*13*, *14*). It appears to mimic well the major supply processes from the soil to the plant, diffusion and desorption. By using DGT as an investigative tool to characterize the dynamics of soil−solution interactions, it should be possible to further the understanding of the soil mechanisms that control supply of metals to plants.

So far, DGT has only been used to provide simultaneous kinetic and pool size information on a single soil (*9*), where the release of Ni was shown to be kinetically limited. In this study, kinetic parameters derived by DIFS modeling of DGT measurements were determined for Cd, Zn, and Ni in five soils with a wide range of properties. The idea was to establish how pH and other soil properties affect kinetic constants. The constants for partitioning between solid and solution that are automatically derived from this approach were compared to values obtained by isotopic exchange.

Principles of DGT and DIFS

The resin-gel of DGT incorporates Chelex-100 resin that strongly binds labile trace metal species that diffuse through the diffusion layer, consisting of a gel layer and a filter membrane. This leads to the formation of a linear concentration gradient in the diffusive gel layer (Figure 1). The gradient depends on the thickness of the diffusion layer, Δg, and the interfacial concentration of labile trace metal species, C_i (gel side of interface). It determines the flux, $F(t)$, of metal toward the resin-gel according to Fick's first law (eq 1), where ϕ_d is the porosity of the diffusion gel and D_d is the diffusion coefficient of the labile trace metal species in the diffusion layer. Thus, DGT acts as a sink that induces a flux of trace metals from the soil to the DGT probe. F may change during the DGT deployment if C_i changes. The accumulation of trace metals by the resin-gel depletes trace metals in the soil solution adjacent to the DGT interface (Figure 1). With increasing deployment time, trace metals in soil solution may become progressively depleted further away from the interface. Resupply of trace metals from particles to solution counteracts the depletion. The concentration of particulate, labile, trace metal, C_{ls}, available for release, and the kinetics of the adsorption and desorption processes will determine the efficiency with which trace metal concentrations are sustained in soil solution relative to their initial level.

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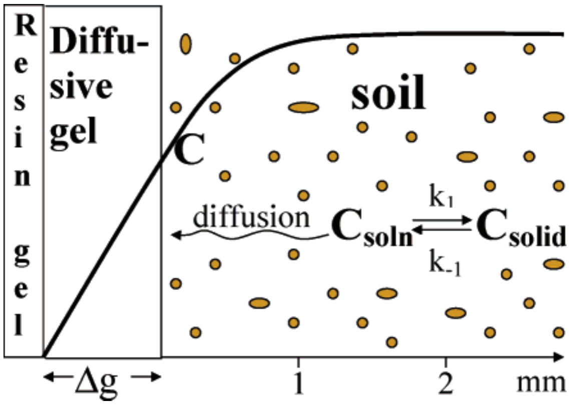

FIGURE 1. Processes induced by deployment of a DGT probe in a soil. The mass of metal per unit area is accumulated by diffusion across the diffusion layer. The mean pseudo-steady-state concentration through the diffusive layer and soil pore waters is shown, with the mean interfacial concentration, C.

DGT continuously accumulates metal on the resin gel during deployment. *M* is the total mass of metal accumulated per unit area, *A*, over the deployment time, *T*, and is given by integrating the flux over the deployment time (eq 2). The time averaged interfacial concentration, C_{DGT}, can be calculated from *M* (eq 3), which is determined analytically after eluting the metal. Comparison of C_{DGT} with the independently measured initial soil solution concentration, C_{soln}, provides a ratio, *R*, which gives an indication of the extent of the depletion of soil solution concentrations at the DGT interface (eq 4).

$$F(t) = \phi_d D_d \frac{C_i(t)}{\Delta g} \tag{1}$$

$$M = \int_{t=0}^{T} F(t)\ \mathrm{d}t \tag{2}$$

$$C_{DGT} = \frac{\int_{t=0}^{T} C_i(t)\ \mathrm{d}t}{T} = \frac{M\Delta g}{\phi_d D_d T} \tag{3}$$

$$R = \frac{C_{DGT}}{C_{soln}} \tag{4}$$

The magnitude of *F* is determined by the concentration gradient at the resin gel/diffusive gel boundary. As, prior to deployment, there is no metal in the diffusive layer, $C_i(t)$ (gel side of interface) and the flux are initially zero. The flux progressively increases to a maximum as the diffusion layer is supplied with metal from the soil. The time to the maximum depends on the kinetics of the metal supply from the soil. The flux subsequently tends to decrease with time, at a rate governed by both the capacity of the solid phase to resupply metal to the soil solution and the rate of this resupply. C_{DGT} and *R* provide integrated measurements of these changes over the deployment time.

The DIFS model quantifies the dependence of *R* on resupply of trace metals from solid phase to solution coupled to diffusional supply to the interface and across the diffusion layer to the resin gel (Figure 1) (*11*, *15*). It uses K_{dl} (eq 5) and the response time, T_c (eq 6), to describe the kinetics of adsorption (rate constant, k_1) and desorption (rate constant, k_{-1}). K_{dl} is the distribution coefficient based on labile solid-phase components that can exchange with the solution phase. It would be expected to be lower than the corresponding value of K_d that is based on the total metal measured in the soil. T_c is the characteristic time for the system to approach equilibrium (*16*).

$$K_{dl} = \frac{C_{ls}}{C_{soln}} = \frac{k_1}{P_c k_{-1}} \tag{5}$$

$$T_c = \frac{1}{k_1 + k_{-1}} = \frac{1}{k_{-1}(1 + K_{dl}P_c)} \approx \frac{1}{k_{-1}K_{dl}P_c} \tag{6}$$

DIFS requires data for C_{soln}, soil porosity (ϕ_s), diffusion layer porosity (ϕ_d), diffusion layer thickness (Δg), particle concentration (P_c), the effective diffusion coefficient in the soil (D_s), the diffusion coefficient in the diffusion layer (D_d), and the deployment time (T). K_{dl} and T_c are supplied as inputs, and DIFS calculates *R*. Distributions of solution- and solid-phase concentrations through the DGT-soil system are calculated for any chosen time.

Methods

DGT Devices. Cylindrical DGT devices were prepared using polyacrylamide gels with 0.12% cross-linker and Chelex-100 resin according to the procedure detailed elsewhere (*17*). The interfacial area, *A*, in contact with the soil is 3.14 cm^2 and $\Delta g = 0.1$ cm. It has been previously established that the porosity of the diffusive gel, $\phi_d = 0.95$ (*17*). D_d for uncomplexed metals has been shown to be slightly less than the corresponding diffusion coefficient in water.

Deployment in Soil Slurry. The selected soils had diverse properties (Table 1) and were part of a set used in a study of metal availability during a 2 year, 3 month time series (*5*). They had been spiked with a common stock solution of metal nitrate salts and then mixed mechanically. The applications (mg kg^{-1}) were Cd = 3, Cu = 135, Ni = 75, Pb = 300, and Zn = 300. Final concentrations in the soils are given in Table 3. The soils were maintained at 80% field capacity in duplicate microcosms throughout this time. This ensured that metal diffusion in soil pore water and aerobic microbial activity were both possible, while anaerobic conditions were avoided (a constant nitrate concentration and no rise in the Fe and Mn concentrations in soil solution during the 2 year, 3 month period). Field capacity was determined by equilibrating an initially saturated soil sample (2 mm seived) on a sand bath held at 0.005 MPa negative pressure (suction) until constant moisture content was achieved.

DGT devices were deployed 3 years after the addition of metals. Plastic pots were filled with 50 g of soil. To provide good contact between DGT and the soils, slurries were prepared by adding deionized water to produce moisture contents in the range of 1.7−3.3 times field capacity (Table 1). The particle concentration, P_c, and the porosity of the soil, ϕ_s, were calculated, assuming a standard particle density of 2.65 g mL^{-1} (*18*). D_s in the slurry was calculated using the relationship $D_s = D_0/(1 - (2 \ln \phi_s))$ (*19*). The slurries were prepared on the day before DGT deployments, to give some time for soil solutions to equilibrate with soil solids. DGT devices were carefully inserted to ensure complete contact with the soil slurry. They were deployed for times between 4 h and 21 days, all at 18 ± 2 °C. As controls, DGT devices were deployed in solutions with known concentrations of metals. The amount accumulated was within ±5% of that predicted by Fick's law and the geometry of the device (*12*). Metal concentrations in blank DGT devices were substantially lower than those measured.

On retrieval, DGT devices were jet-washed with deionized water to remove soil particles and then disassembled. Resin-gels ($V_{gel} = 0.15$ mL) were eluted with 1 M HNO_3 ($V_{HNO_3} = 1$ mL) in closed microvials. The concentration of trace metals in the eluent was measured by ICP-MS (Varian Ultramass) within various calibration ranges after appropriate dilution, using Rh as internal standard. An elution factor of 0.8 was used to calculate the mass of accumulated metal (*17*). C_{DGT}

TABLE 1. Properties of the Soils Used in This Study

soil	type	pH	soil organic carbon (%)	texture	field capacity	% moisture DGT slurry
M	silty loam	4.9	1.45	silty loam	27.6%	46.2
A	brown sand	6.2	0.82	sandy loam	12.7%	24.5
G	pelo-vertic alluvial gley	5.8	3.56	clay	35.0%	115
J	argillic pelosol	7.0	2.58	clay/clay loam	26.4%	77.5
O	humic rendzina	7.1	5.81	clay loam	33.1%	90.1

TABLE 2. Percentages of Metals in Soil Solution in Each Soil Present as Organic Species (Calculated Using WHAM 6)

metal	M	A	G	J	O
Cd	1.5	2.2	2.6	3.9	10
Zn	1.4	1.7	2.0	2.4	6.2
Ni	0.8	0.6	1.0	0.7	1.9

was calculated with eq 3. R was then obtained using the soil solution concentration, C_{soln} (Table 3).

Soil Solutions. Concentrations of metals in soil solutions, C_{soln}, were sampled approximately every second DGT deployment. After retrieval of the DGT device, the slurry was stirred and a fraction (ca. 5−10 mL) was transferred into a 25-mL PTFE tube and centrifuged at 2000 rpm for 10 min. The supernatant was taken up with a plastic syringe and filtered into microvials using 13 mm diameter, 0.45 μm pore size, disposable polysulfone filter assemblies (Whatman Puradisk) and acidified using 2 μL of 1 M HNO_3 in each 100 μL. Soil solutions were analyzed by ICP-MS after appropriate dilution with Rh as internal standard using a MicroMist low uptake (200 μL/min) nebulizer and Cinnabar low volume spraychamber (Glass Expansion). Concentrations of metals in soil solutions showed little systematic change within the 3 weeks of DGT deployment (Table 3), so their averages were used as input parameters for DIFS. Soil pH was measured using a combination electrode on slurries at 220% of the field capacity of each individual soil. After an initial change during the first year after adding metals, pH did not vary substantially (<0.2 pH) with time.

Isotopically Exchangeable Cd and Zn. Cd and Zn that could be exchanged with their added isotopes were determined using established procedures (*20*) on eight occasions after addition of metals. Briefly, 5 g of soil was equilibrated with 25 mL of 0.1 M $Ca(NO_3)_2$ for 5 days. After centrifugation (2200*g*), the supernatant was removed and acidified prior to measurement of Cd and Zn. The remaining electrolyte and soil was resuspended, spiked with ^{65}Zn and ^{109}Cd solution, and shaken for 2 days. After centrifugation, the supernatant was assayed for ^{65}Zn and ^{109}Cd by gamma scintillation. Soil pore solutions were extracted using porous polymer Rhizon soil moisture samplers (Rhizosphere Research Products, Wageningen, The Netherlands) after the moisture content of the microcosm soil was increased to 110% field capacity for 10 days. Results were expressed as distribution coefficients, K_d, by dividing the concentration of isotopically exchangeable metal by the concentration measured in soil solution.

Results and Discussion

Two principal factors control the species measured by DGT, lability and mobility. The lability criterion arises because complexes have to dissociate in the time it takes them to traverse the diffusion layer (typically 15 min) before they can be measured. For complexes to significantly contribute to the DGT measurement, they must also be sufficiently mobile, that is, have values of diffusion coefficients within an order of magnitude of that for the free metal ion.

DGT measures only a proportion of the metal organic complexes in solution, due to their lower diffusion coefficients as compared to inorganic species (*21*). In calculating the ratio, R, of DGT measured concentrations of metals in the whole soil to the concentrations in soil solution, this characteristic of the DGT measurement should be considered. The distribution of species in soil solution has been previously calculated for these soils using the Windermere humic aqueous model (WHAM 6) (*5*). This model combines an inorganic speciation code for aqueous solution (*22*) with the humic ion-binding model VI (*23*). Input files included the master variables [Zn], [Cd], [Ni], [Cu], [Pb], [Cl], [NO_3], [PO_4], SO_4], [NH_4], [Ca], [K], [Mg], [Na], pH, DOC, and P_{CO_2}. The temperature was set at 18 °C. It was assumed that fulvic acid contained 50% carbon, and that 50% of the DOC was fulvic in origin. According to the WHAM predictions (Table 2), the proportion of metals present as fulvic complexes was less than 4% for all soils except for Cd in soil O where it was 10%. Unpublished data have shown that little additional DOC (beyond that already in the pore-water) is released into solution when deionized water is added to soils, but trace metals are released. Consequently, the extent of complexation by fulvic acids in the slurries used for DGT deployments will be less than predicted by these calculations. In all cases, therefore, a DGT measurement of the soil solution would be expected to give a concentration of labile metal that was very similar to the total concentration of metal in solution, making it reasonable to calculate R directly from the DGT and soil solution measurements.

The results for the time series of DGT deployments are shown in Figure 2. The plots show the change in R, the ratio of DGT measured concentration to solution concentration, with increasing deployment time, and the best model fits derived using DIFS. The general trend is a sharp increase in R at short times followed by a decrease after the peak. The increase is due to the establishment of a linear diffusion gradient in the diffusion layer, which is initially free of metal. It is influenced by the rate of release of metal from the solid phase immediately adjacent to the device, as this and diffusion determine the supply from the soil. After the peak, R progressively declines. If there were an infinite supply of metal in the solid phase, R would remain constant. Its decline is due to the reservoir of metals in the layer of soil adjacent to the device (submillimeter to millimeter scale) being successively consumed, increasing the effective diffusive pathway and thereby lowering the flux.

The time dependence of Cd and Zn was similar for the different soils, indicating similar rates of interaction between solid phase and solution. For both metals, interfacial concentrations were sustained best for the clayey soils, O and J, which are characterized by high pH and/or high organic matter content (Table 1). Resupply of Cd and Zn from the solid phase to the DGT interface was relatively poor for the sandy soils A and M, which are additionally characterized by low total organic carbon and pH as compared to the rest of the soils. The time profile of R for soil G, a clay soil with a relatively low pH of 5.8, occupied the intermediate position.

For Ni, the features of Figure 2 were distinctly different. The three clayey soils all had similar R values throughout the time series. The R values for soils with high pH (O and J) were

TABLE 3. Total Concentrations of Metals in Each Soil[a]

soil	M	A	G	J	O
total Cd (mg kg^{-1})	3.25	3.16	3.31	3.18	3.3
soln Cd (μg L^{-1})	60.6 (3.0)	34.5 (4.5)	16.7 (0.9)	3.6 (0.3)	1.2 (0.1)
total Ni (mg kg^{-1})	88	84	121	110	98
soln Ni (μg L^{-1})	2425 (97)	3015 (378)	552 (48)	130 (7)	41 (3)
total Zn (mg kg^{-1})	363	338	417	374	438
soln Zn (μg L^{-1})	12 807 (576)	4245 (424)	1210 (169)	115 (9)	61 (12)

[a] Also shown are the mean (and standard deviation in parentheses) of concentrations in soil solution measured from samples taken at 6, 10, 14, 18, 22, 32, 45, 71, 142, 310, 377, and 468 h during the DGT experiment.

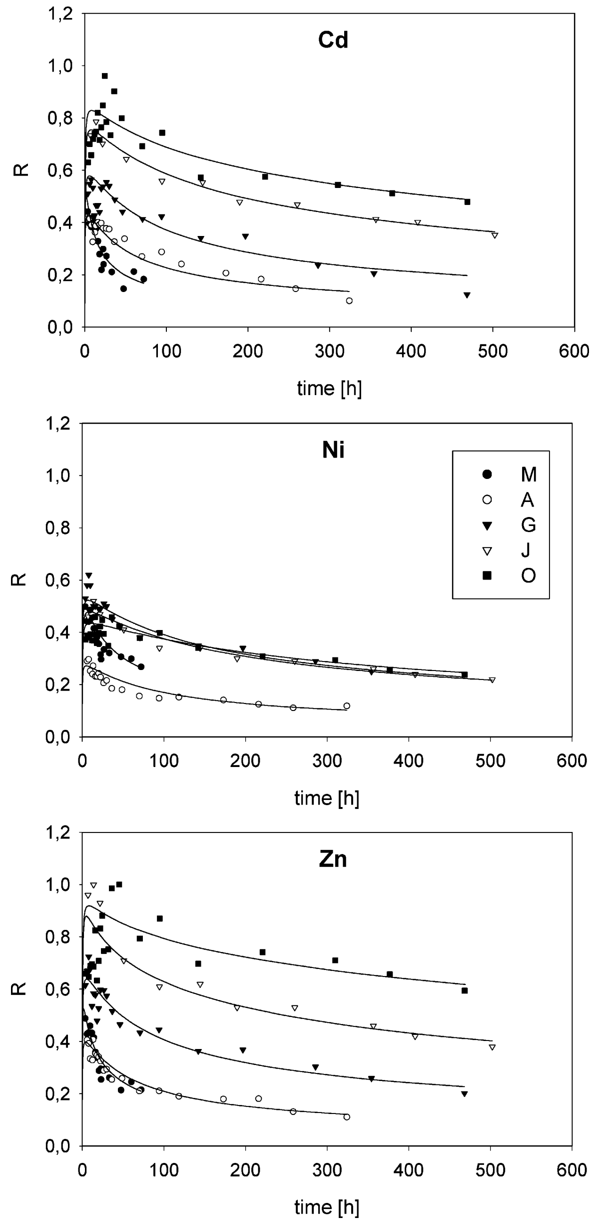

FIGURE 2. Time-dependence of the measured ratio, *R*, which expresses the ratio of metal concentration measured by DGT to total solution concentration. Experimental points are shown for three metals and five soils (M, A, G, J, and O), and the best-fit model lines (DIFS) are included.

TABLE 4. Response Times, T_c (s) Determined by DGT/DIFS, for Trace Metal Interactions in Five Soils

soil	Cd	Zn	Ni
M	300	200	300
A	250	450	1200
G	700	300	800
J	60	<10	700
O	20	<10	1100

lower than those for Zn and Cd, but *R* values for the intermediate pH (5.8) clayey soil (G) were broadly similar for all three metals. The low pH (4.9) sandy soil (M) had *R* values for Ni that were initially similar to those for Zn and Cd, but they declined less steeply with time. The *R* values for the intermediate pH (6.2) sandy soil (A) were slightly lower than those for Zn and Cd.

Kinetics of Trace Metal Exchange. Using DIFS, response times, T_c, for trace metal exchange were derived from the best model fits of *R* versus time (Table 4). The magnitude of *R* at long times is almost exclusively determined by the value of K_{dl}. T_c primarily influences the magnitude at short times and consequently the apparent steepness of the early decline. It is therefore relatively easy to determine unique fits by first optimizing K_{dl} at long times. As this work involved a systematic time series, measurements at each time were not replicated. Replicate DGT measurements of Cd from 22 h deployments had a relative standard deviation of 1.6%. Other workers (*24*) have reported a RSD for DGT deployments in soils of better than 8%. The goodness of fit provides the best error estimates of T_c and K_{dl}. Changing T_c by 30% typically changes the value of *R* by 8%, except where the limiting value is approached. For any given value of K_{dl}, there is a limiting value of T_c. Values of T_c smaller than this threshold have a negligible effect on the value of *R*. This is due to supply from the solid phase being so fast that it no longer limits the amount of metal supplied to the DGT device. The supply then becomes limited by the amount of metal available (labile solid-phase pool concentration via K_{dl}) and the diffusional transport.

For Zn, the short response times (≤10 s) for the high pH soils (J and O) are quoted as maximum values because lowering T_c by an order of magnitude affected the values of *R* by less than 1%. A similar lowering of T_c affected the values of *R* for Cd by 4% (O) and 9% (J) (Table 4). The lower pH soils M, A, and G had longer response times for both Zn and Cd (3−12 min). Selecting order of magnitude shorter response times for soils M and A affected the model fits, but only by a maximum (at short times only) of 11−14% (A) and 9−10% (M). Clearly, the diffusion-limiting case is reached for Zn in soils J and O, and for Cd it is not far from this case in these soils. It cannot be discounted that the diffusion limiting case is reached for soil M and it is close to this case for soil A. For soil G, however, decreasing T_c raised the value of *R* for Cd and Zn by 23−32%. For this soil, there is no doubt that it is the kinetics of desorption, rather than diffusion, that is controlling the supply of these two metals. For all soils, Ni had the longest response times (5−20 min). The difference compared to Cd and Zn was most marked at high pH. In these cases, lowering T_c had a pronounced effect on the value of *R*, showing that a true kinetic limitation exists.

Using the values of K_{dl} and T_c derived from the model fits, it is possible to calculate desorption rate constants (Table 5)

(*11*). Whereas T_c represents the inverse of a rate and therefore embraces the capacity of the labile metal on the solid phase as well as its rate constant of release (see eq 6), the rate constant is a purely kinetic term. The largest value of the desorption rate constant, k_{-1}, for each metal was observed in the sandy acidic soil, M. For Zn and Cd, this soil also had the lowest value of K_{dl}, which affects the overall rate of release and accounts for the long response times observed. This finding of a large desorption rate constant suggests that the intrinsic rate of metal release is higher when there is less binding to the surfaces of soil particles (corresponding to weaker binding for the same adsorption site density). In all cases, Ni had lower rate constants than Cd and Zn. For the more acid soils, the difference was a factor of 2−3, but for the two high pH soils the difference was more marked.

It is difficult to find literature data that can be compared directly to these kinetic measurements. It is not the deployment times of 4 h to 3 weeks that determines the time scale of the measurement, rather it is the time scale of the diffusional transport established by the thickness of the concentration gradient and reflected in the measured response times of 10 s to 20 min. Rates of metal release from soils over short time scales have not often being measured, as stated by Barrow (*25*) and Stumm and Morgan (*26*), and where measurements have been attempted they are usually on suspensions of soil particles in solution. The DGT measurement maintains a realistic soil solution (close to field capacity) in contact with the solid phase. It is sensitive to the rapid supply of metal from the solid phase that can partially buffer the concentration in solution, as metal is removed to the resin sink. This probably corresponds to the fast "desorption" process observed by other workers (e.g., (*26*)) and should be distinguished from the relatively slow release of metal associated with phase change (dissolution) (*27*) or supply from within the particle (*28*).

The best comparative data are associated with response times rather than rate constants. According to Honeyman and Santschi's (*16*) theoretical treatment of sorption, response times in the order of minutes are consistent with values expected for soils. Millward and Liu (*29*) systematically studied the rate of metal release from river and estuarine sediments and estimated best-fit values for response times, T_c, formulated in the same way as this work. Their values of <1 min (Cd), 1.8 min (Zn), and 9.1 min (Ni) are broadly in line with our results for the high pH soils (Table 3), especially when it is considered that high Cl concentrations may have increased the lability of Cd. In their study of Ni detachment from the surface of pyrophyllite, Scheidegger and Sparks (*27*) observed a slow step (months), which they attributed to the dissolution of surface precipitates. A small proportion of the Ni was released within hours, which is still slow as compared to the response times of 5−20 min we observed.

The rapid release of metals is likely to be associated with simple adsorption/desorption processes that can be modeled using surface complexation approaches. Rates of adsorption of metal ions to iron oxides have been shown to be related to their rates of complex formation and release in solution (*30*). The kinetics of metal release from solution complexes is well established. Using the "Eigen mechanism" (*31*), rate constants of Ni release from metal complexes are predicted theoretically to be several orders of magnitude lower than rate constants of release of Cd and Zn from the same complexes, as confirmed experimentally (*32*, *33*). As stated earlier, the rate constants observed in this work for Cd and Zn in soils J and O and possibly M and A are likely to represent minimum values, as the systems appear to be close to diffusional control. It is possible that the true rate of release of Cd and Zn is very fast, mimicking the difference observed between the rates of dissociation of these two metals and Ni in solution.

TABLE 5. Desorption Rate Constants, k_{-1} (10^{-6} s^{-1}), Obtained by DIFS Modeling of DGT Measurements

soil	Cd	Zn	Ni
M	135	113	43
A	22	17	9.2
G	16	25	9.5
J	18	>77	6.5
O	25	>18	3.6

While there is no clear trend in T_c with pH for Ni, there is a reasonably systematic decline in k_{-1} with increasing pH (Tables 4 and 5). This may be associated with the formation of surface precipitates, which form more readily at high pH (*27*). Their formation would ultimately make Ni completely unavailable to DGT (effectively lowers the pool size, see later), but the early stages of formation may simply decrease their rate of release.

Trace Metal Partitioning and Pool Size. The distribution coefficients, K_{dl}, derived from the best model fits of the time dependence of R are shown in Table 6. As varying the value of K_{dl} by 30% produced a typical change in the R value at long times of 10%, they should only be regarded as accurate to ±30%. For soil M, the error could be as much as 50%, as measurements only extended to 72 h. Values of K_{dl} determined by isotopic exchange declined in the first year after metal addition, but were subsequently fairly constant, allowing comparison with K_{dl} values measured 9 months later by DGT (Table 6 and Figure 3).

For Cd, there is good agreement between the two separate estimates of K_{dl} for soils M, A, and G. K_{dl} determined by DGT was higher for soil J, but lower for soil O. Large errors for soil O are associated with the concentration in soil solution being very low (0.24−0.48 μg L^{-1}). In both cases, log K_{dl} increases linearly with pH and the regression lines are similar (Figure 3). Values of K_d, expressed as the ratio of total metal in the soil and the mean concentration in soil solution during the DGT deployment, were higher than K_{dl} in every case, except in comparison to the value derived from isotopic exchange for soil O. Values of K_{dl} derived from isotopic exchange data are based on separate determinations of Cd in soil solution obtained 9 months previous to the DGT measurements.

Log K_{dl} for Zn from both DGT and isotopic exchange increase with pH, but the data obtained from isotopic exchange are generally lower by 0.5 (Figure 3). The difference in K_{dl} values is significant according to the range of values shown in Table 6. It may be due to the extra water that was added to the soil prior to the DGT measurement, which was observed to lower the concentration of Zn (but not Cd) in soil solution. This observation is consistent with the reported phenomena of K_d depending on the concentration of the solid phase, the so-called particle concentration effect (PCE) (*34*). Caution must be exercised in this attribution, however, as the PCE has generally been observed at lower particle concentrations and there is a view that it may simply be due to a failure to account properly for the colloidal component (*35*). There is no significant difference between the two parameters determined on the soil at the same water content and the same time: K_d and K_{dl} from DGT. The similarity indicates that most Zn was available for release to the DGT device.

In the plots of K_{dl} versus pH for Cd and Zn (Figure 3), soil A (pH 6.2) is an obvious outlier for all data, as is, to a lesser extent, soil J (pH 7.0). Soil A had the lowest organic carbon content, and the organic carbon content of soil J was less than half that of the other high pH soil. Thus, the lower partition coefficient for the soils with low total organic carbon suggests less adsorption to the humus.

K_{dl} values for Ni were much lower than those for Cd and Zn for the high pH soils, but similar for the low and

TABLE 6. K_{dl} [mL/g] Determined by DGT/DIFS and Isotopic Exchange and K_d Calculated from Total and Dissolved Concentrations[a]

soil		M	A	G	J	O
Cd	$K_{dl(DGT)}$	11 (6)	45 (14)	100 (30)	700 (210)	1800 (540)
	$K_{dl(IE)}$	10−14	41−42	123−126	198−271	3000−6750
	K_d	54 (3)	92 (12)	198 (11)	883 (74)	2750 (230)
Zn	$K_{dl(DGT)}$	20 (10)	32 (10)	150 (45)	900 (300)	4000 (1500)
	$K_{dl(IE)}$	3.8−5.5	16−18	38−56	340−392	680−925
	K_d	36 (2)	28 (3)	219 (31)	846 (66)	2408 (482)
Ni	$K_{dl(DGT)}$	35 (18)	22 (7)	150 (45)	170 (51)	230 (69)
	K_d	28 (1)	80 (10)	344 (30)	3252 (175)	7180 (525)

[a] Errors in parentheses are estimated from the standard deviation of solution for K_d and the range that gives an acceptable fit for $K_{dl(DGT)}$. The range given for $K_{dl(IE)}$ is based on the duplicate microcosms.

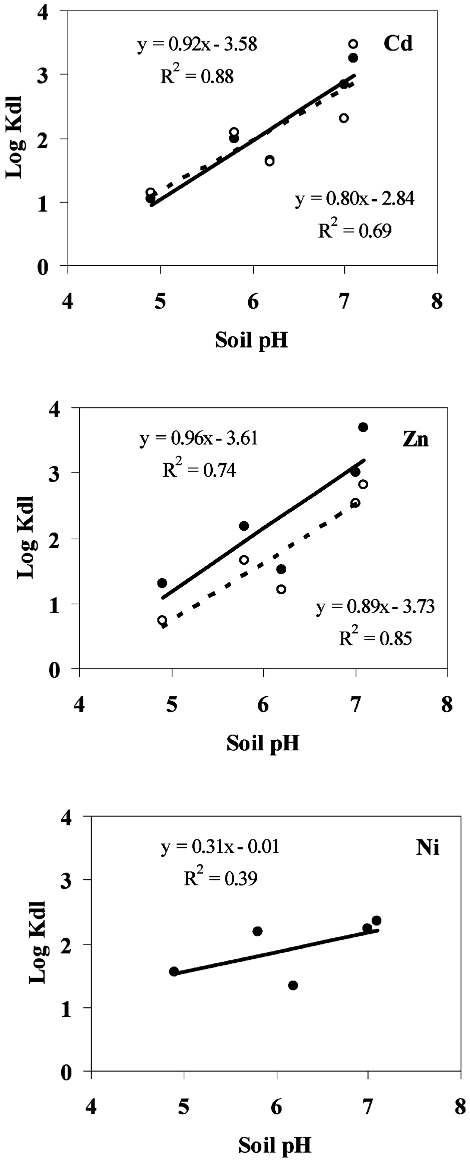

FIGURE 3. Log K_{dl} determined by DGT (solid symbols) and by isotopic exchange (open symbols) versus pH for the five different soils. Regression lines are shown for DGT (solid lines) and isotopic dilution (open lines) data.

intermediate pH soils (Table 6). This resulted in a much lower slope (0.31) for a plot of log K_{dl} versus pH (Figure 3). With all soils the fit was poor ($R^2 = 0.39$), but neglecting soil A resulted in a good fit ($R^2 = 0.81$), with the same slope of 0.31. By contrast, K_d for Ni showed a pH dependence similar to that for Cd and Zn. The concentration of Ni in soil solution (Table 3) also showed a pH dependence similar to that for Cd and Zn. It appears that for the high pH soils only a part of the Ni in the solid phase can be released quickly (minutes) to the DGT device. A possible explanation is that Ni is transferred to a slowly exchangeable form in the higher pH soils. The formation of layered Ni−Al double hydroxides has been shown on kaolinite (*36*). They are resistant to dissolution and form in the presence of humic substances, albeit slowly (*37*). A precursor may make Ni unavailable to DGT, but still allow the concentration of Ni in soil solution to show the expected distribution with pH. The labile pool size of Ni was calculated using K_{dl} estimated from DGT/DIFS, together with the measured concentration of metal in soil solution. It was similar for soils M, A, and G (66−85 mg/kg), but lower for soils J (22 mg/kg) and O (9.4 mg/kg), consistent with Ni being fixed at higher pH. No comparable changes with pH were observed in the solid-phase pool sizes of labile Cd and Zn.

Appraisal of Kinetic Findings

The data for *R* versus time are well-represented by the simple model based on a single K_{dl} and rate constant for metal release. This does not imply that all metal adsorbed by soil can be regarded as being in a single pool with a single rate constant. Rather it indicates that this simple model adequately describes the effective response of the soil system to the induced perturbation of a local sink. There may actually be several pools of metal, with different values of K_d and T_c, but their effect, on the time scale of this experiment, can be described by single values of labile distribution coefficients and response times. Although the experiment lasted 21 days, there is a continuous flux to the device and for any period of a few hours there is an apparent steady-state condition. The characteristic time scale of the measurement can be judged from the response times (Table 4) to be in the range 1−20 min. Thus, processes where metal is more slowly bound within the soil (aging) are not considered in this experiment.

Cd and Zn are released from the solid phase so quickly that it is difficult to distinguish between kinetic and diffusion limitation. By contrast, Ni is released more slowly, allowing its clear distinction from diffusion control. These findings are consistent with other observations of fast release rates for Cd and Zn from solution and surface complexes and slower rates of release for Ni (*31*, *33*). The decline in the dissociation rate constant for Ni with increasing pH is probably due to the formation of surface precipitates, which also appeared to be responsible for lowering the pool size of available Ni. When distribution coefficients are expressed in terms of labile metal on the solid phase, they become conditional on the characteristic time available to measure the labile metal. The broadly similar values observed for Zn and Cd for K_{dl} determined by DGT and isotopic exchange suggest that kinetic processes operating on time scales between 20 min (DGT) and 2 days (isotopic exchange) are not important.

The kinetic findings of this work have implications for assessing the bioavailability of trace metals to plants. DGT measurements have been shown to correlate well with concentrations of metals in plants (*13*, *14*). Although DGT clearly does not mimic all processes involved in plant uptake, including mass flow and root interception, the good correlations indicate that the DGT-soil system effectively mimics the major processes in those soils studied. Thorough interpretation of the physicochemical processes controlling the DGT-soil system can therefore help to identify on a more fundamental basis the factors that control supply of metals to plants. This work has shown that in the case of Ni the kinetics of release from solid phase to solution can control supply to a DGT device. The same constraint would apply to Ni uptake by a plant, if it can rapidly assimilate metal. For Zn and Cd, the speed of release from the solid phase to solution is unlikely to control supply to either a DGT device or a plant. The controls on supply are still complicated, however. They depend primarily on the concentration in soil solution, but other factors are influential. These include the capacity of the solid phase, because even for rapid desorption kinetics of Zn and Cd, the solution concentration adjacent to the DGT device can be considerably depleted within 24 h (Figure 2) when K_{dl} is small.

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