

Supplementary material

The use of ultra-thin diffusive gradients in thin-films (DGT) devices for the analysis of trace metal dynamics in soils and sediments: a measurement and modelling approach

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Diffusive gel preparation

The diffusive gels used in this work were cast to thicknesses of 0.25 and 0.5 mm, using documented procedures.^[1] Briefly, 37.5 mL of acrylamide solution (40 %), 47.5 mL of MilliQ water and 15 mL of DGT cross-linker were mixed together in an acid cleaned vessel. A 10-mL aliquot of the solution was pipetted into another acid-cleaned plastic container, into which 70 μ L of ammonium persulfate solution (10 %, 0.1 g in 1 g of H₂O) and 25 μ L of TEMED (99 %) were added. The solution was then mixed thoroughly and cast between two acid-cleaned glass plates separated by either a 0.25- or 0.5-mm spacer and set in an oven at 45 °C for ~80 min. The gel was then removed from between the glass plates and allowed to hydrate fully for 24 h in MilliQ water, which was changed several times during the hydration cycle. Finally, the diffusive gel was stored in 0.01 M NaNO₃ solution until use. At the end of the hydration cycle, the thicknesses of the gels were 0.4 and 0.8 mm.

Gel drying

The ultra-thin gels were mounted flat on 0.04-cm discs of DGT diffusive gel, which in turn were placed on pre-cleaned 2.5-cm diameter cellulose filter membranes. The filter-diffusive gel-resin gel stacks were left to air dry in a laminar flow hood for 30 min, after which they were placed between white blotting paper and an acid-washed plastic membrane (resin gel facing the plastic membrane) and placed under even pressure overnight. Next the gels were placed in a commercial gel drier (Bio-Rad Laboratories) for 8 h at 60 °C. Finally the gels were mounted on glass microscope slides with double-sided adhesive tape.

Laser Ablation

C-13 has been established previously as an acceptable internal standard for DGT gel LA-ICP-MS analyses^[2,3] and was used again here. Calibration standards were prepared as described by Gao and Lehto.^[3] A beam diameter of 100 μ m was selected to achieve the maximum analyte signal. Ablation intensity was determined by varying the power of the laser using optical attenuation while observing the analyte and C₁₃ signals in accordance with previously established procedures.^[3] Spot analysis of the gel was carried out at 500 μ m intervals (line of spots) using a laser dwell time of 4 s and a 10-s interval between ablations. These parameters were chosen to ensure peaks were easily defined from the background by the instrument software, while keeping the total analysis time to a minimum.

Modelling diffusion in soil

The diffusion coefficients of the dissolved species (D_0) are adjusted to account for the tortuosity (θ^2) of the diffusive pathway in the soil to obtain an effective diffusion coefficient (D_e)^[4] (Eqn S1):

$$D_e = \frac{D_0}{\theta^2} \quad (\text{S1})$$

Model solution

Due to the non-linearity of the continuity equations (Eqns 1–12), a numerical solution is required. The Finite Element Method (FEM) was used to solve the systems of non-linear partial differential equations (PDE) by applying the COMSOL Multiphysics (v3.2b) package supplied by COMSOL, UK. COMSOL Multiphysics applies dynamic unstructured adaptive-grid methods to optimise the numerical solution. The total number of elements varies depending on the size of the diffusive and resin layers considered and on the accuracy required. At the resin-layer–diffusive-layer and the diffusive-layer–soil interfaces the spatial resolution of the calculations was 10^{-7} cm and the temporal resolution varied from 0.001 to 10s. For the purposes of modelling the deployment of a DGT_{0.001} probe, with the soil subdomain extending 10 cm away from the DGT-probe interface, a mesh resolution consisting of a total of 10254 elements was required.

With the input parameters listed in Tables S1–3 the model can be used to calculate the concentrations of all five species at any time and point within the model domain. The total amount of metal taken up by the resin layer is calculated by integrating the total mass of metal-resin complex formed at $-\Delta r \leq x \leq 0$ over the simulated deployment time.

The boundary condition at $x = n$ was specified as a constant concentration with regards to $[M]$, $[L]$, $[ML]$ and $[MS]$. Concentrations of these variables at point n were observed for each model run to ensure that they remained unchanged from the initial concentrations for the duration of the simulation.

Table S1. WHAM VI^[5] (v6.1.2.) input parameters

Analyte	Concentration (mM)
Cl ⁻	0.44
NO ₃ ⁻	0.18
HCO ₃ ⁻	5.30
SO ₄ ²⁻	0.18
Na ⁺	0.4
K ⁺	0.56
Ca ²⁺	1.94
Mg ²⁺	0.7
Ni ²⁺	0.353×10^{-3}
Cu ²⁺	2.282×10^{-3}
Zn ²⁺	0.710×10^{-3}
Cd ²⁺	0.227×10^{-3}
DOC	28.99 mg L ⁻¹
pH	6.13

Table S2. Kinetic parameters

	Parameter	Cu	Cd	Units
Porewater ionic strength ^A	I	6.16×10^{-3}		mol cm^{-3}
Metal–fulvic stability constant ^A	K_{ML}	2.47×10^5	1.3×10^8	$\text{cm}^3 \text{mol}^{-1}$
Metal–resin stability constant ^B	K_{MR}	10^{21}	10^{21}	$\text{cm}^3 \text{mol}^{-1}$
Stability constant for outer–sphere complex ^B	K_{OS}	5.164×10^{-2}	5.164×10^{-2}	cm^{-3}
Rate of dissociation of water molecules ^B	k_w	3×10^8	1×10^9	s^{-1}
Association rate constant ^B	$k_f (= K_{\text{OS}} \times k_w)$	1.55×10^7	5.16×10^7	$\text{cm}^3 \text{s}^{-1} \text{mol}^{-1}$
Dissociation rate constant of metal–fulvic complex ^B	$k_{\text{dis f}} (= k_f / K_{\text{ML}})$	64.53	0.396	s^{-1}
Dissociation rate constant of metal–resin complex ^B	$k_{\text{dis R}} (= k_f / K_{\text{MR}})$	1.55×10^{-14}	5.16×10^{-14}	s^{-1}
Concentration of resin binding sites	$[R]$	0.11×10^{-3}		mol cm^{-3}

^ADerived from WHAM IV results.

^BFor further explanation of parameters, see Morel and Hering.^[6]

Table S3. Soil parameters

	Equation	Value	Units
MWHC (η)	–	43.0	%
Soil Density (ρ)	–	2.65	g cm^{-3}
Particle Concentration (P_c)	–	2.907	g cm^{-3}
Porosity (ϕ)	$\phi = \frac{\rho}{P_c + \rho}$	0.477	–
Tortuosity (θ^2)	$\theta^2 = 1 - 2 \ln(\phi)$	2.481	–

Table S4. Equations that describe the behaviour of metal, ligand and complex in the soil, the diffusive gel and the resin gel

Species	Domain	Equation	Eqn number
Free metal in soil	$(\Delta g < x < n)$	$\frac{\partial[M_x]}{\partial t} = (k_{de} \times P_c \times [MS_x] - k_{ad}[M_x]) + (k_{dis}[ML_x] - k_f[M_x][L_x]) + \frac{\partial}{\partial x} \left(D_{M-s} \frac{\partial[M_x]}{\partial x} \right)$	1
Solid phase-bound metal	$(\Delta g < x < n)$	$\frac{\partial[MS_x]}{\partial t} = \frac{k_{ad}}{P_c}[M_x] - k_{de}[MS_x]$	2
Free ligand in soil	$(\Delta g < x < n)$	$\frac{\partial[L_x]}{\partial t} = k_{dis}[ML_x] - k_f[M_x][L_x] + \frac{\partial}{\partial x} \left(D_{L-s} \frac{\partial[L_x]}{\partial x} \right)$	3
Metal–ligand complex in soil	$(\Delta g < x < n)$	$\frac{\partial[ML_x]}{\partial t} = k_f[M_x][L_x] - k_{dis}[ML_x] + \frac{\partial}{\partial x} \left(D_{ML-s} \frac{\partial[ML_x]}{\partial x} \right)$	4
Free metal in diffusive gel	$(0 < x < \Delta g)$	$\frac{\partial[M_x]}{\partial t} = k_{dis}[ML_x] - k_f[M_x][L_x] + \frac{\partial}{\partial x} \left(D_{M-g} \frac{\partial[M_x]}{\partial x} \right)$	5
Free ligand in diffusive gel	$(0 < x < \Delta g)$	$\frac{\partial[L_x]}{\partial t} = k_{dis}[ML_x] - k_f[M_x][L_x] + \frac{\partial}{\partial x} \left(D_{L-g} \frac{\partial[L_x]}{\partial x} \right)$	6
Metal–ligand complex in diffusive gel	$(0 < x < \Delta g)$	$\frac{\partial[ML_x]}{\partial t} = k_f[M_x][L_x] - k_{dis}[ML_x] + \frac{\partial}{\partial x} \left(D_{ML-g} \frac{\partial[ML_x]}{\partial x} \right)$	7
Free metal in resin gel	$(-\Delta r < x \leq 0)$	$\frac{\partial[M_x]}{\partial t} = k_{dis-R}[MR_x] - k_{f-r}[M_x][R_x] + k_{dis}[ML_x] - k_f[M_x][L_x] + \frac{\partial}{\partial x} \left(D_{M-g} \frac{\partial[M_x]}{\partial x} \right)$	8
Free ligand in resin gel	$(-\Delta r < x \leq 0)$	$\frac{\partial[L_x]}{\partial t} = k_{dis}[ML_x] - k_f[M_x][L_x] + \frac{\partial}{\partial x} \left(D_{L-g} \frac{\partial[L_x]}{\partial x} \right)$	9
Metal–ligand complex in resin gel	$(-\Delta r < x \leq 0)$	$\frac{\partial[ML_x]}{\partial t} = k_f[M_x][L_x] - k_{dis}[ML_x] + \frac{\partial}{\partial x} \left(D_{ML-g} \frac{\partial[ML_x]}{\partial x} \right)$	10
Free Chelex in resin gel	$(-\Delta r < x \leq 0)$	$\frac{\partial[R_x]}{\partial t} = k_{dis-R}[MR_x] - k_{f-r}[M_x][R_x]$	11
Metal–Chelex complex in resin gel	$(-\Delta r < x \leq 0)$	$\frac{\partial[MR_x]}{\partial t} = k_{f-r}[M_x][R_x] - k_{dis-R}[MR_x]$	12

Table S5. Initial and boundary conditions

	Conditions for x, t	Location
Initial conditions		
$[M](x, 0) = 0$	$-\Delta r < x < \Delta g, t = 0$	Resin and diffusive layer
$[L](x, 0) = 0$	$-\Delta r < x < \Delta g, t = 0$	Resin and diffusive layer
$[ML](x, 0) = 0$	$-\Delta r < x < \Delta g, t = 0$	Resin and diffusive layer
$[MR](x, 0) = 0$	$-\Delta r < x < 0, t = 0$	Resin gel
$[R](x, 0) = [R_0]$	$-\Delta r < x < 0, t = 0$	Resin gel
$[M](\Delta g, 0) = [M_0]$	$\Delta g < x < n, t = 0$	Soil porewater
$[L](\Delta g, 0) = [L_0]$	$\Delta g < x < n, t = 0$	Soil porewater
$[ML](\Delta g, 0) = [ML_0]$	$\Delta g < x < n, t = 0$	Soil porewater
Boundary conditions		
$[M](n, t) = [M_0]; \forall t$	$\forall t$	Distance n from diffusive layer–soil interface
$[L](n, t) = [L_0]; \forall t$	$\forall t$	Distance n from diffusive layer–soil interface
$[ML](n, t) = [ML_0] \forall t$	$\forall t$	Distance n from diffusive layer–soil interface
$\nabla[M](-\Delta r, t) = \nabla[L](-\Delta r, t) = \nabla[ML](-\Delta r, t) = 0; \forall t$	$\forall t$	End of resin gel
$D_M \nabla([M](x, t)) _{x=0-}, \Delta g- = D_M \nabla([M](x, t)) _{x=0+}, \Delta g+$	$\forall t$	Interfacial condition
$D_L \nabla([L](x, t)) _{x=0-}, \Delta g- = D_L \nabla([L](x, t)) _{x=0+}, \Delta g+$	$\forall t$	Interfacial condition
$D_{ML} \nabla([ML](x, t)) _{x=0-}, \Delta g- = D_{ML} \nabla([ML](x, t)) _{x=0+}, \Delta g+$	$\forall t$	Interfacial condition
$[M](0-, t) = [M](0+, t); [L](0-, t) = [L](0+, t); [L](0-, t) = [L](0+, t)$	$\forall t$	Interfacial condition
$\nabla[M](0, t); \nabla[L](0, t); \nabla[ML](0, t); \forall t$	$\forall t$	Interfacial condition

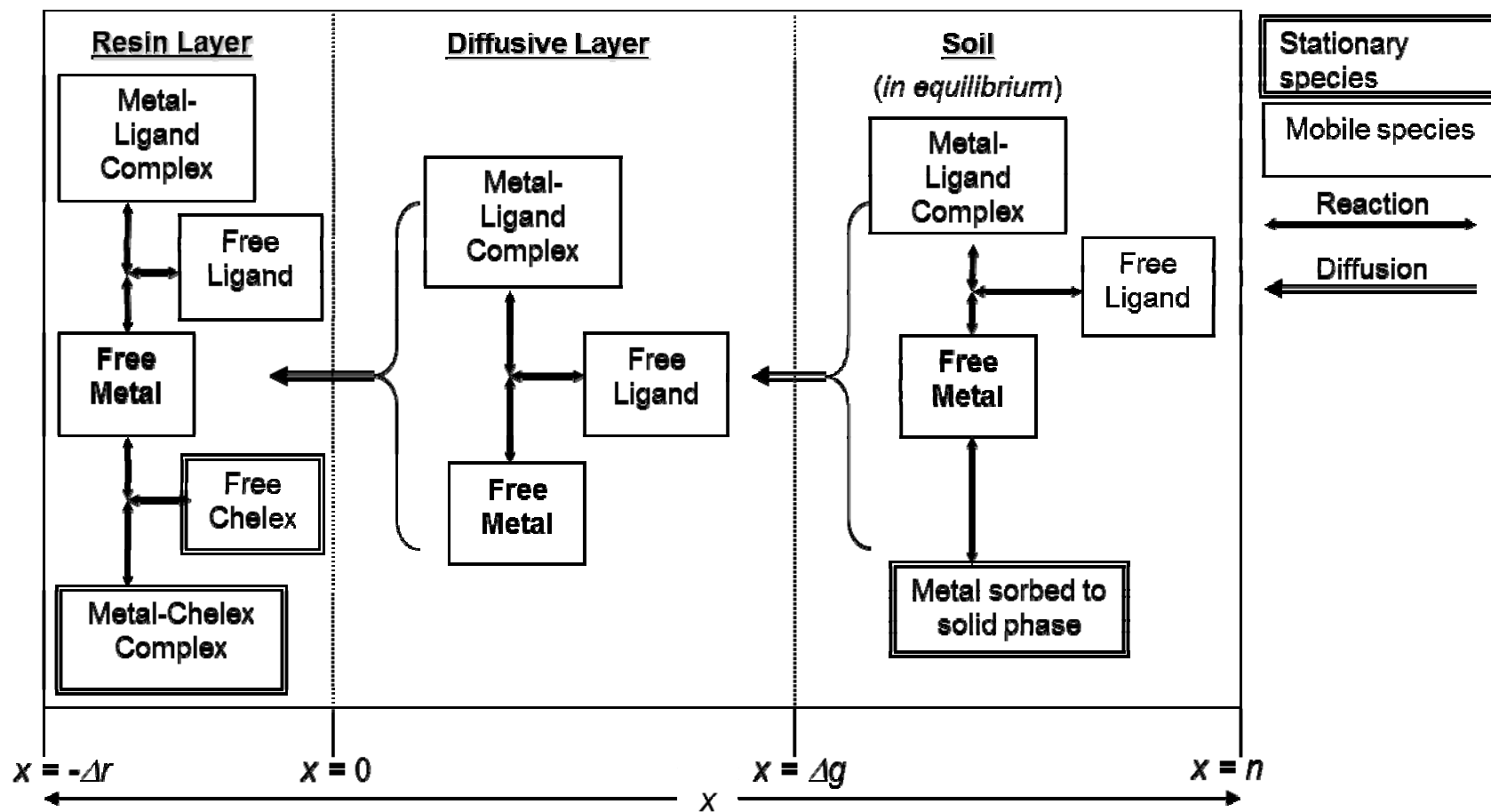


Fig S1. The model domain.

References

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