Diffusion Gradient in Thin Films (DGT) from single ligand systems to mixtures.

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Plants survival: Nutrients availability

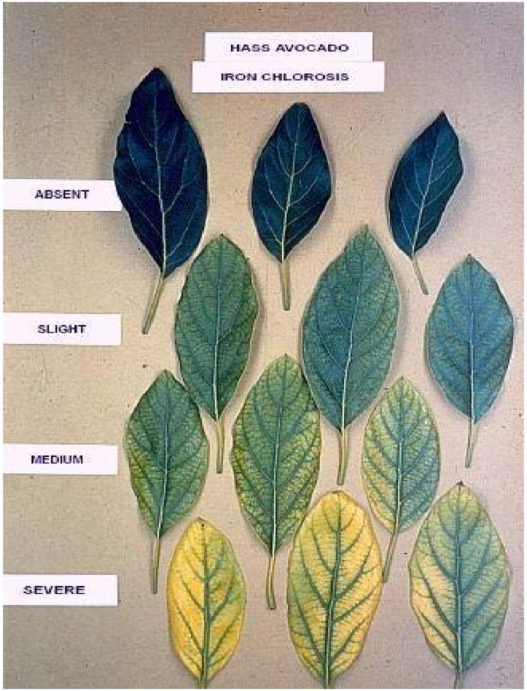
Micronutrients Uptake: Fe

Plant strategy for iron uptake:

- Uptake of **free iron** (Fe^{+3})
- Generation of siderophores(via chelating agents)

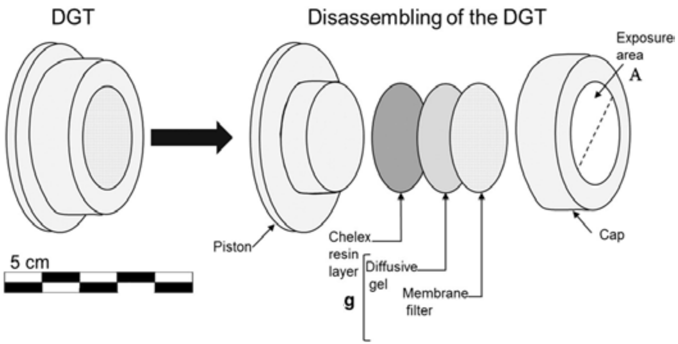
Lack of free iron (Fe^{+3}) in soil?

Iron chlorosis, Yellowing of plants leaves



J.Morrissey and M. L. Guerinot, *Chemical Reviews* **2009** 109 (10), 4553-4567

DGT technique



Use in soils

Chelex Resin ⟶ Metal accumulation ⟶ Elution with an acid solution

ICP-MS/ ICP-OES ⟶ Effective concentration (c_{DGT})

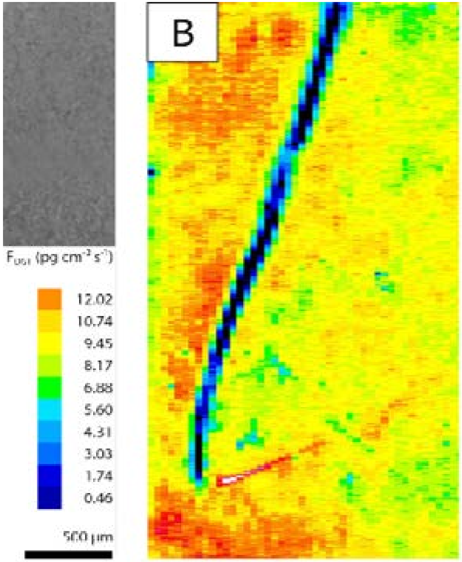
DGT applications

Screening of phosphate uptake by a maize root

12.02 $\frac{pg}{cm^2 s}$

6.88 $\frac{pg}{cm^2 s}$

0.46 $\frac{pg}{cm^2 s}$

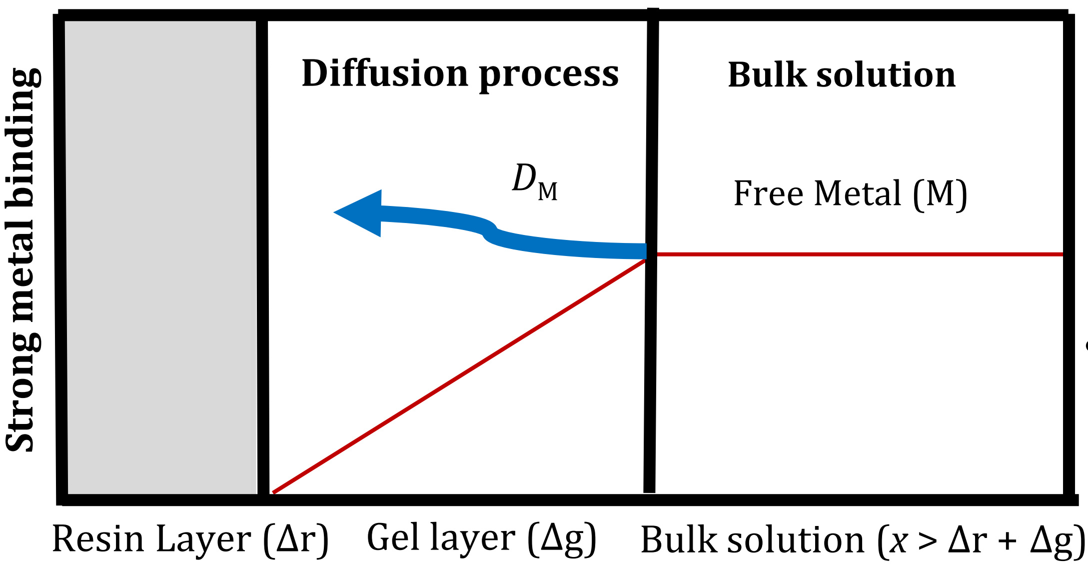


J. Santner et al. *Analytica Chimica Acta* 878 (**2015**) 9–42.

E. D. Amato, et al *Environmental Science & Technology* **2016** *50* (6), 3055-3064

How metal accumulation (n) is computed only considering free metal ion?

Metal accumulation $J = \frac{D_M c_M^*}{g}$ $n = AtJ$



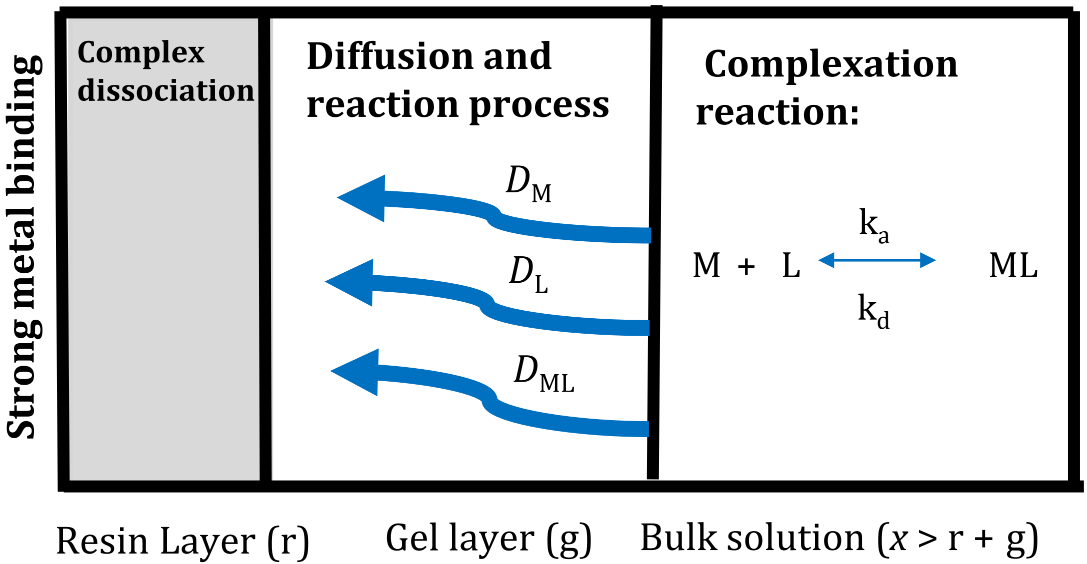
- **Free metal concentration drops to zero** due to the **strong** and **fast** binding of M to resin beads.

M+R⇌MR

- **Diffusion process** of free metal ion along the diffusive **gel**

How c_{DGT} is related to the concentration of species?

Metal accumulation $\quad J = \dfrac{D_{\mathrm{M}} c_{\mathrm{DGT}}}{\mathrm{g}} \qquad n = AtJ$



- **Diffusion-reaction processes** along the diffusive **gel**

  $\mathrm{M+L \rightleftharpoons ML}$

- The **free metal concentration drops to zero** due to the **strong** and **fast** binding of M to resin beads.

  $\mathrm{M+R \rightleftharpoons MR}$

Objectives

- Interpretation of the effective c_{DGT} concentration in terms of species of the natural media.

- Design and test some strategies in experimental systems where using DGT devices with different “g” and “r” thicknesses we could be able to determine concentrations/mobilities or labilities of species present in natural waters.

Tools to fulfill the objectives

- To develop an algorithm to compute the concentration profiles of system mixtures containing mixtures of ligands in high and low ionic strength conditions (using Nernst-Planck equation).
- To develop approximate analytical expressions to compute the flux contribution of free metal ion and it's complexes at the resin layer for systems of 2 ligands or more.
- To develop simple approximate analytical expressions to compute the lability degree of each metal species for an experimental designed system.
- To conduct experimental measurements in simple mixture systems.

Methodology

Application of Finite Element Method (FEM) on transport equations

Considering the simplest complexation reaction (single ligand system):

$$\mathrm{M} + \mathrm{L} \underset{\mathrm{k_d}}{\overset{\mathrm{k_a}}{\longleftrightarrow}} \mathrm{ML}$$

$\mathrm{r} > x > \mathrm{r} + \mathrm{g}$ $$\frac{\partial c_{\mathrm{M}}}{\partial t} = \mathrm{D_M} \frac{\partial^2 c_{\mathrm{M}}}{\partial x^2} - \mathrm{k_a} c_{\mathrm{M}} c_{\mathrm{L}} + \mathrm{k_d} c_{\mathrm{ML}}$$

$0 > x > \mathrm{r}$ $$\frac{\partial c_{\mathrm{M}}}{\partial t} = \mathrm{D_M} \frac{\partial^2 c_{\mathrm{M}}}{\partial x^2} - \mathrm{k_a} c_{\mathrm{M}} c_{\mathrm{L}} + \mathrm{k_d} c_{\mathrm{ML}} - \mathrm{k}_{a_R} c_M c_R + \mathrm{k}_{d_R} c_{MR}$$

$0 > x > \mathrm{r} + \mathrm{g}$ $$\frac{\partial c_{\mathrm{L}}}{\partial t} = \mathrm{D_L} \frac{\partial^2 c_{\mathrm{L}}}{\partial x^2} - \mathrm{k_a} c_{\mathrm{M}} c_{\mathrm{L}} + \mathrm{k_d} c_{\mathrm{ML}}$$

$0 > x > \mathrm{r} + \mathrm{g}$ $$\frac{\partial c_{\mathrm{ML}}}{\partial t} = \mathrm{D_{ML}} \frac{\partial^2 c_{\mathrm{ML}}}{\partial x^2} + \mathrm{k_a} c_{\mathrm{M}} c_{\mathrm{L}} - \mathrm{k_d} c_{\mathrm{ML}}$$

$\mathrm{D_M}$: metal diffusion coeficient.

$\mathrm{D_{ML}}$: complex diffusion coeficient.

$\mathrm{D_L}$: ligand diffusion coeficient.

$\mathrm{k_a}$: association rate constant

k_d: dissociation rate constant

DGT initial and boundary conditions

$t = 0 \qquad c_{\mathrm{i}}(\mathrm{r}+\mathrm{g},t) = c_{\mathrm{i}}^{*}$ $\qquad c_{\mathrm{R}}(x \leq \mathrm{r},t) = c_{\mathrm{TR}}$

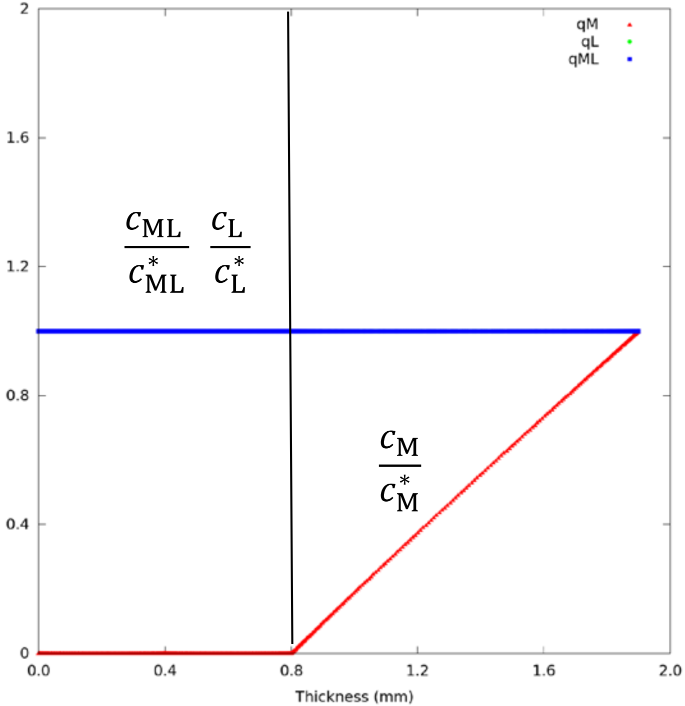
$t = 0 \qquad c_{\mathrm{i}}(x < \mathrm{r}+\mathrm{g},t) = 0$ $\qquad \mathrm{R} \equiv$ Chelex Resin

$$x = 0 \qquad \mathrm{D_i}\frac{\partial c_{\mathrm{i}}(x,t)}{\partial x} = 0$$

$$x = \mathrm{r} \qquad \mathrm{D_i}\frac{\partial c_{\mathrm{i}}(x,t)}{\partial x}_{(x=\mathrm{r}^-)} = \mathrm{D_i}\frac{\partial c_{\mathrm{i}}(x,t)}{\partial x}_{(x=\mathrm{r}^+)}$$

$$x \geq \mathrm{r}+\mathrm{g} \qquad c_{\mathrm{i}}(x,t) = c_{\mathrm{i}}^{*}$$

Simulations in excess of ligand conditions



Resin layer (r) Gel layer (g)

$$\mathrm{K} = 21322$$

$$\mathrm{k_a} = 10^{-2}\,\frac{m^3}{mol}$$

$$\mathrm{k_d} = 46.9\mathrm{x}10^{-8} s^{-1}$$

$$\mathrm{D_M} = \mathrm{D_{ML}} = \mathrm{D_L} \equiv \frac{m^2}{s}$$

Total metal flux at x=r

$$\boxed{\mathrm{J_1} = \mathrm{D_M}\frac{c^*_{\mathrm{M}}}{\mathrm{g}}}$$

Simulations in excess of ligand conditions

$$K = 21322$$

$$k_a = 10^6 \frac{m^3}{mol} \qquad D_M = D_{ML} = D_L$$

$$k_d = 46.9\ s^{-1}$$

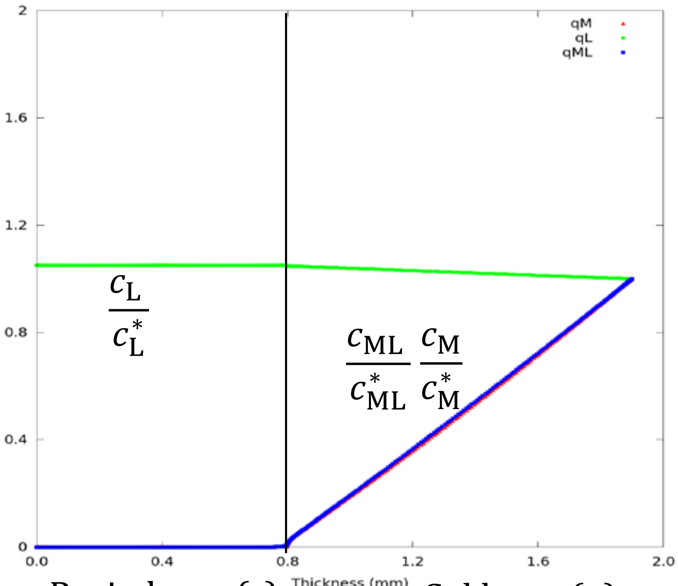
For fully labile complexes

Local Equilibrium

$$\frac{c_{ML}}{c^*_{ML}} = \frac{c_M}{c^*_M}$$

Total metal flux at x=r

$$\boxed{J_3 = D_M \frac{c^*_M}{g} + D_{ML} \frac{c^*_{ML}}{g}}$$



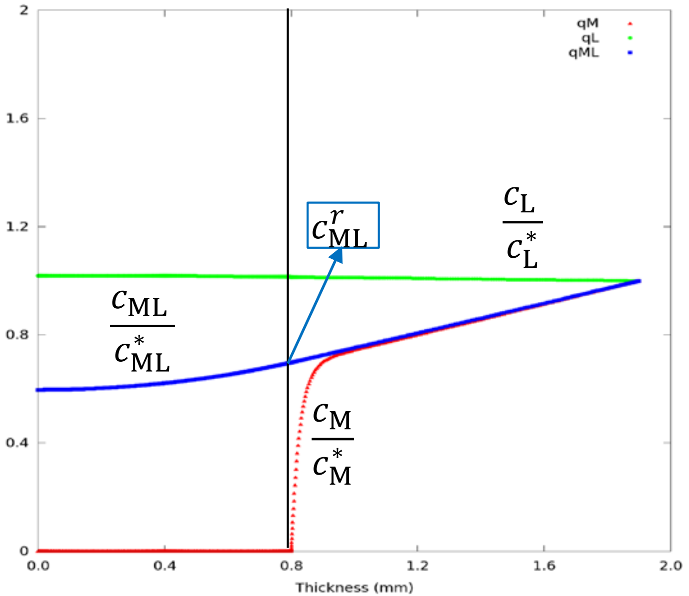
Resin layer (r) Gel layer (g)

Simulations in excess of ligand conditions

$$K = 21322$$

$$k_a = 10^2 \frac{m^3}{mol} \qquad D_M = D_{ML} = D_L$$

$$k_d = 46.9x10^{-4} s^{-1}$$



Resin layer (r) Gel layer (g)

Total metal flux at x=r

$$\boxed{J_2 = D_M \frac{c_M^*}{g} + D_{ML} \frac{c_{ML}^* \xi}{g}}$$

$\xi \equiv$ lability degree

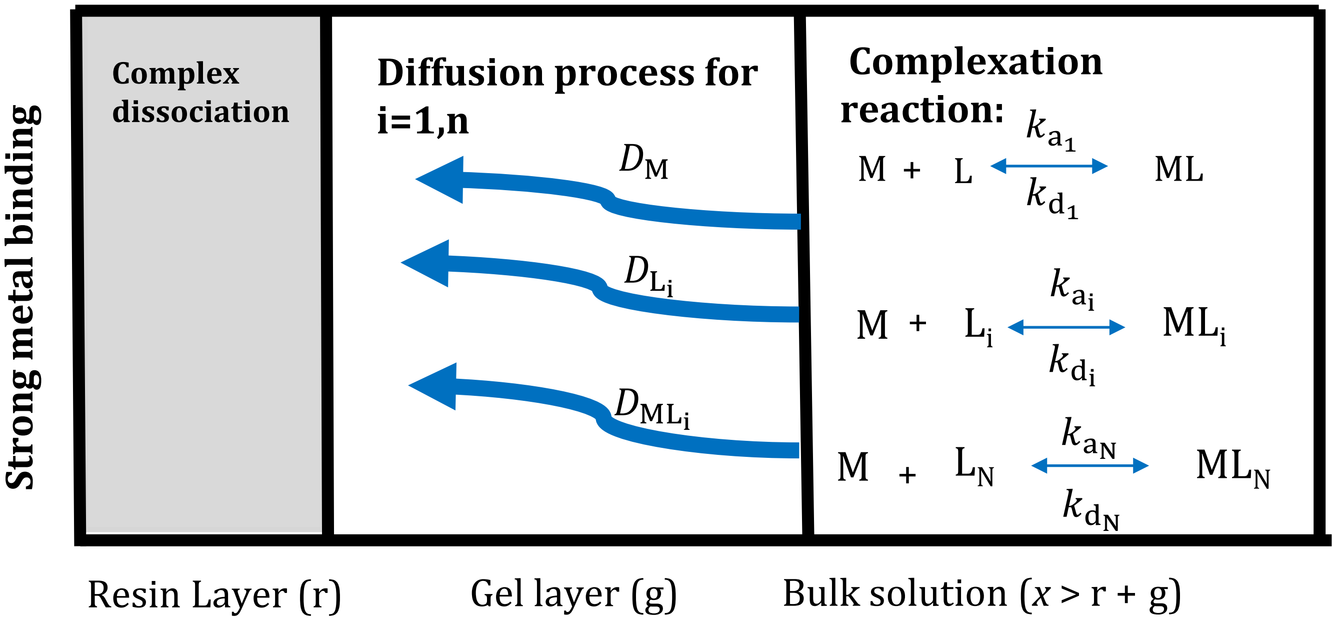
$$\xi = 1 - \frac{c_{ML}^r}{c_{ML}^*}$$

Comparison of total metal flux at x=r with previous simulations

$$J_3 > J_2 > J_1$$

For a system of n ligands

Metal accumulation $\quad n = AtJ \quad J = \dfrac{D_M c_M^*}{\Delta g} + \sum_{i=1}^{N} \dfrac{D_{ML_i} c_{ML_i}^*}{\Delta g} \xi_i$



For a system of n ligands

Analytical expression for total metal flux.

$$J = \frac{D_{\mathrm{M}} c_M^*}{\mathrm{g}} + \sum_{\mathrm{i=1}}^{\mathrm{N}} \frac{D_{\mathrm{ML_i}} c_{\mathrm{ML_i}}^*}{\mathrm{g}} \xi_{\mathrm{i}}$$

Expression for total metal flux considering an effective metal concentration.

$$J = \frac{D_{\mathrm{M}} c_{\mathrm{DGT}}}{\mathrm{g}}$$

Relationship of effective metal concentration (c_{DGT}) with the concentration of the species of this system.

$$\boxed{c_{DGT} = c_M^* + \sum_{\mathrm{i=1}}^{\mathrm{N}} \frac{D_{\mathrm{ML_i}}}{D_{\mathrm{M}}} c_{\mathrm{ML_i}}^* \xi_{\mathrm{i}}}$$

Work Plan

Topics	Time Waste
Formation courses	2 months
Concentration profiles of mixture systems. Dependence of the lability degree on the composition of the mixture	6 -8 months
Effect of low ionic strength in DGT accumulations from first principles	6 -8 months
DGT measurements in mixture model systems and in natural waters.	6-8 months
Research Stay	3 months
Articles and Thesis	7 months

Acknowledgements

- Support from MCIU is gratefully acknowledged

- Support from UdL for the scholarship of 3 years is gratefully acknowledged

- Thanks for your attention!