THESIS PLAN:

MEASURING THE AVAILABILITY OF METALS IN LARGE MIXTURES WITH DIFFUSIVE GRADIENTS IN THIN FILMS (DGT) DEVICES.

Jordi Sans-Duñó
Chemistry Department, ETSEA, UdL, Lleida
e-mail: (jsd@quimica.udl.cat)

1. Description and problem treatment.

Natural waters contain a varied diversity of compounds, such as inorganic compounds (*e.g* metal ions, inorganic complexes with simple ligands), small organic molecules, macromolecules, colloids and particles. Macromolecular organic matter usually come from decomposition processes of dead plants and animals. As the identification of individual molecules is not practical, organic fractions of homologous compounds are measured as sets of compounds with similar physicochemical properties (Morel 1983).

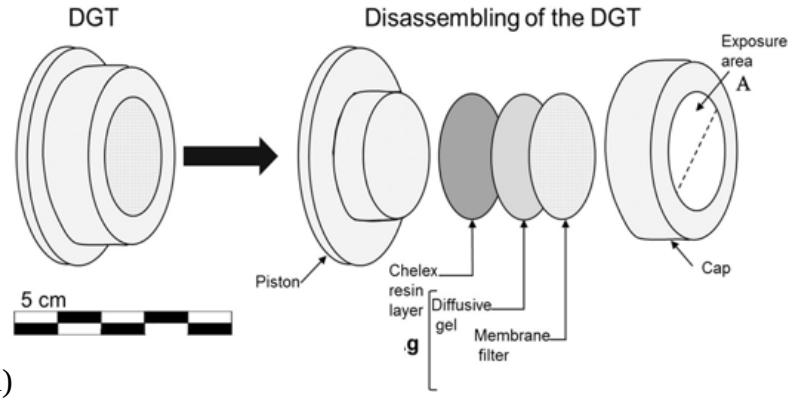
Plants present several ways of assimilating micronutrients such as metal ions. The most common way consists on direct absorption of free metal ion through a porous membrane as a result of a chemical potential gradient. In very few cases, evidences of direct absorption of a complex have been reported (Campbell 1995). However, in general, internalization is dependent on the speciation, on the mobility and on the dissociation kinetics of the complexes, so that the nutritive or toxicological properties of an element in a medium depend on the flux received by the organism, plant, algae etc (Buffle, Wilkinson and van Leeuwen 2009).

It is interesting to have analytical techniques able to measure the metal flux received by limiting surfaces (Unsworth, Zhang and Davison 2005). So, voltammetric techniques have been widely used as mimetics of the natural availability (Town, van Leeuwen and Buffle 2012).

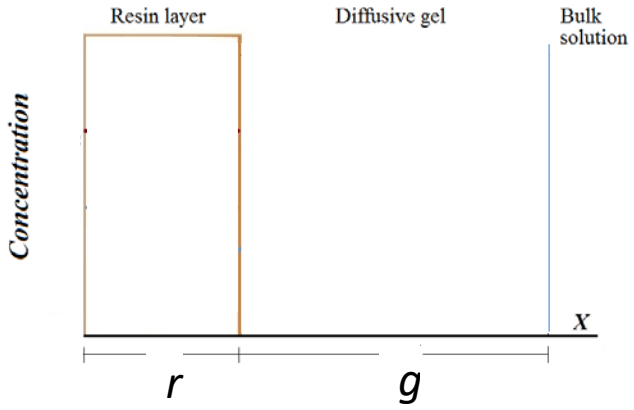
In the last two decades, passive samplers have also been developed to measure in situ metal speciation in natural media. Among them, Diffusive Gradients in Thin Films (DGT) has reached great popularity due to its simplicity (Davison and Zhang 1994). DGT is a tiny device composed of a membrane filter, a gel layer and a resin layer (Fig. (1)). The deployment of several devices allows to measure the accumulation of a metal ion with time. The presence of the diffusive gel between the solution and the resin layer is a key element, because, with an appropriate gel thickness, the rate of mass transport is controlled by diffusion and the system hydrodynamics becomes negligible (Davison and Zhang 1994).

Fig. 1 Graphical scheme of the geometrical structure of each part of a DGT device.

When accumulation takes place under steady-state and perfect sink conditions, the first law of diffusion indicates that



a)



b)

$$n = \frac{AtD_{\mathrm{M}}c_{\mathrm{M}}^{*}}{\mathrm{g}} \qquad (1)$$

where n stands for the number of mols of metal accumulated in the resin disc, t for the deployment time, D_{M} for the diffusion coefficient of the metal, c_{M}^{*} for the free metal ion concentration at the bulk solution. Finally, A and g stand for the area and gel layer thickness of the DGT device.

Eqn. (1) indicates that the sole knowledge of the diffusion coefficient of the metal ion together with the geometrical properties of the device (thickness of the gel layers) permits to compute the flux received by the chemical sensor (Galceran and Puy 2015).

2. Mathematical Formulation.

Different metal species are usually present in natural waters and all of them can contribute to the accumulation depending on the respective diffusion coefficients and dissociation rate constants. To account for these cases, Eqn. (1) is rewritten replacing

c_{M}^{*} with c_{DGT}^{*} which labels the effective or apparent metal concentration that would lead to the same accumulation when only free metal is present in the system.

$$n = \frac{AtD_{\mathrm{M}}c_{\mathrm{DGT}}}{\mathrm{g}} \qquad (2)$$

A first aim of this project is the interpretation of c_{DGT} in terms of the concentration of the species in natural media, *i. e.*, we would like to understand which species and up to which extent do they contribute to the metal accumulation.

As starting point, we will consider the diffusion-reactions equations that describe the transport and reaction processes taking place in a DGT device. A rigorous numerical algorithm to solve this set of diffusion-reaction equations for a set of specific initial and boundary conditions will be developed. Finite Element Methods (FEM) will be used in this numerical tool.

3. Numerical Simulation

The Finite Element Method will be used to numerically solve the system of diffusion reaction equations resulting from the mathematical formulation of the processes taking place in a DGT device.

The main idea of this method is to divide the spatial domain, on which the equations are described, in a set of discrete parts with some privileged points, not necessarily equally spaced, called nodes. If the unknown functions are represented by a linear combination of polynomic functions within each interval, the system of differential equations is transformed into a system of algebraic equations where the unknowns are the values of the functions at the nodes of the grid. The problem is solved on each element to obtain the solution in each node.

2.1 Application of the Finite Element Method to the formulation of the processes taking place in a DGT device deployed in a system with a metal ion and a ligand.

To reduce the complexity of the description, let's consider the simplest case which involve a solution of a metal ion (M) that reacts with a ligand (L) to produce a complex (ML).

$$\mathrm{M} + \mathrm{L} \leftrightharpoons \mathrm{ML} \tag{6}$$

Let us start writing the set of continuity equations that describes the simplest complexation scheme

$$\frac{\partial c_{\mathrm{M}}}{\partial t} = D_{\mathrm{M}}^{g} \frac{\partial^2 c_{\mathrm{M}}}{\partial x^2} + k_{\mathrm{d}} c_{\mathrm{ML}} - k_{\mathrm{a}} c_{\mathrm{M}} c_{\mathrm{L}} \qquad for \quad r < x < r + g \tag{7}$$

$$\frac{\partial c_{\mathrm{M}}}{\partial t} = D_{\mathrm{M}}^{r} \frac{\partial^2 c_{\mathrm{M}}}{\partial x^2} + k_{\mathrm{d}} c_{\mathrm{ML}} - k_{\mathrm{a}} c_{\mathrm{M}} c_{\mathrm{L}} - k_{\mathrm{a}_r} c_{\mathrm{M}} c_{\mathrm{R}} + k_{\mathrm{d}_r} c_{\mathrm{MR}} \quad for \quad 0 < x < r \tag{8}$$

$$\frac{\partial c_{L}}{\partial t} = D_{\mathrm{L}} \frac{\partial^2 c_{\mathrm{L}}}{\partial x^2} + k_{\mathrm{d}} c_{\mathrm{ML}} - k_{\mathrm{a}} c_{\mathrm{M}} c_{\mathrm{L}} \tag{9}$$

$$\frac{\partial c_{\mathrm{ML}}}{\partial t} = D_{\mathrm{ML}} \frac{\partial^2 c_{\mathrm{ML}}}{\partial x^2} - k_{\mathrm{d}} c_{\mathrm{ML}} + k_{\mathrm{a}} c_{\mathrm{M}} c_{\mathrm{L}} \tag{10}$$

where r stands for the thickness of the resin disc and g for the thickness of the diffusive disc (see Fig. (1b)). In Eqns. (7-10) k_{a} and k_{d} are the kinetic constants of association and dissociation of the complexation reaction. In Eqn. (8) c_{R} and c_{MR} are the concentration of resin beads and the concentration of metal ions bonded to the resin beads respectively and the sum of both concentrations is defined as c_{TR}. Then, $k_{\mathrm{a_R}}$, $k_{\mathrm{d_R}}$ are the kinetic constants of association and dissociation of the complexation reaction of the metal ion with the resin beads.

In order to solve these equations for a DGT device the corresponding initial and boundary conditions have to be defined. The initial conditions of the concentration functions of each species are defined as

$$c_i(x,0) = 0 \quad for\ \ x < r + g \tag{11}$$

$$c_{\mathrm{R}}(x,0) = c_{\mathrm{TR}} \quad for\ \ x \leq r \tag{12}$$

$$c_i(x,t) = c_i^* \quad for\ \ x \geq r + g \tag{13}$$

At x=r+g Dirichlet boundary conditions are used, since we are assuming that the concentration is instantaneously restored to the bulk value (c_i^*) at the diffusive disc-sample solution interface due to the transport phenomena arising in the solution.

There is null flux for each species at x=0 so that:

$$D_i^r \frac{\partial c_i}{\partial x}_{|x=0} = 0 \tag{14}$$

because there cannot be a transfer of matter outside the DGT. At x=r, there is a change of phases from the diffusive gel to a resin domain. Therefore, conditions of flux continuity and continuity of the concentrations have to be imposed.

$$D_i^r \frac{\partial c_i}{\partial x}_{|x=r^-} = D_i^g \frac{\partial c_i}{\partial x}_{|x=r^+} \tag{15}$$

In Eqn(14) and Eqn(15) D_i^g and D_i^r stand for the diffusion coefficient of the resin and gel layer. Before computing the solution of the set of partial differential equations (7-9), bulk concentrations have to be determined from total concentrations and equilibrium constants. In the simulation, we will assume that total concentrations and equilibrium constants are known.

2.2 Simulation results: inert complexes

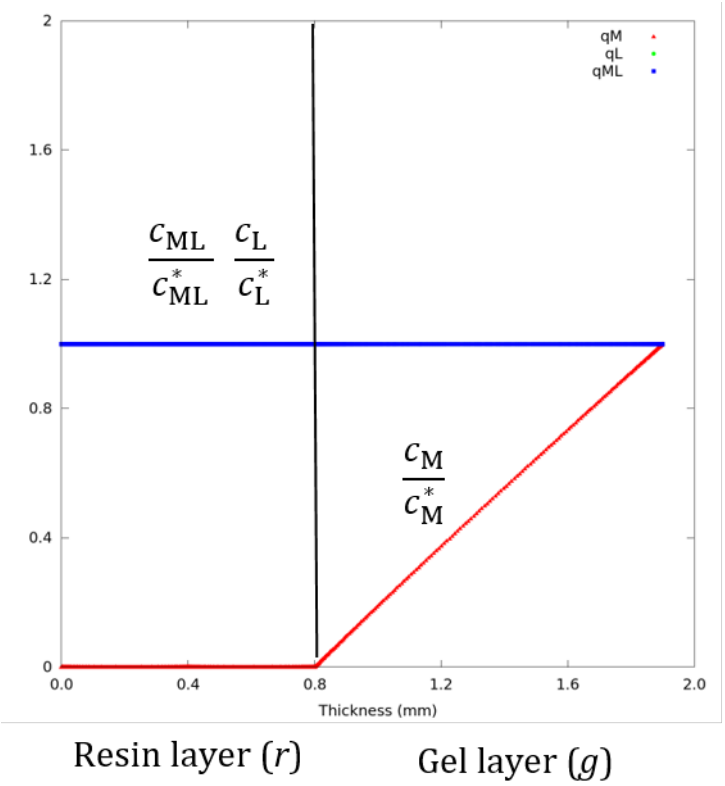


Fig. 2 Normalized concentration profiles $\left(\frac{c_i}{c_i^*}\right)$ in a DGT device in excess of ligand (when $c_L^* > c_M^* + c_{ML}^*$) and quasi-steady state conditions has been obtained with the developed simulation tool. Red triangles stand for normalized free metal (M) concentration, blue dots label the normalized complex concentration (ML) and green dots the normalized ligand concentration (L). $k_a = 10^{-2}\,\frac{m^3}{mol\,s}$, $k_d = 46.9x10^{-8}\,s^{-1}, D_M = 6.08x10^{-10}\,\frac{m^2}{s}$, $D_{ML} = 6.08x10^{-10}\,\frac{m^2}{s}, D_L = 6.08x10^{-10}\,\frac{m^2}{s}$.

As we can see in Fig. (2) An inert complex is simulated by taking very low reaction rates, dissociation of the complex is negligible, although the metal concentration drops to zero at the diffusive gel – resin disc interface. Therefore, the complex is not contributing to the metal flux, which can then be written as

$$J = \frac{D_M c_M^*}{g} \tag{16}$$

2.4 Simulation results: fully labile complexes

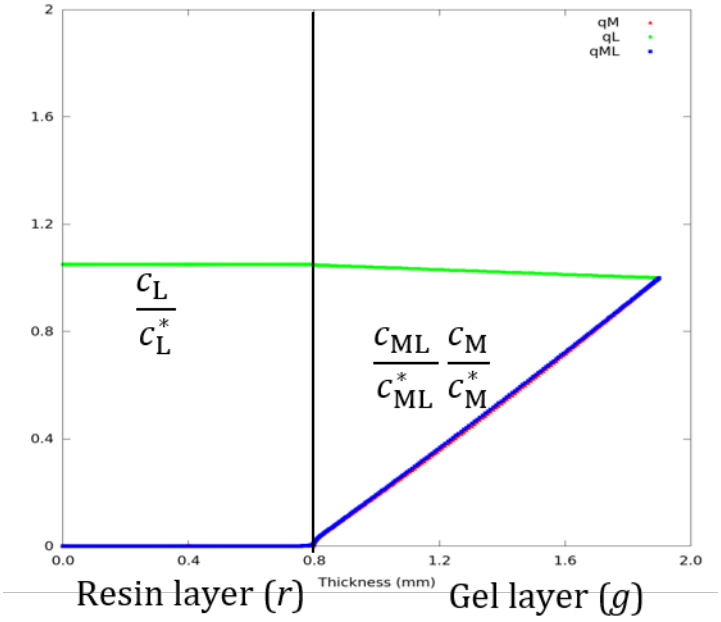


Fig. 3 Normalized concentration profiles (c_i/c_i^*) in a DGT device in excess of ligand and quasi-steady state conditions. Red dots stand for the normalized free metal (M) concentration, blue dots label the normalized complex concentration (ML) and green dots the normalized ligand concentration (L). $k_a = 10^6 \frac{m^3}{mol\ s}$, $k_d = 46.9\ s^{-1}$, $D_M = 6.08x10^{-10}\ \frac{m^2}{s}$, $D_{ML} = 6.08x10^{-10}\ \frac{m^2}{s}$, $D_L = 6.08x10^{-10}\ \frac{m^2}{s}$.

The labile case is achieved with very large k_a and k_d. As seen in Fig. (3), the metal and the complex concentration profiles converge. This indicates that dissociation has proceeded until the complex reaches equilibrium with the metal in all the spatial positions. As both profiles are linear,

$$J = \frac{D_M c_M^*}{g} + \frac{D_{ML} c_{ML}^*}{g} \qquad (17)$$

And this is the maximum flux that can arise in the system, where D_{ML} is the diffusion coefficient of the complex, c_{ML}^* is the bulk concentration of the complex.

2.3 Simulation results: partially labile complexes.

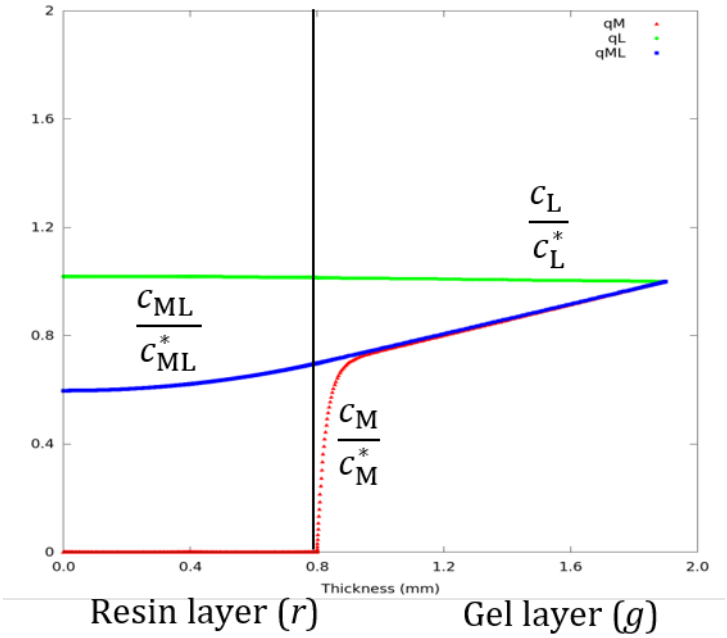


Fig. 4 Normalized concentration profiles (c_i/c_i^*) in a DGT device in excess of ligand and quasi-steady state conditions. Red triangles stand for the normalized free metal (M) concentration, blue dots label the normalized complex concentration (ML) and green dots the normalized ligand concentration (L). $k_a = 10^2 \frac{m^3}{mol\ s}$, $k_d = 46.9x10^{-4}\ s^{-1}$, $D_M = 6.08x10^{-10}\ \frac{m^2}{s}$, $D_{ML} = 6.08x10^{-10}\ \frac{m^2}{s}$, $D_L = 6.08x10^{-10}\ \frac{m^2}{s}$.

As we can see in Fig. (4), there is a partial dissociation of the complex, so that there is a contribution of these species on the metal flux.

For partially labile complexes we can then write the flux as (Galceran et al. 2001)

$$J = \frac{D_M c_M^*}{g} + \frac{D_{ML} c_{ML}^*}{g}\ \xi \qquad (18)$$

where ξ stands for the so called lability degree, which indicates the fraction of the current complex contribution respect to the maximum contribution that could arise if the complex was labile, *i.e.* , if dissociation was fast enough to reach equilibrium with the metal in all spatial positions.

Mixtures

For a mixture system, adding all the diffusion-reaction equations in terms of fluxes, a simple expression for accumulation can be obtained (Altier et al. 2018, Uribe et al. 2013):

$$n = At\left(\frac{D_{\mathrm{M}}c_{\mathrm{M}}^{*}}{g} + \sum_{i=1}^{\mathrm{N}}\frac{D_{\mathrm{ML}}c_{\mathrm{ML}}^{*}}{g}\xi_i\right) \quad (19)$$

where

$$\xi_i = 1 - \frac{C_{\mathrm{ML}}^{r}}{C_{\mathrm{ML}}^{*}} \quad (20)$$

Simulation tools will be developed and used during the Thesis to compute the lability degree of complexes in mixtures and to find approximate analytical expressions for the dependence of the lability degree on the composition of a mixture and on the thickness of the resin and diffusive gel discs.

A comparison of Eqn. (2) with Eqn. (19) gives a simple expression for c_{DGT} in terms of concentration of real species.

$$c_{\mathrm{DGT}} = c_{\mathrm{M}}^{*} + \sum_{\mathrm{i}=1}^{\mathrm{N}}\frac{D_{\mathrm{ML_i}}}{D_M}\frac{c_{\mathrm{ML_i}}^{*}}{\mathrm{g}}\xi_{\mathrm{i}} \quad (21)$$

Different DGT devices with different geometrical dimensions yield several c_{DGT} values of a system and this information can be used to determine concentrations, mobilities or labilities of the species present in the system(Baeyens et al. 2018).

This procedure will be developed in this Thesis to gain knowledge of the natural systems.

3. Work Schedule

Topics	**Time invested**
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 -8months
DGT measurements in mixture model systems and in natural waters.	6 -8 months
Formation courses	2 months
Research Stage	3 Months
Articles and Thesis	7 months

4. References

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