

Supplementary Electronic Information:

Radium analysis by sector field ICP-MS in combination with the diffusive gradient in thin films (DGT) technique

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1. General information about Diffusive Gradients in Thin Films (DGTs)

DGT principles for use in waters

The DGT technique is based on a simple device that accumulates solutes on a binding agent (a resin immobilised in a thin layer of hydrogel) after passage through a hydrogel, which acts as a well defined diffusion layer of thickness Δg . Between the diffusive gel and the bulk solution there is a diffusive boundary layer (DBL), of thickness δ where transport of ions is solely by molecular diffusion. Within a few minutes of immersion, a steady state linear concentration gradient is established between the solution and the resin gel. By exploiting this simple steady state condition the DGT technique can be used to measure concentrations in situ. The flux, J ($\text{mol cm}^{-2} \text{s}^{-1}$), of an ion through the gel is given by Fick's first law of diffusion (Equation 1), where D is the diffusion coefficient ($\text{cm}^2 \text{s}^{-1}$) and dC/dx (mol cm^{-4}) is the concentration gradient.

$$J = D \, dC/dx \quad (1)$$

In practice the DGT device is deployed for a fixed time, t (s). On retrieval the binding-gel layer is peeled off and the mass of the accumulated ions in this layer is measured. Their mass (M) can be measured for example in the case of radionuclides by direct counting or more commonly, after elution with a known volume, V_e (ml), of solution (1 or 2M HNO_3 in the case of metals bound to Chelex resin) by ICPMS or a similar technique. Knowing M , A (cm^2), the area of the exposed diffusive layer, Δg , the thickness of the diffusive gel layer, t , the deployment time and D , the diffusion coefficient, one can calculate the bulk concentration (C) of the solute:

$$C = (M \, \Delta g) / (D \, t \, A) \quad (2)$$

Principles for use in sediments and soils

The interpretation of DGT measurements is not as straightforward in sediments as in solution. The well mixed conditions that exist in solutions enable the interpretation of DGT measurements as concentrations. Pore waters are not well

mixed and as a result the concentration adjacent to the DGT device may become depleted. The application of DGT in sediments and soils can be subdivided into two types, characterized by different objectives and methodologies. The first one applies to homogeneous systems or bulk deployments. Hence, the objective is to measure directly the flux to the DGT device and interpret it as an effective concentration experienced by the device. The second one applies to heterogeneous systems or high-resolution deployments. Here the more conventional objective is to use *in situ* DGT measurements to provide vertical pore water concentration profiles at very high resolution.

In this paper we will only test our method on bulk deployments. Soils were initially well mixed to ensure homogeneity, placed in a plastic container, and sufficient water is added to ensure saturation. The DGT probe is pushed gently into the soil with enough space between the container wall and the probe. It is also important that no air pockets remain between the probe and the soil, and that the soil does not dry out during the deployment.

The deployment time for direct flux and concentration measurements is usually 1 day. If deployment is significantly extended beyond 1 day, there are risks associated with exhausting the available pool of solute (which reduces the flux to the DGT device), of saturating the resin if the concentration of metal is high, and of changing the redox conditions due to saturation.

Sediments versus solutions

To interpret DGT measurements in homogenized soils or sediments it is instructive to consider two significant differences from the use of DGT in water.

1. Due to the lack of mixing it must be assumed that, in general, pore water concentrations adjacent to the DGT device (C_a) become depleted. The local depletion in pore water concentrations induces remobilisation of solutes from the sediment solid phase. One measures thus not the real pore water concentration but also the amount remobilized from the solid phase.
2. If it is assumed that C_a remains relatively constant during the deployment due to a constant, fully sustained, resupply from the solid phase, the theory developed for solution can be adapted to deployments in sediments, using the interfacial pore water concentration between the DGT device and sediment, C_a , rather than the bulk solute concentration. The larger the remobilization flux, the closer C_a to the initial bulk pore water concentration.

2. Preparation of the Diffusive Gradients in Thin Films (DGTs)

1) diffusive gel ($\Delta g = 0.8$ mm)

To 10 ml gel solution (15% acrylamide and 0.3% DGT cross-linker from DGT Research Ltd, Lancaster) 70 μ l 10% ammoniumpersulfate solution and 25 μ l N,N,N,N-tetraethylenediamine (TEMED) are added. The solution is mixed and cast between two glass plates (dimensions are 20cm x 10cm x 0.4cm (thickness)) with a 0.5 mm spacer separating the plates. The assembly is

placed in an oven at 45°C for 1h. When the gel is completely set, it is removed from the plates and hydrated in deionized water for one day and then stored in 0.01M NaNO₃.

2) resin gels ($\Delta g=0.4$ mm)

To 10 ml gel solution (15% acrylamide, 0.3% DGT cross-linker) initially about 3 g Chelex 100 resin and 0.75 g MnO₂, Ln or Actinide resin is added and mixed well. The optimal amount has to be determined for each resin in order to obtain a uniform distribution of the resin on the gel. Then 50 µl 10% ammoniumpersulfate solution and 15 µl N,N,N,N-tetraethylenediamine (TEMED) is added. The solution is mixed and cast between two glass plates with a 0.25 mm spacer separating the plates. The assembly is placed in an oven at 45°C for 1h, and then hydrated in deionized water for at least one day until use.

3) Assembling DGT units for solution deployment

Gels are cut into 2.5 cm circles with a plexi-glass gel cutter. The resin gel is mounted on the moulding base with the resin side face up. Then the diffusive gel is placed on top of the resin gel and covered by a Millipore Durapore membrane filter (HVLP). The cap is then placed on the moulding and pressed down to the bottom of the base.