

DGT – for measurements in waters, soils and sediments

What is it?

DGT stands for diffusive gradients in thin films. Simple, but precision plastic DGT devices accumulate dissolved substances in a controlled way. Conventional analysis in the laboratory provides the in situ concentration at the time of deployment.

Uses?

- ◆ For measuring, trace metals, phosphate, sulphide and radionuclides.
- ◆ Measures average concentrations (hours to weeks) in freshwaters and seawater.
- ◆ Measures both fluxes and concentrations in soils and sediments.
- ◆ Measures effective solution concentrations (bioavailable fraction).
- ◆ Measures at high spatial resolution (microns to centimetres).

Origins?

DGT was invented in Lancaster by Bill Davison and Hao Zhang. The patent filed by Lancaster University in 1993 is granted throughout the World.

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About DGT products

DGT Research Ltd manufactures and supplies DGT products. It supplies two types of products. Complete units are supplied ready for use in soils, sediments and waters. To allow use of DGT for research purposes, separate components are supplied to allow self-assembly of DGT units.

For up to date prices consult the live web pages.

Patents

Patents for DGT applicable worldwide have been granted or are under application.

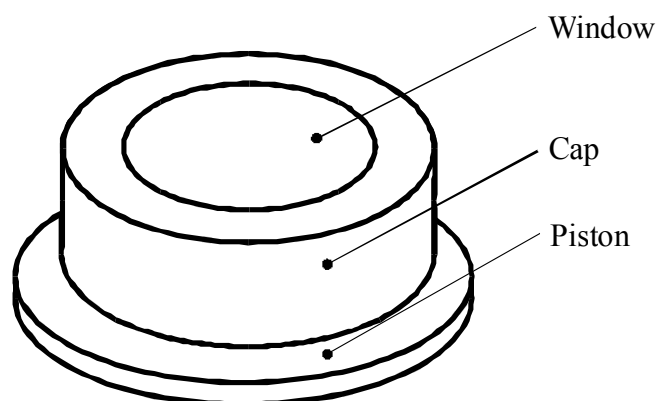
Trademark

DGT™ is a registered trademark in Australia and is under application for the rest of the world.

Products

1. Solution deployment mouldings

A plastic base (2.5 cm diameter) can be loaded with resin gel, diffusive gel and filter and then the plastic top securely push fits over it to leave a 2.0 cm diameter window. The mouldings have been designed to accommodate a 0.4 mm resin gel layer, 0.8 mm diffusive gel layer and 0.135 mm filter. A 0.4 mm thick diffusive layer can be used if a 0.4 mm thick spacer is placed at the back of the resin layer.



2. Gel discs

Pre-cast and hydrated diffusive gels and resin gels are available in disc form (2.5 cm diameter) for solution or soil deployment mouldings. The shelf life is 12 months.

There are six types:

- diffusive gel (open pore);*
- restricted gel (restricted pore for measuring labile inorganic only);*
- Chelex gel (for metals);*
- Fe-oxide gel (for phosphorus);*
- AMP gel (for Cs);*
- AgI gel (for sulphide).*

3. Gel strips

Pre-cast and hydrated diffusive gel strips (about 7 cm x 22 cm, sufficient for 20 gel discs) and resin gel strips are available for DET and DGT sediment probes. Each strip is sufficient for making two sediment probes. The shelf life is 12 months.

There are five types:

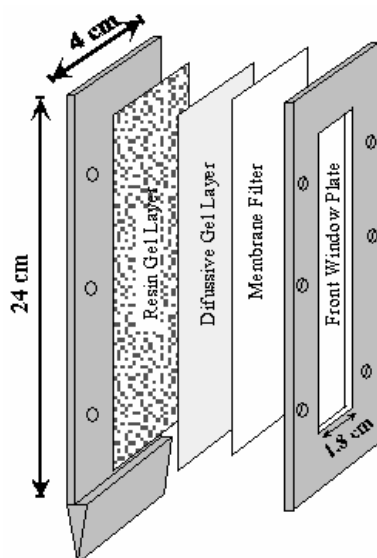
- diffusive gel;*
- Chelex gel (for metals);*
- Fe-oxide gel (for phosphorus);*
- AMP gel (for Cs);*
- AgI gel (for sulphide).*

4. Gel sheets (for diffusive gel only)

Pre-cast and hydrated diffusive gels are available in sheets (13cm x 13cm) for using in Solution Deployment Mouldings. There is sufficient material in each sheet supplied to make about 25 diffusive gel discs. The shelf life is 12 months.

5. Sediment probe

A plastic assembly with an open window of 1.8cm x 15cm is suitable for deploying DGT or DET in sediments. Overall dimensions when loaded are 24 x 4 x 0.5 cm. The holder can accommodate either DET or DGT gel systems.



6. Constrained sediment probe

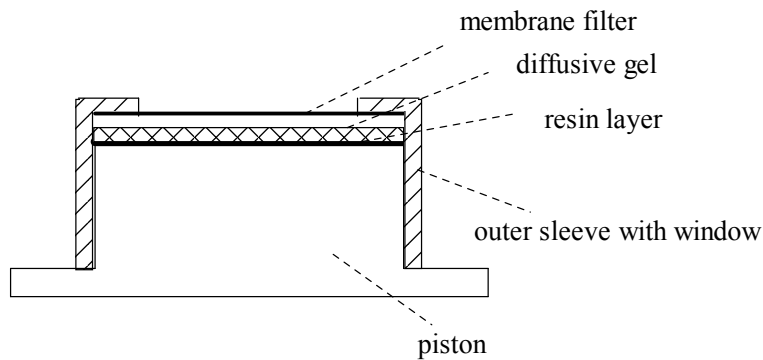
A plastic assembly with slits (0.1cm x 0.1cm x 1.8cm) on a base plate and an open window of 1.8cm x 15cm is designed for sampling major anions, cations and metals with high concentrations (such as Fe and Mn) in pore waters using the DET technique. The slits can be filled with agarose gel which is dimensionally stable during deployment.

7. Loaded sediment probes

The sediment probe can be supplied pre-loaded with DGT (containing both diffusive gel and Chelex or Fe-oxide gel, as shown in figure below) or DET (with diffusive gel only) gels. The shelf life is at least 6 months.

8. Loaded solution deployment mouldings

The solution deployment mouldings can be supplied pre-loaded with DGT gels. The shelf life is at least 6 months.



9. Soil deployment mouldings

These are a redesigned version of the solution deployment moulding that have been designed to work well when pressed directly onto the surface of a wet soil. They can be supplied to fit three different thicknesses of diffusive gel:

0.8mm (standard thickness that is supplied as default if not specified)

0.4mm

2.0mm

(Note: these mouldings can be used for deployment in solution if required. Their surface area (2.54cm^2) is less that of the standard solution mouldings (3.14cm^2))

10. Loaded soil deployment mouldings.

The soil deployment moulding can be supplied pre-loaded with DGT gels. They can be supplied with five different thicknesses of diffusive gel:

0.8mm (standard thickness that is supplied as default if not specified)

0.4mm

1.2mm

1.6mm

2.00mm

(Note: these mouldings can be used for deployment in solution if required. Their surface area (2.54cm^2) is less that of the standard solution mouldings (3.14cm^2))

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What can DGT do?

DGT can be used for many different purposes, including:

- ◆ In situ measurements
- ◆ Monitoring (time averaged concentrations)
- ◆ Speciation (labile inorganic and/or organic species)
- ◆ Bioavailability (effective concentration)
- ◆ Fluxes in sediments and soils
- ◆ Kinetic and thermodynamic constants
- ◆ High spatial resolution measurements (sub-mm)
- ◆ 2D concentration images.

Its capabilities depend on the medium, how it is deployed and the question being asked. Outlines of its capabilities in waters, sediments and soils are provided.

Section

Waters

Sediments

Soils

Capabilities of DGT in Waters

How does it work?

The simple device uses a layer of Chelex resin impregnated in a hydrogel to accumulate the metals. The resin-layer is overlain by a diffusive layer of hydrogel and a filter. Ions have to diffuse through the filter and diffusive layer to reach the resin layer. It is the establishment of a constant concentration gradient in the diffusive layer that forms the basis for measuring metal concentrations in solution quantitatively without the need for separate calibration.

How is it used?

The simple plastic DGT device is deployed for a known time and then the mass of metal on the resin layer is measured after elution with acid by, for example, AAS or ICP-MS. Providing the temperature is known, the concentration in solution can be calculated precisely. DGT devices have usually been deployed by simply suspending them from a rope or string.

What can it measure in water?

When deployed in water DGT measures labile species (Zhang and Davison, 1995). Above a low threshold value, the measurement is independent of solution flow. DGT has been deployed in situ in rivers, lakes, estuaries and the deep sea. Its in-built pre-concentration gives it excellent sensitivity (10^{-12} moles/litre) and avoids contamination problems. For these solution applications a simple, small (1.5 cm deep, 4.0 cm diameter) plastic moulding is used to house the gel layers and filter. Parallel deployment of two DGT units of different diffusive layer thickness allows accurate measurement under low flow conditions. DGT provides time-averaged concentrations that are ideal for regulatory monitoring.

It will measure all those species that are in labile equilibrium with the species that can bind to the binding agent. For example Cu^{2+} binds to Chelex resin. In a natural water Cu exists as inorganic species (eg CuOH^+ and CuCO_3) and as organic complexes that can dissociate quickly (labile) or slowly (inert). DGT measures all the inorganic species and the labile organic species. These are the forms that can be bioavailable.

By using different types of gel for the diffusive layer the inorganic species in solution can be measured separately from the organic species (Zhang and Davison, 2000, 2001). Free ion activities can then be calculated.

In situ?

As DGT can be configured as a simple, robust plastic device, it is readily deployed in situ. The discrimination between species occurs in situ, as DGT accumulates metals. The analysis of the separated species is performed under well-controlled laboratory conditions.

What is the relevance to water quality regulations?

Currently total or total dissolved metals are measured. Ideally we should measure those metal species that are available to organisms. Uptake of trace metals across living

membranes is determined by free ion concentrations when membrane transport is slow and by the total concentration of labile species when membrane transport is fast. Deployment of twin DGT devices with different diffusive gel layers can provide an in situ measurement of both labile inorganic and total labile species. Free ion activities can be calculated from labile inorganic concentrations.

The DGT approach measures directly what is needed to assess water quality for trace metals.

Is biofouling a problem?

It depends on your system and the duration of the deployment. DGT has been deployed for several months (Murdock et al, 2001). Although a film developed on the surface, the device continued to work satisfactorily. It is likely that the flux from solution to the device is sufficiently large that any uptake or release of metals by a biofilm will be negligible. If a biofilm is thick enough to affect significantly the diffusion layer thickness, correction can be made by deploying several devices simultaneously (Davison et al, 2000).

Has DGT been validated?

Yes. DGT has been used since 1993 by several groups of workers who have made comparisons in both laboratory and field and published the results in leading journals (see publications, p42). DGT differs from most other measurements by providing labile metal. The closest technique is anodic stripping voltammetry. Comparative measurements have shown good agreement (Davison and Zhang, 1994, Zhang and Davison, 1995, 2000), especially when the slighter greater time window of DGT is considered. Good agreement with dissolved metals measured by filtration or in situ dialysis is achieved when the natural waters contain low proportions of metals present as colloids or strong complexes (Gimpel et al, 2003).

What substances can be measured?

Any dissolved species for which there is a selective binding agent. For trace metals this includes Al, As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Zn for which data are available (see references). Many more metals are possible, including rare earth elements. Results for calcium, magnesium, phosphate, sulphide and cesium have been published and other inorganic species are under investigation.

Can DGT be used in all natural waters?

Almost. Seawater and most freshwaters are ideal media. There are some data that suggest that there can be problems when making measurements on very dilute solutions with an ionic strength less than 0.2 mmol l^{-1} (Alfaro-De la Torre, 1999; Peters et al., 2003). These would be exceptionally dilute freshwaters and for most freshwaters there are no problems (Denny et al, 1999, Gimpel et al, 2003). The pH range that can be used depends on the measured species and binding agent. Most metals should be measured accurately up to pH 11, above which there are gel stability problems. Note, however, there is likely to be little metal in true solution at pH values between 8 and 11 because of adsorption and solubility considerations. The lower pH limit is determined by the competition between metals and hydrogen ions for the binding agent. Cd binds relatively weakly and can only be measured down to pH 4.5. Cu binds very strongly and can be measured down to pH

2. Other metals usually lie between these extremes (Gimpel et al, 2001). Phosphate can be measured over a wide pH range (2-9).

What concentrations can be measured?

DGT can measure a wide range of concentrations. Use of long deployment times accumulates more metal and lowers the detection limit. For a one day deployment the detection limit for a typical DGT device (0.8mm thick diffusion gel), allowing for substantial dilution (to 1ml) on elution, will be $0.01 \mu\text{g l}^{-1}$ for a detection limit of the final instrumental measurement of $0.1 \mu\text{g l}^{-1}$. By optimizing procedures, DGT detection limits can be several orders of magnitude lower than this. The maximum concentration that can be measured depends on the capacity of the resin. For a 1 day deployment with a typical DGT device it is 0.5mmol l^{-1} . This equates to 30 to 100mg l^{-1} , depending on the metal.

Capabilities of DGT in sediments

How does it work?

The simple device uses a layer of Chelex resin impregnated in a hydrogel to accumulate the metals. The resin-layer is overlain by a diffusive layer of hydrogel and a filter. Ions have to diffuse through the filter and diffusive layer to reach the resin layer. The concentrations of metal ions in the sediment adjacent to the device are lowered. This can induce supply of metal ions from the solid phase to solution in the layers of sediment near to the device. The total metal accumulated during the deployment is measured.

How is it used?

DGT devices fabricated as slim probes can be inserted into the sediment. The simple plastic DGT device is deployed for a known time and then the mass of metal on the resin layer is measured after elution with acid by, for example, AAS or ICP-MS. Providing the temperature is known, the interfacial concentration in solution can be calculated precisely.

What can it measure?

DGT measures directly the *mean flux of labile species* to the device during the deployment. This can be interpreted directly as the *mean concentration of labile metal at the interface* between the device surface and the sediment, during the deployment. For the situation where supply from sediment particles to solution is rapid, this interfacial concentration is the same as the *concentration of metal in bulk pore-water*.

For a given device and deployment time, the interfacial concentration can be related directly to the *effective concentration of labile metal*, C_E (Zhang *et al.*, 2001). C_E represents as a concentration the supply of metal to any sink, be it DGT or an organism, that comes from both diffusion in solution and release from the solid phase.

In-situ?

DGT can be deployed in undisturbed sediments. It will then provide information related to the local structure and heterogeneity. Deployment can be directly by hand on site for shallow systems (Davison *et al.*, 1997). For deep water DGT units can be deployed into retrieved sediment cores (Zhang *et al.*, 1995) or a submersible lander can enable in situ deployment (Fones *et al.*, 2001).

Relevance to sediment quality regulations?

The effective concentration, C_E , measured by DGT has been shown to correlate very well with uptake by biota (Davison *et al.*, 2000, Zhang *et al.*, 2001). DGT mimics the main mechanism of uptake by lowering the concentration locally and inducing diffusive supply and release from the solid phase. Although this is a dynamic measurement that depends on both the rate of transport and the rate of release, it can be used to provide an effective concentration, C_E . C_E is a measure of what the solution concentration would have to be to produce the observed accumulation of metal if there was no supply from the solid phase. C_E may therefore be related through water quality toxicity tests to a quality standard. C_E is

measured directly and simply. It automatically accounts for all sediment properties, including pH and organic matter content.

First published studies?

The first application of DGT in sediments (Zhang et al, 1995) presented the theory, demonstrated that the porewater concentration of metals could be buffered by rapid resupply from the solid phase and showed that trace metals could exhibit substantial structure when measured on a fine (mm) scale. Use of a beam technique (PIXE) that enabled measurements to be made at fine spatial resolution (100 microns) and in two dimensions provided evidence for highly localised point-source microniches of metal remobilization and of metal remobilization at the surface of a microbial mat (Davison et al, 1997). Phosphate was measured using an iron oxide binding agent (Zhang et al, 1998) and sulfide using silver iodide as the binding agent (Teasdale et al, 1999). A numerical model (DIFS) of the DGT device in contact with the sediment was developed and used to extend the theoretical understanding (Harper et al, 1998, 1999, 2000).

Kinetic and thermodynamic constants?

The extent of release of metal from the solid phase depends on the rate constant for transfer from solid to solution and the size of the labile pool of metal in the solid phase. The distribution coefficient, $K_{d\ell}$, for the labile metal can be related directly to the labile solid phase pool size. By deploying DGT for different times in soils where the concentrations of metals in the pore-waters are separately measured, it is possible to provide direct estimates of $K_{d\ell}$ and the re-supply rate constant (Teasdale *et al.*, in preparation). The calculation involves simulation of the diffusive transport regime in the diffusive layer and soil allied to the solid/solution exchange that occurs in the soil. A dynamic, numerical model that does this for saturated soils and sediments has been created and is known as DIFS (DGT induced fluxes in soils) (Harper *et al.*, 1998, 2000). It is freely available for general use on the web (<http://www.es.lancs.ac.uk/wdgroup/aquach.htm>).

High spatial resolution?

DGT probes can be inserted directly into sediments. On retrieval the resin-gel layer can be sliced and metal measured in each slice. Slicing cannot be undertaken at intervals less than 1mm (Zhang *et al.*, 1995, Fones *et al.*, 2001, Zhang et al, 2002). However, even at this spatial resolution detailed structure can be observed. This is partly because the effective volume of soil sampled is very small: only 10 $\mu\ell$. Local variations in concentrations and properties (heterogeneity) are therefore revealed. Measurements have been made at much finer spatial resolution and in two dimensions by measuring the metal in the resin gel by a beam technique (PIXE or laser ablation ICP-MS) (Davison *et al.*, 1997, Fones *et al.*, 2002, Motelica-Heino et al, 2003).

Capabilities of DGT in soils

How does it work?

The simple device uses a layer of Chelex resin impregnated in a hydrogel to accumulate the metals. The resin-layer is overlain by a diffusive layer of hydrogel and a filter. Ions have to diffuse through the filter and diffusive layer to reach the resin layer. The concentrations of metal ions in the soil adjacent to the device are lowered. This can induce supply of metal ions from the solid phase to solution in the layers of soil near to the device. The total metal accumulated during the deployment is measured.

How is it used?

Soils can be mixed into a slurry with a known amount of water. If soils are sufficiently wet (at field capacity) DGT devices can be pressed onto or inserted into the soil. The simple plastic DGT device is deployed for a known time and then the mass of metal on the resin layer is measured after elution with acid by, for example, AAS or ICP-MS. Providing the temperature is known, the interfacial concentration in solution can be calculated precisely.

What can it measure?

DGT measures directly the *mean flux of labile species* to the device during the deployment. This can be interpreted directly as the *mean concentration of labile metal at the interface* between the device surface and the soil, during the deployment. For the situation where supply from soil particles to solution is rapid, this interfacial concentration is the same as the *concentration of metal in bulk pore-water*.

For a given device and deployment time, the interfacial concentration can be related directly to the *effective concentration of labile metal*, C_E (Zhang *et al.*, 2001). C_E represents as a concentration the supply of metal to any sink, be it DGT or a plant, that comes from both diffusion in solution and release from the solid phase.

In-situ?

DGT can be deployed in undisturbed soils. It will then provide information related to the local structure and heterogeneity. For more representative averaged information soils should be mixed. As the soils are not treated with any reagents prior to the measurement, they are undisturbed relative to other procedures.

Relevance to soil quality regulations?

The effective concentration, C_E , measured by DGT has been shown to give a better correlation to plant uptake than any other measurement (Davison *et al.*, 2000, Zhang *et al.*, 2001). DGT mimics the main mechanism of plant uptake by lowering the concentration locally and inducing diffusive supply and release from the solid phase. Although this is a dynamic measurement that depends on both the rate of transport and the rate of release, it can be used to provide an effective concentration, C_E . C_E is a measure of what the solution concentration would have to be to produce the observed accumulation of metal if there was no supply from the solid phase. C_E may therefore be related through water quality toxicity

tests to a quality standard. C_E is measured directly and simply. It automatically accounts for all soil properties, including pH and organic matter content.

First published studies?

The first application of DGT in soils (Zhang *et al.*, 1998) showed that in soils where sludge had been applied, Cd and Zn were present in two separate pools with different kinetic availabilities. A detailed study of deployments of DGT in soils at different moisture contents (Hooda *et al.*, 1999) showed that DGT worked down to 50% of the maximum water holding capacity, but below 80% capacity the increased tortuosity lowered the response. A follow-up study of plant uptake of Cu, Cd, Co, Zn, Pb and Ni at different moisture contents (Davison *et al.*, 2000) showed that the change in plant uptake with moisture content was more closely related to the observed change in DGT uptake than to soil solution concentration. The concept of C_E was introduced by Zhang *et al.*, (2001). They showed that measurements of C_E in a wide range of soils contaminated to various extents with Cu were a very good predictor of Cu uptake by plants.

Kinetic and thermodynamic constants?

The extent of release of metal from the solid phase depends on the rate constant for transfer from solid to solution and the size of the labile pool of metal in the solid phase. The distribution coefficient, $K_{d\ell}$, for the labile metal can be related directly to the labile solid phase pool size. By deploying DGT for different times in soils where the concentrations of metals in the pore-waters are separately measured, it is possible to provide direct estimates of $K_{d\ell}$ and the re-supply rate constant (Ernstberger *et al.*, 2002, 2003). The calculation involves simulation of the diffusive transport regime in the diffusive layer and soil allied to the solid/solution exchange that occurs in the soil. A dynamic, numerical model that does this for saturated soils and sediments has been created and is known as DIFS (DGT induced fluxes in soils) (Harper *et al.*, 1998, 2000). It is freely available for general use on the web (<http://www.es.lancs.ac.uk/wdgroup/aquach.htm>).

High spatial resolution?

DGT probes can be inserted directly into soils. On retrieval the resin-gel layer can be sliced and metal measured in each slice. So far slicing in soils has only been undertaken at 0.5 cm intervals (Zhang *et al.*, Ernstberger *et al.*, in preparation). However, even at this spatial resolution detailed structure can be observed. This is partly because the effective volume of soil sampled is very small: only 50 $\mu\ell$. Local variations in concentrations and properties (heterogeneity) are therefore revealed. In sediments measurements have been made by slicing (Zhang *et al.*, 1995) and at much finer spatial resolution and in two dimensions by measuring the metal in the resin gel by a beam technique (PIXE or laser ablation ICP-MS) (Davison *et al.*, 1997, Fones *et al.*, 2002, Motelica-Heino *et al.*, 2003).

How to use DGT?

Practical guides for assembling, testing and deploying DGT devices have been developed (see this web site). They are not exhaustive. Further details and examples of usage can be found in the individual publications. The review by Davison et al (2000) is particularly useful. See the key papers on measurements in soils for practical details for this medium (Zhang et al, 1998, Hooda et al, 1999, Zhang et al, 2001, Ernstberger et al., 2002). Diffusion coefficients of metal ions for various temperatures in the standard DGT diffusive gel now supplied are provided in a table.

Sections

Practical guide for measuring metals in water
Practical guide for measuring metals in sediments
Practical guide for measuring phosphates
Diffusion coefficients of metal ions

PRACTICAL GUIDE FOR USING DGT UNITS TO MEASURE METALS IN WATER

ASSEMBLING DGT UNITS FROM GELS (strips, sheets or discs)

GEL STORAGE:

- 1) Chelex gels should be stored in MQ or deionised water in a refrigerator (4°C).
- 2) Diffusive gel should be stored in 0.01-0.1M NaNO₃ (or NaCl) at room temperature.
They can be stored under these conditions for about 12 months

CUTTING GEL DISCS:

Discs must be cut to a diameter of 2.5cm. Place the gel on a clean (acid washed) perspex plate. Press the gel cutter directly onto the gel. (The Sterilin tubes containing the supplied gel sheets or strips can be used as a gel cutter).

Useful tricks:

- 1) Gels can be easily handled on a polyethylene sheet with a drop of water. Avoid lifting them, rather tease them out on the surface.
- 2) When the gel disc cutter is used for cutting the resin gel, you need to press and twist the cutter at the same time to ensure a clean cut.

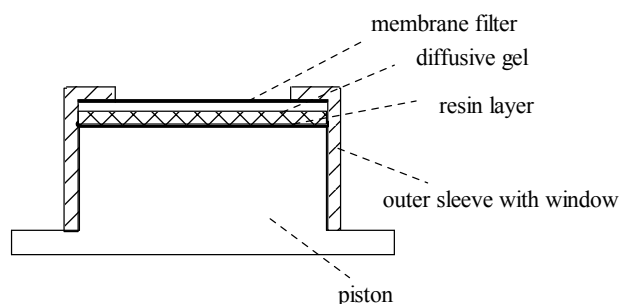


Figure 1. Schematic representation of a section through the DGT assembly.

ASSEMBLING DGT UNITS FOR SOLUTION DEPLOYMENT:

- 1) Wet the filter membrane disc (d=2.5cm) with MQ water (or deionised water).
Note: The filter can be a cellulose nitrate or polysulfone membrane. For field deployments > 24 hours the polysulfone membrane is preferable. The pore size of the filter membrane is 0.45 µm.
- 2) Arrange gels and filter membrane on the moulding base as shown in Figure 1. Place the Chelex gel on the base first and make sure the resin side (see useful tricks below) is face up. Then place the diffusive gel on top of the Chelex gel followed by the filter membrane.
- 3) Carefully put the cap on ensuring it is horizontal. Then apply even force and press it down to the bottom of the base.

Useful tricks:

The Chelex gel was made by settling the resin on one side of the gel. The side with resin is much rougher than the other side. Normally you can see the roughness when you put it on a flat surface. If you find it is difficult to tell, take a piece of clean tissue paper and allow it to touch a small area of the gel to take up the excess water on the surface. You will see the roughness due to resin particles on the resin side.

STORAGE OF DGT UNITS

- 1) Store the units in a refrigerator (4°C). The DGT units provided are kept in the sealed clean plastic bags containing a few drops of 0.01M NaNO₃ solution. Do not open them until immediately prior to deployment.

- 2) Check the units about once a week to make sure they are under moist conditions. Add a few more drops of trace metal clean 0.01M NaNO₃ solution if it is necessary.

If the DGT units are accidentally dried out or over the shelf life (6 months), they need to be revived before deployment.

Procedures for reviving the DGT units:

- 1) Prepare an acid washed plastic box to accommodate the units.
- 2) Prepare 0.01M NaNO₃ solution with MQ water in an acid washed clean container.
- 3) Add Chelex-100 into the above NaNO₃ solution (about 5 to 10 grams into 1 litre) and stir overnight to clean the solution.
- 4) Soak the units in MQ water (use the acid washed plastic box) for 4 to 6 hours.
- 5) Pour the MQ water away and fill the box with the trace metal clean NaNO₃ solution from step (3) (Decant the NaNO₃ solution out carefully from the Chelex-100 beads). Soak the units overnight or 24 hours.
- 6) Deploy the units immediately after they have been revived.

TESTING DGT PERFORMANCE IN YOUR LABORATORY

Experimental Procedures

- 1) Into a 3 L plastic container, mix 2 L of MQ water (or deionised water) and 20 ml of 1M NaNO₃ solution. Spike an appropriate amount of Cd standard solution (or mixed metal standard) to make up a 10 ppb solution (make sure that the pH of the solution is above 5, but less than 7). Now you have created an immersion solution containing 0.01M NaNO₃ with 10 ppb of Cd (or mixed metals). You can also use synthetic lake water or synthetic seawater rather than NaNO₃ solution.
- 2) Place the testing DGT units in the immersion solution. Ensure the plane of the filter is vertical, parallel to the container walls and facing towards the centre of the container (*you need to design a device to fix DGT units in the container*). Note down the time and solution temperature. Make sure the solution is well stirred but not cavitating.
- 3) At the beginning of the experiment take an aliquot of the immersion solution for subsequent analysis.
- 4) After about 4 hours, sample the immersion solution once again for subsequent analysis. Take the DGT units out of the solution and rinse the surface with MQ water.
- 5) Note down the time of retrieval and measure the solution temperature at the end of the experiment.
- 6) The DGT units are designed for disposable use. To retrieve the resin gel after deployment insert a screw driver into the groove in the cap and twist it. The cap will be broken at the weak point and the resin gel can be retrieved.
- 7) Place the Chelex gel in a clean sample tube (*we use 1.5ml micro centrifuge vials*) and add 1ml of 1M HNO₃ solution. Leave it overnight (at least) before analysis. The Cd concentration in the eluent acid should be about 20 ppb if you have followed the above procedures and assuming the test was performed at about 25°C.

Calculating the DGT Measured Concentrations:

- 1) First calculate the mass of metal. The mass of metal in the resin gel (M) can be obtained using equation (1)

$$M = C_e (V_{\text{HNO}_3} + V_{\text{gel}}) / f_e \quad (1)$$

where C_e is the concentration of metals in the 1M HNO₃ elution solution (in µg/l), V_{HNO_3} is the volume of HNO₃ added to the resin gel, V_{gel} is the volume of the resin gel, typically 0.16 ml, and f_e is the elution factor for each metal, typically 0.8.

- 2) The concentration of metal measured by DGT (C_{DGT}) can be calculated using Equation (2).

$$C_{\text{DGT}} = M \Delta g / (D t A) \quad (2)$$

where Δg is the thickness of the diffusive gel (0.8mm) plus the thickness of the filter membrane (0.13 mm), D is the diffusion coefficient of metal in the gel (see Table 1), t is deployment time and A is the exposure area ($A=3.14 \text{ cm}^2$).

- 3) Compare C_{DGT} with the immersion solution concentration analysed in the samples taken during the experiment. If the difference is within 10%, well done. If there is a big discrepancy, run the experiment again.

INSTRUCTIONS FOR DEPLOYING DGT UNITS IN THE FIELD

(Handling, Deployment and Retrieval)

Handling

- 1) Store DGT units in a refrigerator prior to use.
- 2) Do not remove from the sealed plastic bag until immediately (minutes) prior to deployment.
- 3) Only get hold of the DGT unit with clean hands.
- 4) Do not touch the white filter at the face of the unit and do not let it come into contact with anything else.

Deployment

- 1) The DGT unit can be simply suspended by attaching a fishing line to the small hole in the base. Alternatively it can be placed in or attached to any suitable holder. Once removed from its plastic bag, it must be deployed immediately (minutes).
- 2) Ensure the unit is deployed in flowing (or moving) water, but avoid excessive turbulence, particularly bubbles.
- 3) Ensure that the white face of the DGT unit is fully immersed during the whole deployment period.
- 4) Provide an accurate record to the nearest minute of the deployment time and the temperature of the water during deployment. If the variation is within $\pm 2^{\circ}\text{C}$ a mean (or start and end temperature) will suffice. If the variation is greater, ideally the mean temperature should be obtained from an integrated record of temperature (data logger or chart recorder). Although it is not essential, it is sensible to measure the pH of the water.

Retrieval

- 1) On retrieval of any holding assembly, remove the DGT unit immediately (minutes), taking care not to touch the face filter.
- 2) Rinse the DGT unit with a stream of distilled/deionised water from a wash-bottle and shake off obvious surface water (do not dry it).
- 3) Place in a clean plastic bag and seal with minimum air space. Mark the sample details on the bag. Store it in a refrigerator.

PROCEDURES FOR ANALYSING FIELD DGT SAMPLES

Sample Treatment and Analysis

- 1) To retrieve the resin-gel after deployment insert a screw driver into the groove in the cap and twist it. The cap will be broken at the weak point. Remove the broken cap and then peel off the filter and diffusive gel layer to reveal the bottom resin-gel layer.
- 2) Place the resin gel in a clean sample tube and add at least 0.6 ml of 1M HNO_3 solution (if 1.5 ml centrifuge tubes are used). Make sure the resin gel is fully immersed in the HNO_3 solution. Leave it 24 hours at least before analysis.
- 3) Pipette an aliquot from the sample tube and dilute it at least 5 times with Milli-Q (or deionised water) prior to analysis by AAS or ICP-MS.

Calculation of the DGT Measured Concentration

- 1) First calculate the mass of metal accumulated in the resin gel layer (M) using equation (1)

$$M = C_e (V_{\text{HNO}_3} + V_{\text{gel}}) / f_e \quad (1)$$

where C_e is the concentration of metals in the 1M HNO_3 elution solution (in $\mu\text{g/l}$), V_{HNO_3} is the volume of HNO_3 added to the resin gel, V_{gel} is the volume of the resin gel, typically 0.15 ml, and f_e is the elution factor for each metal, typically 0.8.

- 2) The concentration of metal measured by DGT (C_{DGT}) can be calculated using Equation (2).

$$C_{DGT} = M\Delta g / (DtA) \quad (2)$$

where Δg is the thickness of the diffusive gel (0.8mm) plus the thickness of the filter membrane (typically 0.14 mm), D is the diffusion coefficient of metal in the gel (see Table 1), t is deployment time and A is exposure area ($A=3.14 \text{ cm}^2$).

PRACTICAL GUIDE TO ASSEMBLING & USING DGT SEDIMENT PROBES

GEL STORAGE:

- 1) Chelex gels should be stored in MQ or deionised water in a refrigerator (4°C).
 - 2) Fe-oxide gels (for phosphate) should be stored in MQ or deionised water at room temperature.
 - 3) AgI gels (for sulphide) should be stored in MQ or deionised water at room temperature.
 - 4) Diffusive gels should be stored in 0.01-0.1M NaCl at room temperature.
- They can be stored under these conditions for about 12 months*

CUTTING THE GEL:

Place the gel on a clean (acid washed) perspex plate. Press the gel cutter directly onto the gel.

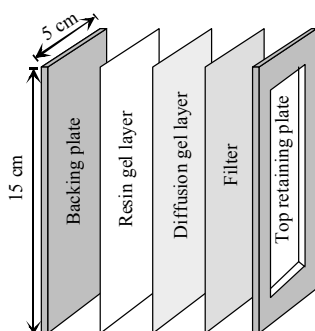


Figure 1. Schematic representation of a section through the DGT assembly.

ASSEMBLY OF DGT SEDIMENT PROBE (see Figure 1):

- 1) Cut the filter membranes (*cellulose nitrate or polysulfone membrane*) to appropriate size (2.7cm x 16.1cm if you use the probe provided by DGT Research Ltd) using scissors/razor/knife. Wet the filter membranes with MQ water or deionised water.
- 2) Lay the Chelex gel strip on a clean Perspex plate with the resin side facing down. Carefully put the filter membrane on top of the Chelex gel strip. They will stick together automatically.
- 3) Cut the gel around the filter membrane using a gel cutter such as a Teflon coated razor blade.
- 4) Pick them up gently and place them on to the base plate of the probe with the filter membrane at the bottom. The resin side is facing up now.
- 5) Place a strip of diffusive gel on top of the Chelex gel and follow it by another piece of filter membrane (wet).
- 6) Put the window plate on top of the assembly and press them together gently.

Useful tricks:

The Chelex gel was made by settling the resin on one side of the gel. The side with resin is much rougher than the other side. Normally you can see the roughness when you put it on a flat surface. If you find it is difficult to tell, take a piece of clean tissue paper and dip it on a small area of the gel to take up the excess water on the surface. You will see the roughness due to resin particles on the resin side.

For Fe-oxide gels, both sides can be used. The Fe-oxide gel is very fragile and more difficult to handle. Avoid lifting them, rather tease them out on the surface.

DGT PROBE STORAGE:

Keep the probes in a clean plastic bag with a few drops of 0.01M NaCl solution and seal the bag properly. Store the probes in a refrigerator.

- 1) Check the probes once a week to make sure they are under moist conditions. If they have dried out, use the following revival procedures.

PROCEDURES FOR DEOXYGENATING THE PROBE:

- 1) Prepare an acid washed plastic bottle (1 L, wide neck) to accommodate the probe and plastic tubing for introducing gas.
- 2) Prepare 0.01M NaCl solution and add 5 to 10 grams Chelex-100 into the solution and stir it overnight. Alternatively purchase extra clean NaCl.
- 3) Fill the acid washed bottle with the trace metal clean 0.01M NaCl solution from step (2) and immerse the probe in the solution. Bubble nitrogen or argon gas moderately through the solution for 24 hours. Make sure the bottle is capped while it is bubbling or carry out the degassing in a glove bag.
- 4) Deploy the probe immediately after degassing.

Note:

A DGT solution monitoring unit should be introduced together with the probe during degassing for use as a BLANK/CONTROL.

PROCEDURE FOR DEPLOYING THE PROBE INTO SEDIMENT (Box or Core):

- 1) If necessary, use an extension for the probe handle (such as plastic paper binder).
- 2) Make a mark (a fine line) on the side at 1 to 2 cm below the top of the window.
- 3) Push the probe gently and smoothly into the sediment until the mark is in line with the sediment/water interface. Keep the probe as vertical as possible during the insertion.
- 4) Note down the temperature and deployment time.

Notes:

- (i) *It is advisable to carry out step 1) and 2) before degassing the probe.*
- (ii) *Always wear clean gloves when handling the probe to avoid contamination.*

PROCEDURE FOR RETRIEVAL:

- 1) Pull the probe out and rinse the surface with MQ water. Make sure there are no particles left on the surface of the probe, especially the window area.
- 2) Put the probe in a cleaned plastic bag and keep it in a refrigerator.

PROCEDURE FOR SLICING:

- 1) Make a cut at the sediment/water interface mark using a Teflon coated blade.
- 2) Cut the gels and the filter membranes along the window edges without disassembling the probe.
- 3) Carefully lift the gels together with the filter membranes out of the window and lay them on a clean flat surface. Peel the top filter membrane and the diffusive gel off and leave the resin gel on the bottom filter membrane.
- 4) Cut the resin gel at the resolution required (no less than 1 mm).
- 5) Put each gel sliver into a micro centrifuge tube (0.5ml) and add 200µl to 300µl 1M HNO₃ solution, ensuring that the gel slivers are fully immersed. Leave them for at least 24 hours before analysis.

Note: Rather than slicing, the resin gel can be dried onto a filter membrane using a gel dryer. It can then be analysed using PIXE or ICPMS-laser ablation at the required resolution.

PRACTICAL GUIDE FOR USING DGT IN SOILS

STORAGE

- 1) Store the units in a refrigerator (4°C). The DGT units provided should be kept in the sealed clean plastic bags containing a few drops of 0.01M NaNO₃ solution. Do not open them until immediately prior to deployment.
- 2) Check the units about once a week to make sure they are under moist conditions. Add a few more drops of trace metal clean 0.01M NaNO₃ solution if it is necessary.

DGT DEPLOYMENT IN SOILS

(Handling, Deployment and Retrieval)

Handling

- 1) Store DGT units in a refrigerator prior to use.
- 2) Do not remove from the sealed plastic bag until immediately (minutes) prior to deployment.
- 3) Only get hold of the DGT unit with clean hands.
- 4) Do not touch the white filter at the face of the unit and do not let it come into contact with anything else.

Deployment

- 1) Wet the soils to 100% field capacity and mix the soil well to make a smooth paste or slurry.
- 2) Equilibrate the soils for 24 hours.
- 3) Take the DGT unit out the plastic bag and rinse it with MQ water. Smear some soil paste gently onto the exposure window (filter membrane) surface of the DGT unit. Press gently onto the soil surface by hand and make sure there is a good contact between the soil and the membrane of the DGT unit.
- 5) Record, to the nearest minute, the deployment time and the temperature of the environment during deployment. If the variation is within $\pm 2^{\circ}\text{C}$ a mean will suffice.

Retrieval

- 1) On retrieval, remove the DGT unit immediately (minutes) and avoid touching the exposure window.
- 2) Rinse the DGT unit with a stream of MQ water from a wash bottle and remove any obvious surface water by gently blotting with a clean tissue paper.
- 3) If the soil paste is very sticky, and it is difficult to clean the DGT unit with MQ water, simply wipe the unit with clean tissue paper to get ride of most of the soil.
- 4) Perform "Sample Treatment" immediately.

Sample Treatment

- 1) To retrieve the resin gel after deployment insert a screw driver into the groove in the cap and twist it. The cap will be broken at the weak point. Remove the broken cap and then peel off the filter and diffusive gel layer to reveal the bottom resin-gel layer.
- 2) Place the resin gel in a clean sample tube and add at least 0.6 ml of 1M HNO₃ solution (if 1.5 ml centrifuge tubes are used). Make sure the resin gel is fully immersed in the HNO₃ solution. Leave it for at least 24 hours before analysis.

PROCEDURES FOR ANALYSING DGT SAMPLES

Sample Analysis

Pipette an aliquot from the sample tube and dilute it at least 5 times with MQ (or deionised water) prior to analysis by AAS or ICP-MS.

Calculation of the DGT Measured Fluxes or Concentrations at the Interface of DGT and Soil

- 1) First calculate the mass of metal accumulated in the resin gel layer (M) using equation (1)
$$M = C_e (V_{\text{HNO}_3} + V_{\text{gel}}) / f_e \quad (1)$$

where C_e is the concentration of metals in the 1M HNO_3 elution solution (in $\mu\text{g/l}$), V_{HNO_3} is the volume of HNO_3 added to the resin gel, V_{gel} is the volume of the resin gel, typically 0.15 ml, and f_e is the elution factor for each metal, typically 0.8.

- 2) The flux of metal measured by DGT (F) can be calculated using Equation (2)

$$F = M/(tA) \quad (2)$$

- 3) The concentration of metal measured by DGT (C_{DGT}) at the interface of the DGT unit and soil can be calculated using Equation (3).

$$C_{\text{DGT}} = F\Delta g/D \quad (3)$$

where Δg is the thickness of the diffusive gel (0.8mm) plus the thickness of the filter membrane (0.14 mm), D is the diffusion coefficient of metal in the gel (see Table 1), t is deployment time and A is the exposure area ($A=3.14 \text{ cm}^2$).

Note: Procedures for calculating the effective solution concentration, C_E , and kinetic parameters will be available later

PRACTICAL GUIDE TO USING DGT FOR MEASURING PHOSPHATE IN WATERS

GEL STORAGE:

- 1) Fe-oxide gels (for phosphate) should be stored in MQ or deionised water at room temperature.
- 2) Diffusive gels should be stored in 0.01-0.1M NaNO₃ (or NaCl) at room temperature.
They can be stored under these conditions for about 12 months

TO CUT THE GEL:

Place the gel on a clean perspex plate. Press the gel cutter directly onto the gel.

Useful tricks:

- 1) Gels can be easily handled on a polyethylene sheet with a drop of water. Avoid lifting them, rather tease them out on the surface.
- 2) When the gel disc cutter is used for cutting the Fe-oxide gel, you need to press and twist the cutter at the same time to ensure a clean cut.

TO ASSEMBLE DGT UNITS FOR SOLUTION DEPLOYMENT:

- 1) Cut the gel to the correct size (d=2.5cm) using a disc gel cutter and wet the filter membrane disc (d=2.5cm) with MQ water (or deionised water).
Note: The filter can be a cellulose nitrate or polysulfone membrane. For field deployments > 24 hours the polysulfone membrane is preferable. The pore size of the filter membrane is 0.45 μm.
- 2) Arrange gels and filter membrane on the moulding base as shown in Figure 1. Place the Fe-oxide gel on the base first. Then place the diffusive gel on top of the Fe-oxide gel followed by the filter membrane. Make sure there are no air bubbles trapped between layers.
- 3) Carefully put the cap on ensuring it is horizontal. Then apply even force and press it down to the bottom of the base.

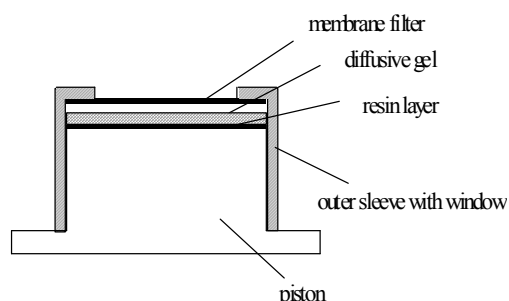


Figure 1. Schematic representations of a section through the DGT assembly.

TESTING DGT PERFORMANCE IN YOUR LABORATORY

Experimental Procedures

- 1) Into a 3 L plastic container, mix 2 L of MQ water (or deionised water) and 4 ml of 100 ppm P (KH₂PO₄) solution to make up a 200 ppb immersion solution. Stir for at least one hour before DGT deployment.
- 2) Place the DGT units under test in the immersion solution. Ensure the plane of the filter is vertical, parallel to the container walls and facing towards the centre of the container (*you need to design a device to fix DGT units in the container*). Note down the time and solution temperature. Make sure the solution is well stirred, but not cavitating.
- 3) At the beginning of the experiment measure the temperature and take an aliquot of the immersion solution for subsequent analysis.
- 4) After about 4 hours, sample the immersion solution again, for subsequent analysis. Take the DGT units out of the solution and rinse the surface with MQ water.
- 5) Note down the time of retrieval and measure the solution temperature at the end of the experiment.

- 6) The DGT units are designed for disposable use. To retrieve the resin-gel after deployment insert a screw driver into the groove in the cap and twist it. The cap will be broken at the weak point and the resin gel can be retrieved.
- 7) Place the Fe-oxide gel in a clean sample tube (*We use 25 ml Sterile tubes supplied from Merck*) and add 10ml of 0.25M H₂SO₄ solution. Before analysis, shake it for at least 2 hours or leave it overnight. The concentration of P in the eluent acid should be about 50 ppb if you have followed the above procedures and assuming the test was performed at about 20°C.

Analysis of P

The phosphate concentration can be determined using a molybdenum blue batch method. Two different mixed reagents have to be used, one for the immersion solution (no H₂SO₄) and the other for the elution solution (contains 0.25M H₂SO₄).

- A) H₂SO₄ (2.5M)
- B) Ammonium molybdate (20g into 500ml water)
- C) Potassium antimonytartrate (0.28g into 100ml water)
- D) Ascorbic acid (1.76g into 100ml water)

Mixed reagent (1) for immersion solution

10ml A + 3ml B + 1ml C + 6 ml D

Add 2 ml of the mixed reagent (1) into 10 ml of sample, wait for 15~20 minutes for colour to develop and then measure.

Mixed reagent (2) for elution solution (contains 0.25M H₂SO₄)

10ml water + 3ml B + 1ml C

Add 1.4ml of reagent (2) into 10ml of elution solution followed by 0.6ml of reagent D (ascorbic acid). Wait for about 15 ~ 20 minutes for colour to develop and then measure.

Calculating the DGT Measured Concentrations:

- 1) First calculate the mass of P in the resin-gel (M) using equation (1)

$$M = C_e (V_{\text{acid}} + V_{\text{gel}}) / f_e \quad (1)$$

where C_e is the concentration of P in the 0.25M H₂SO₄ elution solution (in $\mu\text{g/l}$), V_{acid} is the volume of 0.25M H₂SO₄ added to the Fe-oxide gel, V_{gel} is the volume of the Fe-oxide gel, typically 0.16 ml. f_e is the elution factor for P, which is 1 in this case.

- 2) The concentration of P measured by DGT (C_{DGT}) can be calculated using Equation (2).

$$C_{\text{DGT}} = M \Delta g / (D t A) \quad (2)$$

where Δg is the thickness of the diffusive gel (0.8mm) plus the thickness of the filter membrane (typically 0.13 mm), D is the diffusion coefficient of P in the gel (see Table 1), t is the deployment time and A is the exposure area ($A=3.14 \text{ cm}^2$).

- 3) Compare C_{DGT} with the concentration in the immersion solution obtained by analysis of the samples taken during the experiment. If the difference is within 10%, well done. If there is a big discrepancy, run the experiment again.

Table 1. Diffusion coefficient of H_2PO_4^- in DGT diffusive gel at various temperatures.

Temperature ($^{\circ}\text{C}$)	D ($\text{E}-6 \text{ cm}^2/\text{sec}$)
1	2.82
2	2.93
3	3.04
4	3.15
5	3.27
6	3.38
7	3.50
8	3.62
9	3.75
10	3.87
11	4.00
12	4.13
13	4.27
14	4.40
15	4.54
16	4.68
17	4.82
18	4.97
19	5.12
20	5.27
21	5.42
22	5.57
23	5.73
24	5.89
25	6.05
26	6.21
27	6.38
28	6.55
29	6.72
30	6.89

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April 2003

Table 2. Diffusion coefficients of metal ions in the DGT gel (15% acrylamide & 0.3% cross-linker) at different temperatures from 1 to 35°C

Temp °C	D (E-6 cm ² /sec)										
	Ag	Al	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
1	6.58	2.22	2.84	2.77	2.36	2.91	2.85	2.73	2.69	3.75	2.84
2	6.83	2.30	2.95	2.88	2.45	3.02	2.96	2.83	2.80	3.89	2.94
3	7.09	2.39	3.06	2.99	2.54	3.13	3.07	2.94	2.90	4.04	3.05
4	7.35	2.48	3.18	3.10	2.63	3.25	3.18	3.05	3.01	4.19	3.17
5	7.62	2.57	3.29	3.21	2.73	3.36	3.30	3.16	3.12	4.34	3.28
6	7.89	2.66	3.41	3.32	2.82	3.48	3.42	3.27	3.23	4.49	3.40
7	8.17	2.75	3.53	3.44	2.92	3.61	3.54	3.39	3.34	4.65	3.52
8	8.45	2.85	3.65	3.56	3.02	3.73	3.66	3.50	3.46	4.81	3.64
9	8.74	2.94	3.78	3.68	3.13	3.86	3.79	3.62	3.58	4.98	3.77
10	9.04	3.04	3.90	3.80	3.23	3.99	3.91	3.74	3.70	5.14	3.89
11	9.34	3.14	4.03	3.93	3.34	4.12	4.04	3.87	3.82	5.31	4.02
12	9.64	3.25	4.16	4.06	3.45	4.26	4.18	4.00	3.94	5.49	4.15
13	9.95	3.35	4.30	4.19	3.56	4.39	4.31	4.12	4.07	5.67	4.29
14	10.27	3.46	4.43	4.32	3.67	4.53	4.45	4.26	4.20	5.85	4.42
15	10.59	3.57	4.57	4.46	3.79	4.68	4.59	4.39	4.33	6.03	4.56
16	10.92	3.68	4.72	4.60	3.91	4.82	4.73	4.52	4.47	6.21	4.70
17	11.25	3.79	4.86	4.74	4.03	4.97	4.87	4.66	4.60	6.40	4.85
18	11.59	3.90	5.01	4.88	4.15	5.12	5.02	4.80	4.74	6.60	4.99
19	11.93	4.02	5.15	5.02	4.27	5.27	5.17	4.95	4.88	6.79	5.14
20	12.28	4.14	5.30	5.17	4.39	5.42	5.32	5.09	5.02	6.99	5.29
21	12.64	4.26	5.46	5.32	4.52	5.58	5.47	5.24	5.17	7.19	5.44
22	13.00	4.38	5.61	5.47	4.65	5.74	5.63	5.39	5.32	7.40	5.60
23	13.36	4.50	5.77	5.63	4.78	5.90	5.79	5.54	5.47	7.61	5.76
24	13.73	4.62	5.93	5.78	4.91	6.06	5.95	5.69	5.62	7.82	5.92
25	14.11	4.75	6.09	5.94	5.05	6.23	6.11	5.85	5.77	8.03	6.08
26	14.49	4.88	6.26	6.10	5.19	6.40	6.28	6.01	5.93	8.25	6.24
27	14.88	5.01	6.43	6.27	5.32	6.57	6.45	6.17	6.09	8.47	6.41
28	15.27	5.14	6.60	6.43	5.47	6.74	6.62	6.33	6.25	8.69	6.58
29	15.67	5.28	6.77	6.60	5.61	6.92	6.79	6.50	6.41	8.92	6.75
30	16.08	5.41	6.94	6.77	5.75	7.10	6.96	6.66	6.58	9.15	6.92
31	16.49	5.55	7.12	6.94	5.90	7.28	7.14	6.83	6.74	9.39	7.10
32	16.90	5.69	7.30	7.12	6.05	7.46	7.32	7.00	6.91	9.62	7.28
33	17.32	5.83	7.48	7.29	6.20	7.65	7.50	7.18	7.09	9.86	7.46
34	17.75	5.98	7.67	7.47	6.35	7.84	7.69	7.36	7.26	10.10	7.64
35	18.18	6.12	7.85	7.66	6.51	8.03	7.87	7.53	7.44	10.35	7.83

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How does DGT work?

The simple device uses a layer of binding agent impregnated in a hydrogel to accumulate the solutes. The binding-layer is overlain by a diffusive layer of hydrogel and a filter. Ions have to diffuse through the filter and diffusive layer to reach the resin layer. It is the establishment of a constant concentration gradient in the diffusive layer that forms the basis for measuring metal concentrations in solution quantitatively without the need for separate calibration.

The detailed theory has been developed in several papers, most notably for waters: Zhang and Davison (1995, 2001), Davison et al (2000), Scally et al (2003) and Tusseau-Vuillemin et al (2003), for sediments: Zhang et al (1995), Harper et al (1998, 1999, 2000) and for soils: Zhang et al (1998, 2001) and Harper et al (1998).

The basic theory is given below for use in waters. The theory of operation in sediments is provided: the same theory is taken to apply to saturated soils. A separate section on the principles of bioavailability discusses use of DGT as a surrogate for uptake by biota, using plants as the main example.

Sections

Theory in waters

Theory in sediments and soils

Theory of surrogate for bioavailability

Principles for use in waters

DGT works by automatically accumulating the measured component while the DGT device is deployed in solution. On return to the laboratory the measured component can be released from the device and measured conventionally. DGT is special because it is designed to (a) bind selectively only the substances of interest and (b) accurately control the transport of the substances to the device. These features allow accurate calculation of the concentration in solution during deployment from the laboratory measurement. As this procedure has been well validated by more than 60 publications and 10 PhD theses, no additional calibration is required. Different binding agents with selectivity for different substances can be deployed. Examples to date include Chelex resin for trace metals (Zhang and Davison, 1995), iron oxide for phosphate and arsenic (Zhang et al, 1999, Fitz et al, 2003), ammonium molybdophosphate (AMP) for radioactive cesium (Murdoch et al, 2001) and silver iodide for sulphide (Teasdale et al, 1999). The principles of its use for measurement of solutes in solution are outlined below. Further details can be found in Zhang and Davison (1995) and Davison et al, (2000). The applications in soils and sediments involve additional concepts.

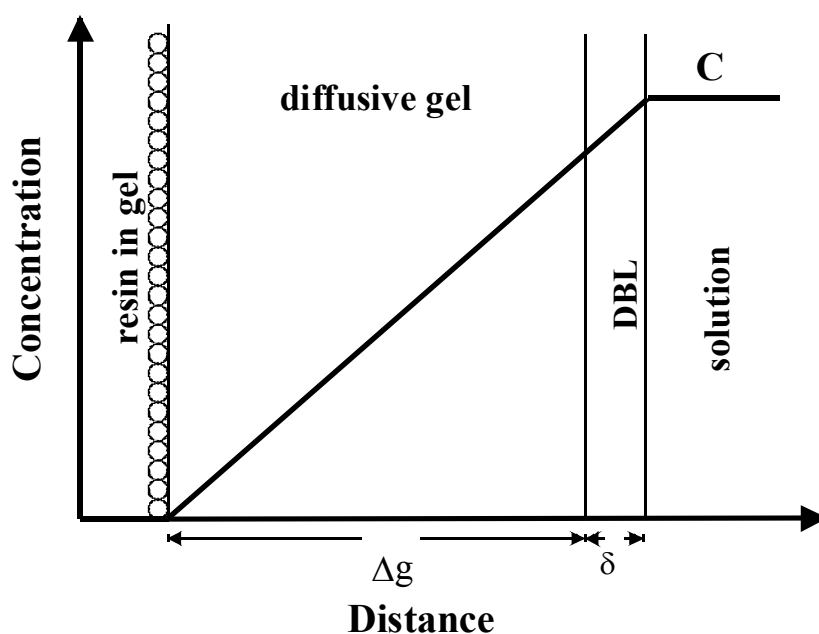


Figure 1 Schematic cross-section through a DGT device in contact with solution, showing the steady-state concentration gradient. The diffusive layer is shown as a single layer of gel, but it can include a gel layer and filter. The thickness of the diffusive boundary layer (DBL) in solution depends on the rate of water movement.

The DGT technique is based on a simple device that accumulates solutes on a binding agent after passage through a hydrogel which acts as a well defined diffusion layer (Figure 1). A binding agent such as a resin, selective to the target ions in solution, is immobilised in a thin layer of hydrogel (binding-gel). It is separated from solution by an ion permeable hydrogel layer (diffusive gel) 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.

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

If diffusion coefficients of ions in the diffusive gel are the same as in water, the flux is given by Equation 2, where C (mol cm^{-3}) is the bulk concentration of an ion and C' is the concentration at the boundary between the binding-gel and the diffusive gel.

$$J = D (C - C') / (\Delta_g + \delta) \quad (2)$$

If the free metal ions are in rapid equilibrium with the binding agent, with a large binding constant, C' is effectively zero, providing the binding agent is not saturated. In well stirred solutions the boundary layer thickness, δ (cm), is negligibly small compared to the thickness of the diffusive layer, Δ_g (cm) of ~ 0.1 cm. Equation (2) then simplifies to Equation (3).

$$J = D C / \Delta_g \quad (3)$$

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. The mass can be measured directly in the binding-gel layer by drying it and using a beam technique such as laser ablation ICP-MS or in the case of radionuclides by direct counting. More commonly, ions in the binding-layer are eluted with a known volume, V_e (ml), of solution (1 or 2M HNO_3 in the case of metals bound to Chelex resin). The concentration of ions in the eluent, C_e , are then measured by any suitable analytical technique after appropriate dilution. As the elution is in batch mode only a fraction of the bound ions are retrieved. The ratio of the eluted to bound metal is known as the elution factor, f_e . Values of f_e of 0.8 have been reported for Zn, Cd, Cu, Ni and Mn and 0.7 for Fe when using 1 or 2 M HNO_3 to elute from Chelex resin. They were obtained by loading a known amount of metal onto a resin-gel by immersing it directly for 24 hours in a stirred solution and measuring metal concentrations before and after immersing. Ideally values of f_e should be measured by each individual research group, especially if conditions such as acid strength are varied. Taking the elution factor into account the accumulated mass (M , moles) of ions in the binding-layer can be calculated from Equation (4) where V_g is the volume of gel (ml) in the binding-layer.

$$M = C_e (V_g + V_e) / f_e \quad (4)$$

M can be used to calculate the flux through the known area of the exposed diffusive layer, A (cm^2) (Equation 5).

$$J = M / At \quad (5)$$

Equating (3) and (5), and rearranging gives, Equation (6) which demonstrates that the concentration in the bulk solution can be calculated from the known values of Δ_g , D (see Table 3) and A , the measured deployment time, t , and accumulated mass, M .

$$C = M\Delta_g / DtA \quad (6)$$

This feature of DGT whereby concentration is calculated from the measured mass and deployment time make it ideal for *in situ* use. The relationship of external concentration to measured mass is determined by the values of Δ_g and A , which are simple, fixed geometric quantities, and the diffusion coefficient in the gel, which can be measured for each temperature. It does not depend on the concentration of other components in the solution and therefore individual calibration in different media is unnecessary.

In practise a filter separates the diffusive gel layer from solution to provide some protection. In most of the work reported to date the DGT devices have used gels and filters which permit free diffusion of ions with diffusion coefficients little different from their values in water. The diffusive boundary layer thickness in solution adjacent to the filter has been negligible due to effective mixing. These conditions facilitate the simple use of equation (6). For the case where the diffusive boundary layer thickness is not negligible and the diffusion coefficients in the gel (D_g), filter (D_f) and water (D_w) are all different, equation (7) applies, where Δ_g and Δ_f are the thicknesses of the gel and filter layers respectively.

$$\frac{1}{M} = \frac{1}{CA t} \left(\frac{\Delta_g}{D_g} + \frac{\Delta_f}{D_f} + \frac{\delta}{D_w} \right) \quad (7)$$

Speciation

The theory underlying the use of DGT for making speciation measurements has been developed considerably (Zhang et al, 2000). DGT distinguishes between species both kinetically (according to their lability) and by size (whether they can pass through the diffusive gel layer). By using different gel compositions Zhang et al (2000) have been able to effectively measure inorganic and organically complexed metal species separately *in situ*. These capabilities offer substantial advances in our ability to make simple measurements for bioavailability and regulatory purposes. Twiss and Moffett (2002) and Odzak et al (2002) have compared DGT to other speciation techniques.

Kinetics

DGT can be used to determine the rates of dissociation of metals from their complexes. Scally et al (2003) developed a simplified theory when determining the

dissociation kinetics of NiNTA complexes, while Tusseau-Vuillemin et al (2003) have presented a fuller theoretical treatment.

Principles in sediments and soils

This section discusses the theoretical background to using DGT in sediments and saturated soils. More details can be found in Davison et al (2000) and Zhang et al (2001). The theory relating to surrogate biological uptake should be accessed from the bioavailability heading (previous page). For simplification the term sediments is usually used to include both media, unless stated otherwise. 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, characterised by different objectives and methodologies:

1. Homogeneous systems (or bulk deployments). The objective is to measure directly the flux to the DGT device and interpret it as an effective concentration experienced by the device. DGT can also be used to investigate quantitatively key sediment processes and properties. This is achieved by combining DGT measurements made at different times or with different gel layer thicknesses in an ideally well mixed sediment, with independent pore water measurements and using a model of sediment-water interactions to fit the results.
2. Heterogeneous systems (or high-resolution deployments). Here the more conventional objective is to use *in situ* DGT measurements to provide vertical (and/or horizontal) pore water concentration profiles at very high resolution.

Methodology

Methodology in homogeneous systems

The piston type DGT assemblies used in solution have also been deployed in well mixed saturated soils (Zhang *et al.*, 1998). Soils were initially well mixed to ensure homogeneity, placed in a plastic container, and sufficient water added to ensure saturation. The DGT device was pushed gently into the soil. The dimensions of the container should be sufficient to ensure that the depletion of the pore water does not progress to the edges of the container (≥ 2 cm between the exposed filter and the container sides will be sufficient for a 24 hour deployment, assuming the worst possible case of supply by diffusion alone). It is also important that no air pockets remain between the device 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. If less than a day, the DGT device may not attain a time invariant response, although if resupply from the solid phase is rapid a pseudo-steady state can be attained within 1 hour. To determine kinetic parameters and solid phase pool sizes a range of deployment times between hours and weeks are used. As soils are well aerated, they can be homogenised quite

simply. Similar homogenisation of sediments would generally be difficult due to their anoxic or sub-oxic conditions.

Methodology in heterogeneous systems

DGT devices must be deoxygenated prior to deployment in most heterogeneous sediments due to the potential presence of anoxic or sub-oxic horizons. During the deoxygenation process, any contamination of the deoxygenated water, particularly by the more ubiquitous trace elements such as zinc and copper, will result in their accumulation by the DGT device, and therefore significant contamination of the resin prior to deployment. Deoxygenation also needs to be carried out in an electrolyte similar to the sampled water (*e.g.* synthetic lake water or synthetic sea water) to ensure the correct diffusional properties for the gel. This is normally incompatible with the objective of minimising contamination. The ideal deoxygenation solution would be a filtered sample of the water in which the DGT assembly is to be deployed with the species to be measured removed (*e.g.* trace metals can be removed by the addition of Chelex resin). Synthetic waters of similar ionic strength that have been rigorously cleaned can also be used.

Principles: homogeneous systems

Sediments vs. solutions

When considering the operation of DGT in sediments it is instructive to review the principles of its use in solutions. The resin layer binds solutes diffusing through the diffusive gel layer, removing them from solution. This sets up a steady state linear concentration gradient through the diffusion layer, and therefore a steady state flux to the resin layer, enabling the calculation of the solute concentration external to the DGT device. This estimation of concentration requires that the solute concentration adjacent to the DGT device remains constant and effectively equal to that in the bulk solution beyond the influence of the DGT device. For *in situ* deployments in natural waters there is a diffusive boundary layer where there is a concentration gradient between the well mixed water and the device. The above condition is satisfied because this diffusive boundary is often negligibly thin. In the pore waters of sediments there are usually no fast mixing processes and therefore the zone of solute depletion adjacent to the device is usually significant. Consequently the principles of using DGT in sediments are quite different from those in solution.

When developing their ideas on how DGT operates in sediments and what it measures, Zhang *et al.* (1998, 1995), and Harper *et al.* (1998) first considered, for simplicity, that the pore water and solid phase concentrations were uniform throughout the sediment. Such a situation has been created by homogenising soils (Hooda *et al.*, 1998; Zhang *et al.*, 1998). Alternatively it might apply to sediments with little heterogeneity and local structure.

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

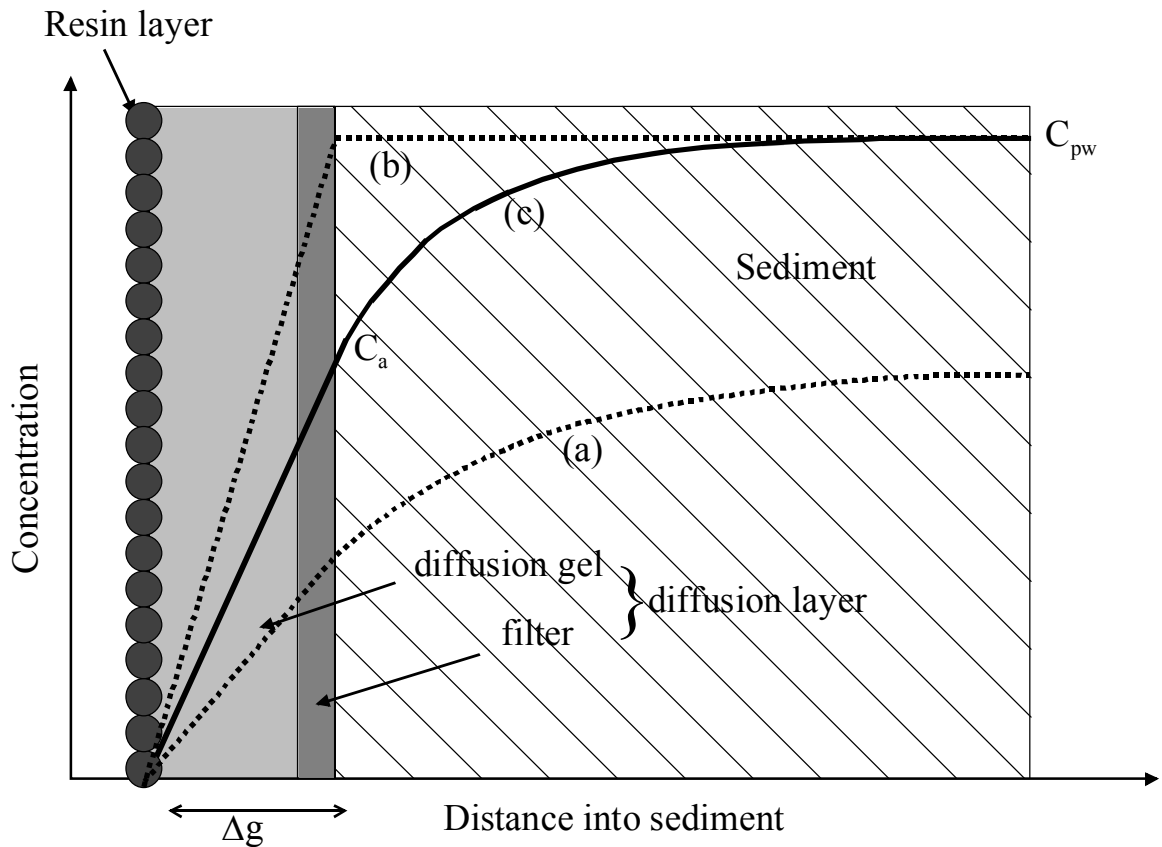


Figure 1. Schematic representation of a cross section through a DGT device in contact with a soil or sediment. Pseudo steady-state concentration gradients are illustrated for three cases: (a) unsustained, (b) sustained and (c) the general or partially sustained case. C_a is the interfacial pore water concentration between the sediment and DGT device.

1. Due to the lack of mixing it must be assumed that, in general, pore water concentrations adjacent to the DGT device become depleted (cases (a) and (c) in Figure 1). If there is no mechanism of supply of solutes other than diffusion, the zone of depletion adjacent to the DGT device becomes progressively larger with time. The flux to the DGT device, which is driven by the concentration gradient through the gel layer, therefore progressively decreases with time. It has been shown (Harper *et al.*, 1998) that in the absence of any resupply of solutes to the pore water, after 24 hours deployment of the standard DGT sediment probe $C_a \approx 0.06C$, where C_a is the interfacial pore water concentration between the sediment and DGT device, and C is the labile pore water concentration in the bulk solution. In practice C_a is usually much greater than this (Zhang and Davison, 1995; Zhang *et al.*, 1998), implying that significant resupply of solutes is occurring. The local depletion in pore water concentrations induces remobilisation of solutes from the sediment solid phase.
2. If it is assumed that C_a remains relatively constant during the deployment due to a constant 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. Assuming steady state throughout the deployment, C_a can

be calculated from the measured DGT mass (Equation 1) by analogy with Equation 3.6. Therefore the concentration measured by DGT, C_{DGT} , is the pore water concentration adjacent to the DGT device, C_a , rather than the bulk pore water concentration, C .

$$C_{DGT} = C_a = \frac{M\Delta g}{DtA} \quad (1)$$

However in practice the steady state condition does not hold throughout deployment (*i.e.* C_a changes with time) and the DGT measured concentration, C_{DGT} , effectively is a time averaged value of C_a . If it is assumed that the flux to the resin layer at any given time is governed by C_a (as for simple solution deployment), then it is more correct to write:

$$C_{DGT} = \frac{1}{t} \int_{t_i=0}^t C_a(t_i) dt \quad (2)$$

where $C_a(t_i)$ is C_a expressed as a function of time and t is the deployment time. In practice C_{DGT} will increase rapidly in the first few minutes as the steady state is established, and possibly decrease gradually after several hours as the capacity of the solid phase to resupply solutes becomes depleted. The initial increase in C_{DGT} has been shown to have negligible effect on the DGT measured concentration when deployments are for greater than 1 hour (Zhang *et al.*, 1995). The greatest difference between C_a and C_{DGT} is in the absence of any solute resupply when, after 24 hours, $C_a = 0.06C$, but $C_{DGT} = 0.1C$ (Harper *et al.*, 1998). Hereafter the term C_{DGT} is used to represent DGT measured concentrations. This is equivalent to the mean interfacial concentration during the deployment time. It can, however, in the great majority of cases where deployment times are restricted to days, be thought of as the interfacial concentration, C_a .

Buffering

The DGT interpreted concentration, C_{DGT} , will be less than or equal to the concentration of labile species in the pore water, C . Where independent measurements of C are available, DGT measurements can be interpreted in terms of the ratio R (Equation 3).

$$R = \frac{C_{DGT}}{C}, \quad 0 < R < 1 \quad (3)$$

R may be obtained experimentally and used to characterise the deployment as one of the three cases described below. These cases are illustrated in Figure 1, which shows a cross section through a DGT device during deployment.

- (a) **Unsustained case ($R = R_{diff}$).** There is no resupply of solutes to the pore water. The DGT device is therefore supplied only by the diffusion of solutes through the pore waters, which become progressively depleted. The exact value of R_{diff} depends on the solute diffusion coefficient in the sediment, the design of the DGT device, and the deployment time. Harper *et al.* (1998) estimated that for a typical sampler design in a high porosity sediment, $R_{diff} = 0.1$ (*i.e.* $C_{DGT} = 0.1C$) for a 24 hour deployment.
- (b) **Sustained Case ($R > 0.95$).** The pore water concentration adjacent to the DGT device is sustained at the bulk pore water concentration throughout the deployment. This can occur if (a) solute mixing rates in the sediment are fast (*e.g.* from tidal pumping, bioirrigation), or (b) the rate of resupply from the solid

phase is fast compared to the rate of removal to the DGT device, and that the capacity of the solid phase to resupply the pore water is large. Efficient pore water mixing will only occur exceptionally in some surficial estuarine and riverine sediments, so the sustained case will normally imply rapid resupply. The DGT measured concentration can be interpreted as the concentration of labile metal species in the pore waters. Note that the theoretical upper limit, of $R = 1$, is never fully achieved as it would require instantaneous resupply from an infinite capacity reservoir adjacent to the DGT device

(c) **Partially Sustained Case ($R_{diff} < R < 1$).** Significant resupply of the solute from the solid phase occurs, but it is insufficient to sustain fully pore water concentrations. The precise value of R is a quantitative measure of the ability of the solid phase to resupply the pore water in response to the depletion induced by the DGT sink.

R values

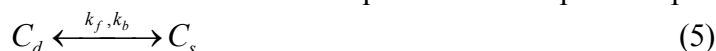
The ratio, R , of DGT measured to bulk concentration depends on a number of factors, including diffusion coefficients, sampler design, and the kinetics and capacity of solid phase resupply. If standardised methodologies and sampler designs are used, R can be interpreted in terms of the capacity of the solid phase to resupply solutes to the pore water and the kinetics of this transfer. This is possible only if simplifying assumptions are made about the interactions of solutes in the pore water with those sorbed to the solid phase. The response of the sediment and DGT device to the latter's deployment can then be modelled. A fuller discussion of the methodology and limitations of this approach is given in Harper *et al.* (1998).

Two studies have interpreted R using such methods. Zhang *et al.* (1998) proposed the relationship

$$R = K_D K_1 \quad (4)$$

where K_D is a distribution coefficient that characterises the partitioning of labile metal between solid phase and pore water, and K_1 is a constant incorporating the resupply rate constant from solid phase to pore water. The former is thus a capacity term, the latter a kinetic term. Note that K_1 will also be dependent on factors such as sampler design, solute diffusion coefficients, and Δg . Equation 4 yields qualitatively useful information when comparing DGT deployments made with the same equipment in similar media (see Zhang *et al.*, 1998).

An extension of this method was developed by Harper *et al.* (1998), based upon a simple model of solute exchange between solid phase and pore water, commonly used in fitting experimental sorption and desorption data (Nyffeler *et al.*, 1984; Jannasch *et al.*, 1998). The DIFS (DGT Induced Fluxes in Sediments or soils) model used by Harper *et al.*, (1998) is available from the web (<http://www.es.lancs.ac.uk/wdgroup/aquach.htm>). The exchange is considered to be a 1st order reversible process between a dissolved phase (pore water concentration, C_d) and a solid phase (sorbed concentration, C_s), described by Equation 5 where k_f and k_b are the rate constants for sorption and desorption respectively.



The modelled response of the DGT device (R) was quantitatively related to K_D and the response time T_c of the (de)sorption process. T_c is defined (Equation 6) as the reciprocal of the sum of k_f and k_b .

$$T_c = \frac{1}{k_f + k_b} \quad (6)$$

Quantitative interpretations based on 1D numerical models require that the deployment conforms as closely as possible to a 1D case. Pore water concentrations adjacent to the DGT assembly are depleted by the DGT device. Close to the edges of the exposure window this depletion may be less than in the centre due to enhanced resupply by diffusion from a greater area of sediment. At the centre, resupply will be essentially one dimensional (1D), at the edges 2D. The distance from the edge of the exposure window over which supply will be 2D will approximately equal the distance, x , to which pore water concentrations are depleted by the DGT device. This has been estimated (Harper *et al.*, 1998) to be $3 \times \Delta g \times (1-R)/R$. For typical DGT assemblies with $\Delta = 0.5$ mm, and $R = 0.3, 0.6,$ and 0.9 , x will be 3.5 mm, 1 mm and 0.17 mm respectively. In order to ensure that 1D interpretations are appropriate, it is advisable to discard an appropriate amount of the resin layer next to the exposure window.

It is important to appreciate that in terms of the interpretations presented above, K_D is based on a reservoir of labile metal associated with the solid phase that is available *in situ*. This may differ from more conventional measurements of K_d (Honeyman and Santschi, 1988).

Pore water concentrations

Although in general the DGT measured concentration, C_{DGT} , is less than the bulk concentration, C , it is possible to estimate C from several DGT measurements using devices with different diffusion layer thicknesses, Δg (Davison et al, 2000).

Principles: heterogeneous systems

By slicing the resin-gel prior to analysis it is relatively easy to use DGT to make measurements of solutes at high vertical resolution. DGT has been most frequently used in sediments to investigate vertical structure. Typically, high resolution (HR) DGT measurements are reported as vertical flux profiles at a resolution of ~ 1 mm, although measurements on the scale of 1 - 5 mm can be classed as HR when compared to conventional techniques, such as dialysis, which sample at cm resolution. It is important to note that the volumetric resolution of DGT measurements is much greater than conventional measurements. DGT usually only affects the sediment within 1 mm of the device. Slicing a 1 cm wide gel at 5 mm intervals therefore represents sediment volumes of 50 μ l. By comparison, slicing a 10 cm diameter core at 5 mm interval would sample a sediment volume of 40 ml. The volumetric resolution of DGT is therefore finer by 3 orders of magnitude. Examples of heterogeneous structure are much more likely to be observed at this high resolution. The interpretation of results in a system that exhibits structure in solute concentrations differs from that in a homogeneous system.

Fine scale structure in sediment pore water concentrations is created by the action of localised sources, such as the release of trace-metals from decomposing organic matter. Persistent concentration gradients are created between these sources and sinks, which could include a well mixed overlying water column, or sorption to a solid phase. As the principal objective in using DGT in HR (or VHR) mode is usually to reproduce fine scale structure in vertical pore water concentration profiles, two aspects of DGT performance are of particular importance: its ability to represent accurately the shape of concentration profiles in the sediment; and its ability to

measure accurately pore water concentrations. These can be termed ‘profile shape fidelity’ and ‘concentration fidelity’ respectively.

Profile Shape Fidelity

Profile shape fidelity refers to the extent to which DGT measured profiles accurately reflect the shape of pore water concentration profiles. Relaxation of the profile shape is caused by the process of *lateral diffusion* within the diffusion layer that has been described previously in the context of DET (Harper et al, 1997). Lateral diffusion occurs in the vicinity of steep concentration gradients. The effect is less in DGT than DET due to immobilisation of the solute by the resin layer. The smallest scale feature measurable using HR DGT depends on the thickness of the diffusion layer. A very sharp peak in pore water concentrations adjacent to the DGT device will spread as it diffuses through the diffusion layer, before being immobilised by the resin. Due to lateral diffusion then, the sharp pore water peak is ultimately represented in the resin layer by a much broader one.

Experimental quantification of the profile shape fidelity at the mm scale is technically very difficult, as it would involve accurate measurement of *in situ* DGT and solute pore water profiles at a μm scale. An alternative approach has been to model numerically the interaction between DGT and sediment (Harper *et al.*, 1998). Although the use of a model inevitably oversimplifies the complexities of DGT-sediment interactions, it can serve to give a useful indication of the reliability of DGT measurements. The profile shape fidelity depends on the thickness of the diffusion layer (Δg), the vertical scale of pore water structures, and the characteristic time of the processes responsible for generating the vertical structure.

Diffusion modelling of a point source adjacent to the DGT device has shown (Harper *et al.*, 1998) that for a typical thickness ($\Delta g = 0.5 \text{ mm}$) the minimum measurable peak width is $\sim 1 \text{ mm}$. Consequently spikes of a single data point in a 1 mm resolution profile may represent real features. This analysis was based on a one dimensional model of pore water structure, in reality diffusion in 3 dimensions may produce much sharper features (Harper et al, 1999).

Concentration Fidelity

As discussed earlier, DGT measured concentration profiles underestimate actual pore water concentrations by a ratio, R , which can vary between ~ 0.1 and 1. One method of estimating pore water concentrations from DGT measurements is to divide the DGT measured concentration, C_{DGT} , by R . This is possible only if independent measurements of pore water concentrations, and therefore R values, are available at several different depths, and if those R values do not vary significantly with depth. While in homogeneous systems, C_{DGT}/R is by definition C (Equation 3), the action of lateral diffusion means that this is not necessarily the case in the presence of vertically structured pore water concentrations. Notwithstanding these limitations, Harper *et al.* (1998) found that the ratio C_{DGT}/R was generally at least 90% of C for peak widths $> 10 \text{ mm}$.

Very High Resolution

Very high resolution (VHR) DGT (Davison *et al.*, 1997, Motelica-Heino *et al.*, 2003) resolves finer scale pore water features than is possible using HR DGT. It also better defines coarser features, which are partially degraded at lower resolution, reproducing gradients more accurately and therefore providing more reliable estimates of vertical fluxes.

Because lateral diffusion within the diffusion layer acts to smooth out fine scale structure it is essential that the thickness of the diffusion layer is minimised. For example, with a diffusion layer of 0.1 mm (*i.e.* comprising just the filter) diffusion modelling suggests (Harper *et al.*, 1998b) that a sharp (10 μm) wide pore water peak ‘relaxes’ by lateral diffusion to become a 0.4 mm wide peak in the resin layer (it would become a 1 mm wide peak with a 0.5 mm diffusion layer). These calculations assume a one dimensional pore water structure. Variability in 2 or 3 dimensions would lead to sharper features in the DGT profile as demonstrated by Harper *et al.*, (1999). The observation of finer scale features is leading to a new understanding of the three dimensional structure of solutes in porewaters sustained by microniches within the solid phase.

Principles for Bioavailability – soils and sediments

The concepts introduced here can be found in more detail in Zhang et al (2001) and Davison et al (2000). The ideas are described for soils, but they apply equally to biota in sediments where the uptake is via a membrane.

Risks associated with heavy metal contamination in soils are difficult to assess. In most ecotoxicological studies, the toxic effects of heavy metals have been related to total soil concentrations or some operationally defined extractable fractions. Although existing legislation or guidelines on heavy metals in soils are also primarily based on total concentrations, they are beginning to recognise that the total metal content of soil embraces large fractions which are unavailable to plants, microorganisms or soil fauna. Extraction of soil solution from soil isolates the aqueous phase to which plant roots and microorganisms are exposed, and there is some evidence that measurements of free ion activities in soil solution provide a better indication of metal availability. However, measurements of metals in soil solution fail to account for the ability of the soil to sustain the solution concentration following depletion by uptake.

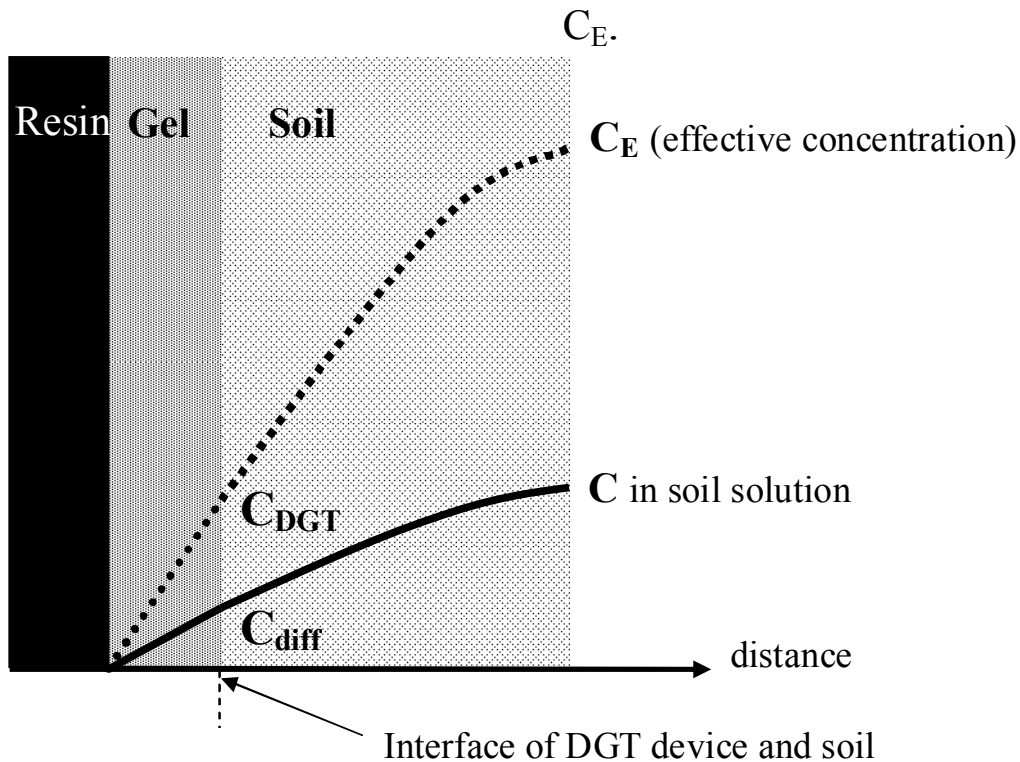
A proportion of metal will only be available from the solid phase if plant uptake is fairly rapid compared to diffusional supply. Then depletion of its concentration in solution in the immediate vicinity of the roots allows transfer from solid phase to solution. For the component associated with the solid phase to contribute to plant uptake, it must be capable of rapid transfer to solution. This solid phase metal is then said to be kinetically labile. Some plants may actively mobilize nutrients, such as Fe, Cu and Zn, from the solid phase under deficiency condition. Under non-deficiency or excess conditions, however, it is soil rather than plant properties that determine what fraction of the metal responds to local depletion. Characterization of these properties may provide an assessment of the potential hazard of a soil contaminated with heavy metals.

The contribution of an element from pools other than soil solution, has been long recognised and led to the concepts of intensity, quantity and capacity. However, the assessment of hazards posed by contaminated soils has been hampered by the lack of simple realistic procedures that assess the rates and extent to which metals can be released from soil particles and supplied to biota. Extraction procedures provide a simple classification of soil metal fractions, but these are based on arbitrary responses to chemical reagents rather than on a true reflection of metal lability. Like plants, DGT locally lowers metal concentrations in the soil solution and responds to metal re-supplied from labile species in solution and the labile metal pool in the solid phase. The measured DGT flux of metals in the soil can be quantitatively related to a new term called the effective concentration, C_E .

Calculation of C_E from DGT measurements.

DGT devices are deployed in a soil for a given period of time during which metal ions accumulate in the resin layer. The mass of accumulated metal, M , is measured. A full numerical model in one and two dimensions of the time dependent interaction of a DGT device of variable geometry with soils or sediments having various properties has been developed and described in detail (*Harper et al. 1998, 2000*). Known as DIFS (DGT induced fluxes in soils and sediments), it is freely available in one-dimensional form, via the internet (<http://www.es.lancs.ac.uk/wdgroup/aquach.htm>). It simultaneously considers, at any

Schematic illustration of how the measured quantity, C_{DGT} , relates to the effective concentration in the soil solution, C_E .



location and point in time, diffusion of metal ions in the soil solution in response to induced concentration gradients. Exchange of metal ions between solid phase and solution is assumed to be governed by first order kinetics. C_{soln} and C_{LP} are the concentrations of metal ions in soil solution and associated with the labile particulate phase respectively. The rate of re-supply, given by $k_{-1}C_{LP}$, clearly depends on both the solid to solution transfer rate constant, k_{-1} and the concentration of labile metal in the solid phase reservoir.

Simulations using DIFS for a typical soil have shown how concentration gradients of a metal through the DGT diffusive layer and the soil solution change with time (Zhang et al, 2001). If there is no resupply of metal from the solid phase the metal concentration at the DGT surface declines appreciably in 24 hours. When there is resupply from the solid phase the concentration does not decline so much. There is effective buffering by the solid phase. Higher values of C_{LP} or k_{-1} provide a better buffer. These representations of concentration profiles extending into solution being buffered to different extents by the solid phase are analogous to those presented in the standard texts treating diffusional supply of nutrients to plants. The idea that a substantial fraction of elements taken up by plants comes from pools other than in solution is long-established. In older literature it was presented as a capacity term. Similarly, that the exchangeable metal can contribute to the effective diffusible transport of metals is well known. When exchangeable metal was measured rather than dissolved concentrations in soil solution, the exchange with the solid phase was regarded as retarding diffusion of the total exchangeable fraction. This is why effective diffusion coefficients that embrace exchangeable metal are lower in soils than solution. By contrast, molecular diffusion coefficients, as used in the DIFS model, refer only to the solution phase and are unaffected by sorption. Indeed

sorption processes enhance the overall flux compared to supply by molecular diffusion alone.

A major advantage of having the diffusive layer in DGT devices is that it simplifies calculations and allows interpretation of the measured mass without resort to numerical simulations. We now show with the aid of the Figure how it is possible to derive an effective concentration, C_E .

If metal is solely supplied from the soil solution it will be depleted near to the surface of the device from its initial concentration, C_{soln} , down to C_{diff} at any deployment time. If the diffusion coefficient in the gel and filter layer is the same, as previously found (*Zhang and Davison, 1999*), at any instant in time after the initial few minutes a pseudo steady state is established and the concentration through the diffusive gel and filter layer is linear, with the flux, F (moles $\text{cm}^{-2} \text{s}^{-1}$), given by Fick's law (equation 2).

$$F = DC_{\text{diff}} / \Delta g \quad (2)$$

D ($\text{cm}^2 \text{s}^{-1}$) is the diffusion coefficient in the diffusive layer of thickness Δg (cm), and C_{diff} (moles cm^{-3}) is the instantaneous concentration at the surface of the device. The mean flux during the DGT deployment can be represented by the same equation, where C_{diff} then represents the mean interfacial concentration (interface between device and soil). The mean flux, F , can also be calculated from the measured accumulated mass of metal, M (moles), the deployment time, t (s), and the exposed area of the gel, A (cm^2) (equation 3).

$$F = M/(At) \quad (3)$$

Consequently the mean interfacial concentration for the diffusion-only case can be calculated directly, using equation (4).

$$C_{\text{diff}} = M\Delta g/(DA t) \quad (4)$$

The ratio of the mean interfacial concentration due to re-supply by diffusion only to the initial or bulk concentration, C_{soln} , can be expressed as R_{diff} .

$$R_{\text{diff}} = C_{\text{diff}}/C_{\text{soln}} \quad (5)$$

R_{diff} is determined by the geometry of the device, deployment time and soil tortuosity. It may be calculated using a numerical solution of the diffusion equations (*Harper et al, 1998*). The local depletion of metal may, however, induce its re-supply from the solid phase. Generally when DGT is deployed, the measured accumulated mass of metal will be greater than in the case of solely diffusional supply due to the contribution from the solid phase. The mean interfacial concentration shown as C_{DGT} in the Figure is then given by equation (6).

$$C_{\text{DGT}} = M\Delta g/(DA t) \quad (6)$$

C_{DGT} reflects supply from both solid phase and solution and is maintained approximately constant, providing the kinetically labile reservoir is not substantially depleted close to the device. In this general case of solid phase and solution resupply, the bulk soil solution concentration, C_{soln} , does not represent the effective concentration that a sink like a DGT device or a plant root experiences. An effective concentration, C_E , is proposed to embrace both soil solution concentration and its enhancement from the solid phase. Just as C_{diff} can be converted to C_{soln} by dividing by R_{diff} , an effective solution concentration, C_E , can be obtained by dividing C_{DGT} by R_{diff} (equation 7).

$$C_E = C_{\text{DGT}}/R_{\text{diff}} \quad (7)$$

Conceptually, C_E is the concentration that would have to be present in the soil solution to supply the same mass of metal accumulated by DGT in case (ii) of the Figure solely by diffusion. Thus the DGT device provides a direct measurement of the effective concentration, C_E . This new concept of an effective concentration that

can be measured is soundly based on our accumulated understanding of diffusional plant uptake processes. If the mechanism of plant uptake also locally lowers soil concentrations, C_E can be expected to relate directly to plant uptake. This situation of transport-limited plant uptake is the worst case, as metal is supplied from both soil solution and the solid phase, which is why C_E provides an assessment of the *potential* hazard for that particular soil.

Validation of theory.

Measurements of Cu as its effective concentration (C_E), its soil solution concentration, by EDTA extraction and as free Cu^{2+} in soil solution were made on 29 different soils covering a large range of copper concentrations (Zhang et al, 2001). They were compared to Cu concentrations in the plant material of *Lepidium heterophyllum* grown on the same soils. Plant concentrations were linearly related and highly correlated with C_E , but were more scattered and non-linear with respect to Cu^{2+} , EDTA extraction or soil solution concentrations. These results demonstrated that the dominant supply processes in these soils were diffusion and labile metal release, which the DGT-soil system mimics. Similar measurements have been performed for different metals, plants and soils (Fitz et al, 2003; Nolan et al, 2003; Zhang et al, 2003). DGT also predicts the dependency of metal uptake by plants on soil moisture content (Davison et al, 2000).

The work showed that insight into the supply of metals from soils can be gained by using DGT as a physical surrogate for plant uptake. DGT only depletes metal in a narrow zone (typically < 1mm) adjacent to the device and so only a small fraction of the solid phase of the soil is involved. Plants can be expected to affect concentrations by diffusive processes over similar distances from root surfaces. The prime difference between DGT and a resin strip is that in DGT a diffusive layer is interposed between the soil and resin layer. This simple device provides a well-defined geometry that allows precise calculation of fluxes and places a limit on the maximum flux. When a resin is exposed directly to a soil, initial fluxes may be massive, as there is no limit other than diffusional control which only regulates progressively with time. Plants never experience such a shock of very high supply. As they progressively grow in a medium they are continually regulated by an established diffusional zone. The thickness of this diffusional zone is similar to the 0.9 mm diffusional layer thickness (gel plus filter) of the DGT devices typically used. Moreover, the membrane transfer rate will have a finite limit, while the chemical uptake rate effective directly at a resin surface is so fast as to be effectively infinite.

The kinetically labile solid phase pool of metal clearly plays an important role in plant uptake and is included in the DGT measurement. DGT offers the possibility of a simple test procedure for soils. The kinetic perturbation of solute concentrations in the soil system is most likely similar to that occurring during plant uptake. The new measure of effective concentrations, C_E , that can be obtained easily using simple DGT devices, may provide a major step forward in assessing hazards posed by metals in contaminated soils.

PUBLICATIONS INVOLVING DGT

It is our policy to update this list annually. We welcome being supplied with new reference or those that we may have overlooked. w.davison@lancaster.ac.uk

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DET – for measurement of solute concentrations

What is it?

DET stands for diffusive equilibration in thin films. A single sheet of gel supported in a holder is inserted into water, sediment or soils. The gel is 95% water. Solutes in the surrounding solution diffuse into the gel until the concentrations in the gel and water are equal. The technique is similar to dialysis, but in DGT the solution is incorporated within the relatively thick gel membrane (typically 0.8mm) rather than being in a separate compartment linked by a membrane to the external solution. Compared to dialysis it has the advantage of relatively fast (within a day) response times and the ability to perform measurements at high spatial resolution.

Uses?

Measurements of solute concentrations at high spatial resolution.

Origins

DET was invented by Bill Davison when he was employed by the Institute of Freshwater Ecology at Windermere (Davison et al, 1991).

Sections

Basic information

Practicalities

Deployment

Basic information on DET

A detailed review of the principles, performance and applications of DET, and its relationship to both DGT and dialysis is provided in a substantial book chapter (Davison et al, 2000). These subjects are touched on very briefly below.

Assemblies

DET is used mainly for sediments. The holders are similar to those used for DGT, comprising a flat probe with an open window. A filter membrane is usually placed on top of the gel sheet for physical protection and to prevent it being contaminated with adhering solid phases. When deployed in sediments, it must be thoroughly deoxygenated prior to insertion.

Measurement

On retrieval the DET gels are usually sliced to the required spatial resolution. The slices of gel are then back equilibrated by inserting them into a small volume of solution. The minimum time depends on the precise volumes used (Harper et al 1997), but is typically a day. Solutes in the resulting eluent are then measured by any appropriate technique. When iron and manganese are fixed with NaOH, an acidic eluent is used (Davison et al, 1994). The first report of DET used a beam technique (PIXE) to measure Fe and Mn in the dried gel (Davison et al, 1991), achieving sub-mm resolution. The more sensitive technique of laser ablation-ICP-MS has been used in recent work (Motelica-Heino and Davison, 2002). A wide sheet of gel has also been sliced into 3mm x 3mm squares to provide a 2 dimensional image of concentrations of Fe and Mn in the pore-waters of sediments (Shuttleworth et al, 1999).

Equilibration times

Harper et al (1997) modelled the equilibration of solutes in DET probes deployed in sediments. The two extreme cases are when there is only diffusive supply from the pore waters or when there is rapid re-supply from solid phase to solution. The main physical factor affecting the equilibration time is gel layer thickness, but the sediment porosity also has an effect. Usually equilibration will be virtually complete in a day, but Davison et al (2000) and Harper et al (1997) should be consulted for details.

Profile fidelity

Several factors (see Harper et al, 1997) contribute to the measured spatial variation in concentration being slightly different from the true in situ variation in concentration. The main one is that diffusion will continue to occur after retrieval of

the device, as demonstrated experimentally (Davison et al, 1994). If left unchecked this will eventually remove all the spatial structure of the solutes. The problem has been overcome in three ways. Firstly, for measuring Fe and Mn, DET probes can be immediately inserted into a NaOH solution. It allows rapid hydrolysis and oxidation of Fe and Mn, fixing them in the solid phase (Davison et al, 1994).

Secondly, the gels may be rapidly sliced (Krom et al, 1994). Thirdly, the probe may comprise a series of individual compartments that can contain separate small volumes of gel so that no re-equilibration can occur (Mortimer et al, 1998). Generally the best spatial resolution obtained by DET with reasonable fidelity is 1mm. However, by using a micro DET assembly with 0.2mm wide compartments, much better resolution was achieved (Fones et al, 1998). A beam technique, in this case PIXE, had to be used to measure the concentration of metal in the gel.

Sensitivity

Rather than solutes being concentrated by DET, they are diluted during elution. This has so far excluded the measurement of trace metals at background levels and limited measurements mainly to Fe, Mn, major cations and anions and nutrients. Trace metals have been measured in a very polluted site (Yu et al, 2000). It is now becoming possible to measure metals at trace levels by using highly sensitive ICP-MS with and without laser ablation (Motelica-Heino and Davison, 2002). The major problem is contamination.

Applications

DET can be used to measure virtually any solute where there is a sensitive technique for analysing very small volumes (see reference list and Davison et al, 2000). It has been used in both freshwater (Davison et al, 1991, Davison et al, 1994, Krom et al, 1994, Fones et al, 1998, Zhang et al, 1999, Shuttleworth et al, 1999) and marine environments (Mortimer et al, 1998, Shuttleworth et al, 1999, Fones et al, 2001, Zhang et al, 2002). Deployment in situ in shallow systems has been by hand insertion (Fones et al, 1998, Shuttleworth et al, 1999). For deep systems, various approaches have included use of divers (Krom et al, 1994), insertion into retrieved sediment cores (Davison et al 1994) and remote deployment with sediment landers (Fones et al, 2001, 2002).

PROCEDURES FOR USING DET SEDIMENT PROBES

DET Probe Storage:

- 1) Keep the probes in a clean plastic bag with a few drops of 0.01M NaCl and seal the bag properly. Store the probes in a refrigerator.
- 2) Check the probes once a week to make sure they are under moist conditions. If they appear to lack moisture add a few more drops of 0.01M NaCl solution.

Procedure for Deoxygenating the Probe:

- 1) Prepare an acid washed plastic bottle (1 L, wide neck) to accommodate the probe and plastic tubing for introducing gas.
- 2) Fill the bottle with clean 0.01M NaCl solution and immerse the probe in the solution. Bubble nitrogen or argon gas moderately through the water for 24 hours. Make sure the bottle is capped while it is bubbling or carry out the degassing in a glove bag.
- 3) Deploy the probe immediately after degassing.

Procedure for Deploying the Probe into Sediment (Box or Core):

- 1) If necessary, fix an extension to the handle.
- 2) Make a mark (a fine line) on the side at 1 to 2 cm below the top of the window.
- 3) Push the probe gently and smoothly into the sediment until the mark is in line with the sediment/water interface. Keep the probe as vertical as possible during the insertion.

Note:

- a) *It is advisable to carry out step 1) and 2) before degassing the probe.*
- b) *Always wear clean gloves when handling the probe to avoid contamination.*
- c) *The deployment time should be at least 2 to 3 days for probes with 0.8mm thick gels.*

Procedure for Retrieval and Fixing

(for Constrained Probes "Fixing" and "Slicing" are not required)

Pull the probe out of the sediment and put it into a fixing solution (10mM NaOH for fixing Fe and Mn) straight away without rinsing the surface. Leave it in the solution for several hours to fix.

Procedure for Slicing:

- 1) Make a cut at the sediment/water interface mark using a Teflon coated blade.
- 2) Cut the gels and the filter membranes along the window edges without disassembling the probe.
- 3) Carefully lift the gels together with the filter membranes out of the window and lay them on a clean flat surface. Peel the top filter membrane off and leave the gel on the bottom filter membrane.
- 4) Cut the gel at the resolution required (no less than 1 mm).
- 5) Put each gel strip into a centrifuge micro tube (0.5ml or 1.5 ml) and add elution solution. Leave it for at least 24 hours before analysis.

Note: *The gel can be dried onto a filter membrane without slicing using gel dryer. It can then be analysed using PIXE or ICPMS - laser ablation at the required resolution.*

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April 2003

PUBLICATIONS INVOLVING DET

It is our policy to update this list annually. We welcome being supplied with new reference or those that we may have overlooked. w.davison@lancaster.ac.uk

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