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1

Introduction to DGT

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1.1 Origins

DGT has its origins in sediment geochemistry. From 1970 to 1990, there were notable advances in the chemistry of sediments as scientists tried to unravel the processes controlling early diagenesis. The seminal works of Aller [1] and other workers on anoxic sediments provided a framework that led to refined models of oxidation of organic material by a series of electron acceptors [2]. Much of the understanding relied on measurements of solutes in porewaters, obtained by squeezing or centrifuging a slice of sediment typically about 1 cm deep and from 3 to 10 cm diameter. An alternative approach of inserting into sediments assemblies of dialysis cells, referred to by Hesslein [3] et al. as peepers, was developed. Solutes were allowed to equilibrate between the porewaters and individual compartments of solution in Perspex blocks, separated from the sediment by a filter membrane. These compartments were quite large, with typically 1 cm × 10 cm windows, resulting in equilibration times of two to three weeks. Inspired by mm-scale measurements of authigenetic solid phases on plastic substrates [4], hydrogels were used for dialysis instead of peepers [5]. In this new technique, which became known as DET (diffusive equilibrium in thin-films) [6], solutes were equilibrated with the non-bound water of the hydrogels. Like the most commonly encountered hydrogels, contact lenses, the DET gels can be easily handled. They can be sliced at the mm scale and the solutes can be back-equilibrated for analysis [7]. Consequently measurements can be made at a much higher spatial resolution than for peepers, and their small scale (∼1-mm thick gel) allows equilibration within days [8].

The idea for the technique of DGT (diffusive equilibration in thin-films), which includes a binding layer to accumulate solutes (Figure 1.1), stemmed from the need to improve the sensitivity of DET, especially for trace metals present in porewaters at very low concentrations. However, the first step in its development was as a solution device for measuring trace metals in seawater [9]. The parallels between DGT and voltammetry were clear at the outset and an analogous theory was developed. It is now recognised that, from a physical chemistry perspective, DGT and voltammetry can both be classed as dynamic techniques that initiate and respond to a flux of solute to the device [10]. Whereas DET relies on establishing equilibrium between solutes in the solution and in the device, in DGT solutes

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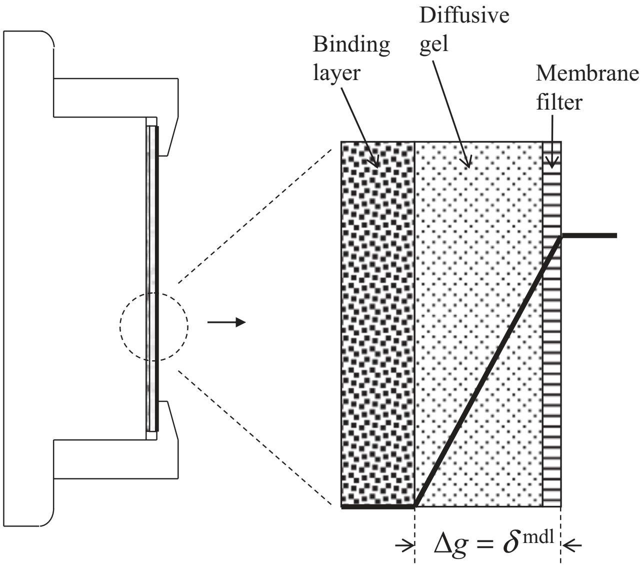

Figure 1.1 Schematic diagram of a DGT piston assembly, with an exploded view of the binding and diffusion layers, showing the concentration gradient of the analyte.

continuously diffuse across a well-defined diffusion layer and are progressively accumulated. The ideas behind DGT were patented worldwide with a filing date in 1993, and the trademark DGT® is registered in many countries and should be displayed when DGT is used commercially. However, this does not prevent the research use of DGT, and the simple initials DGT will be used throughout this book.

In principle, there is little difference between DGT and a range of passive samplers that have been developed for monitoring components in air [11] and organic substances in water [12]. However, the theoretical approach to the interpretation of the DGT measurement has taken a different path, and DGT has been used much more extensively than other devices for the measurement of predominantly inorganic solutes in natural waters. The detailed interpretation of the measurement in terms of equilibrium speciation and dissociation kinetics of complexes has been possible because of the firm theoretical developments. Moreover, the use of DGT has been extended to soils and sediments where it has provided unique information. These applications in particular demonstrate that the description ‘passive sampler’ is inappropriate. As DGT continually removes solute from its deployment medium, it perturbs the system. The accumulated solute that is eventually measured reflects this perturbation. It is this feature that allows it to provide information on speciation in solution and solid–solution interactions in soils and sediments.

This chapter sets out a simplified view of the basic principles of DGT that have been at the heart of most of its applications for measuring solutes in solution. The later chapters provide more thorough treatments of the principles and practise of the measurement in waters, sediments and soils and consider in detail the underlying assumptions.

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1.2 Basic Principles

There are really only two essential parts of DGT: a layer which selectively binds the solute or solutes of interest, known as the binding layer, and a layer which permits diffusion of the solutes prior to binding, known as the diffusion layer. Details of the required properties of these layers and of the types that have been used are provided in Chapters 3 and 4. The original work, aimed at measuring trace metals, used a polyacrylamide hydrogel for both layers [9]. Hydrogels, as their name implies, are largely composed of water. The particular type used was 95% water, allowing virtually unimpeded diffusion of simple cations. Chelex resin binds trace metals more strongly than major cations (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}). It was incorporated into a hydrogel during the casting process to form a dense layer of resin beads at one surface of the resin sheet. These binding and diffusion layers were held together in a plastic holder, with only the diffusion layer exposed to solution through a circular ‘exposure window’. As the first deployments in estuarine conditions showed that the diffusive gel layer was prone to clogging by particles, it was overlain by a protective membrane filter, which had similar diffusion properties to the gel. Figure 1.1 shows a cross-section through a commonly used, commercially available version of the device for measurements in solution. The cylindrical plastic assembly, which is injection moulded in ABS (acrylonitrile butadiene styrene) plastic, is sometimes referred to as a piston holder. The top cap with the exposure window fits tightly over the base, which supports the sandwich of binding layer, diffusion layer and membrane filter.

The simple and robust DGT device is readily deployed in situ in natural waters or in solutions in the laboratory. After deployment, the piston holder is washed and pulled apart to retrieve the binding layer, which, for measurement of metals, is immersed in a small volume (typically 1 mL) of usually 1 M nitric acid. The mass of metal, M, on the binding layer, of volume V^{bl}, is calculated from the measured concentration of metal, c_{e}, in the acid eluent, of volume V_{e}, using equation 1.1. The fraction of bound metal released, f_{e}, known as the elution factor, can be established for controlled conditions:

$$M = \frac{c_{\mathrm{e}}(V^{\mathrm{bl}} + V_{\mathrm{e}})}{f_{\mathrm{e}}} \tag{1.1}$$

As the DGT device is deployed for a known time, t, and the area that is exposed to solution is determined by the area of the window in the device cap, A_{p}, it is simple to calculate the flux of solute, J (mass per unit area per time), passing through the device (equation 1.2).

$$J = \frac{M}{A_{\mathrm{p}}t} \tag{1.2}$$

To appreciate how to convert the measured mass and associated flux to the concentration in solution during deployment, we consider Figure 1.1. It shows the steady-state concentration gradient of the solute being measured that is established through the device when it is deployed in solution. Fick’s first law of diffusion [13] states that the flux, J, through such a system is simply the diffusion coefficient of the solute in the diffusion layer, D^{mdl}, times the concentration gradient, $\mathrm{d}c/\mathrm{d}x$, where c is the concentration of solute and x represents

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distance (equation 1.3). Material diffusion layer (MDL) is used in the superscript to make the distinction between diffusion in the materials of the device and diffusion in solution, as explained in more detail in Chapter 2.

$$J = D^{\mathrm{mdl}} \frac{\mathrm{d}c}{\mathrm{d}x} \tag{1.3}$$

Usually the solute of interest binds so strongly to the binding layer that its concentration at the interface between the diffusion and binding layers is negligibly small. To a first approximation, convection ensures that the concentration of solute in solution, c^{soln}, is effectively constant. Consequently for the region corresponding to the thickness of the diffusion layer, the gradient is simply $c^{\mathrm{soln}}/\Delta g$, allowing equation 1.3 to be expressed in known quantities (equation 1.4).

$$J = \frac{D^{\mathrm{mdl}} c^{\mathrm{soln}}}{\Delta g} \tag{1.4}$$

Although Δg has usually been used to designate the total thickness of the MDL, comprising gel and filter membrane, for consistency in nomenclature, and to distinguish it from individual layers where diffusion occurs (see Chapter 2), it will usually be designated as δ^{mdl} in the rest of the book. If it is assumed that the time required to reach steady state is negligible, an expression for the concentration in solution can be obtained by equating 1.2 and 1.4 and rearranging (equation 1.5). The term c_{DGT} is used in equation 1.5 because this DGT-measured concentration is an interpreted quantity which, depending on the conditions, may not equate to c^{soln}. For example, in more complex media not all species of a solute might diffuse and bind.

$$c_{\mathrm{DGT}} = \frac{M \Delta g}{D^{\mathrm{mdl}} A_{\mathrm{p}} t} \tag{1.5}$$

In principle, however, equation 1.5, which has become known as the DGT equation, allows the concentration in the deployment medium to be calculated by simply measuring the amount of solute that binds to the gel. The diffusion layer thickness and area are obtained from the geometry of the device, while time can be accurately measured. The diffusion coefficients in the MDL of a wide range of solutes of interest are known for a range of temperatures (Chapter 3 and Appendix). For simple solutions, the value of D^{mdl} can be regarded as a calibration factor, as it can be obtained by deploying DGT devices in known solutions. A sample calculation is shown in Table 1.1, which illustrates that concentrations should be expressed per millilitre for conformity with distance units of centimetre.

Equation 1.5 has been shown to work well for deployments in stirred or flowing solutions when using the standard device equipped with a 0.8-mm thick gel and 0.14-mm filter membrane [14] (see Chapter 2.2). It predicts that the measured mass increases linearly with time, which has been verified by numerous workers [6]. The slope of this plot, $c^{\mathrm{soln}} D^{\mathrm{mdl}} A_{\mathrm{p}} / \Delta g$, provides an estimate of c^{soln} if it is unknown or of D^{mdl} where deployments are made in known solutions. The conditions that give rise to deviations from linearity are treated in Chapters 4 and 5. According to equation 1.5 the measured mass is inversely

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Table 1.1 *Example values and units used in calculating the DGT-measured concentration, c_{DGT}, where the concentration in the diluted eluent measured analytically is 0.9 mg L^{-1}. The deployment time and concentration in the eluent for a particular measurement are shown with typical units (unit 1) and the units necessary for the calculation (unit 2).*

Set values		Experiment	Unit 1	Unit 2	Calcn	eqn	value
D^{mdl} (cm^2/s)	5.29E–06	Time	24 h	86400 s	M	1.1	12.7 µg
A_{p} (cm^2)	3.14	c (analysis)	0.9 mg L^{-1}	0.9 µg mL^{-1}	c_{DGT}	1.5	0.83 µg mL^{-1}
Δg (cm)	0.094	Dilution	10×				
f_{e}	0.8	c_{e}	9.0 mg L^{-1}	9 µg mL^{-1}			
V_{e} (mL)	1						
V^{bl} (mL)	0.126						

proportional to Δg. Again this has often been verified, but we will see later (Chapter 2); there are more appropriate equations that should be used when diffusive gel thicknesses differ from 0.8 mm or the water is not fast flowing.

1.3 Measurements in Natural Waters

The robust design of DGT devices makes them easy to deploy in situ. Moreover for simple solutions, where the diffusion coefficient of the solute being measured is known, no calibration other than normal quality control checks is necessary. When the environmental concentration changes with time, as might occur in a river, the DGT device provides the time weighted average (TWA) concentration for the deployment time. These characteristics, allied to the low cost of DGT devices, have contributed to their use in monitoring programmes [15, 16]. The fairly long diffusive path, approaching 1 mm in a standard device, ensures that the DGT measurement is almost insensitive to the rate of solution flow above a threshold flow of 2 cm s^{-1}. A further attractive feature for monitoring purposes is the ease of analysis. If the binding layer for a standard device is eluted into 1 mL of 1M HNO_3, which is then diluted by a factor of 10, the matrix is ideal for analysis by atomic absorption spectroscopy (AAS) and inductively coupled plasma (ICP) (both optical and mass spectrometry (MS)). For a twenty-four-hour deployment of the standard device fitted with a 0.8-mm thick diffusive gel and 0.14-mm thick filter, the concentration measured by the analytical technique in the diluted eluent will be similar to the concentration in the deployment solution, assuming a diffusion coefficient of 5×10^{-6} cm^2 s^{-1} and an elution factor of 0.8, typical for transition metals, as illustrated in Table 1.1. Unless deployment times extend to several days or weeks, the analytical advantage of the DGT measurement lies in the well-defined matrix as much as the enhancement of the concentration.

Although DGT was originally used for measuring trace metals, it has proved to be very versatile. Garmo et al. [17] showed that the original binding layer containing Chelex resin can be used to measure fifty-five elements. Alternative binding layers have been

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used for sulphide [18], Cs [19], Hg [20], Tc [21] and oxyanions (e.g. phosphate [22] and arsenate [23]). Chapter 4 considers in detail the range of possible analytes, which have recently been extended to hydrophilic organic compounds [24].

From the outset, it was recognised that DGT can be used as a speciation tool. At a simple level, it can be used to provide a direct measure of solutes that are both mobile and labile [10]. The term mobile refers to the fact that they must be capable of diffusing at a reasonable rate through the diffusion layer. The term labile is used to denote species which can interconvert, within the timescale of their diffusional transport, to a form that can bind. Gradually the theory has advanced, as detailed in Chapter 5, to allow more sophisticated interpretation in terms of the distribution of species in solution and the rates at which they interconvert [25].

1.4 Applications to Soils and Sediments

DGT has been used extensively to perform measurements in sediments [26] and in soils that are usually fully hydrated [27]. Solutes are supplied from the porewaters, but as there is no convective supply to sustain their concentration, they are depleted adjacent to the device. Interpretation in terms of the concentrations in the porewaters prior to the DGT perturbation is then not so simple. The solute accumulated by DGT is determined by both the concentration of labile and mobile solutes in the porewaters and the rate of supply of solute from the solid phase, as detailed in Chapter 7. The positive aspect of this dependency is that, with a systematic set of measurements and appropriate modelling, information can be obtained about the dynamics of solute interaction with the solid phase [28]. The advantage of using DGT to do this is that it is readily deployed in situ in sediments and in soils that are hydrated to their maximum water-holding capacity.

While the DGT measurement can be treated analytically to derive its component contributions, including kinetic and speciation effects, it can also be viewed holistically. In this case, the interpretation is simply that c_{DGT} reflects directly the response of the soil or sediment system to the perturbation imposed by DGT of removing solute in a controlled way. This approach has been used most successfully by considering that DGT mimics the way that plant roots perturb solutes in a soil system, leading to DGT being used as a tool to predict uptake of solutes by plants and to understand how the dynamics of uptake affects the soil [29]. The underlying processes and assumptions that determine relationships between uptake by DGT and by biota are discussed in Chapter 9.

Most work in soils has involved homogenisation of the sample prior to deployment. The intense redox gradients in sediments and their sensitivity to oxygen prevent this approach. The focus has been in performing DGT measurements at high spatial resolution to inform understanding of early diagenesis. The complexities of the different contributions to the accumulated DGT mass, the steep concentration gradients and the inherent heterogeneity of solute distributions have hindered progress. Measurements at high spatial resolution (sub-mm scale) have revealed apparently stochastic distributions of localised high concentrations of solutes, termed microniches. Ironically, while the technique of DGT grew out of sediment work, advancing understanding of the processes occurring in this medium has been most difficult. However, with more systematic experiments [30], the use of rapid colorimetric techniques of two-dimensional imagery [31], and the development of three-dimensional models of sediments to simulate the localised DGT signals [32] and the distribution of solutes in microniches [33], progress is now being made, as demonstrated in Chapter 8. Two-dimensional imagery of solute concentrations has been extended to soils where it is being used to advance understanding of processes at plant roots [34, 35].

1.5 This Book

Even with this brief introduction, it is clear that DGT is a tool that can be used at various levels of application and interpretation. For simple monitoring, where the aim is to obtain the DGT measurement of labile and mobile solutes, the theory represented by equations 1.1–1.5 will suffice in many cases. The following chapters examine in detail the assumptions associated with these basic forms of the equations and provide more complete treatments. The generic performance characteristics of DGT are examined followed by the consideration of specific factors associated with individual solutes. Further chapters explore the interactions of DGT with its deployment media and provide the principles for understanding the dynamic exchange between species in solution and the dynamics of solute interactions between solution and the solid phases in soils and sediments. Key examples of the application of these principles are provided, with particular emphasis on the information that can be obtained at various spatial scales. The role of DGT in mimicry of biological uptake is considered as an example of holistic measurement. Important in all these developments is sound experimental practice, and so the last chapter is devoted to the practicalities of using DGT.

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