

**An Assessment of the Feasibility of
Using DGT Procedures to Measure
Trace Metals and Radionuclides in
Rivers**

**Environmental Sciences
Lancaster University**

R&D Technical Report P92

An Assessment of the Feasibility of Using DGT Procedures to Measure Trace Metals and Radionuclides in Rivers

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The project examined the feasibility of using the new procedure of diffusive gradients in thin films (DGT) for the measurement of trace metals and radionuclides in water. The information from the project is for use by Agency staff and any others involved on the development of methodology for the measurement of trace metals and radionuclides in water.

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EXECUTIVE SUMMARY

Background Sampling and analysis of waters for trace metals and radionuclides is a difficult, costly procedure requiring skilled personnel. Monitoring is restricted to a series of point samples whereas ideally a continuous or integrated record is required. The availability of trace metals and radionuclides to biota depends on their chemical speciation and this may change during the sampling and handling steps. There is a requirement for an *in situ* procedure which can provide a quantitative integrated record of well-defined solution species of trace metals and radionuclides.

The development of quality standards and risk assessments protocols for the impacts of metals in contaminated waters is hampered by the absence of a simple chemical diagnostic for potential metal toxicity. Measurements of total metals are inappropriate because toxicity depends on the availability of the metal to the biota, and hence the amount of free or weakly bound metal. There is a requirement for a device capable of acting as a surrogate for bio-available metal.

The new procedure of diffusive gradients in thin-films (DGT) has recently emerged. It collects solutes on an immobilized binding agent after diffusion through a thin-film of gel. Because the geometry is well defined the measured mass of metal accumulated after a known deployment time can be used to calculate the time averaged mean concentrations of solutes in the exposure solution. Concentrations can be calculated theoretically, overcoming the difficult problems of *in situ* calibration. DGT responds to labile metal. Like biota it continuously removes the metal from solution, so it may be a good chemical surrogate for bioavailability.

Objectives Prior to this contract, DGT had only been partially tested for zinc and cadmium and its application was restricted to seawater. The aims of the research were to develop DGT into a practical device and to establish its feasibility for measuring several metals in freshwater, including cadmium and mercury. Particular attention was to be placed on the verification of the basic principles and to establishing practical performance characteristics.

Results A simple plastic assembly capable of manufacture by injection moulding was developed. It was tested principally with solutions of cadmium in synthetic freshwater. The concentration measured using DGT was in good quantitative agreement with the known concentration in solution. The measured mass of accumulated metal in the resin-gel layer increased linearly with exposure time and was inversely proportional to the diffusion layer thickness. The measurement was independent of pH between 5 and 9. Temperature dependence was governed solely by the known diffusion coefficient of the solute and was therefore predictable. The DGT response was almost independent of the flow rate in the solution. Theoretical responses were observed over wide ranges of concentrations and

deployment times, up to 1 month. By using ICP-MS for the final laboratory measurement it was possible to measure zinc, cadmium, copper, lead, cobalt and nickel simultaneously. Mercury gave the theoretical response at high concentrations. When DGT assemblies were deployed in situ in the Trent - Mersey canal, sensible and reproducible concentrations of cadmium and mercury were obtained. The capabilities for high sensitivity while avoiding contamination were demonstrated. The potential for DGT to measure radionuclides was also demonstrated. Chelex can not be used to measure cesium. When a general cationic exchange resin was incorporated in the resin layer, both stable strontium and cesium and the radionuclides Sr-90 and Cs-137 could be measured. Use of such a non selective resin limits the deployment time of DGT in natural waters to a few hours, but the principle is established for selective resins which should allow deployment times of several weeks.

Conclusion DGT is a cheap reliable device which can be used to measure quantitatively, *in situ* labile species of trace metals and potentially radionuclides. Further work is required to test DGT devices in a range of field conditions, to improve its use for mercury, to extend its use to anionic species and nutrients and to test its ability for use as a surrogate test for bioavailability.

Key words: *in situ* measurement, polyacrylamide gel, trace metals, cadmium, mercury, diffusive gradients in thin-films (DGT), ion-exchange resin.

1. INTRODUCTION

1.1 Background

Reliable measurements of trace metals in natural waters are essential for the assessment and control of pollutants, understanding metal availability to biota and as inputs to environmental fate models. Since concentrations of mercury and cadmium are regulated to sub-ppb levels, specialised analytical equipment is needed and dedicated clean facilities are required to avoid contamination. The acts of sampling and storage prior to analysis can change the distribution and nature of the chemical species and introduce contamination. Consequently a device which permits *in situ* sampling and measurement is highly desirable.

The majority of present sampling regimes are limited to spot sampling, and therefore they potentially miss pulses of contaminant. Clearly there is a requirement for a technique which provides an integrated record. USA regulations have recently recognised that only a fraction of the metal contamination in the environment is biologically available, and the emphasis now lies with dissolved (0.45- μm filter) rather than total metal levels. Even this may represent an over-estimation as it includes colloidal metal and metal bound to organics, which are potentially capable of remaining inaccessible depending on the competitive equilibrium between the biota and the ligand. There is growing pressure from industry against over regulation. The availability of a simple procedure for measuring truly bio-available metal would greatly benefit the water industry and its industrial users.

A new technique for measuring trace metals was recently developed by Davison and Zhang (1994). It has the potential to make measurements of trace metals *in situ*. It continuously integrates metal concentrations, measures only labile, dissolved metals and incorporates preconcentration, overcoming analytical and contamination problems. This procedure, called DGT, employs a diffusion gradient in a thin film of polyacrylamide gel. The metal ions are allowed to freely diffuse through the gel diffusion layer of thickness Δg , before binding to a layer of resin. The chemical reaction with the metal, occurs *in situ*. It is this initial *in situ* measurement step which defines the chemical speciation. The diffusion boundary layer, δ , which exists at the interface between the bulk solution and the gel layer is sufficiently thin, when compared with that of the gel diffusion layer, that it can be ignored. Consequently, transport of the ions to the resin is controlled by the gel thickness rather than any irregular convective processes in the solution. That is the measurement should be independent of flow. If the free metals are in rapid equilibrium with the resin, with a large binding constant, the concentration at the resin-diffusion gel interface is effectively zero, and a linear diffusion gradient is established from the bulk solution to the resin (Figure 1.1) (Zhang and Davison, 1995). Therefore the flux (F) can be expressed by (1).

$$F = D C_b / \Delta g \quad (1)$$

where D is the diffusion coefficient in the gel and C_b is the bulk solution concentration.

The mass (M) diffusing through an area (A) after a given time (t) can be expressed, according to the definition of flux ($F=M/At$), by (2).

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

The mass of metal in the resin layer can be measured by eluting with acid followed by conventional AAS or ICP-MS analysis, and therefore the concentration in the bulk solution can be calculated from (3).

$$C_b = M \Delta g / D t A \quad (3)$$

The ultimate analytical measurement is undertaken in the laboratory under controlled conditions, but the first analytical step, the chemical fractionation of the metal, occurs *in situ*. Moreover, the metal is accumulated *in situ*, simplifying the ultimate analysis and avoiding contamination.

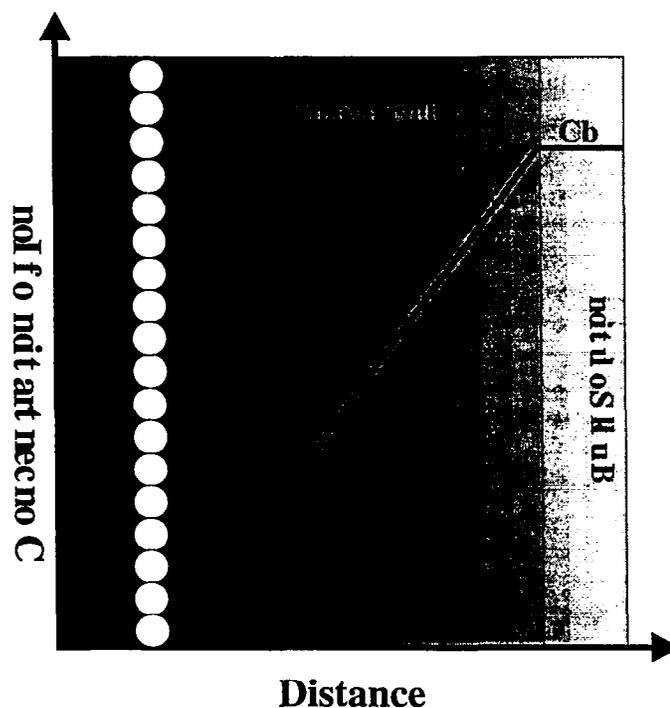


Figure 1.1 Theoretical representation of the diffusion gradient between the bulk solution and the resin layer.

The holders can potentially be deployed for any duration of time, ranging from half an hour to one month (see section 3.6), giving an integrated time-averaged concentration. The device can simultaneously accumulate a variety of metals, depending on the properties of the chelating resin. The analytical measurements are made under controlled laboratory conditions and, with the aid of ICP-MS to analyse the eluted resin, a full multi-element capability is possible. Due to the relatively large pores sizes of the polyacrylamide gel, small ions can diffuse freely through the gel at rates indistinguishable from those through water. Labile complexes will dissociate as they contact the chelating resin. Metal is continuously removed from solution across a membrane, resembling the uptake by biota.

1.2 Objectives

At the end of January 1995 Her Majesty's Inspectorate of Pollution contracted Lancaster University to provide an assessment of the feasibility of using the DGT technique to monitor trace metals and radionuclides in rivers. At this stage preliminary trials had used the procedure to measure zinc in the marine environment (Davison and Zhang, 1994). However, it had essentially been developed as a research tool, and therefore a systematic investigation and characterisation of the device was required to assess its practical capabilities. The main aims of this feasibility study were to test the predictions of the underlying theory, and to develop a practical monitoring tool. Consequently the objectives were defined as follows.

1. To develop a holder to encapsulate the DGT assembly. It should be water tight, and capable of being produced cheaply using injection moulding.
2. To establish the elution efficiency and working capacity of the resin impregnated gel.
3. To verify the theoretical linear relationships between the accumulated mass of metal and
 - a) the diffusion layer thickness
 - b) the exposure time.
4. To assess the flow dependence of DGT by conducting trials in a flume.
5. To assess the pH dependence of DGT.
6. To perform preliminary field trials.
7. To assess the feasibility of using DGT for radionuclides.

2. METHOD

2.1 Gel preparation and DGT assembly

A polyacrylamide hydrogel comprising 15% acrylamide (Boehringer) and 0.3% AcryLAide agarose cross-linker (Flow Gen Instruments) was used for the diffusion layer and to encapsulate the chelating resin. To initiate polymerisation of the gel, 35 µl of freshly prepared (10%) ammonium persulphate initiator and 12 µl of TEMED catalyst were added to 5 ml of gel solution. The solution was injected immediately between two sheets of glass held apart by plastic spacer, and allowed to set at 42 °C for 45-60 minutes. The set gel was subsequently removed from the caste and hydrated in deionised water for at least 24 hours prior to use. The water was usually changed at least twice during this hydration period to ensure that any unreacted reagents were completely washed out.

Chelex-100 (Bio-Rad Laboratories, 100-200 wet mesh, spherical 75-150 µm) resin beads were chosen for accumulating the metal because:

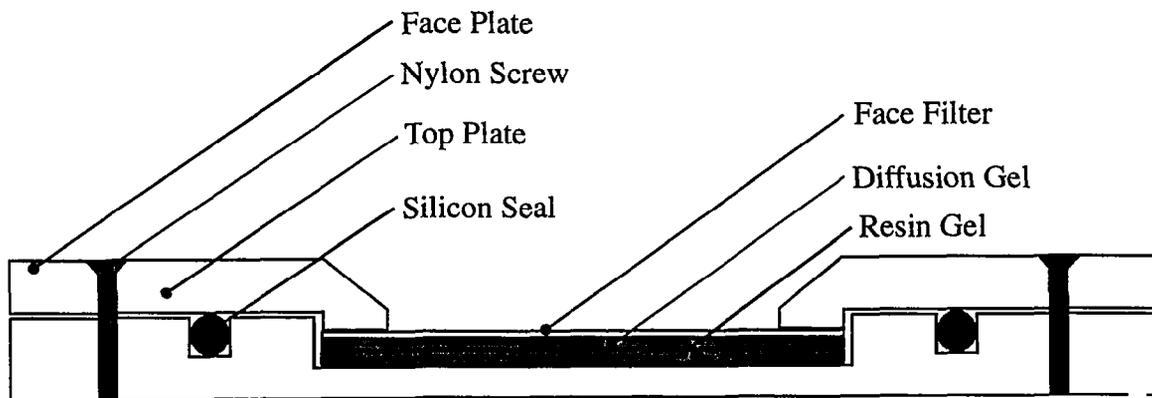
- (1) it is highly selective for trace metals,
- (2) it can bind more than 10 metals simultaneously and
- (3) metals are readily eluted with acid.

Preparation of the resin gel was identical to that of the diffusion gel, with the exception that 1 gram of Chelex-100 resin was added to the 5 ml of gel solution prior to casting. The castes were placed horizontally during setting, allowing the denser resin particles to settle and form a thin layer of closely-packed beads. The gels expanded during hydration resulting in a final water content of approximately 95%.

Unless otherwise stated a 0.7 mm thick diffusion layer and a 0.4 mm thick resin layer were used in the assemblies. A disc of resin gel was placed, with the layer of Chelex beads facing upwards, upon a Millipore cellulose nitrate filter. A disc of diffusion gel was then placed over this and finally a second filter was placed on top. The face filter was required to prevent particles in the natural waters adhering to the gel diffusion layer. The combination of the rear and face filter also assisted in holding the gel layers flat when sealed within the holder. Davison and Zhang (1994) had shown that the filter behaved as an extension of the gel layer and that the diffusion coefficient for transport through the filter was the same as that through the gel. The complete gel assembly was then placed within a holder.

During the initial trials the DGT assembly was held in a perspex holder (Figure 2.1a) comprising two 10 cm diameter plates. The base plate had a 6 cm well cut centrally into it to accommodate the gel assembly, with a concentric recess, into which fitted a silicon O-ring. A chamfered window (5 cm diameter) was cut into the top plate, exposing the diffusion layer to the test solution. The combination of the O-ring, and a lip incorporated into the top plate pressing down onto the gel layer, prevented any leakage of the solution directly to the Chelex layer. The two plates were secured together with six nylon screws.

(a)



(b)

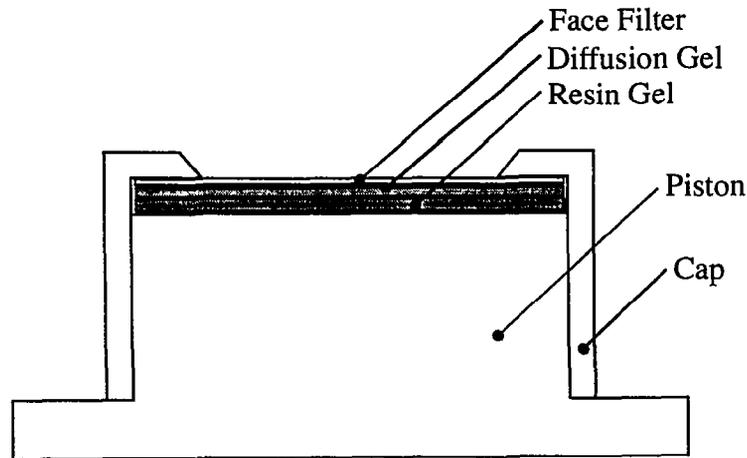


Figure 2.1 Cross-sectional view through holder 1 comprising two perspex discs (a) and holder 2 comprising a piston and cap (b).

The development of a simpler holder was required for routine work. A smaller assembly, based on a squat piston which fitted tightly into a cap with a 2 cm diameter window (Figure 2.1b), was designed. The gel assembly was placed on the piston face and the cap forced down tightly over it to form a friction fit. A series of trials was undertaken at this stage to optimise the compression to allow a good seal between the cap and the face filter without

distorting the gel assembly. The new design was quick to assemble and could be produced cheaply by injection moulding.

The holders were tested in a various solutions, which were well-mixed using a magnetic stirrer bar. During the initial trials the solutions consisted mainly of deionised water spiked with cadmium chloride. Subsequently a synthetic lake water was used. Upon retrieval, the holders were thoroughly rinsed and dried prior to disassembly. The recovered Chelex-gel discs were then eluted with nitric acid (usually 2M for 2 hours), and analysed along with a sample of the test solution by either Zeeman furnace atomic absorption spectroscopy (ZFAAS, Perkin Elmer 4100 ZL) or Inductively-Coupled Plasma Mass Spectrometry (ICP-MS, Varian Ultramass).

2.2 Elution efficiency experiments

Individual discs of Chelex resin-gel of 2.5 cm diameter were placed in sealed PVC vials containing a known volume and concentration of cadmium chloride. These were then shaken for 24 hours to allow the complete uptake of metal from the solution. After disassembly the resin-gel disks were carefully dabbed with a tissue to remove any excess solution, prior to being eluted with nitric acid. The elution time, acid volume and molarity were varied with separate batches of resin-gel disks, to determine the optimum conditions for the maximum elution efficiency.

2.3 Working capacity experiments

Sets of moulded holders were immersed for 10 hours in varying concentrations of cadmium chloride, ranging from 1.5 µg/l to 150 mg/l. 0.4-mm thick gel diffusion layers were used in all the holders and a constant solution temperature (20 ± 1 °C) maintained throughout all the trials. If the capacity is not exceeded the mass of metal accumulated within the resin gel should increase linearly with the bulk solution concentration.

2.4 Diffusion layer thickness experiments

A series of moulded holders were assembled with six different thicknesses of diffusion gel ranging from 0.4 mm to 2.0 mm. In addition to these, a set of holders containing a single 135 µm thick Millipore cellulose nitrate filter as the diffusion layer were also included. All seven types of assemblies were exposed to a 14 µg/l cadmium chloride solution for 24 hours.

2.5 Determination of the diffusion coefficient of cadmium in polyacrylamide gel

Two identical open-topped chambers were constructed from perspex measuring 2.5 cm by 2.5 cm by 11 cm of such a design that they could be clamped together (Figure 2.2). A 1 cm diameter chamfered hole in the adjoining vertical wall of both cells provided direct access between them. A 0.7-mm sheet of polyacrylamide gel with a silicon seal surrounding it was sandwiched between the two cells. They were subsequently clamped together with sufficient pressure to prevent leakage of solution from the cells, while ensuring that the gel layer was not compressed. A 50-ml sample of synthetic lake water spiked with cadmium chloride was poured into one of the cells. The other cell was filled with 50 ml of un-spiked synthetic lake water. A twin stirrer assembly was placed in the cells to ensure complete mixing of the two solution. Aliquots of solution were then taken at set time intervals from both cells and analysed. A diffusion coefficient for the transport of cadmium through the gel could then be calculated.

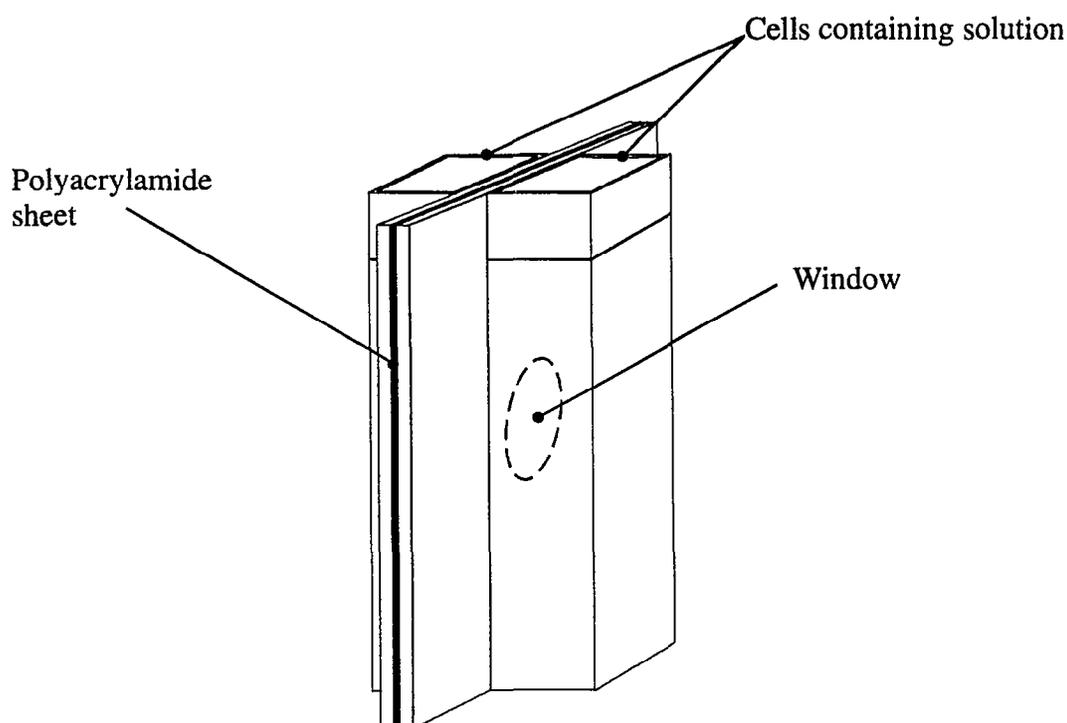


Figure 2.2 Cross-section of the perspex diffusion cell used to determine the diffusion coefficient through polyacrylamide gel.

2.6 Time dependence experiment

A 100 litre drum was fitted with a magnetically-coupled PTFE stirring rod. The drum was filled with a synthetic lake water spiked with 2.5 $\mu\text{g/l}$ cadmium chloride and allowed to equilibrate for 48 hours. A batch of moulded holders was then placed in the drum and exposed to the test solution for varying periods of time up to 1 month. The large initial volume ensured no significant removal of metal from solution.

2.7 Flow dependence

Theoretically the DGT response should be independent of flow above some threshold level. Sufficient cadmium nitrate was spiked into tap water in a 600-l Armfield glass-sided tilting flume to give a bulk solution concentration of approximately 10 µg/l. The flume was subsequently run for 48 hours to allow for equilibration with the surfaces in contact with the solution. A series of three trials investigated the flow-dependence of DGT and the impact of varying the holder's orientation and construction.

Trial 1. A series of moulded holders were assembled with a glass filter paper impregnated with Rhodamine dye replacing the gel diffusion layer. These were placed vertically in the flume in line with the flow and the pattern of release of dye observed at increasing flow rates.

Trial 2. Four different types of DGT holders were used. The first two were as out-lined in Section 4.1 consisting of a 10 cm diameter perspex holder and a moulded holder. Samples of resin gel were taken from the centre of the window and around the perimeter to examine effects due to variations in mixing over the surface of the filter. The third type comprised a standard moulded holder with additional flutings cut into the cap around the window running concentricity inwards (Figure 2.3a). The fourth holder was of the type developed for sediment sampling, and consisted of layers of resin gel, diffusion gel and filter encased in a polythene membrane and clamped between two sheets of 5-cm by 12-cm perspex. The upper sheet had a 1 cm by 10 cm window cut through it allowing the exposure of the diffusion layer to the bulk solution. These four forms of holders were suspended vertically in the flume with the gel surface parallel to the flow and tested at varying flow velocities ranging from zero to 0.35 m/sec.

Trial 3. A series of moulded holders were suspended vertically in the flume at 60° to and in line with the direction of flow. The flow velocity was again increased from zero to 0.4 m/sec and the impact on the mass of accumulated metal monitored. At the slowest velocity of 0.005 m/sec extra holders were placed at 30° to and perpendicular to the direction of flow. A control was included in this trial in the form of a series of holders attached to a continuously rotating rod suspended in the solution. This gave a set flow rate virtually independent of the flume velocity.

Samples of the immersion solution were collected at various stages during the trials and filtered through a 0.45 µm Millipore cellulose nitrate filter directly prior to analysis using Anodic Stripping Voltammetry (ASV). An Autolab (PSTAT10, DAC124, Ecochemie) electrochemical system and a Metrohm hanging mercury drop electrode (663 VA stand) were used.

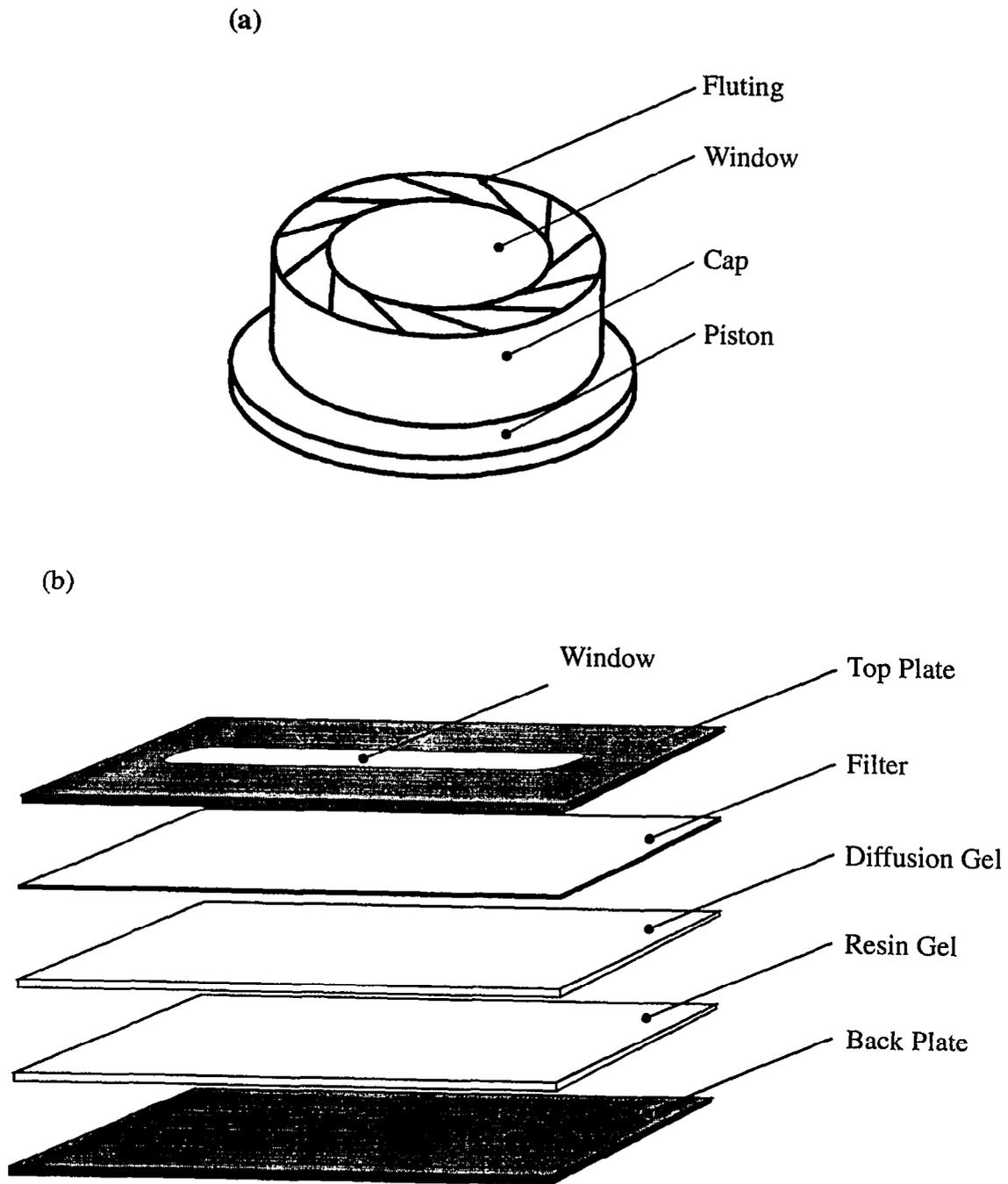


Figure 2.3 (a) Diagram of moulded holder illustrating modifications to cap, and (b) exploded view of sediment sampler.

2.8 Measurement of other metals

Elution efficiencies were determined for cadmium, zinc, nickel, copper, strontium and barium measured by ICP-MS. The DGT response of these metals was checked by exposing them to known solutions for various times.

A well-stirred solution of 20 µg/l mercury chloride was allowed to equilibrate in a container for 12 hours. A set of DGT units were then exposed to the solution for 3.5 hours. Following disassembly and elution, 0.2 mg/l of gold chloride was added to the eluent and samples of solution to minimise loss through volatilisation.

2.9 Full field-deployment in a fluvial environment

A series of designs where DGT units were mounted on a mobile vane were initially tested as possible rigs to hold the DGT assemblies, but were ultimately rejected due to their tendency to snag water-borne debris. A subsequent design used a rectangular funnel mounted 3 cm above a concrete slab (Figure 2.4). A cross-sectional ratio of 5 to 1 between the funnel mouth and the tube holding the DGT devices aided the transport of smaller debris through the funnel, thus much reducing the risk of fouling. Larger bed load would tend not to be carried into the funnel because of its elevated position above the river bed.

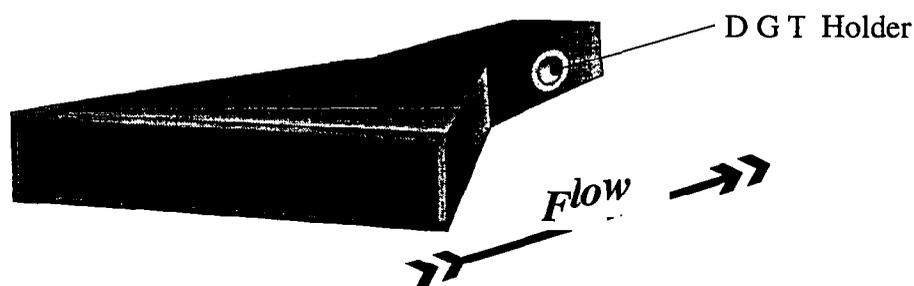


Figure 2.4 Representation of “Funnel rig” as deployed in river.

A bulk water sampler designed to sample continuously the river water was deployed alongside the DGT assemblies to permit a direct comparison. The initial field trial took place in the Trent - Mersey canal at Middlewich (SJ 721 639) which according to NRA data had measurable concentrations of cadmium and mercury. DGT was deployed for a period of eight days. Upon retrieval the assemblies were processed as usual, and the integrated river sample filtered as described in Section 2.7. As before, 0.2 mg/l of gold chloride was spiked into the eluent and the integrated river sample to minimise loss of mercury through

volatilisation. The samples were subsequently analysed using ICP-MS to obtain total metal concentrations of mercury and cadmium.

2.10 Laboratory validation for radionuclides

Chelex resin can not be used for cesium. The only available resins that can simultaneously accumulate cesium and strontium are general cation exchangers. While it is recognised that such general resins may not be suitable for long term deployment in natural waters containing competing cations, they offer the opportunity of testing the principles of the measurement of radionuclides by DGT. A non-selective cation-exchange resin, AG50W-X8 (Biorad), was therefore incorporated into the resin gel layer instead of the Chelex-100 resin, to permit the accumulation of strontium and cesium. A series of moulded holders were assembled with gel diffusion layer thicknesses ranging from 0.4mm to 2.22 mm. These were then exposed to a synthetic lake water spiked with 300 µg/l of stable strontium chloride and cesium chloride for a period of 3 hours. Following disassembly the resin gel disks were eluted with 2M nitric acid and analysed. Similarly prepared DGT units were also exposed to solution containing Cs-137 and Sr-90 of known activities. The resin-layer was dried and then placed directly on the γ counter.

2.11 pH and temperature

The effect of pH was investigated by immersing assemblies in cadmium chloride solutions of various acidities (pH 2.3-8.3). To determine the temperature response assemblies were exposed to a cadmium chloride solution maintained at various temperatures in the range 5-35°C.

2.12 Storage

A series of identical DGT assemblies were prepared and split into two batches. Holders in the first batch were placed on glass fibre filter papers impregnated with deionised water and sealed in individual plastic bags. They were stored in a fridge (4 °C). The remaining batch was immersed completely in de-ionised water in sealed plastic bags and placed in the fridge. Holders were subsequently removed and tested at various intervals over a two month period.

3. RESULTS

3.1 Introduction

During the initial stages of the contract a series of trials were completed to establish the procedures to be used in the main body of the work. These were mainly associated with the development of the new moulded holder and formalising gel preparation procedures. The production of a sealable holder which could be easily assembled, yet was simple enough to injection mould was an early priority. The level of compression exerted on the gel assembly once encapsulated in the holder was clearly important in ensuring a good seal between the face filter and the cap. Over-compression was found to lead to distortion of the gel layers and leakage, while under-compression allowed the un-controlled exchange of solution. After a period of several months of development a simple, but effective holder (design in Fig 2.1) which could easily be injection moulded was fabricated.

Key point. An effective DGT holder can be simply and cheaply fabricated by injection moulding.

Various trials comparing the DGT response from different batches of gel showed our current gel preparation procedures to be fully reproducible under controlled conditions. The diffusion gel was shown to maintain its dimensions and properties for at least a month when hydrated in Milli-Q prior to assembly, thus allowing the bulk production of gel.

The initial trials were completed using a solution composed of de-ionised water spiked with the test metal. However, because of the lack of any buffering, such solutions are prone to large fluctuations in pH, especially where equipment had been acid-washed. Subsequent work used a well-buffered synthetic lake water to avoid this problem. Dramatic improvements in the precision and accuracy of the device were apparent after August 1995 when the design of DGT units had been finalised and synthetic lake water was used. (Figure 3.1).

Key point: DGT precision for trace metals is equal to that of the analytical procedure, typically $\pm 5\%$.

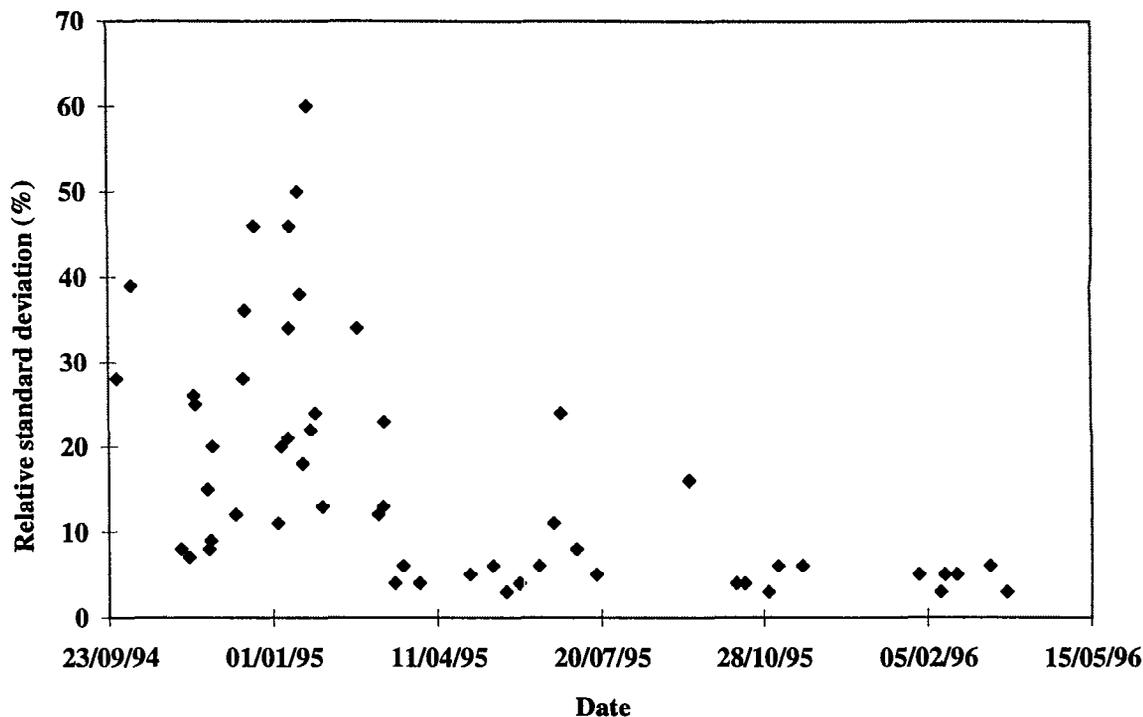


Figure 3.1 Illustration of the improvements in precision after the initial developmental stages.

3.2 Elution efficiency

Metal ions are usually eluted from ion-exchange resins by either batch elution, where the resin is exposed to an excess of leachate, or by column elution where the leaching solution passes through a column containing the resin. The column method is the most efficient, usually giving nearly 100 % recovery, but can clearly not be used on a small disc of resin-impregnated gel. The trials comparing varying elution times, acid volumes and molarities, illustrated that the acid strengths and elution times (1M and 2M for 2 hours) that had been initially chosen gave the most consistent and greatest elution efficiencies for resin incorporated into polyacrylamide gel. Minor adjustments to the elution conditions resulted in no significant variations in elution efficiency (Table 3.1).

Table 3.1 Dependence of elution efficiency on, eluent molarity, volume and elution time.

Molarity	Elution Efficiency ¹	Volume (ml)	Elution Efficiency ¹	Time (hrs)	Elution Efficiency ¹
0.5	92	0.3	90	1	91
1	91	0.75	89	5	90
2	89	1	87	18.5	91
3	90	1.5	87	14	90
4	89	2	90	48	86

Notes: ¹ Ratio of metal bound to metal eluted as a percentage.

Key point: The elution efficiency of 90% is robust and insensitive to small variations in conditions.

3.3 Working capacity

The mass of cadmium accumulated in the resin gel increased linearly with increasing bulk solution concentration up to 150 mg/l, where it plateaued (Figure 3.2). This represents the maximum capacity of the DGT device, corresponding to 0.63 mg of cadmium which agrees well with the manufacturer's stated capacity for this volume of Chelex of 0.56 mg. The linear relationship illustrates that the accumulation of metal in the resin is as predicted by the DGT theory, and is independent of the loading of the resin providing saturation is not reached. Using typical concentrations of Chelex-exchangeable metals in polluted river systems, the maximum deployment time for a DGT device was estimated to be in excess of one month (equation 2). The minimum deployment times of one hour is due to the linear diffusion gradient between the bulk solution and the resin gel taking several minutes to establish (Figure 1.1). After 1 hour the effects due to the initial change in concentration gradient are negligible.

Key point: The accumulation of metal in the DGT device is independent of the loading of the resin providing saturation is not reached.

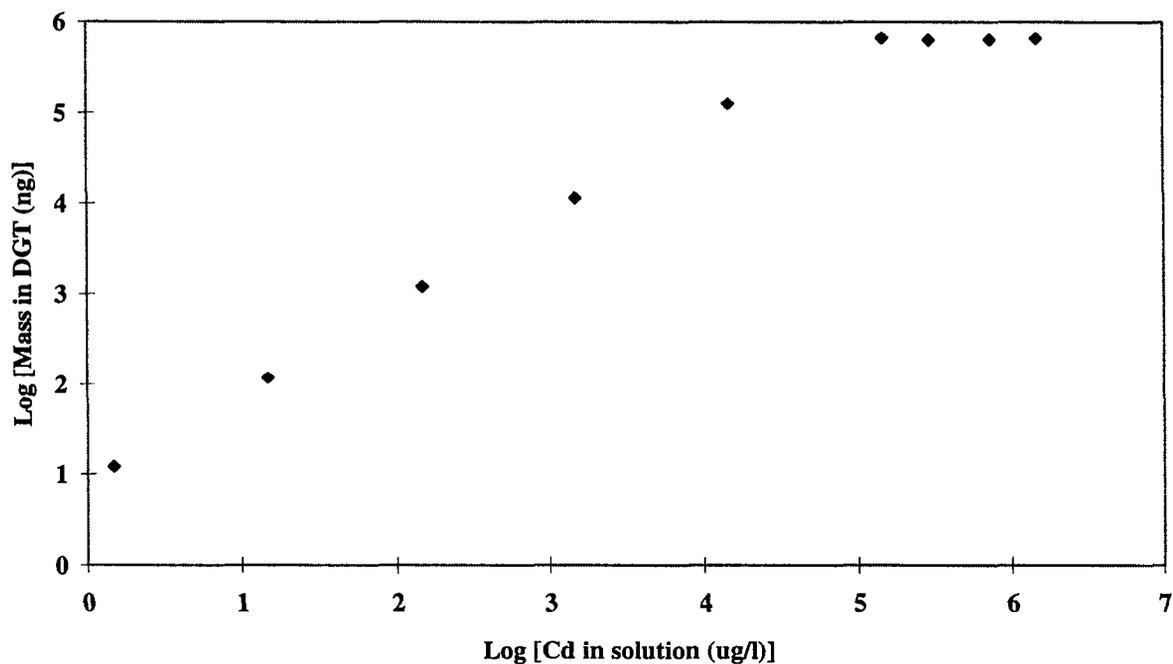


Figure 3.2 Capacity of DGT presented as a log/log plot of mass of cadmium accumulated in the resin gel versus the solution concentration.

3.4 The diffusion layer thickness

The results showed (Figure 3.3) that the mass of accumulated metal is inversely proportional to the thickness of the diffusion layer as predicted by Fick's first law of diffusion upon which the DGT theory is based (equation 2).

Key point: The measured mass of accumulated metal is inversely proportional to the diffusion layer thickness.

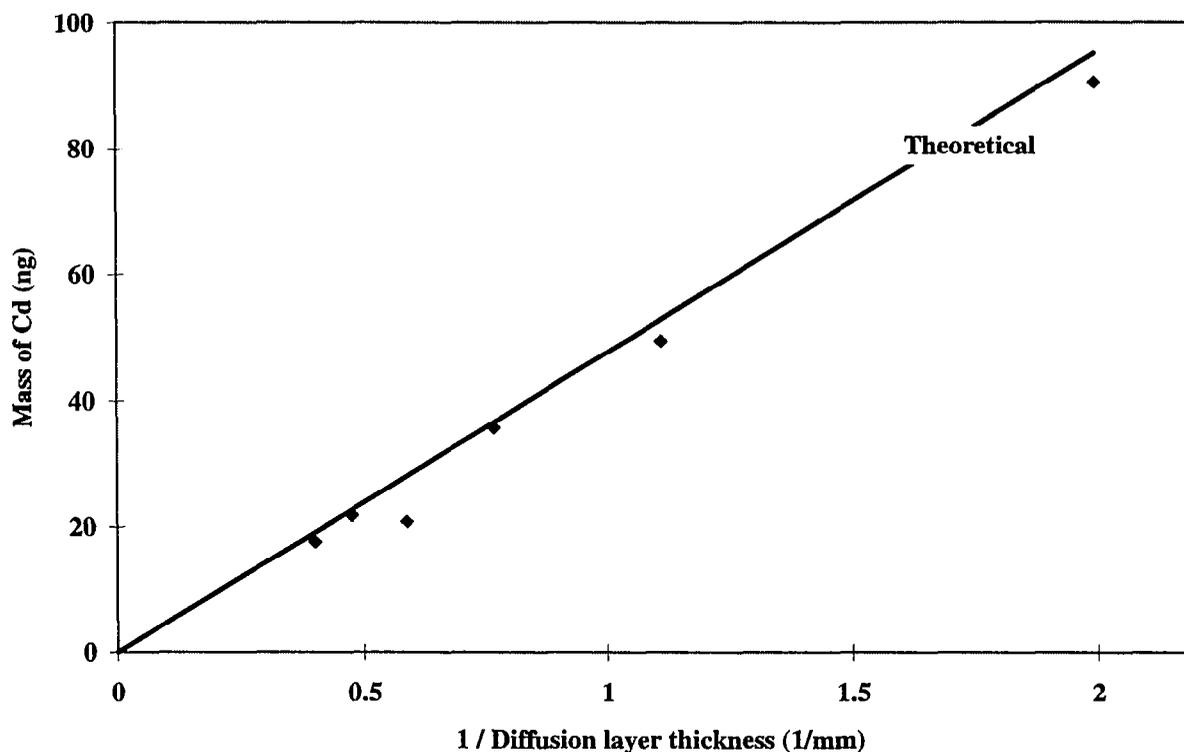


Figure 3.3 Dependence of the measured mass of cadmium accumulated in the resin layer on the reciprocal of diffusion layer thickness. The theoretical response calculated using eqtn (2) is shown by the solid line.

3.5 Measurement of the diffusion coefficient of a metal ion in polyacrylamide gel

The measured mass of Cadmium transferred between the two compartments of the flow cell separated by a polyacrylamide gel increased linearly with time (Fig. 3.4). The slope of the plot gives the flux. The DGT temperature response depends on the known way that D varies with temperature. The diffusion coefficient calculated from the measured flux of metal through the polyacrylamide gel, was equal to that of a cadmium ion in pure water (Li and Gregory, 1974).

Key point: The diffusion coefficients of simple ions in polyacrylamide-agarose gel and water are indistinguishable.

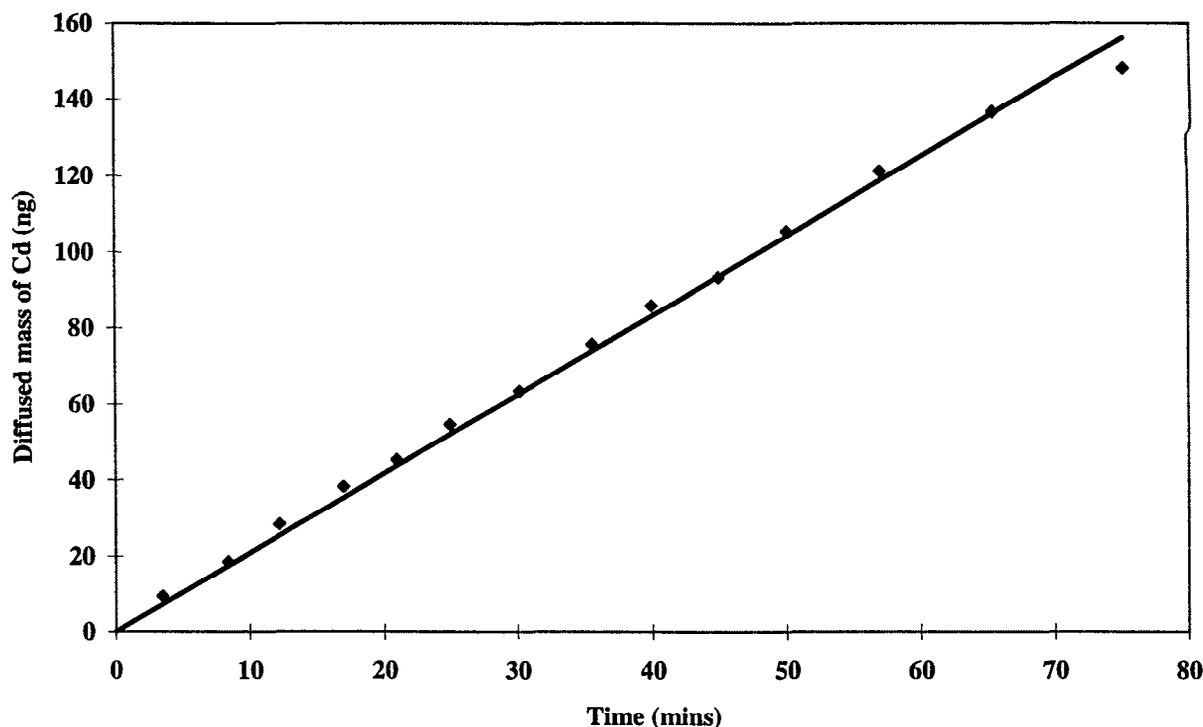


Figure 3.4 Time dependence of mass of cadmium chloride diffusing through a polyacrylamide gel layer. The line is calculated from the known concentration of cadmium.

3.6 Time dependence

The linear relationship between the mass of accumulated metal and the period of exposure as predicted by equation 2 is clearly illustrated, (Figure 3.5). The linearity over the complete test period illustrates the high capacity for binding metal that the current density of Chelex resin possesses. It was noted that the resin gel recovered from the later assemblies showed a mild green colouration, initially believed to be algal growth. However, although it auto-fluoresced under certain wave-lengths of light, usually an indicator of the presence of Chlorophyll, no DNA were identified when stained with DAPI (4'6-Diamiano-2-Phenylindole). The green colouration did not influence the DGT performance.

Key point: A mean concentration can be determined for any period of deployment from 1 hour to 1 month.

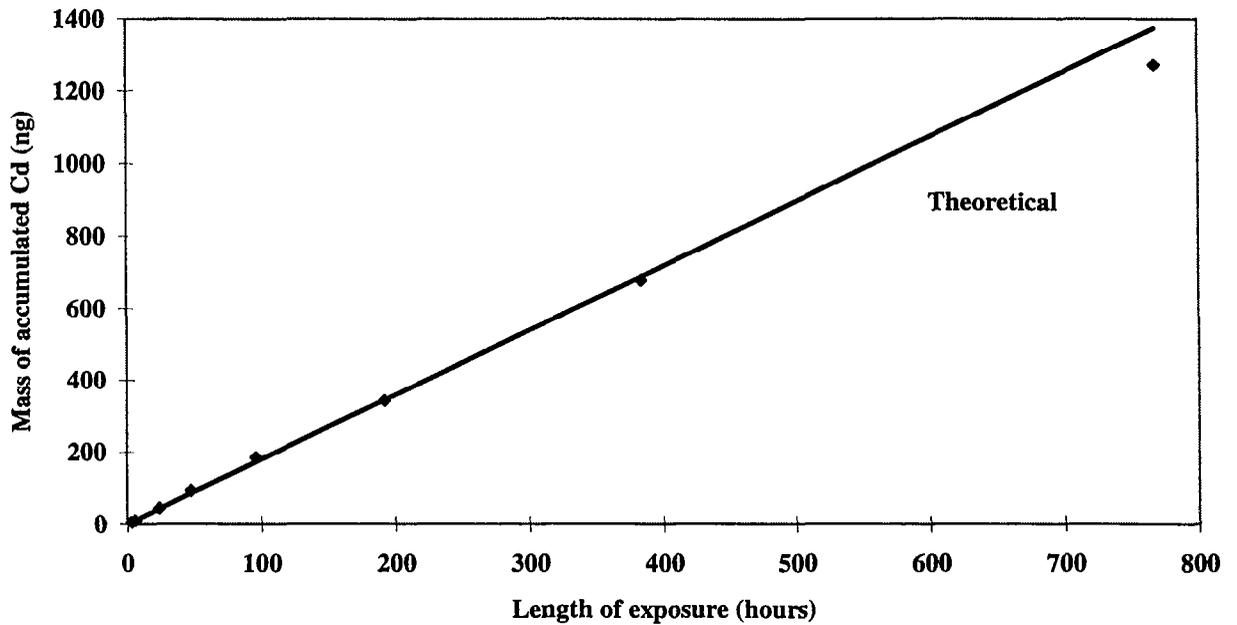


Figure 3.5 Relationship between measured mass of accumulated cadmium and exposure time. The line is calculated from the known exposure concentration using equation 2

3.7 Flow dependence

Trial 1 using Rhodamine dye to observe the flow of solution over the standard moulded holders, suggested that the design of the holder influenced the formation of a turbulent flow in the vicinity of the window. Trial 2 showed that the response of the standard and fluted holders were virtually identical and independent of flow (Figure 3.6). Larger holders had a lower response. Resin-gel collected from the centre of the larger perspex holders had a slightly better response than from the outside, indicating perhaps some shielding of flow at the edges of the gel in this deeply recessed assembly.

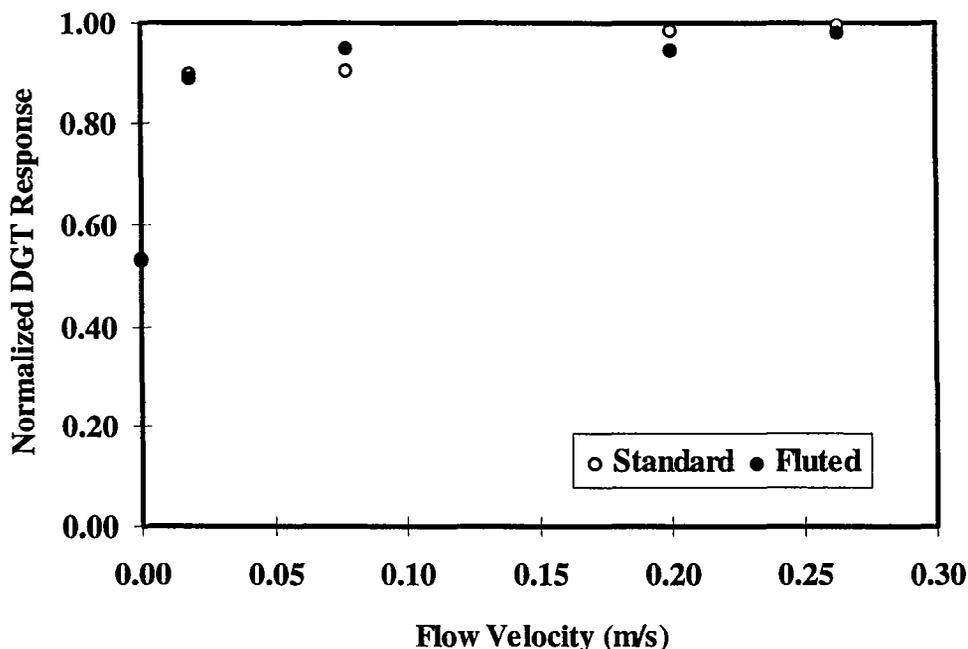


Figure 3.6 A comparison of the performance of two styles of holders at varying flow velocities, normalized to the response of the normal holder at 0.26 m/s.

The data illustrates that above a low threshold flow the effect of flow on the DGT response is small. Reducing the flow to zero results in a 50 % decline in accumulation independent of holder design. These general observations were replicated in trial 3 which showed that varying the angle of the DGT unit with respect to flow had only a small effect.

Key point: With the optimum holder design the effect of flow on the DGT response is minimal.

3.8 Measurement of other metals

Good, reproducible elution efficiencies were obtained for zinc, copper, lead, nickel and cobalt. For all of these metals the measured mass increased linearly with time and was theoretically predicted from the measured concentration in the exposure solution using equation 2.

Measurements of mercury at trace levels were initially complicated by apparent loss from the exposure solution by adsorption to container walls. Elution with acid spiked with gold was necessary to avoid mercury loss. At higher concentrations a theoretical DGT response was obtained.

Keypoint: DGT can measure zinc, copper, lead, nickel and cobalt simultaneously.

3.9 Full field-deployment in a fluvial environment

The newly designed funnel rig (Figure 2.4) worked well with no fouling by debris. Concentrations of cadmium and mercury measured in the Trent - Mersey canal by DGT were within expected ranges for this polluted system (Fig. 3.2). The mean concentration of dissolved (0.45µm filtered) cadmium measured in samples collected at the start and end of deployment was 0.59ppb. The mean DGT measurement was 64% of this value, which is excellent agreement when it is remembered that the DGT measurement excludes strongly bound and colloidal metal. Comparative measurements of both cadmium and mercury using an integrated sampler could not be relied upon, due to suspected contamination problems associated with the sampler. Mercury measured on samples collected at the start and end of deployment was below the limit of detection. Note that, due to in-built preconcentration, the concentration of both cadmium and mercury measured in the DGT eluent was much higher than in the canal, illustrating how DGT overcomes problems of both sensitivity and contamination.

Key point: Initial field trials demonstrated that DGT produces sensible results.

Element	Replicate	Concn in eluent	Concn in Canal
Cd	1	5.57ppb	0.337ppb
Cd	2	5.15ppb	0.330ppb
Cd	3	6.19ppb	0.396ppb
Hg	1	0.51ppb	0.032ppb
Hg	2	0.40ppb	0.025ppb
Hg	3	0.41ppb	0.026ppb

Table 3.2 Measurement of cadmium and mercury by insitu deployment of DGT in King's Loch on the Trent - Mersey canal from 7 August 1996. Concentrations measured in the DGT eluent are given as well as the derived insitu concentrations in the canal. Deployment time was for 142.5 hours at a mean temperature of 18°C.

3.10 Laboratory validation for radionuclides

Results for stable strontium and cesium were similar to those of cadmium. Good, reproducible elution efficiencies were obtained; the mass of elements accumulated in the resin gel was quantitatively predicted by equation 2 and it increased inversely with gel layer thickness (figure 3.8). The diffusion coefficient in the gel was measured to be the same as that in water and its temperature dependence predicted the DGT response.

DGT was shown to work with resins other than Chelex. However, because AGSOW-X8 is a general cation exchange resin it soon becomes saturated by cations such as calcium when used in a natural water. In these conditions the linear response with increasing exposure time is only valid up to 12 hours. Use of more selective resins for strontium and cesium will overcome this problem.

The response of the radionuclides was also theoretical (Fig. 3.9).

Key point: The DGT device has the potential to measure radionuclides.

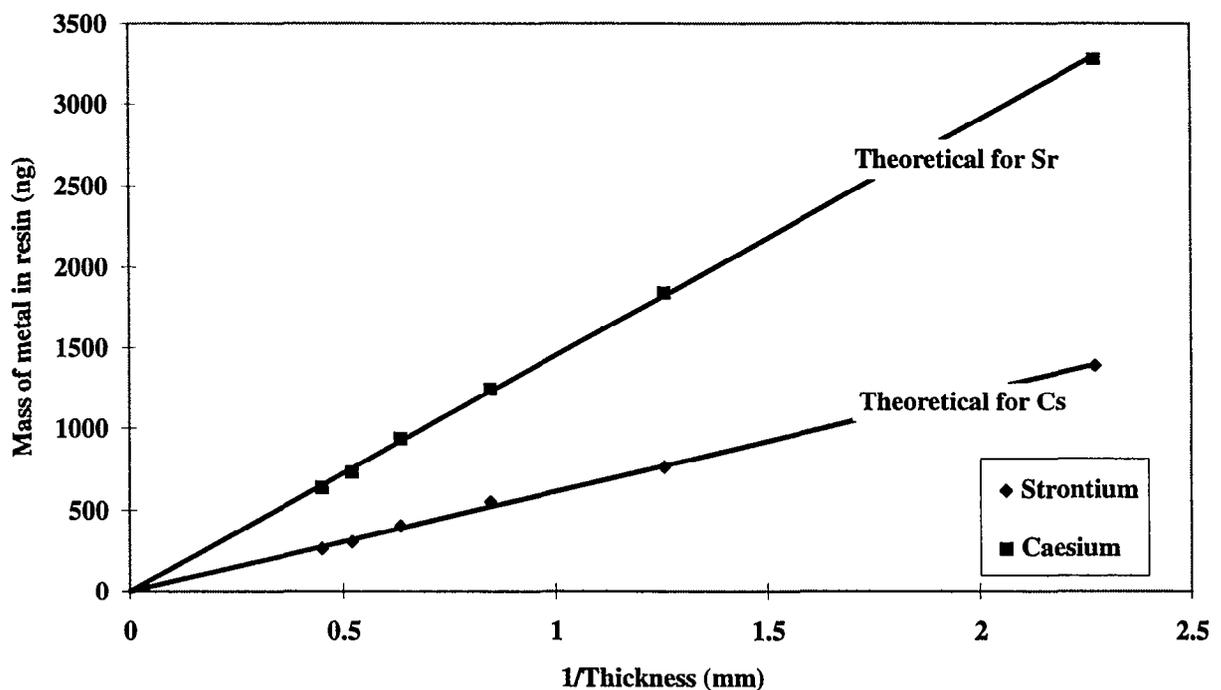


Figure 3.7 Dependence of measured mass of strontium and cesium accumulated in the resin layer on the reciprocal of diffusion layer thickness. The lines are theoretically predicted from the known concentrations in the exposure solution.

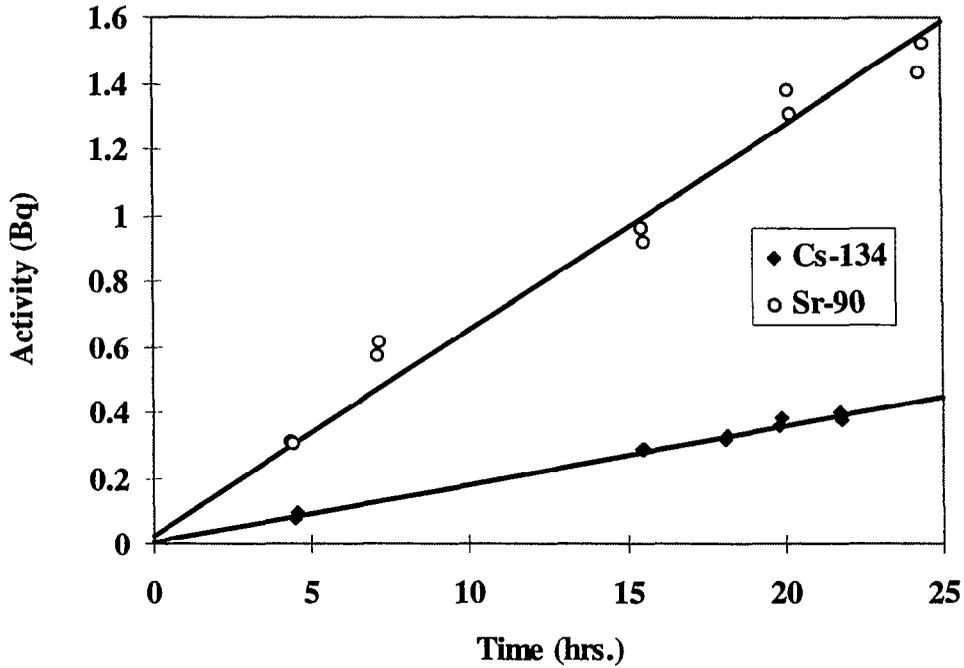


Figure 3.8 Measured activity of Cs-134 and Sr-90 accumulated in the resin layer for different deployment times. The lines are theoretically predicted from the known activities in the exposure solution.

3.11 pH and temperature

Between pH 4 and 8.3 a near theoretical response was obtained. These results are consistent with the properties of Chelex 100, which binds metals less efficiently at low pH.

The temperature dependence of the DGT measurement could be predicted from equation 3 and the known dependence of the diffusion coefficient on temperature.

Keypoint: The DGT response can be predicted for a given temperature and is independent of pH.

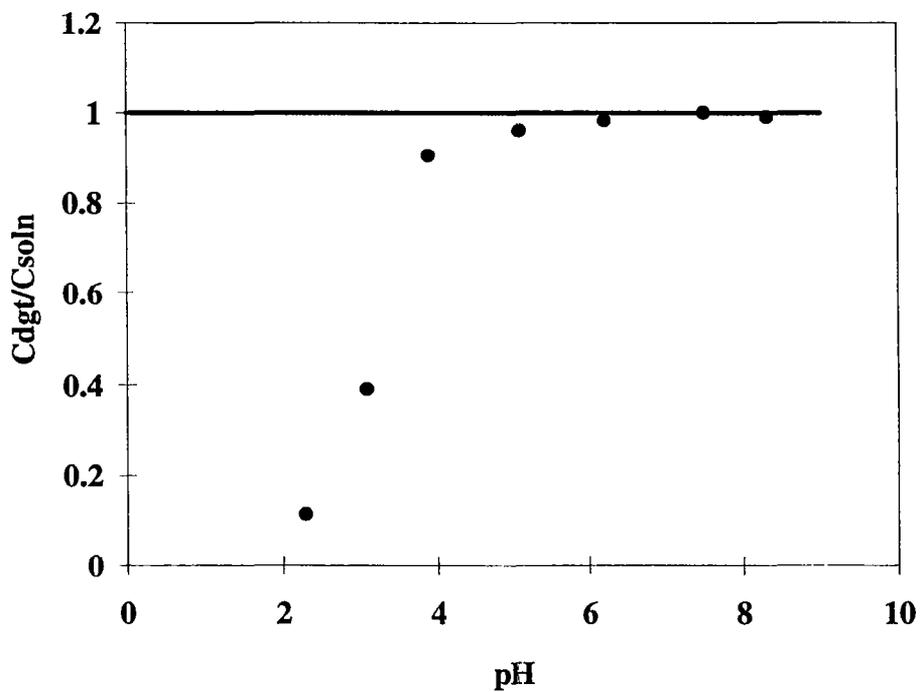


Figure 3.9 Effect of pH on DGT measurements assessed by the ratio of cadmium concentrations measured by DGT to the concentrations measured directly in solution using AAS.

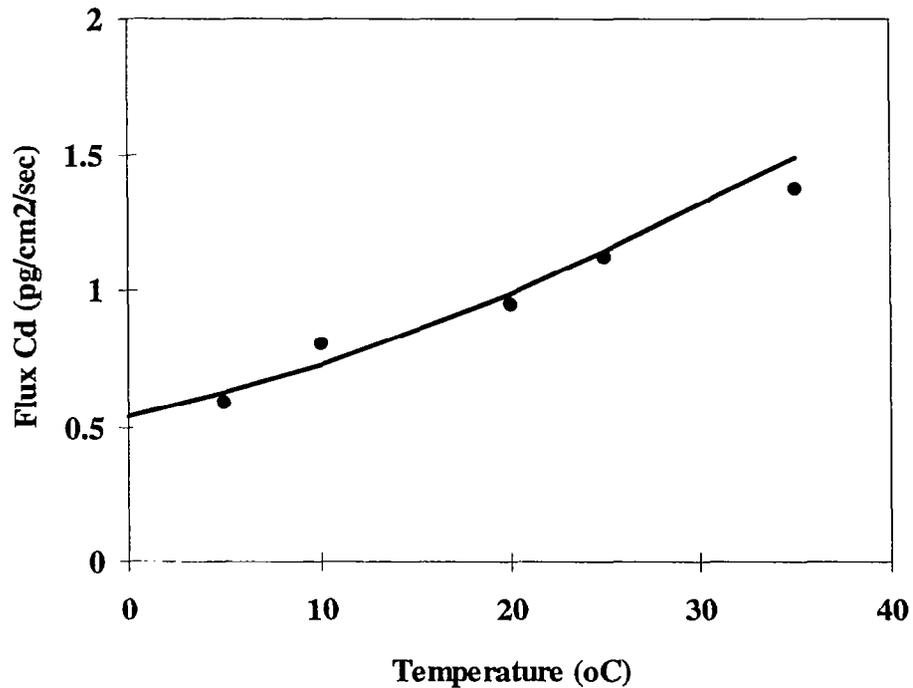


Figure 3.10 Temperature dependence of the diffusive flux of cadmium in CdCl₂ solution (8μg/l). The solid line is the theoretical line.

3.12 Storage

There was no significant difference between measurements made using freshly prepared DGT units and those which had been stored in sealed plastic bags for up to two months.

Keypoint: DGT units can be stored prior to deployment.

4. DISCUSSION

There are a number of factors that need to be considered in assessing the suitability of DGT as a practical *in situ* measuring and monitoring tool for metals in aquatic systems.

- **Ease of use.** Simple, cheap DGT units fabricated from plastic by injection moulding have been shown to be easy to use and to work reliably.
- **Calibration.** A major problem when using most *in situ* devices is calibration. With DGT this problem is overcome because the concentration is calculated from first principles each time. The only requirements are a knowledge of the precise geometry of the device, the time of deployment and the diffusion coefficient, D , for each solute. D is known for a given temperature. Measurements in the laboratory under a wide range of conditions have verified the theoretical prediction of the DGT response and the linear increase in the measured mass with both time and the reciprocal of the diffusion layer thickness.
- **Hydrodynamics.** Ideally the response of a measuring device should be independent of flow. Above a low threshold flow (<0.02 m/s) the DGT response shows relatively little dependence on flow. Such a finding is consistent with the design of DGT where diffusive transport of ions is controlled by the thickness of the gel layer. There will also be a diffusive boundary layer in the solution adjacent to the filter covering the gel, but if this is thin, relative to the gel layer thickness, its effect will be negligible. For all but the lowest flows this is likely to be the case. Generally DGT devices with thicker gel layers should be less dependent on flow.
- **Precision.** The precision achievable using DGT for the replicate measurement of trace metals of $\pm 5\%$ is good, as this variability includes the uncertainty of the final analytical measurement. At trace levels, AAS and ICP-MS rarely have much better precision than this. Moreover the DGT precision automatically includes other uncertainties, such as variations in the mixing regime and elution efficiencies. Whenever DGT is used essentially the same matrix is available each time for analysis by ICP-MS or AAS. Matrix problems are therefore minimised irrespective of the matrix of the water analysed.
- **Elution.** Although batch elution is not an ideal procedure, with DGT it produces remarkably consistent results. The consistency may in part be due to the reproducible nature of the resin-gel and the conditions, including acid strength, volume and exposure time.
- **Capacity and exposure time.** For a selective resin, such as Chelex, the capacity of DGT is sufficiently great to enable it to be deployed in principle for several weeks. It has been shown to measure cadmium quantitatively, irrespective of the exposure time, from one hour to one month. In a natural water such long exposures may be impractical due to biofilm formation, but the quantitative influence of such effects has yet to be tested. The DGT response is not affected by the extent of prior loading, providing saturation is not reached. For a non-selective resin, such as the general cation exchanger used for cesium and strontium, DGT can only be deployed for short times (<12hours) in freshwater. Other ions present at high concentration such as calcium quickly load the resin.
- **Multi-element.** In principle DGT can be used to measure any solute which binds strongly and rapidly to the resin being used. Chelex can bind several metals simultaneously. The features of DGT are therefore best exploited when it is allied to a multi-element analytical tool such as ICP-MS. Good elution characteristics and a linear DGT response with exposure

time have been demonstrated for zinc, cadmium, copper, lead, cobalt and nickel. Initial trials for chromium were not so successful. It is too early yet to decide whether the problem is due to analytical difficulties or whether DGT can be used in this way for chromium. Results for mercury were good at relatively high concentrations when mercury was measured directly in the solid phase rather than eluted. It is difficult to verify low-level mercury measurements in the laboratory due to loss of mercury by adsorption, although use of gold solutions appears to overcome this problem.

- Field trials. Measurement of cadmium and mercury in the Trent - Mersey canal using DGT was successful. Reasonable and reproducible values were obtained (cadmium 0.35 and mercury 0.028 ppb). It is impossible to field test fully the accuracy of DGT because there is no accepted equivalent technique which can be used. This is partly because DGT measures dissolved labile metal *in situ* and automatically provides a time-averaged mean concentration for the entire deployment period. Collected bulk samples for the period can never provide a fully equivalent mean concentration and the speciation of the metal may change in the stored samples.
- Radionuclides. Strontium and cesium were selected as elements with important cationic radionuclides. With a non-selective resin both elements gave theoretical DGT responses. More selective resins are likely to be required for natural samples. Chelex is probably suitable for strontium and there are selective binding agents for cesium. Sr-90 and Cs-137 were used to show that it is possible to measure radionuclides by counting the resin gel directly without elution. It should always be possible to count γ -emitters in this way, even for natural samples, but some pretreatment may be necessary for β -emitters. The dried thin film of resin has an ideal geometry for maximum counting efficiency and reproducibility. If a binding agent is very selective, sample separation could be sufficiently good *in situ* to allow direct counting with no further treatment. In principle it should be possible to measure any radionuclide by DGT, providing a suitable binding agent is available.

5. CONCLUSIONS

The feasibility of using DGT to measure trace metals in natural waters has been demonstrated. Although it is very simple in design and application, it can potentially be deployed for any duration of time, ranging from an hour to one month, giving fully-quantitative, time-averaged concentrations simultaneously for a variety of metals including zinc, cadmium, copper, lead, nickel, and cobalt and possibly mercury. While the initial analytical step and characterisation of the sample is made *in situ*, the final analytical measurements are made under controlled laboratory conditions. Since the device is able to accumulate trace metals to concentrations many times greater than the background levels, analysis is simplified and the potential for contamination is much reduced. It's ability to sample *in situ* overcomes the problems of changes in the nature of the chemical species during sample collection, preservation, and analysis. Concentrations are calculated from knowledge of the deployment time, temperature and measured mass of accumulated metal, so the often intractable problems of *in situ* calibration are avoided. Measurement of trace metal is fully quantitative in the tested pH range of 5-9 and the DGT response is almost independent of flow rate. Cadmium and mercury have been successfully measured in a river with an 8 day DGT deployment. The radionuclides Sr-90 and Cs-137 can be measured using DGT. DGT offers great potential as an *in situ* field device for monitoring concentrations of trace metals and radionuclides. The labile species which DGT measures are likely to be similar to the species available to biota, suggesting that DGT is likely to be a good surrogate measurement for bioavailability.

6. RECOMMENDATIONS

1. DGT should be more fully tested in a wide range of field conditions.
2. There should be further development work on the measurement of mercury and chromium by DGT.
3. Its use as a speciation tool and its potential use as a surrogate for bio-available metal should be investigated.
4. Its capability for measuring of Sr-90 and Cs-137 under field conditions should be investigated.
5. DGT should be further developed to include the measurement of a wider range of radionuclides including anionic species.
6. Its capability for measuring inorganic pollutants such as ammonia, nitrate and phosphate should be investigated.
7. The use of DGT to measure fluxes of potentially biologically available elements, including metals in sediments, should be investigated.
8. Commercial exploitation of the DGT device to make it widely available should be promoted.

7. REFERENCES

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