The use of diffusive gradients in thin films (DGT) for monitoring U and other trace metals in freshwater creeks potentially impacted by mining activities

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Further information

For further information on the use of diffusive gradients in thin films (DGT) for monitoring uranium and other trace metals in freshwater creeks potentially impacted by mining activities, please contact Associate Professor DL Parry and Dr NC Munksgaard at Charles Darwin University and Dr Claudia Sauerland at the Environmental Research Institute of the Supervising Scientist.

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1 Introduction

1.1 Ranger Uranium Mine

Ranger Uranium Mine is located on the Ranger mining lease within the Alligator Rivers Region (ARR), Northern Territory (Figure 1.1). The ARR comprises of an area of almost 33,000 km^2 which is roughly defined by the catchments of the East, South and West Alligator Rivers, a significant portion of which is occupied by Kakadu National Park (van Dam *et al.*, 2002).
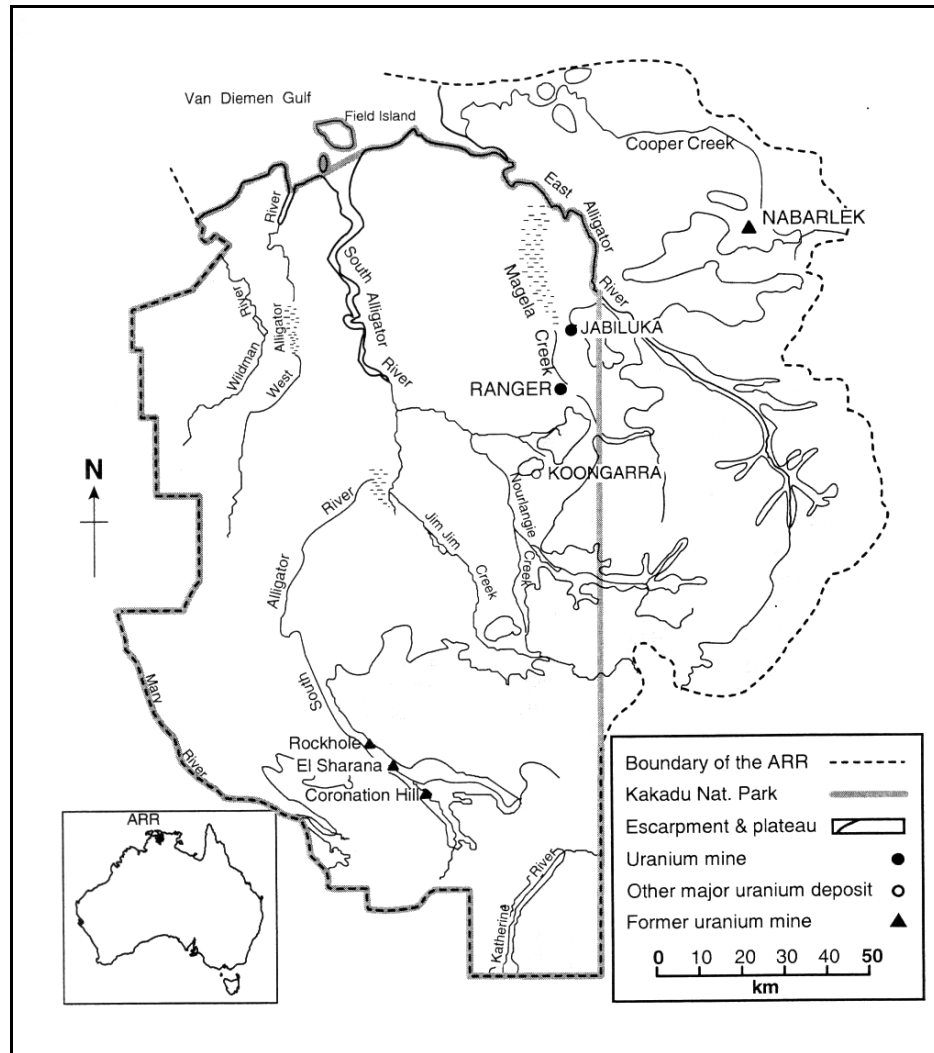
Figure 1.1 Alligator Rivers Region in northern Australia.

The main risk identified for ecosystems surrounding the mine site is from dispersion of mine waste waters to streams and shallow wetlands during the intense wet seasons associated with the tropical monsoonal weather of Northern Australia (Supervising Scientist, 2002a). This study focuses on the monitoring of potential mining impacts on Magela and Gulungul Creeks, which both lie within close vicinity to the Ranger site (Figure 1.1).

1.1.1 Natural input of metals

Prior to commencement of mining at the Ranger site, concentrations and loads of iron (Fe), manganese (Mn), zinc (Zn), cadmium (Cd) and copper (Cu) in Magela Creek were investigated by Hart *et al*. (1982). The results showed that dissolved (< 0.45 µm) metal concentrations in Magela Creek were low, with ranges of < 10 - 35 µg/L Fe, 2.5 - 8.2 µg/L Mn, 1.3 - 2.9 µg/L Zn, 0.16 - 0.45 µg/L Cu and 0.01 - 0.07 µg/L Cd. Hart *et al.* (1982) attributed these low levels to the undisturbed nature of the pristine catchments.

1.1.2 Mine related input of metals

The principle waste products from the Ranger site include uranium (U), magnesium (Mg), sulphate (SO_4^{2-}), and calcium (Ca) (Supervising Scientist, 2002a). Other metals, including Cu and lead (Pb) can be present in ore and waste rock with the potential of becoming mobilised in runoff water.

Each year Magela Creek receives mine-related effluent from a number of sources. The main source is RP1 from which mine waste water is passively released into Magela Creek via a near by Billabong during the later months of the wet season (Supervising Scientist, 2002a). Other contaminants that are washed into Magela Creek originate from waste rock and a land application area within close proximity to Magela creek (Supervising Scientist, 2002a; Energy Resources Australia, 2003).

Mine related effluent is never released into Gulungul creek, however it may receive mine related contaminants from two sources: (i) surface expression of groundwater which originates from tailings-dam seepage into a shallow aquifer, and (ii) overland flow of runoff from the external waste-rock surface of the tailings-dam (Supervising Scientist, 2002a).

1.2 Environmental monitoring of mining impacts

The discharge of mine waste into natural waters can have impacts on water quality in the environment and potentially threatens the survival of the ecosystem supported by that environment. Effective environmental monitoring is essential so that the impact of mining can be accurately measured and relevant mitigation procedures can be carried out.

1.2.1 The Water Quality Guidelines

Monitoring and assessment of aquatic environments involves the sampling, analysis and evaluation of water constituents and conditions with regards to specific water quality objectives as outlined in ANZECC and ARMCANZ Water Quality Guidelines (WQG) (ANZECC and ARMCANZ, 2000). The WQGs provide strategies for monitoring biological and physico-chemical indicators of water quality to ensure protection of the ecological health of aquatic ecosystems (ANZECC and ARMCANZ, 2000).

Aquatic ecosystems are affected by physical and chemical variations that can occur naturally within the environment, or due to human intervention. The consequent risk posed to the health of the ecosystem can be assessed by monitoring physical, chemical and biological aspects of water and sediment, based on a number of indicators. These include biological (e.g. fish and macro

invertebrates), physical and chemical (e.g. physico-chemical parameters) and toxicants (e.g. metals) (ANZECC and ARMCANZ, 2000).

Water quality monitoring is often conducted using integrated methods that combine assessment of the above mentioned indicators, however this study focuses on the assessment and monitoring of toxicants, specifically metal. Metals are monitored based on comparison of measured indicator values to guideline trigger values as outlined by the WQGs (Table 1.1) (ANZECC and ARMCANZ, 2000). Trigger values are determined using a three tiered structure of preferred approaches, 1) local biological effects, 2) reference site data and 3) default values tailored to local conditions (ANZECC and ARMCANZ, 2000). Site specific trigger values for Magela Creek have been derived for U using the first above mentioned approach, based on site specific toxicity data and for Mn using the second approach, based on statistical distribution of reference site data collected over the past 20 years (van Dam, 2000; Klessa, 2000). For other metals, trigger values are derived using the third approach, by tailoring default guidelines to suit specific local environmental conditions. The default guidelines for toxicants in water are derived from biological effects databases from Australia/New Zealand and overseas (ANZECC and ARMCANZ, 2000). The waterways within Kakadu National Park, which is a World Heritage listed site of very high conservation/ecological value, are monitored at the highest level of protection (for 99% of all species) as outlined in the WQG (ANZECC and ARMANZ, 2000).

Table 1.1 ANZECC and ARMCANZ (2000) recommended trigger values for metals of concern (for protection of 99% of all species)

Metal	Trigger values for freshwater (µg/L)
Manganese	32*
Aluminium	27
Uranium	5.8^
Zinc	2.4
Lead	1.0
Copper	1.0
Cadmium	0.06

* Site specific trigger value based on reference site data (Klessa, 2000).

^ Site specific trigger value based on biological effect data (van Dam, 2000).

1.2.2 Water sampling

Water samples for monitoring metal concentrations should ideally be representative of the natural environment. This includes taking into account natural temporal and spatial variations that occur in the environment (Cornelis *et al.*, 2003). Wet season stream flows of Magela and Gulungul Creeks typically comprise of a series of peak flows superimposed on the base flow (Supervising Scientist, 2004). This hydrological fluctuation of stream flow causes variation in total loads and concentrations of metals in the creek water (Hart *et al.*, 1982). Therefore the sampling regime of a monitoring program must take into account the rise and fall of water and metal concentrations.

Grab sampling and composite sampling

Grab sampling measures the instantaneous characteristic of the sampled water at the specific time of sample collection whereas composite sampling provides a means of continuous representative measurements over time (ANZECC and ARMCANZ, 2000). Where quality and accuracy are of major concern grab sampling is preferred, however maximum effects are only measured when the sampling is carried out during flows that are likely to contain maximum metal concentration, which can be difficult to achieve. In contrast, composite sampling is better where the interest is in means, trends and overall loads on the environment.

Regardless of the sampling method used, a problematic aspect of water sampling is the preservation of sample constituents to ensure that the water analysed in the laboratory is truly representative of the water in the environment (Emons, 2003). During sample collection, transport and storage, physical changes occur (e.g. variation in temperature and partial pressure of carbon dioxide) that cause fluctuation of physico-chemical parameters such as pH, ionic strength and dissolved oxygen. Changes in pH reflect changes in acid-base equilibria and coupled redox and complex formation reaction equilibria which can significantly affect the species distribution of metals present in the sample (Cornelis *et al.*, 2003).

1.3   Metal speciation and toxicity

In water quality monitoring for ecosystem protection the interest lies primarily in toxic forms of metals. The toxic affect of a metal depends not only on its abundance but also on its bioavailability, defined as the ability of a metal to bind to or traverse the cell surface of an organism (Sunda and Huntsman, 1998). The effect of a metal on the ecosystem depends on its exact chemical form, or speciation. Species that are typically available for uptake by organisms include free metal ions (e.g. $[M(H_2O)_6]^{n+}$ for octahedral coordination of metal ion M^{n+}) and labile complexes (e.g. $[ML_6]^{n+}$ for octahedral coordination of metal ion M^{n+} with a neutral ligand, L) (Bailey *et al.*, 2002).

The most basic operational definition of metal speciation is the fractionation of species on filtration through a 0.45µm filter membrane. The < 0.45µm filtrate is referred to as the dissolved fraction and contains free metal ions, metals complexed to inorganic and organic ligands, and fine colloidal matter. The > 0.45 µm fraction that is excluded is classified as particulate matter and can contain a variety of material including micro-organisms, large organic molecules, clays, carbonates and metal oxides (most commonly Al, Fe and Mn) (Sondi and Pravdić, 1998). The concentration of metals in the dissolved fraction is generally considered to be of greater importance as it contains the majority of bioavailable species. Metals in the particulate fraction are generally strongly associated with or adsorbed to large colloidal and suspended material, which substantially reduces their bioavailability (Nolan *et al.*, 2003).

However, the dissolved concentration is not directly indicative of toxicity as only the bioavailable fraction (free-metal ions or labile complexes) contribute to toxicity (Nolan *et al.*, 2003). Other constituents of the dissolved fraction, such as fine colloidal matter and stable complexes are not bioavailable and therefore, do not contribute to toxicity (Sunda and Huntsman, 1998).

1.3.1 Models describing the role of the free metal ion and labile metal complex in toxicity

Both the free ion activity model (FIAM) and the biotic ligand model (BLM) show that a large proportion of the bioavailable fraction of the total metal concentration is made up of the free metal ion, and that weakly bound metal complexes, or labile complexes, are also able to interact with cell surface binding sites potentially inducing toxicological effects.

Free ion activity model

The FIAM was developed to rationalize and explain the importance of free metal-ion activities in determining the uptake and toxicity of trace metals. The FIAM has effectively shown the role of the activity of the free metal ion in regulation of interactions between metals and aquatic organisms (Nolan *et al*., 2003). The activity of the free metal ion is based on its interaction with cell surface-binding sites, with which free metal ions are believed to be in rapid equilibrium (Sunda and Huntsman, 1998). In contrast, metal species present as colloidal matter or complexed to strongly binding ligands are considered to be biologically inactive as they are not available to interact with the cell surface-binding sites (Nolan *et al.*, 2003).

Biotic ligand model

The BLM is a mechanistic approach to understanding the partitioning and uptake kinetics of metals in solution (Duffus, 2003). Biotic ligand models are essentially based on the hypothesis that metal toxicity is related to both metal-ligand complexation in solution as well as metal interactions with competing cations for the surface cell receptor (Playle, 1998). These models are developed by mathematically integrating the interaction of a metal with ligands affecting its speciation and its subsequent interaction with receptor sites on the organism, which are also treated as a ligand and referred to as the biotic ligand (Nolan *et al.*, 2003). The amount of metal that is available to bind to a cell surface receptor is determined by the competition for metal ions between the biotic ligand and other aqueous ligands as well as the competition for the biotic ligand between the toxic metal ion and the other cations in solution (Nolan *et al*., 2003).

1.3.2 Factors influencing metal speciation

Ultimately, metal speciation is dependant on the physical and chemical properties of the metal (e.g. oxidation state, size) and a number of physico-chemical variables (e.g. pH, dissolved oxygen, ionic strength) (Bailey *et al.*, 2002). The properties of a metal define its interactions with the physical environment while the physico-chemical variables control complex equilibrium reactions that influence metal speciation.

Metal complexation

Metal speciation in freshwaters is largely controlled by complexation reactions (Davidge *et al.*, 2001). A metal complex is essentially the product of a Lewis acid-base reaction in which ligands donate electrons to form a coordinate covalent bond with a central metal ion. Metal complex formation and stability is dependent on the chemical properties of both the ligating molecules and the metal ions, with each expressing varying affinities for the other. The stability of metal complexes can be defined by the stability constant (K_s), which is the equilibrium constant associated with the formation reaction of a metal complex from the ligand and the free metal ion (Grzybowski, 2000; Davidge *et al.*, 2001). Compared to organic complexation, the formation constants for inorganic complexes are well known (Antelo *et al.*, 2000).

Ionic strength and water hardness

Ionic strength is related to the total concentration of dissolved inorganic ions (mainly Na^+ and Cl^-, but also Ca^{2+}, Mg^{2+}, K^+, CO_3^{2-} and SO_4^{2-}) and is measured as electrical conductivity (EC). The concentration of major divalent cations (Ca^{2+} and Mg^{2+}) alone is referred to as water hardness. These cations are able to compete with metals of similar charge (e.g. Fe^{2+}) for cell binding sites of aquatic organisms (Sunda and Huntsman, 1998). In this way, the ionic strength and more specifically water hardness are able to mitigate metal uptake by biota.

Total organic matter

Organic matter in freshwaters is typically measured as total organic carbon (TOC) or dissolved organic carbon (DOC). Trace metals in natural waters are commonly complexed by natural and anthropogenic organic molecules (Antelo *et al.*, 2000; Zhang and Davison, 2001). Naturally occurring humic substances dominate organo-metallic binding in pristine freshwaters where anthropogenic input of organic matter is limited (Bailey *et al.*, 2002). Humic substances are macromolecular aromatic rings that originate from decaying vegetation and have high capacity for binding metal ions due to oxygen, hydroxyl, carboxyl and nitrogen functional groups (Tipping *et al.*, 2002). The most important of these functional groups are the carboxcylic acids which due to their low pK_a values (the equilibrium constant for the ionization reaction), are mostly dissociated in natural waters of circum-neutral pH. The negative charge of the resulting carboxylate ion enables the organic compound to bind heavy metals (Davis, 1984).

pH

The pH is a measure of the hydrogen ion concentration in solution and essentially gives an indication of the relative concentrations of hydrogen (H^+) and hydroxide (OH^-) ions present (Bailey *et al.*, 2002). Neutral water has pH 7 and indicates equal concentrations of hydrogen ($[H^+]$) and hydroxide ions ($[OH^-]$), whilst acidic waters have low pH (< 7) with high $[H^+]$ and basic waters have high pH (> 7) with high $[OH^-]$.

Changes in pH can affect the toxicity of metals by influencing the stability of metal complexes (ANZECC and ARMCANZ, 2000). When the anion of a typically stable complex is the conjugate base of a weak acid, a decrease in pH can cause the dissociation of the complex into the anion base and free metal ion, hence increasing the concentration of free metal ions in solution (Bailey *et al.*, 2002).

Alkalinity

Alkalinity is the acid neutralizing capacity of natural waters and is based on the concentration of bicarbonates (HCO_3^-) and to a lesser extent, carbonates (CO_3^{2-}) and hydroxides (OH^-) (Bailey *et al.*, 2002). These species are able to buffer pH change by binding and removing excess H^+ from solution. Metal availability can be influenced by alkalinity due to the formation of insoluble metal carbonate complexes (e.g. $CuCO_3$ and $PbCO_3$) (Riethmuller *et al.*, 2001).

Suspended particulate matter

Suspended particulate matter (SPM) consists of insoluble particles that are greater than 0.45μm, such as suspended clay, silt, phytoplankton and detritus (ANZECC & ARMCANZ, 2000). Metals can be strongly adsorbed to SPM reducing the concentration of free metal ions in solution (Sondi and Pravdić, 1998). Suspended particulate matter also acts as an efficient transport medium, carrying metals through aquatic systems (Hart *et al.*, 1982). The concentration of SPM

is flow dependant and increases with flood events as sediment is either washed into the creeks from catchments or is re-suspended from creek bed deposition (Evans *et al.*, 2003).

1.3.3 Speciation analysis for metals in freshwater

Methods for metal speciation in solution include analytical analysis and thermodynamic modelling.

Analytical Methods

Typical methods for species determination and measurement are strictly limited to complex laboratory analysis. There are essentially two approaches to analysis of metal species in collected water samples. The first is the direct measurement of free or labile metal ions (e.g. anodic stripping voltametry) and the second is an indirect measurement where a new metal species is formed on addition of a competitive ligand that is then quantified (e.g. competitive ligand analysis) (Alfaro-De la Torre *et al.*, 2000). Although analytical methods are useful for species determination and measurement they are limited by availability, reliability and sensitivity. This has lead to an increase in the use of thermodynamic modelling techniques for speciation of metals in specific environments.

Thermodynamic Methods

Thermodynamic models are essentially an indirect mathematical method for estimating metal speciation based on measured total dissolved ligand and cation concentrations along with reference to extensive speciation databases (Hunter *et al*., 1999). The accuracy of these types of methods depends on the accuracy of the identification and quantification of ligands present in natural waters. At this stage little is known about the nature of many of these ligands nor the complex equilibrium constants that describe metal interactions with natural ligands, particularly dissolved organic molecules such and humic substances (Antelo *et al*., 2000).

Both analytical and thermodynamic speciation methods require *ex situ* analysis of water samples. Therefore both methods are limited by the alteration of metal speciation during sample collection, transport and storage.

1.4 Diffusive gradients in thin films (DGT)

The diffusive gradients in thin films (DGT) technique is a unique method designed by Davison and Zhang (1994) allowing for *in situ* measurement of dissolved free metal ions and labile metal complexes, representing bioavailable metals.

1.4.1 DGT theory

The DGT sampler comprises of a gel assembly that is enclosed in a piston-like plastic casing (Figure 1.2). The plastic casing comprises of separate base and cap components which when pressed together exclude water from within device except through a 20 mm diameter exposure window in the cap. The gel assembly consists of a high affinity cation exchange binding resin (Chelex-100) embedded in a polyacrlyamide hydrogel which is separated from the bulk solution by a polyacrlyamide diffusive gel of standard uniform pore size and thickness, and a cellulose nitrate 0.45µm membrane filter (to exclude particulate matter).
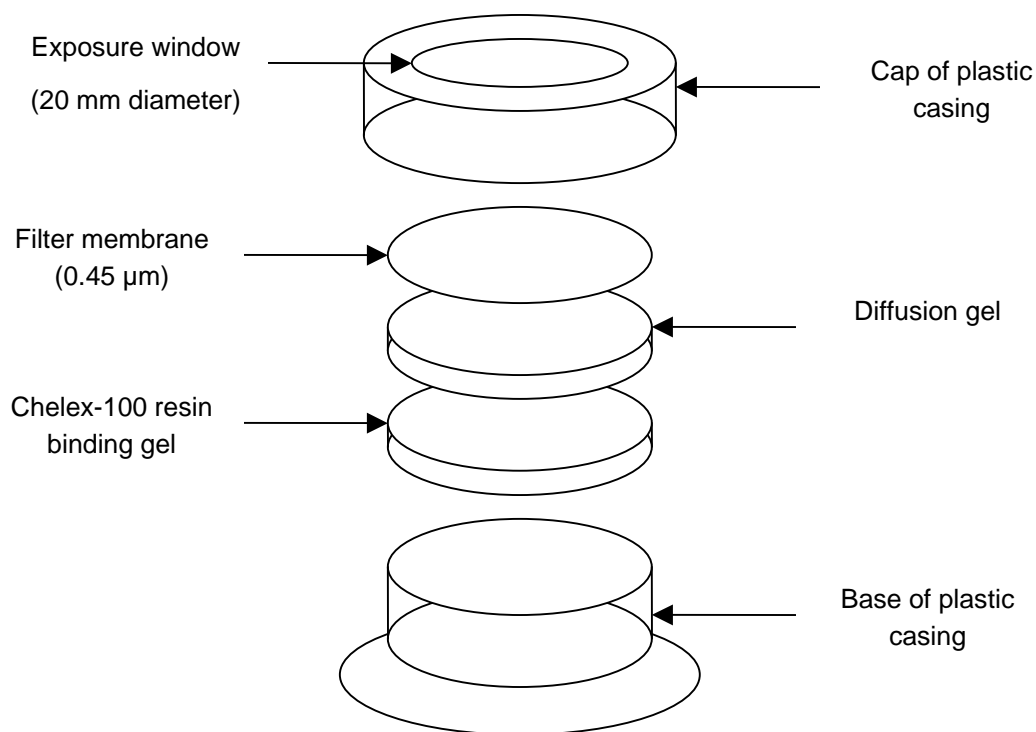
Figure 1.2 DGT assembly

When DGT devices are submerged in solution, water and its constituent dissolved (< 0.45 µm) metal species are able to diffuse into the device via the exposure window. After traversing the diffusive layer metals ions that come in contact with the Chelex-100 become bound and permanently immobilized by binding sites on the resin (Bio-Rad Laboratories, 2000). Assuming the metal ions bind quickly and efficiently to the resin gel, the concentration of metals at the resin-diffusion gel interface effectively remains as zero, resulting in the formation of a linear concentration gradient across the diffusive layer and hence continuous metal uptake until the resin reaches saturation (Figure 1.3) (Zhang and Davison, 1995). The capacity of Chelex-100 resin is 0.4 meq/mL, therefore the maximum capacity of the binding gel is determined by the amount of Chelex-100 resin it contains, which is approximately equal between individual devices (Bio-Rad Laboratories, 2000).
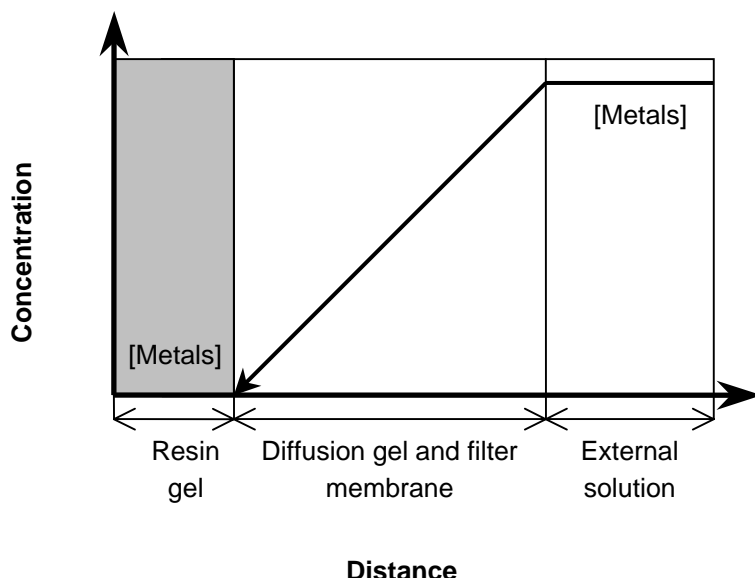
Figure 1.3 Linear concentration gradient for metals across the diffusive gel, where [Metals] is metal concentration.

The DGT measures the amount of metal that diffuses into the device over a period of time per unit area. The kinetics of metal transport into the DGT is controlled by the diffusive gel through which metals diffuse at rates based on their respective diffusion coefficients, as defined by the size of the metal compared to the pore size of the gel (typically 2-5 nm) (Zhang and Davison, 1999). The measured flux of metals accumulated in the resin gel over a given period of time is used to calculate the concentration of metals in the bulk solution to which the DGT was exposed.

1.4.2 Advantages of DGT technique

The DGT technique offers a number of advantages over the current methods for water sampling and assessment for the purposes of water quality monitoring.

The metals measured by DGT are referred to as DGT-labile metals and include free metal ions and labile metal complexes, which comprise the fraction of dissolved (< 0.45 μm) metals that are available for uptake by biota and thereby capable of causing a toxic response. Essentially the DGT-labile concentration is an approximation of the bioavailability of a metal (Luider *et al.*, 2004).

Free metal ions present in solution are able to easily diffuse into the DGT device where they are bound and immobilized in the resin gel (Zhang and Davison, 1994). Metal complexes are also able to enter the device, however their measurement depends on their stability and whether or not the complex undergoes dissociation during the time taken to traverse the diffusion layer (Zhang and Davison, 1994; Zhang and Davison, 1995). Labile complexes have low stability constants and therefore undergo rapid ligand exchange reactions during which the metal ion becomes available to bind with the resin gel (Zhang and Davison, 1995). The ligand exchange for stable complexes is much slower and therefore the metal ion may not become available during its residency in the diffusion layer.

In contrast to conventional metal speciation measurements which involve analysis of water samples, the DGT device is capable of *in situ* speciation by the differentiation and uptake of

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DGT-labile species during deployment in solution. The DGT technique also avoids the problematic behavior of metal species in collected water samples as metals that are bound to the resin gel are unaffected by changing physical parameters.

Because of the large capacity of the binding gel, DGT devices are able to be deployed for substantial periods of time, over which they continue to accumulate metals (Zhang and Davison, 1995). Therefore the resultant DGT measurement is a time integrated average of metal concentrations over the whole deployment period, including the variations caused by changes in hydrology (Meylan *et al.*, 2004).

1.4.3 Parameters affecting DGT measurement

Temperature
The rate of mass uptake is influenced by temperature as it is proportionally related to the diffusion coefficient of the analyte. Values for diffusion coefficients of metals through the polyacrylamide hydrogel are based on those in pure water (Zhang and Davison, 1994; DGT-Research Ltd., 2003).

Flow rate
In quiescent waters with flow < 0.02 m/s, a diffusive boundary layer (DBL) develops at the interface between the solution and the solid surface of the DGT sampler (Gimpel *et al.*, 2001). Formation of a DBL essentially increases the thickness of the diffusion layer and therefore interferes with the mass transport. Gimpel *et al.* (2001) found that above a low threshold flow of 0.02 m/s the mass of metals measured by the DGT was virtually independent of flow, whereas reducing the flow to zero resulted in the DGT only measuring 50% of the solution concentration. Therefore, if flow is maintained above the low threshold value of 0.02 m/s, the thickness of the DBL is assumed be negligible.

pH
The DGT technique has been found to work accurately for a number of metals over the pH range 4.5 – 9 (Zhang & Davison, 1995; Gimpel *et al.*, 2001). Chelex-100 is less efficient at binding metals at low pH as metal ions are in competition with high concentration of hydrogen ions present in solution for binding sites in the resin (Gimpel *et al.* 2001; Bio-Rad Laboratories, 2000). At lower pH Chelax-100 preferentially binds metals in the order $Cu > Pb >>> Zn > Cd$ (Bio-Rad Laboratories, 2000).

Ionic strength
Recent studies have shown that DGT measurement is inaccurate in synthetic laboratory solutions of low ionic strength, as adjusted using soluble sodium and calcium salts (e.g. $NaNO_3$ and $CaCl_2$) (Alfaro De la Torre *et al.*, 2000; Sangi *et al.*, 2002; Peters *et al.*, 2003). A number of theories have been suggested to explain DGT behaviour at low ionic strength.

Alfaro De la Torre *et al.* (2000) suggested that the DGT technique was not reliable for quantitative measurements of metals in solutions with ionic strength (Σ [Mg^{2+}, Na^+, K^+, Ca^2]) less than 0.2 mM. DGT performance in low ionic strength solutions is thought to be hindered by interference in metal diffusion by the counter-diffusion of Na^+ across the diffusive layer. The overall effect is an increase in the diffusion coefficients of the metals entering the DGT.

Peters *et al.* (2003) have suggested that the erratic behavior observed at low ionic strength is due to the ability of the diffusion gel to competitively bind cations with a low affinity for metal ions, thus the binding of metal ions is increased when there are insufficient excess cations present in solution to saturate the binding sites.

The ionic strength effect is of great importance in this study because the ionic strength of the natural waters in the ARR is extremely low. Hart *et al* (1982) found the electrical conductivity (EC) range of Magela Creek was 10.3 to 21.3 µS/cm, which is in agreement with the conductivity ranges observed more recently (Supervising Scientist, 2002b).

1.5 Objectives

This study focuses on the improvement of the water quality monitoring program of freshwater environments potentially impacted by the mining of uranium at Ranger. Specifically, this study investigates the use of DGT devices as tools for continuous monitoring of DGT-labile metal concentrations in Magela and Gulungul Creeks.

This is achieved by laboratory validation of DGT method under controlled conditions, focusing on the effects of low ionic strength. The DGT technique is then assessed under field conditions in trials involving deployment of the DGT devices in Magela and Gulungul Creeks for one week periods over a total of seven weeks. Metal concentrations measured by DGT are compared to concentrations measured in unfiltered and filtered (< 0.45 µm) water samples obtained using grab sampling technique to draw conclusions on the suitability of the method for ongoing monitoring.

2 Methods

2.1 Study design

This study consisted of laboratory based DGT method evaluation and subsequent field trials. Method evaluation involved experiments using either synthetic or filtered (< 0.45 µm) creek water test solutions in order to investigate DGT performance under controlled conditions. Field trials were conducted to investigate DGT performance under natural environmental conditions. For both components DGT performance was assessed by comparing metal concentrations measured by DGT with that in grab water samples collected simultaneously to DGT deployment.

2.2 Cleaning methods for plasticware and glassware

All plasticware and glassware was initially rinsed with high purity deionised Milli-Q (MQ) water (< 8 MΩ/cm) prior to soaking in 5% (v/v) nitric acid (HNO_3) for at least 24 hours. Items used for laboratory experiments were then thoroughly rinsed with MQ water followed by soaking in fresh MQ water for at least 24 hours before final rinsing. Items used for collection and analysis of field samples were soaked for a further 24 h in 5% (v/v) hydrochloric acid (HCl) prior to MQ rinsing and soaking. The DGT casings were soaked in 5% (v/v) HCl only, followed by MQ rinsing and soaking, as HNO_3 was found to 'stain' the plastic.

2.3 DGT preparation and analysis

The procedure used for assembly of fresh DGT devices and disassembly and analysis of exposed DGT devices were consistent for all DGTs used throughout this study. All DGT manipulations were carried out in a class-100 clean room within a laminar flow hood using trace metal clean procedures.

2.3.1 DGT components

The plastic casings used to enclose the gel assembly were similar to the piston-type described by Zhang and Davison (1995), with a 20 mm diameter exposure window.

Cellulose nitrate (0.45 µm, GN - 6 Metricel, Pall Gelman Laboratory) filter membranes (thickness 0.0153 cm) were used in DGT devices. They were cleaned by soaking in 3% HNO_3 for 1 hour followed by successive soaking and rinsing with MQ water.

The gel components were obtained from DGT Research Ltd. (Lancaster, UK). The Chelex -100 resin gel was supplied in pre-cut 25 mm diameter discs that were stored in 0.01 M sodium nitrate ($NaNO_3$) at < 4 °C. The diffusive gel (agarose polyacrylamide, thickness 0.08 cm) was supplied in 13 cm^2 sheets which were stored in 0.01 M $NaNO_3$ at room temperature.

2.3.2 DGT assembly

Assembly was carried out on an acrylic plate using clean pipette tips for handling the gel and filter components. An acrylic disc cutter (DGT Research Ltd.) was used to cut 25 mm diameter discs from the diffusive gel sheets. The acrylic plate and pipette tips were stored in 5% (v/v) HCl

and the disc cutter was stored in 5% (v/v) HNO_3. Prior to use, the plate, tips and cutter were rinsed thoroughly with MQ water until the conductivity of the run off was less than 0.6 µS/cm.

DGT devices were assembled by placing the resin gel disc on top of the piston so that the embedded layer of Chelex-100 resin was on the surface. The diffusive gel disc and filter membrane were then placed on top of the resin gel successively and the cap was carefully pushed over the piston and pressed to ensure a good seal. The quality of the seal between the cap and the filter membrane was routinely tested by placing a few drops of MQ water on the exposure window surface of each DGT and checking for leakage. DGT devices were stored in polypropylene (PP) jars with a few drops of MQ water to prevent drying out.

2.3.3 DGT disassembly

DGT disassembly was carried out on the same acrylic plate used for assembly. The cap was pulled from the piston and using clean pipette tips, the entire gel assembly was lifted and flipped over onto the acrylic plate so that the resin gel was on the top. Using pipette tips, the resin gel was transferred into a 15 mL vial and the diffusion gel and filter membrane were discarded.

2.3.4 DGT resin gel elution

Metals accumulated in the resin gel were eluted using acid extraction by adding 2 mL 10% HNO_3 (Aristar grade, Merck) to the gel in the 15 mL vial, which was then placed in a temperature controlled orbital shaker at 30 ℃ and 100 rpm for 12 h. The 2 mL eluent was then diluted and analysed for metals using Inductively Coupled Plasma – Mass Spectrometry (ICP-MS) (see 2.6.2).

2.3.5 DGT calculations

Using the concentration of metals accumulated in a DGT device (as measured by ICP-MS analysis of DGT eluate), the metal concentration in the bulk solution to which the DGT sampler was exposed was calculated using the procedure of Zhang and Davison (1995) and DGT Research Ltd. (2003).

In practice, only a fraction of the bound metals are eluted from the Chelex-100 resin in the binding gel (Zhang and Davison, 1995). The efficiency of the elution, f_e, is given by the ratio of the eluted metal to the remaining bound metal, which is typically 0.8. The concentration of metal ions in the eluent, C_e (µg/L) was measured using ICP-MS and converted to mass, M (µg) using equation (2.1).

$$M = \frac{C_e\left(V_e + V_g\right)}{f_e}$$
(2.1)

where V_e was the volume (L) of eluent and V_g was the volume (L) of the binding gel (which was negligible compared to the volume of the eluent).

The flux, J, of the metal ions diffused through the gel layer was calculated from the M diffused through the given surface area, A (cm^2) after deployment time, t (s),

$$J = \frac{M}{At}$$
(2.2)

Fick's law of diffusion can also be used to calculate the flux,

$$J = \frac{D(C_b - C')}{\Delta g} \qquad (2.3)$$

where Δg is the thickness of the diffusion layer (diffusion gel + membrane filter) (cm), D is the diffusion coefficient (cm^2/s) of the diffusing metal, C_b is the concentration (μg/mL) of DGT-labile metal in the bulk solution and C' is the concentration of the metal ion at the interface between the binding gel and the diffusion gel. Because of the high affinity of Chelex-100 resin for metal ions, metals adjacent the binding gel are assumed to be bound quickly and efficiently, thus the concentration of metals (C') is assumed to be zero. Therefore, flux is given by,

$$J = \frac{DC_b}{\Delta g} \qquad (2.4)$$

Equations (2.2) and (2.4) can be rearranged to equation (2.5), which allows determination of the concentration of metals in the bulk solution during the time of deployment.

$$C_b = \frac{M\Delta g}{DAt} \qquad (2.5)$$

Throughout this study the diffusion coefficients of metals used to calculate the concentration in bulk solution were those recommended by DGT Research Ltd. (2003).

2.4   Laboratory methods

Experiments were performed by deploying DGT devices for varying periods of time in either synthetic or filtered (< 0.45 μm) creek water test solutions.

2.4.1 Laboratory test solution preparation

Synthetic test solutions

Standard mixed metal (Al, Fe, Mn, Cd, Cu, Zn, Pb and U) stock solutions (10 mg/L) were prepared from 1000 mg/L metal standards (BDH, Merck) using MQ water. Synthetic test solutions were prepared in 4 L low density polyethylene (LDPE) containers by spiking 4L MQ water with mixed metal stock solution to concentrations of 10 or 100 μg/L. The ionic strength of the test solutions was adjusted using analytical grade NaNO$_3$, to concentrations of 0.2, 2 and 20 mM. The pH of test solutions was adjusted using 0.1M sodium hydroxide (NaOH) solution.

Creek water test solutions

The creek water was collected in acid washed high density polyethylene (HDPE) 20L barrels from Gulungul Creek and was filtered using 0.45 μm filter membranes (Gelman, Pall Laboratory) and stored at < 4 ºC until use. The creek water test solutions were prepared by spiking 4 L filtered creek water to 10 or 50 μg/L using 10 mg/L mixed metal stock solution (as above). The pH was adjusted to 4.0, 4.5, 6.0 and 6.5 using 0.1 M HNO$_3$ or 0.1 M NaOH. The range included the minimum and maximum pH extremes observed in Gulungul and Magela Creeks over the 2002-2003 wet season (Supervising Scientist, 2002b).

Details for the composition of test solutions used for various experiments are given in Table 2.1.

Table 2.1 Composition of synthetic and creek water test solutions

Laboratory experiment	Spiked metals	Nominal metal concentration (μg/L)	Ionic strength as represented by NaNO$_3$ concentration (mM)	DGT deployment period (h)
Initial validation experiment*	Al, Fe, Cu, Mn, Cd, Zn and U	10	0.2, 2 and 20	7, 25, 45 and 71
Component investigation	Cu, Zn, Cd, Pb and U	100	20	8
Leakage assessment	Cu, An, Cd, Pb and U	100	20	8
Ionic strength effect	Cu, Zn, Cd, Pb and U	10	0.2, 2 and 20	7, 24, 32, 48, and 71
Filtered (< 0.45 μm) creek water experiment	Cu, Zn, Cd, Pb and U	10 and 50	NA	8, 25, 30, 50 and 73

*During initial experiments Al, Fe and Mn were seen to precipitate out of solution, so they were omitted from all following experiments.

Each fresh test solution was allowed to equilibrate prior to commencement of the test by stirring overnight.

Physico-chemical analysis

The temperature, pH and EC of test solutions were monitored throughout the duration of each experiment. In order to prevent contamination of test solutions, these measurements were carried out on 20mL aliquots taken from test solutions using acid washed syringes. Temperature was measured using a standard mercury thermometer and pH and conductivity were measured using pH and conductivity probes and meter (WTW, Germany) that were calibrated using standard calibration solutions (BDH, Merck).

2.4.2 DGT deployment in laboratory test solutions

The DGT devices were deployed in test solutions by suspending them in the middle of the test container from a nylon line fixed to a small hole in the outer edge of the base of each device. The number of DGTs placed in any one test container ranged from two to six. During DGT deployment test solutions were stirred by means of a Teflon coated magnetic stirrer bar activated by magnetic stirring plates.

The DGT devices were removed after various deployment periods ranging from 4 to 73 h. After removal the devices were rinsed thoroughly with MQ water and placed into clean PP containers and stored at < 4 ºC until analysis.

2.4.3 Water sampling of laboratory test solutions

Water samples (10 mL) were taken from each test solution simultaneously with DGT removal to measure metal concentrations in solution. Unfiltered water samples were collected in 15 mL vials using a clean 60 mL syringe. Filtered water samples were collected in 15 mL vials using a clean 60 mL syringe coupled with a syringe filtration assembly consisting of filter holders loaded

with clean 25 mm diameter 0.45 μm cellulose nitrate filter membranes (GN-6, Metricel). All water samples were acidified to 0.13% (v/v) HNO_3 (Aristar grade, Merck).

2.5   Field methods

2.5.1 Field Sites

Sites sampled in this study include Magela Creek upstream, Magela Creek downstream, Gulungul Creek downstream and the RP1 spillway (Figure 2.1). The Gulungul Creek upstream site was not sampled due to logistical limitations.

Magela Creek runs through the north eastern aspect of the Ranger lease with its 1765km^2 catchment incorporating the majority of the mine site (Hart *et al.*, 1982). Gulungul creek runs along the western side of the mine with its catchment area including the tailings dam.
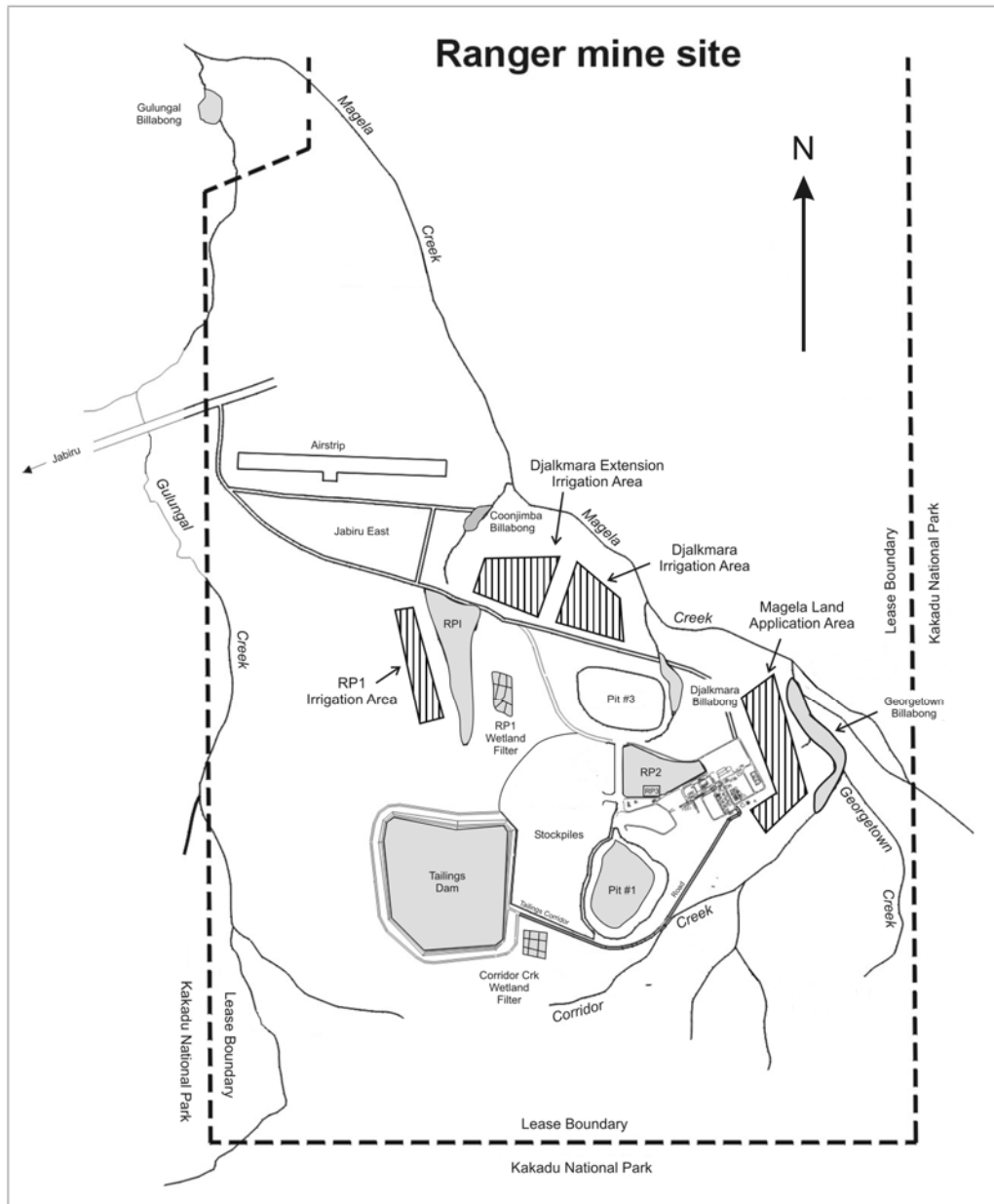
Figure 2.1 Ranger mine lease.

The main source of mine-related effluent is RP1 from which uncontrolled release occurs to Coonjimba Billabong via the RP1 spillway (Figure 2.1). The sites along Magela and Gulungul Creeks are established as monitoring compliance sites and are used by the Supervising Scientist and Energy Resources Australia (ERA) for routine water quality monitoring (Supervising Scientist, 2002b; Energy Resources Australian Ltd., 2003).

Gulungul Creek hydrology data was obtained from a gauging station located between the upstream and downstream sites (not shown in Figure 2.1). This data provides information on the

discharge (m^3/s), which is the rate of flow of the volume of water through the cross sectional area of the creek bed that fluctuates in relation to rain events.

2.5.2 Weekly monitoring

DGT devices were deployed at each of the three field sites in Magela and Gulungul creeks for one week periods (168 hours). The first batch was deployed on the 17th February 2004 and the last batch was removed on the 6th April 2004, coinciding with the middle of the wet season. Filtered and unfiltered water samples and measurement of physico-chemical properties were taken during DGT deployment and removal which was carried out on the same day and approximately the same time each week. During the third week of monitoring the Gulungul Creek Downstream site became flooded, restricting access to the site. As a result no water samples were obtained and the DGT devices that were deployed at the site the previous week were left in place for a further week, being removed during the fourth week of monitoring.

2.5.3 Retention pond 1 trial

DGT devices were deployed in RP1 for a period of 6 h and a period of 43 h. Unfiltered and filtered water samples were collected at the commencement and end of the 6 h deployment and at various times throughout the 43 h deployment.

2.5.4 DGT deployment in the field

DGT Holders
The DGTs were deployed in the field using custom made polyvinylchloride (PVC) DGT holders that were able to secure up to six DGTs at one time.

Figure 2.2 PVC DGT holder used for field deployment of DGT devices.

The holders were tied in place via a stainless steel eyelet at the top of a cement filled shaft which acted as a weight ensuring that the holder remained submerged at all times. The depth at which the holder was deployed could be adjusted by shortening or lengthening the rope. The holder design allowed for simple manipulation of the DGTs as the base could be removed completely from the shaft and then handled on the boat.

a)   b)
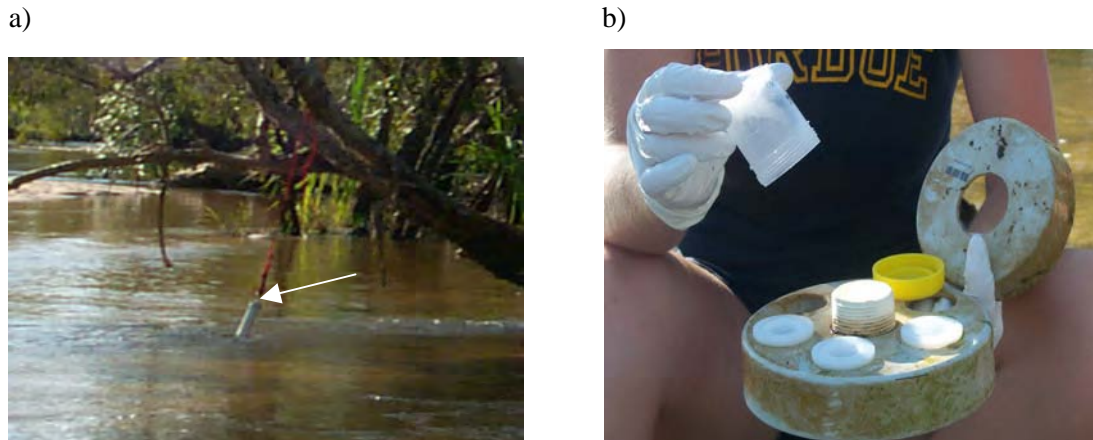
Figure 2.3 a) DGT deployment mid-stream. b) Detachable base of DGT holder.

The DGT devices were transported into the field in PP containers. At each site the devices were placed into the holder by inverting the open PP container above the hole in which the DGT sat, preventing direct handling of the devices. The empty PP containers were sealed in zip locked bags and transported back to the laboratory where they were stored until the DGTs were to be retrieved.

For retrieval of DGT devices at the end of their deployment, the PVC holder was removed from the water and the base was detached from the shaft. Each DGT was removed individually and rinsed with MQ water to remove any excess creek water and debris before being placed back into the PP containers. The containers were sealed in zip locked bags and placed into an esky with a cold pack for transport back to the laboratory. Each DGT was rinsed a second time with fresh MQ water on return to the laboratory.

2.5.5 Water Sampling in the field

The sample bottles (LDPE, 1 L and 60 mL) were filled with 0.1% HCl immediately after acid washing to reduce the risk of metals binding to the container walls during transportation into the field. Prior to sampling, the 0.1% HCl was discarded (either downstream from the boat or on the bank) and the bottles were rinsed thoroughly with sample water to ensure that all acid was removed.

Water sampling was carried out by collecting 1 L of sample water and sub-sampling into 60 mL sample bottles. Direct sampling of water (1 L) from the creeks was conducted using a sampling pole, while a peristaltic pump was used for sampling of RP1 where the use of the pole was not practical.

Collection of 1 L sample

The sampling pole was constructed using PVC and nylon line.

Figure 2.4 Collection of 1 L sample using sampling pole.

The 1 L sampling bottle was placed in the holder at the end of the pole and secured using nylon line and elastic rope. The upside down bottle was submerged in the water to an approximate depth of 30 cm where the pole was rotated so that the opening of the bottle was facing upstream, allowing air captured within the bottle to be expressed and replaced with water. The full bottle was removed from the water and the cap was replaced.

The peristaltic pump with acid washed tubing was enclosed in a sealed plastic container with a switch located on the outside and holes for the inlet and outlet tubes. The end of the inlet tubing was placed in the water at a depth of approximately 30 cm and the whole system was allowed to flush for at least 10 minutes before collection of a 1 L sample.

Collection of 60 mL unfiltered and filtered sub-samples

For unfiltered samples, the 60 mL bottles were rinsed thoroughly with aliquots of sample water poured directly from the 1 L bottle. After rinsing, the 60 mL sample bottle was filled from the 1 L bottle.

For filtered samples the sub-sample from the 1 L bottle was passed through a syringe filtration apparatus. Filter papers (0.45µm, GN-6 Metricel) and filter paper holders were transported into the field separately where they were assembled using stainless steel forceps.

a) b)

Figure 2.5 a) Filter apparatus preparation. b) Syringe filtration into 60 mL sampling bottle.

Water from the 1L bottle was used to rinse the syringe prior to filling it to the 60mL mark. The filter holder loaded with filter paper was then attached to the syringe and three aliquots of 30 mL of sample water were pushed through and into the 60mL sample bottle for rinsing. After rinsing the syringe was refilled with water from the 1 L bottle and approximately 60 mL was passed through the filtration apparatus and collected in the 60 mL bottle.

The 60 mL sub-samples were sealed individually in zip-locked plastic bags and placed in an esky with a cold pack for transportation back to the laboratory. On arrival all samples were acidified in a class 100 clean room within a laminar flow cabinet using Ultra-Pure HNO_3 (BDH, Merck). Unfiltered samples were placed in an oven at 60 ºC for 24 h, after which they were stored with the filtered samples at < 4ºC until analysis.

Physico-chemical analysis

At each site during DGT deployment and retrieval temperature, EC, pH and dissolved oxygen (DO) were measured using Quanta field probes (Hydrolab, USA). The field meter was calibrated in the laboratory prior to each field trip using standard calibration solutions (BDH, Merck).

2.6   ICP-MS analysis

Metal analysis was performed using ICP-MS on a Perkin Elmer ELAN 6000 instrument with an AS90 auto-sampler (Perkin Elmer, USA). The instrument was operated according to manufacturers specifications (Table 2.2) and prior to use the nebuliser gas flow and ion lens voltage were optimised to give maximum sensitivity.

Table 2.2 Elan 6000 ICP-MS instrument conditions

Instrument parameter	Setting
Power (W)	1050
Argon plasma gas flow (L/min)	17
Argon axillary gas flow (L/min)	1.2
Argon nebuliser gas flow (L/min)	0.7
Sample rinse (s at 48 rpm)	20
Sample uptake (s at 48 rpm)	20
Scan mode (s at 16 rpm)	20
Sweeps/reading	6
Replicates	3
Dwell time (ms)	100

Table 2.3 shows the isotope masses analysed and the masses that were selected for quantification in order to avoid interferences caused by spectral overlaps by non-analyte ions with analyte ions. Interference is particularly important for analysis of iron as the ionization of argon from the plasma forms argon isotopes that interfere with the most abundant iron isotope, ^{56}Fe (Vanhaecke and Köllensperger, 2003).

Table 2.3 Isotopes measured by ICP-MS and those selected to avoid spectral interferences

Element	Isotope measured	Isotope selected to avoid spectral overlap
Al	27	27
Fe	54 + 57	54
Mn	55	55
Cu	63 + 65	63
Zn	64 + 66	64
Cd	111 + 114	111
Pb	206 + 207 + 208	208
U	235 + 238	238

The accuracy of all ICP-MS measurements was checked using custom made 'Calcheck', a standard solution of known metal concentration.

2.6.1 ICP-MS analysis of water samples

Sample preparation was carried out in a class 100 clean room using trace metal clean procedures. To each sample, 1 mL of an internal standard solution (400 µg/L Rhodium, Indium and Rhenium) was added per 10 mL of water sample.

Standards for ICP-MS analysis of water samples were made using mixed metal stock solutions prepared from 1000 mg/L metal standards (BDH, Merck) in MQ water. For each analysis a blank

and three standards were prepared by serial dilution of the mixed metal stock solution, using MQ water in 15 mL vials with HNO_3 and internal standard added to match the matrix of the samples.

The standard concentrations used were determined based on estimated analyte concentrations in the sample. Metal concentrations in water samples from laboratory experiments were estimated based on the nominal spiked concentration of the test solution from which they were collected. For example, a test solution containing a nominal spiked concentration of 10 µg/L metals, standards of 1, 10 and 100 µg/L were prepared. Metal concentrations in water samples from the field were estimated based on the typical natural distribution of metals present in the creeks studied (Table 2.4).

Table 2.4 Natural distribution of metals in freshwater creeks of ARR*

Metal	Typical distribution ratio	
	Unfiltered samples	*Filtered samples*
Fe and Al	150	30
Mn, Zn and Cu	10	10
Pb, Cd and U	1	1

* (Supervising Scientist, 2002b)

2.6.2 ICP-MS analysis of DGT resin gel eluent

Sample preparation was carried out in a class 100 clean room using trace metal clean procedures. The 2 mL metal eluent was diluted by adding 2 mL of internal standard solution (40 µg/L Rhodium, Indium and Rhenium) and 1 mL MQ water. After dilution the gel was removed from the eluent solution by inverting the 15 mL vial and allowing the resin to adhere near the opening at the top. Once the resin adhered, the vial was returned to upright position and the gel was removed using a clean pipette tip.

Standards for ICP-MS analysis of the metal eluent were made up similarly to those described for water samples (see 2.6.1). The concentrations of the standards were determined based on an estimation of the concentration of accumulated metal in the binding gel.

2.7   Quality control

2.7.1 DGT blanks

Blanks

After the assembly of a batch of DGT devices, three devices were randomly selected and stored in the laboratory (< 4 ºC) as blanks. The triplicate blank DGTs were analysed simultaneously to DGT devices from the same batch that were exposed to analyte solution.

Sample blanks

DGT sample blanks were collected for each laboratory experiment and for each set of triplicate DGT devices deployed in the field. The DGT sample blanks were essentially transported and handled in the same way as DGT devices that were deployed, however they were not exposed to analyte solutions.

2.7.2 Water blanks

Filter blanks

Filter blanks were taken to check for contamination from the filtration apparatus used for sampling test solutions in the laboratory and creek water in the field. In both cases, MQ water was passed through the filtration apparatus and collected for analysis. In the field, MQ blanks were collected for unfiltered samples as well.

Container and NaNO$_3$ blanks

In laboratory experiments contamination from the test containers and the NaNO$_3$ used to adjust ionic strength was monitored. The container blank was taken directly after filling the 4L test container with MQ water, prior to spiking with either sodium nitrate or metals. The NaNO$_3$ blank was taken after spiking with sodium nitrate and prior to spiking with metals.

2.7.3 Sample replication

In laboratory experiments replication was achieved by deploying replicate DGT devices in the same test container (where space permitted) or by deploying DGT devices in replicate test solutions in separate containers. Triplicate DGT devices were deployed at each site for all field deployments. Duplicate water samples were taken throughout the laboratory experiments and field trials.

3 Results and discussion

3.1 DGT Method validation experiments

3.1.1 Quality Control

All sample blanks taken during water sampling were below detection limits, showing that there was no contamination introduced by sampling methods. Average blank values and detection limits for all water and DGT analyses are reported in Table 3.1.

Table 3.1 Summary of average sample blank concentrations (µg/L) and detection limits (µg/L) for water samples and DGT

Water samples	Cd	Pb	Mn	U	Cu	Zn	Al	Fe
Average detection limit	0.0070	0.024	0.045	0.088	0.12	0.32	0.98	2.1
Average sample blank*	<D.L.	<D.L.	<D.L.	<D.L.	<D.L.	<D.L.	<D.L.	<D.L.
DGT Detection limits	**Cd**	**Pb**	**Mn**	**U**	**Cu**	**Zn**	**Al**	**Fe**
10 h	0.13	0.099	0.019	0.033	0.54	2.2	2.5	3.8
20 h	0.065	0.050	0.0095	0.016	0.27	1.1	1.2	1.9
30 h	0.043	0.033	0.0063	0.011	0.18	0.74	0.82	1.3
40 h	0.032	0.025	0.0047	0.0081	0.13	0.55	0.62	0.96
50 h	0.026	0.020	0.0038	0.0065	0.11	0.44	0.49	0.77
70 h	0.019	0.014	0.0027	0.0047	0.076	0.32	0.35	0.55

* Includes filter blanks, container blanks and $NaNO_3$ blanks.

The DGT detection limits were calculated for various deployment periods using three times the standard deviation of the average mass measured in blank DGT devices.

3.1.2 DGT leakage

The results for DGT deployment in synthetic test solutions at varying ionic strength spiked to 10 µg/L metals (Al, Fe, Mn, Cu, Zn, Cd, Pb and U) are shown in Figure 3.1. Some results for Fe were omitted due to low sensitivity of ICP-MS measurement for this metal.
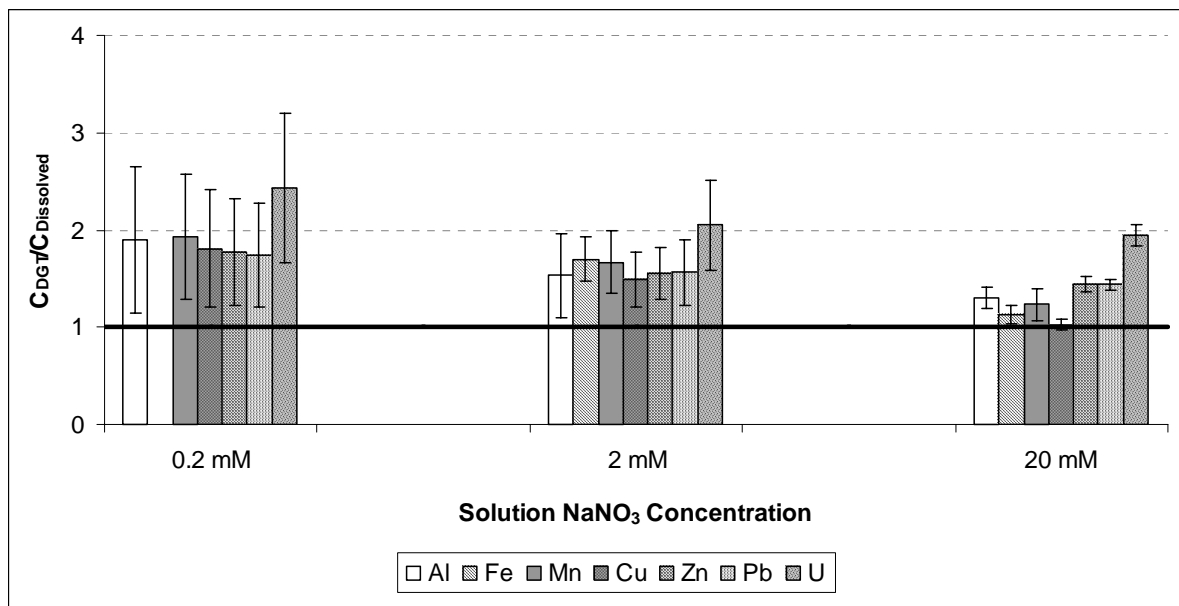
Figure 3.1 Response of DGT to solutions of varying ionic strength spiked with 10 μg/L metals, expressed by the ratio of DGT measured concentration (C_{DGT}) to dissolved concentration ($C_{Dissolved}$). Error bars represent the standard deviation ($\sigma = 1$) of time averaged DGT measurements. The solid line represents the theoretical DGT response ($C_{DGT}/C_{Dissolved} = 1$).

Measurements in all test solutions were erratic and apparently random with respect to time, as shown by the large standard deviation of the time averaged values (Figure 3.1). The ratio of DGT measured concentration to dissolved concentration was generally greater than 1 for all metals in each test solution, showing that the DGT measurement was overestimating the solution concentration. The overestimation occurring at the lowest ionic strength (0.2 mM NaNO$_3$) agrees with observations in other studies that have found DGT measurement to be enhanced due to low ionic strength (Alfaro-De la Torre *et al.*, 2000; Sangi *et al*, 2002; Peters *et al*., 2003). In contrast, the enhanced DGT overestimation occurring in the two higher ionic strength solutions was unexpected as DGT measurement should be independent of ionic strength above 0.2 mM NaNO$_3$ (Alfaro-De la Torre, *et al.*, 2000).

For DGTs working theoretically, metal uptake is linearly related to time, as shown in equation 2.5. The time-dependence of the mass of Cu accumulated in DGT devices exposed 0.2, 2 and 20 mM NaNO$_3$ solutions is shown in Figure 3.2.
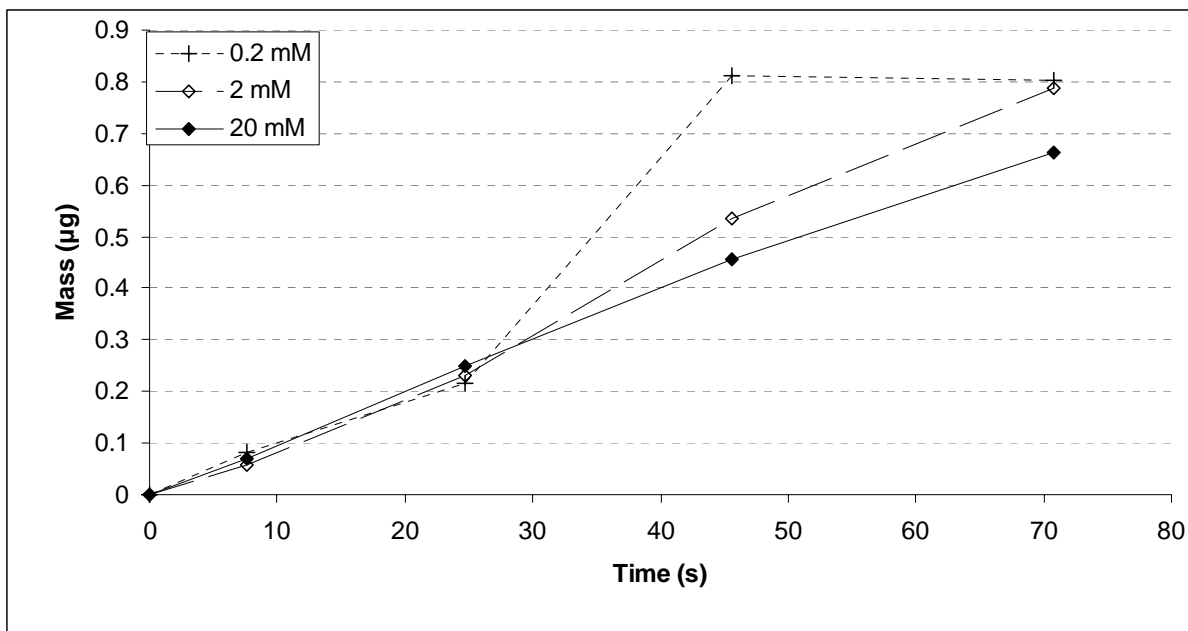
Figure 3.2 Mass of Cu (μg) accumulated in DGT resin gels over time during deployment of DGT devices in 10 μg/L mixed metal test solutions of ionic strength 0.2, 2 and 20 mM NaNO$_3$.

The uptake of copper was linear with respect to time in the 20 mM NaNO$_3$ solution but deviated from linearity in the 2 and 0.2 mM solutions (Figure 3.2). The occurrence of non-linear uptake suggested that the DGTs were not performing as theoretically predicted by equation (2.5). These results were consistent for all metals measured under the same conditions and prompted investigation into the mechanical functioning of the DGT devices.

The performance of individual DGT components, including the diffusive gel, the resin gel, the filter membrane and the plastic DGT casing, was investigated by comparing components from the batch supplied in June 2003 for this study to an older batch of components that were supplied in 2002. DGT devices from the older batch were treated as controls as their accuracy was demonstrated during a study conducted by Munksgaard and Parry (2002). Experiments were performed in test solutions spiked to 100 μg/L metals, with high ionic strength (20 mM NaNO$_3$) to eliminate the ionic strength effect as the cause of overestimation.
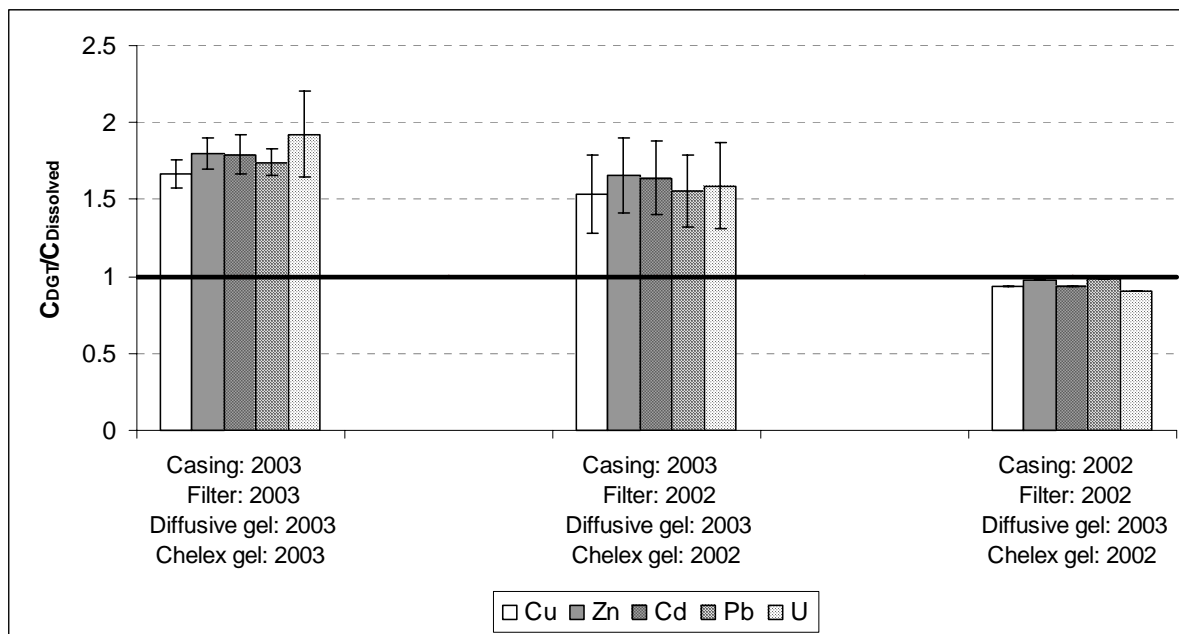
Figure 3.3 Effects of varying DGT components, expressed by the ratio of DGT measured concentration (C_{DGT}) to dissolved concentration ($C_{Dissolved}$). Error bars represent standard deviation ($\sigma = 1$) between duplicate DGT measurements. The solid line represents the theoretical DGT response ($C_{DGT}/C_{Dissolved} = 1$).

The DGT devices assembled within the 2003 casings consistently measured metal concentrations that overestimated the solution concentration while the control devices assembled within the 2002 casings performed as expected (Figure 3.3). These results indicated that the plastic casings supplied in 2003 were the cause of the unexpected overestimation of DGT measurement.

The possibility of leakage occurring in the DGT casings from the seal between the piston and the cap was investigated by performing a series of simple experiments using DGT casings loaded with tissue paper in place of the gel assembly. These pseudo DGTs were placed in a coloured dye solution for 8 h, to a depth that submerged the seal between the base of the piston and the bottom of the cap, leaving the top of the device, including the exposure window, above surface. Leakage from the top of the DGT device (i.e. under the lip of the cap) was not investigated experimentally because it was routinely monitored during DGT assembly (see 2.3.3).
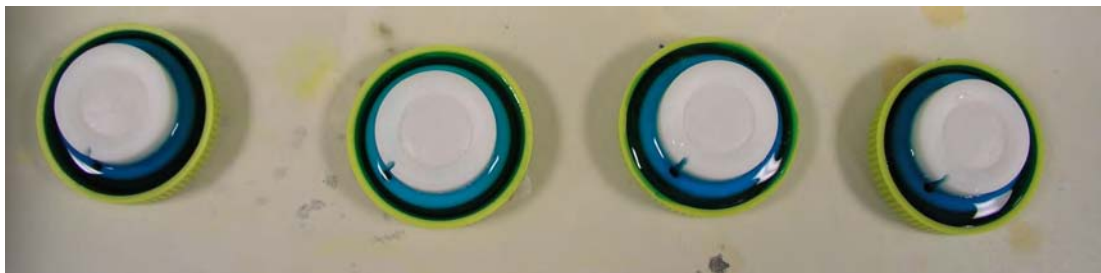
Figure 3.4 DGT casing loaded with tissue paper in place of the gel assembly at time = 0 hours.

Figure 3.5 DGT casing loaded with tissue paper in place of the gel assembly at time = 8 hours.

Figures 3.4 and 3.5 clearly indicate that the dye solution was able to enter the DGT via the seal between the base of the piston and the bottom of the cap, reaching the pseudo-gel assembly within. It can be seen in this extremely simplified scenario of DGT deployment that the leaked solution was generally contained within the outer ring of the tissue paper and that the extent of leakage was variable between DGT devices.

To examine the effects of this leakage on DGT measurement of metals in solution, duplicate DGT devices were deployed for 8 h in synthetic test solutions spiked with 100 µg/L metals (Cu, Cd, Zn, Pb and U) at ionic strength 20 mM NaNO$_3$. After removal from test solutions the resin gels were divided into two sections during DGT disassembly (see 2.3.2), a 5 mm thick annular ring and a 19 mm diameter internal disc, that were eluted and analysed separately (Figure 3.6).
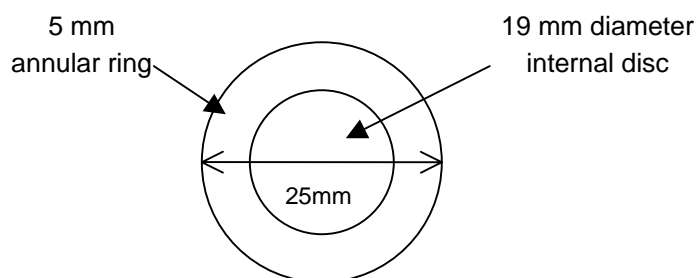
Figure 3.6 Diagram representing 25mm diameter resin gel divided into the 19 mm diameter internal disc and the 5 mm thick annular ring subsections. 1 mm was lost due to cutting.

The results of analysis of the annular ring and internal disc sections are shown in Figure 3.7.
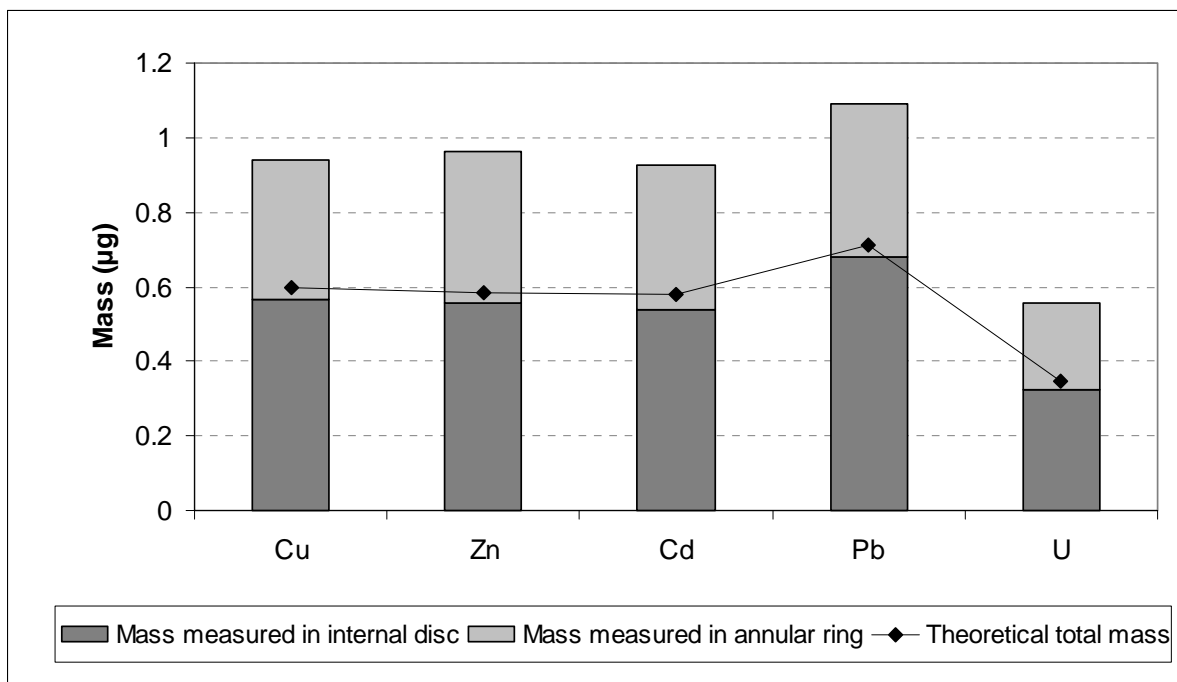
Figure 3.7 Stacked columns showing relative contributions of accumulated mass (µm) from the annular ring and the internal disc segments of the resin gels of duplicate DGT devices exposed to 100 µg/L mixed metal solution at 20 mM NaNO₃. The solid line represents the theoretical accumulated mass calculated using equation 3.4.

Figure 3.7 shows the total mass accumulated in the whole resin gel as the sum of the mass measured in the annular ring and internal disc segments. The annular rings from the duplicate DGT devices contained substantial amounts of metals, contributing, on average, approximately 40% of the total mass accumulated in the whole resin gel (Figure 3.7). The relative standard deviation ($\sigma = 1$) of the average mass accumulated in the annular ring of duplicate DGT devices was equal to the average for all metals, showing that the leakage is highly variable between different DGT casings.

The theoretical mass shown if Figure 3.7 was calculated using equation (2.5) with the given deployment period (8 h), the measured concentrations of each metal in the external solution and the theoretical exposure area (3.14 cm^2). The results show that the mass of metals accumulated in the internal disc agrees with the expected theoretical mass indicating that the leaked mass of metal was essentially contained within the annular ring (Figure 3.7). It was concluded that removal of the annular ring section was sufficient to ensure that only metal ions entering the DGT device by the process of diffusion via the exposure window were measured.

The DGT manufacturers (DGT Research Ltd.) were contacted and informed of these findings and were able to confirm that their manufacturing methods had recently been changed and that this particular batch of DGT casings was 'looser' than others they had produced.

3.1.3 Ionic strength effect on DGT measurement in synthetic test solution

An experiment was performed in order to examine the effects of ionic strength on DGT measurement. DGT devices were deployed in synthetic test solutions at varying ionic strength

(0.2, 2 and 20 mM NaNO$_3$) all spiked to 10 µg/L metals (Cu, Cd, Pb, Zn and U). The 5mm annular ring was removed from all resin gels prior to elution and analysis to exclude leaked metals.
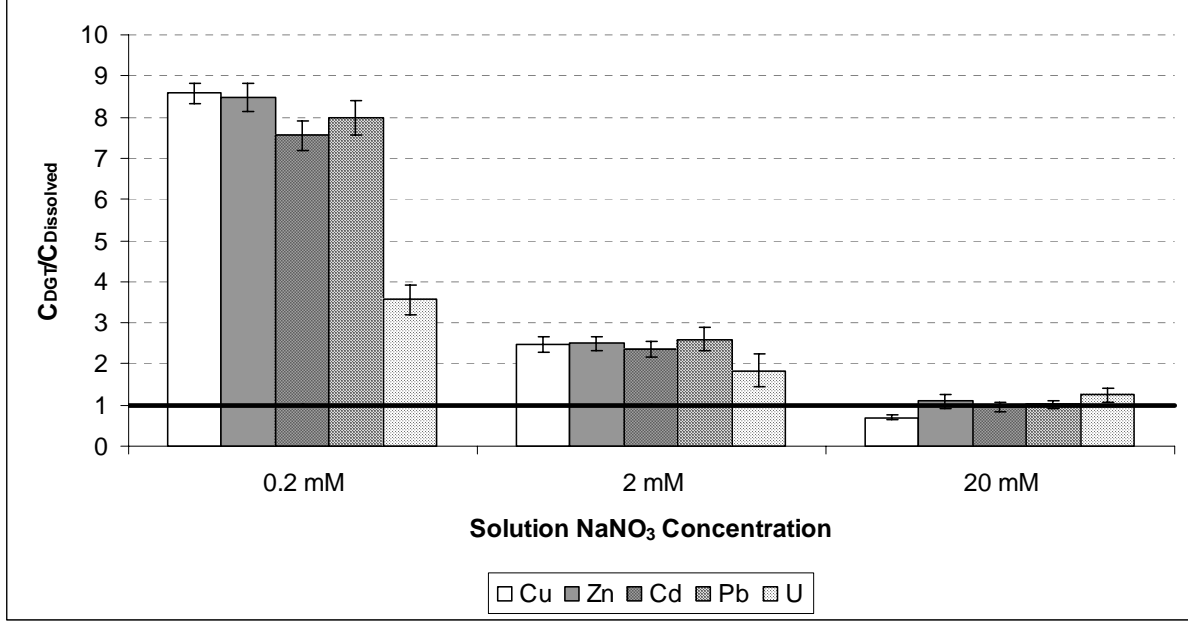
Figure 3.8 Response of DGT devices exposed to 10 µg/L mixed metal solutions of varying ionic strength, analysed after removal of the annular ring, expressed by the ratio of DGT measured concentration (C$_{DGT}$) to dissolved concentration (C$_{Dissolved}$). Error bars represent standard deviation (σ = 1) between time averaged DGT measurements. The solid line represents the theoretical DGT response (C$_{DGT}$/C$_{Dissolved}$ = 1).

The DGT measured concentrations for each metal agreed with the solution concentration at the highest ionic strength (20 mM NaNO$_3$) with good precision, however overestimation was observed for DGT devices deployed in test solutions of ionic strength < 20 mM NaNO$_3$ (Figure 3.8).

The rate of metal uptake by DGT devices deployed in solution can be defined by the mass of metal (µg) bound to the resin gel over time (s), M/t. Throughout all deployment periods the concentration of metals in the bulk solution (C_b) was constant, as were the exposure area (A) and diffusive gel thickness (Δg), therefore, M/t is proportional to the diffusion coefficient (D) as shown by the rearrangement of equation 2.5:

$$\frac{M}{t} = \frac{DAC_b}{\Delta g} \tag{3.1}$$

Therefore the rate at which a metal is taken up by the DGT device (M/t) is a measurable characteristic of its diffusion coefficient in the diffusion gel, hence an observed increase in M/t can be related to an increase in D.

The rate of metal uptake, M/t, can be measured as the slope of the plot of mass accumulated in the resin gel against deployment time. Figure 3.9 shows the time-dependence of the mass of metals

accumulated in the DGT devices exposed to 0.2, 2 and 20mM $NaNO_3$ solutions (with the annular ring removed).
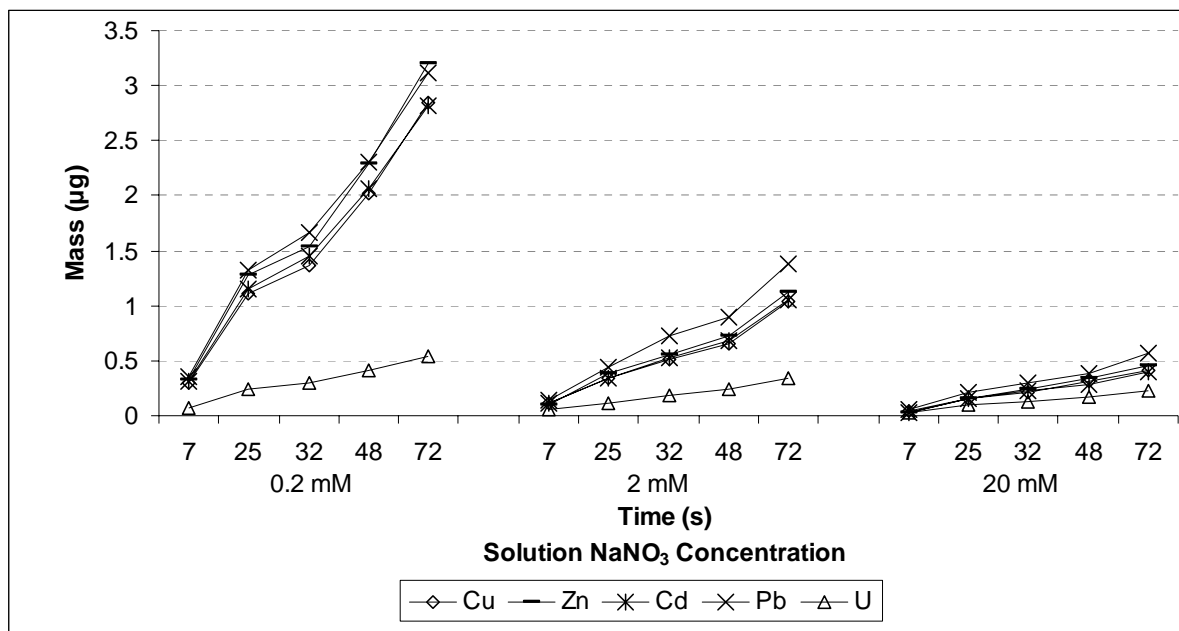
Figure 3.9 Mass (µg) of metal accumulated in the resin gel over time for DGT devices deployed in 10 µg/L mixed metal concentration at varying ionic strength.

As expected from equation (2.5), the mass uptake of each metal was relatively linear with respect to time. The results show that the gradients of the slopes increase with decreasing $NaNO_3$ concentration in the external solution, indicating an increase in the rate of uptake (and diffusion coefficient) for each metal.

Table 3.2 shows the effective diffusion coefficients of Cu, Zn, Cd, Pb and U at ionic strength 0.2, 2 and 20 mM $NaNO_3$, which were calculated by solving equation (2.5) for D using the rate of metal uptake as measured by the slopes obtained from the equations of the lines of best fit for the data represented in Figure 3.9 and the measured metal concentration in the external solution.

Table 3.2 Recommended* and measured diffusion coefficients (x 10^{-6} cm^2/s) for Cu, Zn, Cd, Pb and U at varying ionic strength (mM $NaNO_3$) at 27 ºC

Metal	Recommended*	20 mM	2 mM	0.2 mM
U	4.5	4.8	6.9	14
Cd	6.4	5.7	14	46
Zn	6.4	6.8	15	53
Cu	6.6	4.3	15	54
Pb	8.5	7.9	21	64

*(DGT Research Ltd., 2003).

The measured diffusion coefficients were similar to recommended values at 20 mM $NaNO_3$, however at 0.2 mM $NaNO_3$ there were significantly higher. These results agree with those obtained by Alfaro-De la Torre *et al.* (2000), showing the effective diffusion coefficient of a

metal diffusing through the diffusion gel of a DGT device is increased when DGTs are deployed in solution of low ionic strength. This explains the enhanced metal measurement as observed in Figure 3.8.

It has been suggested that the increase in diffusion coefficient is caused by the efflux of Na ions from within the DGT devices into the external solution. The source of the Na in DGT devices is the resin gel, which contains the Chelex-100 ion exchange resin in its Na form, in which the binding sites are saturated with Na ions from pre-treatment with 0.01M NaNO$_3$ (Peters *et al.*, 2003). As a result of this pre-treatment, the pores in the resin gel surrounding the Chelex-100 resin are saturated with sodium and nitrate ions (Na$^+$NO$_3^-$). Thus the total concentration of sodium within the resin gel is made up of the Na ions bound to the Chelex-100 resin beads ([Na]$_{bd}$) and the free Na ions ([Na$^+$]$_r$) within the pores of the hydrogel.

Alfaro-De la Torre *et al.* (2000) suggest that when DGT devices are exposed to a solution with Na concentration ([Na$^+$]$_b$) less than the free Na concentration in the resin gel (i.e. [Na$^+$]$_b$ < [Na$^+$]$_r$), Na equilibrium across the diffusion gel is reached via efflux of Na ions into the external solution along a concentration gradient in the opposite direction to that of incoming metals.
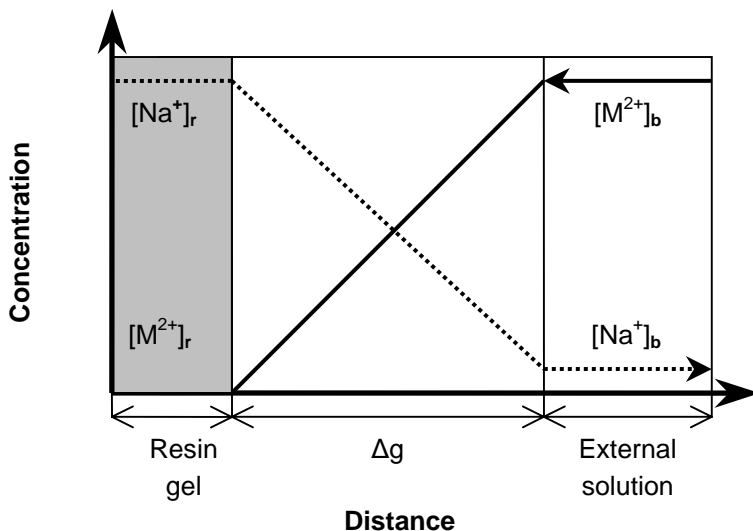
Figure 3.10 Representation of DGT gel assembly (resin gel, diffusive gel and membrane filter) deployed in solution of high metal ion concentration ([M^{2+}]$_b$) and low sodium ion concentration ([Na$^+$]$_b$). The solid line (—) represents the positive concentration gradient for metal entering the DGT device and the dotted line (……) represents the negative concentration gradient for Na ions leaving the device. [Na$^+$]$_r$ and [M^{2+}]$_r$ are the free sodium ion concentration and free metal ion concentrations in resin gel respectively.

The efflux of Na ions out of the DGT causes the formation of a transmembrane potential, where the inside of the membrane becomes more negatively charged compared to the outside. It is possible that in the presence of a transmembrane potential, metal ion transport across the diffusion gel is influenced by electrical gradients, essentially increasing the rate of diffusion of metals from the external solution into the DGT in order to neutralize the charge difference across the membrane.

Figure 3.8 shows that DGT measurement becomes independent of ionic strength between 2 and 20 mM NaNO$_3$, which is higher than observed in other studies. For example, DGT measurement

was found to be independent of ionic strength above low threshold values of 1 mM (Sangi *et al.*, 2002), 0.2 mM (Alfaro de la Torre *et al*., 2000), 0.1 mM (Peters *et al.,* 2003), and 0.01 mM (Zhang and Davison, 1995).

The low threshold value of 0.2 mM $NaNO_3$ obtained by Alfaro-De la Torre *et al*., (2000) was based on predictions of ion transport in the diffusion gel using equation:

$$D_i, eff = D_i - D_i z_i C_i \times \left[\frac{\left(\sum_{j=1}^{n} z_j D_j \left(\frac{\left(\frac{dC_j}{dx} \right)}{\left(\frac{dC_i}{dx} \right)} \right) \right)}{\left(\sum_{j=1}^{n} z_j^2 D_j C_j \right)} \right] \tag{3.2}$$

which describes the diffusion coefficient of a given ion ($D_{i,\ eff}$) in a medium where *n* ions are co-diffusing. *D* and *z* are the diffusion coefficient and charge respectively, of all ions, *j*, including the ion of interest, *i*. Essentially the equation shows that the effective diffusion coefficient of an ion is influenced by the concentrations (*C*), the concentration gradients (*dC/dx*) and diffusion coefficients of all diffusing ions.

Theoretically this equation could be used to predict the effective diffusion coefficients of metals under low ionic strength conditions, thus allowing for accurate DGT measurement. However, such predictions depend on the precise knowledge of all variables within the equation, including $[Na^+]_r$.

Using equation (3.2) with time-integrated mass uptake rate data from a 7 h experiment, Alfaro-De la Torre *et al.*, (2000) calculated the $[Na^+]_r$ to be 0.22 mM. They then used the estimated $[Na^+]_r$ value in equation (3.2) to predict how effective diffusion coefficients of metals would vary in solution of constant metal concentration and varying major cation concentration (Mg^{2+}, Ca^{2+}, Na^+, K^+). Their predictions showed that the electrical gradient contribution to the diffusion coefficients of incoming metals caused by counter-diffusion of Na, should be expected to occur in solutions with total major cation concentration less than 0.2 mM (Σ [Ca, Mg, K, Na] $\leq$ 0.2 mM).

These predications have been questioned by Peters *et al.*, (2003) who experimentally quantified the Na ion concentrations in both the resin and diffusion gels (typically stored in 0.01 M $NaNO_3$). They reported a value for $[Na^+]_r$ of 0.258 mM, which is consistent with the estimated value of 0.22 mM calculated by Alfaro-De la Torre *et al*., (2000). However their results revealed that input of Na into the external solution from the resin gel was considerably small compared to a large flux of Na from the diffusion gel.

Sodium efflux from the diffusion gel is caused by equilibration of the high $NaNO_3$ concentration in the pores of the diffusive gel with the external solution. Peters *et al.* (2003) suggest that during this equilibration, electroneutrality will be maintained through co-diffusion of both Na^+ and NO_3^- out of the diffusion gel, and therefore the Na within the diffusion gel should not contribute to the

electrical effects that have been proposed to increase effective diffusion coefficients of incoming metals.

The test solutions prepared in this study were spiked with metals in the form of nitrate salts dissolved in MQ water resulting in a high NO_3^- concentration in the external solution. Therefore, equilibration of the $NaNO_3$ in the diffusion gel with the external solution would comprise mainly of Na^+ efflux.

In summary, the electroneutrality effects described by Alfaro-De la Torre *et al*., (2000) are able to explain the enhancement of DGT measurement observed in this study. The reason that enhancement occurred at ionic strengths greater than the minimum low threshold of 0.2 mM $NaNO_3$ given by Alfaro-De la Torre *et al.*, (2000) may be explained by the fact that their threshold value was predicted based on a value for $[Na^+]_r$ that underestimated the actual free sodium concentration within the DGT device because sodium release from the diffusion gel was not taken into consideration.

The magnitude of DGT overestimation at the lowest ionic strength (0.2 mM $NaNO_3$) observed in this study was much higher than that reported by other researchers, with ratios ranging from 4 for uranium to between 8 and 9 for cadmium, lead, zinc and copper (Figure 3.8). The maximum ratio of DGT concentration to solution concentration observed by Peters *et al.*, (2003) in test solutions with Ca concentration 0.05 mM ($CaCl_2$) was approximately 3 for Cu and 2.5 for Cd. Further, the rate of mass uptake for Cu and Cd observed in this study at 0.2 mM $NaNO_3$ were 1.5 and 5.4 times that observed for Cu and Cd respectively, at same ionic strength by Alfaro-De la Torre *et al.*, (2000).

The high overestimation observed in this study may be associated with the leakage that was found to occur in these particular DGT devices. Table 3.3 shows the approximate rates of mass uptake for each metal in the internal disc and annular ring segments of DGT devices exposed to solutions of varying $NaNO_3$ concentrations.

Table 3.3 Summary of approximate rate of mass uptake (x 10^{-3} µg/h) for Cu, Zn, Cd, Pb and U in the 19 mm internal disc and 5 mm annular ring segments at varying ionic strength (mM $NaNO_3$)

19 mm Internal Disc	U	Cd	Cu	Zn	Pb
20	3.4	5.9	6.1	6.7	8.1
2	4.9	14.7	14.4	15.7	19.4
0.2	8.1	41.3	40.9	46.1	46.3
5 mm Annular Ring	U	Cd	Cu	Zn	Pb
20	1.3	2.5	2.5	2.9	3.4
2	2.1	5.2	4.7	5.4	5.7
0.2	9.1	9.9	8.8	10.3	10.5

These results show that the rate of metal uptake in the annular ring (via the leak) is increased with decreased ionic strength, which may be due to depletion of $[Na^+]_r$ from within the annular ring, causing accumulation of net negative charge in the vicinity of the leak that may drive the uptake of metals.

For DGT devices exposed to 20 mM solutions, exclusion of the outer ring was found to be sufficient in eliminating the excess mass of metals absorbed to the resin due to leakage (Figure 3.7). It may be possible that in lower ionic strength solutions the increased mass of metals entering the DGT devices are not restricted to the binding gel within the annular ring and may bind within the designated exposure area of the internal disc. Therefore leaked metals may contribute to the mass measured in the internal disc causing further enhancement of metal uptake at low ionic strength. To assess this possibility the capacity of the annular ring was calculated.

The capacity of Chelex-100 resin is 0.4 meq/mL (Bio-Rad Laboratories, 2000). Using this value the total capacity of the resin within the annular ring was calculated to be approximately 0.0053 meq. The total capacity was then converted to weight using the sum of molecular masses and average valence of the metals in the test solution (Cu, Cd, Zn, Pb and U), giving 1.51 mg. Thus the annular ring has the capacity to bind a maximum total mass of 1.51 mg Cu, Cd, Zn, Pb and U. The total mass of these metals in the 4 L test solution when each was spiked to 10 µg/L, was approximately 0.2 mg, well below the maximum capacity of the annular ring. However if leakage occurs locally in small areas of the annular ring adjacent to the site of water ingress, the theory of leaked mass entering the internal disc may still be valid.
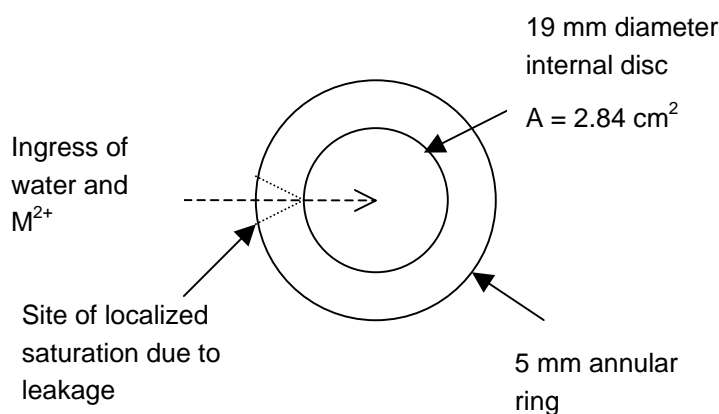
Figure 3.11 Diagrammatic representation of localised saturation of Chelex-100 resin within the annular ring adjacent to the site of leakage.

The volume of Chelex-100 within the localised area may become saturated within a short duration, after which the leaked metals may be able to bind to Chelex-100 resin within the 2.84 cm^2 area of the internal disc. Thus at ionic strength 0.2 mM removal of the annular ring may not be effective in counteracting the problem of leakage.

3.1.4 DGT performance in filtered Gulungul creek water

An experiment was performed in pH adjusted filtered (< 0.45µm) Gulungul Creek water spiked with metals in order to examine DGT performance in natural water of low ionic strength. The creek water had extremely low ionic strength, with an average EC of 35.5 µS/cm (n = 25), which is less than the average EC of the 0.2 mM $NaNO_3$ synthetic test solutions (approximately 50 µS/cm).
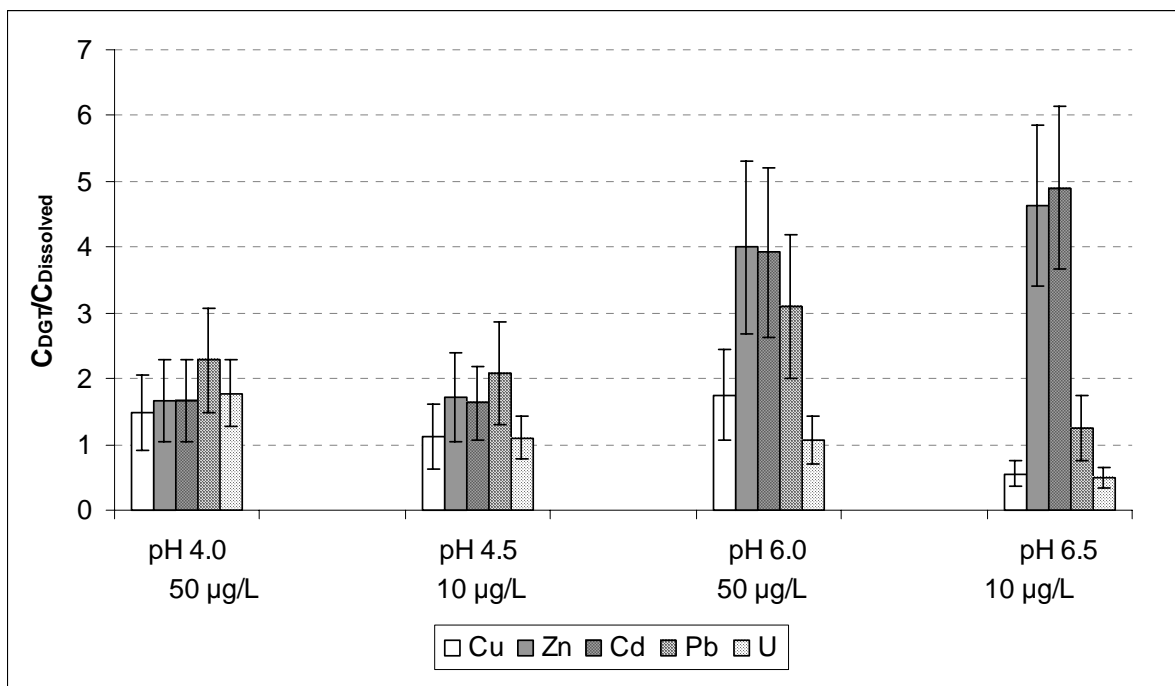
Figure 3.12 DGT performance in filtered Gulungul Creek water at varying pH and spiked metal concentration, expressed as the ratio of $C_{DGT}/C_{Dissolved}$. Error bars represent standard deviation ($\sigma = 1$) between time averaged DGT measurements (n=5).

The results showed that DGT overestimation of metal concentration in the filtered creek water was not as profound as that observed in synthetic test solutions with similar EC. Spiked metals in the synthetic solutions are present as free metal ions whilst in the filtered creek water the free metal ion concentration will be reduced due to the formation of complexes with natural dissolved ligands. Complex formation can reduce the amount of metals in solution that are available for uptake by DGT (DGT-labile) if they are inert, aggregate into particulate matter or are large enough that their diffusion through the diffusive layer is significantly impeded.

The presence of particulates was monitored in spiked filtered creek water test solutions by taking filtered ($< 0.45 \mu m$) and unfiltered water samples throughout the duration of the experiment. For most metals the unfiltered (total) concentration was similar to the filtered (dissolved) concentration, however at pH 6.0 and 6.5, 20% of Pb present was in particulate form. This may be due to formation of insoluble inorganic complexes of Pb (e.g. $PbCO_3$).

Low particulate concentration indicates that metal species formed in the filtered creek water test solution comprise of dissolved complexes. Because the Chelex-100 resin is assumed to exclusively bind free metal ions the measurement of a metal complex, ML, only occurs if the stability constant of the complex is sufficiently low that it undergoes dissociation, releasing the bound metal ion during its residency in the diffusion gel (Sangi *et al.*, 2002). The time taken for diffusion of a species, t_c, is given by the equation:

$$T_c = \frac{(\Delta g)^2}{\pi D} \qquad (3.3)$$

where Δg is the diffusion layer thickness and D is the diffusion coefficient of the species. The pore size of the diffusion gel is such that small complexes are able to diffuse freely at similar rates to free metal ions, however the diffusion of larger organic complexes may be impeded (Zhang and Davison, 2000).

These assumptions should remain relevant for DGT uptake at low ionic strength however the exact effects of the formation of the proposed electrical gradients on the diffusion of metal complexes would be difficult to determine. It may be assumed that the ionic strength effect is more profound on positively charged or highly polar species which may experience a greater attraction to the negative net charge within the DGT device. If this is true, the electrical gradients may influence free metal ions to a greater extent than metal complexes because all free metal ions exhibit positive charge and have a high charge to mass ratio compared to larger metal complexes, which may also be neutral or anionic.

Gimpel *et al.* (2001) studied the effect of pH on Cd and Cu in the pH range of 2 – 5 and Mn and Zn in the range 1 – 5. They found that DGT measurement of Cd was accurate between pH 5 and pH 10 but decreased below pH 5 due to a decline in uptake efficiency of the binding resin, which was also observed by Zhang and Davison (1995). Copper was measured accurately from pH 2 to pH 10 while Mn and Zn were measured accurately in the pH range 3.5 - 5. These findings all suggest that DGT measurement should be independent of pH within the range of 4.0 to 6.5, except for Cd for which DGT uptake is expected to decrease in the pH 4 test solutions.

Figure 3.12 shows a large difference in metal recovery measured by DGT between the different pH levels. The pH 4 and pH 4.5 treatments gave similar results for all metals, with Zn and Cd remaining constant over both spike concentrations, however Pb, Cu and U decreased slightly in the test solution with lower metal concentration (10 µg/L).

At pH 6 and pH 6.4, DGT overestimation for Cd and Zn was high compared to the other metals and increased with decreasing metal concentration. Similarly to the pH 4 and pH 4.5 test solutions, the DGT measured Pb, Cu and U decreased with decrease in metal concentration, with Cu and U showing less than 100% recovery.

These results show that there are three significantly different trends occurring in relation to pH change. DGT measurement of Zn and Cd increases with pH, independent of bulk solution concentration. Similarly, DGT measurement of Cu and Pb increases with increasing pH but not exclusively of bulk solution concentration while DGT measurement of U is independent of pH but varies slightly with external solution concentration.

Zinc and Cadmium

In the low pH solutions the DGT measured concentration for zinc and cadmium were similar at pH 4.0 and pH 4.5, with $C_{DGT}/C_{Dissolved}$ ratio of approximately 1.7. As pH increased, the recovery for Zn and Cd also increased, to a ratio of 4 at pH 6 a ratio of approximately 5 at pH 6.5. The results indicate that Cd and Zn present in the creek water as labile complexes. Both metals have d^{10} electron configuration, thus complexation with ligating species (other than H_2O) is not favoured as it offers no stabilization (Bailey *et al*., 2002). Therefore the metals are essentially weakly binding and complexes formed have low stability constants, showing that Zn and Cd are DGT-labile in filtered creek water.

Lead and Copper

In contrast to the behaviour of Cd and Zn, DGT recovery for Pb and Cu appear to be effected by the metal concentration in solution as well as pH. The overall trend for Pb and Cu with respect to increasing pH is an increase in DGT measurement, as shown by the increase in $C_{DGT}/C_{Dissolved}$ ratio for these metals as pH is increased from 4.5 to 6.0 (Figure 3.12). However recoveries for these metals at either end of the pH range decreased with the decrease in bulk solution concentration, from 50 to 10 µg/L.

This indicates that Pb and Cu are forming inert complexes with material in the creek that are not DGT-labile. Copper and Pb recovery is greater when their concentration in external solutions is greater at both pH extremes. Because these test solutions were made using the same batch of filtered creek water it is assumed that the concentration of potential binding material is the same in each test solution, regardless of the spiked metal concentration. The trend observed for Pb and Cu could be due to the relative differences in concentration of metals and ligating material at each spiked concentration. In solutions with low spiked concentration (10 µg/L), the concentration of ligating material may be in excess, therefore binding the majority spiked metals. At the high spike concentration (50 µg/L), it is likely that the metals are in excess of the ligating material, thus only a fraction of the metals present are bound. Once the ligands in the test solution become saturated, the remaining metal is available for uptake by DGT, probably as aquated metal ions.

Because there is a greater concentration of DGT-labile metals present at high solution concentration the overestimation effect due to low ionic strength is more profound than that observed at lower solution concentration, where a significant proportion of the metal is bound in inert complexes.

Figure 3.12 also shows that in the low spike concentration solutions (10µg/L) the recovery for Pb and Cu is higher at pH 4.5 compared to pH 6.5. This may be explained by the low stability and consequent dissociation of metal complexes at lower pH, yielding free metal ions.

Uranium

DGT measurement of U appears to decrease with increasing pH as the ratio of DGT concentration to solution concentration is reduced significantly from 1.7 at pH 4.0 to 1.1 at pH 6.0. These results suggest that U may form inert complexes at higher pH which bind the majority of U making it unavailable for DGT uptake. The increased uptake observed at lower pH indicates increase in the concentration of U in DGT-labile forms. It is likely that the inert complexes that are formed at pH > 6 have low stability at the lower end of the pH scale, similar to Pb and Cu complexes as described above. Also similar to Pb and Cu, the recovery of U is decreased when bulk solution concentration is decreased. This is likely to be due to the saturation of available ligands in the creek water test solution at the higher metal concentration (50 µg/L).

3.1.5 Summary

It was observed that under ideal conditions DGT measurement was effected by leakage of metals into the device via inefficient seals between the piston base and the cap. The effect of leakage was counteracted in following experiments by removal of the outer 5mm thick annular ring of resin gel, which was found to contain the leaked mass of metals at ionic strength > 0.2 mM.

The DGT measurement (with annular ring removal) was found to become independent of ionic strength between 2 and 20 mM NaNO$_3$. This did not agree with the low threshold 0.2 mM major

cations suggested by Alfaro-De la Torre *et al.*, (2000) however it has been shown that their calculated prediction may not be sufficient in accounting for low ionic strength effects.

DGT devices deployed in creek water with EC 35.5 μS/cm (equivalent to < 0.2 mM $NaNO_3$) were subject to substantial overestimation in metal measurement due to the effects of low ionic strength. However, information on the complexation capacity of the filtered Gulungul creek water for specific metals was derived from DGT measurement. It was observed that Cd and Zn are present primarily as labile complexes. At higher pH Pb, Cu and U form inert complexes that are not measurable by DGT.

3.2 Field Trials

3.2.1 Detection limits

The detection limit of an analytical technique is essentially the minimum amount of analyte that is detectable for measurement (Houk, 2003). Analytical analyses with lower detection limits are more sensitive to low analyte concentration compared to those with high detection limits.

Table 3.4 Average blank concentrations (µg/L) and detection limits (µg/L) for water samples and DGT over the monitoring period

Water samples	U	Pb	Cd	Cu	Mn	Zn	Al	Fe
Detection limit	0.00046	0.016	0.0080	0.0061	0.014	0.097	0.10	1.6
Unfiltered sample blank	<D.L.	<D.L.	<D.L.	0.014	0.016	<D.L.	0.20	<D.L.
Filtered sample blank	<D.L.	<D.L.	<D.L.	<D.L.	0.036	<D.L.	<D.L.	<D.L.
DGT detection limits	**U**	**Pb**	**Cd**	**Cu**	**Mn**	**Zn**	**Al**	**Fe**
6 h	0.0040	0.025	0.0058	0.12	0.061	0.62	5.3	23
43 h	0.00044	0.0023	0.0014	0.036	0.11	0.24	0.73	1.7
168 h	0.00010	0.00069	0.00037	0.0066	0.0081	0.053	0.19	0.43

Because DGT devices continuously accumulate metals throughout the deployment period, they effectively pre-concentrate metals within the binding gel (Zhang and Davison, 1995). As a result of time-integration, DGT detection limits may be significantly lower than those obtained for water sampling. The average DGT detection limits over a typical deployment period (168 h) were less than those for water samples (Table 3.4). DGT detection limits are inversely proportional to time, which explains why the detection limit for the 6 h deployment in RP1 were higher than those obtained in the 43 h deployment.

3.2.2 Ionic strength

Laboratory validation experiments performed in this study have shown that DGT measurement is independent of ionic strength in solutions with $NaNO_3$ concentration 20 mM, which is equivalent to an EC of approximately 2000 µS/cm. Magela and Gulungul Creeks typically have a EC < 20 µS/cm, therefore it is expected that the DGT devices deployed in natural creek water may be influenced by the ionic strength effect observed in the laboratory experiments, causing enhanced DGT measurement (Table 3.5).

Table 3.5 Average (± SD) *in situ* physico-chemical parameters for each study site over the monitoring period

Parameter	RP1 (n = 2)	Magela creek upstream (n = 9)	Magela creek downstream (n = 9)	Gulungul creek downstream (n = 9)
PH	6.7 ± 0.35	5.9 ± 0.4	6.0 ± 0.5	6.0 ± 0.3
EC (µS/cm)	240 ± 2.1	9.9 ± 1.2	12 ± 1.6	13 ± 1.3
DO (mg/L)	7.1 ± 0.22	6.8 ± 0.2	6.7 ± 0.2	7.0 ± 0.3

The DGT validation studies showed that at EC 250 µS/cm (similar to EC of RP1) the degree of overestimation of DGT-labile metal concentration was reduced significantly compared to overestimation observed at EC of 30 µS/cm (similar to that of Magela and Gulungul Creeks). These results suggest that the ionic strength effect will be less profound in RP1 compared to the creek water, allowing for higher accuracy of DGT measurement in RP1.

In filtered (< 0.45 µm) creek water (EC = 35.5 µS/cm) the DGT overestimation was less profound compared to that observed in synthetic test solutions. This is an illustration of DGT speciation capability, showing that in creek water, which has significant complexation capacity compared to synthetic test solutions, the influence of dissolved (< 0.45 µm) ligating species decreases the overestimation of the DGT measurement.

In summary, the low ionic strength of the natural creek water may cause overestimation in the measurement of DGT-labile species. However, even though the DGT-labile concentration measured is not quantitative it can still be used to provide information on metal speciation and bioavailability.

3.2.3 RP1 Input

Release of water from RP1 during the wet season is the major potential source of mine related contaminants in Magela creek (Supervising Scientist 2002b). RP1 was monitored to obtain information on the concentration and speciation of metals being released from this point source into Magela creek.

Previous studies conducted on Magela Creek have shown that background levels of metals are low (Hart *et al.*, 1982) (Table 3.6).

Table 3.6 Summary of metal concentrations in Magela Creek prior to commencement of mining*

Metal	Total	Dissolved (<0.45µm)	Percent of the total that was dissolved
	Mean ± SE	Mean ± SE	Mean
Fe	281 ± 122	0	0
Mn	7.8 ± 3.33	4.7 ± 1.6	60
Zn	2.8 ± 0.7	1.9 ± 0.4	68
Cu	0.41 ± 0.16	0.30 ± 0.09	73
Cd	0.04 ± 0.02	0.04 ± 0.01	100

* (Hart *et al.* 1982)

In later years Le Gras and Noller (1989) reported dissolved Zn concentrations of 0.3 µg/L. The initial high concentrations reported in Table 3.6 were probably caused by contamination during sample collection, which is common for Zn as well as Al and Mn if preventative measures are not taken (Emons, 2003). With the exception of Fe, values for total and dissolved concentrations of all metals in Table 3.6 are higher than the averaged results obtained from water sampling conducted in this study, probably because trace metal clean procedures were carried out for sampling and analysis in order to minimize potential contamination (Table 3.7).

Triplicate DGT devices were deployed in RP1 for a period of 6 h and another period of 43 h. DGT measurements for most metals during the 6 h deployment were below DGT detection limits. The results of the 43 h deployment are shown in Figure 3.13.
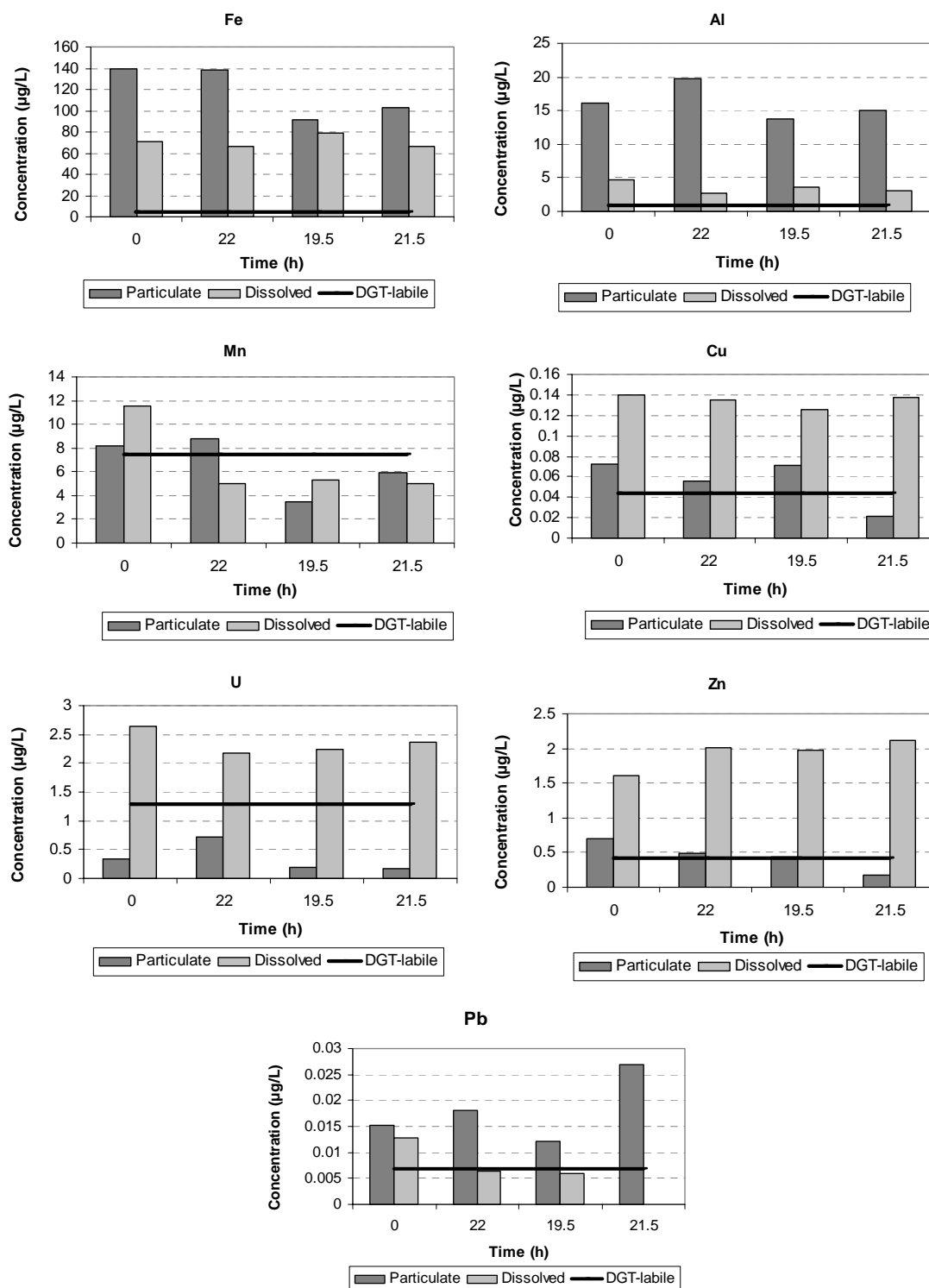
Figure 3.13 Particulate, dissolved and DGT-labile metal concentrations measured in RP1 over 43 h deployment of triplicate DGT devices.

The total concentration of Fe in RP1 was high, with particulate concentrations ranging from 80 – 140 µg/L and dissolved concentrations ranging form 60-80 µg/L. The DGT-labile concentration of Fe was low, indicating absence of available species. Similar results were seen for Al, however particulate forms of Al clearly dominated, with soluble Al concentration < 5 µg/L. For Mn the particulate and dissolved concentrations were relatively similar over the monitoring period, with DGT-labile concentrations grossly overestimated indicating high concentration of available species. Total U, Zn and Cu concentrations were dominated by dissolved species, of which a substantial amount was DGT-labile.

The input of RP1 water into Magela Creek occurs via the Coonjimba Billabong inlet (Figure 2.1) which is located between the upstream and downstream sites. Therefore impact of RP1 release is assessed by comparative monitoring between the unaffected upstream site and the potentially affected downstream site.

Elevated levels of metals observed at the downstream site during this study may be partly attributed to input from RP1 but also from the other potential sources such as runoff from land application of RP2 water (Supervising Scientist, 2002a).

3.2.4 Metal Speciation assessment

Basic speciation assessment was carried out for each of the three sampling sites using the monitoring data obtained. Metals occur as a variety of species, including free metal ions and complexes with inorganic and organic compounds that can exist in soluble, colloidal or particulate forms (Bailey *et al*., 2002). The total concentration of a metal is obtained from unfiltered water samples and comprises of particulate and dissolved species. The dissolved metal concentration is ascertained from the filtered (< 0.45 µm) water samples, which includes free metal ions, soluble inorganic and organic metal complexes and colloidal material that is small enough to pass through the filter.   The particulate concentration, which is calculated by subtracting the dissolved concentration from the total concentration, comprises of large (> 0.45 µm) colloidal material and suspended particles such as clay and silt.

The DGT devices offer further division of metal species by measuring the DGT-labile fraction of the dissolved concentration, which is an approximation of bioavailable concentration that includes free metal ions and labile (weakly bound) metal complexes (Nolan *et al.*, 2003). Due to the low ionic strength of the waters studied it is likely that the DGT measurement is overestimated, giving enhanced DGT-labile concentrations. The overestimation is higher when metals are present in greater concentrations in DGT-labile form.

Table 3.7 Summary of averaged total, dissolved (< 0.45μm) and DGT-labile metal concentrations (μg/L) with percent of dissolved concentration that was DGT-labile (*% DGT-labile*)* in RP1 (43 h deployment), Magela Creek Upstream, Magela Creek Downstream and Gulungul Creek Downstream (168 h deployment)

RP1	Fe	Cu~	Al	U	Mn
Total	190	0.19	20	2.7	13
Particulate	120	0.060	17	0.3	6.3
Dissolved	71	0.13	3.5	2.4	6.7
DGT-labile	4.4	0.040	0.95	1.3	7.4
% DGT-labile	*6.2*	*33*	*27*	*55*	*110*

Magela Creek Upstream	Fe	Cu~	Al	U	Mn
Total	310	0.22	150	0.025	4.5
Particulate	210	0.080	95	0.0071	0.99
Dissolved	96	0.14	56	0.018	3.5
DGT-labile	4.0	0.0080	4.2	0.0014	6.6
% DGT-labile	*4.1*	*6.0*	*7.9*	*7.8*	*190*

Magela Creek Downstream	Fe	Cu~	Al	U	Mn
Total	360	0.27	200	0.056	4.9
Particulate	250	0.12	140	0.12	1.4
Dissolved	110	0.15	57	0.047	3.5
DGT-labile	2.5	0.0080	3.1	0.0043	6.4
% DGT-labile	*2.2*	*4.6*	*5.5*	*9.3*	*180*

Gulungul Creek Downstream	Fe	Cu~	Al	U	Mn
Total	220	0.15	120	0.12	3.1
Particulate	130	0.039	58	0.022	0.75
Dissolved	90	0.11	59	0.095	2.4
DGT-labile	1.9	0.013	3.1	0.0081	2.3
% DGT-labile	*2.2*	*12*	*5.3*	*8.8*	*100*

* % DGT-labile values were calculated from raw dissolved and DGT-labile concentration data for each week.

~ Cu was consistently below detection limits of DGT measurement.

In Table 3.7 the bold values represent the fraction of the dissolved concentration that was measured by DGT. In general the results show that DGT measured concentrations were less than dissolved concentrations for the majority of metals, indicating that the DGT-labile concentrations of most metals in natural creek water was low.

Exceptions were Mn and Zn in Magela Creek which were measured by DGT at greater than 100% recovery of the dissolved concentrations. DGT overestimation caused by low ionic strength is more important when metals are present in solution as free metal ions, suggesting in

Magela Creek, a reasonable proportion of Mn and Zn present in the dissolved fraction may exist as free metal ion species. It may also indicate that the majority of Mn and Zn is bioavailable.

Uranium

Uranium is the primary mine related toxicant of concern (Supervising Scientist, 2002b.). Results for weekly U monitoring are shown in Figure 3.14.
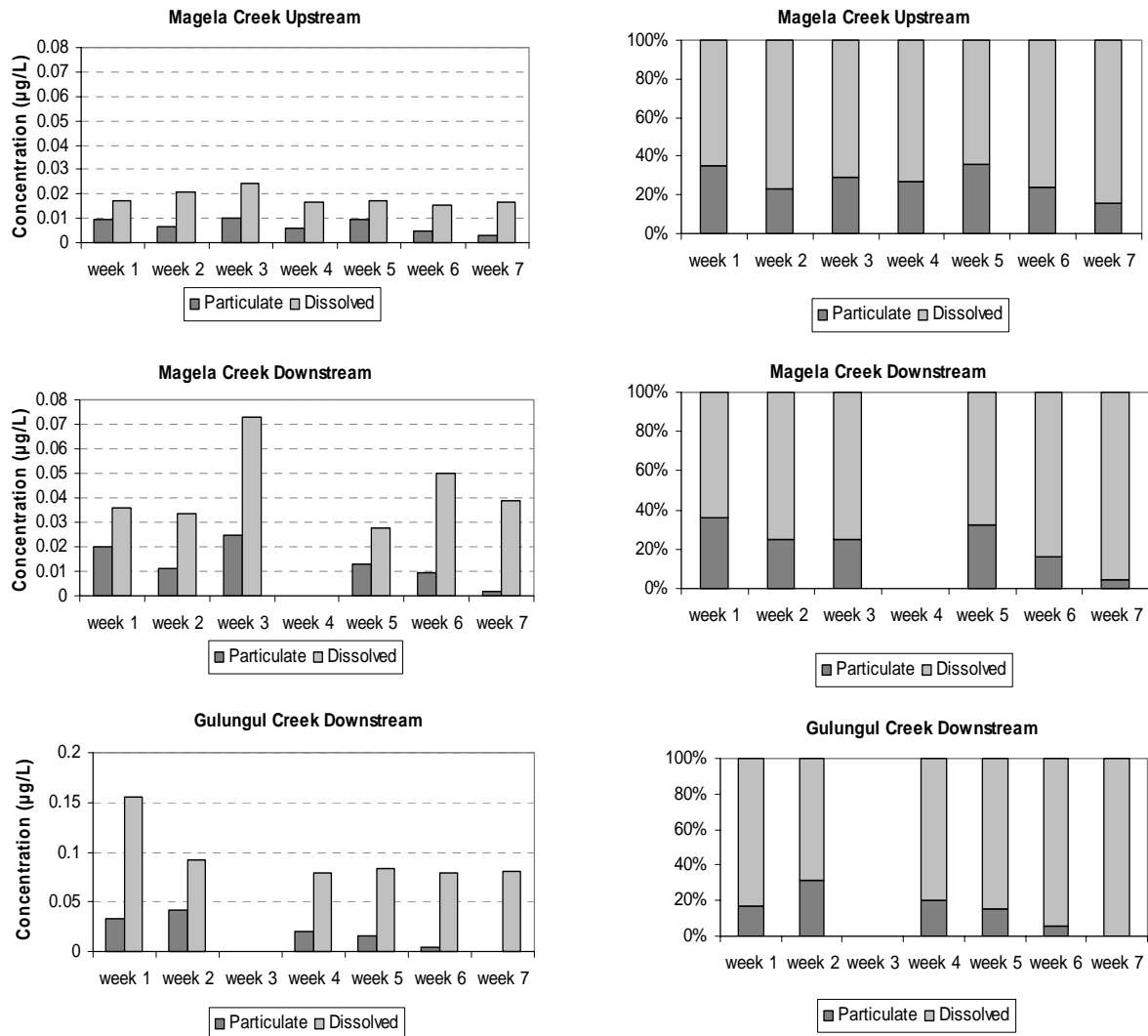
Figure 3.14 Concentrations of particulate and dissolved U and the relative fraction of each contributed to total concentration over the seven week trial period. Erroneous data obtained at week 4 for Magela Creek Downstream are not shown. Water samples were not obtained from Gulungul Creek Downstream at week 3 due to flooding.

Total U concentration is higher and more variable over time at the Magela Creek downstream site compared to the upstream site where particulate and dissolved concentrations both remained relatively constant over time. This suggests mine related input of U into the Magela Creek system, possibly originating from RP1.

For both creeks U was present predominantly in dissolved forms over the monitoring period, with particulate U only contributing up to 40% of the total concentration. Towards the end of the monitoring period the concentration of particulate U was further decreased with almost all U present in dissolved form.

The concentration of dissolved U was consistently higher in Gulungul Creek compared to Magela Creek, possibly indicating mine related input. The main sources of mine related input in Gulungul Creek are surface expression of groundwater contaminated by tailings dam seepage and runoff from the external waste rock surface of the tailings dam (Supervising Scientist, 2002b). The highest dissolved U concentration observed in Gulungul creek occurred at the beginning of the monitoring period which coincided with significant rainfall (Figure 3.14), hence the source of U is more likely to be overland flow of waste-rock runoff.

a)

b)

Figure 3.15 Percent of dissolved (< 0.45 μm) U concentration that was DGT-labile over seven week trial period in a) Magela Creek upstream (MCUS) and Magela Creek downstream (MCDS) and b) Gulungul Creek downstream (GCDS).

The DGT-labile concentration of U present in both creeks was relatively low, ranging from 4 to 16 % of the dissolved concentration. The overestimated concentrations were < 0.01 μg/L (Table 3.7) which indicates that the actual concentration of DGT-labile U must be extremely low.

Uranium in oxic surface waters may exist as the free uranyl ion (UO_2^{2+}), or inorganic uranyl complexes including hydroxides, carbonates and phosphates (Bailey *et al.*, 2002). Stable organic uranyl complexes also exist in soft, low-alkaline, organic rich surface waters with pH 5-7 (ANZECC and ARMANZ, 2000). The free uranyl ion and uranyl hydroxide (UO_2OH^+) are considered to be the most toxic forms of U because they are more bioavailable than the U complexes (Markich, 2002).

Work by Riethmuller *et al.*, (2001) predicted U speciation in synthetic water that simulated the physico-chemical properties (pH 6, alkalinity 4.0 mg/L $CaCO_3$) and inorganic composition of Magela Creek. Of the total U concentration in the synthetic solution, approximately 10% was present as the free uranyl ion (UO_2^{2+}). This is in agreement with the average DGT measured fractions of total dissolved U presented in this study, being approximately 8 % for Magela Creek upstream and 9 % for Magela Creek downstream and Gulungul Creek.

Figure 3.16 Weekly dissolved (< 0.45μm) (♦) and DGT-labile (──) concentrations (μg/L) of U against daily discharge (m³/s) and rainfall volume (mm) at Gulungul Creek Downstream.

Figure 3.16 shows that dissolved and DGT-labile U concentrations in Gulungul Creek were relatively constant over the monitoring period, with little variation in relation to the fluctuating discharge except for the first two weeks where both dissolved and DGT-labile concentrations were slightly increased.

Manganese

Manganese is only moderately toxic, however it is a common constituent of the mine related discharge from retention ponds 1 and 2 (Bailey *et al.*, 2002; Hart, 1982)

Figure 3.17 Concentrations of particulate and dissolved Mn and the relative fraction of each contributed to total concentration over the seven week trial period. Erroneous data obtained at week 4 for Magela Creek Downstream are not shown. Water samples were not obtained from Gulungul Creek Downstream at week 3 due to flooding.

The total concentration of Mn in Magela and Gulungul Creeks was low, with particulate concentration ranging from 0.5 – 1 µg/L and dissolved concentrations ranging from 2 – 4 µg/L.

Mn was present primarily in dissolved form, contributing approximately 60 – 80% of total Mn concentration. This agrees with previous studies of metal speciation in Magela Creek (Hart *et al.*, 1982; Noller *et al.*, 1985; Speers 1995).
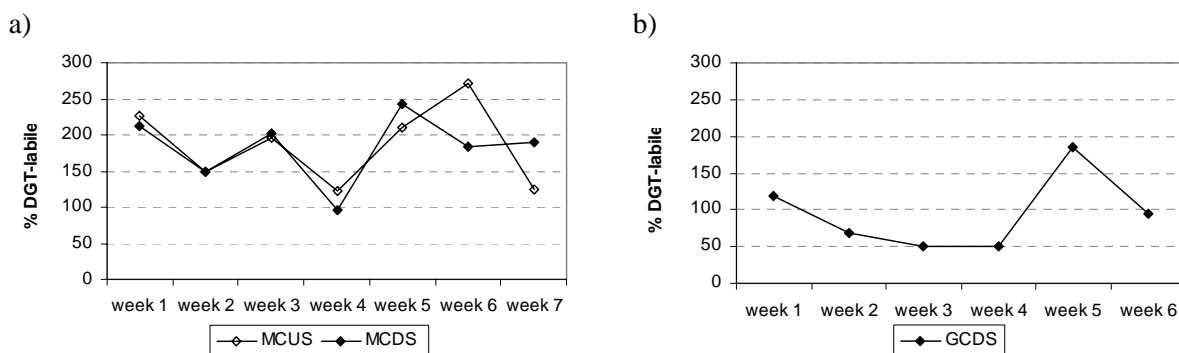
Figure 3.18 Percent of dissolved (< 0.45 µm) Mn concentration that was DGT-labile over seven week trial period in a) Magela Creek upstream (MCUS) and Magela Creek downstream (MCDS) and b) Gulungul Creek downstream (GCDS).

Results of DGT measurement show DGT-labile concentrations greater than the dissolved concentrations, which is an artefact of the low ionic strength effect causing DGT overestimation (Figure 3.18). Because the overestimation observed is high, it can be suggested that a reasonable proportion of Mn is present in DGT-labile form. This was also suggested by Noller *et al.* (1985) who used filtration fractionation methods to discern Mn speciation. They found that of the average 6.0 µg/L dissolved (< 0.4 µm) Mn in Magela Creek, 53 % (3.2 µg/L) was present as hydrated Mn oxides (< 0.05 µm fraction) and 31 % (1.9 µg/L) was present as ionic Mn or soluble Mn complexes (< 0.015 µm fraction). Mn hydroxides are stable in waters with circum-neutral pH so they are not detectable by DGT (Bailey *et al.*, 2002). This indicates that the DGT-labile concentration of Mn measured in this study may comprise of similar species measured in the < 0.015 µm fraction by Noller *et al.* (1985).
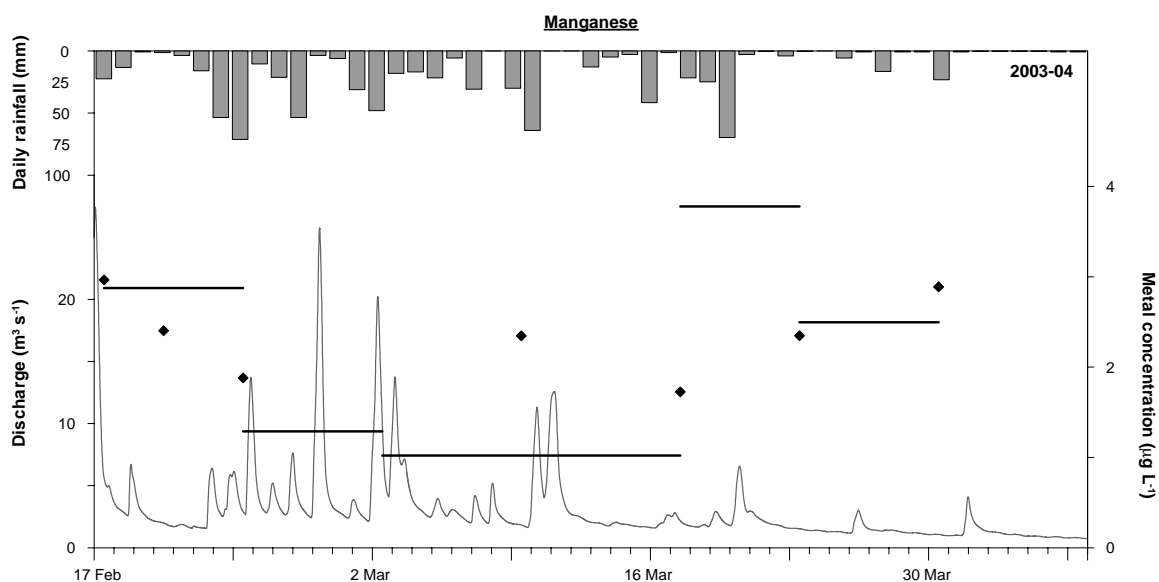
Figure 3.19 Weekly dissolved (< 0.45µm) (♦) and DGT-labile (——) concentrations (µg/L) of Mn against daily discharge (m^3/s) and rainfall volume (mm) at Gulungul Creek Downstream.

Dissolved Mn concentrations increased towards the end of the monitoring period which is clearly correlated to decrease in discharge (Figure 3.19). This agrees with the results of Speers (1995),

who found that as ground water contribution to creek flow is increased the concentration of dissolved Mn increases, suggesting that the main source of dissolved Mn is groundwater. Figure 3.19 clearly shows that DGT-labile Mn concentration also increases with decreased discharge, indicating that labile Mn species originate from groundwater.

Aluminium

Al is generally considered to be non-toxic because of the high stability of Al complexes, however under acidic conditions Al is known to become more bioavailable leading to natural fish kills (Noller *et al.*, 1985). Results for Al are shown in Figure 3.20 as particulate and dissolved concentrations and relative contributions of each to the total concentration.
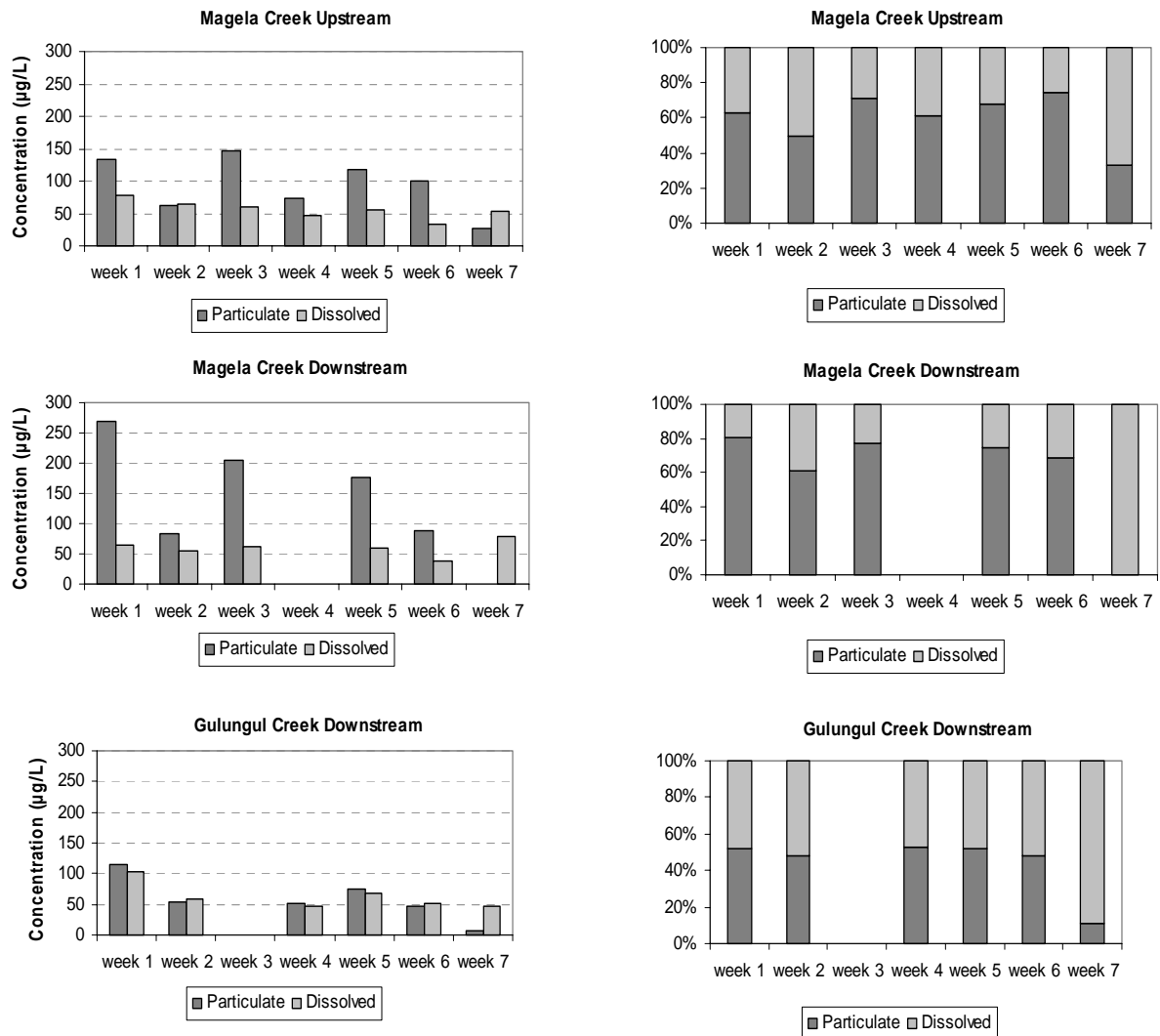
Figure 3.20 Concentrations of particulate and dissolved Al and the relative fraction of each contributed to total concentration over the seven week trial period. Erroneous data obtained at week 4 for Magela Creek Downstream are not shown. Water samples were not obtained from Gulungul Creek Downstream at week 3 due to flooding.

The concentration of particulate Al was more variable in Magela Creek than Gulungul Creek, ranging from 30 – 150 µg/L at the upstream site and 100 – 205 µg/L at the downstream site. It

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was suggested by Hart *et al.* (1992) that the source of Al in Magela Creek was probably from erosion mechanisms in the highly weathered and extensively laterized catchment and that during high flow, particulate Al is present in Magela Creek as aluminosilicates which are readily mobilized from laterite. In Gulungul Creek the contribution of particulate Al to the total concentration (approximately 50%) was consistently lower than that observed in Magela Creek, possibly reflecting differences in the catchments of the two creeks.

The peaks in particulate Al concentration observed in Magela Creek at weeks 1, 3 and 5 (Figure 3.20) may be due to an increased input of erodable materials in runoff from the catchment caused by rainfall. Hart *et al.* (1982) observed a general trend towards higher concentrations of suspended solids at higher flows. They also observed that peak concentrations of particulates reduced over the wet season, which may describe the decrease in particulate Al concentrations over weeks 5, 6 and 7 at all sites (Figure 3.20).

The concentration of dissolved Al was relatively constant (approximately 50 µg/L) in each creek over the seven week sampling period. The fraction of dissolved Al that was DGT-labile in Magela and Gulungul creeks is shown in figure 3.21.

a)   b)
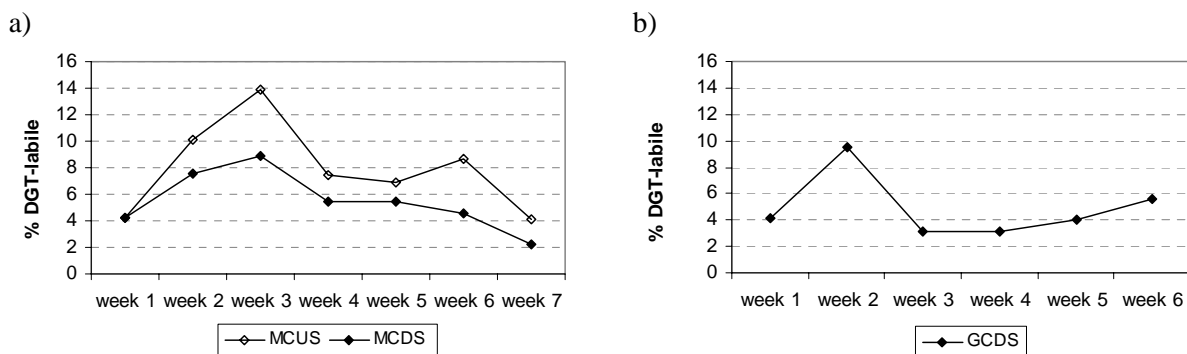
Figure 3.21 Percent of dissolved (< 0.45 µm) Al concentration that was DGT-labile over seven week trial period in a) Magela Creek upstream (MCUS) and Magela Creek downstream (MCDS) and b) Gulungul Creek downstream (GCDS).

In both creeks 2 – 14% of the dissolved concentration was found to be DGT-labile. These relatively low DGT-labile concentrations suggest that bioavailable forms of Al are not significant. Because Al is an oxophilic element it binds preferentially and strongly to oxygen atoms, thus in oxic natural waters Al is present as stable oxides and oxo anion species (Bailey *et al.*, 2002). This was confirmed by computer modelling (MINTEQA2) predictions of Al speciation which showed that hydroxy complexes were the dominating species of dissolved Al in Magela Creek (Speers, 2000). Organic complexation of Al was investigated by Tipping *et al.* (2002), who demonstrated that $AlOH^{2+}$ was the principle form of Al bound to DOM. Therefore, it is not surprising that the DGT-labile concentration of Al (average of 3.46µg/L over both creeks) is low.

In Figure 3.22 the dissolved concentration of Al is compared to discharge in Gulungul Creek.
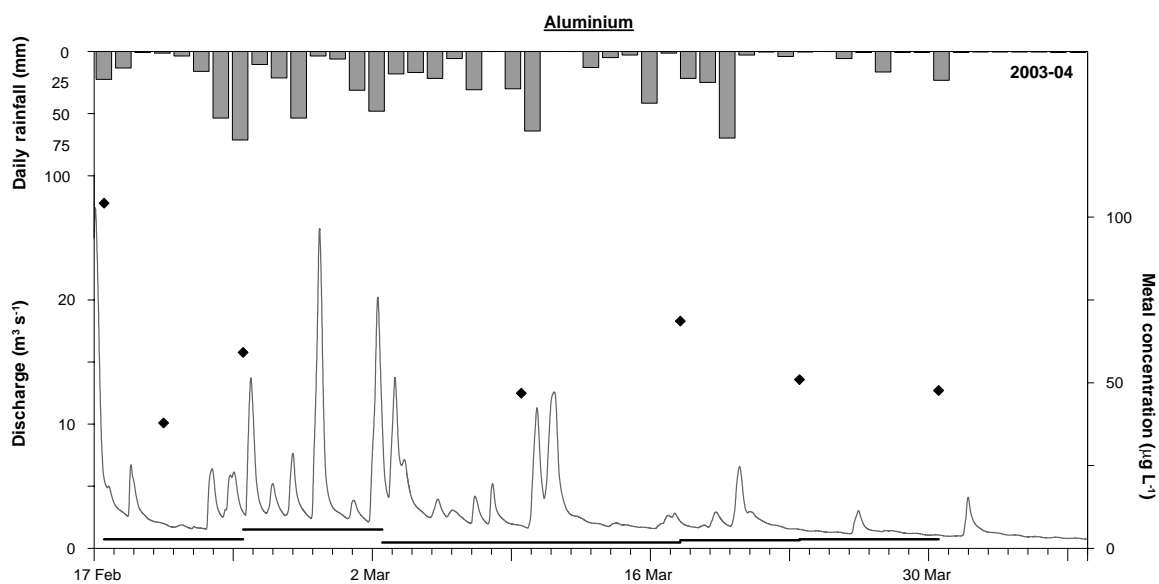
Figure 3.22 Weekly dissolved (< 0.45 µm) (♦) and DGT-labile (——) concentrations (µg/L) of Al against daily discharge (m³/s) and rainfall volume (mm) at Gulungul Creek Downstream.

DGT were able to detect higher concentrations of DGT-labile aluminium during periods of high discharge, such as that related to the flood events that occurred over the second week of monitoring (Figure 3.22).

Iron

Many of the trends observed for Fe were similar to those previously described for Al. This is because of similar laterite source for each of these metals as well as the formation of stable Fe hydroxides (Hart *et al.*, 1982; Baiely *et al.*, 2002). Results for Fe are shown in Figure 3.23 as particulate and dissolved concentrations and relative contributions of each to the total concentration.
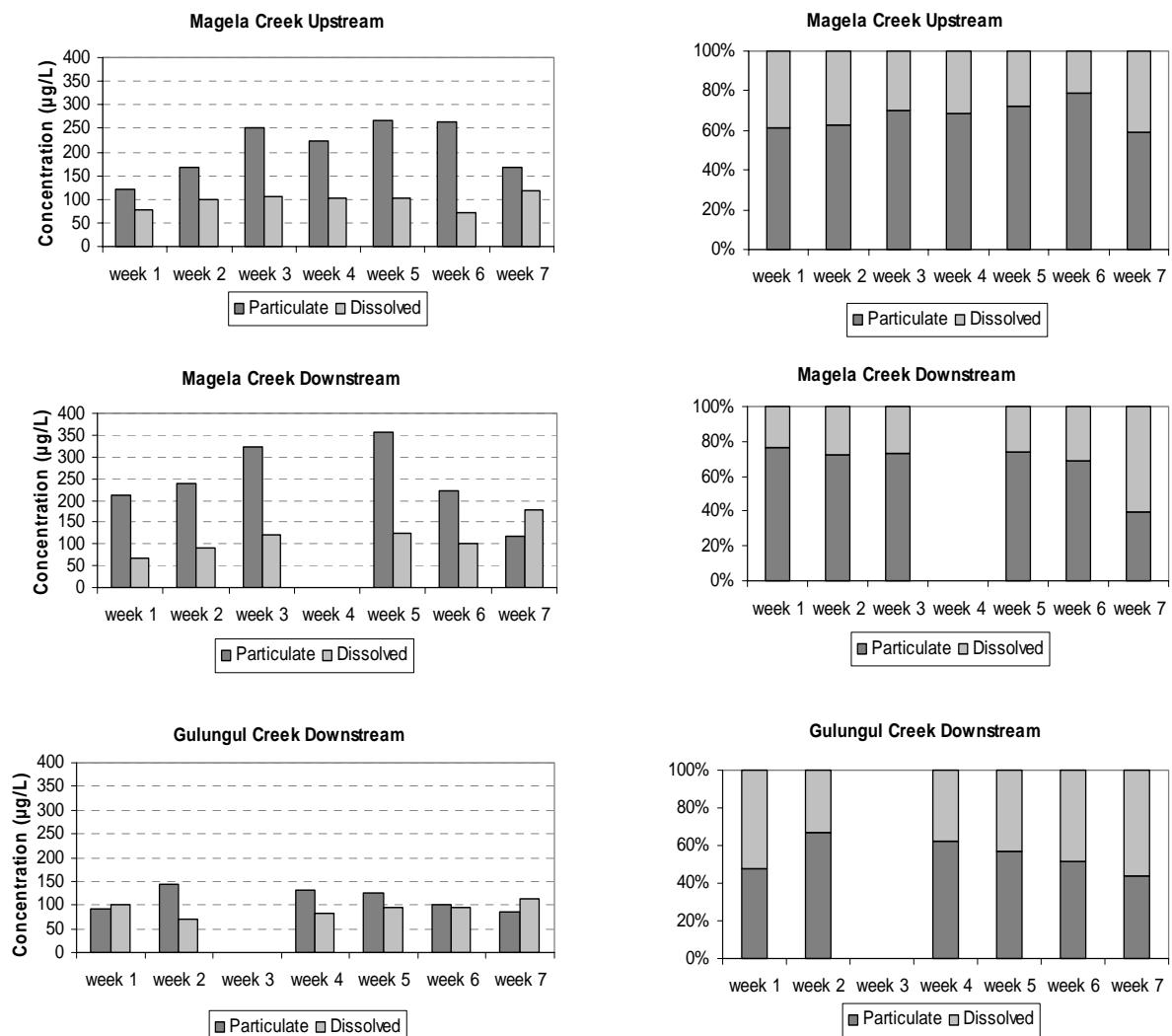
Figure 3.23 Concentrations of particulate and dissolved Fe and the relative fraction of each contributed to total concentration over the seven week trial period. Erroneous data obtained at week 4 for Magela Creek Downstream are not shown. Water samples were not obtained from Gulungul Creek Downstream at week 3 due to flooding.

Fe is present predominantly in particulate forms at similar concentrations in both Magela and Gulungul Creeks, contributing 40–80 % of the total concentration in Magela Creek and 40–60% in Gulungul Creek. In Magela Creek the concentrations of particulate Fe varied over the seven week monitoring period, with a reduction observed over the final three weeks. Similarly to Al, this variation may be related to rainfall runoff from the catchment. Also similar to Al, the particulate Fe concentrations in Gulungul creek (90–150 μmg/L) were lower than Magela Creek concentrations (100–350 μg/L), suggesting different sources of Fe from the different catchment areas.

In contrast to the particulate concentration, the dissolved concentration of Fe was relatively constant in both creeks over the monitoring period, ranging from 50 – 100 µg/L.

DGT measurement showed that 1 – 5 % of the dissolved Fe concentration was in DGT-labile form (Figure 3.24).
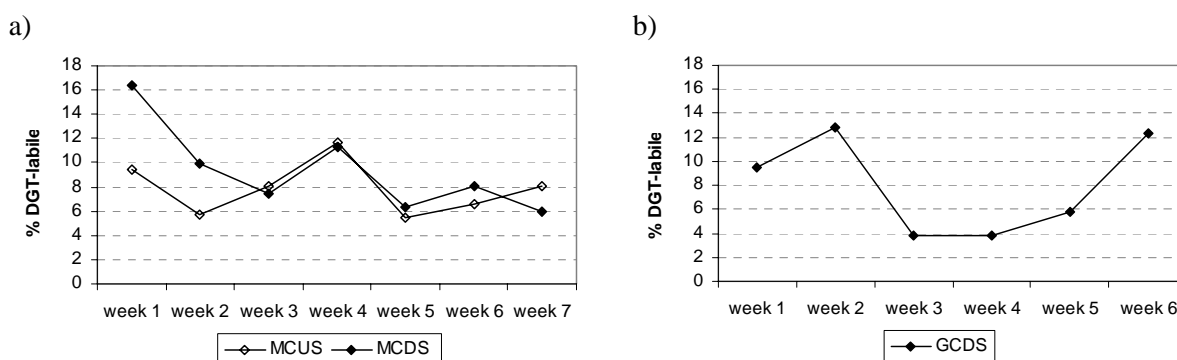
a)

b)
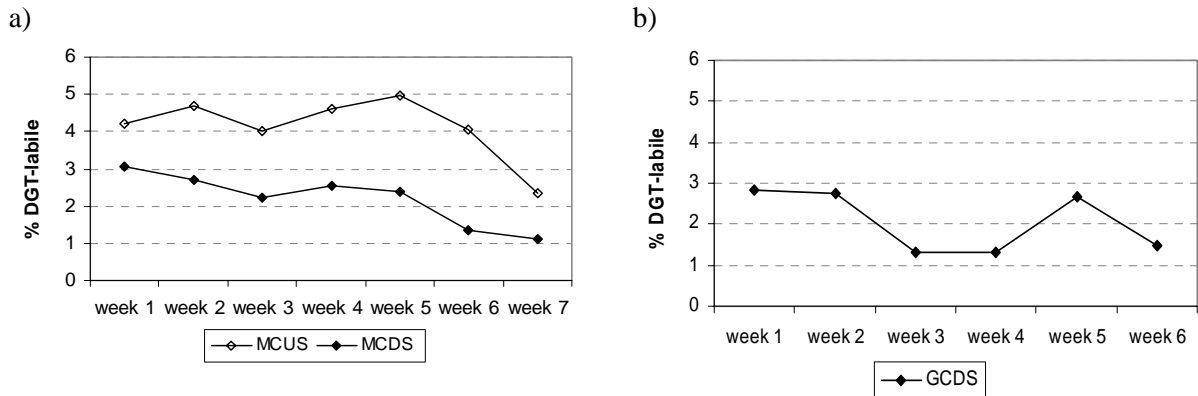
Figure 3.24 Percent of dissolved (< 0.45 µm) Fe concentration that was DGT-labile over seven week trial period in a) Magela Creek upstream (MCUS) and Magela Creek downstream (MCDS) and b) Gulungul Creek downstream (GCDS).

These results are supported by the computational speciation analysis conducted by Speers (1995), which found Fe hydroxides were the dominant Fe species in Magela Creek. An important Fe (III) species in freshwater is ferric hydroxide, FeO(OH), which is a stable polymerized hydrolysis product of hexaqua Fe, $[Fe(H_2O)_6]^{3+}$. Fe is also believed to form strong bonds with DOM, particularly $FeOH^{2+}$, resulting in stable organic complexes (Jansen *et al.*, 2001; Tipping *et al.*, 2002). The stability of Fe hydroxides, including ferric hydroxide, and organic Fe complexes may explain the low DGT-labile concentrations.
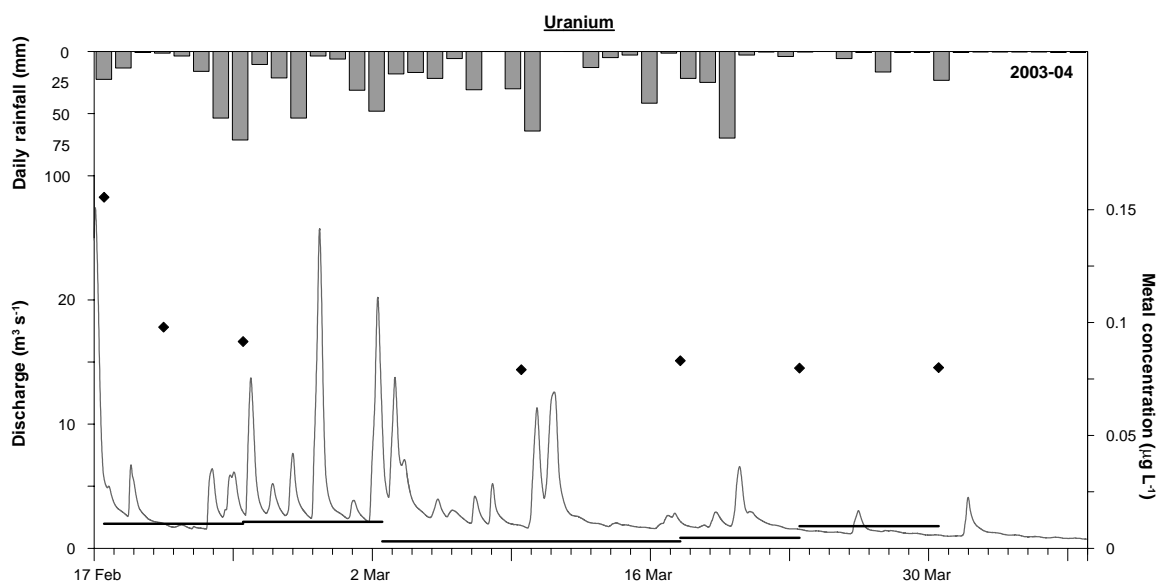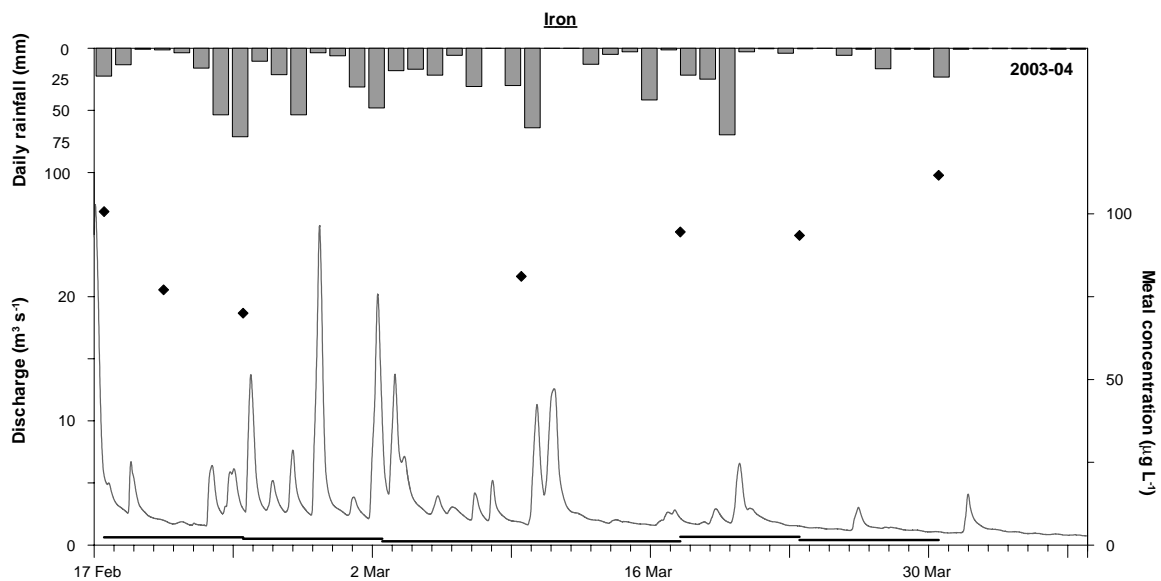

Figure 3.25 Weekly dissolved (< 0.45µm) (♦) and DGT-labile (——) concentrations (µg/L) of Fe against daily discharge (m³/s) and rainfall volume (mm) at Gulungul Creek Downstream.

Comparison of DGT measurement to discharge reaffirms the low DGT-labile Fe concentration and shows that there was no discernable relationship between DGT-labile concentration and discharge (Figure 3.25).

Copper

Copper occurs naturally at low levels, with the free hydrated Cu ion and the hydroxo species thought to be the most toxic (ANZECC and ARMCANZ, 2000).
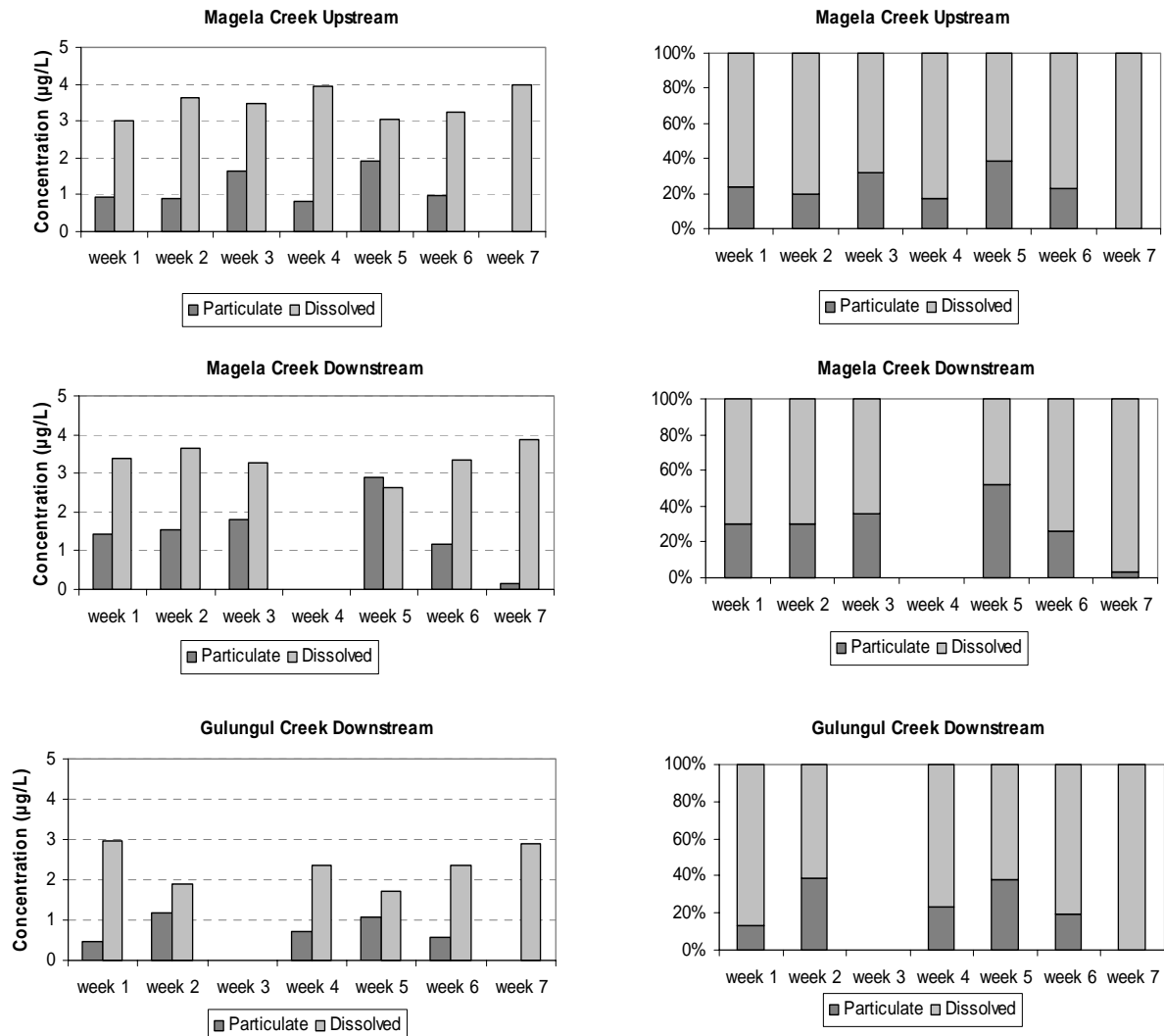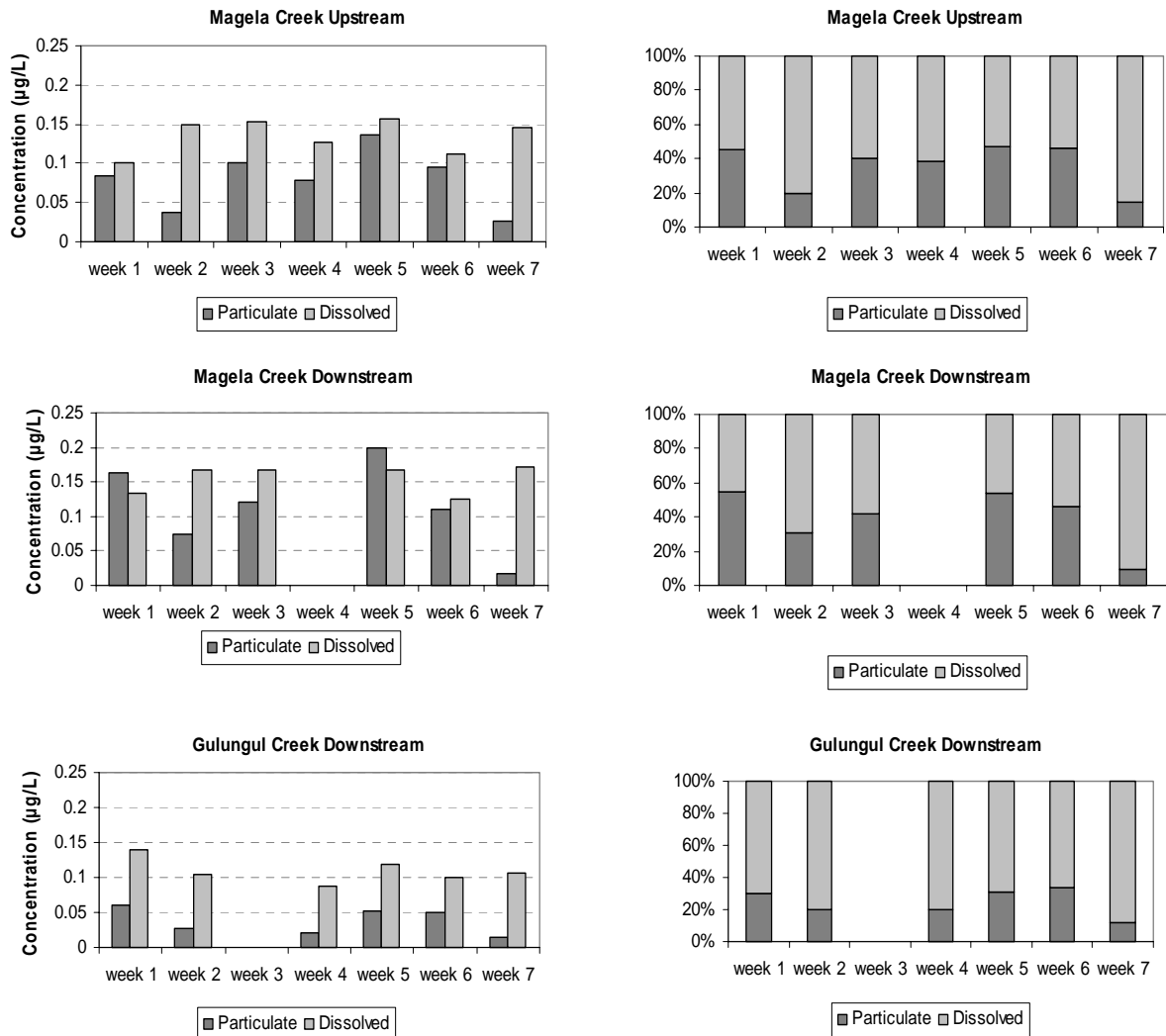

Figure 3.26 Concentrations of particulate and dissolved Cu and the relative fraction of each contributed to total concentration over the seven week trial period. Erroneous data obtained at week 4 for Magela Creek Downstream are not shown. Water samples were not obtained from Gulungul Creek Downstream at week 3 due to flooding.

Figure 3.26 shows that Cu is present in Magela Creek at approximately equal amounts of dissolved and particulate speices. In Gulungul Creek the majority of Cu is in dissolved form. DGT-labile Cu concentration was consistently below detection limits (0.006µg/L) throughout the

monitoring period, suggesting that dissolved Cu is generally present in forms that are unavailable for uptake by aquatic biota.

Most copper in natural waters is present as complexes bound to DOM including humic substances (ANZECC and ARMCANZ, 2000; Bailey *et al.*, 2002). The binding affinities between Cu ions and organic ligands are influenced by pH, with the stability constants of organic Cu complexes increasing with increasing pH (Cao *et al.*, 2004). De la Rosa *et al*. (2003) demonstrated that pH values of 4 and 5 were the most favourable for the binding of Cu by humic substances. The natural content of dissolved organic ligands present in surface waters are commonly in excess of the dissolved copper concentration promoting formation of complexation and thus reducing concentrations of bioavailable copper (ANZECC and ARMCANZ, 2002).

Copper complexation by inorganic material is also important. Hunter *et al.* (1999) show that formation of stable inorganic Cu complexes (e.g. $Cu(OH)_2$ and $CuCO_3$) becomes important just below pH 7.

Zinc, lead and cadmium

Zinc, Pb and Cd were all frequently measured near or below analytical detection limits for water and DGT analysis. These results were not surprising due to the low background levels of these metals (Hart *et al.*, 1982). Further, Klessa (2000) showed that the Zn and Pb concentrations in mine waters were so low that they do not pose a significant risk as contaminants. This study shows that the same may be suggested for Cd.

Table 3.8 Summary of averaged total, dissolved (< 0.45µm) and DGT-labile metal concentrations (µg/L) with percent of dissolved concentration that was DGT-labile (*% DGT-labile*)* at RP1 for 43 h deployment and Magela Creek Upstream, Magela Creek Downstream and Gulungul Creek Downstream for 168 h deployment

RP1 43 h deployment	Pb	Zn	Cd
Total	0.024	2.2	< DL
Particulate	0.016	0.30	-
Dissolved	0.008	1.9	< DL
DGT-labile	0.0069	0.41	< DL
% DGT-labile	*86*	*21*	*-*

Magela Creek Upstream	Pb	Zn	Cd
Total	0.036	0.18	< DL
Particulate	0.024	0.012	-
Dissolved	0.013	0.17	< DL
DGT-labile	0.0017	0.28	0.0010
% DGT-labile	*20*	*130*	*-*

Magela Creek Downstream	Pb	Zn	Cd
Total	0.044	0.21	< DL
Particulate	0.035	0.035	-
Dissolved	0.0069	0.18	< DL
DGT-labile	0.0014	0.24	0.0010
% DGT-labile	*25*	*130*	*-*

Gulungul Creek Downstream	Pb	Zn	Cd
Total	0.046	0.26	< DL
Particulate	0.030	0.096	-
Dissolved	0.015	0.16	< DL
DGT-labile	0.0030	0.16	0.0010
% DGT-labile	*22*	*27*	*-*

* % DGT-labile values were calculated from raw dissolved and DGT-labile concentration data for each week.

Table 3.8 shows that DGT measured Zn concentrations in Magela Creek were grossly overestimated with respect to dissolved concentrations. As with Mn, this indicates that a reasonable portion of the Zn present exists in DGT-labile forms. This was not observed in RP1 or Gulungul Creek, where DGT-labile Zn was 21% and 27% respectively. This suggests that the complexation capacity for Zn is higher in RP1 and Gulungul Creek compared to Magela Creek.

Total lead concentrations in each of the creeks and RP1 was low (average < 0.05 µg/L), with concentrations measured in filtered water samples and DGT below detection limits of 0.02 µg/L and 0.002 µg/L respectively for each technique. Water samples that were above detection limits showed that particulate matter dominated Pb speciation, with particulates contributing $> 80\%$ of total Pb in Magela Creek, whilst in Gulungul Creek 50 – 80% of the total Pb concentration was present in particulate form. This suggests the presence of common insoluble Pb salts, such as carbonate, hydroxide and sulphide (Bailey *et al.*, 2002).

The average DGT-labile Pb concentration (0.002 µg/L) contributed 20 -25 % of the average dissolved concentration (0.012 µg/L) for both creeks, however these measurement are so close to detection limits that their accuracy may be questionable.

Cadmium concentrations were below water sample detection limits (0.007 µg/L) in both creeks and RP1 over the monitoring period. However, DGT measurement was able to detect concentrations of 0.001 µg/L at all sites. This may suggest that the small amount of Cd present exists in DGT-labile forms.

3.2.5 Water quality guidelines

Direct comparison of DGT measured concentrations obtained in this study to WQG trigger values is not an ideal assessment of metal toxicity due to the inaccuracies caused by the low ionic strength of the creek waters. However, the DGT measured concentrations, even though overestimated, were all lower than the current ANZEEC and ARMCANZ (2000) trigger values and site-specific (Table 3.9).

Table 3.9 Comparison of measured DGT-labile concentrations (µg/L) with current ANZECC and ARMCANZ* and site-specific[^#] trigger values (µg/L)

	Cd	Cu	Pb	Zn	U	Al	Mn
Trigger values for freshwater*	0.06	1.0	1.0	2.4	5.8^	27	32#
Magela Creek upstream	0.0010	0.0080	0.0017	0.28	0.0014	4.2	6.6
Magela Creek downstream	0.0010	0.0080	0.0014	0.24	0.0043	3.1	6.4
Gulungul Creek downstream	0.0010	0.013	0.0030	0.16	0.0081	3.1	2.3

* WQG recommended trigger values (for protection of 99% of species) (ANZECC and ARMCANZ, 2000).

^ Site-specific trigger value derived for Magela Creek in accordance with national WQG (ANZECC and ARMCANZ, 2000) from toxicity testing of local aquatic species (van Dam, 2000).

Site-specific trigger value derived for Magela Creek in accordance with national WQG (ANZECC and ARMCANZ, 2000) from distribution of reference site data (Klessa, 2000).

These trigger values are used in the assessment of metal toxicity to the aquatic environment and ideally represent the concentrations at which dissolved metals are of environmental concern. Comparison of the trigger values with the overestimated DGT-labile concentrations measured in this study suggest that there is very little bioavailable metal present in either Magela or Gulungul Creek.

3.2.6 Summary

It was shown in this study that DGT devices provide low detection limits, which for all metals were lower than detection limits obtained using grab sampling methods. Comparisons made between grab sampled concentrations and DGT-labile concentrations over varying stream discharge showed that DGT measurement may be able to detect increases in DGT-labile concentration in relation to increased flow. Such increases were only detected by grab samples when the sample was taken at the time of increased flow. This shows that the time integrated concentrations measured by DGT are sensitive to changes in concentration throughout deployment.

It is also important to mention that average DGT labile concentrations for each metal measured in this study were below recommended trigger values. Based on the assumptions of metal speciation ability, this essentially shows that concentrations of bioavailable metals in Magela and Gulungul Creeks were low.

4 Conclusions

The use of DGT technique as a monitoring tool for mine related metal contamination in freshwater creeks of low ionic strength was investigated. The DGT technique is a new and innovative method for *in situ* measurement of free metal ions and labile metal complexes in natural waters, offering an approximation of metal bioavailability. As well as their unique capability for *in situ* speciation, it has been reported that DGT offer a number of other advantages over grab sampling methods, including higher sensitivity and the ability to detect concentration variation over irregular flow (Zhang and Davison, 1995; Meylan *et al.*, 2003).

This study has provided further information on the effects of low ionic strength on DGT measurement, which is a recently discovered limitation of DGT application in pristine freshwaters (Alfaro-De lat Torre *et al.*, 2000; Sangi *et al*., 2002; Peters *et al.*, 2003). Under low ionic strength conditions, metal diffusion into the DGT device is enhanced which causes overestimation in the measurement of the DGT-labile concentration.

Field trails were conducted to asses the DGT technique as a potential monitoring tool to supplement water quality monitoring procedures currently carried out on Magela and Gulungul Creeks (Supervising Scientist, 2002b). The results show that the low ionic strength of the creeks may have caused inaccuracies in the measurement of DGT-labile concentration, however the overestimated DGT measurements were still useful for speciation assessment. The observed DGT-labile concentration for Mn and Zn was high with respect to dissolved (< 0.45 μm) concentrations measured in water samples, thus it was assumed that a substantial proportion of these metals were present in DGT-labile form. The DGT-labile concentrations of U, Al and Fe were low with respect to dissolved concentrations and therefore, it was assumed that these metals were present mostly bound in stable complexes.

Thus while DGT may be incapable of measuring quantitative DGT-labile concentrations at low ionic strength, the occurrence of different levels of overestimation may still be useful in obtaining speciation information and indeed assessing toxicity as shown by comparison of DGT-labile concentrations with water quality trigger values where DGT-labile concentrations were well below guideline trigger values. From this observation it can be assumed that the actual bioavailable concentrations present in these waters are well below guideline values.

In summary, while DGT technique may not offer quantitative measurement of DGT-labile concentrations under low ionic strength conditions, it gives a conservative overestimation which may still be useful in monitoring maximum potential DGT-labile concentrations.

References

Alfaro-De la Torre, M.C., Beaulieu, P.Y. and Tessier, A. (2000) In situ measurement of trace metals in lakewater using the dialysis and DGT techniques. Analytica Chimica Acta. 418, 53-68.

Antelo, J.M., Arce, F. and Penedo, F.J. (2000) Effect of pH on the complexation parameters for organic matter dissolved in river water. *Chemical Speciation and Bioavailability*. 12, 9-15.

ANZECC and ARMCANZ (2000). *Australian and New Zealand guidelines for fresh and marine water quality*. National Water Quality Management Strategy Paper No 4, Australian and New Zealand Environment and Conservation Council & Agriculture and Resource Management Council of Australia and New Zealand, Canberra, Australia.

Bailey, R.A., Clark, H.M., Ferris, J.P., Krause, S. and Strong, R.L. (2002) *Chemistry of the Environment*. (2nd ed.). Harcourt/Academic Press, London. 566-567.

Bio-Rad Laboratories. (2000) Chelex 100 and Chelex 20 chelating ion exchange resin: Instruction manual. http://www.bio-rad.com/webmaster/pdfs/9184_Chelex.PDF. 2004.

Cao, J., Lam, K.C., Dawson, R.W., Liu, W.X. and Tao, S. (2004) The effect of pH, ion strength and reactant content on the complexation of Cu^{2+} by various natural organic ligands from water and soil in Hong Kong. *Chemosphere*. 54, 507-514.

Cornelis, R.C., Crews, H.M., Caruso, J.A. and Heumann, K.G. (2003) Introduction (Ch1.). In *Handbook of Elemental Speciation: Techniques and Methodology*. Eds Cornelis, R., Crews, H., Caruso, J. and Heumann, K. John Wiley and Sons, Chichester, West Sussex. 1-5.

Davidge, J., Thomas, C.P. and Williams, D.R. (2001) Conditional formation constants or chemical speciation data? *Chemical Speciation and Bioavailability*. 13, 129-134.

Davis, J.A. (1984) Complexation of trace metals by adsorbed natural organic matter. *Geochimica et Cosmochimica Acta*. 48, 679-691.

Davison, W. and Zang, H. (1994) In situ speciation measurements of trace components in natural waters using thin-film gels. *Letters to Nature*. 367, 546-548.

de la Rosa, G., Peralta-Videa, J.R. and Gardea-Torresdey, J.L. (2003) Utilization of ICP/OES for the determination of trace metal binding to different humic fractions. *Journal of Hazardous Materials*. 97, 207-218.

Denney, S., Sherwood, J. and Leyden, J. (1999) In situ measurements of labile Cu, Cd and Mn in river water using DGT. *The Science of the Total Environment*. 239, 71-80.

DGT Research Ltd. (2003) DGT-for measurements in water, soils and sediments: Users guide for DGT technique. http://www.dgtresearch.com. April 2003.

Duffus, J.H. (2003) Environmental risk assessment and the bioavailability of elemental species (Ch 9.). In *Handbook of Elemental Speciation: Techniques and Methodology*. Eds Cornelis, R., Crews, H., Caruso, J. and Heumann, K. John Wiley and Sons, Chichester, West Sussex. 605-628.

Emons, H. (2003) Sampling: Collection, Processing and Storage of Environmental Samples (Ch.2). In *Handbook of Elemental Speciation: Techniques and Methodology*. Eds Cornelis, R., Crews, H., Caruso, J. and Heumann, K. John Wiley and Sons, Chichester, West Sussex. 7-22.

Energy Resources Australia Ltd. (2003) *Ranger mining management plan*.

http://www.energyres.com.au. Energy Resources Australia, November 2003.

Evans K.G., Moliere, D.R., Saynor, M.J., Erskine, W.D. and Bellio, M.G. (2003) Assessing impacts of catchment disturbance on mud transport in a seasonal stream. In *National Environment Conference 2003 Proceedings*, Brisbane, 18-20 June 2003, Environmental Engineering Society (Queensland chapter), Brisbane, CD.

Gimpel, J., Zhang, H., Davison, W. and Edwards, A. C. (2003) In situ trace metal speciation in lake surface waters using DGT, dialysis and filtration. *Environmental Science and Technology*. 37, 138-146.

Gimpel, J., Zhang, H., Hutchinson, W. and Davison, W. (2001) Effect of solution composition, flow and deployment time on the measurement of trace metals by the diffusive gradient in thin films technique. *Analytica Chimica Acta*. 448, 93-103.

Grzybowski, W. (2000) Comparison between stability constants of cadmium and leak complexes with humic substances of different molecular weight isolated from Baltic Sea water. *Oceanologia*. 42, 473-482.

Hart, B.T. and Davies, S.H.R. (1984) *Capacity of water in the Magela Creek system to complex copper and cadmium*. Technical memorandum 7, Supervising Scientist for the Alligator Rivers Region, AGPS, Canberra.

Hart, B.T., Davies, S.H.R. and Thomas, P.A. (1982) Transport of iron, manganese, cadmium, copper and zinc by Magela Creek, Northern Territory, Australia. *Water Research*. 16, 605-612.

Hunter, A.K., Jonathan, P.K. and Malcom R.R. (1999) Factors influencing the inorganic speciation of trace metal cations in fresh waters. *Marine and Freshwater Research*. 50, 367-372.

Houk, R.S. (2003) Elemental speciation by inductively coupled-mass spectrometry with high resolutions instruments (Ch.5). In *Handbook of Elemental Speciation: Techniques and Methodology*. Eds Cornelis, R., Crews, H., Caruso, J. and Heumann, K. John Wiley and Sons, Chichester, West Sussex. 378-416.

Jansen, B., Kotte, M.C., van Wijk, A.J. and Verstraten, M.V. (2001) Comparison of diffusive gradients in thin films and equilibrium dialysis for the determination of Al, Fe(III) and Zn complexes with dissolved organic matter. *The Science of the Total Environment*. 277, 45-55.

Klessa, D.A. (2000) *The chemistry of Magela Creek: A baseline for assessing change downstream of Ranger*. Supervising Scientist Report 151, Supervising Scientist, Canberra.

LeGras, C.A.A. and Noller, B.N. (1989) *The determination of zinc in Magela Creek water*. Technical memorandum 24, Supervising Scientist for the Alligator Rivers Region, AGPS, Canberra.

Luider, C.D., Crusius, J., Playle, R.C. and Curtis, P.J. (2004) Influence of natural organic matter source on copper speciation as demonstrated by Cu binding to fish gills, by ion selective electrode, and by DGT gel sampler. *Environmental Science and Technology*. 38, 2865-2872.

Markich, S.J. (2002) Uranium speciation and bioavailability in aquatic systems: an overview. *Scientific World Journal*. 2, 707-729.

Markich, S.J. and Camilleri, C. (1997) *Investigation of metal toxicity to tropical biota: Recommendations for revision of the Australian water quality guidelines*. Supervising Scientist Report 127, Supervising Scientist, Canberra.

Meylan, S., Odzak, N., Behra, R. and Sigg, L. (2004) Speciation of copper and zinc in natural freshwater: comparison of voltametric measurements, diffusive gradients in thin films (DGT) and chemical equilibrium models. *Analytica Chimica Acta*. 510, 91-100.

Munksgaard, N.C. and Parry, D.L. (2002) Monitoring of labile metals in turbid coastal seawater using diffusive gradients in thin-films. *Journal of Environmental Monitoring*. 4, 1-6.

Noller, B.N., Currey, N. and Le Gras, C. (1985) Speciation of manganese in Magela Creek and Ranger Uranium mine waters. 1984-1985 Annual Research Summary, Alligator Rivers Region Research Institute, AGPS, Canberra. 70-74.

Nolan, A.L., Lombi, E. and McLaughlin, M.J. (2003) Metal bioaccumulation and toxicity in soils-Why bother with speciation? *Australian Journal of Chemistry*. 56, 77-91.

Peters, A.J., Zhang, H. and Davison, W. (2003) Performance of the diffusive gradients in thin films technique for measurement of trace metals in low ionic strength freshwaters. *Analytica Chimica Acta*. 478, 237-244.

Playle, R.C. (1998) Modelling metal interactions at fish gills. *The Science of the Total Environment*. 219, 147-163.

Riethmuller, N. (2000) The effects of true water hardness and alkalinity on the toxicity of Cu and U to two tropical Australian freshwater organisms. Masters Thesis. Northern Territory University, Northern Territory.

Riethmuller, N., Markich, S.J., van Dam, R.A. and Parry, D.L. (2001) Effects of water hardness and alkalinity on the toxicity of uranium to a tropical freshwater hydra (*Hydra viridissima*). *Biomarkers*. 6, 45-51.

Sangi, M.R., Halstead, M.J. and Hunter, K.A. (2002) Use of diffusion gradient thin film method to measure trace metals in fresh waters at low ionic strength. *Analytica Chimica Acta*. 546, 241-251.

Sondi, I. and Pravdić, V. (1998) The colloid and surface chemistry of clays in natural waters. *Croatica Chemica Acta*. 71, 1061-1074.

Speers, A.C. (1995) *The speciation of manganese, iron and aluminium in Magela Creek, Northern Territory and its implication to contaminant transport*. Honours Thesis. Northern Territory University, Northern Territory.

Sunda, W.G. and Huntsman, S.A. (1998) Processes regulating cellular metal accumulation and physiological effects: Phytoplankton as model systems. *The Science of the Total Environment*. 219, 165-181.

Supervising Scientist. (2002a.) Annual Report 2001-2002. Supervising Scientist Division, Darwin, NT, Australia. 9-19.

Supervising Scientist. (2002b.) Supervising Scientist Monitoring Program. http://www.deh.gov.au/ssd/monitoring/pubs/env-mon-prog-backgroun.pdf. Supervising Scientist Division, Department of the Environment and Heritage. May 2002.

Supervising Scientist. (2004) Introduction to the Alligator Rivers Region. http://www.deh.gov.au/ssd/about/arr/index.html#hydrology. Supervising Scientist Division, Department of the Environment and Heritage. June 2004.

Tipping, E., Rey-Castro, C., Bryan, S.E. and Hamilton-Taylor, J. (2002) Al(III) and Fe(III) binding by humic substances in freshwater, and implications for trace metal speciation. *Geochimica et Cosmochimica Acta.* 66, 3211-3224.

Vanhaecke, F. and Köllensperger, G. (2003) Detection by ICP-Mass Spectrometry (Ch.5). In *Handbook of Elemental Speciation: Techniques and Methodology*. Eds Cornelis, R., Crews, H., Caruso, J. and Heumann, K. John Wiley and Sons, Chichester, West Sussex. 281-312.

van Dam, R.A. (2000) *Derivation of a site-specific water quality trigger value for uranium in Magela Creek*. Internal Report 350, Supervising Scientist, Darwin. Unpublished paper.

van Dam, R.A., Humphrey, C.L. and Martin, P. (2002) Mining in the Alligator Rivers Region, northern Australian: Assessing potential and actual effects on ecosystem and human health. *Toxicology*. 181-182, 505-515.

Zhang, H. (2004) In-situ speciation of Ni and Zn in freshwaters: comparison between DGT measurements and speciation models. *Environmental Science and Technology*. 38, 1421-1427.

Zhang, H. and Davison, W. (1994) In situ speciation of trace components in natural waters using thin-film gels. *Letters to Nature*. 367, 546-548.

Zhang, H. and Davison, W. (1995) Performance characteristics of diffusion gradients in thin films for the in situ measurement of trace metals in aqueous solution. *Analytical Chemistry*. 67, 3391-3400.

Zhang, H. and Davison, W. (1999) Diffusional characteristics of hydrogels used in DGT and DET techniques. *Analytica Chimica Acta.* 398, 329-340.

Zhang, H. and Davison, W. (2000) Direct in situ measurements of labile inorganic and organically bound metal species in synthetic solutions and natural waters using diffusive gradients in thin films. *Analytical Chemistry*. 72, 4447-4457.

Zhang, H. and Davison, W. (2001) In situ measurements. Using diffusive gradients in thin films (DGT) to determine inorganically and organically complexed metals. *Pure and Applied Chemistry*. 73, 9-15.

Appendices

Appendix 1: Dissolved (<0.45µm) metal concentrations for validation experiment

Test Solution	Sample time (h)	Dissolved concentration (µg/L)						
		Al	Fe	Mn	Cu	Zn	Pb	U
1	0	9.3	< DL	9.0	9.1	9.5	9.2	9.0
	7	9.4	< DL	9.4	9.3	9.8	9.1	9.0
	25	10.5	< DL	9.4	9.5	10.0	9.2	9.4
	45	9.5	< DL	8.8	9.0	9.4	8.9	9.0
	71	9.1	< DL	8.7	8.9	9.1	8.7	8.6
2	0	11.2	< DL	8.9	9.2	9.3	8.7	8.9
	7	9.4	< DL	8.7	9.0	9.4	8.7	8.8
	25	9.9	< DL	9.2	9.6	9.8	9.1	9.4
	45	9.9	7.8	9.0	9.6	9.8	8.7	8.8
	71	9.2	< DL	9.1	9.3	9.3	8.9	9.0
3	0	11.3	13.7	9.5	13.1	10.2	9.6	9.5
	7	11.7	13.7	9.4	13.0	9.9	9.1	8.8
	25	11.3	13.9	9.7	13.6	10.5	9.6	9.5
	45	10.4	11.6	9.3	12.5	9.6	9.0	8.9
	71	10.4	12.6	9.2	12.7	9.6	9.1	9.1
4	0	16.3	11.0	9.1	12.9	9.8	9.5	9.4
	7	11.6	16.1	10.1	14.1	11.3	9.9	9.6
	25	10.6	11.3	9.2	12.6	9.7	9.0	8.9
	45	11.7	14.7	9.4	13.1	10.0	9.1	9.2
	71	10.8	13.8	9.4	13.8	10.2	9.4	9.4

Appendix 2: DGT-labile metal concentrations for validation experiment

Test Solution	DGT deployment period (h)	DGT-labile concentration (µg/L)						
		Al	Fe	Mn	Cu	Zn	Pb	U
1	0	ND	ND	ND	ND	ND	ND	ND
	7	13.5	7.8	14.9	14.3	15.6	13.3	19.5
	25	12.6	8.4	12.9	12.1	12.7	11.9	16.1
	45	28.5	22.0	26.1	24.7	24.8	22.8	32.3
	71	18.4	14.1	16.6	15.7	15.4	15.4	20.3
2	0	ND	ND	ND	ND	ND	ND	ND
	7	10.2	5.6	11.1	10.2	11.2	10.2	13.2
	25	14.3	11.4	13.9	13.0	14.0	12.3	16.8
	45	20.1	14.8	17.9	16.3	17.3	16.3	22.5
	71	17.3	13.8	16.7	15.5	16.2	16.2	21.0
3	0	ND	ND	ND	ND	ND	ND	ND
	7	17.8	16.1	16.8	15.9	17.3	15.7	20.9
	25	15.4	13.7	13.1	14.0	16.0	13.4	18.9
	45	15.0	13.9	7.3	12.9	13.0	12.5	16.8
	71	12.2	10.6	7.8	11.0	11.5	11.0	14.0
4	0	ND	ND	ND	ND	ND	ND	ND
	7	10.3	13.7	10.3	9.9	11.0	9.9	13.1
	25	16.8	19.2	12.1	14.6	15.9	14.0	18.8
	45	18.3	16.4	14.0	15.1	16.3	15.5	21.1
	71	19.1	16.8	12.3	15.2	16.6	15.8	20.7

Appendix 3: Dissolved (<0.45μm) metal concentrations for component investigation experiments

Test Solution	Sample time (h)	Dissolved concentration (µg/L)				
		Cu	Zn	Cd	Pb	U
1a	0	107.4	106.6	108.1	106.2	110.1
	4	104.4	102.7	105.1	101.6	102.4
	8	106.7	107.7	111.3	106.9	109.7
2a	0	104.0	109.8	111.7	100.1	93.3
	4	101.5	104.2	107.4	98.7	94.8
	8	103.2	105.4	105.8	101.1	99.5
1b	0	97.2	96.6	99.3	94.1	93.9
	8	97.8	97.9	95.3	89.9	84.0
2b	0	97.6	97.1	98.1	91.7	84.4
	8	100.0	101.7	98.3	87.7	77.2

Appendix 4: DGT-labile metal concentrations for component investigation experiments

Test Solution	DGT deployment period (h)	Components used in each DGT device	DGT-labile concentration (µg/L)				
			Cu	Zn	Cd	Pb	U
1a	4	All 2002	279.4	276.7	255.0	257.5	323.4
	4	Casing: 2002 Filter: 2002 Diffusive gel: 2003 Chelex gel: 2002	219.2	209.7	211.9	196.5	222.8
	4	All 2003	249.9	244.6	235.9	233.9	282.7
	4	Casing: 2003 Filter: 2003 Diffusive gel: 2002 Chelex gel: 2003	195.4	191.9	185.6	180.9	226.3
1a	8	All 2002	119.5	131.0	130.4	116.7	106.8
	8	Casing: 2002 Filter: 2002 Diffusive gel: 2003 Chelex gel: 2002	96.3	104.2	101.0	98.8	87.0
	8	All 2003	246.1	248.1	238.0	223.6	241.5
	8	Casing: 2003 Filter: 2003 Diffusive gel: 2002 Chelex gel: 2003	187.2	187.6	175.6	171.6	165.1
1b	8	All 2003	156.0	167.7	165.4	155.0	153.3
	8	Casing: 2003 Filter: 2002 Diffusive gel: 2003 Chelex gel: 2003	206.5	214.6	211.9	191.0	202.0
	8	Casing: 2003 Filter: 2003 Diffusive gel: 2003 Chelex gel: 2002	186.6	189.0	191.3	178.4	179.7
	8	Casing: 2003 Filter: 2002 Diffusive gel: 2003 Chelex gel: 2002	167.5	177.5	175.7	158.6	158.8
	8	Casing: 2003 Filter: 2003 Diffusive gel: 2003 Chelex gel: 2003 Annular ring removed	105.1	102.6	98.3	95.7	88.7
	8	Removed annular ring	17.3	20.5	18.8	15.8	14.7
1b	8	All 2002	170.9	185.7	184.9	161.5	171.4
	8	Casing: 2003 Filter: 2002 Diffusive gel: 2003 Chelex gel: 2003	288.5	311.3	305.6	272.3	297.9
	8	Casing: 2003 Filter: 2003 Diffusive gel: 2003 Chelex gel: 2002	193.8	209.6	209.6	185.6	194.7
	8	Casing: 2003 Filter: 2002 Diffusive gel: 2003 Chelex gel: 2002	133.7	147.6	144.4	124.9	112.7
	8	Casing: 2003 Filter: 2003 Diffusive gel: 2003 Chelex gel: 2003 Annular ring removed	81.5	85.7	83.4	77.7	69.8
	8	Removed annular ring	104.9	114.8	110.3	88.6	98.2

Appendix 5: Dissolved (<0.45µm) metal concentrations for ionic strength experiment

Test Solution	Sample time (h)	Dissolved concentration (µg/L)				
		Cu	Zn	Cd	Pb	U
1	0	7.5	9.1	9.2	7.4	6.4
	7	7.5	9.2	9.1	7.3	6.2
	24	6.3	7.4	8.0	5.9	5.1
	32	6.5	7.6	8.2	6.3	5.8
	48	5.9	7.3	7.4	5.4	5.0
	71	5.6	6.7	7.0	4.7	4.7
2	0	7.8	8.9	9.4	7.8	5.8
	7	7.4	8.5	8.4	7.4	5.1
	24	7.0	7.8	8.0	6.9	4.9
	32	6.1	6.7	7.4	6.1	4.3
	48	6.4	7.8	7.4	6.0	4.3
	71	6.3	6.7	7.3	5.9	4.6
3	0	8.6	9.4	9.4	8.6	7.0
	7	8.8	9.5	9.4	8.7	6.5
	24	8.1	8.7	9.1	8.2	6.1
	32	9.3	9.6	9.6	8.8	6.4
	48	8.3	8.7	8.7	8.1	5.9
	71	7.9	9.4	8.3	7.4	5.8
4	0	12.3	8.7	9.2	8.9	6.8
	7	13.0	9.0	9.4	9.4	6.5
	24	12.8	9.0	9.3	9.1	6.2
	32	12.2	8.6	9.2	9.2	6.2
	48	12.4	8.6	9.4	9.1	6.1
	71	12.7	8.7	9.1	9.1	6.1

Appendix 6: DGT-labile metal concentrations for ionic strength experiment

Test Solution	DGT deployment period (h)	DGT-labile concentration (µg/L)				
		Cu	Zn	Cd	Pb	U
1	0	ND	ND	ND	ND	ND
	7	64.1	73.4	70.2	58.9	22.6
	24	68.2	81.6	73.5	61.8	20.3
	32	62.0	72.9	69.7	57.3	19.3
	48	59.4	70.4	62.9	50.9	16.6
	71	52.8	63.1	57.1	46.1	14.9
2	0	ND	ND	ND	ND	ND
	7	61.5	68.6	65.1	58.3	24.9
	24	58.2	66.9	59.5	54.1	19.1
	32	62.1	69.8	65.7	60.2	20.6
	48	60.1	68.8	62.0	55.2	19.6
	71	59.4	66.1	56.3	49.5	16.3
3	0	ND	ND	ND	ND	ND
	7	22.6	22.6	23.4	23.7	16.8
	24	19.6	22.1	19.7	19.2	10.1
	32	23.5	25.8	24.5	25.5	12.6
	48	19.6	22.2	20.8	20.8	10.3
	71	20.5	22.7	21.3	21.1	9.9
4	0	ND	ND	ND	ND	ND
	7	7.8	7.5	7.7	8.5	9.6
	24	9.2	9.5	8.9	9.4	8.4
	32	10.0	11.4	10.3	10.5	8.6
	48	9.2	10.3	8.7	9.0	7.2
	71	8.1	9.2	8.1	8.6	6.5

Appendix 7: Dissolved (<0.45μm) metal concentrations for creek water experiment

Test Solution	Sample time (h)	Dissolved concentration (μg/L)				
		Cu	Zn	Cd	Pb	U
1	0	0.6	16.4	< DL	0.1	< DL
	8	0.6	15.7	< DL	0.2	0.1
	25	0.6	13.4	< DL	0.1	0.1
	35	0.5	13.2	< DL	0.1	0.1
	50	0.6	14.0	< DL	0.1	0.1
	73	0.6	12.6	< DL	0.1	0.1
2	0	11.1	33.1	10.1	7.9	8.4
	8	9.2	28.0	9.2	7.3	8.3
	25	10.4	30.3	8.6	6.7	8.3
	35	10.1	30.9	9.2	6.2	8.6
	50	10.3	26.8	8.7	6.7	8.5
	73	10.8	28.1	8.7	7.1	8.6
3	0	47.5	69.6	49.4	38.5	35.5
	8	42.9	65.0	44.7	30.2	27.9
	25	40.4	57.4	42.6	32.0	32.8
	35	42.1	59.1	40.3	32.1	33.0
	50	44.7	59.4	42.8	31.5	33.8
	73	42.0	56.9	40.4	30.1	31.7
4	0	17.6	52.9	16.1	14.3	12.9
	8	10.6	30.6	9.7	7.7	7.3
	25	9.2	27.4	8.6	7.3	6.9
	35	10.5	30.2	9.2	8.1	8.0
	50	10.0	29.9	9.6	7.4	7.5
	73	10.7	31.4	8.9	7.7	8.0
5	0	48.9	67.4	50.6	40.4	40.1
	8	47.6	63.1	46.5	39.0	39.4
	25	45.4	65.2	44.9	37.8	37.7
	35	48.9	66.7	43.2	41.9	44.1
	50	50.6	67.6	45.1	42.1	45.1
	73	50.3	70.3	46.0	40.9	42.1

Appendix 8: DGT-labile metal concentrations for creek water experiment

Test Solution	DGT deployment period (h)	DGT-labile concentration (µg/L)				
		Cu	Zn	Cd	Pb	U
1	0	ND	ND	ND	ND	ND
	8	< DL	66.9	< DL	< DL	0.0035
	25	< DL	42.7	< DL	< DL	
	35	< DL	58.1	< DL	< DL	0.0013
	50	< DL	56.7	< DL	< DL	0.0036
	73	< DL	27.8	< DL	< DL	0.0055
2	0	ND	ND	ND	ND	ND
	8	8.3	185.0	58.4	14.3	6.1
	25	6.0	139.5	47.7	9.6	3.9
	35	6.1	149.1	49.8	10.1	4.4
	50	2.6	80.3	25.7	3.7	2.7
	73	5.5	146.0	46.4	7.3	3.3
3	0	ND	ND	ND	ND	ND
	8	118.8	367.8	246.0	150.4	49.7
	25	93.0	314.7	221.8	125.1	39.3
	35	36.1	133.6	91.8	50.0	19.8
	50	62.7	205.6	141.0	86.3	30.1
	73	74.9	254.9	182.8	105.2	31.8
4	0					
	8	8.4	39.6	13.8	14.0	8.3
	25	7.4	38.5	11.6	11.5	6.4
	35	18.3	81.5	24.4	23.5	11.9
	50	17.8	81.0	21.6	25.2	12.1
	73	15.4	65.2	18.5	22.4	10.2
5	0	ND	ND	ND	ND	ND
	8	88.6	143.5	105.9	116.2	88.6
	25	47.7	73.3	50.3	61.1	55.2
	35	90.6	130.5	91.5	113.4	82.8
	50	94.9	141.6	99.9	112.8	87.7
	73	35.9	59.4	42.5	50.3	44.7

Appendix 9: Physico-chemical parameters of test solutions in the validation experiment

Test Solution	Sample time (h)	Validation experiment		
		[NaNO3] (mM)	EC (µS/cm)	pH
1	0	0.2	ND	4.5
	7	0.2	ND	4.6
	25	0.2	40	4.6
	45	0.2	40	4.6
	71	0.2	40	4.6
2	0	2	ND	4.5
	7	2	250	4.6
	25	2	250	4.5
	45	2	249	4.6
	71	2	250	4.6
3	0	20	ND	4.5
	7	20	2190	4.5
	25	20	2190	4.6
	45	20	2190	4.5
	71	20	2200	4.5
4	0	20	ND	4.5
	7	20	2190	4.6
	25	20	2200	4.6
	45	20	2190	4.6
	71	20	2210	4.6

Appendix 10: Physico-chemical parameters of test solutions in the component investigation experiments

Test Solution	Sample time (h)	Component investigation experiment 1		
		[NaNO3] (mM)	EC (µS/cm)	pH
1	0	20	2100	5.1
	4	20	2100	5.1
	8	20	2100	5.1
2	0	20	2070	6.2
	4	20	2070	6.2
	8	20	2070	6.2

Test Solution	Sample time (h)	Component investigation experiment 2		
		[NaNO3] (mM)	EC (µS/cm)	pH
1	0	20	2060	5.4
	8	20	2070	5.4
2	0	20	2060	6.0
	8	20	2070	6.0

Appendix 11: Physico-chemical parameters of test solutions in the ionic strength experiment

Test Solution	Sample time (h)	Ionic strength experiment		
		[NaNO3] (mM)	EC (µS/cm)	pH
1	0	0.2	31	6.8
	7	0.2	ND	ND
	24	0.2	32	6.7
	32	0.2	ND	ND
	48	0.2	ND	ND
	71	0.2	33	6.7
2	0	0.2	29	6.6
	7	0.2	ND	ND
	24	0.2	32	6.4
	32	0.2	ND	ND
	48	0.2	ND	ND
	71	0.2	32	6.3
3	0	2	237	6.4
	7	2	ND	ND
	24	2	240	6.2
	32	2	ND	ND
	48	2	ND	ND
	71	2	239	6.2
4	0	20	2170	5.9
	7	20	ND	ND
	24	20	2180	5.8
	32	20	ND	ND
	48	20	ND	ND
	71	20	2130	5.8

Appendix 12: Physico-chemical parameters of test solutions in the creek water experiment

Test Solution	Sample time (h)	Filtered creek water experiment	
		EC (µS/cm)	pH
1	0	21	6.7
	8	ND	ND
	25	21	6.8
	35	ND	ND
	50	21	6.9
	73	21	6.8
2	0	22	6.4
	8	ND	ND
	25	22	6.6
	35	ND	ND
	50	22	6.6
	73	22	6.5
3	0	36	5.8
	8	ND	ND
	25	36	6.0
	35	ND	ND
	50	36	6.0
	73	36	6.1
4	0	40	4.5
	8	ND	ND
	25	40	4.5
	35	ND	ND
	50	40	4.5
	73	40	4.5
5	0	59	4.1
	8	ND	ND
	25	58	4.2
	35	ND	ND
	50	59	4.1
	73	58	4.2

Appendix 13: Detection limits for water samples over the seven week monitoring period

Date	Sites	Detection limit (µg/L)							
		Al	Fe	Mn	Cu	Zn	Cd	Pb	U
17/02/2004	All sites	0.19	1.53	0.011	0.018	0.029	0.012	0.012	0.0007
24/02/2004	All sites	0.14	1.77	0.020	0.003	0.132	0.008	0.004	0.0005
2/03/2004	All sites	0.14	1.77	0.020	0.003	0.132	0.008	0.004	0.0005
9/03/2004	All sites	0.14	1.77	0.020	0.003	0.132	0.008	0.004	0.0005
17/03/2004	All sites	0.03	1.45	0.006	0.005	0.028	0.010	0.033	0.0004
23/03/2004	All sites	0.03	1.45	0.006	0.005	0.028	0.010	0.033	0.0004
23/03/2004	Unfiltered and RP1 only	0.03	0.81	0.028	0.009	0.177	0.003	0.006	0.0004
30/03/2004	All sites	0.03	1.45	0.006	0.005	0.028	0.010	0.033	0.0004
30/03/2004	Unfiltered only	0.20	2.60	0.010	0.003	0.183	0.005	0.017	0.0005

Appendix 14: Weekly unfiltered metal concentrations measured at each site over the seven week monitoring period

Date	Site	Al	Fe	Mn	Cu	Zn	Cd	Pb	U
		Unfiltered concentration (µg/L)							
17/02/2004	MCUS	216.5	208.6	3.9	0.18	0.19	< DL	0.032	0.027
17/02/2004	MCUS	204.2	185.4	4.0	0.19	0.18	< DL	0.033	0.027
17/02/2004	MCDS	341.7	288.6	5.1	0.29	0.30	< DL	0.062	0.056
17/02/2004	MCDS	323.9	266.4	4.5	0.30	0.25	< DL	0.056	0.056
17/02/2004	GCDS	218.6	192.2	3.4	0.20	0.15	< DL	0.066	0.188
20/03/2004	GCDS	93.0	277.3	3.7	0.15	< DL	< DL	0.050	0.136
24/02/2004	MCUS	126.8	276.9	4.7	0.19	< DL	< DL	0.021	0.028
24/02/2004	MCUS	127.9	257.6	4.4	0.18	< DL	< DL	0.020	0.027
24/02/2004	MCDS	139.6	332.1	5.2	0.24	< DL	< DL	0.028	0.044
24/02/2004	MCDS	136.7	326.6	5.2	0.24	< DL	< DL	0.027	0.045
24/02/2004	GCDS	114.2	212.3	3.1	0.13	< DL	< DL	0.048	0.134
2/03/2004	MCUS	220.1	369.8	5.1	0.26	< DL	< DL	0.047	0.034
2/03/2004	MCUS	190.2	347.3	5.1	0.25	0.30	< DL	0.049	0.034
2/03/2004	MCDS	263.6	434.9	5.1	0.29	0.14	< DL	0.051	0.094
2/03/2004	MCDS	270.9	448.2	5.1	0.29	0.36	< DL	0.061	0.101
9/03/2004	MCUS	116.8	313.2	4.6	0.20	< DL	< DL	0.019	0.022
9/03/2004	MCUS	125.6	337.7	4.9	0.21	< DL	< DL	0.020	0.024
9/03/2004	MCDS	8.8	17.5	2.7	2.17	< DL	< DL	0.221	0.229
9/03/2004	MCDS	310.5	407.5	18.4	14.74	< DL	< DL	1.521	1.664
9/03/2004	GCDS	98.4	213.8	3.1	0.11	< DL	< DL	0.039	0.099
16/03/2004	RP1	20.9	210.7	19.8	0.21	2.30	< DL	0.028	2.990
17/03/2004	MCUS	166.8	354.8	4.8	0.28	< DL	< DL	< DL	0.025
17/03/2004	MCUS	182.4	382.6	5.1	0.31	0.04	< DL	0.040	0.029
17/03/2004	MCDS	260.9	491.1	5.4	0.37	0.16	< DL	< DL	0.041
17/03/2004	MCDS	212.1	472.4	5.7	0.36	0.12	< DL	< DL	0.040
17/03/2004	GCDS	143.3	219.7	2.8	0.17	< DL	< DL	0.034	0.098
17/03/2004	RP1	22.6	204.7	13.8	0.19	2.49	< DL	0.024	2.892
10.20 AM 18/03/2004	RP1	17.4	170.2	8.7	0.20	2.41	< DL	0.018	2.420
12.30 AM 18/03/2004	RP1	14.7	163.3	10.7	0.15	2.26	< DL	< DL	2.538
12.30 AM 18/03/2004	RP1	21.4	175.1	11.2	0.17	2.34	< DL	0.027	2.509
23/03/2004	MCUS	160.8	348.6	4.3	0.23	< DL	< DL	0.049	0.020
23/03/2004	MCUS	110.0	320.2	4.1	0.19	< DL	< DL	0.034	0.020
23/03/2004	MCDS	136.6	327.9	4.4	0.25	< DL	< DL	0.035	0.061

Appendix 14: Continued

Date	Site	Al	Fe	Mn	Cu	Zn	Cd	Pb	U
		Unfiltered concentration (µg/L)							
23/03/2004	MCDS	115.9	317.9	4.6	0.22	< DL	< DL	0.033	0.058
23/03/2004	GCDS	106.2	190.6	2.9	0.18	< DL	< DL	0.049	0.086
23/03/2004	RP1	7.9	124.5	9.2	0.26	2.40	< DL	0.033	2.556
23/03/2004	RP1	16.2	118.2	8.7	0.26	2.03	< DL	0.027	2.547
30/03/2004	MCUS	85.9	305.5	3.9	0.17	0.21	< DL	< DL	0.021
30/03/2004	MCUS	75.1	267.1	3.7	0.17	0.19	< DL	< DL	0.018
30/03/2004	MCDS	74.9	291.1	3.8	0.18	0.19	< DL	< DL	0.041
30/03/2004	MCDS	80.3	303.1	4.2	0.20	< DL	< DL	< DL	0.040
30/03/2004	GCDS	54.0	210.7	2.9	0.11	< DL	< DL	0.027	0.078
30/03/2004	GCDS	53.3	185.0	2.9	0.13	0.36	< DL	0.042	0.080

Appendix 15: Weekly filtered (<0.45μm) metal concentrations measured at each site over the seven week monitoring period

Date	Site	Filtered concentration (μg/L)							
		Al	Fe	Mn	Cu	Zn	Cd	Pb	U
17/02/2004	MCUS	76.1	71.2	2.8	0.09	0.12	< DL	< DL	0.016
17/02/2004	MCUS	80.0	81.5	3.3	0.11	0.16	< DL	< DL	0.019
17/02/2004	MCDS	72.2	76.5	3.0	0.12	0.13	< DL	< DL	0.034
17/02/2004	MCDS	55.7	55.6	3.7	0.15	0.16	< DL	< DL	0.037
17/02/2004	GCDS	104.2	100.7	3.0	0.14	0.16	< DL	0.031	0.155
20/03/2004	GCDS	37.8	77.1	2.4	0.10	< DL	< DL	0.008	0.098
24/02/2004	MCUS	55.0	81.9	3.5	0.14	0.16	< DL	0.016	0.020
24/02/2004	MCUS	73.3	115.8	3.8	0.16	0.25	< DL	0.014	0.022
24/02/2004	MCDS	53.9	92.2	3.6	0.17	0.16	< DL	0.005	0.036
24/02/2004	MCDS	54.2	88.7	3.7	0.16	0.14	< DL	< DL	0.031
24/02/2004	GCDS	59.2	70.0	1.9	0.10	< DL	< DL	0.009	0.092
2/03/2004	MCUS	55.8	97.7	3.4	0.15	< DL	< DL	0.009	0.023
2/03/2004	MCUS	62.1	115.1	3.5	0.16	0.57	< DL	0.013	0.025
2/03/2004	MCDS	67.3	125.7	3.3	0.17	< DL	< DL	0.011	0.072
2/03/2004	MCDS	56.4	114.4	3.2	0.16	< DL	< DL	0.007	0.074
9/03/2004	MCUS	40.5	86.1	3.8	0.13	< DL	< DL	< DL	0.016
9/03/2004	MCUS	53.3	116.2	4.0	0.12	< DL	< DL	< DL	0.017
9/03/2004	MCDS	45.3	114.3	4.2	0.14	< DL	< DL	< DL	0.074
9/03/2004	MCDS	42.4	99.7	4.0	0.13	< DL	< DL	< DL	0.067
9/03/2004	GCDS	46.8	81.2	2.3	0.09	< DL	< DL	0.013	0.079
16/03/2004	RP1	4.7	71.2	11.6	0.14	1.61	< DL	< DL	2.650
17/03/2004	MCUS	58.8	108.4	3.1	0.15	< DL	< DL	< DL	0.018
17/03/2004	MCUS	53.5	94.2	3.0	0.16	< DL	< DL	< DL	0.016
17/03/2004	MCDS	61.8	129.2	2.7	0.17	< DL	< DL	< DL	0.028
17/03/2004	MCDS	59.4	122.9	2.6	0.16	< DL	< DL	< DL	0.027
17/03/2004	GCDS	68.6	94.5	1.7	0.12	< DL	< DL	< DL	0.083
17/03/2004	RP1	2.7	66.5	5.0	0.13	2.00	< DL	< DL	2.181
10.20 AM 18/03/2004	RP1	3.5	79.0	5.3	0.13	1.98	< DL	< DL	2.240
12.30 AM 18/03/2004	RP1	2.9	64.5	4.9	0.14	2.10	< DL	< DL	2.332
12.30 AM 18/03/2004	RP1	3.2	67.2	5.2	0.14	2.14	< DL	< DL	2.395
23/03/2004	MCUS	43.7	99.5	3.3	0.12	0.03	< DL	< DL	0.016
23/03/2004	MCUS	24.9	42.5	3.2	0.11	0.27	< DL	< DL	0.015
23/03/2004	MCDS	51.5	140.5	3.4	0.13	< DL	< DL	< DL	0.053

Appendix 15: Continued

Date	Site	Filtered concentration							
		(μg/L)							
		Al	**Fe**	**Mn**	**Cu**	**Zn**	**Cd**	**Pb**	**U**
23/03/2004	MCDS	26.8	58.5	3.3	0.12	< DL	< DL	< DL	0.047
23/03/2004	GCDS	63.4	118.8	2.4	0.10	< DL	< DL	< DL	0.083
23/03/2004	GCDS	38.4	68.2	2.3	0.10	0.71	< DL	< DL	0.077
23/03/2004	RP1	2.2	56.7	4.8	0.17	1.60	< DL	0.016	2.286
23/03/2004	RP1	1.8	52.1	4.5	0.15	1.71	< DL	0.014	2.264
30/03/2004	MCUS	60.5	136.6	4.0	0.15	< DL	< DL	< DL	0.017
30/03/2004	MCUS	47.8	98.0	4.0	0.14	< DL	< DL	< DL	0.016
30/03/2004	MCDS	94.0	199.4	3.9	0.18	0.27	< DL	< DL	0.040
30/03/2004	MCDS	60.9	158.6	3.8	0.16	0.21	< DL	< DL	0.038
30/03/2004	GCDS	60.9	138.2	3.1	0.12	< DL	< DL	< DL	0.084
30/03/2004	GCDS	34.4	85.2	2.7	0.10	< DL	< DL	< DL	0.076

Appendix 16: Detection limits for DGT over seven week monitoring period

Date	Deployment period	Site	Detection limit (µg/L)							
			Al	Fe	Mn	Cu	Zn	Cd	Pb	U
17/2 - 20/2	72 h	GCDS	0.14	0.65	0.002	0.025	0.41	0.0201	0.0190	0.01088
17/2 - 24/2	168 h	MCUS	0.06	0.30	0.001	0.012	0.04	0.0004	0.0007	0.00010
17/2 - 24/2	168 h	MCDS	0.06	0.30	0.001	0.012	0.04	0.0004	0.0006	0.00010
17/2 - 24/2	168 h	GCDS	0.06	0.29	0.001	0.011	0.04	0.0003	0.0006	0.00009
24/3 - 2/3	168 h	MCUS	0.32	0.46	0.000	0.001	0.04	0.0006	0.0004	0.00003
24/3 - 2/3	168 h	MCDS	0.32	0.46	0.000	0.001	0.04	0.0006	0.0004	0.00003
24/3 - 2/3	168 h	GCDS	0.30	0.43	0.000	0.001	0.04	0.0005	0.0004	0.00003
2/3 - 9/3	168 h	MCUS	0.32	0.46	0.000	0.001	0.04	0.0006	0.0004	0.00003
2/3 - 9/3	168 h	MCDS	0.31	0.45	0.000	0.001	0.04	0.0006	0.0004	0.00003
9/3 - 17/3	168 h	MCUS	0.20	0.47	0.030	0.010	0.07	0.0004	0.0006	0.00012
9/3 - 17/3	168 h	MCDS	0.20	0.47	0.030	0.010	0.07	0.0004	0.0006	0.00012
2/3 - 17/3	336 h	GCDS	0.10	0.23	0.015	0.005	0.03	0.0002	0.0003	0.00006
16/3 - 18/3	43 h	RP1 43 h	0.72	1.74	0.110	0.036	0.24	0.0014	0.0023	0.00044
17/3 - 23/3	168 h	MCDS	0.20	0.48	0.030	0.010	0.07	0.0004	0.0006	0.00012
17/3 - 23/3	168 h	GCDS	0.20	0.48	0.030	0.010	0.07	0.0004	0.0006	0.00012
23/3 - 23/3	6 h	RP1 6 h	5.31	23.29	0.061	0.118	0.62	0.0058	0.0246	0.00399
23/3 - 30/3	168 h	MCUS	0.08	0.17	0.003	0.008	0.09	0.0001	0.0012	0.00014
23/3 - 30/3	168 h	MCDS	0.08	0.16	0.003	0.008	0.09	0.0001	0.0012	0.00014
23/3 - 30/3	168 h	GCDS	0.08	0.16	0.003	0.008	0.09	0.0001	0.0012	0.00014
30/3 - 6/4	168 h	MCUS	0.20	0.90	0.002	0.005	0.02	0.0002	0.0010	0.00015
30/3 - 6/4	168 h	MCDS	0.20	0.88	0.002	0.004	0.02	0.0002	0.0009	0.00015

Appendix 17: Weekly DGT-labile concentrations measured at each site over the seven week monitoring period

Week	Deployment period	Site	DGT-labile concentration (µg/L)							
			Al	Fe	Mn	Cu	Zn	Cd	Pb	U
3 day deployment	17/2 - 20/2	GCDS	2.3	1.9	4.7	< DL	< DL	< DL	< DL	0.012
3 day deployment	17/2 - 20/2	GCDS	2.6	2.5	4.9	< DL	< DL	< DL	< DL	0.012
3 day deployment	17/2 - 20/2	GCDS	3.1	2.9	6.6	< DL	< DL	< DL	< DL	0.014
1	17/2 - 24/2	GCDS	2.8	2.4	3.1	< DL	0.07	< DL	0.0009	0.011
1	17/2 - 24/2	GCDS	3.2	2.8	3.1	< DL	0.09	< DL	0.0027	0.012
1	17/2 - 24/2	GCDS	2.3	1.9	2.4	< DL	0.05	< DL	0.0020	0.010
1	17/2 - 24/2	MCUS	2.8	3.2	6.5	< DL	0.18	< DL	0.0022	0.002
1	17/2 - 24/2	MCUS	3.2	4.0	8.6	< DL	0.19	< DL	< DL	0.001
1	17/2 - 24/2	MCUS	3.0	3.8	7.5	< DL	0.26	< DL	0.0029	0.003
1	17/2 - 24/2	MCDS	2.7	2.7	8.0	< DL	0.27	0.0006	0.0024	0.006
1	17/2 - 24/2	MCDS	2.5	2.2	6.8	< DL	0.24	< DL	0.0024	0.006
1	17/2 - 24/2	MCDS	2.3	2.2	7.5	< DL	0.18	0.0014	0.0019	0.005
2	24/3 - 2/3	MCUS	6.5	5.3	4.7	< DL	0.30	0.0013	0.0043	0.001
2	24/3 - 2/3	MCUS	6.0	4.3	5.9	< DL	0.24	0.0007	0.0014	0.001
2	24/3 - 2/3	MCDS	4.7	3.3	3.8	< DL	0.26	0.0007	0.0014	0.006
2	24/3 - 2/3	MCDS	4.8	3.2	6.1	< DL	0.31	0.0010	0.0016	0.006
2	24/3 - 2/3	MCDS	3.5	2.1	5.5	< DL	0.19	< DL	0.0011	0.004
2	24/3 - 2/3	GCDS	5.4	1.6	0.9	< DL	0.29	0.0010	0.0026	0.010
2	24/3 - 2/3	GCDS	6.1	2.2	2.2	< DL	0.27	0.0012	0.0031	0.013
2	24/3 - 2/3	GCDS	5.5	1.9	0.8	< DL	0.25	0.0010	0.0049	0.012
3	2/3 - 9/3	MCUS	7.2	3.7	7.1	< DL	0.41	0.0010	0.0021	0.001
3	2/3 - 9/3	MCUS	7.6	4.8	8.2	< DL	0.33	0.0012	0.0024	0.001
3	2/3 - 9/3	MCUS	7.2	4.0	6.5	< DL	0.33	0.0011	0.0015	0.002
3	2/3 - 9/3	MCDS	4.6	2.1	7.9	< DL	0.26	0.0008	0.0012	0.006
3	2/3 - 9/3	MCDS	4.5	2.1	7.2	< DL	0.28	0.0007	0.0013	0.005
3	2/3 - 9/3	MCDS	4.9	3.3	7.0	< DL	0.26	0.0006	0.0008	0.005
3 and 4	2/3 - 17/3	GCDS	1.8	1.0	1.1	< DL	0.09	0.0007	0.0016	0.003
3 and 4	2/3 - 17/3	GCDS	1.8	1.3	1.0	0.005	0.11	0.0004	0.0023	0.003
3 and 4	2/3 - 17/3	GCDS	1.7	1.1	0.9	< DL	0.09	0.0004	0.0020	0.003
4	9/3 - 17/3	MCUS	3.5	4.1	4.5	< DL	0.25	0.0008	0.0010	0.002
4	9/3 - 17/3	MCUS	4.3	4.7	4.7	< DL	0.19	0.0007	< DL	0.002
4	9/3 - 17/3	MCUS	3.7	5.1	3.7	< DL	0.30	0.0008	0.0009	0.002
4	9/3 - 17/3	MCDS	2.8	3.0	3.6	< DL	0.17	0.0004	0.0010	0.005
4	9/3 - 17/3	MCDS	3.0	3.3	4.4	< DL	0.31	0.0007	0.0008	0.006

Appendix 17: Continued

Week	Deployment period	Site	DGT-labile concentration (µg/L)							
			Al	Fe	Mn	Cu	Zn	Cd	Pb	U
4	9/3 - 17/3	MCDS	2.8	2.7	1.7	< DL	0.21	0.0005	0.002	0.006
43 h	16/3 - 18/3	RP1 43 h	17.9	4.6	8.4	0.044	0.55	< DL	0.010	1.043
43 h	16/3 - 18/3	RP1 43 h	1.0	3.3	6.2	< DL	0.26	< DL	0.005	1.280
43 h	16/3 - 18/3	RP1 43 h	0.9	5.2	7.8	< DL	0.43	< DL	0.006	1.556
5	17/3 - 23/3	MCUS	2.9	4.4	6.5	0.011	0.27	0.0010	0.002	0.001
5	17/3 - 23/3	MCUS	3.0	3.9	5.3	< DL	0.22	0.0010	0.002	0.001
5	17/3 - 23/3	MCUS	3.5	4.5	8.1	< DL	0.41	0.0010	0.001	0.001
5	17/3 - 23/3	MCDS	2.0	2.3	6.3	< DL	0.27	0.0006	0.001	0.002
5	17/3 - 23/3	MCDS	2.4	2.7	8.2	< DL	0.24	0.0007	0.001	0.002
5	17/3 - 23/3	MCDS	3.7	3.0	7.3	< DL	0.24	0.0007	0.001	0.002
5	17/3 - 23/3	GCDS	3.5	3.5	3.8	< DL	0.22	0.0007	0.003	0.006
5	17/3 - 23/3	GCDS	1.9	1.9	3.6	0.021	0.14	0.0006	0.002	0.004
5	17/3 - 23/3	GCDS	2.0	2.2	3.9	< DL	0.17	0.0005	0.003	0.004
6	23/3 - 30/3	MCUS	4.3	3.9	12.5	< DL	0.30	0.0016	< DL	0.001
6	23/3 - 30/3	MCUS	3.6	3.5	8.3	< DL	0.27	0.0012	< DL	0.001
6	23/3 - 30/3	MCUS	3.6	4.0	8.6	< DL	0.27	0.0014	< DL	0.001
6	23/3 - 30/3	MCDS	2.8	2.4	6.8	< DL	0.25	0.0097	< DL	0.002
6	23/3 - 30/3	MCDS	2.6	1.8	5.6	< DL	0.12	0.0004	< DL	0.004
6	23/3 - 30/3	MCDS	2.6	1.5	7.5	< DL	0.11	0.0006	< DL	0.004
6	23/3 - 30/3	GCDS	2.7	1.7	2.7	< DL	< DL	0.0002	< DL	0.010
6	23/3 - 30/3	GCDS	2.9	1.4	2.2	< DL	< DL	0.0003	< DL	0.010
6	23/3 - 30/3	GCDS	2.6	1.5	2.6	< DL	0.09	0.0029	< DL	0.009
6 h	23/3 - 23/3	RP1 6 h	< DL	< DL	6.7	< DL	1.86	< DL	0.047	1.342
6 h	23/3 - 23/3	RP1 6 h	< DL	< DL	9.8	< DL	3.29	< DL	0.070	1.273
7	30/3 - 6/4	MCUS	2.4	2.7	4.8	< DL	0.23	0.0009	0.002	0.001
7	30/3 - 6/4	MCUS	2.2	2.9	3.8	0.009	0.29	0.0009	0.001	0.001
7	30/3 - 6/4	MCUS	2.1	2.6	6.3	0.002	0.21	0.0008	0.001	0.001
7	30/3 - 6/4	MCDS	2.0	2.4	8.6	0.008	0.27	0.0008	0.001	0.003
7	30/3 - 6/4	MCDS	1.6	1.6	6.5	0.006	0.19	0.0005	< DL	0.002
7	30/3 - 6/4	MCDS	1.6	2.0	6.9	0.010	0.29	0.0010	0.004	0.002

Appendix 18: Physico-chemical parameters measured at each site over the seven week monitoring period

Date	Magela Creek Upstream				Magela Creek Downstream				Gulungul Creek Downstream			
	Temperature	pH	EC	DO	Temperature	pH	EC	DO	Temperature	pH	EC	DO
17/02/2004	27.5	4.8	8.0	6.8	27.4	4.8	9.0	6.7	29.7	5.5	12.0	7.3
24/02/2004	27.8	5.3	8.0	7.0	28.2	5.3	10.0	6.5	32.2	5.9	16.0	6.5
2/03/2004	27.7	5.9	10.0	6.7	28.2	6.1	13.0	6.5	27.6	6.1	11.0	7.1
8/03/2004	29.1	6.0	10.0	6.9	29.5	6.3	13.0	6.7	30.6	6.5	14.0	7.2
17/03/2004	27.9	6.0	10.0	7.1	27.7	6.2	12.0	6.9	27.5	6.2	13.0	6.8
23/03/2004	28.2	6.1	10.0	7.3	28.7	6.3	13.0	6.9	29.0	6.3	13.5	6.5
30/03/2004	28.2	6.2	11.0	6.0	29.5	6.2	14.0	6.6	ND	ND	ND	ND
6/04/2004	27.9	6.2	13.0	7.2	28.6	6.2	15.0	7.0	28.8	6.2	15.0	7.4