

# Instructions for DGT

## 1 Essential things to know about DGTs

### 1.1 What is a DGT?

DGT (diffusive gradients in thin films) are small, simple passive sampling devices (Figure 1) that accumulate dissolved substances and provide a time-weighted average (TWA) concentration over the deployment period. They do not require any power supply to work and are small enough (~40 mm in diameter) to be deployed in many locations.

The DGTs have three layers:

- A membrane filter to keep out solid particles;
- A diffusive gel layer which controls the diffusion of solutes; and
- A binding layer or gel, which selectively binds the solutes of interest.

DGTs are available for metals (cationic and oxyanions), some nitrogen and phosphorus species, and selected polar organic compounds. For metals, the binding layer is Chelex, which binds trace metals more strongly than major cations. This allows the metals to accumulate over the deployment period to higher concentrations, thus enabling measurement of trace concentrations in water. The devices have been used extensively in rivers and streams though somewhat less in stormwater.



**Figure 1:** DGT device for sampling water. Photo credit Stuart Mackay, NIWA.

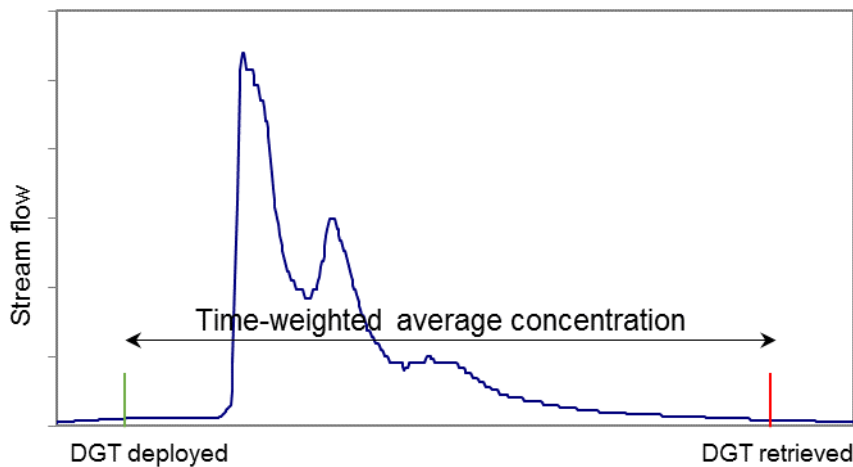
### 1.2 How do you use a DGT?

The DGT devices need to be deployed in the field for several hours to weeks to accumulate contaminants. They then need to be retrieved and shipped to a laboratory where they are disassembled under clean conditions, the contaminants are extracted from the binding layer, and the accumulated mass of contaminants is measured by routine methods. This mass, along with water temperature and the length of time deployed, is used to calculate the time-weighted average concentration in the waterbody.

### 1.3 How does a DGT help me?

A DGT continuously absorbs and concentrates dissolved contaminants from the water column and provides an indication of the in-stream concentration throughout the entire period the DGT device

was installed (Figure 2). It does not provide any information on peak concentrations or the range in concentrations throughout a storm.



**Figure 2:** Example stream hydrograph showing period of DGT measurement.

#### 1.4 Where can I use a DGT?

- Streams, including those tidally-influenced (depending on the variables being measured);
- Stormwater drains;
- Stormwater pipes;
- Pumped stormwater discharges.

#### 1.5 What else do I need to know?

Some key features of DGTs:

- DGTs can be damaged by sharp objects (e.g., sticks, scissors) which can pierce the outer membrane layer. Treat them carefully prior to deployment.
- DGTs must not dry out, either before or during deployment, as this will affect the ability of the gel to take up contaminants.
- At least one field blank and one laboratory blank need to be included with each batch of samples (where a batch is  $\leq 10$  and  $\leq 4$  sites).
- You can contaminate a DGT through incorrect handling, just as you can contaminate a water sample. Gloves (powder-free) need to be worn at all times when handling. Zinc-containing sunscreen should be avoided when sampling for metals.
- To calculate water concentrations, you need to know the water temperature during deployment. Ideally this is recorded at the location. Inaccuracies of  $> 2^{\circ}\text{C}$  will give an error of more than 5% (see Section 3.1).
- You need to record the length of time the DGT was deployed (underwater), see Section 3.3.

- At this stage, we recommend deploying DGTs in duplicate (with at least one site in triplicate) to enable the identification of outlying results (for example from a damaged DGT).
- DGTs can be stored in the refrigerator after deployment for several weeks prior to sending to the laboratory. Therefore it is safe to retrieve DGTs on a Friday, and refrigerate over the weekend.

## 2 Preparatory work

The level of detail in the descriptions below vary depending on the application. For applications that are expected to be the most commonly used, these instructions provide relatively complete information regarding how and when to implement this approach. For applications that are expected to be more rarely used, the details will depend on the specific situation and only general guidance is provided.

### 2.1 Selecting and purchasing DGTs

DGTs can be purchased from DGT Research, based at Lancaster University, who provide these for research and commercial purposes. The DGTs are produced in China and generally shipped about 3 weeks from order. There are many different types available, including multiple types for the same contaminants, with different gels and requiring different extraction methods. The DGTs that are recommended for use in NZ in stormwater and urban stream applications are listed in Table B-1 with their codes for clarity when ordering.

**Table 2-1: DGTs commercially available from DGT Research suitable for stormwater and urban stream applications. .**

<b>DGT code</b>	<b>Water quality variables measured</b>
LSNM-NP	Metals incl. Cd, Cr, Cu, Fe, Ni, Zn
LSNX-NP	Phosphorus, metals & metalloids (wide range incl. As, Cd, Cr, Cu, Fe, Ni, Zn)
LSNN-AP	Nitrate-N

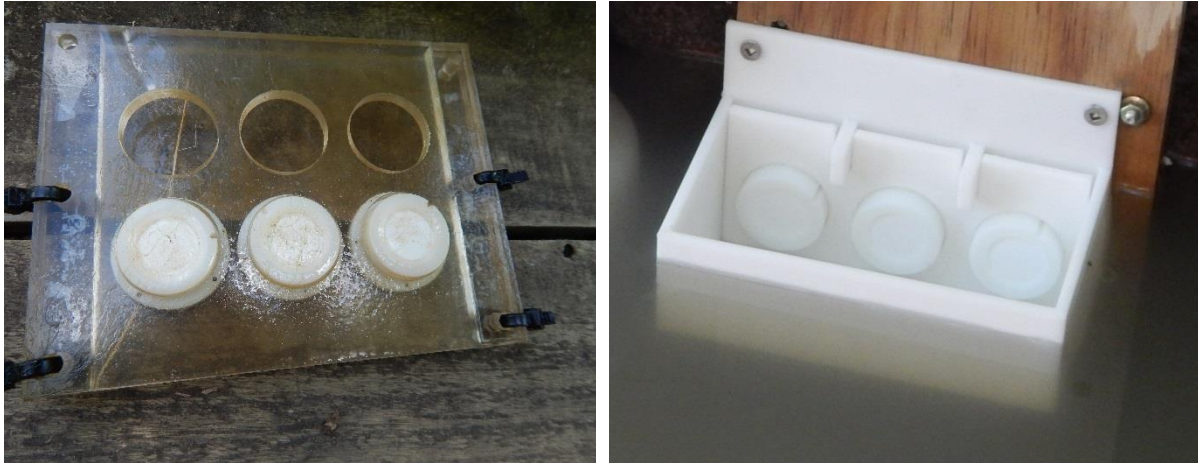
DGTs have an expiry date that is typically about 3 months after purchase. Within this period the DGTs are not expected to dry out when stored refrigerated. They may still be suitable for use after expiry, however the devices should be carefully checked to ensure they are not dry. The filter membrane should have good contact with the cap and if there is any visible gap then the gels have dried out and need to be either revived (instructions at [dgtresearch.com](http://dgtresearch.com)) or discarded.

### 2.2 Site selection and mounting considerations

This section contains information on considerations when selecting a site, and for positioning and mounting the equipment at the selected site.

#### 2.2.1 DGT holders

In stream and stormwater deployments, DGT holders are recommended (Figure 3). In marine deployments, DGTs can be simply deployed on a rope using nylon threaded through the DGT back plates.



**Figure 3: Housings for DGTs for monitoring of stream water (a) and stormwater (b).**

### 2.2.2 Mounting in streams and rivers

The following factors should be considered:

**Flow:** A constant flow of water is required past the face of the DGT. Therefore, the device should be deployed in a flowing reach of stream (run or riffle) and never in a pool or backwater. Excessive turbulence, particularly bubbles should be avoided.

**Point sources and dead zones:** The deployment location should be away from the immediate influence of point sources, tributary stream and drain confluences and dead zones (e.g. backflow eddies) that will not have completely mixed in the stream channel.

**Water depth:** The DGTs should ideally be deployed at mid-depth of the stream. They should not be sitting on or directly above the stream bed. They should also be at a depth that ensures they will remain underwater for the duration of deployment. Pay close attention to this in locations where the water level is affected by the tide or downstream control structures such as pumps to ensure they remain underwater during all parts of the tidal (or pumping) cycle.

**Attachment:** The acrylic holder can be cable-tied to a permanent structure within the stream, such as a heavy log or tree root, or an intake pipe at a water level recording site, as long as these are in a flowing reach of stream and oriented as required. Alternatively, a waratah may be banged into the stream and the holder can be cable tied to the waratah at the required depth and orientation.

**Orientation:** The DGTs should be deployed in an acrylic plastic holder that is mounted at a depth to ensure that the DGTs are always submerged. The holder should be mounted in line with the stream flow to optimise flow past the face of the DGTs. The holder should not be placed inside any other object (such as a minnow trap) which might reduce the flow and affect contaminant uptake. The holder should be mounted so that the membrane surface of the DGTs is vertical, to minimise sediment deposition on the membrane, which can also affect contaminant uptake rates<sup>1</sup>.

<sup>1</sup> British Standard (2011). Water quality - Sampling. Part 23: Guidance on passive sampling in surface waters (ISO 5667-23:2011). 23 p.

### 2.2.3 Mounting in stormwater networks

The following factors should be considered:

**How to keep the DGT wet:** For a stormwater location that is dry except during storm conditions, such as a stormwater pipe or drain, DGTs should be deployed in a housing to keep the DGTs wet prior to the storm commencing. DGTs can be deployed in the NIWA-designed and made trough housing which holds clean fluid during dry weather flow and is rapidly inundated at storm flows. The DGTs should be mounted vertically in this housing, to minimise sediment deposition on the membrane, which could affect contaminant uptake rates.

**Dead zones:** The deployment location have a steady flow past but not be too turbulent.

**Water depth:** The DGT housing can be placed on the pipe floor or wall. Ensure that it is not deployed too high – it should be underwater for most of the storm event, not just for the very peak flow.

**Attachment:** The trough housing needs to be attached to a solid structure, such as the side of the culvert or the bed of the stormwater pipe. For a temporary installation, extendable pipe can be used with the DGT trough attached to that (see Figure 4a). For a more permanent (frequently used) installation, a piece of timber could be dynabolted into the concrete stormwater structure, and the DGT trough screwed into this at the desired height (see Figure 4b).

**Orientation:** The DGT housing should be oriented with its longest dimension parallel to the stream flow. Stormwater will flow in one end, past the three DGTs and then out the other end. This is to optimise flow past the face of the DGTs.

All equipment used in the housings, to attach the DGTs or to attach the housings, should be stainless steel or acid-washed plastic.



**Figure 4:** DGT trough holder mounted to (a) extendable pipe inside a stormwater pipe for a temporary installation and (b) timber bolted to stormwater outlet wing-wall for a more permanent deployment location.

#### 2.2.4 Slow velocity waters

In areas where the stream or water flow is very slow, the DGTs could under-estimate water concentrations (as the diffusive boundary layer becomes thicker and no longer negligible). This can result in uncertainties of around 20% and for this reason, slow reaches of water should be avoided. For some purposes, such as initial screening, this level of additional uncertainty due to low flows may be acceptable. However for other purposes, a higher level of precision may be required. If there are no locations with faster flow, then this issue can be minimised by deploying DGTs with two different diffusive gel thicknesses. This provides information on the diffusive boundary layer thickness which can be used in a more sophisticated calculation of in-stream concentrations. We recommend consulting experts in DGTs if this is required.

### 2.3 Equipment and Field Record Forms

Equipment lists are provided in Sections 3.1 and 4.1, specific for deployment and retrieval, respectively. The equipment required differs depending on the location of deployment, either in a stormwater pipe / drain or in a constantly-flowing stream. Check that you have all the equipment needed prior to your field trip.

A standard field form should be used to record field visit metadata, including essential information on the timing of deployment. An example form is provided in Attachment 1. This form provides a record that verifies the location and timing under which deployment was carried out, along with other factors that may influence the data being collected. This record is also essential for later reconciliation with water quality results received from the laboratory. Waterproof paper is recommended for field forms.

A photograph of the DGT deployment site also provides a useful record.

### 2.4 Health and Safety

Collection of field measurements and water samples from rivers has some elements of danger that should be considered in a Health and Safety Plan, prepared in accordance with your own organisational processes. Safe access to routine monitoring sites in all weather conditions is particularly important. Special attention to safety is needed when sampling of rivers is conducted from the shore, a bridge, a boat or by wading during high, swift and/or turbid conditions. Only trained personnel shall be involved in fieldwork and suitable lone worker procedures are required if lone work is unavoidable. Appropriate personal protection equipment, such as hi-visibility clothing and floatation aids, should be provided to ensure safety. Gloves should be worn when sampling all river waters, from pristine to heavily contaminated. This is to protect samples from potential contamination and the sampler from potential harm. For further guidance on safety precautions when collecting discrete water samples refer to the NEMS Code of Practice Safe Acquisition of Field Data In and Around Fresh Water. <http://www.nems.org.nz/assets/Documents/NEMS-12/Safe-Aquisition-of-Field-Data-in-and-Around-Fresh-Water-v11.pdf>

When sampling for metals in summer, ensure that sunscreen being used is not a zinc-containing formula. The very high zinc content of these sunscreens has potential to easily contaminate samples.

## 3 Field Deployment

### 3.1 Equipment List

For DGT deployment, you need to have a record of the water temperature, ideally throughout the deployment period. If there is a temperature recorder at or near the site of interest, this can be used, otherwise a temperature recorder should be deployed, for example an EXO Sonde or a Hobo Tidbit. If using DGTs for nitrate-N and there is doubt about the salinity of the waterbody, it should be checked prior to DGT deployment to ensure it is below 1 ppt.

Gear list for deployment	
DGTs in sealed plastic bags	
Chilly bin packed with frozen slicker pads	
Disposable, powder-free nitrile, latex or vinyl gloves	
Side-cutters or scissors for snipping cable ties	
Tidbit temperature logger (if no temperature sensor near site)	
Mobile phone or watch to note time (in NZST)	
Waterproof field sheets and pencils	
Stormwater application (above water during dry weather)	Stream water application (underwater during dry weather)
3-D printed trough* & stainless screws	Acrylic mounting plates (purchased from DGT Research*)
Screw-driver	Medium cable ties and long cable ties in a different colour if possible.
Small cable ties	Elbow length gloves
Chelex-cleaned DGT fluid *	Clean plastic bag or sheet, approx. 30 cm x 20 cm to place DGTs
Ruler to measure deployment depth	Waders (chest or thigh, depending on stream depth)
Waratah & waratah hammer if needed	Waratah & waratah hammer if needed

\* Can be supplied by NIWA

## 3.2 Transport

DGTs should be transported to the site in their supplied zip-locked bags to ensure they are not contaminated and do not dry out. DGTs can be housed in a plastic container (such as a lunch box) to ensure they are not damaged by knocks during transport and placed within a chilly bin with slicker pads to ensure they remain cool.

## 3.3 Deployment

### 3.3.1 Stream deployment

If required, install waratah or other mounting structure in the stream.

Next insert the DGTs into the acrylic mounting plates:

1. Place a clean sheet of plastic on the ground or on a chilly bin lid to use as a clean work surface.
2. Place acrylic mounting plate on plastic sheet and open up.
3. Put on disposable gloves (powder-free), to be worn at all times when handling the DGT devices.
4. Taking care not to touch the face of the DGT, remove one DGT from its zip-lock bag and place face-down in hole of acrylic plate. Close zip-lock bag and return to chilly bin (this will be used on sampler retrieval).
5. Repeat for second and third DGTs, placing all in a single line of the DGT holder.
6. Place the flat plate over the DGTs to squeeze into place.
7. Put cable ties through the plate holes to keep DGTs locked into the acrylic holder and pull all ties tight. Snip tails from cable ties to reduce collection of debris (Figure 5a).
8. If using a Tidbit, attach this to the acrylic plate with small cable ties (Figure 5b).

If the face of the DGT comes into contact with anything (e.g., is dropped on the ground) the device should be discarded and replaced with a clean device.

Next deploy the acrylic mounting plate containing DGTs in the stream. Enter stream from a location downstream of the sampling zone where possible. Carry DGTs in plate into stream taking care not to touch the DGTs (you could place the DGTs and mounting in a clean plastic bag while working in the stream). Place underwater and cable tie into position using the holes in the corners of the acrylic plate (Figure 5c). If a different colour of cable tie is available, use this, to assist on retrieval. The holder can be oriented with DGTs in either top or bottom row depending on water depth, but when using triplicates, the plate should be oriented with three places across and two down so that all triplicates are at the same depth. Ensure that DGTs are not too close to the water surface (in case water level drops prior to the storm or prior to sampler retrieval) and not too close to the stream bed to avoid contaminants within the sediment influencing results. Snip tails from cable ties to reduce collection of debris. Note the time of deployment (in NZ Standard Time (NZST) for later cross referencing with hydrological records).



(a)



(b)



(c)



**Figure 5:** Deployment steps showing (a) DGTs contained within acrylic plate (b) with temperature recorder attached and (c) and plate attached to waratah.

### 3.3.2 Stormwater deployment

There are two main steps to deployment: attaching the holder at the stormwater site and inserting DGTs into the holder. This can be done in either order, depending on the accessibility of the deployment location. If this is not very accessible, it may be easier to insert the DGTs into the trough first then carefully take to the deployment location. However, in cases where it may be fiddly to attach the trough, it may be easier to attach the trough first, then insert the DGTs, to ensure that DGTs are not contaminated (or dried) while attaching.

Step 1 (or 2): Insert the DGTs into the trough housing:

1. Put on disposable gloves (powder-free), to be worn at all times when handling the DGT devices.
2. Taking care not to touch the face of the DGT, remove one DGT from its zip-lock bag and place face-down in hole of trough insert plate. Close zip-lock bag and return to chilly bin (this will be used on sampler retrieval).
3. Repeat for second and third DGTs, keeping the plate flat so the devices don't fall out.
4. Carefully insert the plate into the sampler trough ensuring the plate is locked in behind the raised bump and trough tabs are through the slots.
5. Put cable ties through the holes in the trough tabs and pull tight to lock DGTs in place.
6. If using a Tidbit, attach this to the tabs with small cable ties.
7. Snip tails from all cable ties to reduce collection of debris.

Step 2 (or 1): Attach the DGT trough to the structure you have selected (see Section 2.1). Ensure the trough is horizontal (use a small level if you like). Measure and record the distance from the water surface (if any) or bed of pipe to the top of the trough (Figure 6).

Step 3: Fill the trough with the clean DGT fluid.

If the face of the DGT comes into contact with anything (e.g., is dropped on the ground) the device should be discarded and replaced with a clean device.

Note the time of deployment (in NZST).



**Figure 6:** Installing trough on an adjustable pipe and measuring deployment height.

### 3.3.3 Quality Assurance

Field blanks and laboratory blanks are used to assess potential contamination at each stage of the field study.

Field blanks are DGTs taken into the field, removed from their zip-lock bags and exposed to the air, then replaced into the bag. At least one field blank should be used with every batch of up to 10 samples. If deploying DGTs at multiple sites, expose the field blank at the site that has highest risk of contamination during DGT deployment. This could be a site near an industrial area with higher dust levels. For deployments in multiple catchments a field blank should be prepared for *each catchment*. For deployments on multiple days a field blank should be prepared for *each day* of field work.

Laboratory blanks consist of sampling devices that have not left the laboratory and are analysed alongside each batch of samples analysed.

### 3.4 Water sampling

When using DGTs for metals, it is useful to have data on the Dissolved Organic Carbon (DOC) content of the water, particularly for comparing results between different streams. In locations where there is permanent flow (e.g., streams) a sample can be collected at the time of deployment or retrieval. Samples for DOC analysis should be collected in laboratory-supplied glass bottles for measurement of Dissolved Organic Carbon (analysed as DNPOC, dissolved non-purgeable organic carbon), with bottles filled and capped under water to remove any air gap. These samples should be sent to the laboratory as soon as possible as DOC is not stable until filtered. If there is no permanent flow, a sample could be collected at high flow with a Nalgene stormwater sampler with a glass sampling bottle.

When sampling is targeted to storm events, and DGTs are deployed and retrieved at baseflow, much of the time that they are accumulating contaminants will be during baseflow. To assist in understanding of the storm flow concentrations, it is useful to collect water samples at the time of deployment and retrieval. These are analysed for the same contaminants as the DGTs. These water samples provide information on the concentrations during baseflow and can be compared to the DGT concentrations integrated over the entire deployment period.

### 3.5 Records

The field sheet attached in Attachment A, or similar, should be filled in. Record the time (in NZST) that the DGTs are deployed to the nearest 5-10 minutes.

## 4 Field Retrieval

### 4.1 Equipment List

Gear list for retrieval	
Plastic bags for DGTs	
Clean plastic bag or sheet, approx. 30 cm x 20 cm to place DGTs	
Chilly bin packed with frozen slicker pads	
Disposable, powder-free nitrile, latex or vinyl gloves	
Side-cutters or scissors for snipping cable ties	
Camera	
Mobile phone or watch to note time	
Field sheets and pencils	
Squirty bottle filled with ultra-pure water (Milli-Q or equivalent, can be obtained from a commercial laboratory or supplied by NIWA for this project)	
Stormwater application (above water during dry weather)	Stream water application (underwater during dry weather)
Screw-driver	Elbow length gloves
	Waders

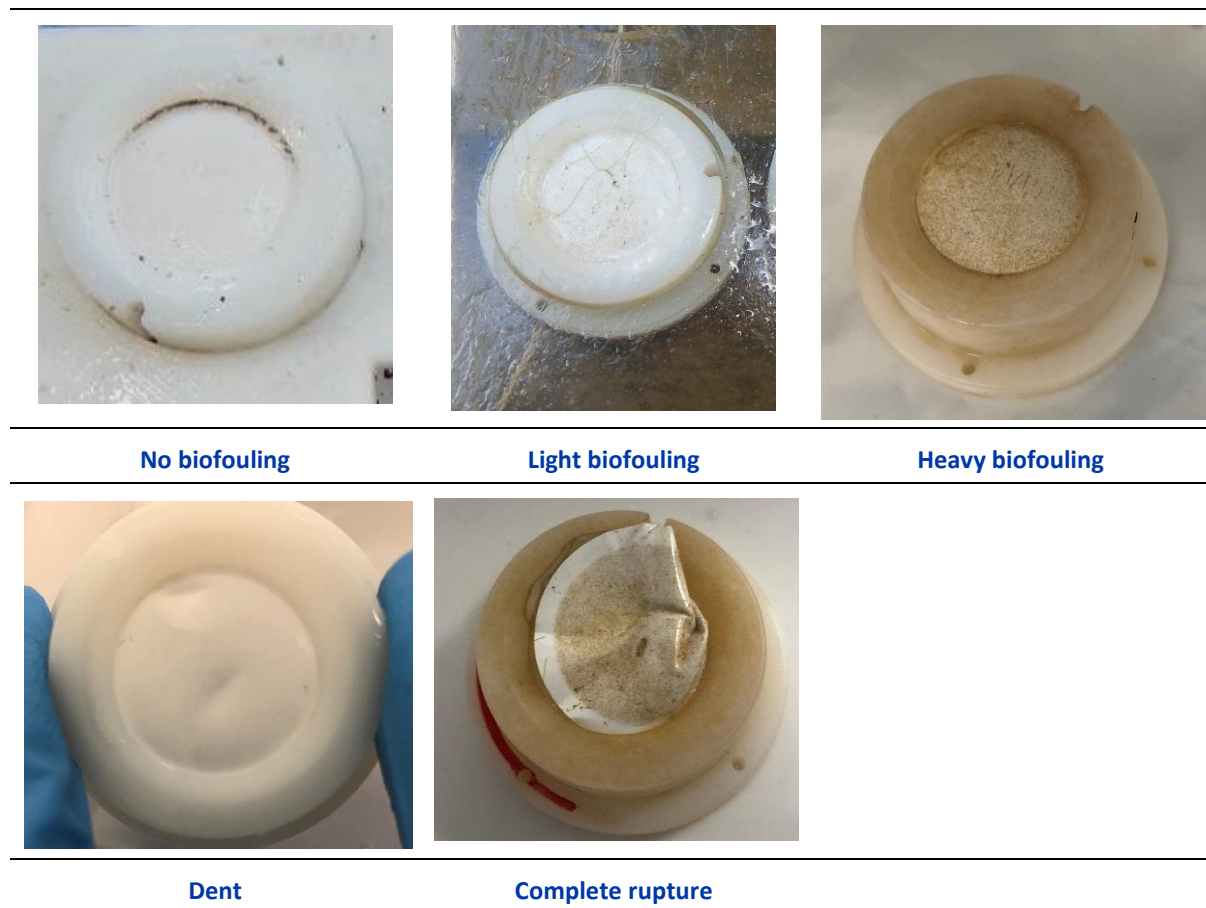
### 4.2 Retrieval Steps

#### 4.2.1 Stream retrieval

1. Prior to retrieval, the zip-lock plastic bags should be labelled with the site name and a number corresponding to each DGT replicate. Label from 1-3 from upstream to downstream to indicate the position the DGT was deployed in for future understanding.
2. Put on disposable gloves (elbow length if needed depending on water depth) for retrieval.
3. Wading into the stream, retrieve the DGT acrylic holder containing the DGTs by cutting the cable ties that attach it to the waratah or other permanent structure. Take care to only snip the cable ties that connect it, and not the cable ties that tie the plates together. Note that the DGT holder sinks so take care to grip the holder so that it and the cable ties are not lost. Return to the stream bank.
4. In a suitable location on the stream bank, lay out a clean plastic bag as a work surface and place the DGT holder onto it with the DGTs face up for inspection.
5. Document the extent of biofouling in each DGT (Figure 7) both on the field form and by taking photographs. After noting biofouling, thoroughly rinse each DGT with Milli-q water to remove

visible sediment and examine the integrity of each device. Note and photograph any damage, for example any scratches or ruptures in the membrane.

6. Snip the cable ties holding the acrylic plates together and carefully open the plates, ensuring that DGTs do not fall out onto the ground. Rinse back of DGTs if necessary to remove any trapped sediment. Place each DGT back into its labelled zip-lock bags and seal with minimum air space. Note on the field form which sampler is which.
7. Record the time of collection to the nearest 5 minutes.



**Figure 7: Biofouling and damage of DGTs.**

#### 4.2.2 Stormwater retrieval

1. Prior to retrieval, the zip-lock plastic bags should be labelled with the site name and a number corresponding to each DGT replicate. It may be easiest to label from 1-3 from upstream to downstream.
2. Put on disposable gloves for DGT retrieval.
3. Retrieve the DGT trough housing.
4. In a suitable location, lay out a clean plastic bag as a work surface. Snip the cable ties holding the DGTs in place and remove the holder insert keeping the DGTs on top / face down in order to not drop them.

5. Place DGTs in insert onto clean plastic bag with the DGTs face up for inspection.
6. Document the extent of biofouling in each DGT (as shown above in Figure 7) both on the field form and by taking photographs. After noting biofouling, thoroughly rinse each DGT with Milli-q water to remove visible sediment and examine the integrity of each device. Note and photograph any damage, for example any scratches or ruptures in the membrane.
7. Rinse back of DGTs if necessary to remove any trapped sediment. Place each DGT back into its labelled zip-lock bags and seal with minimum air space. Note on the field form which sampler is which.
8. Record the time of collection to the nearest 5-10 minutes.

### 4.3 Sample Transport and Handling

During transport to the laboratory, the DGTs should be stored in an insulated container with slicker pads or bagged ice. On return from the field, DGTs can be safely stored in a laboratory fridge for up to four weeks.

At present there are two laboratories in New Zealand that can analyse DGTs: Hill Hill Laboratories (Hamilton) and Lincoln University. DGTs, along with field and laboratory blanks, should be shipped with appropriate chain of custody documentation and laboratory request forms.

### 4.4 Data and Records

#### 4.4.1 Temperature

If a tidbit temperature logger has been used on site, download the data using the Hobo shuttle.

If temperature is continuously monitored on the site by some other means, download the data.

## 5 Laboratory Analysis

### 5.1 Extraction

The laboratory will disassemble the DGT sampler by breaking the cap then peeling off the filter and diffusive gel layer to reveal the bottom resin-gel layer.

These resin-gel layer contains the contaminants and is extracted using methods specific to the type of contaminants. For metals (code LSNN-NP), the resin gel is immersed in 1 ml of 1M HNO<sub>3</sub> solution for 24 hours. Following this, an aliquot removed and diluted for metal analysis. For nitrate-N DGTs (code LSNN-AP), the resin gel is extracted with 5 ml of 5% NaCl (m/v) for 16 hours. For mixed resin gel DGTs (LSNX-NP), there are two extractions: first with 1mL of 1 M HNO<sub>3</sub> for 24 hours (for analysis of metals) then with 1 mL of 1M NaOH for 24 hours (for analysis of DRP).

### 5.2 Analysis

Once extracted from the gel, the analysis is by standard laboratory methods. For metals, this is ICP-MS analysis at trace level. For nitrate-N, analysis is of total oxidised nitrogen by automated cadmium 61-80 reduction, Flow injection analyser.(APHA 4500-NO<sub>3</sub>- I modified).

The laboratory supplies the results as a concentration in the extraction fluid.

## 6 Data analysis and use

This chapter describes how to convert the concentrations obtained from the laboratory to an in-water concentration; the sources of uncertainty in DGT measurements and potential uses of the data.

### 6.1 Calculation of water concentration

Calculation of the in-stream concentration requires the following information:

1. The concentration of contaminants in the extraction fluid;
2. The length of time deployed; and
3. The average temperature during the deployment period.

Concentrations of each element in the blanks (specific to each batch) should be subtracted, then the mass of metal (or other contaminant) accumulated in the resin gel layer (M) calculated using Equation 1:

$$M = C_e \frac{(V_{HNO_3} + V_{gel})}{f_e} \quad \text{Equation 1}$$

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

The values of  $f_e$  when eluted with 1 mL of 1M  $HNO_3$  for 24 hours are 0.89 for copper and 0.9 for zinc.

Next the metal concentration in the water column is calculated using Equation 2:

$$C_{DGT} = \frac{(M \Delta g)}{(DtA)} \quad \text{Equation 2}$$

where  $\Delta g$  is the thickness of the diffusive gel (0.078 cm) plus the thickness of the filter membrane (0.014 cm),  $D$  is the diffusion coefficient of metal in the gel,  $t$  is deployment time (in sec) and  $A$  is the exposure area ( $A=3.14 \text{ cm}^2$ ).

Diffusion coefficients were from the DGT research website and are reproduced in Table 2.

**Table 2: Diffusion coefficients (D) of metal ions in DGT gel (open pore) at different temperatures from 12 to 25°C.** (Units are  $E^{-6} \text{ cm}^2/\text{sec}$ )

°C	Cd	Cu	Ni	Pb	Zn
12	4.16	4.26	3.94	5.49	4.15
13	4.30	4.39	4.07	5.67	4.29
14	4.43	4.53	4.20	5.85	4.42
15	4.57	4.68	4.33	6.03	4.56
16	4.72	4.82	4.47	6.21	4.70
17	4.86	4.97	4.60	6.40	4.85
18	5.01	5.12	4.74	6.60	4.99
19	5.15	5.27	4.88	6.79	5.14

°C	Cd	Cu	Ni	Pb	Zn
20	5.30	5.42	5.02	6.99	5.29
21	5.46	5.58	5.17	7.19	5.44
22	5.61	5.74	5.32	7.40	5.60
23	5.77	5.90	5.47	7.61	5.76
24	5.93	6.06	5.62	7.82	5.92
25	6.09	6.23	5.77	8.03	6.08

## 6.2 Uncertainty in measurements

As with any measurement, there are multiple sources of uncertainty in DGT measurements. The primary sources are reported to be related to the elution of the DGT and issues in estimating the cross-sectional area of the DGT<sup>2</sup>, neither of which can be controlled by users of DGTs.

We have found that contamination of the DGTs can be a major source of uncertainty, particularly in locations where low metal concentrations are found. Field blanks are highly recommended as described in Section 3.3.3. Ideally multiple field blanks are prepared, for each site or small number of sites. Concentrations in blank DGTs should ideally be below 10% of the concentration in sample DGTs. When field blanks contain metal concentrations above this, the results for samples in that batch should be viewed with caution. DGTs deployed for long periods of time (e.g., a week) accumulate metals to higher concentrations, which are more likely to be above the concentrations in field blanks, however this may not be compatible with a project objective that targets storm events (which typically have a short duration). Therefore, when deploying DGTs in locations where metal concentrations are expected to be at lower concentrations (e.g., in peri-urban streams or rural streams upstream of an urban area), extreme care should be taken when handling DGTs and multiple field blanks prepared.

Damage to the DGT membrane can affect the results by increasing the uptake of metals. If damage was noted on the field sheets during retrieval, results should be viewed with caution, particularly when higher than expected (for example, higher than replicates from the same location). Biofouling may decrease the uptake of metals by the DGTs and where there is extensive biofouling, the results should be considered as a lower estimate when comparing to guidelines or between sites.

Slow water velocity also affects the diffusion of metals into the DGTs and concentrations may be under-estimated in locations with slow velocities.

The water temperature during that deployment affects the calculation of the in-water concentrations as this influences the diffusion coefficient. Inaccuracies of > 2°C will give an error of more than 5%, and inaccuracies of 5°C will give an error of about 15%. Therefore, measuring water temperature at each site is recommended where high accuracy is required. On the other hand, accuracy in the time of deployment and retrieval is less important, with negligible differences in metal concentrations for discrepancies of even an hour, when deployed for at least 12 hours.

<sup>2</sup> Knutsson, J.; Rauch, S.; Morrison, G.M. (2014). Estimation of Measurement Uncertainties for the DGT Passive Sampler Used for Determination of Copper in Water. *International Journal of Analytical Chemistry* 2014: 7.

Kreuzeder, A.; Santner, J.; Zhang, H.; Prohaska, T.; Wenzel, W.W. (2015). Uncertainty Evaluation of the Diffusive Gradients in Thin Films Technique. *Environmental Science & Technology* 49(3): 1594-1602.



### 6.3 Using the data

The information collected using DGTs is ideal for comparing between locations as it integrates over time. Where there are large differences in the water chemistry between sites, the concentrations may be less comparable, as some aspects of water chemistry affect metal speciation and therefore the concentrations measured by DGT. In particular, differences in DOC between sites will affect the concentrations of copper and to a lesser extent, zinc.

Concentrations calculated using DGTs are suitable for assessing metal toxicity as DGT concentrations more closely represent the bioavailable concentrations than total dissolved metal concentrations do<sup>3</sup>. Water quality guidelines, including the Australia New Zealand Guidelines for Water Quality, are almost all based on dissolved concentrations. However, a more advanced step in comparing water quality data to the guidelines includes considering the bioavailable fraction for toxicants. For metals, one of the methods recommended is to measure metal concentrations using DGTs<sup>4</sup>, therefore the data obtained with DGTs can be directly compared to these guidelines.

## Attachment 1: Field Sheet

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<sup>3</sup> Degryse, F.; Smolders, E. (2016). DGT and bioavailability. In: Davison, W. (ed.). Diffusive gradients in thin-films for environmental measurements, pp. 216-262. Cambridge University Press, Cambridge.

<sup>4</sup> <http://www.waterquality.gov.au/anz-guidelines/guideline-values/default/water-quality-toxicants/local-conditions#bioavailable-fraction>

## Water Quality Data Sheet – DGT Deployment & Retrieval

### Site details

Site Location Code	Description

	Deployment	Retrieval
Date		
Person recording data		
Person deploying samplers		

### DGTs details

Sample codes	Location	Deployment height	Time deployed	Time retrieved	Observations (eg biofilm, dents, holes)

Water samples collected for:

	Deployment		Retrieval	
	Water samples collected	Sample labels	Water samples collected	Sample labels
Dissolved metals (field filtered, <0.45 µm filters)				
DOC				