




Guidelines

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A Good Practice Guide for the Use of DGTs. Sampling of metals in transitional and coastal waters by Diffusive Gradient in Thin films (DGT) technique

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A Good Practice Guide for the Use of DGTs

Sampling of metals in transitional and
coastal waters by Diffusive Gradient
in Thin films (DGT) technique



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MONITOOL PROJECT

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SUMMARY

This document provides guidance on best practice for the use of Diffusive Gradient in Thin films (DGT) passive samplers devices in sampling of transitional and coastal waters for water quality monitoring. The methodology¹ to be addressed in this guide was developed by the consortium of the European Union's Interreg MONITOOL Project in order to ensure comparability and reproducibility of the data obtained from each project Partner in different regions. The guide provides practical and detailed information on all the aspects to be considered before the deployment of these devices and the essential steps for their deployment, retrieval and subsequent sample processing for the analysis of trace metals. Although it is not aimed as a standard protocol, these guidelines address the need for a common approach and the intention to promote best practice.

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1. Introduction

1.1. Background

According to the EU Water Framework Directive (WFD, 2000/60/EC), good chemical status of water bodies is achieved when the concentrations of priority substances do not exceed the relevant Environmental Quality Standards (EQS) established by Directive 2008/105/EC (subsequently amended by Directive 2013/39/68 EU). Regarding metals, the EQS refers to the dissolved concentration, i.e., the metal concentrations measured in a water sample previously filtered through a 0.45 μm filter or subjected to any equivalent pre-treatment.

The most commonly used approach to monitoring compliance with the requirements of the WFD for metals, relies on water samples obtained by spot sampling, followed by filtration (dissolved metal), preconcentration and instrumental analysis². The limitations of low-frequency spot sampling, such as the lack of representativeness in dynamic systems and the inability to account for bioavailability and potential toxicity of the contaminants, have been discussed elsewhere^{3,4}. Thus, the inclusion of complementary methodologies, which integrate the environmental metal fluctuations and/or measure the metal speciation that can be more easily related to ecotoxicological effects, might improve the quality of the assessment.

As an alternative, passive samplers have been used for measuring labile metal concentrations in waters⁵. The Diffusive Gradients in Thin films, DGT⁶, is the most extensively used sampler for *in situ* labile metal measurements⁷. DGT samplers accumulate metals continuously during the deployment time, usually ranging from several days to weeks. This provides time-weighted average metal

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concentrations and enables the achievement of lower limits of quantification compared with low-volume water samples⁸. In addition, DGT samplers only accumulate free metal ions and easily dissociable metal complexes, operationally known as metal labile concentration, which has been related to observed toxicity in different types of organisms^{9,10,11}. These advantages might favour the inclusion of DGT technique within monitoring programmes.

On the other hand, the fact that in the year 2011 the International Organization for Standardization (ISO) released the document ISO 5667-23:2011¹² specifying procedures for the determination of time-weighted average concentrations and equilibrium concentrations of the free dissolved fraction of organic and organometallic compounds and inorganic substances, including metals, in surface water by passive sampling, followed by analysis, seems to be a clear indicator of the trend today to seek more suitable sampling methods for monitoring water quality.

Finally, Directive 2013/39/EU¹³, with regard to priority substances in the field of water policy, specifies that “Novel monitoring methods such as passive sampling and other tools show promise for future application, and their development should therefore be pursued”.

1.2. Scope

This good practice guide is focused on the DGT devices, which are the most widely used passive sampler for metals, covering the following aspects:

- Principle
- Handling passive sampling devices for metals
- Estimation of appropriate field deployment time

- Passive sampling device preparation and assembly
- Selection of sampling site and safety precautions
- Passive sampling device deployment and retrieval
- Extraction of analytes from passive sampling devices
- Analysis
- Calculations

2. DGT Passive Samplers

The acronym DGT stands for Diffusive Gradient in Thin films. A DGT is a simple and robust plastic device that accumulates dissolved substances in a controlled way, providing the *in situ* concentration during the time of deployment.

They are used since 1994, when Hao Zhang and William Davison (Lancaster University) developed the DGT technique to detect metals in marine environments. Since then, the DGT technique has expanded to a significant number of elements and the devices have been modified, developing different types and configurations used for: analysis of waters, dry soils, sediments and flooded soils (Image 1).

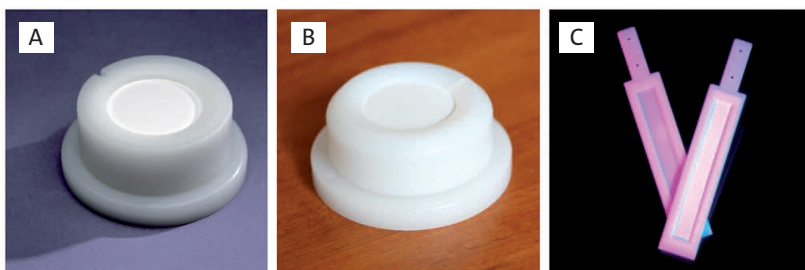


Image 1. Some examples of DGT devices: (A) piston-type DGT device used for analysis of waters, (B) piston-type DGT device used in dry soils and (C) Flat-type DGT used for sediments and flooded soils. Source: dgtresearch.com

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With more than 800 scientific publications, it has been confirmed throughout the world that DGTs work for a wide range of substances. Today, they constitute a research and monitoring tool widely used by scientists, agencies, industry, consultants, etc.

This guide will focus on the piston-type DGTs used for analysis of waters (or solutions). They consist of a base and a tight-fitting circular cap with an opening (DGT window). As shown in Image 2 below, a binding gel layer (e.g. Chelex-100), diffusive gel and filter membrane are stacked onto the piston (or base), and the cap is placed over the assembly. The elements or compounds of interest pass through the membrane filter and diffusive gel and are bound/accumulated in the binding gel in a rate-controlled manner.

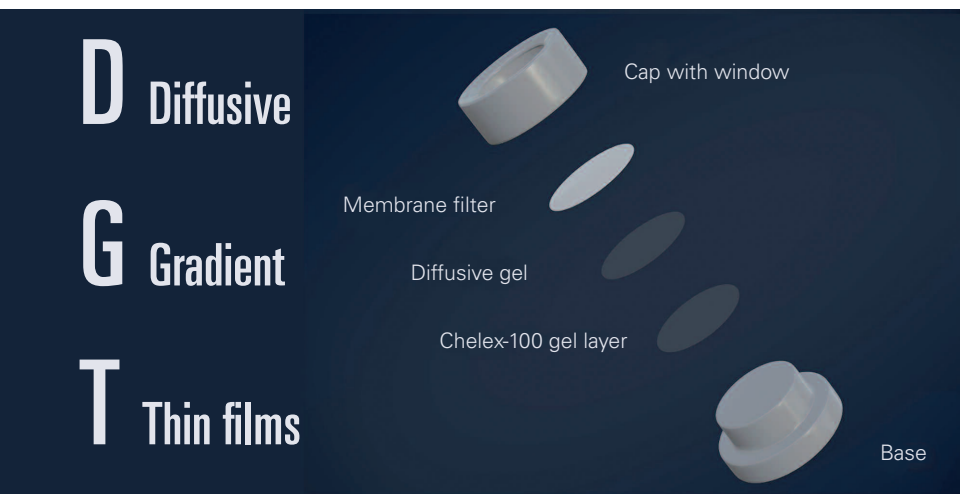


Image 2. DGT for metals components. Source: MONITOOL project.

By using different types of filter membranes, diffusive gels and binding layers, a wide range of analytes can be determined (Table 1):

Table 1. Available Loaded DGT® devices for deployment in solution

	Possibility to measure	Filter membrane	Diffusive gel	Binding layer
LSNM-NP Loaded DGT device for metals (A)	Up to 30 metals, including: Cd, Co, Cu, Fe, Mn, Ni, Pb, Zn, etc.	PES (Polyether-sulphone)	0.8 mm APA (Agarose cross-linked polyacrylamide)	Chelex-100
LSNP-NP Loaded DGT device for P and metals (B)	P and metals present as oxy-ions, including: As, Mo, Sb, Se, U, V, W, etc.	PES	0.8 mm APA	Iron oxide
LSNT-NP Loaded DGT device for P, metals (B) and glyphosate	P and metals present as oxy-ions or strongly hydrolysed, including: Al, As, Mo, Sb, Se, U, V, W. Also, glyphosate	PES	0.8 mm APA	Titanium oxide (Metsorb)
LSNZ-NP Loaded DGT device for P and metals (B)	P and metals present as oxyanions, including: As, Mo, Sb, Se, V, etc.	PES	0.8 mm APA	Precipitated zirconium oxide
LSNX-NP Loaded DGT device for metals (A and B) and P	Phosphate and polyphosphates and up to 40 metals, including: Al, As, Cd, Co, Cu, Fe, Mn, Ni, Pb, Sb, Se, U, V, W, Zn, etc.	PES	0.8 mm APA	Mixed binding layer of Chelex-100 and titanium oxide (Metsorb)
LSNY-NP Loaded DGT device for metals (A and B) and P	Phosphate and polyphosphates and up to 40 metals, including: As, Cd, Co, Cu, Fe, Mn, Ni, Pb, Sb, Se, U, V, W, Zn, etc.	PES	0.8 mm APA	Mixed binding layer of Chelex-100 and iron oxide (ferrihydrite)
LSNB-AP Loaded DGT device	Hg ²⁺ and methyl mercury and As (III)	PES	0.8 mm agarose	3-mercapto-propyl functionalised silica gel

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	Possibility to measure	Filter membrane	Diffusive gel	Binding layer
LSNE-NP Loaded DGT device	Cr (VI) in the presence of Cr (III)	PES	0.8 mm APA	N-methyl-D-glucamine (DMDG) functional resin
LSNV-NP Loaded DGT device	Technetium (Tc)	PES	0.8 mm APA	Dispersed TEVA resin
LSNN-AP Loaded DGT device	Nitrate in freshwater	PES	0.8 mm agarose	SIR-100-HP resin styrene (divinyl-benzene-based absorbent with amine functional groups)
LSNH-NP Loaded DGT device	Sulphide	PES	0.8 mm APA	Silver iodide
LSNC-AP Loaded DGT device for antibiotics and illicit drugs	A range of polar compounds, including antibiotics and some illicit drugs	PES	0.8 mm agarose	XAD-18 resin
LSND-AP Loaded DGT device for pharmaceuticals other than antibiotics	A range of polar compounds, including pharmaceuticals other than antibiotics	PES	0.8 mm agarose	HLB (hydrophilic-lipophilic-balanced binding agents)
LSNR-AT Loaded DGT device	Bisphenols	Polytetrafluoroethane (PTFE)	0.8 mm agarose	Activated charcoal
LSND-AN Loaded DGT device	Household and personal care products	Nuclepore polycarbonate	0.8 mm agarose	HLB
LSND-AG Loaded DGT device	Pesticides and herbicides	Hydrophylic polypropylene (GHP)	0.8 mm agarose	HLB

Source: Compiled by authors based on information in dgtresearch.com.

3. DGT METHODOLOGY

3.1. DGT Passive Samplers

Principle

Metals in the water can be present in either dissolved (soluble) or particulate (insoluble) state. The dissolved metals are in a free ionic form or forming inorganic or organic complexes in the solution.

The basic principle of DGTs for dissolved metals in the solution is that, once DGT devices are deployed directly in the water, during the entire deployment period, the metal complexes in solution can diffuse in the DGT's gel layer. The complexes, which dissociate during their migration in the diffusive gel will be fixed irreversibly onto the binding layer. These complexes are said to be labile (potentially available to biota)^{14,15}.

Type selected

The passive sampler selected in MONITOOL project and in this guide is the LSNM-NP Loaded DGT device for cationic trace metals in waters, consisting of a standard DGT plastic holder with (Image 3):

- Diffusive gel: 0.8 mm agarose cross-linked polyacrylamide (APA)
- Filter membrane: polyethersulphone (PES) 0.45 µm pore size
- Binding gel layer: chelex-100

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These DGT devices are provided by DGT® Research Ltd (Lancaster, UK) at: <https://www.dgtresearch.com/product/lsnm-loaded-dgt-device-for-metals-a-in-solution/>

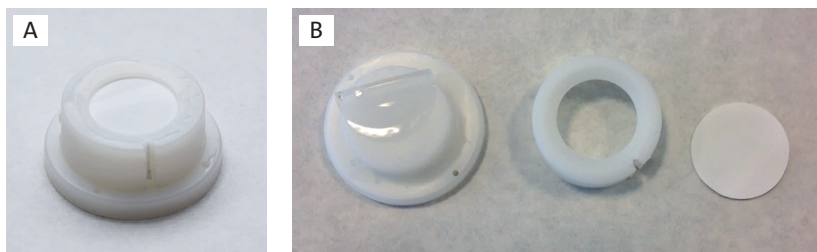


Image 3. (A) DGT assembled and (B) DGT disassembled showing its different components. Source: MONITOOL project.

This DGT device can be used to measure up to thirty metals. Figure 1, below, shows the specific metals measured in MONITOOL project:

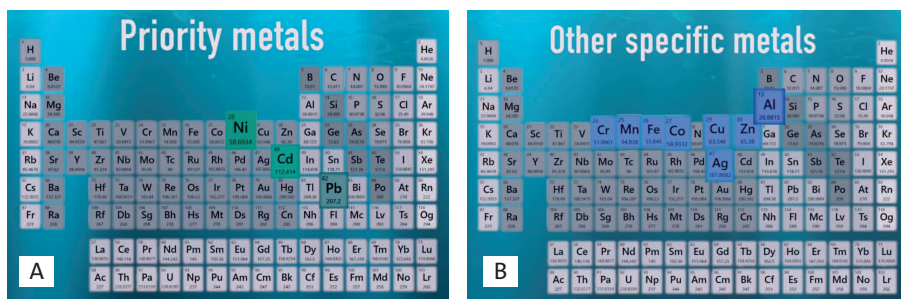


Figure 1. (A) WFD priority metals and (B) Other metals measured by DGTs in MONITOOL project.

Storage of the DGTs in laboratory pre-deployment

The DGT devices are supplied in sealed, clean plastic bags containing a few drops of 0.01M NaNO₃ (or 0.01M NaCl) solution.

In order to prevent contamination of the DGT devices, direct contact with them must be minimised:

- Store the DGT units under refrigerated conditions (4°C), avoid freezing as performance can be affected.
- Check the DGT units about once a week to ensure that moist conditions are maintained. Add a few more drops of trace metal clean 0.01M NaNO₃ (or 0.01M NaCl) solution if necessary.
- Always wear powder-free, preferably uncoloured, gloves when handling DGT units to avoid contamination.

Units needed

A minimum of eight DGT devices will be required per sampling site:

- 3 DGTs laboratory blanks
- 1 DGT field blank per location
- 4 DGTs for deployment per location: 3 DGTs for the analysis of trace metals by ICP-MS and 1 DGT to be kept as “reserve”

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NOTES:

- **DGT laboratory blanks** are unexposed DGT devices. A minimum of three DGT Laboratory Blanks are recommended for the detection of anomalous values (such as metal contamination resulting from the manufacturing process).
- **DGT field blank** is designed to identify the potential contamination that might affect to the DGT devices exposed to air briefly, but not deployed:
 - At laboratory during handling and assembly of the DGTs to be deployed.
 - At the sampling site, during those DGTs deployment and retrieval.
 - At laboratory during the dismantling of those deployed DGTs.

It is advisable to have at least one field blank for each test series.

3.2. Other reagents, materials and equipment

Reagents needed:

- Nitric acid (HNO_3), 69%, ultrapure grade
- Water, ultrapure, type I or better ($\geq 18 \text{ M}\Omega\cdot\text{cm}$ resistivity)

Materials needed:

- Gloves, powder-free (preferably uncoloured)
- DGT holders (*): provided by DGT® Research Ltd (Lancaster, UK) at: <https://www.dgtresearch.com/product/ds6-holder-for-up-to-6-solution-dgt-devices/>

- Clamps (*), uncoloured (e.g. cable tie)
- Plastic bags (*)
- Netting (*), uncoloured or white (optional)
- Plastic tweezers/forceps (*), white if possible
- Micro-centrifuge tubes (*), plastic, 1.5 and 5 ml
- Pipette tips (*), 100 µl, 1 ml and 5 ml
- Ropes, weights, etc.
- Cool box
- Ice packs
- Plastic screwdriver (or metal screwdriver covered with plastic or glove)

NOTE: Material with (*) must be cleaned as described:

- Analytical grade HNO_3 (69%) must be used to make up a 10 % (v/v) aqueous HNO_3 bath, where the material to be used in the laboratory and sampling campaigns will be immersed for 4 hours to overnight. Materials must be rinsed with deionised water and stored in cleaned and sealed plastic bags until utilisation.

Equipment needed:

- Laminar flow hood, positive pressure
- Variable volume automatic pipettes: 100 µl, 1 ml and 5 ml
- Water temperature measurement device

3.3. Deployment site location

The location for DGT-based sampling should comply with the following requirements:

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- Restricted access and/or discreet place for persons, swimmers, etc.
- Possibility of attaching the system.
- A minimum depth of 2 meters.
- Flowing (or moving) water, but avoiding excessive turbulence, particularly bubbles.
- Away from any metallic structure as much as possible.
- Possibility of working from land, boat and/or with a diver.
- In the case of ports, without risk of entanglement of the system on motor ships that can circulate near the exposed DGTs.

3.4. DGT based passive sampling

General DGT handling guidelines

To avoid contamination:

- Direct contact with the DGT devices must be minimised.
- Clean handling procedures should be adopted during the entire DGT manipulation (preparation, deployment, retrieval and laboratory processing steps).
- Always wear powder-free, preferably uncoloured, gloves when handling DGT units.
- Do not open or remove DGT units from the sealed plastic bag until immediately (minutes) prior to assembly or deployment.
- Do not touch or let anything come into contact with the white filter membrane at the face of the DGT unit.

DGT holder assembly

DGT devices are assembled pre-deployment in a clean laboratory environment (Image 4), preferably under a laminar flow cabinet

or, alternatively, in a clean plastic bag to avoid contamination from air exposure.

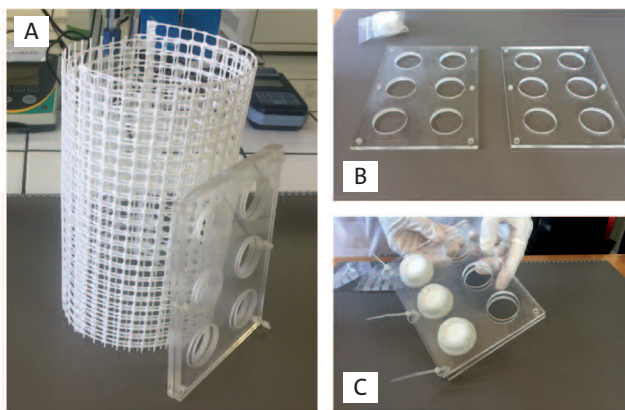


Image 4. Structure for the deployment of DGTs: (A) DGT holder and net; (B) detailed photograph of the DGT holder; (C) placing of DGTs in the DGT holder (Source: UNICA).

When mounting the DGT devices onto the holder for each sampling site:

- Open the individual bag and expose DGT field blank on a clean surface, for the entire duration of the holder/DGT assembly (i.e. simultaneously exposed while manipulating the DGTs before their deployment).
- All DGTs to be exposed (3 + 1 reserve) should be mounted onto the holder in the laboratory, keeping the individual plastic bags to store the DGT once exposed after the retrieval stage.
- The whole assemblage must be stored in sealed clean plastic double bag and refrigerated before deployment.
- Transfer the DGT field blank back in its original plastic bag and store it refrigerated.

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NOTE: As noted before, DGT field blanks (1 per sampling site) are further exposed (but not deployed) in the field during the DGTs deployment and retrieval processes and in the laboratory during the holder/DGT disassembly.

Depending on the sampling site considered, it can be recommended to cover the holder with a net (white, as well as the needed clamps) before deployment, in order to prevent damage and protect the DGT devices from side impact and accelerated degradation by fish and other organisms in the deployment zone.

Pre-assembly of the nets should be performed in the laboratory to speed up the DGT deployments and to limit exposure of devices to ambient air.

Transport to deployment site

Sealed plastic bags with each DGT assemblage (DGT, holder and net) and DGT field blanks must be transported to the field in a clean cool box/polystyrene box with ice packs (Image 5).

Designated deployment structure

The easiest deployment system consists of the use of moorings, buoys or other fixed structures (Figure 2, B), where the DGT assembly is attached with a rope presenting a weight at the end. Another option is to place the DGT assembly between a weight resting on the bottom and a buoy in order to keep the DGTs at the desired height (Figure 2, A).



Image 5. Double bag DGT assembly and other needed material in cooler box (Source: ITC).

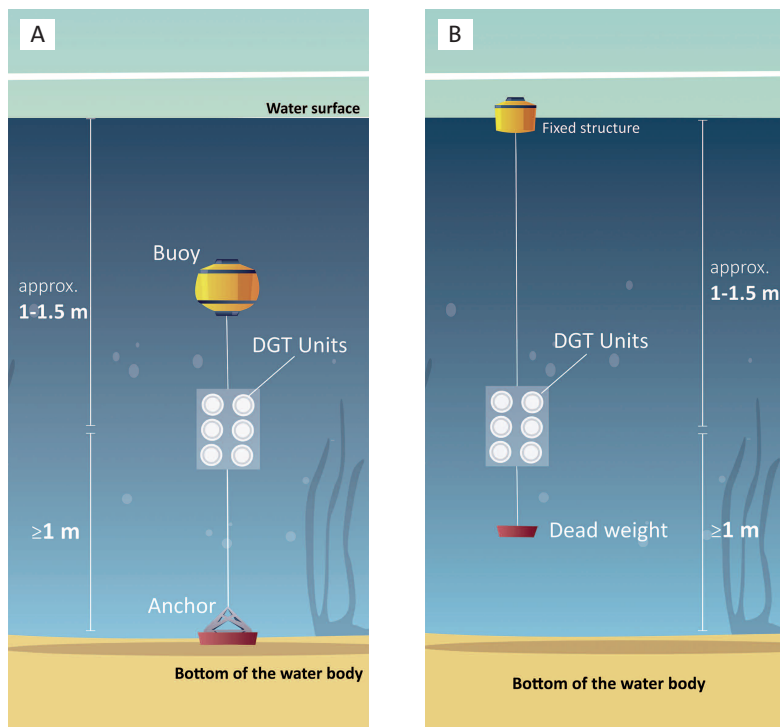


Figure 2. Designated structures options for DGT deployment: (A) From the bottom and (B) From the surface (Source: ITC).

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- If deploying from a boat, all the preparation must be done with the engine switched off.
- Ensure that the sampling windows of the DGTs are fully immersed during the deployment period, therefore:
 - Deploy the DGT ideally at a depth of 1-1.5 m below the surface and at least 1 m above the seabed.
 - In shallow areas (depth <1 m), ensure that the DGT devices are fully immersed and at least 0.3-0.5 m above the seabed.

However, sampling site characteristics must be considered for the selection of the most suitable sampling depth (e.g., in harbours, choosing a greater depth might guarantee a reduction in potentially high variability associated to shipping).

In Image 6 real examples of DGT holder assembling during MONITOOL project's sampling campaigns are shown.

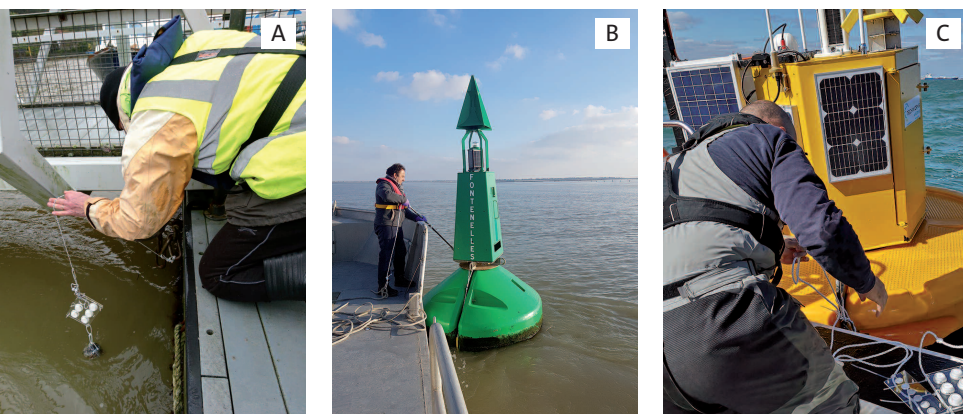


Image 6. DGT deployment structures used in MONITOOL: (A) Fal Estuary, UK (Source: CEFAS); (B) Fontelles, France (Source: IFREMER); (C) Dublin Bay, Ireland (Source: DCU).

Sampling duration

Deployment times between 3 and 21 days are generally suitable, although optimum deployment time depends on various factors:

- On one hand, longer deployment periods allow a higher concentration of metals in the Chelex-100, which results in lower detection limits. Furthermore, as it is a time-weighted average sampling, it is more representative of the real situation as it integrates the contaminant fluctuations occurring during the deployment time.
- On the other hand, long deployment periods can lead to fouling problems (Image 7) and/or reaching the maximum capacity of DGT devices (approximately 0.5 mg of metals¹⁶).

The protocol used during MONITOOL sampling campaigns fixed the DGT deployment time to four days (i.e. 4 x 24 h).

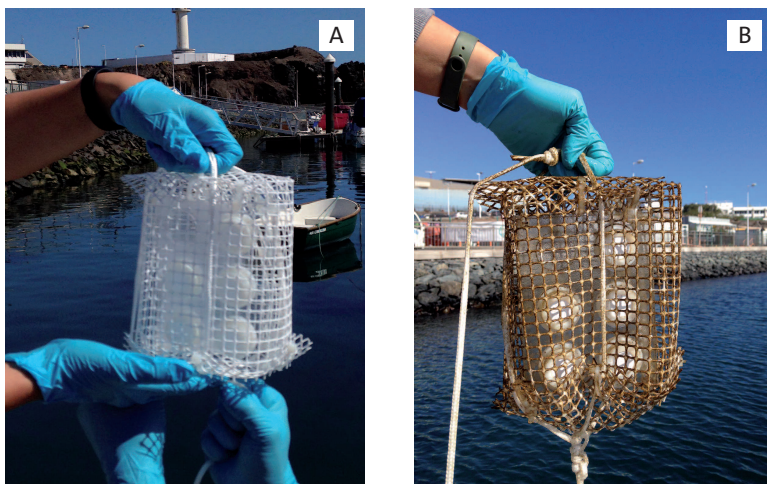


Image 7. Biofilm growth on DGT assemblage at Taliarte (Gran Canaria): (A) Before deployment and (B) After 7 days of exposure (Source: ITC).

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NOTE: If the concentrations of the metals are very low, as in an offshore marine environment, and there is no indication of biofilm growth on the surface of the devices, longer deployment times may be appropriate.

3.5. DGT deployment

The DGTs should be deployed in accordance with the following instructions:

- Wearing powder-free (preferably uncoloured) gloves, expose the DGT field blank on a clean surface (Image 8) until the DGTs assemblage is submerged in the water.
- Remove the DGT assemblages from their plastic bag and attach the DGT holder (with or without the net) onto the designated structure.
- Deploy the DGT devices immediately.
- Record accurately the deployment time to the nearest minute.
- After that, put the DGT field blank back in its original plastic bag and store refrigerated until the DGT retrieval day.
- Keep the original plastic bag (clearly labelled and sealed) to store the DGT assemblages at the retrieval stage.
- Record the depth of deployment and temperature of the water.
- If the temperature variation during the deployment period is within $\pm 2^\circ\text{C}$, a mean (or start and end temperature) will suffice. If the variation is greater, ideally the mean temperature should be obtained from an integrated record of temperatures (e.g. data logger).

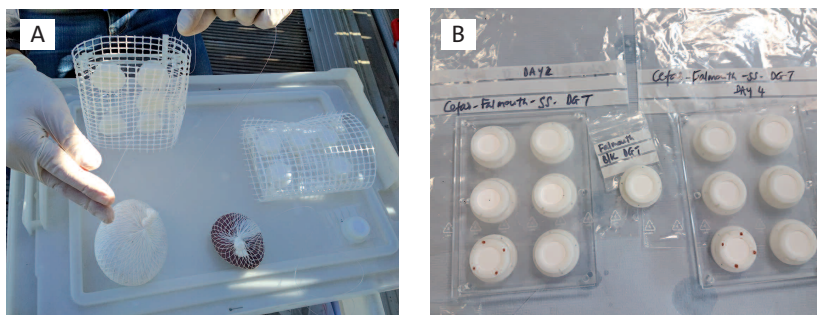


Image 8. (A) DGT assembly at Tagus location (Source: IPMA) and (B) Exposing of the field blank (Source: CEFAS).

3.6. *In-situ* physico-chemical parameters

If in addition to the temperature, other *in-situ* physico-chemical parameters of water are recorded at the DGT sampling depth, an adequately calibrated multiparametric probe should be used at each location (Image 9). The usual physico-chemical parameters to be measured are: depth (m), temperature ($^{\circ}\text{C}$), specific conductivity (mS/cm), dissolved oxygen and saturation (mg/L and %, respectively) and pH.

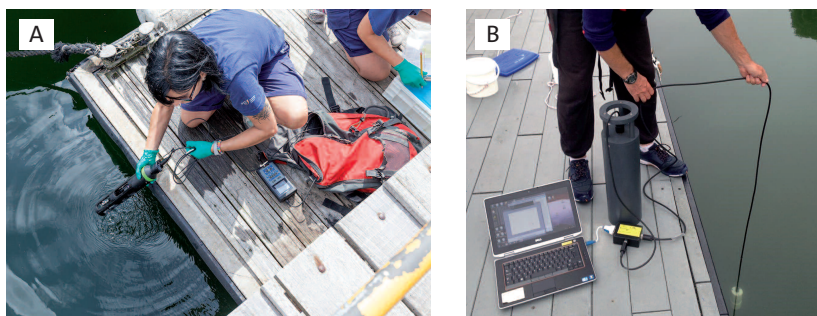


Image 9. Water parameters recording with a multiparametric probe (source: (A) AZTI; (B) CEFAS).

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NOTE: If spot water sampling is also necessary for the determination of other supporting physico-chemical parameters (SPM, DOC, turbidity, etc.), it should be performed first, prior to DGT deployment/retrieval and prior to the *in situ* measurement of physico-chemical parameters:

Spot water sampling → DGT (deployment / retrieval) → *In situ* measurements

3.7. DGT retrieval and transport

Once the deployment time has elapsed, the DGTs retrieval and transport (Image 10) should be performed in accordance with the following instructions.

If a boat is used for the retrieval operations, the engine must be off at all times.

- Expose the DGT field blank (previously exposed during the DGT assembly and deployment) on a clean surface for the entire duration of the retrieval process.
- Remove the DGT holder unit from the deployment structure and take it out of the water wearing gloves (powder free, preferably uncoloured), taking care not to touch the DGTs' filter membrane.
- Record the retrieval time to the nearest minute.
- Rinse the DGT holder immediately after recovery with water from the site by direct immersion of the device (e.g., from the boat, from the dock, etc.) and by shaking the device underwater several times. Alternatively, rinse the DGT holder and DGT units with a stream of uncontaminated distilled/deionised water from a clean wash bottle.
- Shake off obvious surface water (do not dry).

- Place the DGT holder (containing the exposed DGT) in their original plastic double bag and seal with minimum air space. Label the bag with the sampling location.
- DGT field blank is returned in their original plastic bag.
- Record the temperature of the water at the retrieval time.
- Store the DGT field blanks and the DGT holder both in their corresponding bags in a cool box with ice packs for transport to the laboratory.

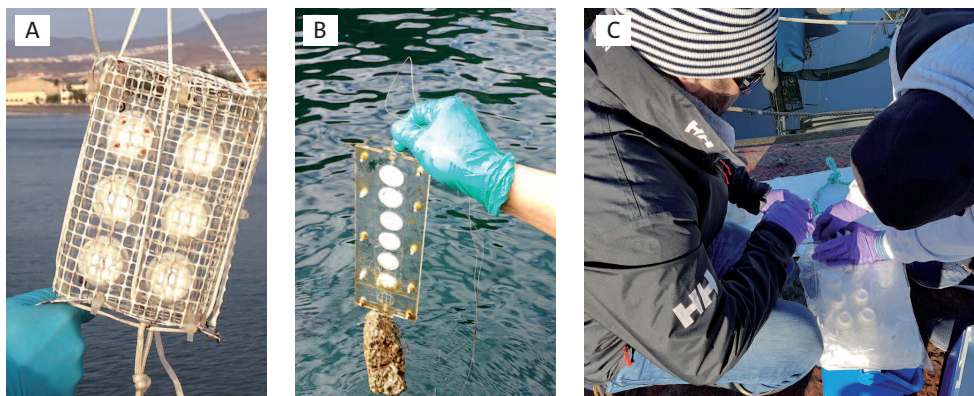


Image 10. DGT retrieval: (A) at Gando location (Gran Canaria, Spain (Source: ITC); (B) at “Museo” Pasaia location, Guipúzcoa, Spain (Source, AZTI); (C) Double bag of the DGTs assembly and field blank DGT at Saint-Nazaire, France (Source: IFREMER).

3.8. DGT holder dismantling and preservation

At the laboratory (Image 11), under a laminar flow hood or in a clean plastic bag, and wearing powder free (preferably uncoloured) gloves:

- Expose the DGT field blank (previously exposed during the DGT assembly, deployment and retrieval processes) on a clean surface for the entire duration of the holder disassembly.

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- Remove the individual DGT devices from its holder unit and put them in individually labelled plastic bags (using the plastic bags provided by DGT® Research Ltd when the DGT devices were received).
- Then, return the DGT field blank back in its original plastic bag.
- Double bag the three exposed DGT devices and the DGT field blank.

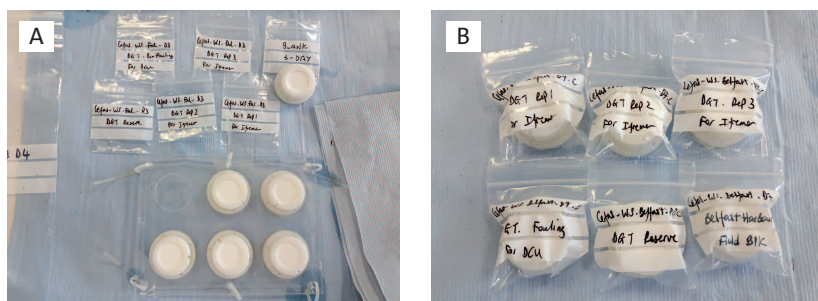


Image 11. (A); Exposing blank and field DGTs in lab; (B) Exposed DGTs in their individually labelled plastic bag; (Source: CEFAS).

- Store in a refrigerator (4°C) until the dismantling of DGTs for extraction and posterior analysis.
- Care should be taken to avoid gels becoming dry, as this can cause the gels to stick to each other and become difficult to separate.

3.9. DGT dismantling and extraction pre-analysis

Powder free and preferably uncoloured gloves must be worn at all time.

The procedure must be conducted in a clean, positive pressure laminar flow hood or, alternatively, in a clean plastic bag to avoid contamination from air exposure. Follow the following order for the dismantling of various DGT devices:

- I. DGT Laboratory Blanks
 - II. DGT Field Blanks
 - III. Deployed DGTs (from least to highest expected contamination)
- To retrieve the resin gel, insert a plastic screwdriver (or metal screwdriver covered with plastic or glove) into the groove in the cap and twist. The cap will break at the weak point (Image 12, A).

NOTE: In the case that DGT plastic housing with groove is too tough to break, use a clean tweezers to break the white filter membrane and pull out the gels directly and retrieve the resin gel from the bottom.

- Remove the broken cap and then peel off the filter and diffusive gel layer to reveal the bottom resin-gel layer. Alternatively, turn over the complete assembly and take only the thin layer of Chelex-100 that is then left on top (Image 12, B).
- Place the resin gel, with the help of the tweezers, in a clean sample tube and add 1 ml of 1M HNO₃ solution (Image 12, C).
- Ensure that the resin gel is fully immersed in the HNO₃ solution. Leave at least 24 hours at room temperature.

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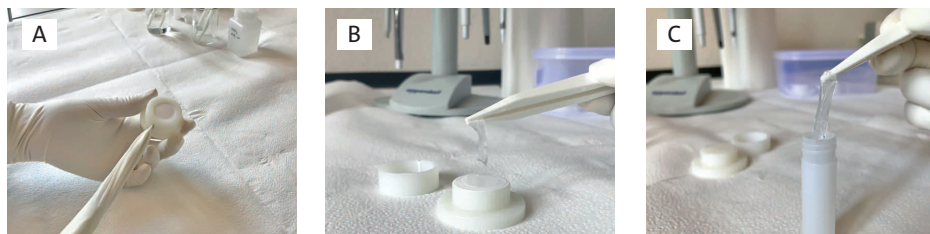


Image 12. (A) DGT opening; (B) Chelex-100 peel off; (C) Chelex-100 being placed in a sample tube (Source: UNICA).

NOTE: For urgent analysis, elute gel for at least 2 hours on a shaker.

- Once the time is expired, pipette an aliquot from the Chelex-100 containing tube into a new clean tube and dilute it the minimum possible with ultrapure water.

NOTES:

- 10 time dilution for salted waters (the salt in resin gel may have matrix effect on ICPMS) and 5 time dilution for freshwater.
- To avoid any broken gel pieces or resin getting into diluted solution, pipette from the top of the sample tube).
- Store solutions refrigerated (4°C) until trace metals analysis by the best available analytical technique.

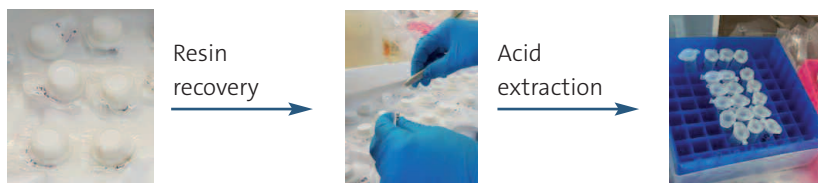


Image 13. General flow chart of DGT dismantling and extraction pre-analysis (Source: IFREMER).

3.10. Determination of trace metals in DGT eluates (a short overview)

Common analytical methods used for trace metal analysis include graphite furnace atomic absorption spectroscopy (GF-AAS), inductively coupled plasma optical emission spectroscopy (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS).

Trace metal analysis in DGT eluates requires highly sensitive analytical equipment. In addition, it must allow the use of a volume of eluate as low as possible to take advantage of the concentration and integration of metals in the Chelex-100 resin, optimizing the concentration factor of the DGT method and achieving the lowest limits of quantification (LOQs).

Due to the above, the analysis of DGT eluates by ICP-MS is the recommended method.

Regardless of the analytical technique used, all reagents, standards, samples and blanks are prepared in Suprapure acids and properly cleaned (low-density polyethylene) LDPE or Teflon flasks.

A multi-point calibration curve, varying with the natural occurrence of each metal, is used for quantification. Standard solutions should be prepared using stock solutions for ICP-MS determinations diluted accordingly in ultra-pure water with 2% (v/v) HNO₃.

The precision and accuracy of the analytical procedures are controlled through repeated analysis of determined elements in certified reference materials. Each batch of samples (10-20 samples, depending on the total number) should include a blank, a certified reference material and a Quality Control (QC) solution. The last two consist in acid based solutions containing the target elements to be quantified.

When using ICP-MS technique, the isotopes used for quantification are subject to minimum isobaric and polyatomic interferences

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(^{111}Cd , ^{208}Pb , ^{60}Ni , ^{27}Al , ^{52}Cr , ^{59}Co , ^{65}Cu , ^{56}Fe , ^{55}Mn and ^{66}Zn). The isotope ^{115}In is regularly used as online internal standard. The solution is prepared with ultrapure water and Suprapure HNO_3 (2% v/v).

Metals in all the diluted DGT eluates can then be measured, including those corresponding to the DGT laboratory and field blanks concentrations to ensure accurate method results (Image 14).

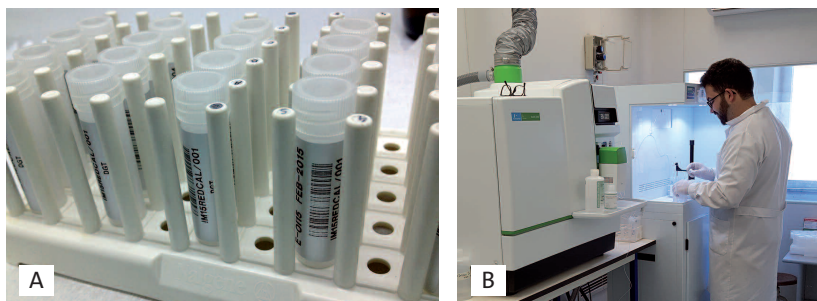


Image 14. (A) DGT elutions ready for analysis (Source: AZTI) and (B) ICP-MS for the metal analysis of DGT eluates (Source: IPMA).

3.11. Calculations of the DGT measured concentration

Calculations are made in two steps:

1. Calculate the mass of metal (M), in g, accumulated in the resin gel layer using the following equation:

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

where:

- C_e is the concentration of metals, in g/L, in the 1M HNO_3 elution solution

- V_{HNO_3} is the volume of HNO_3 added to the resin gel
- V_{gel} is the volume of the resin gel (typically 0.15 ml)
- f_e is the elution factor for each metal (typically 0.8)

II. Calculate the concentration of metal in water, in g/L, measured by DGT device (C_{DGT}) using the following equation:

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

where:

- Δg is the thickness, in cm, of the diffusive gel (Image 15; 0.078 cm) plus the thickness of the filter membrane (0.014 cm)
- D is the diffusion coefficient of metal in the gel (see Table 2 below for open pore gel)
- t is deployment time (in seconds)
- A is the exposure area, 3.14 cm^2 (Image 15)

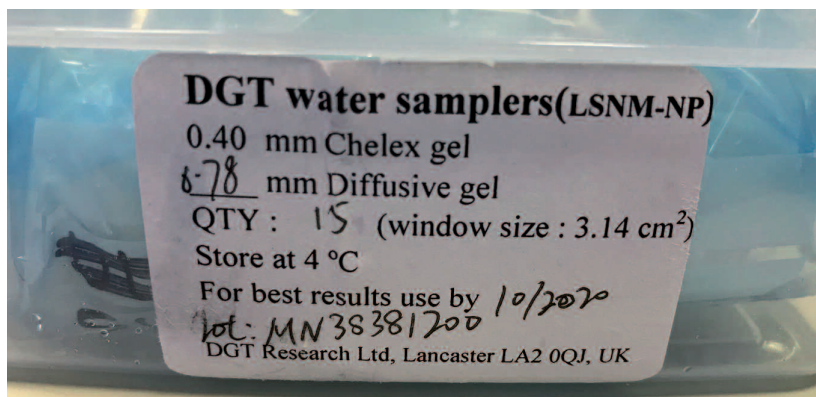


Image 15. DGT label with their specificities (Source: ITC).

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Table 2. Diffusion coefficients of metal ions in DGT gel (open pore) at different temperatures from 1 to 35°C (Unit of D: E-6 cm²/s)

°C	Ag	Al	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
1	6.58	2.22	2.84	2.77	2.36	2.91	2.85	2.73	2.69	3.75	2.84
2	6.83	2.30	2.95	2.88	2.45	3.02	2.96	2.83	2.80	2.89	2.94
3	7.09	2.39	3.06	2.99	2.54	3.13	3.07	2.94	2.90	4.04	3.05
4	7.35	2.48	3.18	3.10	2.63	3.25	3.18	3.05	3.01	4.19	3.17
5	7.62	2.57	3.29	3.21	2.73	3.36	3.30	3.16	3.12	4.34	3.28
6	7.89	2.66	3.41	3.32	2.82	3.48	3.42	3.27	3.23	4.49	3.40
7	8.17	2.75	3.53	3.44	2.92	3.61	3.54	3.39	3.34	4.65	3.52
8	8.45	2.85	3.65	3.56	3.02	3.73	3.66	3.50	3.46	4.81	3.64
9	8.74	2.94	3.78	3.68	3.13	3.86	3.79	3.62	3.58	4.98	3.77
10	9.04	3.04	3.90	3.80	3.23	3.99	3.91	3.74	3.70	5.14	3.89
11	9.34	3.14	4.03	3.93	3.34	4.12	4.04	3.87	3.82	5.31	4.02
12	9.64	3.25	4.16	4.06	3.45	4.26	4.18	4.00	3.94	5.49	4.15
13	9.95	3.35	4.30	4.19	3.56	4.39	4.31	4.12	4.07	5.67	4.29
14	10.27	3.46	4.43	4.32	3.67	4.53	4.45	4.26	4.20	5.85	4.42
15	10.59	3.57	4.57	4.46	3.79	4.68	4.59	4.39	4.33	6.03	4.56
16	10.92	3.68	4.72	4.60	3.91	4.82	4.73	4.52	4.47	6.21	4.70
17	11.25	3.79	4.86	4.74	4.03	4.97	4.87	4.66	4.60	6.40	4.85
18	11.59	3.90	5.01	4.88	4.15	5.12	5.02	4.80	4.74	6.60	4.99
19	11.93	4.02	5.15	5.02	4.27	5.27	5.17	4.95	4.88	6.79	5.14
20	12.28	4.14	5.30	5.17	4.39	5.42	5.32	5.09	5.02	6.99	5.29
21	12.64	4.26	5.46	5.32	4.52	5.58	5.47	5.24	5.17	7.19	5.44
22	13.00	4.38	5.61	5.47	4.65	5.74	5.63	5.39	5.32	7.40	5.60
23	13.36	4.50	5.77	5.63	4.78	5.90	5.79	5.54	5.47	7.61	5.76
24	13.73	4.62	5.93	5.78	4.91	6.06	5.95	5.69	5.62	7.82	5.92
25	14.11	4.75	6.09	5.94	5.05	6.23	6.11	5.85	5.77	8.03	6.08
26	14.49	4.88	6.26	6.10	5.19	6.40	6.28	6.01	5.93	8.25	6.24
27	14.88	5.01	6.43	6.27	5.32	6.57	6.45	6.17	6.09	8.47	6.41
28	15.27	5.14	6.60	6.43	5.47	6.74	6.62	6.33	6.25	8.69	6.58

29	15.67	5.28	6.77	6.60	5.61	6.92	6.79	6.50	6.41	8.92	6.75
30	16.08	5.41	6.94	6.77	5.75	7.10	6.96	6.66	6.58	9.15	6.92
31	16.49	5.55	7.12	6.94	5.90	7.28	7.14	6.83	6.74	9.39	7.10
32	16.90	5.69	7.30	7.12	6.05	7.49	7.32	7.00	6.91	9.62	7.28
33	17.32	5.83	7.48	7.29	6.20	7.65	7.50	7.18	7.09	9.86	7.46
34	17.75	5.98	7.47	7.47	6.35	7.84	7.69	7.36	7.26	10.10	7.64
35	18.18	6.12	7.85	7.66	6.51	8.03	7.87	7.53	7.44	10.35	7.83

Source: dgtresearch.com

3.12. Data treatment

The generated “concentration of metal in water” dataset by site (DGTs in triplicate), may present unusual values, called outliers. As a first step in data treatment, calculation of a coefficient of variation and/or graphical presentation of the data (scatter plots, box plots, etc.) is recommended to identify potential anomalous values.

The anomalous results can be a consequence of a mistake during data collection or it can be just an indication of variance in your data.

In Figure 3 is shown the flow chart of the data treatment process carried out in MONITOOL project to remove outliers from the triplicates of the DGT. Commonly used statistical softwares can be used to assist with this procedure.

Subsequently “Statistical treatment” (either descriptive statistics or inferential statistics) should be applied to the resulting data set (including all the DGT blanks) to help in the interpretation of the results.

Regarding the blank results (DGT laboratory blanks and DGT field blanks), there is not either a unique way to proceed. These blanks may demonstrate high variability in concentrations and there is no agreement so far within the passive sampling community whether or not these corrections should be applied at all.

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For the time being, the safest approach, and the one applied in MONITOOL, has been:

- Checking that the DGT laboratory blanks are largely (ten times) below the values of the field exposed DGTs, and no correction of the amount is made in exposed DGTs.
- Checking the DGT field blanks to assess contamination from the atmosphere during assembling, transport and deployment/retrieval in a qualitative manner. High levels in the DGT field blanks, for example, may indicate a revision of these operations.

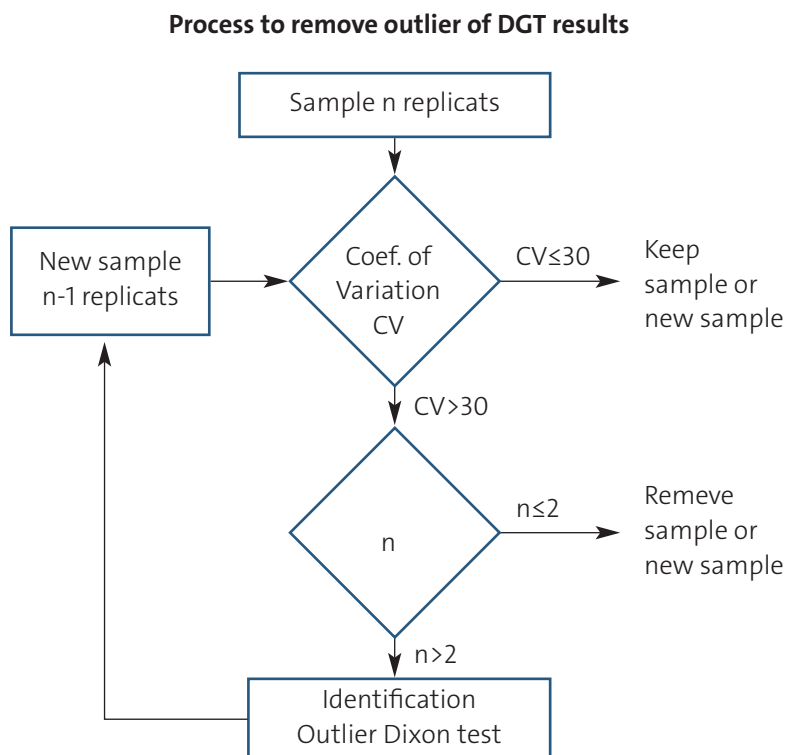


Figure 3. Treatment process summary (Source: IFREMER).

4. MONITOOL project: New tools for water quality monitoring

MONITOOL is a European project whose objective is to provide a robust database of dissolved and labile metal concentrations in transitional and coastal waters for adapting existing Environmental Quality Standards (EQS; 0.45 µm-filtered) for DGT (Diffusive Gradient in Thin-films) passive sampling devices (EQS-DGT) in order to more accurately evaluate the chemical status of the waters under the WFD.

To this end, a survey programme consisting of simultaneous deployment of passive sampling devices and collection of spot samples has been performed by eight Partners, covering the Atlantic region from Canary Islands to the Scottish Highlands & Islands, as well as the Mediterranean area.

A sampling protocol¹ was developed to define a series of guidelines /methodologies that has been followed by all participating Partners in order to guarantee the comparability and reproducibility of data obtained from each Partner in different regions.

More information: <https://www.monitoolproject.eu/>

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