

OVERVIEW OF PASSIVE SAMPLING TECHNIQUES FOR GROUNDWATER MONITORING

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Abstract

This document presents an overview of passive sampling technologies applied in groundwater monitoring. It contains an overview of this innovative sampling technology showing the different background theories for organic and for inorganic contaminants; then, the paper focuses on one device for both types of contaminants, discussing its advantages, limitations, and development status in detail.

Keywords: passive sampling, passive samplers, monitoring, contaminants.

Abbreviations: BTEX, Benzene, toluene, ethylbenzene and xylene; DBL, Diffusive boundary layer; DET, Diffusion equilibrium in thin films; DGT, Diffusive gradient in thin films; LDPE, Low-density polyethylene; MESCO, Membrane-enclosed sorptive coating; nd-SPME, Negligible depletion solid-phase microextraction; PAH, Polycyclic aromatic hydrocarbon; PCB, Polychlorinated biphenyl; PDB, Polyethylene diffusion bag; PIMS, Passive integrative mercury sampler; PLM, Permeation liquid membrane; SBSE, Stir-bar sorptive extraction; SLM, Supported liquid membrane; SLMD, Stabilized liquid-membrane device; SPMD, Semi-permeable membrane device; TWA, Time-weighted average; VOC, Volatile organic compound.

1. Introduction to passive sampler technologies

Sampling and analysis of organic (e.g., chlorophenols, organo-chlorine pesticides, polyaromatic hydrocarbons, polychlorinated biphenyls) and inorganic (e.g., heavy metals and some of their organo-metallic species) compounds represents an ongoing challenge to the environmental chemist. [1]

The passive groundwater sampler is defined as acquiring a sample from a discrete position in a well without active media transport induced by pumping or purging techniques. [2]

Passive samplers usually combine sampling, selective analyte isolation, preconcentration, and, in some cases, speciation preservation in one step. The operations performed at the sampling site are simplified by passive sampling. They eliminate the need for an energy/power supply and allow the entire sampling set-up to be miniaturized. When the samples are collected, further steps in their processing are usually the same as for other sampling preconcentration methods in analysis. They include extraction/desorption of the analytes, final instrumental analysis, and processing of the data.

In the following, several samplers with potential for use in groundwater monitoring programs are presented to illustrate the applications of this technology. [3]

2. Advantages and limitations of passive sampler technologies

Passive sampler technologies have advantages and limitations specific to the nature of each technology. In the following, several pros and cons of passive samplers are cited:

2.1. Advantages of passive sampler technologies

- are relatively easy to use and can be deployed in most wells;
- are practical for use where access is difficult or where discretion is desirable;
- can sample discrete intervals in a well;
- can be deployed in series to provide a vertical contaminant profile;
- have no depth limit;
- reduce field sampling variability, resulting in highly reproducible data;
- allow rapid field sample collection;
- decrease field labor and project management costs for long-term monitoring;
- eliminate purge-water production and thus all or most disposal cost. [4]

2.2. Limitations of passive sampler technologies

- must be submerged in the screened interval during deployment;
- require the aquifer to be in hydraulic communication with the screened portion of the well;
- require special consideration in wells having a layer of free product;
- may have volume/analyte limitations;
- require consideration of contaminant stratification. [4]

3. Classes of passive samplers/ passive sampling devices

The passive samplers in this document will be classified into two categories:

- Passive samplers for organic pollutants
 - Passive diffusion bag samplers
 - Membrane enclosed sorptive coating
 - Semi-permeable membrane devices
 - Negligible depletion-solid phase microextraction
 - Solvent-filled dialysis membranes
 - Solid-phase microextraction applied for the determination of TWA concentrations
 - LDPE and silicone strips
- Passive samplers for inorganic pollutants
 - Diffusion gradients in thin films
 - Permeation liquid membrane
 - Passive integrative mercury sampler
 - Stabilized liquid membrane device
 - Supported liquid membrane and chemcatcher

Tables 1 and 2 below present an overview of devices used to measure organic and inorganic contaminants in water.

3.1. Passive diffusion bag samplers (PDB) for volatile organic compounds (VOCs) elimination

PDB samplers are used for collecting groundwater samples from wells. They offer a cost-effective approach to long-term monitoring of volatile organic compounds (VOCs) at well-characterized sites. [5,6]

Table 1. Passive sampling devices for organic contaminants

Sampler	Name	Purpose	Analytes	Construction	Advantages	Inconvenience	Deployment	Reference
PDB	Passive diffusion bag samplers	Equilibrium sampling in ground-water	Polar organic compounds, VOCs, metals, trace elements	Dialysis membrane or a low-density polyethylene bag filled with distilled water	Relatively inexpensive, and sample recovery is rapid	Not suitable for sampling semi-volatile organic compounds	2 weeks	[7]
MESCO	Membrane – enclosed sorptive coating	Integrative	PAHs, PCBs, organochlorine pesticides	PDMS-coated stir bar used in SBSE or a PDMS rod enclosed in a membrane made of regenerated cellulose or low-density polyethylene	Miniaturized sampler, non-depletive matrix extraction, solventless sample processing, and both non-polar and polar analytes are accumulated in the sampler equipped with a cellulose membrane	Low membrane stability of the sampler variant with a cellulose dialysis membrane	2 weeks	[8]
SPMD	Semi-permeable membrane devices	Integrative	Hydrophobic semi-volatile organic compounds	Flat tube of LDPE filled with triolein	Widely used method, commercially available, well-established standard operation procedures, and calibration data available for many analyte classes, and high sensitivity	Complicated sample cleanup, susceptible to biofouling	1 month	[9]
nd-SPME	Negligible depletion-solid phase microextraction	Equilibrium	Hydrophobic chemicals, including PAHs, PCBs, petroleum hydrocarbons, organochlorine pesticides, aniline, phenols	A fiber coated with a liquid (polymer), a solid (sorbent), or a combination of both	Negligible depletion extraction, a cheap, disposable device	Low sensitivity	Hours	[10]
	Solvent-filled dialysis membranes	Integrative	Hydrophobic organic compounds	Non-polar solvent immiscible with water filled in a cellulose dialysis membrane	Not prone to biofouling	Low sensitivity for very hydrophobic compounds and solvent diffuses out of the sampler during deployment	1 month	[11]

TWA-SPME	Solid-phase microextraction applied for the determination of TWA concentrations	Integrative	BTEX	A fiber coated with a liquid (polymer), a solid (sorber), or a combination of both	No need for extensive laboratory calibrations and sampling rates can be estimated using empirical mass-transfer models		A few minutes	[12]
LDPE and silicone strips		Integrative	Hydrophobic organic compounds	Low-density polyethylene or silicone strips	Simple construction, inexpensive, simple sample processing, and calibration data available for many analyte classes	Smaller sampling capacity than SPMDs	1 month	[13]

Table 2. Passive sampling devices for inorganic contaminants

Sampler	Name	Purpose	Analytes	Construction	Advantages	Inconvenience	Deployment period	Reference
DGT	Diffusion gradients in thin films	Integrative, speciation, screening, mimicking biological uptake	55 metallic elements including the common heavy metals, phosphorous, sulfide, and ⁹⁹ Tc	Two layers of acrylamide gel mounted in a holder device, one containing an acceptor phase, the other acting as a thin diffusion layer	Versatile, well documented	Complicated preparation of the device	1 week	[14]
PLM	Permeation on liquid membrane	Bioavailable metal species	Cu, Pb	Microporous hydrophobic support separating test solution from receiving solution	Selectivity of the sampler can be adjusted using appropriate combination of carrier media and receiving phase	Complicated preparation of device	Hours	[15]
PIMS	Passive integrative mercury sampler	Pre-concentration, screening	Neutral Hg species	LDPE lay-flat tubing	Membrane characteristics may be altered for control of sampling rates	Further development necessary for aquatic conditions	Weeks–months	[16]

SLMD	Stabilized liquid membrane device	Pre-concentration, in situ sampling, determination of labile metal ions in grab samples	Divalent metal ions	LDPE lay-flat tubing containing an acidic solution with high affinity for the target elements		Early development stage	Days–weeks	[10]
SLM	Supported liquid membrane	Integrative field sampling, preconcentration of trace elements, mimicking biological membranes	Doubly charged cations	A strip solution with strong complexing agent is separated from the test solution by a macroporous hydrophobic membrane	Versatile, selectivity of the sampler can be adjusted		Days	[17]
Chem-catcher		In situ sampling, integrative, speciation	Cd, Cu, Ni, Pb and Zn	Comprises an immobilized chelating acceptor resin on a PTFE base and a cellulose acetate membrane filter acting as a thin diffusion layer	Selectivity of the sampler can be adjusted using appropriate combination of membrane and Empore disks, and calibration data available for many chemicals		14 days – 1 month	[18]

The samplers consist of deionized water enclosed in a low-density polyethylene (LDPE) sleeve (Figure 1). They are deployed adjacent to a target horizon within a screened or open interval of a well. The suggested application is for long-term monitoring of VOCs in wells. Where the screened interval is greater than 10 feet (ft), the potential for contaminant stratification and/or intra-borehole flow within the screened interval is greater than in screened intervals shorter than 10 ft. It is important that the vertical distribution of contaminants is determined in wells having 10-ft-long well screens, and that both the vertical distribution of contaminants and the potential for intra-borehole flow be determined in wells having screens longer than 10 ft. The approach is inexpensive and has the potential to eliminate or substantially reduce the amount of purge water removed from the well.

A variety of PDB samplers have been utilized in well applications (Figure 1). Although the samplers vary in specific construction details, a typical PDB sampler consists of a 1- to 2-ft-long LDPE tube closed at both ends and containing laboratory-grade deionized water (Figure 1). The typical diameter for PDB samplers used in a 2-inch-diameter well is approximately 1.2 inches; however, other dimensions may be used to match the well diameter. Equilibration times may be longer for larger diameter PDB samplers. On the outside of the PDB sampler, a low-density polyethylene mesh sometimes is used for protection against abrasion in open boreholes and as a means of attachment at the prescribed depth. The PDB sampler can be positioned at the target horizon by attachment to a weighted line or attachment to a fixed pipe.

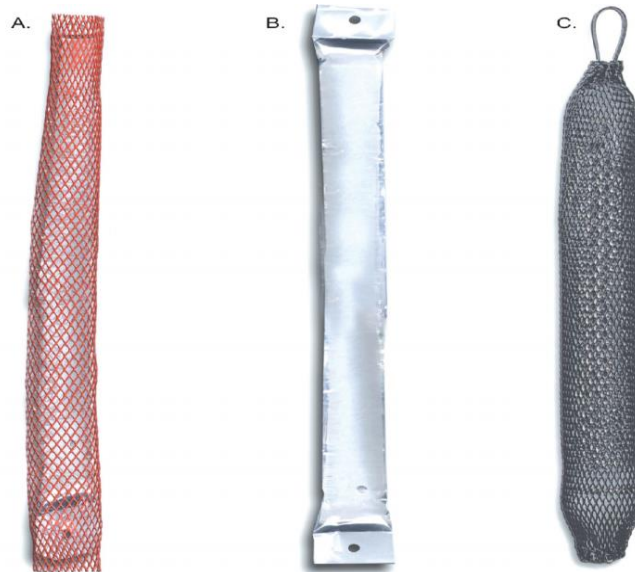


Figure 1. Typical water-filled passive diffusion bag samplers used in wells, including (A) diffusion bag with polyethylene mesh, (B) diffusion bag without mesh, and (C) bag and mesh attached to bailer bottom.

Summary of PDB sampler advantages and limitations:

3.1.1. Advantages

1. PDB samplers have the potential to eliminate or substantially reduce the amount of purge water associated with sampling.
2. PDB samplers are inexpensive.
3. The samplers are easy to deploy and recover.
4. Because PDB samplers are disposable, there is no downhole equipment to be decontaminated between wells.
5. A minimal amount of field equipment is required.
6. Sampler recovery is rapid. Because of the small amount of time and equipment required for the sampling event, the method is practical for use where access is a problem or where discretion is desirable (residential communities, business districts, or busy streets where vehicle traffic control is a concern).
7. Multiple PDB samplers, distributed vertically along the screened or open interval, may be used in conjunction with borehole flow meter testing to gain insight into contaminants movement into and out of the well screen or open interval or to locate the zone of highest concentration in the well. Analytical costs when using multiple PDB samplers can sometimes be reduced by selecting a limited number of the samplers for laboratory analysis based on screening using field gas chromatography at the time of sample collection.
8. Because the pore size of LDPE is only about 10 angstroms or less, sediment does not pass through the membrane into the bag. Thus, PDB samplers are not subject to interference from turbidity. None of the data collected suggests that VOCs leach from the LDPE material or that there is a detrimental effect from the PDB material on the VOC sample.

3.1.2. Limitations

1. PDB samplers integrate concentrations over time. This may be a limitation if the sampling goal is to collect a representative sample at a point in time in an aquifer where VOC concentrations substantially change more rapidly than the samplers equilibrate. [19]. The initial equilibration under field conditions may be longer to allow well water, contaminant distribution, and flow dynamics to restabilize following sampler deployment. [20]
2. Water-filled PDB samplers are not appropriate for all compounds. For example, although methyl-tert-butyl ether and acetone [21,22] and most semi-volatile compounds are transmitted through the polyethylene bag, laboratory tests have shown that the resulting concentrations were lower than in ambient water. A variety of factors influence the ability of compounds to diffuse through the polyethylene membrane. These factors include the molecular size and shape and the hydrophobic nature of the compound. Compounds having a cross-sectional diameter of about 10 angstroms or larger (such as humic acids) do not pass through the polyethylene because the largest (transient) pores in polyethylene do not exceed about 10 angstroms in diameter [23,24,25]. The samplers are not appropriate for hydrophilic polar molecules, such as inorganic ions. Unpublished laboratory test data [26] of semi-volatile compounds in contact with PDB samplers showed a higher concentration of phthalates inside the PDB sampler than outside the PDB sampler, suggesting that the polyethylene may contribute phthalates to the enclosed water. Thus, the samplers should not be used to sample phthalates.
3. VOC concentrations in PDB samplers represent groundwater concentrations in the vicinity of the screened or open well interval that moves to the sampler under ambient flow conditions. This is a limitation if the groundwater contamination lies above or below the well screen or open interval and requires the operation of a pump to conduct contaminants into the well for sampling.
4. In cases where the well screen or open interval transects zones of differing hydraulic head and variable contaminant concentrations, VOC concentrations obtained using a PDB sampler may not reflect the concentrations in the aquifer directly adjacent to the sampler because of vertical transport in the well. However, a vertical array of PDB samplers, used in conjunction with borehole flow meter testing, can provide insight into contaminants movement into or out of the well. This information can then help determine if the use of PDB samplers is appropriate for the well and select the optimal vertical location(s) for the sampler deployment.
5. In wells with screens or open intervals with stratified chemical concentrations, the use of a single PDB sampler set at an arbitrary (by convention) depth may not provide accurate concentration values for the most contaminated zone. However, multiple PDB samplers distributed vertically along the screened or open interval, in conjunction with pump sampling (as appropriate), can be used to locate zone(s) of the highest concentration in the well. Multiple PDB samplers may also be needed to track the zone of maximum concentration in wells where flow patterns through the screened interval change due to groundwater pumping or seasonal water-table fluctuations.

3.2. Diffusive gradients in thin films (DGT)

The diffusive gradient in thin films (DGT) device is a development of a similar sampler – the diffusion equilibrium in thin films (DET) device – initially suggested by Davison and co-workers in 1991 [27]. The first reported use of the improved DGT device was in 1994 for measuring Zn in sea water. The DGT device comprises a gel layer incorporating a binding agent (which acts as a solute sink) and a hydrated acrylamide diffusion gel separating it from the water column. This creates a diffusion layer of well-defined thickness. The initial design of the DGT utilized an ion-exchange resin as the receiving

phase. Later, Zhang and co-workers [28] demonstrated the applicability of the technique to the determination of trace metals (Cd, Cu, Fe, and Mn) in sea water. With a chelating resin embedded in the gel layer, metals could be quantified as low as 4 pmol/L after deployment for 1 h. The subsequent refinement of the design and the extended range of inorganic pollutants that may be sampled indicate the versatility and the widespread use of the DGT device. In principle, it is possible to sample any labile species for which a suitable binding agent can be embedded into the receiving phase gel.

Also, DGT is based on a simple procedure of measuring soluble metals, which diffuse through a filter and accumulate on a binding agent, the hydrogel. DGT is designed to bind only the species of interest selectively and to accurately control the transport of the substances to the device, allowing the concentration in solution during deployment to be calculated from the laboratory measurement. DGT has been successfully applied in a variety of environmental monitoring projects related to hazardous radionuclides, trace metals, organic contaminants to measure chemical release at a controlled rate. [29]

It is also possible to calculate free ion activity by using different diffusive layers (gels) to trap inorganic and organic species separately and then conducting speciation calculations.

3.2.1. DGT theory

The DGT sampler comprises a gel assembly that is enclosed in a piston-like plastic casing (Figure 2). The plastic casing comprises a separate base and cap components which, when pressed together, exclude water from within the 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 polyacrylamide hydrogel, which is separated from the bulk solution by a diffusive polyacrylamide gel of standard uniform pore size and thickness, and a cellulose nitrate 0.45 μ m membrane filter.

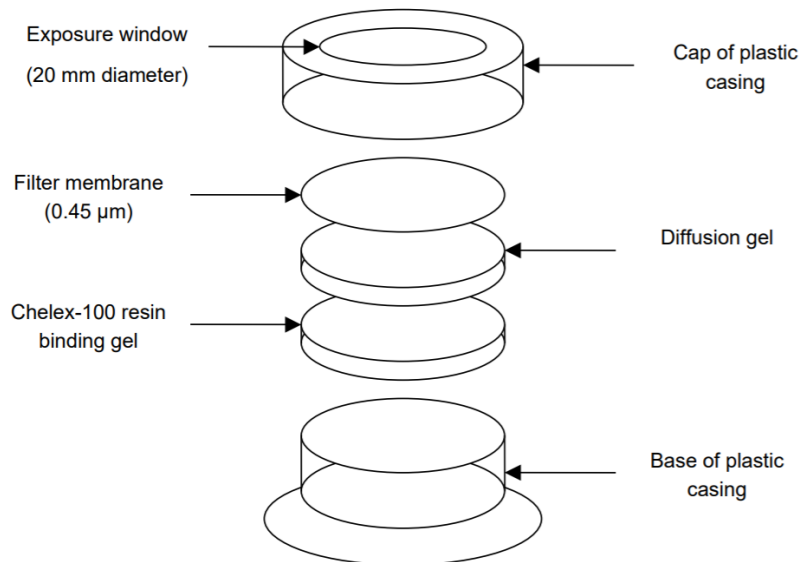


Figure 2. DGT assembly

When DGT devices are submerged in solution, water and its constituent dissolved ($< 0.45 \mu\text{m}$) metal species are able to diffuse into the device via the exposure window. After traversing the diffusive layer, metal ions that come in contact with the Chelex-100 become bound and permanently immobilized by binding sites on the resin [30]. 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 2) [31]. 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 [30].

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) [32]. 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.

3.2.2. Advantages of the 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.

1. The metals measured by DGT are referred to as DGT-labile metals. They include free metal ions and labile metal complexes, which comprise the fraction of dissolved ($< 0.45 \mu\text{m}$) 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 metal [33].
2. Free metal ions present in the solution are able to easily diffuse into the DGT device, where they are bound and immobilized in the resin gel [34]. 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 [31,34]. 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 [31]. 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.
3. 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 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.
4. 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 [31]. Therefore the resultant DGT measurement is a time-integrated average of metal concentrations over the whole deployment period, including the variations caused by hydrology changes [35].

3.2.3. Parameters affecting DGT measurement

Any change or defect in the following parameters will directly affect the DGT measurement.

Temperature

The rate of mass uptake is influenced by temperature as it is proportionally related to the analyte diffusion coefficient. Values for diffusion coefficients of metals through the polyacrylamide hydrogel are based on those. [34,36]

Flow rate

In quiescent waters with flow $< 0.02 \text{ m/s}$, a diffusive boundary layer (DBL) develops at the interface between the solution and the solid surface of the DGT sampler [37]. The formation of a DBL essentially

increases the thickness of the diffusion layer and therefore interferes with the mass transport. Gimpel et al. [37] 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 the flow is maintained above the low threshold value of 0.02 m/s, the thickness of the DBL is assumed to be negligible.

pH

The DGT technique has been found to work accurately for many metals over the pH range of 4.5 – 9 [31,37]. Chelex-100 is less efficient at binding metals at low pH as metal ions are in competition with a high concentration of hydrogen ions present in the solution for binding sites in the resin [31,38]. At lower pH Chelax-100 preferentially binds metals in the order $\text{Cu} > \text{Pb} \gg \text{Zn} > \text{Cd}$ [31].

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) [38,39,40]. Several theories have been suggested to explain DGT behavior at low ionic strength.

Alfaro De la Torre et al. [38] suggested that the DGT technique was not reliable for quantitative measurements of metals in solutions with ionic strength ($\Sigma [\text{Mg}^{2+}, \text{Na}^+, \text{K}^+, \text{Ca}^{2+}]$) 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. [40] have suggested that the erratic behavior observed at low ionic strength is due to the ability of the diffusion gel to bind cations with a low affinity for metal ions competitively; thus, the binding of metal ions is increased when there are insufficient excess cations present in solution to saturate the binding sites.

4. Summary and conclusion

This document contains an overview of passive sampling technologies for organic and inorganic pollutants. Two of these passive samplers technologies are described in detail with their advantages and limitations.

The PDB technique has been shown to be a method for organic contaminants; it offers a cost-effective approach to long-term monitoring of (VOCs) at well-characterized sites. [5,6]

The effectiveness of the use of a single PDB sampler in a well is dependent on the assumption that there is horizontal flow through the well screen and that the quality of the water is representative of the groundwater in the aquifer directly adjacent to the screen. If there are vertical components of intra borehole flow, multiple intervals of the formation contributing to flow, or varying concentrations of VOCs vertically within the screened or open interval, then multiple deployments of PDB samplers within a well may be more appropriate for sampling the well. [41]

The DGT technique is a new and innovative method for in situ measurements of free metal ions and labile metal complexes in groundwater, offering an approximation of metal bioavailability. As well as their unique capability for in situ speciation, it has been reported that DGT offers a number of other advantages over other methods, including higher sensitivity and the ability to detect concentration variation over irregular flow [31,35].

In summary, the development of passive sampling technologies still progressing to monitor a wider range of chemicals.

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