Diffusive gradients in thin films for the measurement of labile metal species in water and soils: a review

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Abstract

The determination of the concentration of an environmental pollutant is not sufficient to assess the related health risk because this pollutant may not be bioavailable. Therefore, methods to determine pollutant bioavailability are more relevant to assess toxicity than measuring the total concentration. For instance, the diffusive gradient in thin films (DGT) is an in situ dynamic technique used to measure the concentration of labile compounds in the environment. Here we review the latest developments achieved in speciation and bioavailability of metals and metalloids using this technique. We detail the technique, common binding agents and diffusive gels. We give laboratory procedures to prepare the gels, and we explain calculations using the DGT-induced fluxes in soils (DIFS) modeling. DIFS models can predict the resupply capacities from soils to porewater, and the uptake of trace elements by plants. Procedures for in situ field deployments, including issues of biofilm growth, are also discussed.

Keywords Passive sampling · Trace metals · Speciation · Bioavailability · Binding layer · Diffusive layer · Environmental field deployment

Abbreviations

APA	Agarose cross-linked polyacrylamide
DGT	Diffusive gradient in thin films
EtHg	Ethylmercury
MeHg	Methylmercury
RDL	Restricted diffusive layer

Introduction

Most of the inorganic chemical pollutants, e.g., trace metals and metalloids, are usually persistent on the Earth's surface and originate mainly from natural and anthropogenic sources, including volcanic eruptions, mining, industrial processes, agriculture. They can bioaccumulate and biomagnificate in organisms. Metal toxicity, including its considerable risks in the environment and human health, has

been widely studied (Díez 2008; Tchounwou et al. 2012; Liu et al. 2013b; Jaishankar et al. 2014; Tóth et al. 2016; Rodríguez and Mandalunis 2018; Herrera-Herrera et al. 2019; Marrugo-Negrete et al. 2020; Pinzón-Bedoya et al. 2020). At this point, it is important to remark that there are two types of metals focusing on its toxicity: on one side metals, such as Cd, Pb and Hg, which are not essential for organisms, and could cause serious damages in neurological, renal, cardiovascular and reproductive systems and genetic effects even at relative low concentrations. On the other hand, metals like Fe, Zn, Cu and Se, among others, have an essential role in the human health, and some of them are also important in the production and protection of DNA and damage caused by free radicals and non-essential metals. It is well known that the determination of total metal concentration is not a good indicator for metal availability for the organisms because toxicity is directly dependent on the bioavailable fraction of metal and this, in turn, of the metal speciation and its mobility in waters, soils, sediments and air.

Although with several exceptions, the free ion activity model states that the free metal ion concentration is the determining factor in metal uptake, and the competition between metal ions at this biotic surface is accounted for the biotic ligand model (Kalis 2006).

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These models have helped scientists to understand the bioavailability as the metal fraction assimilated by an organism causing a physiological response in it. Besides that, models determine (1) the physico-chemical component characterized by sorption/desorption processes, which control metal mobility in soils and determinates the “chemical availability” of metals; and (2) the biological component characterized by a physiologically driven uptake process of a specific biological receptor (Peijnenburg and Jager 2003). Total metal concentration, pH, redox, speciation, mobility and the amount of organic matter are the main factors that directly influence the bioavailability. Likewise, it is important to take into account the environmental media, since the dynamics of metals are different in aqueous media compared to soils, where other factors, such as soil type, porosity and cation exchange capacity, influence metal bioavailability (Kalis 2006).

As briefly noted above, speciation was identified years ago as one of the factors that most influences bioavailability; however, more studies are needed to understand what metal species are responsible for the final interaction with the organism. Speciation has been defined by the International Union of Pure and Applied Chemistry as the distribution of an element among chemical specific form such as isotopic composition, electronic or oxidation state and/or complex or molecular structure in a system (Feldmann et al. 2014; Templeton and Fujishiro 2017). For example, mercury (Hg) may be present in the environment in three different states: mercuric (Hg^{2+}), mercurous (Hg_2^{2+}) and elemental (Hg^0) (WHO 2000), of which the dissolved Hg^{2+} fraction is considered the most available form for subsequent biogeochemical transformations. Besides that, Hg^{2+} can be bound to one or two carbon atoms, naming alkylated forms, such as methylmercury (MeHg) and ethyl mercury as the most common species. However, bioavailability depends not only on the chemical species, but also on cellular interaction with both Hg^{2+} and MeHg, by a mechanism not yet completely understood (Bratkić et al. 2019). For this reason, chemical speciation techniques have been developed in order to measure only a certain fraction of the total metal concentration, i.e., the bioavailable fraction. Based on the free ion activity model, some of the techniques used are only focused on the determination of the free metal ion concentration, like equilibrium ion-exchange technique (Fortin and Campbell 1998), the Donnan membrane technique (Temminghoff et al. 2000), Permeation Liquid Membrane (Parthasarathy et al. 2001) and some electrochemical techniques, such as square wave anodic stripping voltammetry (Ure and Davidson 2002) or direct potentiometric measurements (Rachou et al. 2007). Nevertheless, chemical lability is considered as a proxy for bioavailability too. Labile metal fractions are often the main target, as they contain free ions and easily dissociable

complexes that may be more susceptible to interact with aquatic organisms, entering trophic chains (Fairbrother et al. 2007). Consequently, speciation techniques have been developed focused on determining the labile fractions of a metal, like gel-integrated micro-electrodes (Pei et al. 2000), stripping chronopotentiometry (Van Leeuwen and Town 2002), competing ligand exchange methods (Apte et al. 2005) and the dynamic technique diffusive gradients in thin films (DGT) (Davison and Zhang 1994). DGT is also considered as a passive sampling technique for monitoring.

According to that, passive sampling techniques are considered as an alternative method to traditional sampling techniques (Fernández-Gómez et al. 2012b), which offers high potential as a profitable monitoring tool, avoiding many of the disadvantages of active sampling, including preparation of related samples. In addition, passive sampling has some benefits, such as providing time-averaged contaminant concentrations during operation periods (hours to weeks), serving as an in situ enrichment procedure and protecting analytes from degradation during field transport to the laboratory and storage.

In this context, the DGT technique has proven to be a wide and versatile strategy to better understand the metal speciation. Its simplicity, ease of use during the in situ deployment in the field and its applicability to different environmental matrices and the capability for measuring a wide range of target compounds make this technique a good option for environmental studies. In addition, it is possible to distinguish between labile inorganic and organic species varying the diffusion gel pore size of the DGT devices (Fernández-Gómez et al. 2012b).

It is now nearly 30 years since the invention of the technique of DGT, and some reviews have already emerged. Previous reviews have been focused in different topics such as phosphorus and metals in sediments and soils (Zhang et al. 2014), organic DGT (Guibal et al. 2019), different methods used for the determination of single species (Pesavento et al. 2009), trace metals and accumulation/response by animals (Eismann et al. 2020), metals in waters (Menegário et al. 2017), theoretical approaches and numerical simulations (Galceran and Puy 2015) as well as general reviews devoted to understanding the progress on the use of DGTs (Davison and Zhang 2012; Zhang and Davison 2015; Li et al. 2019). To the best of our knowledge, this review provides a comprehensive overview of DGT passive sampler for metals in waters and soils from its first report in 1994 to the present. Theory, configurations, field deployments procedures and applications of the sampler device and advantages and challenges of DGT technique are detailed and discussed. This review is organized in an easy-to-use format to help scientists to choose the most suitable device for a particular trace element. A list with up to 400 references including all the

published studies from 1994 until 2020 for the determination of a single or multiple trace metals categorized in water and soils is given.

Concepts and theory of diffusive gradient in thin films

The diffusive gradient in thin film (DGT) technique was developed in 1994 by Hao Zhang and William Davison at the Lancaster University, UK, and was first designed for in situ determination of trace metals in water (Davison and Zhang 1994). Since then, this technique has increased its capacity to determine many other elements and compounds, including nutrients (Cai et al. 2017), radionuclides (Leermakers et al. 2016), rare earth elements (Yuan et al. 2018) as well as in further environmental matrices such as sediments and soils.

Therefore, the DGT allows in situ evaluation of labile fractions and by approximation, bioavailability of metal species in aqueous environments, including natural waters (Zhang et al. 1998; Clarisse et al. 2009; Lucas et al. 2012; Turull et al. 2017a, 2018; Bratkič et al. 2019; Gao et al. 2019c), sediments (Harper et al. 1998, 2000; Gao et al. 2009; Yin et al. 2014) and soils (Docekalová et al. 2012; Song et al. 2015; Turull et al. 2019a, b; Babalola and Zhang 2021), based on the behavior of the labile species in the diffusive layer is similar to the behavior in the proximity of biological membrane (Clarisse et al. 2012; Amirbahman et al. 2013; Fernández-Gómez et al. 2015). The DGT passive sampler houses a binding gel and a diffusive gel protected by a membrane filter, that permits the diffusion of free ions and labile complexes through the diffusive layer that are irreversibly uptake by the specific binding layer. The final objective of this technique is to accumulate the target analyte in the binding layer over time following the Fick's first law of diffusion through the diffusive layer (Davison and Zhang 1994). Thus, the speciation of metals using DGT devices depends mainly on two effects: the difference in the diffusion coefficients and the difference in the affinity of the target species with the binding agent (Fernández-Gómez et al. 2012b).

The theoretical foundations for the use of DGT technique in aqueous solutions has been extensively documented (Zhang and Davison 1995; Lehto et al. 2006; Fernández-Gómez et al. 2012b; Shiva et al. 2016; Xu et al. 2020). The DGT technique is based on Fick's first law of diffusion, which relates the diffusive flux to the gradient of the concentration. The DGT device is composed by a binding layer that consists of a selective resin usually fixed in polyacrylamide gel (Zhang et al. 1998; Österlund et al. 2010). As can be seen in Fig. 1, this binding layer is separated from the bulk solution by a diffusive layer with a specific thickness (Δg). The layer between the filter membrane and the solution where ions are transported

Fig. 1 Concentration of ionic species (C_b) through the diffusive layer in contact with aqueous solution. The diffusive gradients in thin film device is composed by a binding layer consisting of a selective resin embedded in a gel which is separated from the bulk solution by a diffusive layer or diffusive gel with a specific thickness (Δg). The layer between the filter membrane and the solution where ions are transported by molecular diffusion is called diffusive boundary layer (BDL). Adapted from Zhang and Davison (1995)

by molecular diffusion is called diffusive boundary layer (BDL). Since a concentration gradient is established in the diffusion layer, then the concentration is equal to the bulk concentration at the filter membrane/water interface (Fig. 1).

In an early study, Zhang and Davison (1995) established the basis to calculate concentrations of labile species using DGT devices. According to the Fick's first law, the flux goes from high concentration to low concentration, with a magnitude that is proportional to the concentration gradient (1). In this equation, J is the flux ($\text{mol cm}^{-2} \text{s}^{-1}$), D is the diffusion coefficient ($\text{cm}^2 \text{s}^{-1}$) and dC/dx (mol cm^{-4}) is the concentration gradient because C is the concentration (mol cm^{-3}) and x is the distance. This gradient induces a constant diffusion flux, which could be different depending on factors such as temperature, physical properties of the gel and concentration of labile metal in the bulk solution.

$$J = D \frac{dC}{dx} \quad (1)$$

If dC represents the variation of free concentration of metal in the bulk solution (C_b) with respect to free concentration of metal in the resin gel layer (C'), then it could be expressed as $(C_b - C')$. If the free metal ions are in a rapid interaction with the resin, with a large binding constant, C' is effectively zero providing the resin is not saturated. In addition, the thickness of the diffusion layer (Δg) and the DBL thickness (δ) may be considered as x . If δ is negligibly small compared to Δg , the flux could be calculated as:

$$J = D \frac{C_b}{\Delta g} \quad (2)$$

According to the flux definition, the total mass of the analyte (M) diffused through an area (A), after given time (t), could be calculated as $J = M/At$. After the DGT device is deployed and retrieved, the binding layer is analyzed and the M could be determined using the most appropriate analytical techniques for each metal. Thus, from Eq. 2, the metal concentration in the bulk solution could be quantified by:

$$C_b = \frac{M\Delta g}{DA t} \quad (3)$$

In practice, DBL could include the effective δ in Eq. 4, as follows:

$$C_b = \frac{M(\Delta g + \delta)}{DA t} \quad (4)$$

The total mass of analyte accumulated on the resin gel may be extracted through elution of the gel using an appropriate volume of eluents (V_e) (e.g., HNO_3). Knowing the concentration of the analyte in the eluent (C_e), the elution factor (f_e) and the volume of the resin gel (V_g), M could be calculated by Eq. 5:

$$M = C_e \frac{(V_g + V_e)}{f_e} \quad (5)$$

Experimentally, A , t and Δg could be measured, and D is the value of the molecular diffusion coefficient in water at a given temperature. A calibration plot of M/C_b versus t could be used to calculate the value of D (Fernández-Gómez et al. 2012a, b; Turull et al. 2017a). Since the temperature influences the diffusion in the gel, D must correct the deployment temperature, T (Zhang and Davison 1995):

$$\log D_T = \frac{1.37023(T - 25) + 8.36 \times 10^{-4}(T - 25)^2}{109 + T} + \log \frac{D_{25}(273 + T)}{298} \quad (6)$$

where D_{25} is the diffusion coefficient at the deployment time at 25 °C.

Device and components of diffusive gradient in thin films

In water, the type of diffusive gradient in thin film (DGT) sampler used is the piston-type device (www.dgtresearch.com) as it is shown in Fig. 2. The device consists in a DGT piston (base) (a) and a DGT cap (e) with an exposure area of 3.14 cm² (Jolley et al. 2016; Turull et al. 2017b). Other

Fig. 2 Structure and assembly direction of a piston-type sampling device commonly used for the application of the diffusive gradients in thin film technique in aquatic and soil systems. The sampler consists in **a** the piston; **b** the binding layer; **c** the diffusive gel; **d** the membrane filter; and **e** the cap

components inside the DGT sampling device are shown in Fig. 2, including a binding layer (b), which is a resin gel supported in the base, responsible for the accumulation of the analytes; a diffusive gel (c) which has a composition up to 95% of water and allows analytes pass through by diffusion; and a filter membrane (d) to protect the gels. Different configurations of these layers are used according to the thickness of each one. Nevertheless, the most common configuration used is the configuration of binding layer (0.4 mm thick), a agarose cross-linked polyacrylamide (APA) diffusive gel (0.8 mm thick) and a 25-mm-diameter polyethersulfone membrane filter 0.45 μm pore size (0.014 mm thick), for a total thickness of 1.34 mm (Jolley et al. 2016). For other type of configurations, another diffusive gel should be placed to compensate the final thickness if is less than 1.34 mm. In this sense, it should be taken into account that the APA gel during the hydration step has an expansion factor of 1.6, and therefore the initial gel is thinner (Fernández-Gómez et al. 2011; Turull et al. 2017a).

Binding agents

A potential binding agent for determining an analyte should be chosen taking into consideration four key characteristics: (1) the binding strength, which is represented by an equilibrium constant for the specific analyte; (2) the intrinsic binding capacity, which relates to the number of sites able to interact with analyte species; and (3) the competition effects, due to the presence of other ions with similar binding strengths (Bennett et al. 2016a). Diverse binding agents have been used to analyze many trace metals (including cations and oxyanionic metals) and other species, such as sulfide or radionuclides (Table 1). Moreover, mixed binding layers have been developed to

Table 1 Binding agents and elements used to study some trace metals with the diffusive gradients in thin film technique

Analyte(s)	Binding agent	Eluent	References
THg/MeHg	3-Mercaptopropyl functionalized silica	Direct analysis	Fernández-Gómez et al. (2011, 2014), Turull et al. (2019a)
	Spheron-Thiol	Direct analysis	Diviš et al. (2010)
	Amberlite GT73 Duolite GT73	Direct analysis	Diviš et al. (2010), Pelcová et al. (2014)
	Iontosorb AV-IM	Direct analysis	Diviš et al. (2010)
	Ambersep GT74	Direct analysis	Pelcová et al. (2014)
	Tulsion CH-95	0.1 M HCL + 2% thiourea	Ren et al. (2018)
	<i>Saccharomyces cerevisiae</i>	0.6 M HCl	Tafurt-Cardona et al. (2015)
Divalent and trivalent ions	Chelex-100	2 M HNO ₃	Zhang and Davison (1995)
Rare earth elements	Chelex-100	2 M HCl	Yuan et al. (2018)
Cu, Cr, Cd, Mn, Ni, Pb, Zn	MMT ^a	1 M HNO ₃	dos Anjos et al. (2017)
Cu, Cd, Co, Mn, Ni, Pb, Zn, Hg	Whatman P81	2 M HNO ₃	Larner and Seen (2005)
Cu, Cd, Co, Ni, Zn, Pb	SPR-IDA ^b	1 M HNO ₃	Gao and Lehto (2012)
Cr	<i>N</i> -methyl-D-glucamine	1 M HNO ₃	Pan et al. (2015)
Au	Activated carbon	Aqua regia	Lucas et al. (2012)
As, Sb, Mo, V, W	Ferrihydrite	1.4 M HNO ₃ + 0.1 M HF	Österlund et al. (2010)
As	Amberlite IRA 910	1.2 M HCl	Rolisola et al. (2014)
As, Se	Metsorb (TiO ₂)	1 M NaOH	Bennett et al. (2010)
As, Sb	3-Mercaptopropyl functionalized silica	H ₂ O ₂ + NaOH	Bennett et al. (2016b)
U	MnO ₂ and Metsorb	1 M H ₂ O ₂ /HNO ₃	Turner et al. (2012)
Tc	TEVA resin ^c	4 M HNO ₃	French et al. (2005)

THg total mercury, MeHg methylmercury

^aNatural clay mineral Montmorillonite (MMT)

^bSuspended particulate reagent-iminodiacetate (SPR-IDA)

^cTrialkyl methylammonium nitrate (TEVA)

perform the determination of a wider range of analytes such as Amberlite IRP69/ferrhydrite to determine P and K (Zhang et al. 2013), Chelex–Metsorb to determine Ni, Cu, Mn, Cd, Co, Mo, Sb, Pb, As, W, V and P (Panther et al. 2014) or Chelex-100–ZrO₂ to determine P, Fe and As (Sun et al. 2015).

The binding agents are usually quasi-homogeneously incorporated into a gel matrix to form the binding layer. Chelex-100 resin was the first binding agent used to measure trace metals by DGT technique because of its advantage on determining a large amount of them, including Ni, Zn, Cu, Mn, Cd, Co, Pb, Fe and Al. This commercial resin has a high selectivity for transition metals over alkali and alkaline earth metals due to the fact that it contains functional groups of iminoacetic acid, thus avoiding analytical interferences in the measurement of trace metals in natural waters (Zhang and Davison 1995). From there, other ion-exchange binding agents have been studied alternatively for the determination of trace metals using the DGT technique, such as the cellulose phosphate-based membrane Whatman P81 (Larner and Seen 2005), the suspended particulate reagent-iminodiacetate resin (SPR-IDA) (Gao and Lehto 2012) and the natural clay mineral montmorillonite (MMT) (dos Anjos

et al. 2017). In general, ion-exchange binding agents are widely used in the DGT technique due to their easy preparation, flexibility and mechanical resistance, compared to other types of binding agents, such as liquid binding phases.

The Hg-determination by the DGT technique has been widely validated since mercury is a global pollutant that affects human and ecosystem health. Docekalová and Diviš (2005) compared the efficiencies of Chelex-100 and Spheron-thiol resins in the determination of Hg(II), finding that Spheron-thiol showed a greater and stronger affinity with mercury species that bind to the thiol (–SH) groups. Although, other thiol functionalized resins used in the binding layer have shown high affinity and selectivity with mercuric species. Later, other studies (Fernández-Gómez et al. 2011, 2014; Clarisse et al. 2012; Turull et al. 2017a, 2019a) have demonstrated the efficacy of 3-mercaptopropyl functionalized silica resin as a binding agent in the Hg-determination by the DGT technique in different environmental matrices. The ion exchange resins Amberlite GT73 (also known as Duolite GT73) (Diviš et al. 2010) and Ambersep GT74 (Pelcová et al. 2014), and the functionalized

macroporous cross-linked polystyrene (Tulsion CH-95, (Ren et al. 2018) can measure several mercury species, with a high adsorption capacity and elution efficiency for Hg(II) and MeHg. In general, the effects of competition between ions with similar binding forces are more probable in binding layers that are based on adsorption or ion-exchange mechanisms compared to those that are based on complexation. In order to choose, a suitable binding agent is also important to consider the binding force, the binding sites available to interact with the analyte to be uptake, and the particle size that allows simple and uniform incorporation into the gel matrix.

Diffusive gels

The hydrogels used in the DGT technique are highly hydrophilic polymers with an intermediate structure between solid and liquid, with polar functional groups that allow them to absorb water and expand their size containing up to 95% of water. Determined by the precise composition, hydrogels can range from a viscous to a more rigid appearance, although all of them are typically flexible and elastic. Hydrogels represent the diffusion layer in the DGT device, being the transport of target analytes from the bulk solution to the binding layer by diffusion as the main function, without interfering with the determination of the target analyte by binding to it (Davison and Zhang 2016).

Various polymers have been applied as diffusion layers in the DGT technique, among which three types of gel stand out for being the most commonly used: polyacrylamide with agarose-derivative cross-linker (APA) (Zhang and Davison 1995; Fernández-Gómez et al. 2014), agarose (Docekalová and Diviš 2005) and polyacrylamide cross-linked with bisacrylamide gels (Shiva et al. 2015; Turull et al. 2019a).

The most used diffusive layer is APA hydrogel, which has an open pore size larger than 5 nm allowing the diffusion of molecules with molecular weights $< 10^6$ (i.e., fulvic acid and some of the humic acid) as well as its advantage of retaining stability in the range of pH 2–9 after 3.2 times swelling due to hydration (Wang et al. 2016b). Some studies have been described the protocol for its preparation (Fernández-Gómez et al. 2011; Turull et al. 2017b), which consists on the addition of the cross-linker and acrylamide (or agarose derivative) to the water, followed by the addition of *N,N,N',N'*-tetramethylethylenediamine solution, which catalyzes the reaction and the ammonium persulfate, which plays the role of initiator of the reaction. The polymerization is carried out at 42–45 °C for 45 min approximately, resulting in a layer which contains 15% monomer and 0.3% cross-linker, although the cross-linker structure of the commercial product is still unknown. Even after an in-depth washing during the preparation, the APA gel maintains a positive charge which interacts electrostatically with the analytes,

interfering with the effective diffusion of metals with low ionic strength due to the formation of the Donnan potential. This electrostatic interaction can be negligible when the ionic strength is greater than 1 mM because of the low charge density in the gel (Zhang and Davison 1999; Wang et al. 2016b). Nevertheless, although the existence of a Donnan potential is often mentioned in the results of cation diffusion through the APA gel, this effect is highly dependent on the pH at which the DGT sampling device is deployed. Negative charges for APA gel are reported in the literature, more specifically, on negatively charged acrylate functions created during the hydrolysis of acrylamide ($pK_a = 4.25$) (Li et al. 2002a; Pommier et al. 2021).

Agarose gel is another standard diffusive layers widely used in DGT technique to determinate inorganic and organic analytes. Agarose is a polysaccharide, generally extracted from certain red seaweed of the genera *Gellidium* and *Gracillaria*. It is a linear polymer formed by repeating units of agarobiose, which is a disaccharide made up of D-galactose, 3,6-anhydro-L-galactopyranose and the lack of sulfate groups. The agarose gel has binding sites that resemble sulfonic functional groups, which are responsible of the complexation with trace metals, and negatively-charged pyruvic functional groups which represent the majority of binding sites in the gel and attractive interactions with cations and repulsive with anions, due to the formation of the Donnan potential (Wang et al. 2016b). The strength of these interactions between the gel and the ions decreases with increasing ionic strength. The lowest ionic strength capable of producing steady-state DGT flux is 0.1 mM for MeHg (Gao et al. 2014), 1.0 mM for MeHg and Hg (Hong et al. 2011) and 5.0 mM for Hg (Colaço et al. 2014). Further, in a comparison between agarose and polyacrylamide gels for the Hg determination using Chelex-100 as a binding layer, the agarose gel showed a lower absorption of Hg compared to the polyacrylamide gel. However, when diffusive polyacrylamide gel was used in DGT units in the same study, it was difficult to interpret the findings due to a possible competition for Hg ions between polyacrylamide gel and Chelex-100 (Docekalová and Diviš 2005; Gao et al. 2011). In another comparative study between agarose and APA gels, Fernández-Gómez et al. (2014) observed statistically significant differences between diffusion coefficients values of MeHg for agarose gel in DGT units in the absence and presence of dissolved organic matter (3.15×10^{-6} and $2.68 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, respectively), and also for APA gel in DGT units (2.49×10^{-6} and $1.69 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, respectively). MeHg diffusion was higher on agarose gel with and without dissolved organic matter in comparison with those observed in APA gel. Even so, DGT based on APA gel seems to be a better choice for eutrophic waters, when the monitoring is in environment with very low concentrations of MeHg, considering its slightly higher uptake capacity.

A polyacrylamide cross-linked with bis-acrylamide gel (*N,N'*-methylene-bis-acrylamide) is the third type of gel used in the DGT technique consisting on two acrylamide molecules linked through their aminocarbonyl groups, and in comparison with the previous two gels, this is much more fragile and its pore size is smaller (~ 1 nm), so it is usually called restricted gel or restricted diffusive layer (RDL). The smaller pore size affects the chemical species that can diffuse through the gel, allowing only free ions and small inorganic complexes to pass through and leaving out larger molecules such as organic complexes (Österlund et al. 2010; Shiva et al. 2015). According to the above mentioned, when using RDL, the difference in diffusion coefficient between the gel and the filter is larger than when using open pore (Österlund 2010), and therefore Eq. 4 can be modified to Eq. 7 as follows:

$$C_b = \frac{M}{At} \left(\frac{\Delta_{\text{gel}}}{D_{\text{gel}}} + \frac{\Delta_f}{D_f} \right) \quad (7)$$

The main difference from Eq. 4 is that the thickness of the diffusion layer, Δg , is divided into Δ_{gel} and Δ_f , corresponding to the diffusive gel and membrane filter thickness, respectively, and D_f is the diffusion coefficient in the membrane filter.

Filter membrane

The most commonly used filter membranes have a pore size of ~ 0.45 μm . The most commonly used filter membranes are: polyvinylidene, cellulose nitrate, cellulose acetate and hydrophilic polyethersulfone filter membranes (Li et al. 2019). This filter protects the diffusion and binding layers inside the DGT device from possible contamination caused by large particles, or simply contains the gels to prevent damage or loss of these during the deployment of the DGT devices. However, they may be susceptible to biofilm formation caused by the microorganism colonization during the deployment of DGT devices in environmental matrices

(Fig. 3). This biofilm must be taken into consideration since it could absorb analytes, restricts absorption of them or act as an extension of the diffusion layer, leading to errors in the determination of analytes. Uher et al. (2012) evaluated the effect of biofilm on the determination of trace metals (Ba, Cd, Co, Cr, Cu, Mn Ni, Pb and Zn) and their results showed that the presence of biofilm in DGTs did not significantly affect diffusion of all metals. Thus, an interaction of metallic species with the biofilm in different degrees of specificity was suggested, based on the biological activity of the microorganisms that constitute the biofilm. Likewise, Díez and Giaggio (2018) showed that Hg-labile uptake in DGT devices had been reduced by up to 35% when deployment times in the field were longer, so a pretreatment of the filter membranes with a silver nanoparticle biocide was implemented. The results demonstrated the effectiveness of silver nanoparticle biocide by showing statistically significant differences between the Hg-concentration in DGT devices with and without treatment, and additionally, the Hg concentrations in treated DGT devices coincided with the theoretically calculated concentrations. However, despite the good results obtained with anti-biofilm agents, these pretreatments do not prevent the clogging of the filter membrane by suspended particulate matter (see last picture in Fig. 3), so they are not widely used, and instead, an optimization of the deployment time is chosen (Li et al. 2005a; Pichette et al. 2009; Österlund et al. 2016; Díez and Giaggio 2018). In this sense, dynamic numerical models used to understand DGT flux and explore the necessary deployment time of DGT devices have been examined in a review by Davison and Zhang (2012), as well as other basic aspects, such as geometry, competition effects and the kinetic limitations of the DGT technique.

In summary, in water and soil the most user sampler is the piston-type device composed of APA as diffusive gel and, depending on target trace metals, different ion-exchange resins as binding layer. Usually, filter membranes of 0.45 μm pore sizes are used as a protective layer to prevent contamination to hydrogels. Clogging of the filter membrane by suspended particulate matter and biofilm growth is difficult

Fig. 3 Growth of biofilm in diffusive gradients in thin film devices deployed for several days in a eutrophic river water. Last picture shows biofilm and suspended particulate matter clogging the filter

to avoid and optimization of the deployment time is the best option.

Deployment of diffusive gradient in thin films in the field

For water and soil studies, the piston-type device is the most common device used to be deployed in freshwater, seawater and agricultural and/or contaminated soils.

Deployment in water

For water, the main objective is usually obtaining time-averaged concentrations of trace metals, whereas for soil the main target has been studying plant yield response to

P fertilizers (Tandy et al. 2011; Zhang et al. 2013) and prediction of trace metals in plants (Zhang et al. 2004; Turull et al. 2019b).

General operation for deployments in the field include transportation of diffusive gradient in thin films (DGT) in individual clean sealed ziplock plastic bag containing few drops of 0.01 M NaCl/NaNO₃ solution, to maintain the devices in adequate humid and ionic strength conditions.

Once in the field, each unit is taken out from the bag and DGT is secure inside a sampling device and submerged at each sampling point. There are several designs to hold and suspend the samplers, one consists of a double methacrylate plate with round holes where DGTs can be attached (Clarisse and Hintelmann 2006; Uher et al. 2018) (Fig. 4a). The methacrylate plate could leave it submerged or fixed to two iron sticks using nylon string and stuck on the sediment

Fig. 4 Different designs for the deployment of diffusive gradients in thin films in the field. **a** Sampler in triplicate fixed in a double methacrylate plate, **b** sampling device driven into the river bed, **c** home-made baskets made of plastic mesh strips; **d** sampler in triplicate in

the methacrylate plate put in a protective basket before deployment, **e** detail of the samples after 1-week deployment and dismantled device with suspended material adhered on the filter membrane

(Fernández-Gómez et al. 2012a) (Fig. 4b), or attached to plastic mesh strips with fishing line (Lucas et al. 2014). Moreover, in other studies, the DGT devices have been attached with fishing line to a buoy (Pichette et al. 2007; Clarisse et al. 2009). The most common design for DGT deployment in natural waters consist of put in the DGTs inside a homemade cylindrical basket made of a plastic net, which is anchored to a rope with a weight on one end and a buoy on the other (Turull et al. 2017b) (Fig. 4c). After retrieval, DGT units are rinsed with distilled water to stop diffusion and also to remove biofilm and suspended material adhered on the DGT filter.

Deployment in soil

For soil applications, the typical piston-type device can be deployed into soils by hand gently pressing after the soil is moistened (Zhang et al. 2004; Turull et al. 2019b). Depending on several studies, the water content could be adjusted either over 90% (Zhang et al. 2004; Turull et al. 2019a) or 70% of the maximum water holding capacity (Zhang et al. 2017a) for 48 h to ensure the equilibrium between fractions and soil (Yao et al. 2016a).

One of the most important uses of DGT devices in soil is to predict the bioavailability of metals to plants. To do that, it is the necessary concept of effective concentration (C_E), which is the concentration that should be present in the soil solution to supply the same mass of metal accumulated by DGT in the partially sustained case (Zhang et al. 2001). Only diffusion concentration is taken into consideration, which is the same process found in the rhizosphere of plants, and therefore C_E can be directly related to the uptake of the plant. To calculate C_E , a relationship between the mean interfacial concentration with the resupply solely by diffusion to the bulk concentration should be calculated as follows:

$$C_E = \frac{C_{DGT}}{R_{diff}} \quad (8)$$

R_{diff} is defined as the ratio of the concentration at the DGT interface to the concentration in the bulk soil solution and should be obtained by the numerical model DIFS (DGT-induced fluxes in sediments) (Sochaczewski et al. 2007).

The software 2D DIFS (version 1.2.3-3, 2005, Lancaster, U.K.) is available online (www.dgtresearch.com) and can be used to simulate values of R , labile distribution coefficient (K_{dl}) and the soil response time to depletion (T_c). Besides DGT measurements, the additional measurable parameters required for DIFS fitting are soil porosity (ϕ_s), diffusive gel porosity (ϕ_d) and thickness (Δg), the effective diffusion coefficient in the soil (D_s) and the diffusion gel (D_d) and deployment time (t).

In summary, DGT devices are normally put in cylindrical basket made of a plastic net for aquatic deployments, whereas for soil deployments, the piston-type device can be applied in the soil individually by pressing gently with the hand after wetting the soil. Moreover, DIFS models are necessary to get valuable data to know the kinetics resupply of solutes to porewater from soil, and therefore to later predict the uptake of metals to plants.

Applications in aquatic ecosystems

Natural waters show a wide variety of ions at different concentrations, as well as a wide range of physicochemical characteristics and parameters, of which it is important to consider such as pH, ionic strength, temperature, dissolved organic matter and total dissolved solids for the application of the diffusive gradient in thin film (DGT) technique. Likewise, it is also important to consider that the binding layers' effectiveness depends essentially on the environmental matrix where the DGT device is deployed. Most of the binding layers mentioned above have been applied only in freshwater, due to the high concentrations of potentially competing ions that are present in more complex matrices such as seawater. In this sense, Österlund et al. (2016) explain in detail how to design a successful DGT sampling program in freshwater, lakes, brackish and marine waters.

In this review, we aim to emphasize the huge number of trace metals that has been determined in different aquatic systems by the DGT technique, which are shown in Table 2. All these studies demonstrate the versatility of DGT passive samplers for the determination of individual trace metals as well as a simultaneous determination of several of them.

Applications in terrestrial ecosystems

Although the diffusive gradient in thin film (DGT) technique was initially developed as a passive sampling technique for water, over the years it has evolved to be applied in soils as well. The piston-type DGT device can also be deployed on wet soil, pressing it manually in such a way that the filter membrane is in contact with the soil slurry (Turull et al. 2019a). For the measurements of trace metals in terrestrial ecosystems by the DGT technique, the same influencing factors considered in aquatic systems should be considered such as the pore size of the gel, interaction between analyte-gel, effect of competition (including H^+) and the ionic strength. The principles and application of the DGT technique in soils are detailed by Lehto (2016), focusing mainly on the influence of solid phases adjacent to the DGT device in the interpretation of analyte measurement results, also considering the important morphological and biogeochemical of soils.

Table 2 Studies of the diffusive gradients in thin film technique applied in aquatic systems for the determination of different species of metals and metalloids (published works found in Web of Knowledge from its development in 1994 up to the present time in 2020)

	Studies in aquatic systems
Mercury species	
Total Hg/Labile Hg	Docekalová and Diviš (2005), Rodríguez Martín et al. (2006), Diviš et al. (2009, 2010), Roig et al. (2011), Fernández-Gómez et al. (2011, 2012a), Gao et al. (2011), Zhou et al. (2013), Colaço et al. (2014), Pelcová et al. (2014, 2017), Tafurt-Cardona et al. (2015), Senila et al. (2017a), Sierra et al. (2017), Turull et al. (2017a, b, 2018), Wu et al. (2017), Díez and Giaggio (2018), Schintu et al. (2018), Muresan et al. (2018), Noh et al. (2020), Reichstädter et al. (2020), Elias et al. (2020)
MeHg	Clarisse and Hintelmann (2006), Clarisse et al. (2009, 2012), Fernández-Gómez et al. (2014, 2015), Gao et al. (2014)
Hg(II)	Colaço et al. (2012), Wu et al. (2017), Tan et al. (2019b), Yao et al. (2020)
MeHg and Hg(II)	Cattani et al. (2009), Hong et al. (2011), Ren et al. (2018), Bratkič et al. (2019), Bretier et al. (2020)
Hg(II), MeHg, ethylmercury, phenylmercury	Pelcová et al. (2015)
Other trace elements	
1 element	
As	Panther et al. (2008a, b), Bennett et al. (2011), Österlund et al. (2012a), Sun et al. (2014b), Liu et al. (2016), Prieto et al. (2016), Senila et al. (2017b), Gorny et al. (2019), Tan et al. (2019a), Smolíková et al. (2020)
Cd	Bradac et al. (2009), Menegário et al. (2010), Fan et al. (2015)
Cr	Ernstberger et al. (2002b), Giusti and Barakat (2005), Chen et al. (2014), Guo et al. (2014), Pan et al. (2015), Devillers et al. (2016), Suárez et al. (2016), Yao et al. (2016b), Gao et al. (2019b)
Cu	Zhang and Davison (2001), Nierop et al. (2002), Luidar et al. (2004), Kraal et al. (2006), Martin and Goldblatt (2007), Fan et al. (2009a), McGifford et al. (2010), Bourgeault et al. (2013), Ferreira et al. (2013), Knutsson et al. (2014), Pérez et al. (2015), Philipps et al. (2018a, b), Strivens et al. (2019, 2020), Macoustra et al. (2020)
Ni	Shafaei Arvajej et al. (2013)
Pb	Scally et al. (2004), Van Der Veecken et al. (2008), Pescim et al. (2012), Sui et al. (2016)
Zn	Wang et al. (2009), Lourino-Cabana et al. (2011), Companys et al. (2018)
2 elements	
Al, Cu	Tonello et al. (2007, 2011)
Cd, Cu	Zhang and Davison (2000), Li et al. (2002a, b, 2005a, b), Peters et al. (2003), Warnken et al. (2005), Fan et al. (2009b), Davison et al. (2015)
Cd, Pb	Jakl et al. (2009), Reichstädter et al. (2020)
Cd, V	Mangal et al. (2016)
Cu, Ni	Österlund et al. (2012b)
Cu, Pb	Philipps et al. (2019)
Cu, Zn	Costa and Wallner-Kersanach (2013), Costa et al. (2013), Paller et al. (2019)
Ni, Zn	Zhang (2004)
Pb, Zn	Desaulty et al. (2015)
3 elements	
Al, As, Fe	Gontijo et al. (2016)
As, Sb, V	Li et al. (2020)
Cd, Co, Ni	Puy et al. (2014)
Cd, Cu, Mn	Denney et al. (1999)
Cd, Cu, Ni	Torre et al. (2000)
Cd, Cu, Pb	Fan et al. (2013), Sui et al. (2013)
Cd, Mg, Ni	Altier et al. (2019)
Cd, Ni, Zn	Uher et al. (2012)
Cu, Ni, Pb	Cleven et al. (2005)
Cu, Ni, Zn	Knutsson et al. (2013)

Table 2 (continued)

4 elements	
As, Cd, Cu, Ni	Buzier et al. (2014)
As, Mo, Sb, V	Zhang et al. (2017b)
As, P, Se, V	Price et al. (2013)
As, Se, V, Sb	Luo et al. (2010a)
Cd, Cu, Ni, Pb	Scally et al. (2006), Unsworth et al. (2006), Kawakami et al. (2008), Schintu et al. (2008), Slaveykova et al. (2009), Dakova et al. (2011), Marras et al. (2020)
Cd, Cu, Ni, Zn	Wallner-Kersanach et al. (2009), Huynh et al. (2010)
Cd, Cu, Pb, Zn	Webb and Keough (2002), Van Leeuwen et al. (2005), Balistrieri and Blank (2008), Gaabass et al. (2009), Schintu et al. (2010)
Cd, Mn, Pb, Zn	Nguyen et al. (2020)
Co, Cu, Ni, V	Hartland et al. (2011)
Cr, Cu, Ni, Zn	Smith et al. (2007)
Cu, Fe, Mn, Zn	Gimpel et al. (2003)
Cu, Mn, Ni, Zn	Forsberg et al. (2006)
Cu, Ni, Pb, Zn	Dunn et al. (2003, 2007), Han et al. (2013, 2014, 2016), Zhu and Guéguen (2016)
5 elements	
As, Cd, Cu, Mg, Mn	Colaço et al. (2012)
As, Cd, Cu, Pb, Zn	Huynh et al. (2012b)
As, Cr, Cu, Pb, V	Xu et al. (2019a)
As, Cu, Mn, Pb, Zn	Chen et al. (2013)
As, Mo, Sb, V, W	Österlund et al. (2010), Panther et al. (2013)
Cd, Co, Cu, Mn, Pb	Munksgaard and Parry (2003)
Cd, Co, Cu, Ni, Pb	Warnken et al. (2004), Garmo et al. (2008), Guéguen et al. (2011), Levy et al. (2012a), Gaulier et al. (2019), Cindrić et al. (2020)
Cd, Co, Mn, Ni, Zn	Omanović et al. (2015), Uher et al. (2017)
Cd, Cu, Fe, Ni, Zn	Stewart et al. (2016)
Cd, Cu, Ni, Pb, Zn	Rodríguez Martín et al. (2006), Sigg et al. (2006), Allan et al. (2007, 2008), Nyein Aung et al. (2008), de Souza et al. (2014), Wang et al. (2014b), Koppel et al. (2019), Yabuki et al. (2019)
6 elements	
Cd, Co, Cu, Mn, Ni, Pb	Hojaji (2012), Levy et al. (2012b), Vannuci-Silva et al. (2017)
Cd, Co, Cu, Ni, Pb, Zn	Sangi et al. (2002), Kim et al. (2016), Cindrić et al. (2017)
Cd, Cr, Cu, Ni, Pb, V	Schintu et al. (2018)
Cd, Cr, Cu, Ni, Pb, Zn	Diviš et al. (2007), Soriano-Disla et al. (2010)
Cd, Cu, Fe, Mn, Pb, Zn	Bradac et al. (2010)
Cd, Cu, Mn, Ni, Pb, Zn	Odzak et al. (2002)
Co, Cu, Mn, Ni, Pb, Zn	Almeida et al. (2012)
7 elements	
Ag, Cd, Cr, Cu, Ni, Pb, Zn	Vystavna et al. (2013)
Al, Cd, Co, Cu, Mn, Ni, Zn	Yabuki et al. (2014)
Al, Cd, Cr, Cu, Fe, Ni, Pb	Buzier et al. (2011)
As, Cd, Cr, Cu, Ni, Pb, Zn	Sierra et al. (2017)
As, Cd, Co, Mo, Ni, Sb, Zn	Schmukat et al. (2013)
As, Cu, Fe, Mn, Pb, Sr, U	Martin et al. (2019)
Cd, Co, Cr, Cu, Fe, Ni, Pb	Buzier et al. (2006)
Cd, Co, Cr, Cu, Mn, Ni, Zn	Bourgeault et al. (2010)
Cd, Co, Cr, Cu, Ni, Pb, Zn	Vystavna et al. (2012), Villanueva et al. (2013, 2015, 2016)
Cd, Co, Cu, Fe, Mn, Ni, Pb	Warnken et al. (2008), Baeyens et al. (2011)
Cd, Co, Cu, Mn, Ni, Pb, Zn	Larner and Seen (2005)
8 elements	
Al, Cd, Co, Cr, Cu, Ni, Pb, Zn	Devillers et al. (2017a)
Al, Cd, Co, Cu, Fe, Mn, Ni, Zn	Öhlander et al. (2012)

Table 2 (continued)

Al, Cd, Cu, Fe, Mn, Ni, Pb, Zn	Warnken et al. (2009)
As, Cd, Cr, Cu, Ni, Pb, Sb, Se	Devillers et al. (2017b)
Cd, Cr, Co, Cu, Mn, Ni, Pb, Zn	Uher et al. (2013, 2018), Dabrin et al. (2016)
9 elements	
Al, As, Cr, Co, Cu, Mn, Pb, Sn, Zn	Larner et al. (2006)
Al, Cd, Co, Cr, Cu, Fe, Ni, Pb, Zn	Liu et al. (2013a)
Al, Cd, Co, Cu, Fe, Mn, Ni, Pb, Zn	Warnken et al. (2007), Sherwood et al. (2009)
Al, Cr, Co, Cu, Mn, Ni, Pb, U, Zn	Agnelli et al. (2014)
Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Zn	Dragun et al. (2008, 2015)
10+ elements	
Al, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Zn	Díaz et al. (2012)
	Garmo et al. (2003), Balistrieri et al. (2007), Casiot et al. (2009), Uribe et al. (2011), Roig et al. (2011), Panther et al. (2014), Shiva et al. (2016, 2017), Lucas et al. (2015), Shiva et al. (2015), Wang et al. (2016b, 2017b), dos Anjos et al. (2017), Schoyen et al. (2017), Cánovas et al. (2020)

Table 3 shows all the published studies applying DGT technique in soil for the determination of metals and metalloids. One of the most prominent applications is the comparison of the amount of metal uptake by plants vs the amount of this metal in adjacent soil by DGT devices, since understanding the metal bioavailability in agricultural soils is key for food security purposes. In this context, the studies developed in foods are outstanding, such as rice (Tian et al. 2008; Liu et al. 2012; Williams et al. 2012; Li et al. 2018; Ma et al. 2020; Peng et al. 2020; Wen et al. 2020), potatoes (Pérez and Anderson 2009a), spinach (Almås et al. 2006), onions (Yi et al. 2020) and lettuce (Koster et al. 2005; Cornu and Denaix 2006; Agbenin and Welp 2012; Turull et al. 2019b).

Studies have indicated that As, Cd, Cu, Zn and Pb are the most common trace metals and metalloids determined in soils by the DGT technique, which in some cases are determined simultaneously related to agricultural soils to predict their uptake in edible crops.

Conclusion

The diffusive gradient in thin film (DGT) technique has been continuously developed for more than 20 years, and the theoretical principles for its effective application in aquatic and terrestrial systems are well established. The development of the DGT technique has been of great importance due to the ease of application, versatility, wide range of analytes that can be determined by a single DGT deployment, even at very low concentrations (i.e., trace metals) in waters. Similarly, the great number of published studies that have been cited in this review indicates that the DGT technique is very useful for the measurement of the labile species of most elements allowing a fast, easy and relatively cost-effective detailed study of the bioavailability and speciation of metals and metalloids in waters

and soils. Later, great progress has been made in terrestrial systems, e.g., in agricultural soils, with the use of DIFS modeling that has opened the possibility of predicting the uptake of trace metals by plants, which in turn is key to the future of security food, just by analyzing the soil.

Although this technique has been developed continuously, however, significant challenges remain for the future development of DGT. Firstly, overcoming the interference to DGT measurements when applying in the field for long period of time is a big challenge since biofilms have been proved could affect analyte diffusion, as well as competition of other ions that also interfere diffusion and final adsorption performance in the binding gel. Likewise, it is necessary to unify the operating procedures for the assembly, deployment and treatment of samples of DGT devices in order to simplify comparison between different studies.

The development and implementation of new materials species-specific as binding layers is also a challenge that will let the determination of even more environmental pollutants/species, e.g., metals, nutrients or even organics. Moreover, while the process of creating a binding layer from a binding agent embedded in a gel matrix has facilitated the wide versatility of this technique, binding agents are often expensive. This could be compensated by using small quantities of them in binding layers' preparation, although not for deployment in high polluted environments as it would reduce the capacity of the DGT device. Nevertheless, it has also been presented as an obstacle for developing the DGT technique worldwide, especially in developing countries with high contamination levels and low investment in research. In addition, it should be considering the evaluation of inexpensive and easily accessible materials as possible binding agents to improve the accessibility of the DGT technique.

Finally, few studies have been conducted trying to understand the relationships between DGT determinations of trace elements and their absorption by different organisms;

Table 3 Studies of the diffusive gradients in thin film technique applied in terrestrial systems for the determination of different species of metals and metalloids (published works found in web of knowledge from its development in 1994 up to the present time in 2020)

	Studies in terrestrial systems
Mercury species	
Total Hg/Labile Hg	Liu et al. (2012), Senila et al. (2013), Hlodák et al. (2015), Ridošková et al. (2017, 2019), Ndu et al. (2018), Huu Nguyen et al. (2019), Pelcová et al. (2019)
MeHg and Hg ²⁺	Cattani et al. (2008)
Labile Hg and inorganic Hg	Turull et al. (2019a, b)
Other trace elements	
1 element	
As	Fitz et al. (2003), Mojsilovic et al. (2011), Moreno-Jiménez et al. (2013), Wang et al. (2014a, 2018a, b), Xu et al. (2014), Zhang et al. (2017a, 2019), Dai et al. (2018), Sun et al. (2018b), Zheng et al. (2019), An et al. (2020)
Cd	Pérez and Anderson (2009a), Song et al. (2015), Yao et al. (2016a, 2017), Wang et al. (2016a, 2017a), Gu et al. (2017), Dai et al. (2018), Gramlich et al. (2018), Wu et al. (2018), Li et al. (2018), Tian et al. (2018), Xu et al. (2019b), Ono et al. (2019), Wen et al. (2020), Yi et al. (2020)
Cr	Amezcuca-Allieri et al. (2005a), Gao et al. (2020), Vogel et al. (2020)
Cu	Zhang et al. (2001), Ma et al. (2006), Zhao et al. (2006), Bravin et al. (2009, 2010, 2012), Amery et al. (2010), Garrido and Mendoza (2013), Le Forestier et al. (2017), Sun et al. (2018a)
Ni	Gao et al. (2018), Zhao et al. (2018)
Pb	Senila (2014), Xu et al. (2019c, d)
Zn	Degryse et al. (2003), Zhang et al. (2004), Sönmez and Pierzynski (2005), Sönmez et al. (2009, 2016), Gramlich et al. (2014), Sun et al. (2014a), Xu et al. (2018), Zhou et al. (2019), García-Gómez et al. (2020)
2 elements	
As, Sb	Ngo et al. (2016, 2020), Zhang et al. (2018)
As, Pb	Liang et al. (2014), Zhang et al. (2017c)
Cd, Cu	Cui et al. (2020)
Cd, Fe	Wang et al. (2020)
Cd, Ni	Pérez and Anderson (2009b), Luo et al. (2010b, 2014), Liu et al. (2018), Ma et al. (2020)
Cd, Pb	Zarrouk et al. (2014), Ridošková et al. (2017)
Cd, Zn	Almás et al. (2006), Cornu and Denaix (2006), Zhang et al. (2006), Muhammad et al. (2012), Williams et al. (2012), Li et al. (2014), Hoefer et al. (2015), Gramlich et al. (2017), Eugene et al. (2018), Grüter et al. (2019)
Co, Ni	Gao et al. (2019a)
Cu, Pb	Fresno et al. (2017)
Cu, Zn	Nowack et al. (2004), Ahumada et al. (2011), Tella et al. (2016), Peng et al. (2020)
3 elements	
As, Cd, Pb	Tang et al. (2019)
As, Cu, Zn	Manzano et al. (2019)
As, Sb, Pb	Lomaglio et al. (2017)
Cd, Cu, Ni	Kovaríková et al. (2007), Senila et al. (2012)
Cd, Cu, Pb	Balistrieri and Blank (2008)
Cd, Ni, Zn	Ernstberger et al. (2005), Welikala et al. (2018)
Cd, Pb, Zn	Fischerová et al. (2005), Puschenreiter et al. (2013), Pavel et al. (2014), Cornu et al. (2016)
Cu, Ni, Pb	Amezcuca-Allieri et al. (2005b)
Cu, P, Zn	Tandy et al. (2011)
4 elements	
As, Cd, Pb, Zn	Neu et al. (2018)
As, Cr, Cu, Zn	Hattab et al. (2014)
As, Cu, Pb, Zn	Bade et al. (2012a, b, 2013), Hattab-Hambli et al. (2016)
As, Fe, Mn, P	Chowdhury et al. (2018)
Cd, Cu, Mn, Zn	Grüter et al. (2017)
Cd, Cu, Ni, Pb	Docekalová et al. (2012)

Table 3 (continued)

Cd, Cu, Ni, Zn	Zhang et al. (1998), Ernstberger et al. (2002a), Black et al. (2011), Huynh et al. (2012a)
Cd, Cu, Pb, Zn	Nolan et al. (2005), Tian et al. (2008), Conesa et al. (2010), Agbenin and Welp (2012), Qiu et al. (2012), Bidar et al. (2019)
Cr, Cu, Ni, Zn	Ahumada et al. (2014)
Cu, Fe, Mn, Ni	Ruello et al. (2008)
5 elements	
Al, Cu, Cd, Ni, Zn	Li et al. (2015)
As, Cd, Cu, Pb, Zn	Huynh et al. (2012b)
As, Cd, Pb, Sb, Zn	Qasim et al. (2016)
Cd, Cr, Cu, Pb, Zn	Guo et al. (2016)
Cd, Cu, Ni, Pb, Zn	Hamels et al. (2014), Zhang et al. (2016), Guan et al. (2018)
6 elements	
As, Cd, Cu, Mn, Pb, Zn	Ciadamidaro et al. (2017)
As, Cd, Cu, Ni, Pb, Zn	Moreno-Jiménez et al. (2016)
As, Co, Cr, Cu, Mo, Zn	Hattab et al. (2015)
Cd, Co, Cu, Ni, Pb, Zn	Hooda et al. (1999)
Cd, Cu, Fe, Mn, Ni, Zn	Zhang and Davison (1995)
Cr, Cu, Fe, Mn, Pb, Zn	Lu et al. (2019)
9+ elements	
Al, Cd, Co, Cr, Cu, Fe, Mn, Ni, Zn	Chapman et al. (2012)
	Docekal et al. (2003), Jakl et al. (2015), Galhardi et al. (2020)

MeHg methylmercury

however, whether DGT represents the definitive bioavailable fraction in aquatic systems remains a matter of debate. Although the DGT data are very valuable to understand the biological process, many efforts should be done to link DGT values to biological responses under field conditions.

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