



Use of diffusive gradient in thin-films (DGTs) to advance environmental mercury research: Development, growth, and tomorrow

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ABSTRACT

An understanding of global environmental pollution requires sensitive high-resolution analytical methods to detect contaminants at trace level concentrations (\leq ppb), to accurately assess potential effects associated with chronic low-level exposure. Additionally, the focus of environmental risk assessments has evolved to consider not only total concentrations but also bioavailable fractions. Diffusive gradient in thin-film passive samplers (DGTs) can be deployed in a variety of matrices to accumulate contaminants through diffusion. Due to their simple design, DGTs can be manipulated and adjusted to fit the experimental or monitoring purpose and contaminant of interest. Mercury (Hg) is a ubiquitous trace element of global concern that accumulates in biota and concentrates through the food chain as organic methylmercury. Existing reviews on environmental Hg research mention DGTs as a promising and successful tool to quantify the flux of labile species over a broad range of environmental matrices. This is the first comprehensive review of current literature describing the development and environmental deployment of mercury specific DGTs. Given the multi-faceted nature of this research, this review discusses the impact of DGT configuration and Hg speciation on the interpretation of analytical data and addresses the application of DGT passive samplers in bioavailability studies.

1. Introduction

Environmental trace element analysis and subsequent risk assessment necessitate an alternative to traditional grab sampling because contaminants may either fall below their respective limit of detection (LOD) or their total concentration may not reflect their environmental impact. Passive sampling is a minimally invasive monitoring technique that deploys well-defined environmental sinks for an analyte of interest with a known uptake capacity over a defined timespan [1]. Additionally, passive samplers are a valuable tool for environmental monitoring in remote places where other adequate sampling methods or preservation are not feasible [2]. Apart from being used to determine levels and even sources of pollution, passive samplers are increasingly used to quantify dynamic concentrations and associated uptake fluxes (known as time-weighted average concentrations; TWACs) [3]. The use of TWACs is less susceptible to short-term concentration fluctuations which could distort the interpretation of single point analyses [4]. The selective accumulation and pre-concentration of analytes also mitigates some of the challenges posed by complex environmental matrices that may perturb trace contaminant analyses [5]. However, correct deployment

and data interpretation of passive samplers is dependent on a suitable pairing of device configuration and analyte matrix, as well as an understanding of the potential artifacts created by inhomogeneous environments, e.g. suspended particulate matter [6–9]. The use of diffuse gradient in thin-film (DGT) passive samplers has gained increased attention, as their facile deployment and production makes them a versatile tool in assessing labile pools and estimate uptake rates [4]. Briefly, DGT samplers are typically composed of two stacked gels, a diffusive phase and a binding phase, mounted inside a plastic housing and shielded by a filter membrane (see Fig. 1A). During sampling, solute ions pass the filter membrane and travel through the diffusive phase to reach the binding phase. The diffusivity is temperature and material dependent. As the binding of diffused ions removes these from solution, their effective concentration in the binding phase remains near zero, thus maintaining a gradient and flux toward further accumulation in the phase (see Fig. 1B). Over time, the binding phase can concentrate the ions of interest, allowing for quantitative trace contaminant determination without the need for low LODs. An exhaustive theoretical background of the DGT principle can be found in Davison and Zhang, [10]. The performance, selectivity, and mode of deployment of DGT

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components are heavily influenced by their nature and configuration. As such they continue to be a crucial parameter in experimental and analytical design.

2. Mercury

Mercury (Hg) is a highly toxic, environmentally persistent, and bioaccumulating element that poses a significant hazard to the biome [7]. Its intrinsic characteristics make Hg a challenging analyte as it readily speciates, and thus changes its chemical behavior, depending on the surrounding environmental conditions [11]. In this manuscript, the term ‘speciation’ refers to the ‘distribution of an element among defined chemical species in a system’ as outlined by IUPAC [12]. In organisms, the most hazardous forms of Hg are organomercurials as they are not readily eliminated from the body and are highly neurotoxic [13]. The most common forms, methylmercury chloride and dimethyl mercury, are here referred to as MeHg. These compounds are bioaccumulated through the food chain, making MeHg a risk for humans, as the increased consumption of seafood has been recognized to increase human exposure [14]. Environmental impact assessments and remediation approaches increasingly focus on active fractions rather than total concentrations, thus putting emphasis on porewater as a proxy for labile and bioavailable pools [11]. In the context of this manuscript, the ‘labile’ fraction is defined as the interchangeable fraction of weakly adsorbed analytes with a short residence time in a solid matrix (i.e. sediment, soil, etc.) and high rate of dissociation into the water column [15]. Given the challenging nature of Hg as an environmental analyte, DGTs offer a promising approach to enable trace quantification and source identification through overcoming matrix effects [3]. This review highlights the research and development of mercury-specific “Hg-DGTs” as well as their deployment in different environments, appropriate interpretation of data, and current limitations.

3. Impact of sampler configuration

3.1. Diffusive boundary layer (DBL)

Solid surfaces in turbulent medium are covered by a boundary layer in which the medium flow is affected by frictional forces, slows down, and may even become laminar (see Fig. 1C). As a result, diffusion becomes the dominant mode of analyte mobility in this layer [16]. The thickness of the DBL depends on the flow pattern or turbulence close to that surface [17]. High turbulence results in a thin DBL, which accelerates total diffusion rates [18]. One of the main concerns during the deployment of any passive sampler in natural aquatic environments is the formation of biofilms (i.e., biofouling), which may affect compound uptake by affecting the diffusive boundary layer. Biofilm formation on Hg-DGTs has been observed after deployment times of 2–3 weeks, leading to a significant underestimation of ambient Hg concentrations [19]. To improve the long-term exposure performance, Díez and Giaggio, [20] used nanoparticulate Ag to prevent biofouling on Hg-DGTs, which significantly inhibited biofilm growth during a deployment time of 24 days without negatively impacting Hg measurements. Comparable results were achieved with copper and silver iodide in phosphorous-specific DGTs, although biofouling processes could only be inhibited for up to 21 days [21]. Nonetheless, DGT biofouling remains an understudied subject with existing studies suggesting a pH dependent effect of biofilms on DGT performance. Both the nature and thickness of formed biofilms are dependent on the surrounding environmental parameters (e.g., water flow) and may divergently affect analyte uptake [22]. Consequently, any long-term DGT deployment requires careful consideration, as these artefacts have a potential to limit analyte accumulation resulting in subsequent data misinterpretation.

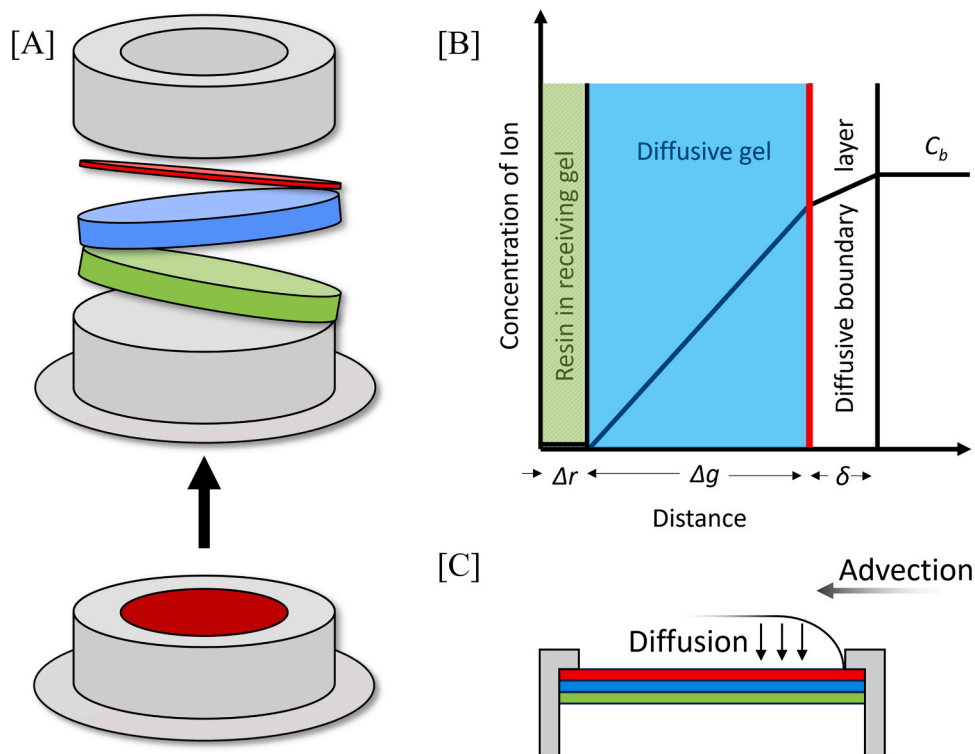


Fig. 1. General structure of piston-type DGT samplers. Part [A] shows an exploded view schematic of a piston-type DGT sampler showing the protective filter membrane (red), the diffusive phase (blue), and the binding phase (green) assembled in a plastic casing (grey). Part [B] illustrates the concentration of free ionic species in a DGT gel assembly in contact with a solution of the concentration C_b . The concentration gradient forms over the distances Δr , Δg , and δ which represent the thickness of the receiving gel (green), diffusive gel (blue), and the diffusive boundary layer respectively. Part [C] shows the formation of a diffusive boundary layer resulting from advection over the DGT surface. The main mode of analyte mobility within the diffusive boundary layer is diffusion.

3.2. Diffusive phase

Most diffusive phases used in the here reviewed Hg-DGT studies are hydrogels on agarose (1.5% m/v) or polyacrylamide (15% m/v) basis with only one study using cellulose acetate [23]. However, the use of both natural and synthetic hydrogels in Hg-DGT research remains challenged due to a significant collateral retention of Hg in both agarose and polyacrylamide gels [24–26]. Fatin-Rouge et al., [27] conducted an in-depth mechanistic study of the influence of agarose functional groups on the diffusivity of divalent ions, including Hg, and concluded that the negatively charged pyruvate groups caused a Donnan effect that effectively retained ions in the gel. It should be noted that for DGTs such effects have only been observed in low ionic strength and low pH solutions and that the effect of gel charge is reduced with increasing ionic strength [28]. The intrinsic amide functional groups of polyacrylamides interact with Hg species [29]. The most evident case of collateral Hg binding to a polyacrylamide diffusive phase was reported by Docekalova and Divis, [30], who noted a 700-fold higher concentration of Hg in the diffusive phase compared to dissolved concentrations. In addition to the chemical composition, the preparation of hydrogels has a major influence on the resulting polymer structure and overall performance of DGTs. For example, by varying the concentration and type of copolymers or the final gel thickness, different analyte diffusivity and gel pore sizes can be achieved [31]. The controlled variation of gel pore sizes, commonly referred to as open or restricted gels, can be achieved by using different cross-linkers such as agarose or bis-acrylamide. The resulting difference in gel porosity has long been proposed to distinguish between the environmental fractions of free ions and large organic complexes [32]. Turull et al., [31,33] found that a differentiation between low molecular species and colloid forms of Hg using restricted and open DGT gels could indeed be made, thus further advancing DGT-based assessments of fractionated environmental Hg pools.

The distribution of reported empirically measured diffusion

coefficients (Fig. 2), demonstrates that individual diffusivity assessments are required to correctly interpret the produced data. In general, the diffusion coefficient ‘is the amount of a particular substance that diffuses across a unit area in 1 s under the influence of a gradient of one unit’ [34].

Given its central role in a diffusion driven process, assessing the diffusion coefficient is particularly important, when unexplored materials such as cellulose acetate are used [23], and the matrix dependent speciation affects the ionic properties [35]. For a detailed discussion on the impact of gel preparation on the performance of diffusive phases see Davison and Zhang, [28].

3.3. Binding phase

The efficiency of Hg binding, directly affecting DGT performance, is dependent on the chemical composition of the binding phase and can thus be readily modified. Initial versions of DGTs used a Chelex-100 resin, with a high affinity for heavy- and transition metals. However, deployment in environmental waters revealed a significantly reduced recovery (< 60%) specifically for Hg [30,36]. This reduced chelation efficiency could be explained by the binding being kinetically limited or the binding affecting hydrolysis [28]. One of the first modifications to increase Hg-binding efficiency was the use of thio-functionalized resins to exploit the thiophilicity of Hg. A direct comparison of the performance of Chelex-100 and Spheron-thiol revealed that the latter accumulated total Hg (tHg, including large organic aggregates), whereas Chelex-100 only captured ionic Hg and weak complexes [24,30]. Subsequent studies confirmed that the otherwise commonly used Chelex-100 failed to compete with sulfur functionalized or other functionalized resins in Hg specific setups [26]. Since then, commercial thio-functionalized resins such as Amberlite GT73, Purolite S924, Ion-tosorb AV, Tulsion® CH-95 and CH-97, HSTY®-TU, and ZXC-620, but also ion exchange membranes (e.g., Whatman P81) have been deployed

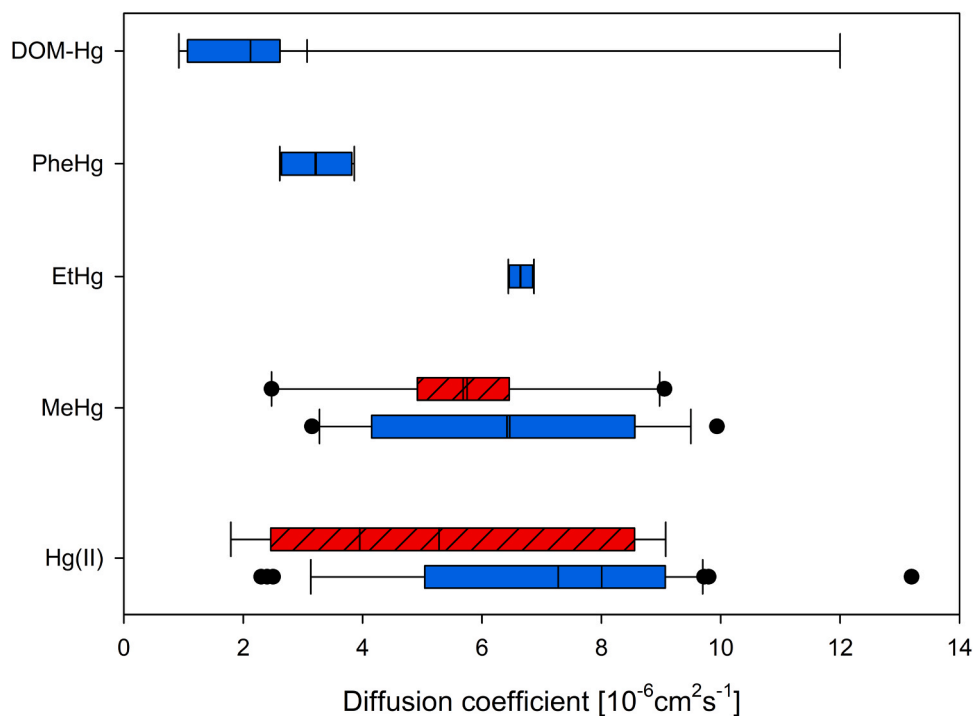


Fig. 2. Published diffusion coefficients of diverse Hg compounds and species in agarose (blue) and polyacrylamide (hatched red) diffusion gels. Hg compounds and species are divalent ionic Hg (Hg^{2+}), methylmercury (MeHg), ethyl mercury (EtHg), phenylmercury (PheHg), and organically complexed Hg ions (DOM-Hg). Scopus, Pubmed, WebOfScience, and the website of the Royal Chemical Society were searched for the term “mercury dgt”, “Hg-DGT”, and “DGT mercury”. 97 relevant peer reviewed articles were found to date (19th October 2023). Diffusion coefficient data were included if they were empirically measured and excluded if they were literature derived or assumed. Data were transformed to 25 °C if determined or published at a different temperature using Stokes-Einstein equation. Raw data can be found in [Supplementary Material 1](#).

as Hg specific binding phases with good reproducibility and little interference by other heavy metals [5,29]. Currently commercially available Hg-DGTs (e.g., DGT®Research Ltd.) use 3-mercaptopropyl-functionalised silica gel binding resins, which have displayed a high degree of Hg affinity and specificity in heavy metal ion interference studies [26,37].

The development of experimental binding resins by functionalizing a polymer or scaffolding, as well as the use of liquid binding layers has also gained interest. Resins with organosulfur moieties such as thio-salicylate, benzoylthiourea, sulfhydryl, and cysteine functional groups have been demonstrated to perform well under variable aquatic conditions, both in laboratory and environmental applications [38–40]. Similarly, short oligonucleotides (aptamers) are used as macromolecular complexing agents for a wide range of elements and small molecules in DNA-based biosensing. Pi et al., [41] immobilized a thymine-rich 24-base single-strand aptamer in polyacrylamide to construct a Hg-specific DGT binding phase, with a higher sorption capacity (9.5 mg Hg disk⁻¹) than thiol-modified resins (4 mg Hg disk⁻¹). Additionally, this configuration allowed for a fluorometric analysis of sorbed Hg. Other studies demonstrating the sensitivity and robustness of Hg DNA-sensing exist, however a wider application of this sensing technique is still lacking.

In a different approach, Tafurt-Cardona et al., [42] used *Saccharomyces cerevisiae* yeast immobilized in agarose to selectively bind MeHg, a method previously demonstrated to be suitable for cadmium and lead sorption by DGTs [43,44]. A confirmation of *S. cerevisiae* as a robust and selective binding phase could elevate and simplify future species specific analyses however, published evidence to date suggests that synthetic sulfur-containing binding phases remain favored in traditional Hg-DGT research. An exhaustive list of commercially available and experimental binding phases used in Hg-DGT research can be found in Table 1.

An additional measure of DGT binding phase performance is the total uptake capacity into the assembled sampler as this has direct implications on deployment duration. For Hg-DGTs, nine publications experimentally determined the total uptake capacity of their assembled samplers, spanning three orders of magnitude (Fig. 3).

4. Impact of speciation and ligands

Environmental deployment of passive samplers like DGTs as well as testing of new DGT configurations requires a matrix specific pre-calibration under controlled laboratory conditions to refine data processing [38]. Variables including flowrate, temperature, pH, salinity, molecular weight, and diffusive phase material may significantly impact empirical Hg diffusion coefficient measurements [29,35,49]. The natural formation of coordinated inorganic Hg complexes can lead to decrease of the effective aqueous diffusion coefficient of up to fivefold by increasing molecular size [1,49]. Empirical data on this can be found in Hong et al., [28]. Additionally, natural waters contain both particulate and dissolved organic matter, which can unselectively complex cations with intrinsic functional groups [1]. In most current works, increased organic ligand availability collaterally decreased Hg diffusion coefficients by up to one order of magnitude [1,25,35,41,49], with only a few studies reporting negligible impacts on Hg-DGT performance [1, 29]. Both DOM and dissolved sulfide reduce the diffusivity of Hg ions in Hg-DGT diffusive phases in a dose dependent manner [1,67]. The DOM: Hg ratio and DOM partitioning coefficient have a significant impact on the effective Hg diffusivity, which can be modelled using partitioning data as shown by Bland et al., [1]. Although ratio-based assessments of organic Hg complexation and its effects on DGT performance have received increasing attention, the influence of chemical composition and functional groups within DOM, which are known to govern Hg-DOM relationships, remains understudied [68]. A more deterministic approach to Hg-DOM related studies, based on functional group characterization could prove helpful in future mercury research.

In the presence of elevated sulfide and DOM concentration, solute Hg

Table 1

Binding phases used in Hg-DGT research. Grey resins are non-commercial, experimental resins.

Name	Chemical composition	Reference
Chelex-100	Styrene-divinylbenzene resin with iminodiacetic groups	[26]
Spheron-Thiol	Thiol functionalized hydroxyethyl methacrylate gel	[25,30, 45–47]
Amberlite GT73	Thiol functionalized styrene-divinylbenzene resin	[48–55]
3MFSG P81	3-mercaptopropyl functionalized silica gel	[35,56,57]
Ambersep GT74	Cellulose phosphate ion exchange membrane	[58]
Iontosorb AV	Thiol functionalized styrene-divinylbenzene resin	[48]
Purolite S294	Modified bead-form cellulose containing aminoaryl- β -ethylsulfone groups	[59]
Tulsion CH-95	Thiol functionalized polystyrene	[5,18]
Tulsion CH-97	Isothiourea functionalized cross-linked polystyrene	[29]
HSTY-TU	Methylene thiol functionalized cross-linked polystyrene	
ZXC-620	Thiol functionalized resin	
ISOLUTE Si-Thiol	1-propanethiol functionalized silica	[1]
Duolite GT73	Thiol functionalized styrene-divinylbenzene copolymer	[60]
SH-SBA	3-mercaptopropyl functionalized mesoporous silica	[26]
SH-PMO	3-mercaptopropyl functionalized ethenylene bridged periodic mesoporous organosilica	
Sumichelate Q10R	Dithiocarbamate functionalized periodic mesoporous organosilica	
Agarose-yeast	<i>S. cerevisiae</i> immobilized in agarose gel	[42]
QuadraSil	3-mercaptopropyl silica resin	[61]
DNA-DGT	Single-stranded acryl-Hg-DNA sequence	[41]
TM-MDH	Thiol-modified metal double hydroxide	[62]
Si(np)-TOMATS	Nanoparticulate silicon dioxide modified with trioctylmethylammonium thiosalicylate	[38,63]
CAS	Cysteine immobilized on 3-amino-functionalised silica	[39]
CAPS	Cysteine immobilized on 3-aminopropyl-functionalised silica	
SH-CNPs	Thiol-modified carbon nanoparticle suspension	[23]
TiO ₂	Titanium dioxide in polyacrylamide	[64]
BTP1	Poly(4-((2-aminonaphthalene-6-carbonothioyl) carbamoyl) benzoil isothiocyanate)	[40]
SiO ₂ -SH cryogel	Sulfhydryl-modified silica nanoparticles embedded into polyacrylamide	[65]
PE-NPAU-LPFG	Poly-electrolyte coated gold nanoparticle long period fiber grating sensor	[66]

is known to complex and potentially precipitate as (nano)particulate mercury sulfide (HgS). This insoluble species has a significant impact on DGT-based measurements, as the particles have been shown to accumulate on the DGT surface, leading to significantly reduced diffusion coefficients of dissolved Hg [6]. The effects of nanoparticles on DGT applications in a field study were observed by Clarisse et al., [67], who noted a 50% decreased MeHg accumulation in DGTs in the presence of high aqueous sulfide concentrations. Macroscopic suspended particulate matter in natural waters binds Hg similar to DOM, which may lead to its photoreduction to elemental Hg⁰ [4], or demethylation due to the photolytic formation of oxygen reactive intermediates [68]. The profound matrix effect of ligand availability and naturally occurring Hg speciation results in a broad range of literature values for aquatic Hg diffusion coefficients (Fig. 1).

5. Hg-DGTs as monitoring tools

DGTs are a favored means to assess labile environmental Hg pools as they possess distinct advantages over other methods such as dialysis samplers and direct porewater extraction which are affected by collateral Hg adsorption onto the device, oxidation, and insufficient sample

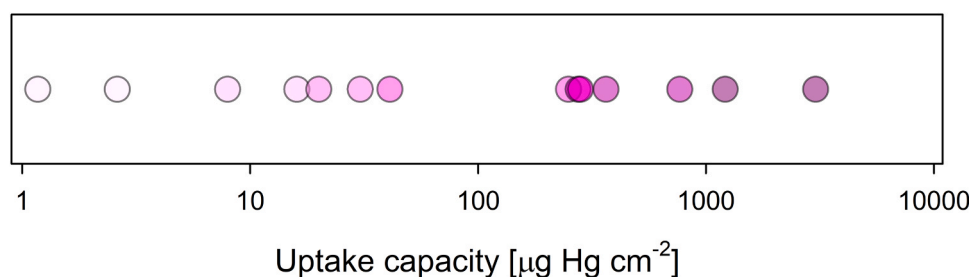


Fig. 3. Uptake capacities [$\mu\text{g Hg cm}^{-2}$] of diverse binding phases used in Hg-DGT research. Capacity data were found in 11 peer reviewed publications and were included if they were given in " $\mu\text{g Hg cm}^{-2}$ " or " $\mu\text{g Hg disk}^{-1}$ ". Data in the latter format was converted by consideration of the DGT sampler area (typically 3.14 cm^2). Data from 9 publications were finally included in this graph. Colouring was done for aesthetic purposes only. Raw data can be found in [Supplementary Material 2](#).

volume as highlighted by others [69]. Hg-DGTs have been evaluated under variable environmental conditions and are increasingly deployed in routine environmental monitoring to assess fluxes and infer available fractions. In a comparative performance study, Liu et al., [8] used dialysis samplers, direct measurement, and DGTs in a field study of MeHg profiles in wetlands. Their results suggest that, although spatio-temporal variability impacted all three methods, DGTs provide more accurate results which was attributed to their preconcentration effect and lowest LOD method. Further studies emphasize that the preconcentration of analytes and matrix robustness achieve low LODs thus overcoming the most common challenges posed by environmental Hg analysis.

Given their high analyte specificity, small footprint, and possibility for long-term deployment [18,20], the use of Hg-DGTs in relevant aquatic environmental studies is expected to further increase over the years (Fig. 4). Although originally devised as a standalone passive sampler, the DGT architecture and its underlying principle have also been used as a platform for novel Hg passive samplers such as sol-gel samplers [70], equilibrium passive samplers [71], or composited LPFG-DGTs [66]. Traditional long-period fiber grating (LPFG) sensors are optical fiber structures with periodically varying properties, which can change light transmission as a response to external effects. Although this sensor type is promising for continuous monitoring approaches, its intricate synthesis and delicate structure preclude it from direct environmental deployment. Tan et al., [66] sought to overcome this disadvantage, by embedding LPFG sensors in a DGT housing, which effectively shielded the brittle sensor from direct environmental forces and allowed for a near real-time assessment of Hg accumulation, a completely novel approach to the DGT concept [4,29,38,39,49].

6. Bioavailability studies

Bioavailability, the measure by which environmental substances are

available for biotic uptake, is a critical concept in risk assessment as it considers effective, and thus more biologically relevant, rather than total concentrations. In the case of Hg, labile, and therefore more bioavailable, species may only make up between 7% and 20–30% of tHg in marine and riverine sediment, respectively [30,45]. The accumulation and concentration of environmental contaminants by DGTs simulates the bioaccumulation process by which the concentration of a chemical in an organism becomes higher than its concentration in the surrounding medium. As DGTs can be deployed in both aquatic and wet sediment/soil systems, they offer a well-defined and standardized sampling medium in diffusion-driven uptake processes. There is a strong correlation between Hg uptake rates in organisms and DGTs, indicating the potential of the system for assessing Hg bioavailability in a specific environment. This has led to an increasing popularity of DGTs in comparative bioavailability studies as reviewed by Menegário et al. [3].

Although the uptake of Hg is dependent on its speciation, intake route and subsequent absorption efficiency, results obtained from DGT-deployment studies have shown a strong correlation with data gathered in studies with organism passively or actively ingesting Hg. Initial studies assessed the lability of organic and inorganic Hg compounds in estuarine sediments and their uptake by macroinvertebrates (amphipods, polychaetes, and clams) and DGTs [9,72]. Both studies reported a strong correlation between DGT and invertebrate uptake rates, thus affirming the applicability of DGTs as biomimetic proxies. Similar conclusions were drawn by Drygiannaki et al., [73], who used DGTs and clams to assess the impact of sediment recontamination due to storm-water discharges. Their results indicate total sediment concentrations to be bad indicators of overall contaminant availability. Finally, Nguyen et al., [74] assessed the impact of organic matter and pH on Hg uptake by *Eisenia fetida* and DGTs and determined that accumulation increased in both systems with decreasing OM content and increasing pH.

While Hg-DGT measurements correlate well with biota accumulation rates under both laboratory and field conditions, their applicability as

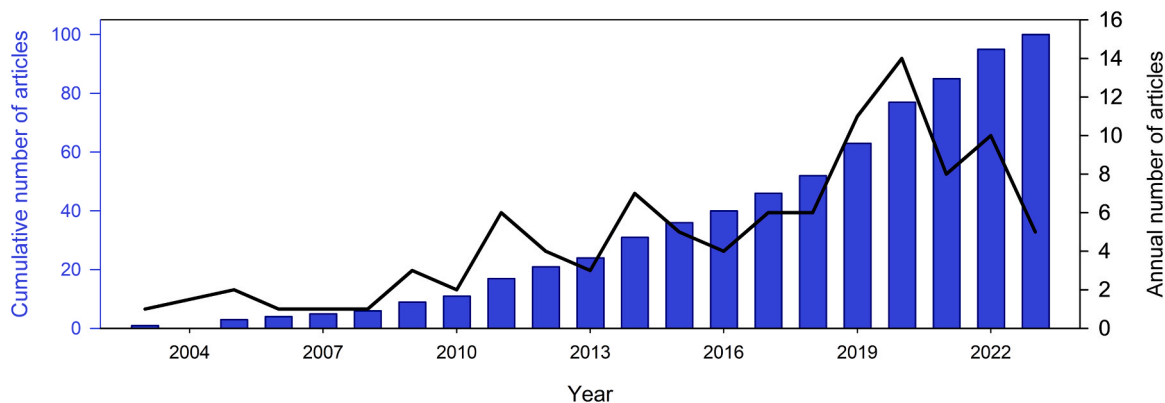


Fig. 4. Cumulative number of research articles on Hg-DGTs (vertical bars) as well as the annual number of published articles using Hg-DGTs (line) over the years of publications presently discussed. Cut-off date for data entry was the 20th of October 2023.

biomimetic proxies may be limited to small organisms with less complex uptake mechanisms. For larger aquatic organisms with differentiated modes of detoxification, individual tissue concentrations that are the result of diffusion driven Hg uptake, such as eyes, gills, scales, and skin correspond with DGT uptake rates, while metabolism driven excretion organs such as kidneys do not [75]. Additionally, the distribution of Hg is known to be organ dependent, thus making it apparent that the use of DGT derived data may not be adequate to extrapolate complex biotic accumulation processes.

The influence of organic complexation on bioavailability has also been reported in plant studies (e.g., [33,55]). In these studies, the presence of high organic carbon ligands resulted in an overall low release of soil-bound Hg and a low plant root availability and accumulation. DGT derived data additionally allows for an estimation of the effective concentration. In the context of environmental DGT studies this refers to a combined term expressing both the soil solution concentration and a resupply flux from the solid phase. Briefly, the effective concentration (C_E) is calculated as the ratio of the DGT-derived concentration (C_{DGT}) and a efflux parameter (R_{diff}) which includes the material porosity and analyte diffusivity.

$$C_E = \frac{C_{DGT}}{R_{diff}}$$

A complete derivation of this concept can be found elsewhere [76]. The advantage of this approach is the inclusion of the resupply flux term, which tackles the potential local analyte depletion in pore water extraction [31]. Initial studies defining this concept concluded a strong correlation between C_E and plant root uptake which has since been corroborated for Hg-DGTs [31,55,60]. In some cases, the C_E approach provided better approximation of root uptake than previously used methods such as sequential extraction and soil solution concentration [33].

It is known that some plants accumulate significant amounts of organomercurials, making them a significant pathway for human exposure. Liu et al., [15] used DGTs to predict the root uptake of MeHg by rice plants (*Oryza sativa*) reporting a strong correlation between measured available fractions of MeHg in soil pore water and concentrations in rice grains.

7. Methylmercury in various systems

Mercury can form organomercurials that show increased biotic resorption and toxicity because of the added organic moiety [7]. In contrast to inorganic Hg species, organomercurials can impede complexation by large organic ligands as their organic moiety inhibits the binding of chelating ligands [77] and empirical studies conclude that organic complexation does significantly impact MeHg accumulation by Hg-DGTs [9,68]. Reported log K values, indicating binding strength, for organic and inorganic Hg-HA complexes are significantly different; 12.15–16.9 [68,78] and 22.6–32.8 [79] respectively. MeHg is formed continuously through pelagic microbial methylation processes, rate controlled by abiotic and biotic parameters in both water column and sediment, making them highly spatiotemporally variable [8,9]. The most fundamental factors influencing MeHg variations and availability are Hg source and local microbiome [14], sediment water holding capacity [80], free sulfide and organic matter concentration [67], and sediment redox conditions [4]. Kinetic studies confirm a close correlation between DGT uptake and microbial Hg methylation rates, suggesting Hg-DGTs to be a good model to estimate microbial methylation potential [14,81]. Given their continuous analyte uptake, Hg-DGTs offer a fit for purpose approach in determining methylation rates without the need for low LOD analytical instrumentation [81].

Apart from the microbial generation of MeHg, which remains difficult to parametrize, its subsequent lability and bioavailability are a key factor in assessing its environmental risk. However, deployment in multi-phase systems, such as soil or sediment, is governed by the

analytes mobility in porous media, which may distort the interpretation of measured DGT concentrations. pH and conductivity [82], sediment depth [24], and organic matter content [80] greatly influence the exchangeable fraction and thus the lability of solute Hg, which is considered to be primarily bioavailable to biota [11].

MeHg continues to be a complex contaminant of concern, as its formation rates are location specific, and its analysis requires pre-processing and sensitive equipment. The microbiological mobilization of sequestered Hg into the water column and food web has been a declared risk factor in environmental risk assessments [55]. If deployed correctly, Hg-DGTs can provide a reliable means of quantifying effective MeHg concentrations as well as their fluxes in both laboratory and field experimental setups. Research into MeHg-specific DGTs, as demonstrated by Tafurt-Cardona et al., [42] may simplify future MeHg research by eliminating further processing pre-analysis.

8. Conclusion and future research direction

DGTs offer diverse experimental approaches to study the environmental fate of Hg, including new analytical techniques, speciation analysis, and lower LODs compared to direct measurement. Currently DGTs are a preferred method to estimate Hg fluxes and bioavailable fractions [15] and have a high predictive power for accumulation rates in comparison to conventional methods such as direct porewater Hg concentration and weak acid extraction [69,80]. Additionally, DGTs are easily deployed, allowing for routine environmental monitoring. Multidimensional stress tests demonstrate the rigidity of the DGT system and its components [83]. Nonetheless, significant parameters in both environmental Hg research as well as DGT development remain underexplored, necessitating further study to fully elucidate the environmental fate of Hg.

The nature, stability, and capacity of organic matter binding remain an increasingly investigated subject [49]. Additionally, while the effect of DOM-Hg stoichiometry on DGT accumulation has been studied [1], researchers point out that the quality rather than the quantity of organic ligands govern Hg bioavailability [68]. Approaches using restricted and open diffusive gels have delivered new insights into possible quantification of availability by discrimination between environmental Hg pools [33]. The presence of nanoparticles significantly alters DGT performance; the process of which is not yet fully understood [6]. These insoluble Hg compounds are currently not accumulated by DGTs at a constant rate, although they are known to be a bioavailable species to microorganisms [14]. Future comparative microbial bioavailability studies should explore the relationship between uptake rates of DGTs and the microorganisms involved [6]. Given the importance of organomercurials due to their bioaccumulation potential [9], Hg-DGT-based research should aim to optimize the accuracy of microbiological methylation measurement to match that achievable for measuring variations in the labile fractions.

CRedit authorship contribution statement

Lenka Mbadugha: Conceptualization, Project administration, Supervision, Writing – review & editing. **Graeme Paton:** Funding acquisition, Project administration, Resources, Supervision, Writing – review & editing. **Christoph Gade:** Conceptualization, Investigation, Visualization, Writing – original draft, Writing – review & editing.

Declaration of Competing Interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Christoph Gade reports financial support was provided by Chevron Corp. Christoph Gade reports a relationship with Chevron Corp that includes: funding grants. If there are other authors, they declare that they have no known competing financial interests or personal

relationships that could have appeared to influence the work reported in this paper.

Data availability

Data is available in the Supplementary Material

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.teac.2024.e00230](https://doi.org/10.1016/j.teac.2024.e00230).

References

- G.D. Bland, B. Rao, D. Reible, Evaluating the transport of Hg(II) in the presence of natural organic matter through a diffusive gradient in a thin-film passive sampler, *Sci. Total Environ.* 749 (2020) 141217, <https://doi.org/10.1016/j.scitotenv.2020.141217>.
- S. Marrugo-Madrid, M. Salas-Moreno, H. Gutiérrez-Mosquera, C. Salazar-Camacho, J. Marrugo-Negrete, S. Díez, Assessment of dissolved mercury by diffusive gradients in thin films devices in abandoned ponds impacted by small scale gold mining, *Environ. Res.* 208 (2022) 112633, <https://doi.org/10.1016/j.envres.2021.112633>.
- A.A. Menegário, L.N.M. Yabuki, K.S. Luko, P.N. Williams, D.M. Blackburn, Use of diffusive gradient in thin films for in situ measurements: a review on the progress in chemical fractionation, speciation and bioavailability of metals in waters, *Anal. Chim. Acta* 983 (2017) 54–66, <https://doi.org/10.1016/j.aca.2017.06.041>.
- M. Bretier, A. Dabrin, G. Billon, B. Mathon, C. Miège, M. Coquery, To what extent can the biogeochemical cycling of mercury modulate the measurement of dissolved mercury in surface freshwaters by passive sampling? *Chemosphere* 248 (2020) 126006 <https://doi.org/10.1016/j.chemosphere.2020.126006>.
- M. Reichstädter, P. Diviš, E. Abdulbur-Alfakhoury, Y. Gao, Simultaneous determination of mercury, cadmium and lead in fish sauce using diffusive gradients in thin-films technique, *Talanta* 217 (2020) 121059, <https://doi.org/10.1016/j.talanta.2020.121059>.
- A.L.-T. Pham, C. Johnson, D. Manley, H. Hsu-Kim, Influence of sulfide nanoparticles on dissolved mercury and zinc quantification by diffusive gradient in thin-film passive samplers, *Environ. Sci. Technol.* 49 (2015) 12897–12903, <https://doi.org/10.1021/acs.est.5b02774>.
- W.-L. Tang, Y.-R. Liu, W.-Y. Guan, H. Zhong, X.-M. Qu, T. Zhang, Understanding mercury methylation in the changing environment: Recent advances in assessing microbial methylators and mercury bioavailability, *Sci. Total Environ.* 714 (2020) 136827, <https://doi.org/10.1016/j.scitotenv.2020.136827>.
- J. Liu, X. Feng, G. Qiu, H. Yao, L. Shang, H. Yan, Intercomparison and applicability of some dynamic and equilibrium approaches to determine methylated mercury species in pore water, *Environ. Toxicol. Chem.* 30 (2011) 1739–1744, <https://doi.org/10.1002/etc.565>.
- O. Clarisse, G.R. Lotufo, H. Hintelmann, E.P.H. Best, Biomonitoring and assessment of monomethylmercury exposure in aqueous systems using the DGT technique, *Sci. Total Environ.* 416 (2012) 449–454, <https://doi.org/10.1016/j.scitotenv.2011.11.077>.
- W. Davison, H. Zhang, In situ speciation measurements of trace components in natural waters using thin-film gels, *Nature* 367 (1994) 546–548, <https://doi.org/10.1038/367546a0>.
- C.S. Eckley, C.C. Gilmour, S. Janssen, T.P. Luxton, P.M. Randall, L. Whalin, C. Austin, The assessment and remediation of mercury contaminated sites: a review of current approaches, *Sci. Total Environ.* 707 (2020) 136031, <https://doi.org/10.1016/j.scitotenv.2019.136031>.
- D.M. Templeton, F. Ariese, R. Cornelis, L.-G. Danielsson, H. Muntau, H.P. van Leeuwen, R. Lobinski, Guidelines for terms related to chemical speciation and fractionation of elements. Definitions, structural aspects, and methodological approaches (IUPAC Recommendations 2000), *Pure Appl. Chem.* 72 (2000) 1453–1470, <https://doi.org/10.1351/pac200072081453>.
- M. Farina, J.B.T. Rocha, M. Aschner, Mechanisms of methylmercury-induced neurotoxicity: evidence from experimental studies, *Life Sci.* 89 (2011) 555–563, <https://doi.org/10.1016/j.lfs.2011.05.019>.
- U. Ndu, G.A. Christensen, N.A. Rivera, C.M. Gionfriddo, M.A. Deshusses, D.A. Elias, H. Hsu-Kim, Quantification of mercury bioavailability for methylation using diffusive gradient in thin-film samplers, *Environ. Sci. Technol.* 52 (2018) 8521–8529, <https://doi.org/10.1021/acs.est.8b00647>.
- J. Liu, X. Feng, G. Qiu, C.W.N. Anderson, H. Yao, Prediction of methyl mercury uptake by rice plants (*Oryza sativa* L.) using the diffusive gradient in thin films technique, *Environ. Sci. Technol.* 46 (2012) 11013–11020, <https://doi.org/10.1021/es302187t>.
- Q. Cao, Z. Shao, D.K. Hensley, N.V. Lavrik, B.J. Venton, Influence of geometry on thin layer and diffusion processes at carbon electrodes, *Langmuir* 37 (2021) 2667–2676, <https://doi.org/10.1021/acs.langmuir.0c03315>.
- O. Sulpis, A. Mucci, B.P. Boudreau, M.A. Barry, B.D. Johnson, Controlling the diffusive boundary layer thickness above the sediment–water interface in a thermostated rotating-disk reactor, *Limnol. Oceanogr. Methods* 17 (2019) 241–253, <https://doi.org/10.1002/lom3.10309>.
- P. Diviš, M. Reichstädter, Y. Gao, M. Leermakers, J. Krikala, Determination of mercury in fish sauces by thermal decomposition gold amalgamation atomic absorption spectroscopy after preconcentration by diffusive gradients in thin films technique, *Food* 9 (2020) 1858, <https://doi.org/10.3390/foods9121858>.
- C. Fernández-Gómez, J.M. Bayona, S. Díez, Laboratory and field evaluation of diffusive gradient in thin films (DGT) for monitoring levels of dissolved mercury in natural river water, *Int. J. Environ. Anal. Chem.* 92 (2012) 1689–1698, <https://doi.org/10.1080/03067319.2011.581369>.
- S. Díez, R. Giaggio, Do biofilms affect the measurement of mercury by the DGT technique? Microcosm and field tests to prevent biofilm growth, *Chemosphere* 210 (2018) 692–698, <https://doi.org/10.1016/j.chemosphere.2018.07.047>.
- C. Pichette, H. Zhang, W. Davison, S. Sauve, Preventing biofilm development on DGT devices using metals and antibiotics, *Talanta* 72 (2007) 716–722, <https://doi.org/10.1016/j.talanta.2006.12.014>.
- E. Uher, H. Zhang, S. Santos, M.-H. Tusseau-Vuillemin, C. Gourlay-Francé, Impact of biofouling on diffusive gradient in thin film measurements in water, *Anal. Chem.* 84 (2012) 3111–3118, <https://doi.org/10.1021/ac2028535>.
- T. Wu, G. Wang, Y. Zhang, M. Kong, H. Zhao, Determination of mercury in aquatic systems by DGT device using thiol-modified carbon nanoparticle suspension as the liquid binding phase, *N. J. Chem.* 41 (2017) 10305–10311, <https://doi.org/10.1039/C7NJ02007D>.
- P. Diviš, M. Leermakers, H. Dočekalová, Y. Gao, Mercury depth profiles in river and marine sediments measured by the diffusive gradients in thin films technique with two different specific resins, *Anal. Bioanal. Chem.* 382 (2005) 1715–1719, <https://doi.org/10.1007/s00216-005-3360-8>.
- C. Fernández-Gómez, B. Dimock, H. Hintelmann, S. Díez, Development of the DGT technique for Hg measurement in water: comparison of three different types of samplers in laboratory assays, *Chemosphere* 85 (2011) 1452–1457, <https://doi.org/10.1016/j.chemosphere.2011.07.080>.
- Y. Gao, E. De Canck, M. Leermakers, W. Baeyens, P. Van Der Voort, Synthesized mercaptopropyl nanoporous resins in DGT probes for determining dissolved mercury concentrations, *Talanta* 87 (2011) 262–267, <https://doi.org/10.1016/j.talanta.2011.10.012>.
- N. Fatin-Rouge, A. Milon, J. Bufflé, R.R. Goulet, A. Tessier, Diffusion and partitioning of solutes in agarose hydrogels: the relative influence of electrostatic and specific interactions, *J. Phys. Chem. B* 107 (2003) 12126–12137, <https://doi.org/10.1021/jp0303164>.
- W. Davison, H. Zhang, Progress in understanding the use of diffusive gradients in thin films (DGT) – back to basics, *Environ. Chem.* 9 (1) (2012), <https://doi.org/10.1021/EN11084>.
- M. Ren, Y. Wang, S. Ding, L. Yang, Q. Sun, L. Zhang, Development of a new diffusive gradient in the thin film (DGT) method for the simultaneous measurement of CH 3 Hg + and Hg 2+, *N. J. Chem.* 42 (2018) 7976–7983, <https://doi.org/10.1039/C8NJ00211H>.
- H. Dočekalová, P. Diviš, Application of diffusive gradient in thin films technique (DGT) to measurement of mercury in aquatic systems, *Talanta* 65 (2005) 1174–1178, <https://doi.org/10.1016/j.talanta.2004.08.054>.
- M. Turull, C. Fontàs, S. Díez, Diffusive gradient in thin films with open and restricted gels for predicting mercury uptake by plants, *Environ. Chem. Lett.* 17 (2019) 1353–1358, <https://doi.org/10.1007/s10311-019-00864-2>.
- H. Zhang, W. Davison, Diffusional characteristics of hydrogels used in DGT and DET techniques, *Anal. Chim. Acta* 398 (1999) 329–340, [https://doi.org/10.1016/S0003-2670\(99\)00458-4](https://doi.org/10.1016/S0003-2670(99)00458-4).
- M. Turull, C. Fontàs, S. Díez, Conventional and novel techniques for the determination of Hg uptake by lettuce in amended agricultural peri-urban soils, *Sci. Total Environ.* 668 (2019) 40–46, <https://doi.org/10.1016/j.scitotenv.2019.02.244>.
- L.S. Ettre, Appendix 12a. Nomenclature | Chromatography (IUPAC Recommendations 1993), in: *Encyclopedia of Separation Science*, Elsevier, 1993: pp. 4712–4753, <https://doi.org/10.1016/B0-12-226770-2/09048-7>.
- Y.S. Hong, E. Rifkin, E.J. Bouwer, Combination of diffusive gradient in a thin film probe and IC-ICP-MS for the simultaneous determination of CH 3 Hg + and Hg 2+ inoxic water, *Environ. Sci. Technol.* 45 (2011) 6429–6436, <https://doi.org/10.1021/es200398d>.
- I. Cattani, S. Spalla, G.M. Beone, A.A.M. Del Re, R. Boccelli, M. Trevisan, Characterization of mercury species in soils by HPLC-ICP-MS and measurement of fraction removed by diffusive gradient in thin films, *Talanta* 74 (2008) 1520–1526, <https://doi.org/10.1016/j.talanta.2007.09.029>.
- O. Clarisse, H. Hintelmann, Measurements of dissolved methylmercury in natural waters using diffusive gradients in thin film (DGT), *J. Environ. Monit.* 8 (2006) 1242, <https://doi.org/10.1039/b614560d>.
- G. Elias, S. Díez, H. Zhang, C. Fontàs, Development of a new binding phase for the diffusive gradients in thin films technique based on an ionic liquid for mercury determination, *Chemosphere* 245 (2020), <https://doi.org/10.1016/j.chemosphere.2019.125671>.

- [39] M. Reichstädter, Y. Gao, P. Diviš, T. Ma, C. Gaulier, M. Leermakers, Cysteine-modified silica resin in DGT samplers for mercury and trace metals assessment, *Chemosphere* 263 (2021) 128320, <https://doi.org/10.1016/j.chemosphere.2020.128320>.
- [40] S. Marrugo-Madrid, C. Fontàs, G. Kurt, C. Salazar-Camacho, M. Salas-Moreno, H. Gutiérrez-Mosquera, J. Marrugo-Negrete, S. Díez, Benzoylthiourea based polymers as new binding agents for diffusive gradients in thin films technique in labile mercury determination in freshwaters, *Environ. Technol. Innov.* 28 (2022) 102911, <https://doi.org/10.1016/j.eti.2022.102911>.
- [41] K. Pi, J. Liu, P. Van Cappellen, Direct measurement of aqueous mercury(II): combining DNA-based sensing with diffusive gradients in thin films, *Environ. Sci. Technol.* 54 (2020) 13680–13689, <https://doi.org/10.1021/acs.est.0c03870>.
- [42] M. Tafurt-Cardona, C.E. Eismann, C.A. Suárez, A.A. Menegário, K. Silva Luko, É. Sargentini Junior, In situ selective determination of methylmercury in river water by diffusive gradient in thin films technique (DGT) using baker's yeast (*Saccharomyces cerevisiae*) immobilized in agarose gel as binding phase, *Anal. Chim. Acta* 887 (2015) 38–44, <https://doi.org/10.1016/j.aca.2015.07.035>.
- [43] G.F. Pescim, G. Marrach, M. Vannuci-Silva, L.A. Souza, A.A. Menegário, Speciation of lead in seawater and river water by using *Saccharomyces cerevisiae* immobilized in agarose gel as a binding agent in the diffusive gradients in thin films technique, *Anal. Bioanal. Chem.* 404 (2012) 1581–1588, <https://doi.org/10.1007/s00216-012-6248-4>.
- [44] A.A. Menegário, P.S. Tonello, S.F. Durrant, Use of *Saccharomyces cerevisiae* immobilized in agarose gel as a binding agent for diffusive gradients in thin films, *Anal. Chim. Acta* 683 (2010) 107–112, <https://doi.org/10.1016/j.aca.2010.10.016>.
- [45] P. Diviš, M. Kadlecová, B. Ouddane, Mercury distribution in the Deûle River (Northern France) measured by the diffusive gradients in thin films technique and conventional methods, *Arch. Environ. Contam. Toxicol.* 70 (2016) 700–709, <https://doi.org/10.1007/s00244-015-0231-y>.
- [46] C. Fernández-Gómez, J.M. Bayona, S. Díez, Comparison of different types of diffusive gradient in thin film samplers for measurement of dissolved methylmercury in freshwaters, *Talanta* 129 (2014) 486–490, <https://doi.org/10.1016/j.talanta.2014.06.025>.
- [47] L. Marziali, L. Valsecchi, Mercury bioavailability in fluvial sediments estimated using chironomus riparius and diffusive gradients in thin-films (DGT), *Environments* 8 (2021) 7, <https://doi.org/10.3390/environments8020007>.
- [48] P. Pelcová, H. Dočekalová, A. Kleckerová, Determination of mercury species by the diffusive gradient in thin film technique and liquid chromatography - atomic fluorescence spectrometry after microwave extraction, *Anal. Chim. Acta* 866 (2015) 21–26, <https://doi.org/10.1016/j.aca.2015.01.043>.
- [49] P. Pelcová, H. Dočekalová, A. Kleckerová, Development of the diffusive gradient in thin films technique for the measurement of labile mercury species in waters, *Anal. Chim. Acta* 819 (2014) 42–48, <https://doi.org/10.1016/j.aca.2014.02.013>.
- [50] A. Ridošková, A. Pelfréne, F. Douay, P. Pelcová, V. Smolíková, V. Adam, Bioavailability of mercury in contaminated soils assessed by the diffusive gradient in thin film technique in relation to uptake by *Miscanthus × giganteus*, *Environ. Toxicol. Chem.* 38 (2019) 321–328, <https://doi.org/10.1002/etc.4318>.
- [51] P. Pelcová, I. Zouharová, A. Ridošková, V. Smolíková, Evaluation of mercury availability to pea parts (*Pisum sativum* L.) in urban soils: comparison between diffusive gradients in thin films technique and plant model, *Chemosphere* 234 (2019) 373–378, <https://doi.org/10.1016/j.chemosphere.2019.06.076>.
- [52] P. Pelcová, R. Kopp, A. Ridošková, J. Grmela, D. Štěrbová, Evaluation of mercury bioavailability and phytoaccumulation by means of a DGT technique and of submerged aquatic plants in an aquatic ecosystem situated in the vicinity of a cinnabar mine, *Chemosphere* (2021) 132545, <https://doi.org/10.1016/j.chemosphere.2021.132545>.
- [53] P. Pelcová, A. Ridošková, J. Hrachovinová, J. Grmela, Fractionation analysis of mercury in soils: a comparison of three techniques for bioavailable mercury fraction determination, *Environ. Toxicol. Chem.* 39 (2020) 1670–1677, <https://doi.org/10.1002/etc.4797>.
- [54] P. Pelcová, P. Vičarová, A. Ridošková, H. Dočekalová, R. Kopp, J. Mareš, E. Poštulková, Prediction of mercury bioavailability to common carp (*Cyprinus carpio* L.) using the diffusive gradient in thin film technique, *Chemosphere* 187 (2017) 181–187, <https://doi.org/10.1016/j.chemosphere.2017.08.097>.
- [55] P. Pelcová, A. Ridošková, J. Hrachovinová, J. Grmela, Evaluation of mercury bioavailability to vegetables in the vicinity of cinnabar mine, *Environ. Pollut.* 283 (2021), <https://doi.org/10.1016/j.envpol.2021.117092>.
- [56] Y. Hong, N.P. Dan, E. Kim, H.J. Choi, S. Han, Application of diffusive gel-type probes for assessing redox zonation and mercury methylation in the Mekong Delta sediment, *Environ. Sci.: Process. Impacts* 16 (2014) 1799–1808, <https://doi.org/10.1039/c3em00728f>.
- [57] S. Noh, Y. Kim, H. Kim, K. Seok, M. Park, M.X. Bailon, Y. Hong, The performance of diffusive gradient in thin film probes for the long-term monitoring of trace level total mercury in water, *Environ. Monit. Assess.* 192 (2020) 66, <https://doi.org/10.1007/s10661-019-7966-2>.
- [58] C. Destro Colaço, L. Nozomi Marques Yabuki, A. Marta Rolisola, A. Antonio Menegário, E. De Almeida, C. Alfredo Suárez, Y. Gao, W.T. Corns, V.F. Do Nascimento Filho, Determination of mercury in river water by diffusive gradients in thin films using P81 membrane as binding layer, *Talanta* 129 (2014) 417–421, <https://doi.org/10.1016/j.talanta.2014.05.025>.
- [59] P. Diviš, R. Szkandera, L. Brulík, H. Dočekalová, P. Matúš, M. Bujdoš, Application of new resin gels for measuring mercury by diffusive gradients in a thin-films technique, *Anal. Sci.* 25 (2009) 575–578, <https://doi.org/10.2116/analsci.25.575>.
- [60] A. Ridošková, A. Ridošková, H. Dočekalová, P. Pelcová, Prediction of cadmium, lead and mercury availability to plants: comparison between diffusive gradient in thin films technique measurement and soil grown plants, *J. Elem.* 22 (2016) 349–363, <https://doi.org/10.5601/jelem.2016.21.2.1075>.
- [61] B. Muresan, E. Metzger, D. Jézéquel, D. Cossa, A multiscale study of mercury transformations and dynamics at the chemocline of the Petit-Saut tropical reservoir (French Guiana), *Sci. Total Environ.* 630 (2018) 1401–1412, <https://doi.org/10.1016/j.scitotenv.2018.02.280>.
- [62] H. Yao, Y. Zhao, C.J. Lin, F. Yi, X. Liang, X. Feng, Development of a novel composite resin for dissolved divalent mercury measurement using diffusive gradients in thin films, *Chemosphere* 251 (2020) 126231, <https://doi.org/10.1016/j.chemosphere.2020.126231>.
- [63] M. Turull, G. Elias, C. Fontàs, S. Díez, Exploring new DGT samplers containing a polymer inclusion membrane for mercury monitoring, *Environ. Sci. Pollut. Res.* 24 (2017) 10919–10928, <https://doi.org/10.1007/s11356-016-6813-z>.
- [64] R. Szkandera, H. Dočekalová, M. Kadlecová, J. Travníková, P. Diviš, A sorption gel with titanium dioxide for mercury determination by the technique of diffusion gradient in thin film, *Chem. Listy* 107 (2013) 160–164.
- [65] H. Lin, M. Li, Y. Zhu, W. Lan, Q. Feng, S. Ding, T. Li, Y. Wang, Y. Duan, J. Wei, M. Li, Development and validation of the DGT technique using the novel cryogel for measuring dissolved Hg(II) in the estuary, *Mar. Environ. Res.* 182 (2022) 105773, <https://doi.org/10.1016/j.marenvres.2022.105773>.
- [66] S.-Y. Tan, S.-C. Lee, H. Kuramitz, F. Abd-Rahman, A novel hybrid long period fiber grating-diffusive gradient in thin films sensor system for the detection of mercury (II) ions in water, *Opt. (Stuttg.)* 194 (2019) 163040, <https://doi.org/10.1016/j.jlloe.2019.163040>.
- [67] O. Clarisse, D. Foucher, H. Hintelmann, Methylmercury speciation in the dissolved phase of a stratified lake using the diffusive gradient in thin film technique, *Environ. Pollut.* 157 (2009) 987–993, <https://doi.org/10.1016/j.envpol.2008.10.012>.
- [68] C. Fernández-Gómez, J.M. Bayona, S. Díez, Diffusive gradients in thin films for predicting methylmercury bioavailability in freshwaters after photodegradation, *Chemosphere* 131 (2015) 184–191, <https://doi.org/10.1016/j.chemosphere.2015.02.060>.
- [69] R. Mason, N. Bloom, S. Cappellino, G. Gill, J. Benoit, C. Dobbs, Investigation of Porewater Sampling Methods for Mercury and Methylmercury, *Environ. Sci. Technol.* 32 (1998) 4031–4040, <https://doi.org/10.1021/es980377t>.
- [70] Y. Zhou, T. Stotesbury, B. Dimock, A. Vreugdenhil, H. Hintelmann, Novel silica sol-gel passive sampler for mercury monitoring in aqueous systems, *Chemosphere* 90 (2013) 323–328, <https://doi.org/10.1016/j.chemosphere.2012.07.022>.
- [71] J.P. Sanders, A. McBurney, C.C. Gilmour, G.E. Schwartz, S. Washburn, S.B. Kane Driscoll, S.S. Brown, U. Ghosh, Development of a novel equilibrium passive sampling device for methylmercury in sediment and soil porewaters, *Environ. Toxicol. Chem.* 39 (2020) 323–334, <https://doi.org/10.1002/etc.4631>.
- [72] A. Amirbahman, D.I. Massey, G. Lotufo, N. Steenhaut, L.E. Brown, J. M. Biedenbach, V.S. Magar, Assessment of mercury bioavailability to benthic macroinvertebrates using diffusive gradients in thin films (DGT), *Environ. Sci. Process Impacts* 15 (2013) 2104, <https://doi.org/10.1039/c3em00355h>.
- [73] I. Drygiannaki, M. Bejar, D.D. Reible, J.A. Dawson, B. Rao, N.T. Hayman, G. H. Rosen, M.A. Colvin, Assessing biota accumulation due to contamination of sediments by storm water heavy metals, *Environ. Toxicol. Chem.* 39 (2020) 2475–2484, <https://doi.org/10.1002/etc.4862>.
- [74] V. Huu Nguyen, S.K. Yee, Y. Hong, D.H. Moon, S. Han, Predicting mercury bioavailability in soil for earthworm *Eisenia fetida* using the diffusive gradients in thin films technique, *Environ. Sci. Pollut. Res.* 26 (2019) 19549–19559, <https://doi.org/10.1007/s11356-019-05180-4>.
- [75] P. Pelcová, P. Vičarová, A. Ridošková, H. Dočekalová, R. Kopp, J. Mareš, E. Poštulková, Prediction of mercury bioavailability to common carp (*Cyprinus carpio* L.) using the diffusive gradient in thin film technique, *Chemosphere* 187 (2017) 181–187, <https://doi.org/10.1016/j.chemosphere.2017.08.097>.
- [76] H. Zhang, F.-J. Zhao, B. Sun, W. Davison, S.P. McGrath, A new method to measure effective soil solution concentration predicts copper availability to plants, *Environ. Sci. Technol.* 35 (2001) 2602–2607, <https://doi.org/10.1021/es000268q>.
- [77] I. Cattani, H. Zhang, G.M. Beone, A.A.M. Del Re, R. Bocelli, M. Trevisan, The role of natural purified humic acids in modifying mercury accessibility in water and soil, *J. Environ. Qual.* 38 (2009) 493–501, <https://doi.org/10.2134/jeq2008.0175>.
- [78] H. Hintelmann, P.M. Welbourn, R.D. Evans, Measurement of complexation of methylmercury(II) compounds by freshwater humic substances using equilibrium dialysis, *Environ. Sci. Technol.* 31 (1997) 489–495, <https://doi.org/10.1021/es960318k>.
- [79] A. Khwaja, P. Bloom, P.L. Brezonik, Binding constants of divalent mercury (Hg²⁺) in soil humic acids and soil organic matter, *Environ. Sci. Technol.* 40 (2006) 844–849, <https://doi.org/10.1021/es051805c>.
- [80] V.H. Nguyen, J. young Seon, G.H. Qasim, H. Fareed, Y. Hong, S. Han, Applying the diffusive gradient in thin films method to assess soil mercury bioavailability to the earthworm *Eisenia fetida*, *Environ. Sci. Pollut. Res.* 28 (2021) 39840–39852, <https://doi.org/10.1007/s11356-021-13344-4>.
- [81] O. Clarisse, B. Dimock, H. Hintelmann, E.P.H. Best, Predicting net mercury methylation in sediments using diffusive gradient in thin films measurements, *Environ. Sci. Technol.* 45 (2011) 1506–1512, <https://doi.org/10.1021/es102730n>.
- [82] M. Bretier, A. Dabrin, F. Bessueille-Barbier, M. Coquery, The impact of dam flushing event on dissolved trace elements concentrations: coupling integrative passive sampling and discrete monitoring, *Sci. Total Environ.* 656 (2019) 433–446, <https://doi.org/10.1016/j.scitotenv.2018.11.303>.
- [83] Y. Wang, S. Ding, M. Gong, S. Xu, W. Xu, C. Zhang, Diffusion characteristics of agarose hydrogel used in diffusive gradients in thin films for measurements of cations and anions, *Anal. Chim. Acta* 945 (2016) 47–56, <https://doi.org/10.1016/j.aca.2016.10.003>.