# Benzoylthiourea based polymers as new binding agents for diffusive gradients in thin films technique in labile mercury determination in freshwaters

Siday Marrugo-Madrid [a], Clàudia Fontàs [b], Gülşah Kurt [c], Carlos Salazar-Camacho [d], Manuel Salas-Moreno [d], Harry Gutierrez-Mosquera [d], Jose Marrugo-Negrete [e], Sergi Díez [a],*

[a] Environmental Chemistry Department, Institute of Environmental Assessment and Water Research, IDAEA-CSIC, E-08034, Barcelona, Spain
[b] Department of Chemistry, University of Girona, C/Maria Aurèlia Capmany 69, 17003 Girona, Spain
[c] Department of Chemistry, Faculty of Arts and Sciences, Aksaray University, Aksaray, Turkey
[d] Faculty of Natural Sciences, Department of Biology, Technological University of Chocó, Quibdó, Colombia
[e] Department of Chemistry, Faculty of Sciences, University of Córdoba, Montería, Colombia

## ARTICLE INFO

## ABSTRACT

In this study, the diffusive gradient in thin film (DGT) has been developed using three new materials derived from benzoylthiourea (PBTU, BTP1 and BTP2) for the determination of bioavailable mercury (Hg). The efficiency of these DGT devices was compared with the well-established 3-mercaptopropyl functionalized silica gel (3MFS) in laboratory and field conditions. It was found that PBTU lacked of consistency for handling and assembling in the DGT device, whereas the other two polymers provided mechanically stable binding gels and extracted satisfactorily Hg. However, BTP2 showed no correlation between Hg uptake and Hg present in the aqueous solution, and therefore, BTP1 gels was chosen as the binding layer used for DGT technique. The calculated diffusion coefficient of DGT-BTP1 was $4.0 \times 10^{-6}$ cm$^2$ s$^{-1}$ at 25 °C in 0.8 mm thick diffusion layer and 2.3% w/v of material in gel, whereas for DGT-3MFS, the D value was $9.1 \times 10^{-6}$ cm$^2$ s$^{-1}$. Moreover, it was found that neither the pH (range 4.5 – 9.5) nor the ionic strength (range 0.005–0.1 mol L$^{-1}$) significantly affected the binding behavior of Hg ($p > 0.05$). Finally, the DGT-BTP1 devices were successfully used for in-situ measurements of Hg in Quito River (Colombia), impacted by artisanal gold mining, and were compared with DGT-3MFS. Results showed a good performance with values of the labile Hg concentration between 5 to 8% of the total Hg in water. This study demonstrates that benzoylthiourea based DGT is a useful tool for in situ monitoring of Hg in freshwaters.
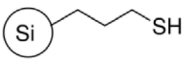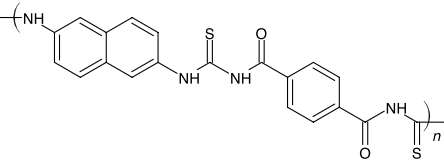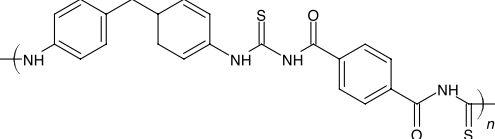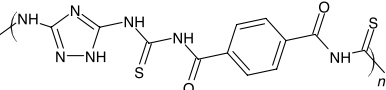
## 1. Introduction

Despite the fact that mercury (Hg) is one of the main pollutants in the world and its use has been discouraged since the Minamata Convention on Mercury (UNEP, 2017), this toxic metal is still widely used in artisanal and small-scale gold

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* Corresponding author.
  *E-mail address:* sergi.diez@idaea.csic.es (S. Díez).

**Table 1**
Chemical structures of the materials used in this study.

| Name | Acronym | Chemical structure | Binding gel composition (% w/v) |
|---|---|---|---|
| 3-Mercaptopropyl functionalized silica | 3MFS | | 12 |
| Poly(4-((2-aminonaphthalene-6-carbonothioyl) carbamoyl) benzoyl isothiocyanate) | BTP1 | | 2.3 |
| Poly(4-((4-(4-aminobenzyl) phenylcarbonothioyl) carbamoyl) benzoyl isothiocyanate) | BTP2 | | 2.3 |
| Polybenzoylthiourea polymer | PBTU | | – |

mining (ASGM) in which Hg amalgamation is used to extract gold from ore. As it has been reported recently (Marrugo-Madrid et al., 2022), to fulfill the objectives of this treaty, there is a need to perform sampling campaigns to monitor Hg contamination in remote ASGM areas (Palacios-Torres et al., 2018; Gutiérrez-Mosquera et al., 2021; Salazar-Camacho et al., 2021, 2017) where the diffusive gradient in thin-films (DGT) technique (Davison and Zhang, 1994) is useful.

The total concentration of Hg is the value commonly used to regulate contamination; however, measuring only the total concentration does not give a useful basis for the assessment of risks because toxicity is related to the concentration of bioavailable metal rather than the total concentration (Marrugo-Negrete et al., 2017; Turull et al., 2019).

The effectiveness of the application of the DGT technique as an analytical method for the determination of bioavailable Hg has been widely demonstrated in previous studies (Clarisse and Hintelmann, 2006; Diviš et al., 2010; Colaço et al., 2014; Fernández-Gómez et al., 2014; Turull et al., 2018; Bratkič et al., 2019; Elias et al., 2020; Marrugo-Madrid et al., 2022). This is based on the use of easily transportable passive sampling devices, which contain a binding layer (resin gel), a diffusion gel and a filter membrane, which protects the gels from the outside. Hg ions, due to a concentration gradient, diffuse through the filter membrane and diffusion gel, until they reach the binding layer, where they accumulate during a certain deployment time.

The 3-mercaptopropyl functionalized silica gel (3MFS) has been one of the most used resins for the preparation of binding layers, because its thiol groups have a high affinity towards Hg (Shade and Hudson, 2005; Clarisse and Hintelmann, 2006; Gao et al., 2011). However, it is important to continue evaluating the selective capacity of other materials with a high affinity for Hg, which could be less expensive and easily incorporated into the DGT technique, such as those derived from thiourea. Kurt (2021, 2019) synthesized polymeric compounds derived from benzoylthiourea that proved to have high thermal stability, resistance to external physical effects and capacity to Hg uptake.

Benzoylthioureas, due to their strong donor groups (carbonyl and thioamide), are promising as coordinating agents. Their ability to coordinate oxygen and sulfur atoms with metal has made them effective in analytical and environmental applications (Fontàs et al., 2005) (Table 1). When we compare the synthesized benzoylthiourea polymers, we observe that the naphthalene structure in BTP1 increases the stability of the complex and the acidity of the ligand, and the triazole heterocycle in PBTU increases the solubility of the polymer. The surfaces of all three polymers are homogeneous and dense (Kurt, 2021, 2019).

For the first time, this study evaluates the possible inclusion of different compounds derived from benzoylthiourea in a DGT passive sampling device. Therefore, the efficiency of DGT devices made of new polymeric materials was compared with 3MFS binding gels in laboratory conditions and in the field. Likewise, an evaluation of the effects of ionic strength and pH on the Hg uptake capacity of the binding layers obtained with the new materials was also carried out. Moreover, since there is a great interest to determine Hg bioavailability in rivers impacted by ASGM, we also evaluated their efficiency in the field.

## 2. Materials and methods

### 2.1. Reagents, gel preparation and mounting of DGT devices

The reagents, gel preparation and mounting of in-house manufactured DGT devices with 3MFS have been described in previous studies (Fernández-Gómez et al., 2011; Turull et al., 2017; Marrugo-Madrid et al., 2022). The different polymers

investigated as binding phase were: Poly (4-((2-aminonaphthalene-6-carbonothioyl) carbamoyl) benzoyl isothiocyanate) (BTP1), Poly (4-((4-(4-aminobenzyl) phenylcarbonothioyl) carbamoyl) benzoyl isothiocyanate) (BTP2) and a polyben-zoylthiourea polymer (PBTU). These polymers were synthesized as described by Kurt (2021, 2019). Prior to their used, they were sieved at 0.125 mm. Table 1 shows the chemical characteristics and the binding gel composition for each compound. The diffusive gels were made with polyacrylamide (0.8 mm thickness). Finally, a nylon filter membrane (0.45 $\mu$m pore size) was used as the outer layer to protect the gels. The piston types with an exposure area of 3.14 cm$^2$ were used (DGT Research Ltd., UK) for assembling the DGT devices. All reagents used were of analytical grade and the solutions were prepared with Milli-Q water (18.25 M$\Omega$ cm).

## 2.2. Determination of the diffusion coefficient

The general procedure used to calculate the diffusion coefficients is described by Fernández-Gómez et al. (2011). In laboratory experiments, 16 DGT devices were deployed in 4 L of a Hg(II) solution at 2 $\mu$g L$^{-1}$ in 0.01 M NaCl, in order to guarantee a constant ionic strength, and two DGTs were retrieved at different times (2 h, 4 h, 8 h, 10 h, 20 h, 30 h, 60 h and 72 h). The initial pH of the solution was 6.8, the temperature was 27 $\pm$ 0.5 °C, and the stir was constant throughout the experiment. Subsequently, the DGT devices were removed and dismantled to extract the binding layers and to determine the mass of Hg on a direct Hg analyzer DMA-80 Evo Milestone. Similarly, the concentrations of Hg(II) solution subsamples, withdrawn at the same time as each DGT device, were also determined with the DMA-80 Evo Milestone.

According Fick's law, the Hg(II) concentration in the solution ($C_{DGT}$) is equivalent to the relationship between the mass of Hg accumulated on binding layer (M), the diffusive layer thickness ($\Delta$g), the diffusion coefficient of the labile Hg (D), the area of exposed surface (A) and the deployment time (t):

$$C_{DGT} = \frac{M\Delta g}{DAt} \tag{1}$$

D can be calculated from the slope of the relationship between Hg accumulated by the DGT devices and the deployment time by Eq. (1). At different temperatures, it is possible to determine D using Stoke-Einstein's equation (Zhang and Davison, 1995).

The entire analytical procedure was validated by analysis of certified reference material (DOLT-5, dogfish liver) samples from the National Research Council of Canada (NRCC). The Hg concentration found in the DOLT-5 was 0.38 $\pm$ 0.10 mg kg$^{-1}$ ($n = 5$), which was in good agreement to the certified value (0.44 $\pm$ 0.18 mg kg$^{-1}$) (mean recovery 86%). This reference material was analyzed in triplicate at the beginning and ends of each set of (usually 10) samples, to ensure the calibration of the instrument during the study. The detection limit (LOD) (0.2 ng mL$^{-1}$ of Hg) was calculated based a series of blank samples.

## 2.3. Effect of ionic strength and pH on the Hg uptake

DGT devices were deployed in triplicate in Hg(II) solutions at 3 $\mu$g L$^{-1}$ with NaCl at different concentrations: 0.005, 0.01 and 0.1 M, in order to evaluate the effect of ionic strength on Hg(II) uptake. The mean initial pH of the solutions was 4.50 $\pm$ 0.03, and the mean temperature was 21.5 $\pm$ 0.5 °C. Constant stirring was maintained during the 6 h that DGTs were immersed in the solutions.

To evaluate the effect of pH, the DGT devices were again deployed in triplicate in Hg(II) solutions at 3 $\mu$g L$^{-1}$ with 0.01M NaCl, and different initial pH (4.5, 6.5, 8.0 and 9.5) previously adjusted with NaOH or HNO$_3$, with a pH-meter GLP 22 Crison. The mean temperature of the solutions was 21.5 $\pm$ 0.5 °C, and constant stirring was maintained during 6 h. All DGT devices were removed and dismantled to extract the binding layers and determine the mass of Hg on a direct Hg analyzer DMA-80 Evo Milestone.

## 2.4. Deployment of the DGT devices in field

The DGT devices manufactured with either 3MFS or BTP1 binding layers were deployed in triplicate at 6 stations in Quito River, tributary of the Atrato River, Colombia (Marrugo-Madrid et al., 2022). Field deployment time was around 92 h, and temperature, pH, dissolved oxygen (DO), conductivity, total dissolved solids (TDS), turbidity, and total mercury concentration in water were determined at the start and end of each deployment with an YSI Pro2030 multiparameter. Furthermore, at each sampling site, a freshwater sample was taken, and 3 DGT devices from the same batch were chosen as traveling blank or "control".

After recovering the DGT devices, they were rinsed with Milli-Q water and returned to individual polythene bags for its conservation. All samples were preserved, transported to the laboratory and refrigerated at 4 °C until analyzed. In Colombia, also a DMA-80 Evo Milestone was used for the determination of the Hg concentration in binding layers from DGT devices and a certified reference material from International Atomic Energy Agency (IAEA-336 Lichen Hg: 0.16–0.24 mg kg$^{-1}$), and a Liquid Mercury Analyzer RA-915M/RP92 Lumex was used in the measurement of Hg in freshwater samples.
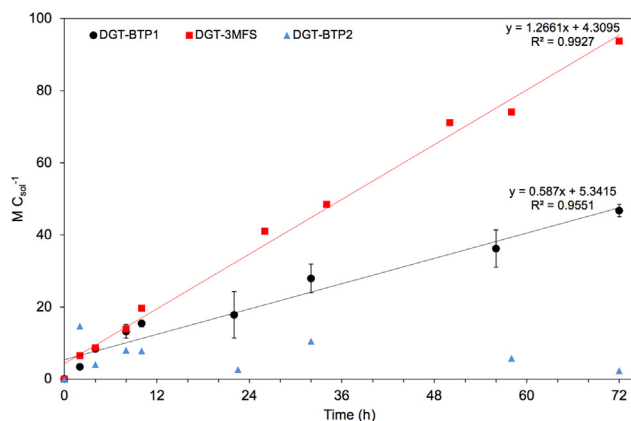
**Fig. 1.** Comparison between the relations of mass of Hg in the binding gel (M) and concentration in the solution ($C_{sol}$) vs. the time for BTP1, BTP2 and 3MFS DGT devices.

## 3. Results and discussion

### 3.1. Comparison of different benzoylthiourea derivative materials

Three different benzoylthiourea derivative materials were tested to prepare stable binding layers. The main difference between PBTU, BTP1, and BTP2 polymers (Table 1) is the triazole unit in the chemical structure of PBTU, which makes it soluble in polar organic solvents, including DMSO and DMF, in contrast with BTP1 and BTP2, which are insoluble in any organic solvent (Kurt, 2021).

The manufacture of the binding gels with three new polymeric materials BTP1, BTP2 and PBTU was done in a similar manner as for DGT-3MFS, according to Fernández-Gómez et al. (2011). In the original procedure, the binding gel of DGT-3MFS is mixed with a polyacrylamide gel solution at a ratio of 12% w/v. Nevertheless, applying the same w/v ratio to the new polymeric materials, it was not possible to obtain stable gels with a similar shape to those of DGT-3MFS. Then, we reduced the amount of mass from the new polymeric materials until we found satisfactory results with the ratio of 2.3% w/v for BTP1 and BTP2. For PBTU, possibly due to its high solubility in organic solvents (Kurt, 2021), it was not possible to obtain a gel with an adequate texture and thickness for its subsequent handling and inclusion in the DGT device, so it was discarded for the following tests (Figure S1).

### 3.2. Diffusion coefficient of Hg in benzoylthiourea derivative gels discs

Manufactured DGT devices must be calibrated under controlled conditions of temperature, pH and concentration of both Hg(II) and NaCl in solution, in order to determine their diffusion coefficients by applying Fick's Law (Eq. (1)). According the Stoke-Einstein's equation (Zhang and Davison, 1995), D values at 25 °C for DGT-BTP1 and DGT-3MFS devices were $4.0 \times 10^{-6}$ and $9.1 \times 10^{-6}$ cm$^2$ s$^{-1}$, respectively. Moreover, calibration test for DGT-BTP2 was also performed, however no correlation was obtained between the Hg amount uptake and deployment time, confirming that BTP2 binding gels are not able to be used as binding gels (Fig. 1).

Even though the D of DGT-BTP1 is about 2-times lower than for DGT-3MFS devices, they are at the same order of magnitude ($10^{-6}$), which are closer to reported D values (Dočekalová and Diviš, 2005; Clarisse and Hintelmann, 2006; Fernández-Gómez et al., 2011; Gao et al., 2011; Pelcová et al., 2014; Turull et al., 2017). Furthermore, it is possible that the difference in D between DGT-BTP1 and DGT-3MFS devices may be due to the w/v ratio of BTP1 binding gels that is almost fivefold lower than the w/v ratio used to prepare the 3MFS binding gels. Fig. 1 shows the comparison between both calibrations for DGT-BTP1 and DGT-3MFS devices. A linear relationship was observed in both DGT devices, with very good R$^2$ correlation coefficients (0.993 for DGT-3MFS and 0.955 for DGT-BTP1). The difference between the D values may indicate that 3MFS has a higher affinity/selectivity for Hg than the BTP1 material, which may, in turn, be influenced by the simplicity of its chemical structure compared to that of BTP1 (Table 1). A comparison of the recently found D values for 3MFS and BTP1 with values already reported in the literature is shown in Table 2.

### 3.3. Effect of ionic strength and pH on Hg uptake

Fig. 2 shows the average values of the ratio between the concentrations in solution, calculated from the mass of Hg in the binding gels of DGT-BTP1 devices ($C_{DGT}$), and the Hg concentration in solution after 6 h ($C_{sol}$). The $C_{DGT}/C_{sol}$ range was between 0.80–1.12 in the evaluated range, at different ionic strengths, with a good performance and a little dispersion at
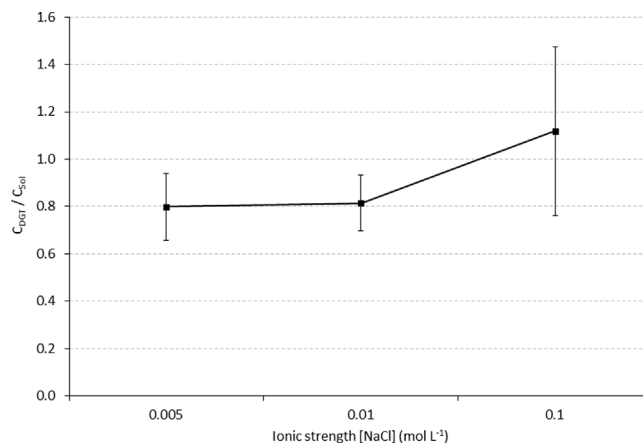
**Table 2**
Comparison between diffusion coefficients (D) reported for Hg(II) in BTP1 vs. resins based on thiol groups.

| Binding gel | Diffusive gel | Medium | pH | T (C) | D ($\times 10^{-6}$; cm$^2$ s$^{-1}$) | |
|---|---|---|---|---|---|---|
| BTP1 | Polyacrylamide | 0.01 M NaCl | 6.8 | 25 | 3.95 | This study |
| 3MFS | Polyacrylamide | 0.01 M NaCl | 6.8 | 25 | 9.08 | This study |
| Spheron-Thiol | Agarose | 0.01 M NaNO$_3$ | 5.0 | – | 9.13 | Dočekalová and Diviš (2005) |
| Spheron-Thiol | Agarose | 0.01 M NaCl | 7.0 | 21.5 | 4.41 | Fernández-Gómez et al. (2011) |
| 3MFS | Agarose | 0.01 M NaCl | 7.0 | 21.5 | 3.86 | |
| 3MFS | Polyacrylamide | 0.01 M NaCl | 7.0 | 21.5 | 2.84 | |
| | Agarose | 0.01 M NaNO$_3$ | 5.0 | 20 | 8.44 | Gao et al. (2011) |
| 3MFS | Agarose | 0.01 M NaNO$_3$ | 7.0 | – | 4.48 | Hong et al. (2011) |
| 3MFS | Agarose | 0.01 M NaCl | 7.7 | – | 4.04 | |
| Ambersep GT74 | Agarose | 0.01 M NaNO$_3$ | 5.0 | 25 | 9.07 | Pelcová et al. (2014) |
| 3MFS | Polyacrylamide | 0.01 M NaCl | – | 20.5 | 1.59 | Turull et al. (2017) |
| 3MFS | Polyacrylamide | 0.01 M NaCl | 7.0 | 20 | 3.08 | Turull et al. (2019) |

BTP1: Poly (4-((2-aminonaphthalene-6-carbonothioyl) carbamoyl) benzoyl isothiocyanate)
3MFS: 3-mercaptopropyl functionalized silica gel.



**Fig. 2.** Effect of ionic strength on Hg uptake by DGT-BPT1 devices. Deployment solution: 3.0 µg L$^{-1}$ of Hg(II) at 21.5 °C and initial pH: 4.5.

ionic strength $\leq 0.01$M. Although at an ionic strength of 0.1 M, the average performance could also be considered suitable, there is a greater dispersion between the measurements, which could reduce the efficiency of the DGT-BTP1 devices in water bodies with a high ionic strength, such as seawater.

The pH is one of the factors that influence the formation of mercuric species in natural waters, so it is also very important to evaluate its influence in the application of DGT devices. The effect of pH on Hg uptake was also tested in triplicate in solutions of 3.0 µg L$^{-1}$ of Hg(II) and 0.01 M of NaCl. Fig. 3 shows the average values of the ratio between $C_{DGT}$ and $C_{sol}$, obtained after 6 h. The $C_{DGT}/C_{sol}$ range was between 0.72–0.96, at different pH, evidencing that DGT-BPT1 devices are not sensitive to variations in pH ($p > 0.05$). The Hg uptake results were better at acidic pH (4.5) and good at slightly acidic pH (6.5), and, therefore, this binding phase is suitable for Hg uptake at the typical pH of natural waters. Moreover, the dispersion between the measurements was minimal in all cases, which could be interpreted as a good efficiency of the devices in the absorption of labile Hg.

### 3.4. Deployment of the DGT devices in field

According to the previous results obtained in the laboratory for the DGT-BTP1 devices, we also evaluated their efficiency in the field, making a comparison with the DGT-3MFS devices under equal deployment conditions. Sampling was carried out in the Quito River, at 6 stations impacted by gold mining activities, for approximately 92 h. The mean values ± SD of temperature, pH, DO, conductivity, TDS, turbidity, and total mercury concentration in water (THg) are shown in Table S1. Labile Hg concentrations calculated from DGT-3MFS and DGT-BTP1 devices and THg in freshwater are shown in Fig. 4. Labile Hg concentrations calculated from both types of DGT devices were similar in most stations, with no statistically significant differences between them ($p > 0.05$). In turn, these values of labile mercury represented between 5 to 8% of the total Hg in water. The results showed a good performance of the DGT-BTP1 devices, which makes them a useful tool for in situ monitoring of Hg in freshwater.
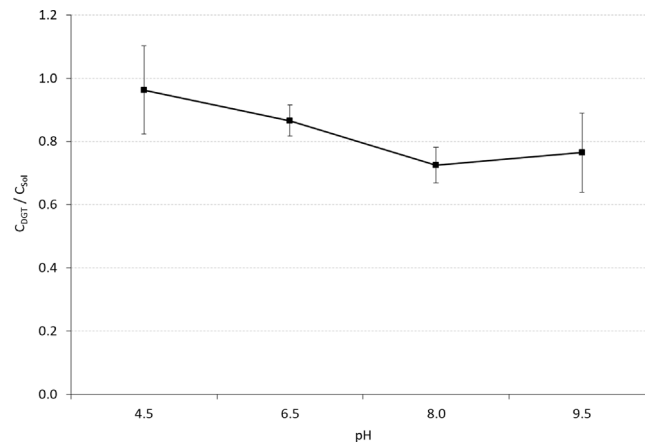
**Fig. 3.** Effect of pH on Hg uptake by DGT-BPT1 devices. Deployment solution: 3.0 $\mu$g L$^{-1}$ of Hg(II) and 0.01M of NaCl at 21 °C.
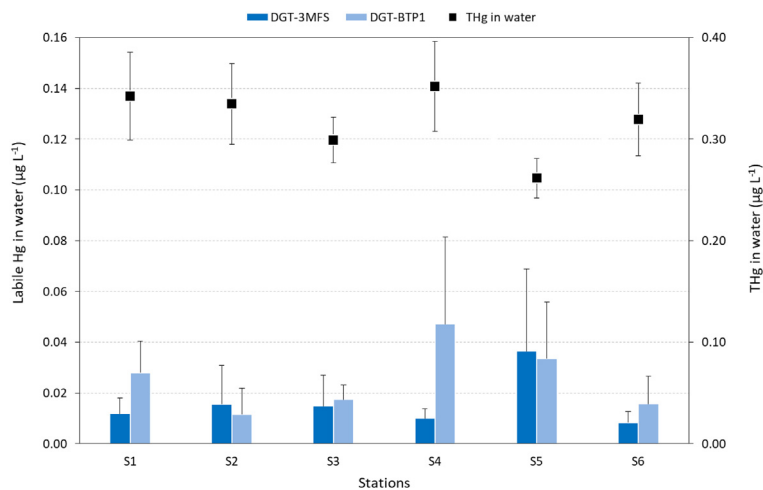


**Fig. 4.** Comparison between labile Hg concentrations calculated from DGT-3MFS, DGT-BTP1 devices and the total mercury concentration in freshwater (THg).

## 4. Conclusions

The proposed DGT method using benzoylthiourea as a binding agent and polyacrylamide gel as a diffusive layer was effective for the determination of labile Hg species, showing a strong linear correlation between the accumulated Hg mass and the deployment time. The polyacrylamide DGT-BTP1 was suitable for aqueous solutions with a wide pH range (4.5–7.5), and ionic strength in the range between 0.005 M and 0.01 M; however, it may not be suitable at aqueous solutions with ionic strength close to 0.1 mol L$^{-1}$, due to the dispersion of measured accumulations Regarding the field deployment, this new DGT showed as a useful tool for bioavailable Hg determination in river water, with matching results with other devices assembled with 3-mercaptopropyl, that have already been proved a high performance in freshwater deployments.

## CRediT authorship contribution statement

**Siday Marrugo-Madrid:** Writing – original draft, Investigation, Formal analysis, Methodology. **Clàudia Fontàs:** Conceptualization, Funding acquisition, Review. **Gülşah Kurt:** Synthesis of new resins. **Carlos Salazar-Camacho:** Support during sampling campaign. **Manuel Salas-Moreno:** Transport and support during sampling campaign. **Harry Gutierrez-Mosquera:** Transport and support during sampling campaign, Contact to local sites. **Jose Marrugo-Negrete:** Conceptualization, Funding acquisition. **Sergi Díez:** Supervision, Conceptualization, Funding acquisition, Writing – review & editing.

## Declaration of competing interest

The authors 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 will be made available on request.

## Acknowledgments

## Appendix A. Supplementary data

Supplementary material related to this article can be found online at https://doi.org/10.1016/j.eti.2022.102911.

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