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Determination of mercury in river water by diffusive gradients in thin films using P81 membrane as binding layer

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ABSTRACT

In this work, a device based on diffusive gradients in thin films (DGT) was evaluated for the determination of Hg(II) in river water. The DGT device was assembled with a cellulose phosphate ion exchange membrane (P81 Whatman) as a binding phase and agarose gel 1.5% (m/v) as a diffusive layer. Laboratory deployments showed that the binding of Hg^{2+} ($[Hg_{DGT}]/[Hg_{solution}]$) by P81 membrane was more effective (97%) than the Chelex 100 resin (80%).The effect of ionic strength, pH and potential interfering ions on Hg binding with DGT's was investigated. The results showed no significant effect on the binding of Hg(II) at pH range from 3.5 to 8.5 and at an ionic strength range from 0.0005 to 0.1 mol L^{-1}. Uptakes of 50 μg L^{-1} Hg(II) by P81 membrane were not affected by Fe, Mn, Zn, Cu, Ca and Mg at the concentration range of 200–1800 μg L^{-1}. Finally, the DGT device using the P81 as the binding layer was applied for *in situ* measurements of Hg in river water. For *in situ* measurements, the labile Hg concentration (from <2 to 13 ng L^{-1}) was lower than 10% of the dissolved fraction (from 155 to 446 ng L^{-1}).

1. Introduction

Mercury is known as one of the most toxic trace metals. It assumes many chemical forms, the most common of which are metallic mercury (elemental mercury), inorganic mercury and organic mercury. Inorganic mercury compounds are considered to be less toxic than organomercury compounds but their selective measurement is important because inorganic mercury compounds can be converted to methylmercury by microbial processes. In aquatic systems, inorganic Hg(II) is the predominant form of mercury in surface waters. Sorption and desorption to suspended matters and subsequent transfer to the bed sediments are important processes for determining the fate of mercury in aquatic systems [1]. Freshwaters with unknown sources of mercury contamination generally contain less than 5 ng L^{-1} of total mercury in aerobic surface waters [2]. However, values higher than 5 ng L^{-1} of total mercury have been reported (0.5–104.3 ng L^{-1}) with the particulate phase being a significant fraction (10–92%) [3]. In addition, typical total dissolved mercury values are 0.5–3 ng L^{-1} in ocean waters and 2–15 ng L^{-1} in coastal waters [4].

Nowadays, the determination of the total dissolved metal in aquatic system is not able to properly quantify its potential risk to the environment and to human health. Assessment of the potential risk of metals requires evaluation using the bioavailable fraction. However, this fraction may be present in extremely low concentrations in the aquatic environment which makes the determination difficult [5,6].

Passive sampling techniques are promising tools for measuring the concentrations of various metal species in the aquatic system. The diffusive gradients in thin films technique (DGT) is an *in situ* sampling techniques that allows the evaluation of the labile fraction of metals. The principle of this technique is based on the diffusion of dissolved species through a porous material (conventionally, a polyacrylamide hydrogel) and their retention on a binding resin (conventionally, Chelex-100 resin) [7,8]. The DGT technique has been widely used to measure labile species of metals in aquatic systems [9-25]. Some advantages of the DGT

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technique include *in situ* speciation, matrix interference removal and time-integrated sampling.

The polyacrylamide diffusive gel commonly used in the DGT technique shows a high affinity with mercury labile species because Hg(II) is covalently bonded to the amide groups of this diffusive gel [26]. This means that the amount of mercury in the diffusive layer (polyacrylamide gel) will increase with the deployment time. As consequence, it is not possible to measure the mercury concentrations based on the conventional DGT theory, because of the competition for Hg(II) by the resin and the polyacrylamide diffusive gel [26].

Agarose has been investigated as a diffusive layer of a DGT device for determination of mercury, in combination with Chelex-100 or Spheron-Thiol binding phases. This approach presented a good performance for determination of labile mercury species [26].

Concerning the binding phase of DGT device for Hg evaluation, the commonly used Chelex-100 resin is possibly a kinetically limited absorbent and this binding phase might affect mercury hydrolysis [27]. The Spheron-Thiol, the GT73 Duolite and 3-mercaptopropyl functionalized silica resins were tested as binding phases of the DGT technique for Hg(II) measurements in rivers [28,29]. Although it was possible to measure Hg with these thiol group based resins, a complicated pre-treatment (graining, sieving, acid washing and incorporating the resin in polyacrylamide gel) is needed. However the 3-mercaptopropyl functionalized silica resin is commercially available but costly [28].

A resin paper-based DGT technique coupled to energy dispersive x-ray fluorescence spectrometry was successfully used for determination of labile Mn, Co, Ni, Cu, Zn and Pb in river water [25]. Also, the P81 ion exchange membrane have been used for the determination of Ba in an oil produced water [30], as well as Cu^{2+} and Cd^{2+} evaluation in natural waters [31]. This P81 membrane showed some advantages compared to the conventional resin gels, such as simple preparation, easy of handling and possible reuse [25,31]. Moreover, the P81 membrane offers homogenous binding sites [25].

This work describes a new DGT approach based on the use of the P81 membrane as a binding phase for the determination of mercury in river water. For that purpose, the effect of ionic strength, pH and potential interfering ions on the P81-Agarose DGT performance for mercury was evaluated, as well its application in the field.

2. Experimental

2.1. Equipment and materials

Mercury was measured by Cold Vapor Atomic Fluorescence Spectrometry (CV-AFS, PS Analytical, Model 10.025 Millennium Merlin, Orpington, England). The pH and conductivity of solutions were measured by a pH/conductivity meter (Jenway, Model 430, England).

DGT polypropylene devices (piston and sleeve) were ordered from DGT Research Ltd., Lancaster, UK. A cellulose phosphate ion exchange membrane P81 (25 mm diameter and 0.2 mm thickness, Whatman International Ltd., England) was used as a binding phase in the DGT technique in this study. A cellulose acetate membrane (0.45 μm Sartorius Stedim Biotech Ltd., German), was put gently over the diffusive layer to protect the gel assembly.

The Hg concentrations in all sample solutions were determined by cold vapor atomic fluorescence spectrometry (CV-AFS) utilizing continuous flow system and $SnCl_2 \cdot 2H_2O$ as a reducing agent.

2.2. Reagents and solutions

The agarose used to prepare the diffusive gel was ordered from Agarose NA (Pharmacia Biotech AB, Georgetown, Canada). Chelex-100 disks (polyacrylamide hydrogels) were purchased from DGT Research Ltd. The HNO_3 and $NaNO_3$ were obtained from Merck, Germany, and $SnCl_2 \cdot 2H_2O$ from Caledon, Georgetown, Canada. All solutions were prepared using 18 MΩ cm purified water and analytical grade reagents.

Hg standard solutions were prepared from 1000 mg L^{-1} standard stock solutions (Specsol, São Paulo, Brazil). For the interfering test, 1000 mg L^{-1} standard stock solutions of Mn, Cu, Zn, Mg and Ca (Specsol, São Paulo, Brazil) were used to prepare the working solutions.

2.3. Gel and membranes

2.3.1. The preparation of the diffusive and binding phases

For preparing the diffusion gel, a 1.5% agarose solution was utilized, as previously described [15]. This solution was cast between two glass plates separated by a 1 mm thickness spacer. After sectioned, the discs were stored in 0.05 mol L^{-1} $NaNO_3$ solution [32]. The thickness of hydrated gels was 1.25 ± 0.05 mm, measured with a micrometer.

The P81 and cellulose acetate membranes were previously decontaminated with 1 mol L^{-1} HNO_3 [33] and then washed with purified water till neutral pH and stored in purified water before use.

2.4. Assembly of DGT devices

A P81 membrane was placed on the DGT piston, and subsequently the agarose gel and the cellulose acetate membrane were put on. Then the polypropylene sleeve was pressed down onto the DGT piston. To avoid contamination, the whole procedure was performed in a laminar flow hood.

2.5. Elution factor and diffusion coefficient

2.5.1. Elution factor

The elution factor was determined by considering the ratio between the eluted and retained mass of Hg on the P81 membranes after 4 h of immersion in 50 mL of a 100 μg L^{-1} of mercury solution. Retained mass was calculated from the difference between the Hg concentrations on those solutions, before and after the immersion. The elution of Hg from P81 membrane was carried out with 5 mL of 2 mol L^{-1} HNO_3 under agitation for 24 h.

2.5.2. Calculations and diffusion coefficient

To determine the diffusion coefficient of Hg, the agarose-P81 DGT devices were deployed in a 4 L 500 μg L^{-1} of Hg^{2+} solution containing 0.05 mol L^{-1} $NaNO_3$ at pH 5. The DGT devices were immersed in the Hg solution, and were sequentially retrieved from the solution at the time point of 6, 9, 15, 18, 21 and 24 h. During the deployment, the test solution was maintained at constant temperature (23 ± 2 °C) under stirring with a Teflon-coated magnetic stirring bar.

After deployments, the mass of Hg accumulated on the DGT binding phase (M) was calculated as follows:

$$M = C_e(V_g + V_e)/f_e \quad (1)$$

where C_e is the Hg concentration in the eluent, V_g and V_e are the volumes of the gel and the eluent, respectively, and f_e is the elution factor.

The bulk Hg concentration (C_b) was calculated as follows:

$$C_b = M\Delta g/DtA \quad (2)$$

where Δg is the diffusive layer thickness (0.138 cm, assuming the thickness of the DBL is negligible), D is the diffusion coefficient, t is

the deployment time and A is the exposure area of the DGT device (3.14 cm^2) [8].

The diffusion coefficient was calculated rearranging Eq. (2)as follows [9]:

$$D = (a\Delta_g)/(C_b A), \quad (3)$$

where D is the diffusion coefficient (10^{-6} cm^2 s^{-1}) and a is the slope of the deployment curve accumulated mass *vs.* time.

2.6. Effect of pH and ionic strength on uptake of Hg^{2+} by agarose-P81 DGT

For the study of pH effect on Hg uptake by agarose-P81-DGT, the DGT devices were immersed in a mercury solution of 200 μg L^{-1} containing 0.05 mol L^{-1} $NaNO_3$ at pH ranging between 3.5 and 8.5. The effect of ionic strength on Hg uptake by this DGT device was studied by adjusting the ionic strength of a mercury solution of 200 μg L^{-1} with $NaNO_3$ in the range of 0.0005–0.1 mol L^{-1}. Four DGT devices were immersed in different ionic strength mercury solutions for 6 h. After this period, the DGT devices were retrieved and the mercury was eluted from P81 membrane.

2.7. Effect of potential interfering metals on uptake of Hg^{2+} by agarose-P81 DGT

In order to check the metal inference on the uptake of Hg by agarose-P81 DGT, the performance of the DGT devices performance were tested in 50 μg L^{-1} Hg solutions (0.01 mol L^{-1} of NaNO3) containing Mn, Cu, Zn, Fe, Ca or Mg in a range of 200–2000 μg L^{-1} at pH 5.5 and temperature 22 ± 2 °C. The deployment was carried out for 5 h.

2.8. Comparison of the performance of the Chelex 100 and P81 membrane binding agents

The chelex-DGT devices were prepared in a similar way as the preparation of P81-DGT by replacing the chelex resin gel with P81 membrane. Two types of DGT devices were immersed in a Hg solution of 50 μg L^{-1} containing 0.05 mol L^{-1} of $NaNO_3$ at pH 5.5. The deployment time was 24 h. Two milliliter of 2 mol L^{-1} HNO_3 was used to elute the Hg from Chelex 100 resin gels [26]

2.9. Field applications

The deployment sites were located at 22°24,39′41″ S latitude and 47°32,19′35″ W, longitude (Ribeirão Claro – SP); at latitude 03°10′30,28″ S and longitude 59°58′39,9″ W (Negro river – AM) and at latitude 03°14′50,5″ S and longitude 60°02′0,42″ W (Solimões river – AM). The DGT units were deployed from 3 to 5 days at 0.5 m below the surface water. For each sites, water samples were collected for the determination of total and dissolved Hg. To evaluate the dissolved Hg content, samples were filtered through a 0.45 μm cellulose acetate membrane. The samples were preserved in 2% (v/v) of HNO_3.

The Agarose – P81 DGT units were deployed *in situ* in the Ribeirão Claro river (São Paulo State, Brazil), and Negro and Solimões rivers (Amazon State, Brazil). The pH, conductivity and temperature of the water column were measured at the beginning and at the end of the deployment (Table 1). In this case, the ionic strength of the water column was estimated by

$$I = 0.013EC,$$

where EC is the electrical conductivity (μS cm^{-1}) and I is the ionic strength (mmol L^{-1}) [34].

Table 1
Average values of pH, ionic strength (IS, mmol L^{-1}) and temperature (°C) measured at the beginning and at the end of sampling in Ribeirão Claro, Negro and Solimões river.

Site Period	Ribeirão Claro October 2011	Ribeirão Claro February 2012	Negro July 2011	Solimões July 2011
pH	7.14	6.5	5.1	7.36
EC (μS cm^{-1})	40.7	62.5	7.18	56.7
IS (mmol L^{-1})*	0.53	0.81	0.093	0.73
*TDS (mg L^{-1})***	*26.05*	40	*4.6*	36.29
Temperature (°C)	25.7	23.1	29.1	28.3
TOC (mg L^{-1})	–	–	10.0 ± 0.1	8.45 ± 0.06

* The IS values estimated according to Griffin and Jurinak [34].
** The total dissolved solids (TDS) values calculated according APHA. (1992) [35].

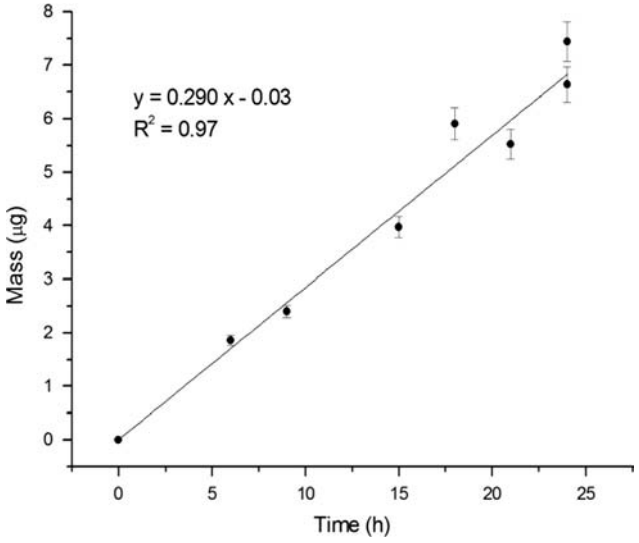

Fig. 1. Hg^{2+} accumulated mass *vs.* deployment time using APA-P81 DGT.

3. Results and discussion

3.1. Elution factor and diffusion coefficient

The elution factor of Hg^{2+} from the P81 membrane was 0.91 ± 0.05. A similar value (> 0.96) was previously reported for Cu^{2+}, Cd^{2+}, Pb^{2+}, Co^{2+}, Zn^{2+}, Mn^{2+}, Ni^{2+}, Ca^{2+}, Mg^{2+}, K^+ and Na^+ utilizing the same elution procedure (5 mL of 2 mol L^{-1} HNO_3 for 24 h) [31,33].

Fig. 1 shows the Hg^{2+} accumulated mass (ng) *vs.* deployment time (h) using Agarose-P81 DGT devices. It can be seen from Fig. 1 that a linear uptake of Hg^{2+} by the P81 membrane ($R^2 > 0.97$) was achieved up to 24 h of deployment time.

Considering the slope of linear line in Fig. 1 and using Eq. (3), the diffusion coefficient (D) of Hg^{2+} using 1.5% of agarose as diffusive layer was 7.8 ± 0.5 × 10^{-6} cm^2 s^{-1}. This value was close to the value of 7.21 ± 0.01 × 10^{-6} cm^2 s^{-1} which was reported by Colaço et al. and slightly lower than the value of 8.44 ± 0.33 × 10^{-6} cm^2 s^{-1} which was reported by Gao et al. In addition, diffusion coefficients of 8.86 ± 0.11 × 10^{-6} cm^2 s^{-1} and 9.08 ± 0.13 × 10^{-6} cm^2 s^{-1} for Hg^{2+} using agarose diffusive gel coupled with Chelex 100 and Spheron-Thiol binding phases respectively were reported [26].

3.2. Effect of pH, ionic strength and interferences on Hg^{2+} measurements

The ratios of the Hg^{2+} concentration obtained from DGTs, to its concentration in the deployment solution ($[Hg]_{DGT}/[Hg]_{solution}$), are shown in Fig. 2, considering the different pH values. There was no significant change on the uptake of Hg^{2+} by the P81 membrane at the pH range of 3.5–8.5.

The binding capacity of the P81 membrane for Hg^{2+} in the presence of Na (I=0.001 mol L^{-1}), calculated according to Li and co-workers [31], was found to be 0.013 μmol cm^{-2}. Even being this value lower than those found by Li and co-workers [31] for other elements (from 0.069 to 0.88 μmol cm^{-2}), this performance does not imply in a practical problem, since the common concentration of Hg^{2+} in river water is very low (less than 0.00002 μmol L^{-1} in aerobic surface waters [2]).

Fig. 3 shows the ratio of $[Hg]_{DGT}/[Hg]_{solution}$ considering the different ionic strength values.

The uptake of the Hg^{2+} by the P81 membrane has not significantly changed at the range of ionic strength (0.0005–0.1 mol L^{-1}), except for the highest ionic strength 0.1 mol L^{-1}.

The effect of Cu(II), Mn(II), Zn(II), Fe(II), Ca(II) and Mg(II) on the Hg^{2+} uptake by the Agarose-P81 DGT is shown in Table 2. No significant interferences from these metals were verified, since satisfactory recoveries of Hg mass were obtained (from 83% to 114%).

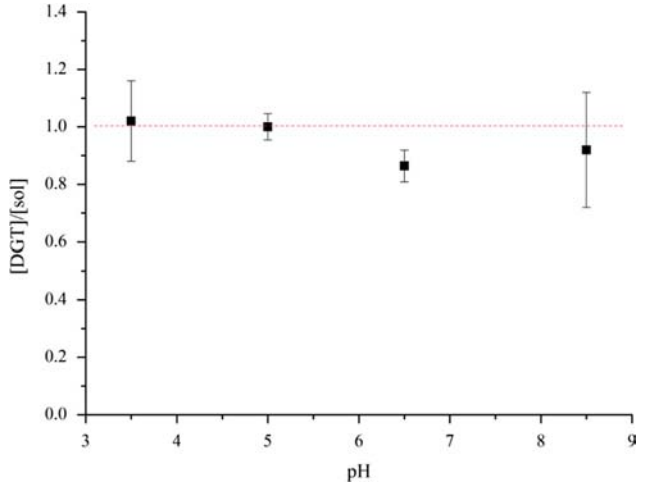

Fig. 2. The ratio of the DGT concentration of Hg^{2+} to its concentration in the deployment solution ([DGT]/[solution]), considering different pH values.

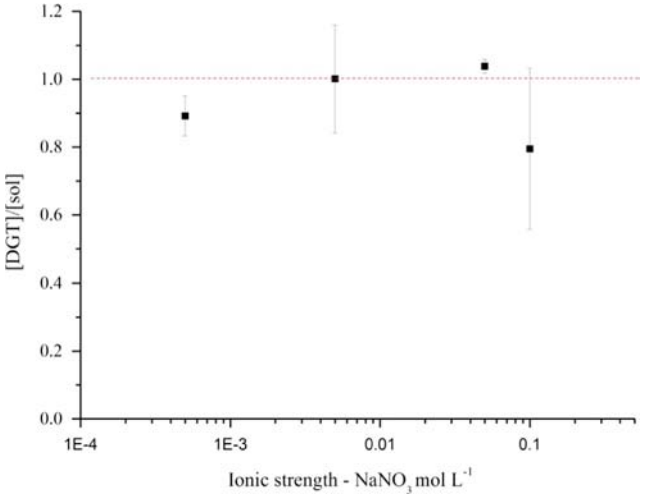

Fig. 3. The ratio of the DGT Hg^{2+} concentration to its concentration in the deployment solution ([DGT]/[solution]), considering different ionic strength values.

3.3. Comparison of the performance of Chelex-DGT to the P81-DGT for Hg uptake

The recovery of Hg^{2+} obtained by P81-DGT was 97%, which is higher than the recovery of 80% obtained by chelex-DGT.

It has been reported previously that the accumulation of Hg^{2+} on the chelex resin is fast at the first two hours deployment in Hg solution, but after four hours, the uptake decreases significantly [36]. It was also reported that Chelex 100 resin is kinetically limited to bind to Hg^{2+} [27]. When the concentration of the labile fraction differs significantly using different binding phases, it may suggest that the labile metal fraction measurement depends on the binding strength of the binding agent [37].

3.4. Field applications

3.4.1. in situ measurements in Ribeirao Claro river

For an immersion time of 72 h and assuming an instrumental limit of detection (LOD) of 20 ng L^{-1}, a LOD for DGT measurements of 2.4 ng L^{-1} was obtained. When instrumental LOD is improved (by increasing the instrumental gain and/or improving the blank solution) to 4.5 ng L^{-1} and immersion time is increased to 90 h, a LOD for DGT measurements of 0.4 ng L^{-1} was obtained.

Table 3 shows total, dissolved and labile (DGT measurements) Hg concentration at four sites. The total and dissolved Hg concentrations measured in October 2011 at sampling site of Ribeirão Claro were lower than the limits of detection (20 ng L^{-1}), while the labile fraction measured by DGT was 1.8 ± 0.71 ng L^{-1}. It was due to the pre-concentration feature of DGT technique. The DGT Hg concentration found on February 2012 was 0.62 ± 0.02 ng L^{-1}. This value was lower than the total and dissolved Hg fractions found in this site: 82 ng L^{-1} and 45 ng L^{-1}, respectively. The different levels of Hg in October (dry season) and in February (rainy season) is corroborated with a previous study carried out in

Table 2
Effect of Cu(II), Mn(II), Zn(II), Fe(II), Ca(II) and Mg(II) on the Hg^{2+} uptake for the Agarose-P81 DGT.

Metal	C_{metal} in solution (μg L^{-1})[a]	Ratio interfering ion and Hg concentration[b]	Recovery of Hg^{2+} (%)[c]
Cu	420	28	105 ± 19
Mn	393	34	95 ± 2
Zn	435	32	96 ± 3
Fe	212	14	115 ± 15
Ca	1490	24	83 ± 1
Mg	1811	78	97 ± 7

[a] Interfering dissolved concentration (mean value) measured in bulk solution before and after deployment.
[b] Calculated from footnote a and Hg(II) concentration (mean value) measured in bulk solution before and after deployment.
[c] The Hg mass recovery was obtained by the ratio between the DGT Hg concentration and the Hg concentration in the deployment solution.

Table 3
Labile (DGT), dissolved and total concentration (ng L^{-1}) of Hg.

Site Period	Ribeirão Claro October 2011	Ribeirão Claro February 2012	Negro July 2011	Solimões July 2011
Labile	1.8 ± 0.7	0.62 ± 0.02	13	< 2.4
Dissolved	< 20	45	155	446
Total	< 20	82	3079	700

Table 4
Comparison of labile (DGT), non-complexed (CHEAQS software speciation), dissolved and total concentration of Hg for synthetic solutions containing humic substances and Solimões river.

Sample	HS, mg L^{-1}	Total Hg, μg L^{-1}	Non-complexed Hg, (%)	
			DGT	CHEAQS
Synthetic 1	0.25	22.0	12 ± 3	9
Synthetic 2	5.0	33.1	4.9 ± 0.2	0.1
Solimões river	8.5	0.7	$< LOD_{DGT}$	0.03

the Xiaxi watercourse, China, in which it has been found that the main responsible for Hg release was high flow events [38].

3.4.2. in situ measurements in Negro river and Solimões river

The total and dissolved Hg concentrations in Negro river were 3079 ng L^{-1} and 155 ng L^{-1}, respectively. Although, the ionic strength of this sampling site has not been within the range of ionic strength studied, it was possible to estimate the level of labile mercury of 13 ng L^{-1} by the DGT technique in Negro river (Table 3). However, it is important to emphasize that in this case, due to the high organic matter content and the low ionic strength of this river, the DGT devices need to be calibrated under the same environmental conditions.

The DGT labile fraction of Hg in Solimões river was lower than its limit of detection (2.4 ng L^{-1}), which shows that despite of the total and dissolved Hg fraction with the values of 700 ng L^{-1} and 446 ng L^{-1} respectively, mercury presents mostly as non-labile species and therefore is not detectable by the DGT technique and has less potential bioavailability to the organisms.

To confirm the results obtained in this work, additional experiments were carried out by employing synthetic samples containing different concentrations of humic substances and compared with speciation using CHEAQS software: two Hg^{2+} synthetic solutions were prepared with FI = 0.05 mol L^{-1} $NaNO_3$ and pH = 5.4 at 22 °C; humic substances were added to those solutions at concentration of 0.25 mg L^{-1} and 5.0 mg L^{-1} respectively. Based on the results showed in Table 4, it can be inferred that only non-complexed mercury species was up-taken by DGT.

4. Conclusions

The Agarose-P81 DGT is easy of handling and less costly as compared to the resins used to determine Hg using the DGT technique. The proposed method was effective for determination of labile mercury species, showing satisfactory linear correlation between the accumulated Hg^{2+} mass and the deployment time.

In addition, the agarose-P81 DGT performance for Hg^{2+} evaluation was acceptable regarding the wide pH and ionic strength ranges. It may not be suitable for waters with ionic strength close to or higher than 0.1 mol L^{-1}. The Hg^{2+} uptake obtained with the proposed device was 97%, which was higher than the one found using Chelex 100 as binding agent. Regarding the *in situ* DGT deployment, although the labile concentration of Hg was low, the quantification was still possible due to the pre-concentration ability of the DGT technique. The approached studied allowed *in situ* labile Hg evaluation, showing a useful tool for Hg speciation in river water.

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