



Development of a novel composite resin for dissolved divalent mercury measurement using diffusive gradients in thin films

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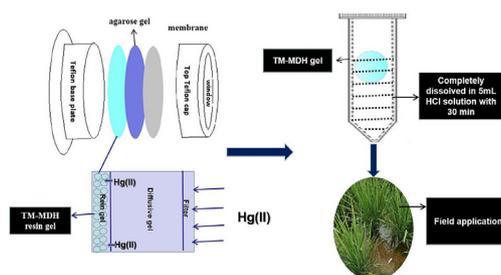
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HIGHLIGHTS

- A novel composite resin has been developed for divalent mercury measurement using DGT devices.
- The resin is a highly uniform substrate and easily digestible for divalent mercury determination.
- The new resin equipped DGT device can accommodate a wide range of environments.
- The DGT method is reliable and cost-effective for measuring divalent mercury in water and sediments.

GRAPHICAL ABSTRACT



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ABSTRACT

In this work, a composite resin gel incorporating thiol-modified metal double hydroxide (TM-MDH) nanoparticles is developed for application in diffusive gradients in thin films (DGT) devices to sample and concentrate divalent Hg (Hg(II)) in water and sediment samples. The DGT device uses the TM-MDH resin as a sorption layer and an agarose gel as a diffusive layer. Complete digestion of the TM-MDH resin after sampling can be achieved in 5 mL of 12 N HCl solution for 30 min for direct aqueous Hg(II) analysis. The recovery of Hg(II) uptake onto the resin in aqueous solution reaches $95.4 \pm 1.9\%$. The effect of ionic strength and pH on the performance of DGT device for Hg(II) is assessed. It is found that there is no significant difference on Hg(II) uptake over a pH range of 3.5–8.5 and an ionic strength range of 1–500 mM NaCl. The diffusion coefficient of Hg(II) at 25 °C was estimated to be $9.48 \times 10^{-6} \text{ cm}^2/\text{s}$ at 50 µg/L solution. The sorption capacity of TM-MDH-DGT for Hg(II) reaches 41.0 µg/cm^2 . Field validations performed in reservoir water and in contaminated paddy soil demonstrate that the developed TM-MDH DGT device can accurately determine Hg(II) concentrations in these samples and outperform traditional sampling methods for both high and low Hg(II) concentrations.

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Abbreviations: Hg(II), Divalent mercury; DGT, Diffusive gradients in thin films; TM-MDH, Thiol-Modified metal Double Hydroxide; SH-Thiol, Spheron Thiol; 3MFS, 3-Mercaptopropyl Functionalized Silica Gel; SH-SBA, 3-Mercaptopropyl SBA15; CVAFS, Cold Vapor Fluorescence; Methylmercury, MeHg; Mercury, Hg.

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1. Introduction

Mercury (Hg), one of the most toxic pollutants in its methylated forms, exists ubiquitously in air, soil, water, sediment and organisms (Driscoll et al., 2013). Once it enters aquatic environment, inorganic divalent mercury (Hg(II)) can be biologically converted into methylmercury (MeHg) (Ullrich et al., 2001), which poses a threat to human health and ecosystem through accumulation and biomagnification in the food chains (Steenhuisen and Wilson, 2015). Therefore, the concentration, mobility and bioavailability of Hg(II) in the aquatic environment need to be monitored for reducing the risk of Hg exposure.

Traditional sampling methods (direct sampling, centrifugation and dialysis sampler) obtain the total analyte concentrations, rather than the labile components that indicate the risk of a target analyte (see Fig. S1) (Li et al., 2018). Direct sampling and centrifugation methods are active *ex-situ* sampling techniques while the dialysis method is considered *in-situ* sampling technique that takes a few weeks to reach chemical equilibrium. These methods are prone to contamination, chemical changes, long sampling time and sensitivity limitation (Liu et al., 2011). Presently, accurate and cost-effective methods for monitoring labile Hg remain a challenge due to a lack of quick, accurate, selective and sensitive methods that are deployable for field measurements (Divis et al., 2016). This limits the understanding of Hg pollution, particularly in remote regions. Therefore, there is a need to develop *in-situ* monitoring methods for aqueous Hg(II).

Diffusive gradients in thin films (DGT) technique is a low-cost, *in-situ* sampling method of trace elements for field monitoring of aqueous Hg(II) (Turull et al., 2017). DGT technology is a passive field sampling technique originally developed in 1994 (Davison and Zhang, 1994). It is well suited for sampling soluble trace metals for determination of concentration and bioavailability of labile metal species in aquatic systems (Jansen et al., 2002). The method resists environmental disturbances and eliminates the need of active media transport (Li et al., 2018) (see Fig. S1). Earlier studies examined experimental resin substrates for field applications. Typical resin materials for Hg(II) adsorption contains thiol groups because of the strong affinity of Hg(II) to the thiol group (Elias et al., 2020). Among the earlier developments, chelex-100 resin is inadequate for reliable Hg(II) sampling (Docekalova and Divis, 2005; Pelcova et al., 2014). The 3-mercaptopropyl functionalized silica gel (3MFS) has preferential selectivity for methylmercury (MeHg) adsorption rather than Hg(II) (Clarisse and Hintelmann, 2006; Liu et al., 2012; Hong et al., 2011). The Spheron-Thiol (SH-Thiol) (Docekalova and Divis, 2005; Fernandez-Gomez et al., 2012), SH-SBA (Gao et al., 2011), and Duolite GT73/Ambersep GT74 (Pelcova et al., 2014; Ridoskova et al., 2017) resin materials are in their developmental stage and often need to be prepared using materials not commercially available, making it infeasible for immediate field applications. Therefore, there is a need to develop new, field deployable resins that can directly applied for measuring aqueous Hg(II) using materials that are readily accessible and demonstrate desired performance.

This work aims at developing a novel composite resin using a thiol-modified metal double hydroxide (TM-MDH) as the resin gel for the determination of Hg(II) in the aqueous phase. For that purpose, the effect of ionic strength, pH, sorption time required for complete sampling, and sampling capacity of the TM-MDH resin is investigated. Field deployment and verification are carried out in an experimental reservoir and in a rice paddy field to examine the performance of the developed DGT device of field application. The analytical results obtained by the DGT method are also compared to the values measured by conventional sampling methods to assess the analytical performance of the DGT device for field application.

2. Experiments

2.1. The preparation of DGT device

DGT devices are comprised of three functional components (filter membrane, diffusive gel and resin gel). The Thiol-Modified metal Double Hydroxide (TM-MDH) resin was synthesized using LDH as the resin gel matrix according to Liang et al. (2010) with modification. Details on the procedure of TM-MDH synthesis are described in the supporting information (SI, Section S1). Other four resin gels were obtained from DGT Ltd. Company (<http://www.dgtresearch.com.cn/>), including 3-Mercaptopropyl Functionalized Silica Gel (3MFS), Spheron thiol (SH-Thiol), Chelex-100 and 3-Mercaptopropyl SBA15 (SH-SBA). The diffusive layer was made of 2% agarose (Fisher Scientific, Inc.) (Section S2 in the SI). The filter membrane with a 0.45 μm pore size polyether sulfone was purchased from Pall company (Pall, U.S.). Moldings where the functional components of the DGT device are housed were acquired from DGT Research Ltd. The DGT components are shown in the supporting information (Section S3 in the SI).

2.2. Sampling efficiency of aqueous Hg(II)

To evaluate the collection efficiency of Hg(II) for the newly developed resin, each gel disc was placed in a 10-mM NaCl solution with different concentrations containing 0.05, 0.5, 2 and 50 $\mu\text{g/L}$ Hg(II) for 24 h under shaking at 25 °C. After a 24-hr uptake period, the gel was removed and rinsed with deionized water, and then digested in 5-mL of 12-N HCl solution for 30 min. The digested solution, which is completely free of suspended solids, was percolated with 2% bromine monochloride (BrCl) until Hg(II) analysis. The final solution can be directly introduced into Brooks Rand III for Hg detection using CVAFS.

The collection efficiency of aqueous Hg(II) is estimated as:

$$fe = \frac{C_e \times V_e}{(C_0 - C_u) \times V_u} \times 100\% \quad (1)$$

fe is the collection efficiency of Hg(II), representing a ratio of the Hg(II) mass sampled by the resin gel to the Hg mass removed from the uptake solution. C_e is the concentration of Hg(II) in the digested solution (ng/L), C_0 is the initial concentration of Hg(II) in the solution before uptake (ng/L), C_u is the residual concentration of Hg(II) in solution after uptake (ng/L), V_e is the combined volume of digestion and BrCl solutions for resin gel digestion (0.025 L), and V_u is the volume of uptake solution (0.04 L). Therefore, the sampled Hg(II) mass (M) can be calculated as:

$$M = \frac{C_e \times V_e}{fe} \quad (2)$$

where M (ng) is the mass transferred through the control area (A , cm^2), t is the time period of the diffusive transport (s). As such, the concentration of analytes in the environmental media can be estimated as:

$$CDGT = \frac{M \times \Delta g}{D \times A \times t} \quad (3)$$

where $CDGT$ is the free concentration of an analyte metal ion in bulk solution ($\mu\text{g/L}$, i.e., ng/cm^3), and Δg is the thickness of the diffusive layer (cm). Based on Eqs. (2) and (3), Hg(II) concentration as measured in the DGT device can be calculated as:

$$CDGT = \frac{C_e \times V_e \times \Delta g}{D \times A \times t \times f_e} \quad (4)$$

The principles of DGT measurements are described in the SI (Section S4).

Potential interference caused by MeHg was also examined. During the experiment, we checked the uptake of 0.05 µg/L MeHg using TM-MDH resin for 24 h at 25 °C. The gel was then removed, rinsed with deionized water, and digested in 5-mL 2% thiourea-0.1 M HCl solution. The final solution was measured for MeHg concentration using GC- CVAFS (Clarisse and Hintelmann, 2006).

2.3. Comparison of Hg uptakes using different resin gels

To evaluate the mass of Hg uptake, we compared the uptake performance of TM-MDH resin gel developed in this work with four resin materials used in earlier DGT devices. Each resin gel was immersed in a 50 µg/L Hg standard test solution containing 10 mM of NaCl at pH 5.0 for 2, 4, 8, and 24 h, thoroughly rinsed with deionized water, and then analyzed for accumulated Hg(II) mass following the procedure described in Section 2.2.

2.4. Effects of ionic strength and pH

Ionic strength measures the concentration of ionic charge in solution and may affect the uptake of metal ion (USEPA, 2017). Therefore, the effect of ionic strength on Hg(II) uptake by DGT device needs to be examined. Ionic strength is expressed as:

$$I = \frac{1}{2} \times \sum C_i \times Z_i^2 \quad (5)$$

where I is the ionic strength (mM, 1 mM = 10⁻³ mol/L), C_i is the concentration of ion (mole/L), Z_i is the valence of ion.

Common cations (e.g., sodium (Na⁺), calcium (Ca²⁺), magnesium (Mg²⁺), potassium (K⁺)) and anions (e.g., chloride (Cl⁻), bicarbonate (HCO₃⁻), carbonate (CO₃²⁻), sulfate (SO₄²⁻)) contribute to ionic strength. In our study, we chose NaCl as the matrix for the ionic strength test. Solutions of 1, 10, 100, 300 and 500 mM NaCl with 2 µg/L of Hg(II) were prepared, and three TM-MDH DGT devices were exposed to each solution for 24 h at pH 5 to test the performance of Hg(II) uptake.

We chose to use the ppt level (2 µg/L) in the experiments to illustrate the uptake capacity and higher analytical accuracy. The effect of pH was evaluated by placing the DGT devices into 2 µg/L of Hg(II) solution at pH 3.5–9.0 with 10 mM NaCl for 24 h. The pH of the solutions was adjusted by using 0.01 mol/L HCl or NaOH solution. We analyzed the pH of the solution before and after the time exposure and the change is insignificant. DGT samples were then analyzed for Hg(II) concentration.

2.5. Diffusion coefficients

To determine the diffusion coefficients of Hg(II) at high and low concentrations, twelve TM-MDH DGT devices were deployed in a 1.5 L of 50 µg/L and 500 ng/L of Hg(II) solution containing 10 mM NaCl at pH 5.0, respectively. During the deployment, every three DGT devices were taken out at different times (4, 8, 16 and 24 h). The solution was maintained at constant temperature (25 °C) under continuously stirring with a Teflon-coated magnetic stirring bar. After deployments, the resin gels were removed from the DGT devices and then analyzed for Hg(II) accumulated mass following the procedure described in Section 2.2.

2.6. Rate and capacity of Hg uptake of the TM-MDH resin

A series of experiments were conducted to examine the time required (4, 8, 16 and 24 h) for Hg(II) uptake in a Hg standard solution (2 µg/L) prepared in 10 mM NaCl using the developed TM-MDH resin. During the experiments, Hg(II) concentrations in the aqueous phase were monitored. For the uptake capacity experiments, the DGT device was immersed in 2 L of well-mixed 10 mM NaCl solutions (pH 5.0, T 25 °C) containing 1–25 mg/L of Hg(II). After 24 h of Hg(II) uptake, the resin gels were digested and then analyzed for Hg(II) following the procedure described in Section 2.2. All experiments were triplicated.

2.7. Field applications

The developed DGT devices were deployed for determining the Hg(II) concentrations in a fresh-water reservoir (Baihua reservoir) and a Hg mining paddy soil (Sikeng district). Both sites locate in the Guizhou, province, Southwest China. Previous studies had reported that the total Hg concentration ranged from 4.34 to 7.91 ng/L in the Baihua reservoir (Long et al., 2018), and the dissolved Hg concentrations in the pore water of mining paddy soil ranged from 38 to 916 ng/L at Hg (Zhao et al., 2016a). The two concentration ranges were selected to examine the performance of the DGT devices under high and low environmental concentrations.

The sampling location in Baihua reservoir was near the dam at N26°40' and E106°32'. The circular DGT units were deployed at 0.5 m below water surface for 7 days. For comparison, separate water samples were collected using a 10-L Niskin sampler at 0.5 m depth each day. The water samples were filtered using a 0.45 µm membrane (Milli-pore) to remove suspended solids and then preserved in 0.4% HCl.

The sampling location for the paddy soil is in the Sikeng Hg mining (N27°30', E109°11'). The rectangular DGT devices were vertically inserted into water saturated paddy soil. After 7 days of sampling, each DGT device was washed with Milli-Q water and preserved at 4 °C in a sealed polythene bag. After transporting the sample back in the lab, the TM-MDH resin in each DGT device was sliced into 1.0 cm strips and each slice was digested and analyzed for Hg(II) concentration. Separate pore water samples were collected from paddy soil cores using the procedure described by Mason et al. (1998). The pore water samples were filtered through 0.45-µm disposable nitrocellulose filter and then treated with 0.4% hydrochloric acid before analysis. Temperature and pH were measured by a portable water quality parameter probe (Clean, USA) at the beginning and the end of each deployment.

2.8. Hg(II) analysis and QA/QC

Hg(II) analysis for all samples was made using a cold vapor fluorescence (CVAFS) detector (Brooks Rand Model III, Brooks Rand Labs, U.S.A) (USEPA, 2001), after each resin gel was digested in HCl (36–38%, Ultra traces analysis) and NaCl (BioXtra, ≥99.5% Sigma-Aldrich) reagents. One hundred ppm of Hg²⁺ standard solution in 10% HCl (Ultra traces analysis) was prepared by diluting a 1000-ppm Hg standard solution (Aladdin, ACS), yieldign 2 or 50 ppb Hg²⁺ in 0.01 M NaCl for test according to the required concentrations. All solutions were prepared in deionized 18.2 MΩ cm (Milli-Q) water with 0.1 M hydrochloric acid, then stored at 4 °C before use. All DGT devices were soaked in a Hg-free NaCl solution (0.03 M) before field deployment of the devices.

Quality control for Hg(II) determination was conducted by duplicate analysis, method blanks, matrix spikes and standard reference materials. Blank spikes and duplicates were taken

regularly (>10% of samples) throughout the chemical analysis. The method detection limits (MDL), based on three times the standard deviation of replicate measurements of a blank solution in the water sample, was 2-pg Hg. The resin gel blank based on Hg uptake in DI water was 6.09 ± 0.44 pg for Hg^{2+} ($n = 6$). Possible contamination during preparation of DGT devices and field deployment were monitored by 6 random samples in the field and no Hg(II) contamination was found. Six DGT devices were utilized for Hg(II) measurement in water samples spiked with 5 ng/L Hg standard. The recoveries were found to range from 93.0% to 105.0%, with a mean (\pm SD) value of $97.0 \pm 5.0\%$. As there is no DGT reference substance, we chose the National Research Council of Canada Lobster Hepatopancreas Standard (NRCC-TORT-2) as the reference to check accuracy of Hg(II) measurement using DGT devices. The measured mean Hg concentration of the standard material was 285 ± 20 ng/g ($n = 3$), comparable to the certified value (270 ± 60 ng/g). Statistical analysis was performed using SPSS 23.0 and Origin 8.0. Statistically significant differences were established at a 5% significance level.

3. Results and discussion

3.1. Collection efficiency of Hg(II) in solution after uptake and digest

The primary advantage of the TM-MDH resin compared to those reported earlier is its digestibility in acid solution for direct chemical analysis. This eliminates the desorption step that frequently leads to incomplete extraction of sampled metals from the resin. TM-MDH uses hydrotalcite-like compounds or anionic clays containing thiol group. The material has a moderate level of alkalinity (Liang et al., 2010) and can be completely dissolved in 12 N HCl solution within 30 min. The resin gels developed earlier (e.g., Spheron, Duolite GT73 and 3MFS) used elution methods and required additional solvents for separating Hg^{2+} from the resin material (e.g., 5%TU-30%KOH or 6 M HCl, etc., Gao et al., 2011; Hong et al., 2011; Pelcova et al., 2015), leaving various quantities of undigestible resin gel in the solution. Using the TM-MDH resin avoids incomplete digestion that leads to analytical uncertainty.

Recovery of Hg(II) sampled by the resin in terms of the ratio of the Hg(II) mass sampled by the resin gel to the Hg mass removed from the uptake solution (Eq. (1)) is estimated using the method described in Section 2.2. The collection efficiency of Hg(II) at different concentration (0.05, 0.5, 2, and 50 $\mu\text{g/L}$) are $95.0 \pm 0.6\%$, $95.3 \pm 2.4\%$, $95.5 \pm 1.9\%$, and $95.5 \pm 2.3\%$ (Mean \pm SD), with an average recovery of $95.4 \pm 1.9\%$ (range from 92.0 to 98.2%). In comparison, Table S1 shows the Hg(II) collection efficiency by TM-MDH and resins developed in earlier studies. Conventional resin gels yield a recovery ranging from 83% to 108%, with an average recovery of $94.7 \pm 5.2\%$. There is no obvious difference compared to the recovery of new developed resin (Paired t -Test, $p = 0.82$). This demonstrates the effectiveness of the new resin in sampling aqueous Hg(II).

The profiles of Hg(II) mass uptake of Hg(II) by the TM-MDH resin and four other reference resins (Chelex-100, 3MFS, SH-SBA, SH-Thiol) with respect to time are shown in Fig. 1. Hg(II) uptake by Chelex-100 and 3MFS resin gel shows a non-linear trend and an decreased rate after 4 h, indicating a weaker affinity and lower capacity for Hg(II) compared to other resins. The new resin material exhibits continuous and linear accumulation of Hg(II) over 24 h (fit-linear-test, $R^2 > 0.999$, $y = 57.94x + 6.04$). There is no difference between the accumulation rate of TM-MDH and the other high-performance resins including SH-Thiol ($R^2 > 0.99$, $y = 53.42x + 25.76$) and SH-SBA ($R^2 > 0.99$, $y = 50.41x + 34.83$) (T-Test, $p > 0.05$). The results show that the performance of TM-MDH, in terms of Hg(II) accumulation rate, compares favorably to those

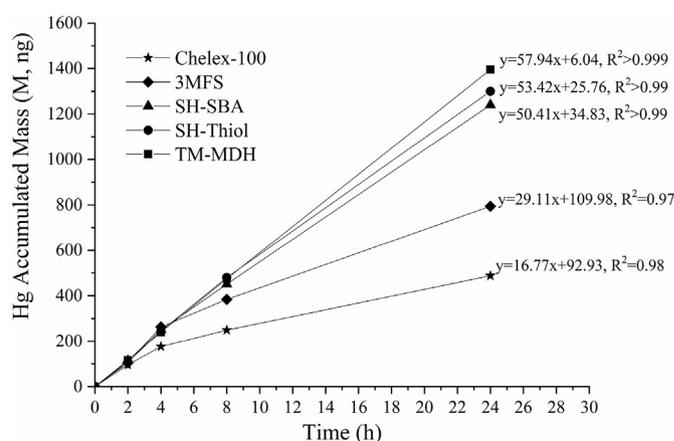


Fig. 1. Mass of Hg(II) accumulation with respect to time using different resin gels. According to Eq. (3), a linear relationship demonstrates the performance of Hg uptake. It is clear that TM-MDH has the best performance based on the linearity of the curve.

achieved by previously reported resins (SH-Thiol and SH-SBA). The SH-Thiol and SH-SBA materials are no longer commercially available, so the new resin gel can serve as the alternative for Hg(II) measurement using DGT devices. In addition, using Eq. (2), the sorption capacity of TM-MDH is estimated to be $6.8 \mu\text{mol}$ given the experimental condition. Earlier reports on the sorption capacities using identical experimental conditions are: $3.9 \mu\text{mol}$ for Chelex-100 resin, $4.3 \mu\text{mol}$ (SH-Thiol), $4.14 \mu\text{mol}$ (SH-SBA), respectively (Divis et al., 2010; Gao et al., 2011). The high capacity of the TM-MDH resin may be responsible for the linear and nearly complete Hg(II) sorption patterns observed in this work.

3.2. Effects of ionic strength and pH on Hg(II) uptake

Both ionic strength and pH can significantly impact the partition of Hg(II) between the aqueous phase and the resin layer (Davison, 2016). The developed TM-MDH resin is examined over the typical ranges of pH and ionic strength found in environmental samples for assessing its applicability during field deployment. This is accomplished by comparing the Hg(II) concentration measured using the DGT (C_{DGT}) method with the concentration measured in solution (C_{Solution}). A ratio of $C_{\text{DGT}}/C_{\text{Solution}}$ ranging from 0.90 to 1.1 is the desirable performance of the DGT sampling method (Davison, 2016).

Fig. 2a shows the $C_{\text{DGT}}/C_{\text{Solution}}$ ratio measured in 1–500 mM of NaCl solutions using the TM-MDH resin gel, with a mean ratio of $97 \pm 0.04\%$. The ratio agrees with the findings reported earlier (Hong et al., 2011; Gao et al., 2011; Colaco et al., 2014; Ren et al., 2018). The performance of the DGT device remains consistent in the examined concentration range of NaCl. The typical ionic strengths in river, lake and seawater water range from 1 mM to 700 mM (Noh et al., 2016). The experimental results indicate that Hg(II) uptake to the TM-MDH resin is unlikely to be affected by the variation of ionic strength in natural freshwater.

Fig. 2b shows the ratio of $C_{\text{DGT}}/C_{\text{Solution}}$ at various pH. As seen, there was no significant change on the uptake of Hg^{2+} by the TM-MDH gel at pH from 3.5 to 8.5 ($p > 0.05$, $n = 14$, T-Test), meeting the requirement for environmental application for DGT (Pelcova et al., 2014; Colaco et al., 2014). The $C_{\text{DGT}}/C_{\text{Solution}}$ values slightly decreased to 0.86 ± 0.06 when pH reached 9.0 or higher, suggesting that Hg(II) uptake is somewhat hindered at $\text{pH} \geq 9.0$. Since the speciation of Hg(II) under the experimental conditions at the pH range and Cl^- concentration (10 mM) was HgCl_2 , a stable form of Hg(II) complex (Holbrey et al., 2003). The slight reduction of Hg(II)

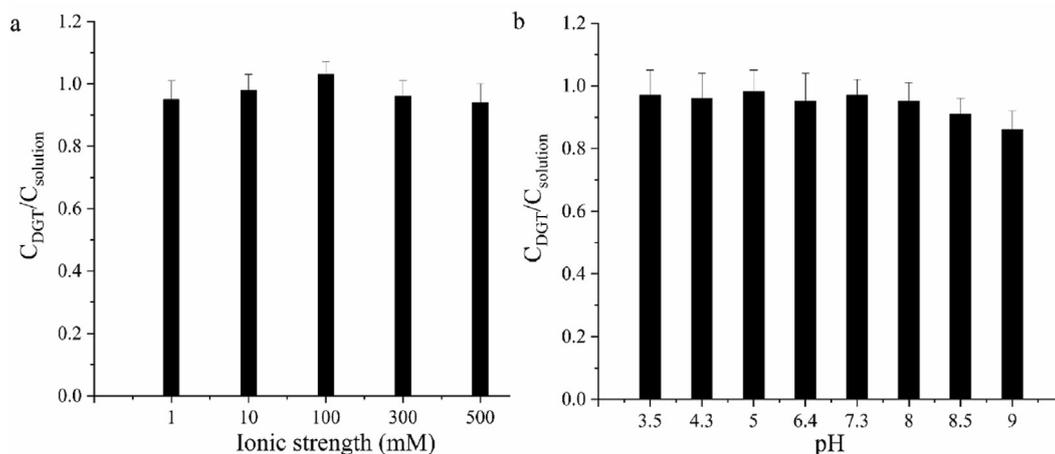


Fig. 2. Effect of the ionic strength pH on uptake of Hg. a) Ionic strength (Deployment time: 24 h, $I = 10$ mM Cl, $V = 1.5$ L, $T = 24$ °C); b) pH (Deployment time: 24 h, $pH = 5.0$, $V = 1.5$ L, $T = 24$ °C).

uptake is most likely caused by the change of material property at the higher pH. The sulfhydryl modification of the LDH is based on the esterification reaction. Since the ester bond can be more readily hydrolyzed under the alkaline condition (Asaff et al., 2014), the adsorption activity may be reduced on the sulfhydryl modified LDH. Given the typical pH values of natural waters in the range 4.5–9.0 (Deluchat et al., 1997), the TM-MDH resin gel is broadly applicable under environmental conditions.

3.3. Diffusion coefficient

The effective diffusion coefficient is determined by the DGT time-series deployment method since the measurement condition associated with this method are similar to that of field measurement. Compared to the diffusion cell method, the DGT time series method is more widely applied because of its field applicability (Shiva et al., 2015; Wang et al., 2016). The accuracy of the DGT measurement is largely determined by diffusion coefficient (Chen et al., 2012, 2018; Zhang et al., 2019). Fig. 3a shows the Hg uptake mass (ng) versus time (h) of the agarose-TM-MDH DGT devices in high concentration Hg(II) solution ($C = 50$ $\mu\text{g/L}$). The response curve in Fig. 3a shows linear uptake of Hg(II) ($R^2 > 0.999$) over the 24-h of deployment time, with the significance level of $p < 0.001$.

The slope of the linear fitting equation (57.9 ng/h) in Fig. 3a is utilized for calculation of the diffusion coefficient according to Eqs. (3) and (S4), yielding a diffusion coefficient (D) of Hg in the agarose diffusive layer of 9.48×10^{-6} cm^2/s at 25 °C.

The concentration of Hg(II) in the aquatic environment is at a trace level. Therefore, it is necessary to evaluate the effectiveness of the TM-MDH-DGT at low concentration of Hg(II). Fig. 3b shows the Hg uptake mass (ng) versus time (h) at low Hg(II) concentration ($C = 500$ ng/L). A linear uptake of Hg(II) ($R^2 > 0.99$) is evident for the 24 h of deployment time with a slope of 0.35 ng/h. Using Eqs. (3) and (S4), the diffusion coefficient of Hg(II) using agarose as the diffusive layer is 5.47×10^{-6} cm^2/s at 25 °C. The diffusion coefficients of Hg(II) appears decreased slightly at low Hg(II) concentration. A pair t -test showed that the difference is significant between the values measured at high and low Hg(II) concentrations ($n = 6$, $p < 0.001$). Measurements of diffusional coefficient can be affected by the consistency of the diffusion layer, mixing condition and mass transfer difference at various concentrations. These factors are part of analytical uncertainty. Typically, the measured diffusion coefficients at lower solute concentrations tend to be somewhat smaller due to a small depletion of bulk concentration that leads to a mass transfer limitation across surface boundary layer. Table S2 shows the diffusion coefficient values reported in

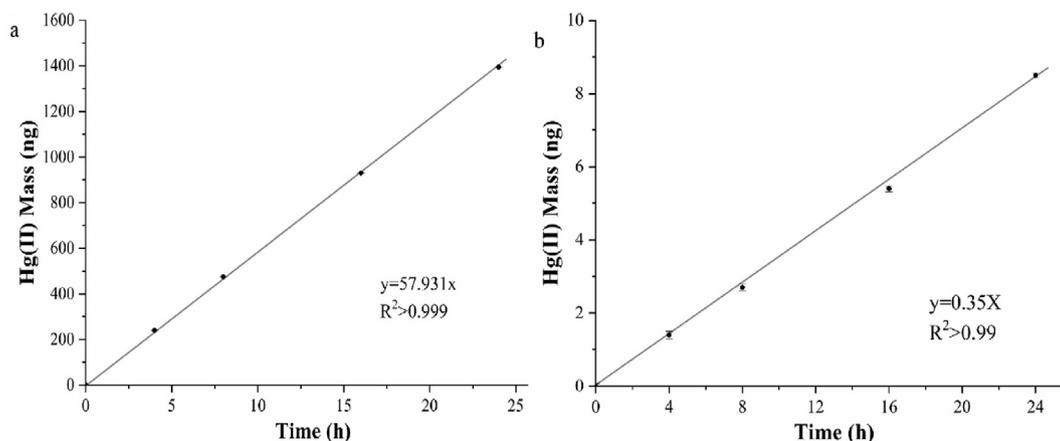


Fig. 3. Hg accumulated masses (M) vs. deployment time (h) using agarose TM-MDH DGT device in different Hg(II) concentrations ($pH = 5.0$; $I = 10$ mM Cl, $V = 1.5$ L, $T = 25$ °C). (a) high concentration ($C_{DGT} = 50$ $\mu\text{g/L}$); (b) low concentration ($C_{DGT} = 500$ ng/L); the black lines are the linear regression used to calculate the diffusion coefficients.

this and earlier works (Docekalova and Divis, 2005; Gao et al., 2011; Pelcova et al., 2014). Our estimates are consistent with the magnitude of previously reported values. This demonstrates that the TM-MDH-DGT can be successfully used in both low and high concentrations Hg(II) solutions.

3.4. Hg(II) uptake capacity of the TM-MDH DGT device

The Hg(II) uptake capacity of the resin gel relates to the number of sites able to interact with Hg(II) at the interface of the diffusive and resin layers. A high binding capacity is particularly important for DGT techniques when the resin's binding strength is low or where common ion competition is likely an issue (Davison, 2016).

In this study, the uptake capacity of Hg(II) by the TM-MDH resin is measured by placing the DGT device in a 2-L solution containing increasing Hg(II) concentration up to 25 mg/L for 24 h. A linear response between the accumulated Hg mass and aqueous Hg(II) concentration indicates that resin has sufficient capacity for Hg(II) uptake based on Eq. (3). As shown in Fig. 4, the linear trend sustains up to 15 mg/L of Hg(II). After that, the accumulated Hg(II) deviates from the linear trend. It was also found that the deviation from linearity increased over time at 20 and 25 mg/L. It is possible that the active binding sites become saturated at high Hg(II) concentrations. Competition by other ions (e.g. H^+ , HCO_3^- , SO_4^{2-} , etc.) in the solution may also be a cause for the decreased capacity through a reduction in available resin binding sites.

Using Eq. (3), the uptake capacity of the developed TM-MDH resin is up to $41 \mu\text{g}/\text{cm}^2$. Using the slope shown in Fig. 6 and a 7-day deployment, the Hg(II) concentration needs to be $> 2 \text{ mg/L}$ to exceed the update capacity of each resin disk. Since the typical Hg(II) concentration of Hg(II) in environmental waters are orders of magnitude lower than 2 mg/L . For example, total Hg concentration in contaminated paddy soil pore water near historical Hg mining area of Wanshan was 20–916 ng/L (Colaco et al., 2014; Zhao et al., 2016a). It is highly unlikely the capacity of the TM-MDH DGT device will be exceeded for environmental measurement.

3.5. Field verification

3.5.1. In-situ measurement in Baihua Reservoir

The TM-MDHDGT device has been deployed for a 7-day

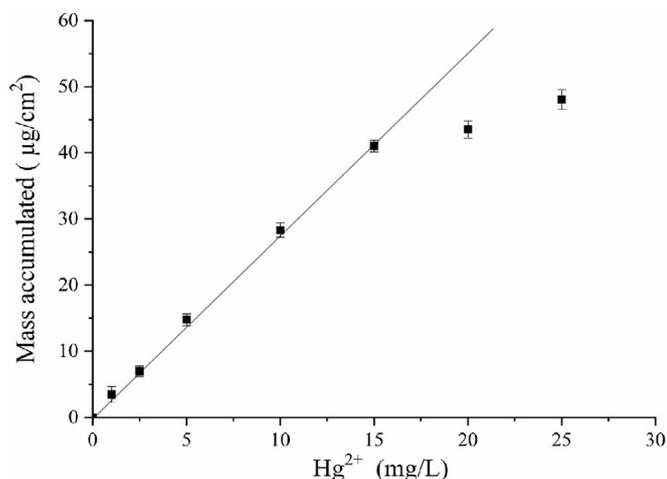


Fig. 4. Mass of Hg accumulated by TM-MDH DGT device at 25°C deployed for 24 h in solution containing 10 mM NaCl and different concentrations of Hg. The solid line is calculated from known concentration by equation (3). Values are mean \pm standard deviation of three replicates ($n = 3$).

sampling period in Baihua Reservoir and the measured concentration is verified against the concentration determined using conventional direct water sampling. During the deployment period, water quality parameters are as follows. The temperature ranges from 8.7 to 22.9°C , with a mean ($\pm\text{SD}$) value of $15.8 \pm 7.08^\circ\text{C}$. The pH value ranges from 7.7 to 8.0 , with a mean ($\pm\text{SD}$) value of 7.84 ± 0.13 . These parameters are applicable based on the laboratory measured characteristics of the TM-MDH-DGT device.

Fig. 5 shows the Hg concentrations measured by the DGT and conventional sampling methods. The Hg(II) mean ($\pm\text{SD}$) concentration measured by DGT is $3.19 \pm 0.06 \text{ ng/L}$ over 7 days, compared to the measured mean concentration of $2.85 \pm 0.83 \text{ ng/L}$ (2.10 – 4.20 ng/L) by direct water sampling. Compared to the previously reported mean concentration of $2.2 \pm 0.9 \text{ ng/L}$ (Yan et al., 2013), the Hg(II) concentration in Baihua Reservoir is similar to those found in uncontaminated aquatic systems (Zhang et al., 2009; Jeremiason et al., 2009). There is no statistical difference between

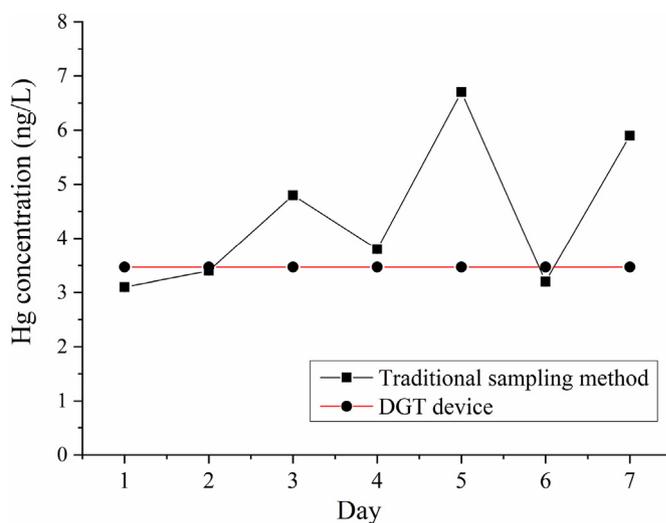


Fig. 5. Hg(II) concentrations measured using the TM-MDH DGT device (red line), it represented the 7-days average concentration; and direct water sampling (black line), it represented each day concentration at 11:00 a.m. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

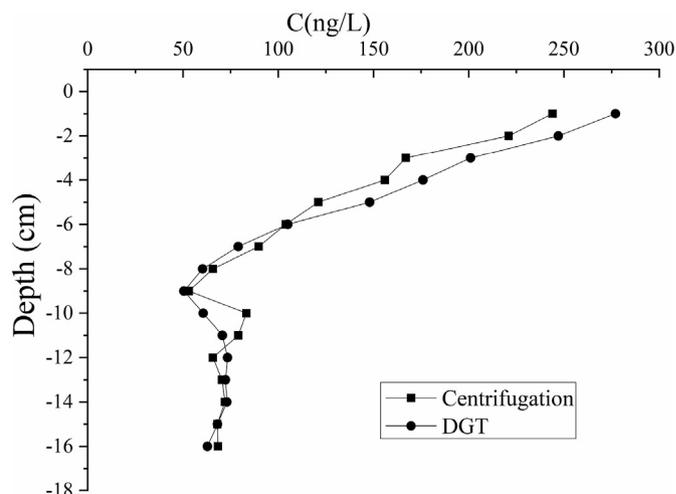


Fig. 6. Vertical distribution of Hg(II) concentrations in paddy pore water as measured by centrifugation and DGT methods.

the concentration measured by the two methods (T-Test, $p > 0.05$), demonstrating the effectiveness of the DGT sampling method.

The measured concentration of Hg(II) concentration using conventional sampling shows greater variability due to environmental changes such as rainfall, surface runoff and flow in the reservoir (Yao et al., 2011). In contrast, the TM-MDH-DGT method gives time-averaged concentration of Hg(II) during the sampling period. The mean Hg(II) concentration measured by the direct water sampling method is approximately 10% smaller than the concentration measured by the DGT method. It is likely that the conventional sampling method underestimates the mean concentrations, possibly due to a loss of Hg(II) during storage and transportation before analysis. The passive DGT sampling method is particularly useful and cost-effective for measuring time-average concentration of Hg(II).

In addition, various Hg species co-exist in environment medias. For example, both Hg(II) and MeHg are present in natural water. The resin gel developed in this study contains the sulfhydryl material and is capable of adsorbing both Hg(II) and MeHg simultaneously. During laboratory verification, the uptake of MeHg using TM-MDH resin is less than 50% at 0.05 $\mu\text{g/L}$ aqueous solution. The concentration of MeHg is typically much smaller than that of Hg(II), i.e., the ratio of MeHg and THg (MeHg/THg) about $5 \pm 0.82\%$ (Long et al., 2018). Given the uptake capacity of the resin, we do not anticipate analytical bias caused by the presence of trace amount of MeHg.

3.5.2. *In situ* measurement in paddy soil

Temperature (T) and pH are monitored at the sampling site for soil paddy. The pH values ranges from 7.2 to 7.4, with an averaged value of 7.32 ± 0.12 in pore water. The temperature ranges from 28.4 to 30.6 $^{\circ}\text{C}$, with a mean value of 29.5 ± 1.10 in pore water. The paddy water is mildly alkaline, and the paddy soil is a yellow brownish, occasionally black, soft mud. The water content is 65%, with an organic carbon content at $4.6 \pm 0.85\%$ (dry wt.). These parameters fall within the range for application of DGT device for Hg(II) measurement.

Fig. 6 shows the vertical profile of Hg(II) concentrations in the paddy porewater using the DGT and centrifugation sampling methods. The DGT technique yields 114 ± 70 ng/L compared to 108 ± 59 ng/L using the centrifugation method. These two methods are statistically consistent with each other (paired *t*-Test, $p > 0.05$). The concentration variation trends are also similar, although the centrifugation-measured concentration is somewhat lower (at ~95% of the DGT-measured concentration). From the vertical concentration-depth profiles (Fig. 6), the highest concentration of Hg(II) in pore water occurs in the surface layer (0–2 cm), decreases with depth, and remains unchanged below the 8 cm (K–S test, $p > 0.05$). It shows that Hg(II) concentration is higher in the top-layer soil, consistent with the results of previous research reported (Zhao et al., 2016b). This is due to the fact that the water column is controlled by atmospheric deposition or human activities (Zhang et al., 2009). The Hg(II) peak appearing at 10-cm depth indicates the release of Hg(II) from deep soil solids due to bio-turbation. The observed differences shown in Fig. 6 may be caused by the two fundamentally different sampling methods. It has been documented that centrifugation method can lead to Hg(II) loss during collection. Because centrifugation method requires soil samples for centrifugation in the lab analysis, the sampling process can be prone to contamination caused by its sample treatment. Using the TM-MDH DGT device eliminates such contamination concern. Although long-term monitoring is necessary to further illustrate the effectiveness of the DGT method, our field results show that the developed resin in this study can effectively sample Hg(II) in both homogeneous and heterogenous environmental media.

4. Conclusions

This work demonstrates a rapidly soluble, highly uniform resin made of thiol-modified metal double hydroxide for collecting Hg(II) in water and saturated soil using DGT devices. The resin is capable of passively concentrating Hg(II) in aqueous and sediment samples over a wide range of ionic strength and pH. Laboratory examination shows that the efficiency of Hg(II) uptake onto the resin in aqueous solution reaches $95.4 \pm 1.9\%$. The diffusion coefficient of Hg(II) measured with a DGT device housing the resin and an agarose gel diffusive layer is $9.48 \pm 0.07 \times 10^{-6} \text{ cm}^2/\text{s}$ at 50 $\mu\text{g/L}$ Hg(II) aqueous solution, consistent with the known values reported in the literature. The adsorption characteristics of the developed resin exhibit excellent linearity between Hg(II) uptake and aqueous concentration, with a capacity of 41.0 $\mu\text{g}/\text{cm}^2$, satisfying the requirement for *in-situ* monitoring of Hg(II) over a wide range of field applications. The developed method has been successfully deployed and verified in two field tests for field sampling in reservoir water and in contaminated paddy soil.

Compared with direct sampling method, the DGT method gives the *in-situ* time-averaged concentration while water sampling yields Hg(II) concentration at the sampling time. DGT devices can be easily packaged and transported to and from remote sites with little possibility of contamination. Once deployed, the Hg(II) can be sampled and concentrated passively without the need of extensive sample preparation. Since the Hg(II) concentration in selected environmental samples may fall below instrumental detection limits for direct determination, using DGT with an extended sampling period *in-situ* helps address the analytical need for environmental measurements. Earlier studies have shown that metal concentration determined using DGT is representative of bioavailable fraction, which is another advantage over direct sampling methods. More field examinations need to be performed, especially in anoxic water and sediments, to further understand the bioavailability of Hg in lake water and paddy soil. The developed DGT resin serves as a useful analytical tool for such studies.

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.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.chemosphere.2020.126231>.

Author contribution

Heng Yao performed the experiments and draft the manuscript, Yujie Zhao designed the experiments and provide technical guidance, Che-Jen Lin performed the data analysis and revised the manuscript ^{c,d,*}, Fengjiao Yi and Xuefeng Liang assisted in the technical assessment, Xinbin Feng oversee the work and review the manuscript.

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