In Situ Measurement of Thallium in Natural Waters by a Technique Based on Diffusive Gradients in Thin Films Containing a δ-MnO₂ Gel Layer

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Supporting Information

ABSTRACT: Thallium (Tl) has been identified as a priority contaminant because of its severe toxic effects. Exact measurement of Tl is a challenge because it is difficult to avoid altering the element’s chemical speciation during sampling, transport, and storage. In situ measurement may be a good choice. Based on the in situ technique of diffusive gradients in thin films (DGT), new DGT devices equipped with novel laboratory-synthesized manganese oxide (δ-MnO₂) binding gels were developed and systematically validated for the measurement of Tl, including Tl(I) and Tl(III) species, in water. Comparison between Chelex binding gel and δ-MnO₂ gel on the uptake kinetics of Tl demonstrated that δ-MnO₂ binding gels could adsorb Tl rapidly and effectively. Removal of Tl from the δ-MnO₂ gels was achieved by use of 1 mol·L⁻¹ oxalic acid, yielding elution efficiencies of 1.0 for Tl(I) and 0.86 for Tl(III). Theoretical responses from DGT devices loaded with δ-MnO₂ gel (δ-MnO₂-DGT) were obtained irrespective of pH (4–9) and ionic strength (0.1–200 mmol·L⁻¹ NaNO₃). δ-MnO₂-DGT showed good potential for long-term monitoring of Tl due to its high adsorption capacity of 27.1 μg·cm⁻² and the stable performance of δ-MnO₂ binding gel kept in solution, containing only 10 mmol·L⁻¹ NaNO₃, for at least 117 days. Field deployment trials confirmed that δ-MnO₂-DGT can accurately measure the time-averaged concentrations of Tl in fluvial watercourses. In summary, the newly developed δ-MnO₂-DGT technique shows potential for environmental monitoring and biogeochemical investigation of Tl in waters.

Thallium (Tl) is a rare, nonessential element and notorious poison, whose toxicity is much higher than that of mercury (Hg), cadmium (Cd), lead (Pb), or copper (Cu), evoking biological damage even at extremely low parts per billion concentrations.¹ Due to its mutagenic, carcinogenic, and teratogenic activity, Tl is listed as a priority pollutant by the U.S. Environmental Protection Agency (EPA) and has been classified as a dangerous substance by the European Union (EU Directive 67/548/EEC).² ³ Anthropogenic sources of Tl in the environment mainly stem from coal combustion, iron and nonferrous mining and smelting, and cement production.⁴ ⁵ The global average Tl concentration in nonpolluted surface waters is typically on the order of a few nanograms per liter.⁶ Nonetheless, there are some geographic differences: for example, the coastal seawaters of Australia possess an average concentration of 13.0 ± 1.4 ng·L⁻¹ Tl, while inland the freshwater levels are typically 4 ng·L⁻¹ Tl.⁶ In Sweden, concentrations of Tl in eight watercourses, comprising a mixture of rivers and lakes, ranged between 11 and 46 ng·L⁻¹.⁷ This is higher than for nonpolluted natural waters in both the United Kingdom⁸ and Italy, with the latter averaging 5.5 ng·L⁻¹.⁹ However, Tl concentrations of up to 534 and 1098 μg·L⁻¹, 5–6 orders of magnitude higher than those of normal river water, were detected in acid mine drainage from an abandoned Pb–Zn mine in the south of France and in deep groundwater within the Tl-mineralized area in Guizhou Province, China, respectively.¹⁰ ¹¹ In order to regulate/minimize exposure to Tl, the U.S. EPA has set its maximum
limit value and the target value for Tl in drinking water at 2 and <0.5 μg L\(^{-1}\), respectively.\(^{13}\) China has a more stringent potable water standard with a maximum limit value of 0.1 μg L\(^{-1}\).\(^{14}\)

Tl exits in two oxidation states in the aquatic environment, Tl(I) and Tl(III), with each species exhibiting significantly different physical, chemical, and toxicological properties.\(^{10,14}\) Compared with one another, Tl(I) is more thermodynamically stable and less reactive than Tl(III).\(^{15}\) It is well documented that Tl(I) predominates in freshwaters.\(^{10,16}\) In oxidizing environments, Tl(III) can exist as Tl(OH)\(_3\) (log \(K_{sp}\) = −45.2) at pH < 7. The occurrence of stable Tl(III) in solution is possible at higher pH, where hydroxide complexes are formed, and in the presence of ligands such as sulfates, chlorides, acetate, and humic acid.\(^{14,17}\) Furthermore, the toxicity of Tl(III) to the unicellular alga Chlorella has been shown to be 50,000 times greater than that of Tl(I).\(^{18}\)

The measurement of Tl species in natural waters presents a number of challenges, principally due to the low Tl concentration present but also because traditional analytical methods have low sensitivity for Tl and suffer from a range of matrix-related interference.\(^{1,19}\) The predominant methods for determining concentrations of Tl in surface waters require preconcentration/separation of Tl in water samples onto specific adsorbents or resins.\(^{20}\) Liquid−liquid extraction,\(^{21}\) cloud-point extraction,\(^{22}\) and solid-phase extraction\(^{23}\) have been developed, and various adsorbents, such as Amberlite XAD resins, Chelex-100 resin, and Chromosorb105 resin, have been used for this purpose.\(^{14,20,24}\) However, these methods are usually laborious and time- and reagent-consuming and require a large sample volume. Therefore, a technique with a low detection limit and a high sensitivity to determine trace concentrations of Tl is a pressing need. As an alternative to the current analytical methods for Tl, the diffusive gradients in thin films (DGT) technique is a passive sampling method for in situ measurement of time-averaged concentration of a broad range of labile metal and metalloid species in solution.\(^{25}\) Based on Fick’s first law of diffusion,\(^{26}\) the DGT technique associates the processes of mass transport through a diffusive gel layer with accumulation within a binding gel layer (i.e., a resin/adsorbent immobilized in a thin layer of a hydrogel). Compared with immediate or grab sampling, in situ measurement with DGT circumvents the measurement biases associated with the former for altering an element’s chemical form during collection, processing, and storage. In dynamic systems (e.g., rivers) where concentrations can change rapidly, grab sampling will not capture the variation in concentration, whereas DGT will incorporate this variation into the time-averaged measurement.\(^{27}\) Finally, even trace or ultratrace concentrations of the elemental target can be measured, because of the absorption/enrichment process that operates within the DGT device. Due to its simplicity, in situ deployment, and robustness, DGT has been successfully applied to measure different analytes in natural waters,\(^{28-29}\) soils,\(^{30-31}\) and sediments.\(^{32,33}\)

It has been reported that Chelex-100 resin can adsorb Tl in water effectively over a strict/limited range of pH (~1.8).\(^{34}\) Although DGT devices equipped with Chelex binding gels (designated Chelex-DGT) have been used to study the high-resolution profiles of Tl in sediments,\(^{35}\) it was reported that Chelex-DGT showed low uptake of Tl, and the authors suggested further characterization of Chelex-DGT performance in the measurement of Tl.\(^{35}\) Δ-MnO\(_2\) has been proven as an excellent adsorbent for Tl in both soil remediation and wastewater treatment\(^{36,37}\) due to its strong oxidation ability, high selectivity, and high surface area. There is no literature on DGT devices equipped with δ-MnO\(_2\) binding gels (designated δ-MnO\(_2\)-DGT) for Tl measurement. In this study, δ-MnO\(_2\) was used for the first time as a binding phase in DGT devices. δ-MnO\(_2\)-DGT devices were evaluated for measuring Tl under different conditions of pH and ionic strength and compared with Chelex-DGT devices as well. Diffusion coefficients of Tl in the diffusive gels were measured by two different methods, for precise evaluation of DGT-measured concentrations. A field trial of δ-MnO\(_2\)-DGT device was performed in natural waters near Tl-polluted sources to assess its performance in a real aquatic environment.

## EXPERIMENTAL SECTION

**Reagents, Materials, and Solutions.** Tl stock solutions were prepared by dissolving Tl(NO\(_3\))\(_3\)·3H\(_2\)O (Acros, Belgium) in 0.1 mol·L\(^{-1}\) HNO\(_3\) (Sigma–Aldrich) and then diluting with Milli-Q water\(^{38}\) (18.2 MΩ·cm, Millipore). Gel-making reagents include 40% acrylamide and bis-acrylamide (99%; Electron, BDH), H\(_3\)PO\(_4\), H\(_2\)C\(_2\)O\(_4\), KMnO\(_4\), and MnSO\(_4\) were purchased from Nanjing Chemical Reagent Co., Ltd. NaOH and NaNO\(_3\) were purchased from Xilongs Scientific, Shantou, China. All reagents were of analytical grade or above. DGT piston moldings were supplied from DGT Research Ltd. (Lancaster, U.K.). Containers and moldings were acid-cleaned twice in an acid bath, containing only 10% (v/v) HNO\(_3\) for about 24 h and then washed with Milli-Q water three times.

**Synthesis of δ-MnO\(_2\).** δ-MnO\(_2\) was prepared according to Cai and Ren,\(^{39}\) by titrating KMnO\(_4\) solution (45 g·L\(^{-1}\)) with MnSO\(_4\) solution (35 g·L\(^{-1}\)) with vigorous stirring to produce δ-MnO\(_2\) precipitate, which was washed and then dried at 103 °C for 12 h. The obtained δ-MnO\(_2\) was characterized and used as the DGT binding phase.

**Analytical Methods.** MnO\(_2\) crystal structures were characterized by X-ray diffraction (XRD; ARL XTRA). Scanning electron microscopy (SEM) was performed on an emission scanning electron microscope (Hitachi S-3400N II, Japan) at 40 kV and 40 mA to detect the homogeneity of δ-MnO\(_2\) binding gel. Inductively coupled plasma mass spectrometry (ICP-MS; NexION 300X, PerkinElmer) was used to analyze total Tl in experiments. All samples were diluted with 0.1 mol·L\(^{-1}\) HNO\(_3\) and indium (In) was added as an internal standard, spiked to give a 50 μg·L\(^{-1}\) concentration. Certified reference material (CRM) BWB2198-2016 river water (National Reference Materials, China) was used to validate the ICP-MS analysis.

**Speciation Modeling.** As a companion approach to DGT speciation measurement, Tl speciation was modeled by use of PhreeQC software parameterized with equilibrium constants obtained from the literature\(^{0,40,41}\) (Table S1). The PhreeQC software was developed for computation of aqueous geochemical speciation in principally low ionic strength media. Caution must be applied, therefore, when the in silico simulation is extended to higher ionic strength conditions, such as seawater.\(^{42}\)
Device Preparation for Diffusive Gradients in Thin Films. A piston DGT device contains a 0.40 mm thick binding gel, a polyacrylamide diffusive gel with 0.80 mm thickness, and a 0.14 mm thick, 0.45 μm pore size hydrophilic poly(ether sulfone) filter membrane (Pall), sandwiched by a DGT plastic base and a cap with a window open area of 2.51 cm². The polyacrylamide diffusive gel was prepared according to previously described procedures[1] (see section S1).

In this study, two different binding gels were used: Chelex-100-based and δ-MnO₂-based. Chelex gel was prepared according to the procedure described by Zhang and Davison[45] (see section S1). Preparation of δ-MnO₂ gels was different from that of Chelex binding gels. Briefly, 0.33 g of dried δ-MnO₂ powder was weighed into 10 mL of gel solution, and then the gel solution was placed in an ultrasonic bath, containing ice to keep the gel solution at low temperature, for at least 8 min to evenly disperse the δ-MnO₂ in the gel solution. After that, 100 μL of 10% daily prepared APS solution and 20 μL of TEMED were added to the gel solution, and the whole mixture was carefully shaken. The solution was then cast into acid-cleaned glass plate assemblies with 0.25 mm thick plastic spacer around three edges, and the molds were then heated in an oven at 42–46 °C for about 36 min. δ-MnO₂ gel hydrated in Milli-Q water for 24 h, with five changes of water. The gels were then cut into discs with a diameter of 2.5 cm and kept in 10 mmol L⁻¹ NaNO₃ at 4 °C for use.

Calculation of Concentrations Measured by Diffusive Gradients in Thin Films. According to the theory of the DGT technique, DGT-measured concentrations, C_DGT, can be calculated through eqs 1 and 2:[44]

\[ C_{\text{DGT}} = M \Delta g / (DA t) \]  
\[ M = C_{\text{e}} (V_{\text{gel}} + V_{c}) / f_{c} \]

where \( M \) (nanograms) is the amount of Tl (which can be calculated in eq 2) adsorbed by the binding gels, \( C_{\text{e}} \) (micrograms per liter) is the Tl concentration in the eluent, and \( V_{\text{gel}} \) and \( V_{c} \) (milliliters) are the volumes of binding gels and eluents, respectively. \( f_{c} \) represents Tl elution efficiency, \( \Delta g \) (centimeters) is the total thickness of diffusive gel and filter membrane, \( A \) (square centimeters) is the window open area of a DGT device, \( t \) (seconds) is the deployment time of DGT immersing into deployment solution, and \( D \) is the diffusion coefficient of the measured metal. In order to precisely calculate the DGT-measured concentrations, it is necessary to measure these parameters during DGT deployment.

Uptake Kinetics and Elution Efficiency. The two kinds of prepared binding gel discs were soaked and shaken in 10 mL of 50 μg L⁻¹ Tl(I) or Tl(III) and 0.01 mol L⁻¹ NaNO₃ for different times from 2 min to 24 h at 25 °C. All samples were in triplicate. Elution efficiency refers to the recovery rate of an analyte from the binding gel. Accurate measurement of elution efficiency is crucial to the calculation of \( C_{\text{DGT}} \). To investigate the stability of elution efficiency, gels loaded with different amounts of Tl were each eluted for 24 h. Different eluents were adopted to elute Tl from the loaded gels to find the best eluent. HNO₃ is usually used to elute metals from Chelex gels,[35] and therefore aliquots (1 mL) of 1, 2, and 3 mol L⁻¹ HNO₃ were adopted to elute Tl preloaded onto Chelex gels. As for δ-MnO₂ gels, aliquots (1 mL) of 2 and 3 mol L⁻¹ HNO₃, 1 mol L⁻¹ oxalic acid (H₂C₂O₄), H₃PO₄, and NaOH, were used for eluents.

Measurement of Diffusion Coefficient. Diffusion coefficients of Tl(I), denoted Tl(I)_D, and Tl(III), denoted Tl(III)_D, across the diffusive layer were measured via the diffusion cell method and the DGT device derivation method according to the reported procedure.[28] A diffusion cell is composed of two glass cells connected by a round hole with a diameter of 1.5 cm. While measuring diffusion coefficients, a piece of 0.8 mm thick diffusive gel was clamped between the two holes of the two cells. After that, 50 mL of 1 mg L⁻¹ Tl solution containing 10 mmol L⁻¹ NaNO₃ was added in a source cell, and 50 mL of Tl-free solution containing 10 mmol L⁻¹ NaNO₃ without Tl was added in a receptor cell. The two kinds of solution had the same pH and temperature. When the solutions were added, the two cells were mixed by use of an overhead stirrer. Solution samples (200 μL) in the two cells were collected at 10 min intervals during the 2 h experiment. The collected samples were measured by ICP-MS. Finally, Tl concentration in the source cell was rarely changed. The diffused mass \( M \) (nanograms) from the source cell to the receptor cell linearily correlated with time \( t \) (seconds). Diffusion coefficient measured by use of this cell device, \( D_{\text{cell}} \), can be calculated from eq 3:

\[ D_{\text{cell}} = \frac{\Delta g}{CA} \]  

where \( \Delta g \) is obtained from the linear plot of the mass of Tl diffused into the receptor cell versus time, \( C \) is the Tl concentration in the source cell, and \( A \) (1.767 cm²) is the open area of the round hole between the two cells.[60]

Another method for measurement of diffusion coefficients uses DGT devices. δ-MnO₂-DGT devices were deployed in a 2 L well-stirred solution of 50 μg L⁻¹ Tl and 0.01 mol L⁻¹ NaNO₃ for 24 h. \( D_{\text{DGT}} \) was calculated from eq 4:

\[ D_{\text{DGT}} = \frac{M \Delta g}{C_{\text{sol}} A t} \]

where \( C_{\text{sol}} \) is the solution concentration of Tl in the container and \( M \) is the mass in the binding gels.

Laboratory Performance Characteristics of Diffusive Gradients in Thin Films. Effects of pH and Ionic Strength. To test environmental conditions of pH and ionic strength on DGT measurements, the two kinds of DGT devices (Chelex-DGT and δ-MnO₂-DGT) were deployed in a well-stirred solution for 4 h. For pH experiments, 2 L solutions, containing 30 μg L⁻¹ Tl and 10 mmol L⁻¹ NaNO₃ with pH ranging from 2 to 9, were used. Solution pH was adjusted/optimized by stirring the solution in the presence of air, followed by a stabilization period of ca. 72 h. During this period, the pH was adjusted at 12 h intervals with 1 mol L⁻¹ HNO₃ and 1 mol L⁻¹ NaOH. As for the ionic strength experiments, 2 L solutions containing 40 μg L⁻¹ Tl and a range of concentrations of NaNO₃ (0.1–200 mmol L⁻¹) were used. After DGT deployment for 4 h, binding gels were retrieved from the DGT devices and eluted for 24 h.

Capacity and Storage Time. High capacity is necessary for long-term deployment of DGT devices in the environment. To measure the capacity of δ-MnO₂-DGT, DGT devices containing 0.8 mm thick diffusive gels were deployed in a series of well-stirred 2 L solutions of pH 5.7 ± 0.2 containing 0.01 mol L⁻¹ NaNO₃ and different concentrations of Tl(I) ranging from 0.1 to 80 mg L⁻¹ for 4 h. In addition, to evaluate effects of storage time of δ-MnO₂ binding gel on δ-MnO₂-DGT performance, δ-MnO₂ gels were stored in 10 mmol L⁻¹ HNO₃ for different times from 2 min to 24 h at 25 °C. All samples were in triplicate. Elution efficiency refers to the recovery rate of an analyte from the binding gel. Accurate measurement of elution efficiency is crucial to the calculation of \( C_{\text{DGT}} \). To investigate the stability of elution efficiency, gels loaded with different amounts of Tl were each eluted for 24 h. Different eluents were adopted to elute Tl from the loaded gels to find the best eluent. HNO₃ is usually used to elute metals from Chelex gels,[35] and therefore aliquots (1 mL) of 1, 2, and 3 mol L⁻¹ HNO₃ were adopted to elute Tl preloaded onto Chelex gels. As for δ-MnO₂ gels, aliquots (1 mL) of 2 and 3 mol L⁻¹ HNO₃, 1 mol L⁻¹ oxalic acid (H₂C₂O₄), H₃PO₄, and NaOH, were used for eluents.
DGT devices were deployed in situ along the creek and the Jiangshui River, which are impacted by a range of industrial activities including pyrite mining, sulfuric acid processing, and cement works. DGT devices were deployed in a 2 L solution with pH 5.7 and 10 mmol·L⁻¹ NaNO₃ for 4 h.

Field Application. To test the applicability of δ-MnO₂-DGT in natural water, DGT devices were deployed in a contaminated creek and the Jiangshui River, which are impacted by a range of industrial activities including pyrite mining, sulfuric acid processing, and cement works. Locations of the eight sampling sites are shown in Figure 1. These sites were chosen on the basis of their distances from the identified industrial pollution point sources, as well as their proximity to other input source such as streams or creeks. DGT devices were deployed in situ along the creek and Jiangshui River in May 2018. Six δ-MnO₂-DGT devices were deployed in each sampling site for 24 h with a button thermometer (DS 1922L, Maxim Integrated Products) to record the temperature at 20 min intervals during the sampling period. To avoid direct contact of DGT samplers with the riverbed sediment, δ-MnO₂-DGTs were deployed in poly(vinyl chloride) (PVC) tubes with an inner diameter of 16 cm and length of about 25 cm. The PVC tubes’ openings were oriented to face the direction of water flow. It was reported that when flow rate exceeds 2 cm·s⁻¹, the effect of diffusion boundary layer (DBL) on DGT measurements will be small, and in this case the thickness of the DBL can be excluded from the calculation of DGT concentration. During our deployments, there were two rainstorm events resulting in estimated river flow rates of ~6–20 cm·s⁻¹; thus the DBL was negligible for calculation in this study. The DGT devices were rinsed thoroughly with Milli-Q water upon retrieval from the field waters. Then these devices were placed in acid-cleaned plastic bags, stored in a refrigerated container at ~4 °C, and transported to the laboratory for further analysis.

To validate the DGT measurements, a conventional grab sampling of water (100 mL) at a depth of about 15 cm (in triplicate) was performed at the beginning (0 h) and end (24 h) of the DGT deployment. In addition, two more grab samplings were conducted for sites 2 and 3 during the 24 h sampling period. The basic physical—chemical parameters [pH, temperature, dissolved oxygen (DO), and electrical conductivity (EC)] of the water samples were measured on-site by a multiparameter portable probe (Orion Star A329 Portable, Thermo Scientific). Before being returning to the laboratory, the water samples were filtered (0.45 μm pore size nitrocellulose membrane), adjusted to pH < 2 with concentrated HNO₃, and then stored in closed polypropylene vessels at 4 °C prior to analysis. Water subsamples without acidification/stabilization treatment were measured for total organic carbon (TOC) on a TOC analyzer (TOC-V CPH, Shimadzu). Concentrations of anions (Cl⁻, SO₄²⁻, and F⁻) and trace metal elements were measured by ion chromatography (ICS-2100, Thermo Fisher) and ICP-MS, respectively.

RESULTS AND DISCUSSION

Structure of δ-MnO₂ and Gel. Crystalline properties (Figure S1) of the synthesized δ-MnO₂ particles in this study, determined by XRD, were similar to the standard sample of synthetic birnessite phase δ-MnO₂ (peaks at 25.06°, 37.16° and 66.12°) suggesting the successful preparation of δ-MnO₂ particles. The synthesized δ-MnO₂ particles have sizes ranging from 100 to 500 nm. The fine size of the δ-MnO₂ particles means they agglomerate easily in the gel solution. SEM analysis of δ-MnO₂ binding gel was carried out to check whether δ-MnO₂ particles dispersed evenly in the gel. Figure S1b shows that δ-MnO₂ particles were homogeneously distributed in the gel.

Blanks and Detection Limits for Diffusive Gradients in Thin Films. The DGT blank concentration was determined from the measured mass of Tl in the binding gel (δ-MnO₂ gel or Chelex gel) assembled in a DGT device with a 0.8 mm thick diffusive gel, a filter membrane (0.14 mm thick), and 2.51 cm² exposure window by assuming a supposed deployment time of 7 days at 25 °C. The method detection limit (MDL) of DGT measurement was calculated as 3 times the standard deviation of the DGT blank concentration. DGT blank concentrations and MDLs of Tl(I) and Tl(III) for δ-MnO₂-DGT and Chelex-DGT are summarized in Table S2. MDLs of Tl(I) and Tl(III) for δ-MnO₂-DGT and Chelex-DGT are summarized in Table S2. MDLs of Tl(I) and Tl(III) for δ-MnO₂-DGT and Chelex-DGT are summarized in Table S2. MDLs of Tl(I) and Tl(III) for δ-MnO₂-DGT and Chelex-DGT are summarized in Table S2. MDLs of Tl(I) and Tl(III) for δ-MnO₂-DGT and Chelex-DGT are summarized in Table S2. MDLs of Tl(I) and Tl(III) for δ-MnO₂-DGT and Chelex-DGT are summarized in Table S2. MDLs of Tl(I) and Tl(III) for δ-MnO₂-DGT and Chelex-DGT are summarized in Table S2. MDLs of Tl(I) and Tl(III) for δ-MnO₂-DGT and Chelex-DGT are summarized in Table S2. MDLs of Tl(I) and Tl(III) for δ-MnO₂-DGT and Chelex-DGT are summarized in Table S2. MDLs of Tl(I) and Tl(III) for δ-MnO₂-DGT and Chelex-DGT were much lower than those for other commonly used methods for total Tl measurement, for example, sequential injection dispersive liquid—liquid microextraction (SI-DLLME; MDL = 0.86 μg·L⁻¹) and the flotation reagent protocol method using hexamethylenediammo-nium hexamethylenedithiocarbamate (HMAHMDTC; MDL = 0.024 μg·L⁻¹) for measurement of total Tl. The MDLs of DGT were lower than the average dissolved Tl concentration.

![Figure 1. Map of sampling sites in Yunfu, Guangdong Province, South China.](image-url)
eluents are listed in Table 1. Generally, the elution efficiencies of Tl(I) and Tl(III) bound onto binding gels and eluted with different eluents cannot elute Tl(I) and Tl(III) from δ-MnO₂ gels, with very low elution efficiencies of <0.008. On the contrary, 1 mol·L⁻¹ H₂C₂O₄ had high elution efficiencies for Tl(I) (1.04 ± 0.06) and Tl(III) (0.86 ± 0.06). The black δ-MnO₂ gel turned to a transparent gel after addition of 1 mL of 1 mol·L⁻¹ H₂C₂O₄ for 20 min, indicating that δ-MnO₂ can react with H₂C₂O₄ and then dissolve the binder releasing the adsorbed Tl into the eluate (MnO₂ + 2H₂C₂O₄ = MnC₂O₄ + 2CO₂ + 2H₂O). In this study, 1 mol·L⁻¹ HNO₃ and H₂C₂O₄ were adopted to elute Tl from Chelex gels and δ-MnO₂ gels, respectively.

Diffusion Coefficients of Tl(I) and Tl(III). Accurate determination of the diffusion coefficients of Tl(I) and Tl(III) is a prerequisite for successful DGT measurement of Tl. The mass of diffused Tl(I) and Tl(III) into the receptor cell increased linearly with time (correlation coefficient r = 0.99 for both Tl(I) and Tl(III), p < 0.05), implying that there was a stable diffusion process of the measured Tl during the experimental period. Diffusion coefficient of Tl(I) in water, D_water, is 15.34 × 10⁻⁶ cm²·s⁻¹ at 25 ºC. Diffusion coefficients, D_gel of Tl(I) and Tl(III) calculated by use of eq 3 are listed in Table S3. D_gel values for Tl(I) and Tl(III) were 14.74 × 10⁻⁶ and 9.02 × 10⁻⁶ cm²·s⁻¹, respectively, at 25 ºC. Similarly, D_DGT values were 13.96 ± 10⁻⁶ and 10.88 × 10⁻⁶ cm²·s⁻¹ at 25 ºC for Tl(I) and Tl(III), respectively. D_gel of Tl(I) was much larger than that of Tl(III), probably due to the ionic radii of labile Tl⁺ (0.150 pm; Tl³⁺; 0.89 pm; Tl(OH)²⁺; 1.80 pm; Tl(OH)⁺; 2.70 pm) in solution, covalent bonding between Tl and OH possesses a radius of 90 nm), and Tl(III) complexes with covalent bonding experienced substantially more difficulty passing through the diffusive gel. Tl(I)D_gel was about 106% of Tl(III)D_gel and the difference between these two values from two different methods was less than 6%, suggesting that measured D here was reasonable. However, Tl(I)D_gel was about 82.9% of Tl(III)D_gel. The ratio of D_gel to D_DGT was similar to that for As(III) and As(V) reported by Bennett et al., in which D_gel/D_DGT for As(III) and As(V) were 79% and 82%, respectively. In order to be consistent in the calculation of DGT measured concentrations, D_gel was used for calculation in eq 1.

Effects of pH and Ionic Strength. According to theory of the DGT technique, in simple solutions without metal organic complexes and colloids, DGT-measured concentrations, C_DGT of analytes should be equal to the corresponding solution concentrations, C₀, indicating that the ratio, or R, value, of C_DGT to C₀ should be 1.0 ± 0.1. Changes of R value with

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<th>eluent</th>
<th>f₂ for Tl(I)</th>
<th>f₂ for Tl(III)</th>
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<tr>
<td>1 mol·L⁻¹ HNO₃</td>
<td>0.85 ± 0.09</td>
<td>0.76 ± 0.05</td>
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<tr>
<td>2 mol·L⁻¹ HNO₃</td>
<td>0.99 ± 0.06</td>
<td>0.72 ± 0.15</td>
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<tr>
<td>3 mol·L⁻¹ HNO₃</td>
<td>1.05 ± 0.07</td>
<td>0.73 ± 0.10</td>
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<td>1 mol·L⁻¹ H₂C₂O₄</td>
<td>0.06 ± 0.04</td>
<td>0.002 ± 0.001</td>
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<tr>
<td>1 mol·L⁻¹ H₂PO₄</td>
<td>0.08 ± 0.004</td>
<td>0.003 ± 0.003</td>
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<td>1 mol·L⁻¹ NaOH</td>
<td>0.004 ± 0.001</td>
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DGT blank concentrations were calculated with 0.8 mm thick diffusive gel, 0.14 mm thick filter membrane, and 2.51 cm² open area at 25 ºC for a presumed deployment time of 24 h.

Table 1. Elution Efficiencies of Tl(I) and Tl(III) Bound onto Binding Gels and Eluted with Different Eluents
different pH are shown in Figure 3a,b. pH in the environment is normally in the range $4.3 \pm 9.4$. If $R$ values obtained in this pH range can be $1.0 \pm 0.1$, it means that DGT can accurately measure the concentrations of analytes in water. For Chelex-DGT, $R$ values for Tl(I) were all below 0.56 when pH ranged from 3.46 to 8.61. Similarly, for Tl(III), $R$ values were still lower than 0.5 in pH conditions of 2–6, though $R$ values can reach $\sim 0.8$ when pH is between 8.17 and 8.75. These data show that Chelex-DGT cannot accurately measure Tl(I) and Tl(III) at pH 2–9. The adsorption mechanism of Chelex to Tl was via ion exchange, while that of $\delta$-MnO$_2$ was via oxidation–reduction reaction. The different mechanisms mean Chelex has a lower adsorption efficiency for Tl, resulting in a lower $R$ value. Contrarily, $R$ values obtained by $\delta$-MnO$_2$-DGT were acceptable in the range of 0.9–1.1 in the studied pH range, except for a slightly low $R$ value of 0.86 $\pm$ 0.04 for Tl(I) at pH 3.46. At pH $< 4.0$, less negative charge is present on the surface of $\delta$-MnO$_2$, resulting in lower adsorption ability. Nonetheless, $\delta$-MnO$_2$-DGT can work well in the studied pH range.

$R$ values associated with different ionic strengths are shown in Figure 3c,d. For Chelex-DGT, measured $R$ values dramatically decreased as ionic strength increased, suggesting that Chelex-DGT cannot precisely measure Tl in many environments, including freshwater systems, due to ionic strength limitations. However, $\delta$-MnO$_2$-DGT showed a good ability to accurately measure both Tl(I) and Tl(III) with acceptable $R$ values of $1.0 \pm 0.1$ when ionic strength ranged from 0.1 to 200 mmol·L$^{-1}$ NaNO$_3$. This comparison study proved that $\delta$-MnO$_2$-DGT was suitable for a wide range of natural water bodies with different pH and ionic strengths.

Considering the realistic deployment time of DGT in the field, it is also important to check the long-time performance of DGT under conditions of varying pH and ionic strengths. Therefore, we carried out an experiment to investigate the effect of longer deployment time on $\delta$-MnO$_2$-DGT performance. The results (Tables S4 and S5) show that $\delta$-MnO$_2$-DGT can still effectively and correctly measure Tl in aquatic systems across ionic strength ranges (0.1–200 mmol·L$^{-1}$) and pH ranges [4–9 for Tl(I) and 2–9 for Tl(III)].

Capacity and Storage Time of $\delta$-MnO$_2$-DGT. High adsorption capacity of DGT devices is very helpful for their long-term deployment in the environment. As indicated in Figure 4a, the mass of Tl(I) accumulated by $\delta$-MnO$_2$-DGT provided a good fit with the theoretical line assessed from known concentrations of Tl(I) in solutions when they were less than 7.10 mg·L$^{-1}$. After that, accumulated mass by $\delta$-$
MnO2-DGT began to deviate from the theoretical line with increasing Tl(I) concentration in solution. Thus, the capacity of δ-MnO2-DGT was assessed at about 27.1 μg·cm−2. For this value of the capacity, δ-MnO2-DGT can be deployed in 2 mg·L−1 Tl(I)-contaminated water for 24 h at 25 °C. If Tl concentration in water was the same as the U.S. maximum limit value of 2 μg·L−1 for water quality, the measured capacity in this study would be reached after 2.6 years of deployment when only time was taken into account. Couture et al. summarized Tl concentrations in aquatic systems in more than 20 regions around the world and found that the highest concentration of Tl in groundwater was 1098 μg·L−1, which was detected in Lanmuchang, Guizhou, China. Even there, δ-MnO2-DGT can be deployed for about 42 h before reaching the adsorption capacity. Due to the low concentrations of Tl in most aquatic systems, this capacity of δ-MnO2-DGT is sufficient for measurement of Tl.

Performance characteristics of DGT devices equipped with δ-MnO2 binding gels, which had been soaked in 10 mmol·L−1 NaNO3 solution for 1, 6, 62, 71, 76, 102, or 117 days since production, are depicted in Figure 4b. R values of δ-MnO2-DGT were in the range 1.0 ± 0.1, implying that storage time of up to 117 days in this study did not affect the characteristics of δ-MnO2 gels. Further experiments are needed to confirm whether the δ-MnO2 DGT still has a stable and acceptable performance when the δ-MnO2 gels were stored for a longer time (>117 days). Therefore, δ-MnO2 gels can be stored in solution, containing only 10 mmol·L−1 NaNO3, at 4 °C for at least 117 days.

Field Deployments of δ-MnO2-DGT. δ-MnO2-DGT was deployed in situ in natural water to verify the robustness of δ-MnO2-DGT performance in a natural aquatic system. Percentages of Tl(I) and Tl(III) species calculated by use of the PhreeQC program incorporating the water physical parameters (Table S6) and the concentration of various ions (Table S7) are listed in Table S8. These data suggested that Tl(III) predominated (>98.5% of total dissolved Tl) over Tl(I) in the eight studied water samples, which was consistent with Tl species measurements taken in the Great Lakes. Therefore, concentrations of Tl measured by DGT devices deployed in the eight studied sampling sites were calculated on the basis of Tl(III) and its diffusion coefficient.

For Tl, C_{DGT} and total dissolved concentrations, C_{grab} of grab sampling water with filtration are shown in Figure 5. C_{DGT} was basically between δ_{C_{grab}} and δ_{C_{grab}} or C_{grab} at different random sampling times, except sites 1 and 8, in which C_{DGT} were marginally lower than C_{grab}. Because grab sampling cannot reflect all the changes in concentration of analytes during sampling periods of DGT deployment, it may at least partially account for the lower ratio of C_{DGT} to C_{grab} at sites 1 and 8. Especially for site 8, the junction of the Jiangshui River and the Xijiang River brings high flow velocity and ever-changing flow direction, indicating low-frequency sampling cannot represent actual changes of concentrations, while DGT-measured concentrations reflect the time-averaged concentrations of analytes at the sampling site.

CONCLUSIONS

In this study, DGT devices equipped with δ-MnO2 binding gels were developed and tested to monitor Tl in water for the first time. H₂C₂O₄ was adopted to elute Tl from the δ-MnO₂ binding gel, and high elution efficiency of 1.04 ± 0.06 for Tl(I) and 0.86 ± 0.06 for Tl(III) was obtained. δ-MnO₂-DGT can...
accurately measure Tl in solutions across a wide range of pH (4–9) and ionic strength (0.1–200 mmol L⁻¹). Its high capacity of 27.1 μg of Tl·cm⁻² implies that δ-MnO₂-DGT is suitable for long-term monitoring of Tl. Although δ-MnO₂ binding gels were stored in solution, containing only 10 mmol·L⁻¹ NaNO₃, for up to 117 days here, much longer storage time can be expected, judging from the stable performance of δ-MnO₂ binding gels after 117 days of storage. Comparison of Chelex-DGT and δ-MnO₂-DGT revealed that Chelex-DGT was greatly influenced by pH and ionic strength and further proved that δ-MnO₂-DGT can be used to measure Tl in the environment. Field trial of δ-MnO₂-DGT in a contaminated creek and Jiangshui River near Yunfu pyrite mine and sulfuric acid plant and Qinzhou cement plant demonstrated the robustness of the DGT method for in situ monitoring of Tl. The results also showed that the method can be used in many circumstances, encompassing Tl-contaminated creeks, lakes, and rivers, through to pristine environments with trace levels of Tl. Although this study proved that δ-MnO₂-DGT can be used in water with high ionic strength and pH, further validation would be required to test the applicability of the method in estuarine or seawater due to higher concentrations of salts in saline waters. The DGT technique can help to monitor the wastewater discharge behavior of factories due to its time-averaged measurement, while grab sampling may fail to capture sporadic discharge events. In principle, this newly developed δ-MnO₂-DGT device can be a powerful tool to exactly measure Tl in aquatic systems.

**ASSOCIATED CONTENT**

* Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.analchem.8b03352.

Four text sections describing preparation of diffusive and Chelex-100 gels and effects of pH, ionic strength, synthetic freshwater, and organic matter on δ-MnO₂-DGT measurement of Tl(I) and Tl(III); three figures showing XRD pattern and SEM images of δ-MnO₂, δ-MnO₂-DGT performance in freshwater solution, and effects of organic matter on measurement; eight tables listing equilibrium constants from PhreeQC, blank concentrations and method detection limits, diffusion coefficients measured by diffusion cell and DGT methods, effects of ionic strength and pH on measurement, physical–chemical parameters and ion concentrations for water samples collected from different sampling sites, and percentages of Tl(I) and Tl(III) in total Tl (DOCX)

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**Notes**

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