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

Deng, H., Luo, M., Shi, X., Williams, P. N., Li, K., Liu, M., Fan, W., Xiao, T., Chen, Y., Ma, L. Q., & Luo, J. (2019). In Situ Measurement of Thallium in Natural Waters by a Technique Based on Diffusive Gradients in Thin Films Containing a δ -MnO₂ Gel Layer. *Analytical Chemistry*, 91(2), 1344–1352. <https://doi.org/10.1021/acs.analchem.8b03352>

Published in:
Analytical Chemistry

Document Version:
Peer reviewed version

Queen's University Belfast - Research Portal:
[Link to publication record in Queen's University Belfast Research Portal](#)

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1 **Novel *in situ* Measurement of Thallium in Natural Waters based on the**
2 **Diffusive Gradients in Thin-Films Technique equipped with a δ -MnO₂ Gel**
3 **Layer**

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19 **ABSTRACT**

20 Thallium (Tl) has been identified as a priority contaminant because of its severe toxic effects. Exact
21 measurement of Tl is a challenge because it is difficult to avoid altering the element's chemical
22 speciation during sampling, transport, and storage. *In situ* measurement may be a good choice. Based on
23 the *in situ* technique of Diffusive Gradient in Thin-films (DGT), new DGT devices equipped with novel
24 laboratory-synthesized manganese oxide (δ -MnO₂) binding gels were developed and systematically
25 validated for the measurement of Tl, including Tl(I) and Tl(III) species, in water. Comparison between
26 Chelex binding gel and δ -MnO₂ gel on the uptake kinetic of Tl demonstrated that δ -MnO₂ binding gels
27 could adsorb Tl rapidly and effectively. Removal of Tl from the δ -MnO₂ gels was achieved using 1 mol
28 L⁻¹ oxalic acid, yielding elution efficiencies of 1.0 and 0.86 respectively for both Tl(I) and Tl(III).
29 Theoretical responses from DGT devices loaded with δ -MnO₂ gel (δ -MnO₂-DGT) were obtained
30 irrespective of pH (4–9) and ionic strength (0.1–200 mmol L⁻¹ NaNO₃). δ -MnO₂-DGT showed good
31 potential for long-term monitoring of Tl due to its high adsorption capacity of 27.1 μ g cm⁻² and the stable
32 performance of δ -MnO₂ binding gel stored in 0.01 mol L⁻¹ NaNO₃ solution for at least 117 d. Field
33 deployment trials confirmed that δ -MnO₂-DGT can accurately measure the time-averaged concentrations
34 of Tl in fluvial watercourses. In summary, the newly developed δ -MnO₂-DGT shows potential for
35 environmental monitoring and biogeochemical investigation of Tl in waters, sediments, and soils.

36 ■ INTRODUCTION

37 Thallium (Tl) is a rare, non-essential element and notorious poison, whose toxicity is much higher
38 than mercury (Hg), cadmium (Cd), lead (Pb) and copper (Cu), evoking biological damage even at
39 extremely low, parts per billion concentrations.¹ Due to its mutagenic, carcinogenic, and teratogenic
40 activity, Tl is listed as a priority pollutant by the United States Environmental Protection Agency (USEPA)
41 and has been classified as a dangerous substance by the European Union (EU Directive 67/548/EEC).^{2,3}
42 The anthropogenic sources of Tl in the environment mainly stem from coal combustion, iron and non-
43 ferrous mining and smelting, and cement production.^{4,5} The global average Tl concentration in non-
44 polluted surface waters are typically in the order of a few ng L⁻¹.⁴ Nonetheless there are some geographic
45 differences for example the coastal seawaters of Australia possess an average concentration of 13.0 ± 1.4
46 ng L⁻¹ Tl, while inland the freshwaters levels are typically 4 ng Tl L⁻¹.⁶ In Sweden, concentrations of Tl
47 in 8 watercourses comprising of a mixture of rivers and lakes, ranged between 11-46 ng L⁻¹.⁷ This being
48 higher than both non-polluted natural waters in the UK,⁸ and Italy with the latter averaging 5.5 ng L⁻¹.⁹
49 However, Tl concentrations of up to 534 µg L⁻¹ and 1100 µg L⁻¹, which are five to six orders of magnitude
50 higher than those of normal river water, were detected in acid mine drainage from an abandoned Pb-Zn
51 mine in the south of France and in deep groundwater within the Tl-mineralized area in Guizhou Province,
52 China, respectively.^{10,11} In order to regulate/minimize exposures to Tl, the USEPA has set its maximum
53 limit value and the target value for Tl in drinking water at 2 µg L⁻¹ and <0.5 µg L⁻¹, respectively.¹² China
54 has a more stringent potable water standard with a maximum limit value of 0.1 µg L⁻¹.¹³

55 Tl exists in two oxidation states in the aquatic environment, Tl(I) and Tl(III), with significantly
56 different physical and chemical characterization and toxicity.^{10,14} Comparison with Tl(III), Tl(I) is more
57 thermodynamically stable and less reactive.¹⁵ It is well documented that Tl(I) predominates in

58 freshwater.^{10,16} In oxidizing environments, Tl(III) can exist as Tl(OH)₃ (log K_{sp} = -45.2) at pH < 7. The
59 occurrence of stable Tl(III) in solution is possible at higher pH, where hydroxide complexes are formed,
60 and in the presence of ligands such as sulphates, chlorides, acetate, and humic acid.^{14,17} Furthermore, it
61 has been elucidated that the toxicity of Tl(III) was 50,000 times of Tl(I) to the unicellular alga *Chlorella*.¹⁸
62 Until now, the study of Tl species in aquatic systems is still challenging.

63 Due to low contents of Tl in the normal surface waters (a few ng L⁻¹ or less), traditional analytical
64 methods have low sensitivity for Tl and may be interfered by other matrix components.^{1,19} The
65 predominant methods for determining concentrations of Tl in surface waters requires
66 preconcentration/separation of Tl in water samples onto specific adsorbent or resin.²⁰ Liquid-liquid
67 extraction,²¹ cloud point extraction,²² and solid phase extraction²³ have been developed and various
68 adsorbents, such as Amberlite XAD resins, Chelex-100 resin, and Chromosorb105 resin, have been used
69 for this purpose.^{14,24,25} However, these methods are usually laborious, time and reagent consuming, and
70 in need of a large sample volume. Therefore, any technique with a low detection limit and a high
71 sensitivity to determine trace concentrations of Tl is a pressing need. As an alternative to the current
72 analytical methods of Tl, the diffusive gradients in thin-films (DGT) technique is an *in situ* passive
73 sampling method for measuring time-averaged concentration of a broad range of labile metal and
74 metalloids species in solution.²⁶ Based on the Fick's first law of diffusion,²⁷ the DGT technique associates
75 the processes of mass transport through a diffusive gel layer with accumulation within a binding gel layer
76 (i.e a resin/adsorbent immobilized in a thin layer of a hydrogel). Compared with grab sampling, *in situ*
77 sampling avoids the change of elemental chemical forms during collection, processing, and preservation.
78 In dynamic systems (e.g. rivers) where concentrations can change rapidly – in these cases grab sampling
79 will not capture the variation in concentration, whereas DGT will incorporate this into the time averaged

80 measurement.²⁸ What's more, trace or ultra-trace substances can be measured by enriching in DGT before
81 reaching DGT capacity. Due to its simplicity, *in-situ*, and robustness, DGT has been successfully applied
82 to measure different analytes in natural waters,^{29,30} soils,^{31,32} and sediments.^{33,34}

83 It has been reported that Chelex-100 resin can adsorb Tl in water effectively at a strict range of pH
84 (~1.8).³⁵ Although DGT equipped with Chelex binding gels (Chelex-DGT) has been used to study the
85 high resolution profiles of Tl in sediments,¹⁹ it was reported that Chelex-DGT showed low uptake of Tl
86 and the authors suggested further characterization of Chelex-DGT performance on measuring Tl.³⁶ δ -
87 MnO₂ has been proven as an excellent adsorbent for Tl in both soil remediation and wastewater
88 treatment^{37,38} due to its strong oxidation ability, high selectivity and high surface area. There is no
89 literature on the DGT devices equipped with δ -MnO₂ binding gels (δ -MnO₂-DGT) for Tl measurement.
90 In this study, δ -MnO₂ was used for the first time as a binding phase in DGT devices. δ -MnO₂-DGT were
91 evaluated for measuring Tl under different conditions of pH and ionic strength and compared with
92 Chelex-DGT as well. Diffusion coefficients of Tl in the diffusive gels were measured, using two different
93 methods, for precise evaluation of DGT-measured concentrations. Field trial of δ -MnO₂-DGT was
94 performed in natural waters near Tl-polluted sources to assess its performance in the real aquatic
95 environment.

96 ■ EXPERIMENTAL SECTION

97 **Reagents, Materials, and Solutions.** Tl stock solutions were prepared by dissolving TlNO₃ or
98 Tl(NO₃)₃·3H₂O (Acros, Belgium) in 0.1 mol L⁻¹ HNO₃ (Sigma-Aldrich, USA) and then diluting with
99 Milli-Q water³⁹ (18.2 MΩ cm, Millipore, USA). Gel making reagents include acrylamide water solution
100 40% (BDH, UK), a patented agarose derived cross-linker 2% (DGT Research Ltd., Lancaster, UK),
101 ammonium persulphate (APS) (BDH, UK) initiator for making a 10% water solution, *N,N,N',N'*-

102 tetramethylethylenediamine (TEMED) catalyst (99%, Electron, BDH, UK), Chelex-100 resin (200–
103 400 mesh, Bio-Rad, USA). H_3PO_4 , $\text{H}_2\text{C}_2\text{O}_4$, KMnO_4 , and MnSO_4 were purchased from Nanjing
104 Chemical Reagent Co., Ltd., China. NaOH and NaNO_3 were purchased from Xilongs Scientific, Shantou,
105 China. All reagents were of analytical grade or above. DGT piston moldings were supplied from DGT
106 Research Ltd. (Lancaster, UK). Containers and moldings were acid-cleaned twice in 10% (v/v) HNO_3 for
107 at least 24 h and rinsed with Milli-Q water for three times.

108 **Synthesis of $\delta\text{-MnO}_2$.** $\delta\text{-MnO}_2$ was prepared according to Cai and Ren,⁴⁰ by titrating KMnO_4
109 solution (45 g L^{-1}) using MnSO_4 solution (35 g L^{-1}) with vigorous stirring to produce $\delta\text{-MnO}_2$ precipitate,
110 which was washed and dried in $103 \text{ }^\circ\text{C}$ for 12 h. The obtained $\delta\text{-MnO}_2$ was characterized and used as
111 DGT binding phase.

112 **Analysis Methods.** The MnO_2 crystal structures were characterized by X-ray diffraction (XRD, ARL
113 X'TRA, Switzerland). Scanning Electron Microscope (SEM) was performed on an emission scanning
114 electron microscope (Hitachi S-3400N II, Japan) at the power of 40 kV and 40 mA to detect the
115 homogeneity of $\delta\text{-MnO}_2$ binding gel. Inductively Coupled Plasma Mass Spectrometry (ICP-MS,
116 NexION 300X, PerkinElmer, USA) was used to analyze total Tl in experiments. All samples were diluted
117 with 0.1 mol L^{-1} HNO_3 and added $50 \text{ } \mu\text{g L}^{-1}$ indium(In) as internal standard to ensure the reliability of
118 the data. For quality control of ICP-MS analysis, river water certified reference material for Tl
119 (BWB2198-2016, National reference materials, China) was analyzed.

120 **Speciation modeling.** Tl species were assessed using the PhreeQC software with a series of
121 equilibrium constants from the literature⁴¹⁻⁴³ (Supporting information (SI), Table S1) for the
122 interpretation of the results. The PhreeQC software was designed to perform aqueous geochemical
123 calculations and works adequately at low ionic strength but may fail at higher ionic strengths (in the

124 range of seawater and above)⁴⁴. It should be treated with caution in the application with high ionic
125 strength.**DGT Preparation.** A piston DGT device contains a 0.40 mm thick binding gel, a
126 polyacrylamide diffusive gel with 0.80 mm thickness and a 0.14 mm thick, 0.45 μm poresize hydrophilic
127 poly (ether sulfone) filter membrane (Pall, USA), sandwiched by a DGT plastic base and a cap with a
128 window open area of 2.51 cm^2 . The polyacrylamide diffusive gel was prepared according to previously
129 described procedures⁴⁵ (see [SI, Experiments 1](#)).

130 In this study, two different binding gels were used: Chelex-100 based binding gels and $\delta\text{-MnO}_2$ based
131 binding gels. The Chelex gel was prepared according to the procedure described by Zhang and Davison⁴⁵
132 (see [SI, Experiments 1](#)). Preparation of the $\delta\text{-MnO}_2$ gels was different from Chelex binding gels. Briefly,
133 0.33 g of dried $\delta\text{-MnO}_2$ powder was weighed into 10 mL gel solution and then the gel solution was in an
134 ultrasonic bath, containing ice to keep gel solution at low temperature, for at least 8 min to dispersing $\delta\text{-}$
135 MnO_2 evenly in gel solution. After that, 100 μL of 10% daily prepared APS solution and 20 μL of
136 TEMED were added to the gel solution with well shaking. The solution was then cast to the acid-cleaned
137 glass plate assembly with a 0.25 mm thick spacer round three edges, and the assembly was heated in an
138 oven at 42–46°C for about 36 min. The $\delta\text{-MnO}_2$ gel was hydrated in Milli-Q water for 24 h by changing
139 water for about 5 times. Moreover, the gels were then cut into discs with a diameter of 2.5 cm and stored
140 in 0.01 mol L^{-1} NaNO_3 at 4°C for further use.

141 **Calculation of DGT measured concentrations.** According to the theory of the DGT technique,
142 DGT measured concentrations, C_{DGT} , can be calculated through [eqs 1 and 2](#).⁴⁶

$$143 \quad C_{\text{DGT}} = M\Delta g / (DA t) \quad (1)$$

$$144 \quad M = C_e (V_{\text{gel}} + V_e) / f_e \quad (2)$$

145 Where M (ng) is the amount of Tl, which can be calculated in [eq 2](#), adsorbed by the binding gels, C_e (μg

146 L^{-1}) is the Tl concentration in the eluent, and V_{gel} and V_e (mL) mean the volume of binding gels and
147 eluents, respectively. f_e presents the Tl elution efficiency, Δg (cm) is the total thickness of diffusive gel
148 and filter membrane, A (cm^2) is the window open area of a DGT device, t (s) means the deployment time
149 of DGT immersing into deployment solution, and D is diffusion coefficient of the measured metal. In
150 order to precisely calculate the DGT-measured concentrations, it is necessary to measure the parameters
151 mentioned above during DGT deployment.

152 **Uptake Kinetics and Elution Efficiency.** The two kinds of prepared binding gel discs were soaked
153 and shaken in 10 mL of $50 \mu g L^{-1}$ Tl(I) or Tl(III) and $0.01 mol L^{-1} NaNO_3$ for different time from 2 min
154 to 24 h at $25^\circ C$. All samples were in triplicate. Elution efficiency refers to the recovery rate of an analyte
155 from the binding gel. Accurate measurement of elution efficiency is crucial to the calculation of C_{DGT} .
156 To investigate the stability of elution efficiency, the gels loaded with different amounts of Tl were eluted
157 for 24 h, respectively. Different eluents were adopted to elute Tl from the loaded gels to find the best
158 eluent. HNO_3 is usually used to elute metals from Chelex gels,⁴⁷ therefore 1 mL of 1, 2, or $3 mol L^{-1}$
159 HNO_3 were adopted to elute Tl preloaded onto Chelex gels. As for δ - MnO_2 gels, 1 mL of 2 and $3 mol L^{-1}$
160 HNO_3 , $1 mol L^{-1}$ oxalic acid ($H_2C_2O_4$), H_3PO_4 , or NaOH, were used for eluents.

161 **Measurement of Diffusion Coefficient.** Diffusion coefficients of Tl(I), $^{Tl(I)}D$, and Tl(III), $^{Tl(III)}D$,
162 across the diffusive layer were measured using the diffusion cell method and the DGT device derivation
163 methods according to the reported procedure.²⁸ Diffusion cell is composed of two glass cells, which were
164 connected by a round hole with a diameter of 1.5 cm. While measuring diffusion coefficients, a piece of
165 0.8 mm thick diffusive gel was clamped between the two holes of the two cells. After that, 50 mL of 1
166 $mg L^{-1}$ Tl solution containing $0.01 mol L^{-1} NaNO_3$ was added in a source cell and 50 mL of $0.01 mol L^{-1}$
167 $NaNO_3$ solution without Tl was added in a receptor cell. The two kinds of solutions had the same pH and

168 temperature. When the solutions were added, two cells were mixed using overhead stirrer. Solution
169 samples (200 μL) in the two cells were collected at intervals of 10 min during a period of 2 h. The
170 collected samples were measured using ICP-MS. Finally, Tl concentration in the source cell was rarely
171 changed. The diffused mass, M (ng), from the source cell to the receptor cell linearly correlated with time,
172 t (s). Diffusion coefficient measured using this cell device, D_{cell} , can be calculated from eq 3,

$$173 \quad D_{\text{cell}} = \text{slope} \frac{\Delta g}{CA} \quad (3)$$

174 Where the slope is obtained from the linear plot of the mass of Tl diffused into the receptor cell versus
175 time, C is the concentration of Tl in the source cell, and A (1.767 cm^2) is open area of the round hole
176 between the two cells.

177 Another method for measurement of diffusion coefficient using DGT devices, D_{DGT} , was based on
178 eq 1. $\delta\text{-MnO}_2$ -DGT devices were deployed in a 2 L well stirred solution of $50 \mu\text{g L}^{-1}$ Tl and 0.01 mol L^{-1}
179 NaNO_3 for 24 h. D_{DGT} was calculated in eq 4.

$$180 \quad D_{\text{DGT}} = M\Delta g / (C_{\text{soln}}At) \quad (4)$$

181 Where C_{soln} is solution concentration of Tl in the container and M is the mass in the binding gels.

182 **Performance Characteristics of DGT in the Laboratory.** *Effects of pH and Ionic Strength.* To test
183 environmental conditions of pH and ionic strength on DGT measurements, the two kinds of DGT devices
184 (Chelex-DGT and $\delta\text{-MnO}_2$ -DGT) were deployed in a well stirred solution for 4 h. For pH experiments,
185 2 L of $30 \mu\text{g L}^{-1}$ Tl and 0.01 mol L^{-1} NaNO_3 solutions with pH ranging from 2 to 9 were used. Solutions
186 with a certain pH was achieved by stirring the solution in the presence of air, and stabilized for about 72
187 h. During the time, the pH was adjusted in the interval of 12 h using 1 mol L^{-1} HNO_3 and 1 mol L^{-1} NaOH .
188 As for ionic strength experiments, 2 L of $40 \mu\text{g L}^{-1}$ solutions containing a range concentrations of NaNO_3
189 from 0.1 to 200 mmol L^{-1} were used. After DGT deployment for 4 h, binding gels were retrieved from

190 the DGT devices and eluted for 24 h.

191 *Capacity and Storage time.* High capacity is necessary for long term deployment of DGT devices in
192 the environment. To measure the capacity of δ -MnO₂ DGT, DGT devices containing 0.8 mm thick
193 diffusive gels was deployed in series of well stirred 2 L solutions of pH 5.7 ± 0.2 containing 0.01 mol L⁻¹
194 ¹ NaNO₃ and different concentrations of Tl(I) ranging from 0.1 to 80 mg L⁻¹ for 4 h. In addition, to
195 evaluate effect of storage time of δ -MnO₂ binding gel on δ -MnO₂-DGT performance, δ -MnO₂ gels were
196 stored in 0.01 mol L⁻¹ NaNO₃ for 1–117 d after production. DGT devices equipped with the long-term-
197 stored δ -MnO₂ gels were immersed in a 2 L solution with pH 5.7 ± 0.2 containing 30 μ g L⁻¹ Tl(I) and
198 0.01 mol L⁻¹ NaNO₃ for 4 h..

199 **Field Application.** To test the applicability of δ -MnO₂-DGT in natural water, DGT devices were
200 deployed in a contaminated creek and Jiangshui River, which are impacted by Yunfu Pyrite Mining,
201 Sulphuric Acid Plant, and Qingzhou Cement Plant.⁴⁸ Locations of eight sampling sites are shown in
202 [Figure 1](#). These sites were chosen considering their distances from the point pollution source as well as
203 the input of other streams of potentially different sources. DGT devices were *in situ* deployed along the
204 creek and Jiangshui River in May 2018. Six δ -MnO₂-DGT devices were deployed in each sampling site
205 for 24 h with a button thermometer (DS 1922L, Maxim Integrated Products) to record temperature at 20-
206 min intervals during sampling period. To avoid direct contacting of DGT with river bed and sludge, the
207 δ -MnO₂-DGTs were deployed in PVC tubes with an inner diameter of 16 cm and length of about 25 cm.
208 PVC tubes' opening was facing the direction of water flow during δ -MnO₂-DGT's deployment It was
209 reported that when flow rate exceeds 2 cm s⁻¹, the effect of diffusion boundary layer (DBL) on DGT
210 measurements will be small and in this case the thickness of DBL can be excluded in the calculation of
211 DGT concentrations expediently.⁴⁹ There were rainstorms for 2 times during sampling and the river flow

212 rates were estimated at 6-20 cm s⁻¹, which were obviously larger than 2 cm s⁻¹, thus, the DBL was
213 negligible for calculation in this study. The DGT devices were rinsed thoroughly with Milli-Q water on
214 retrievals from the field waters. Then these devices were placed in acid-cleaned plastic bags, stored in
215 refrigerated container at ~4°C, and transported to laboratory for further analysis.

216 To validate the DGT measurement, a conventional grab sampling of collecting 100 mL water at a
217 depth of about 15 cm (in triplicate) was performed at the beginning (0 h) and the end (24 h) of the DGT
218 deployment. In addition, two more grab samplings were conducted for sites 2 and 3 at random time
219 during 24 h. The basic physical-chemical parameters (pH, temperature, dissolved oxygen (DO), and
220 electrical conductivity (EC) of the water samples were on-site measured by multi-parameter portable
221 probe (Orion Star A329 Portable, Thermo Scientific, USA). Before returning to the laboratory, the water
222 samples were filtered (0.45 μm poresize nitrocellulose membrane), adjusted to pH <2 with concentrated
223 HNO₃, and then stored in closed polypropylene vessels at 4°C until analysis. Subsequent water sample
224 without acid treatment was for laboratory measurement of total organic carbon (TOC) contents using a
225 TOC analyzer (TOC-V_{CPH}, Shimadzu, Japan). Concentrations of anions (Cl⁻, SO₄²⁻, and F⁻) and trace
226 metal elements were measured using ion chromatography (ICS-2100, Thermo Fisher, USA) and ICP-
227 MS, respectively.

228 ■ RESULTS AND DISCUSSION

229 **Structure of δ-MnO₂ and Gel.** Crystalline properties (Figure S1) of the synthesized δ-MnO₂
230 particles in this study using XRD were similar to the standard sample of synthetic birnessite phase δ-
231 MnO₂ (peaks in 25.06°, 37.16° and 66.12°),^{37,40} suggesting the successful preparation of δ-MnO₂ particles.
232 The synthesized δ-MnO₂ particles have a size ranging from 100 nm to 500 nm. Due to that δ-MnO₂
233 particles agglomerate easily in gel solution, SEM analysis of δ-MnO₂ binding gel was carried out to

234 check whether δ -MnO₂ particles evenly dispersed in the gel. [Figure S1b](#) showed that δ -MnO₂ particles
235 were evenly distributed in the gel.

236 **DGT Blanks and Detection Limits.** DGT blank concentration was the conversion of the measured
237 mass of Tl in the binding gel (δ -MnO₂ gel or Chelex gel) assembled in a DGT device with a 0.8 mm thick
238 diffusive gel, a 0.14 mm thick filter membrane and 2.51 cm² open area by assuming a supposed
239 deployment time of 7 d at 25°C. Three times the standard deviation of the DGT blank concentration is
240 defined as the method detection limit (MDL) of DGT measurement. DGT blank concentrations and
241 MDLs of Tl(I) and Tl(III) for δ -MnO₂-DGT and Chelex-DGT are summarized in [Table S2](#). MDLs of
242 Tl(I) and Tl(III) for both δ -MnO₂-DGT (2.0 ng L⁻¹ for Tl(I) and 0.01 ng L⁻¹ for Tl(III)) and Chelex-DGT
243 (0.6 ng L⁻¹ for Tl(I) and 0.9 ng L⁻¹ for Tl(III)) were much lower than those of sequential injection
244 dispersive liquid–liquid microextraction (SI-DLLME) method (MDL = 0.86 μ g L⁻¹)⁴⁸ and
245 hexamethylenammonium hexamethylenedithiocarbamate (HMAHMDTC) as flotation reagent (MDL =
246 0.024 μ g L⁻¹)⁵⁰ for measurement of total Tl. The MDLs of DGT were lower than the average dissolved
247 Tl concentration (0.020 μ g L⁻¹) in Huron Rivers,³⁶ USA, and the measured concentration range of Yunfu,
248 China (0.01–9.15 μ g L⁻¹ in dry season and 0.03–1.92 μ g L⁻¹ in wet season).⁴⁷ These comparisons show
249 that the DGT blanks and MDLs are low enough for the analysis of Tl in natural water. If Tl concentration
250 is lower than the MDL, prolonging the deployment time or reducing the thickness of diffusive gel can
251 reduce the MDL correspondingly.

252 **Kinetics of Sorption and Elution Efficiency of Binding Gels.** Mass of Tl(I) or Tl(III) adsorbed
253 by δ -MnO₂ binding gels and Chelex binding gels with the increasing time (0–24 h) are shown in [Figure](#)
254 [2](#). δ -MnO₂ binding gels had higher adsorption ability and quicker adsorption rates of both Tl(I) and Tl(III)
255 than Chelex binding gels. δ -MnO₂ binding gels adsorbed about 84% of Tl(I) or Tl(III) in the solutions in

256 the first 15 min and > 93% at 60 min while Chelex binding gels only adsorbed about 23–25% of Tl(I) or
257 Tl(III) in the solution even at 24 h. Adsorption mechanism of Chelex resin was ion exchange for Tl ion³⁵
258 while Tl adsorption by δ -MnO₂ was through oxidation-reduction reactions³⁷. As a chelating agent,
259 Chelex has strict requirements for the adsorption of Tl (for example, pH<2).³⁵ It suggested that δ -MnO₂
260 binding gel could adsorb Tl effectively when it was assembled into DGT devices. Accumulated mass of
261 Tl by δ -MnO₂ gels after 2 min immersion corresponded to a flux of 0.167 ng cm⁻² s⁻¹ for Tl(I) and 0.233
262 ng cm⁻² s⁻¹ for Tl(III). These sorption fluxes were much higher than diffusive fluxes of Tl(I) and Tl(III)
263 (calculated as 0.08 and 0.06 ng cm⁻² s⁻¹)⁵¹ through a 0.8 mm thick diffusive gel of DGT devices deployed
264 in a solution of 500 μ g Tl/L which was exceptionally high and rare in the natural water. This proves that
265 δ -MnO₂ binding gels can rapidly adsorb the diffused Tl, and ensures the concentration at the interface of
266 diffusive gel/binding gel is effectively zero.

267 Elution efficiencies of the studied two binding gels eluted in various eluents are listed in [Table 1](#).
268 Generally, the elution efficiencies of Tl(I) were higher than Tl(III) for all the eluents. HNO₃ is usually
269 used to elute metals from the Chelex binding gels, so here it was used as well for Tl elution from the
270 Chelex binding gels. With the increasing HNO₃ concentration from 1 to 3 mol L⁻¹, the elution efficiencies
271 of Tl(I) from Chelex gels increased from 0.85 \pm 0.09 to 1.05 \pm 0.07. But for Tl(III), increased increasing
272 HNO₃ concentrations did not increase elution efficiency obviously, which was kept around 0.72–0.76.
273 However, 2 or 3 mol L⁻¹ HNO₃ just elutes a little Tl(I) and Tl(III) from δ -MnO₂ gels with low elution
274 efficiencies (<0.17). Besides, 1 mol L⁻¹ H₃PO₄ or NaOH solutions cannot elute Tl(I) and Tl(III) from δ -
275 MnO₂ gels with very low elution efficiencies of <0.008. On the contrary, 1 mol L⁻¹ H₂C₂O₄ had high
276 elution efficiencies for Tl(I) (1.04 \pm 0.06) and Tl(III) (0.86 \pm 0.06). The black δ -MnO₂ gel turned to a
277 transparent gel after adding 1mL 1 mol L⁻¹ H₂C₂O₄ for 20 min, indicating that δ -MnO₂ can react with

278 $\text{H}_2\text{C}_2\text{O}_4$ and then dissolve followed by inducing the adsorbed Tl into the eluate ($\text{MnO}_2 + 2\text{H}_2\text{C}_2\text{O}_4 =$
279 $\text{MnC}_2\text{O}_4 + 2\text{CO}_2 + 2\text{H}_2\text{O}$). In this study, 1 mol L^{-1} HNO_3 and $\text{H}_2\text{C}_2\text{O}_4$ were adopted to elute Tl from
280 Chelex gels and $\delta\text{-MnO}_2$ gels, respectively.

281 **Diffusion Coefficients of Tl(I) and Tl(III).** Accurate determination of diffusion coefficients of Tl(I)
282 and Tl(III) is the prerequisite of DGT measurement. Mass of diffused Tl(I) and Tl(III) in the receptor cell
283 linearly increased with the increasing time (the correlation coefficient, $r^2 = 0.99$ for both Tl(I) and Tl(III),
284 $p < 0.05$), inferring that there was a stable diffusion process of the measured Tl during the experiment
285 period. Diffusion coefficients of Tl(I) in water, D_{water} , is $15.34 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ at 25°C .⁵² Diffusion
286 coefficients, D_{cell} , of Tl(I) and Tl(III) calculated using eq 3 are listed in Table S3. D_{cell} of Tl(I) and Tl(III)
287 were 14.74×10^{-6} and $9.02 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, respectively, at 25°C . Similarly, D_{DGT} were 13.96×10^{-6} and
288 $10.88 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ at 25°C for Tl(I) and Tl(III), respectively. D_{cell} of Tl(I) was much larger than Tl(III)
289 at 25°C probably due to the ionic radii of labile Tl (Tl^+ : 150 pm; Tl^{3+} : 89 pm; $\text{Tl}(\text{OH})^{2+}$: 180 pm and
290 $\text{Tl}(\text{OH})_2^+$: 270 pm, in addition, covalent bonding between Tl and OH possess a radius of 90 nm),⁵³ and
291 Tl(III) complexes with covalent bonding were much more difficult to pass through the diffusive gel.
292 ${}^{\text{Tl(I)}}D_{\text{cell}}$ was about 106% of ${}^{\text{Tl(I)}}D_{\text{DGT}}$ and the difference between these two values from two different
293 methods was less than 6%, suggesting that measured D here was reasonable. However, ${}^{\text{Tl(III)}}D_{\text{cell}}$ was
294 about 82.9% of ${}^{\text{Tl(III)}}D_{\text{DGT}}$. The ratio of D_{cell} to D_{DGT} was similar to that for As(III) and As(V) reported by
295 Bennett et al.,⁵⁴ in which $D_{\text{cell}}/D_{\text{DGT}}$ for As(III) and As(V) were 79% and 82%, respectively. To keep
296 consistency of calculation of DGT measured concentrations, D_{cell} was used for calculation in eq 1.

297 **Effects of pH and Ionic Strength.** According to theory of the DGT technique, in the simple solution
298 without metal organic complexes and colloids, DGT-measured concentrations, C_{DGT} , of analytes should
299 be equal to the corresponding solution concentrations, C_{soln} , indicating that the ratio, R value, of C_{DGT} to

300 C_{soln} should be 1.0 ± 0.1 .⁵⁴ Changes of R value with different pH are shown in [Figures 3a](#) and [3b](#). pH in
301 the environment is normally in the range of 4–9.⁴⁴ If R value obtained in this pH range can be 1.0 ± 0.1 ,
302 it means that DGT can accurately measure the concentrations of analytes in water. For Chelex-DGT, R
303 values for Tl(I) were all below 0.56 when pH ranging from 3.46 to 8.61. Similarly, for Tl(III), R values
304 were still lower than 0.5 in pH of 2–6 though R values can reach to around 0.8 when pH 8.17–8.75. These
305 data show that Chelex-DGT cannot accurately measure Tl(I) and Tl(III) at pH 2–9. Adsorption
306 mechanism of Chelex to Tl was ion exchange³⁵ while $\delta\text{-MnO}_2$ was through oxidation-reduction
307 reactions³⁷. The different mechanisms make Chelex have lower adsorption efficiency on Tl and causing
308 low R value. Contrarily, R values obtained by $\delta\text{-MnO}_2$ -DGT were acceptable in the range of 0.9–1.1 in
309 the studied pH range, except for a little low R value of 0.86 ± 0.04 for Tl(I) at pH 3.46. At pH < 4.0, less
310 negative charge is on the surface of $\delta\text{-MnO}_2$, resulting lower adsorption ability⁵⁶. Nonetheless, $\delta\text{-MnO}_2$ -
311 DGT can work well in the studied pH range.

312 R value assessed with different ionic strength are shown in [Figures 3c](#) and [3d](#). For Chelex-DGT,
313 measured R values dramatically decreased with the increasing ionic strength, suggesting that Chelex-
314 DGT cannot precisely measure Tl in most conditions of ionic strength including freshwater systems.
315 However, $\delta\text{-MnO}_2$ -DGT showed a good ability to accurately measure both Tl(I) and Tl(III) with
316 acceptable R values of 1.0 ± 0.1 when ionic strength ranging from 0.1 to 200 mmol L⁻¹ NaNO₃. The
317 comparison study proved that $\delta\text{-MnO}_2$ -DGT was suitable for a wide range of natural water bodies with
318 different pH and ionic strength.

319 Considering the realistic deployment time of DGT in the field, it is also important to check the long-
320 time performance of DGT under conditions of varying pH and ionic strengths. Therefore, we carried on
321 an experiment to investigate the effect of longer deployment time on $\delta\text{-MnO}_2$ -DGT performance. The

322 results (SI, Tables S4 and S5) show that after 72 and 120 h deployment, δ -MnO₂-DGT can still effectively
323 and correctly measured Tl in aquatic systems under ionic strength range of 0.1-200 mmol L⁻¹ and pH
324 ranges (4–9 for Tl(I) and 2–9 for Tl(III)).

325 **Capacity and Storage Time of δ -MnO₂-DGT.** High adsorption capacity of DGT devices is very
326 helpful for their long-term deployment in the environment. As indicated in Figure 4a, the mass of Tl(I)
327 accumulated by δ -MnO₂-DGT was fitted well with the theoretical line assessed from the known
328 concentrations of Tl(I) in solutions when Tl(I) concentrations in solutions were less than 7.10 mg L⁻¹.
329 After that, accumulated mass by δ -MnO₂-DGT began to deviate from the theoretical line with the
330 increasing Tl(I) concentration in solution. Thus, the capacity of δ -MnO₂-DGT was assessed at about 27.1
331 $\mu\text{g cm}^{-2}$. For the value of the capacity, δ -MnO₂-DGT can be deployed in 2 mg L⁻¹ Tl(I) contaminated
332 water for 24 h at 25°C. If Tl concentration in water was the same as the US maximum limit value of 2 μg
333 L⁻¹ for water quality, the measured capacity in this study can be reached after 2.6 years of deployment
334 while only taking time into account. Couture et al.⁵⁷ summarized the Tl concentrations in aquatic systems
335 in more than 20 regions around the world and found that the highest concentration of Tl in the
336 groundwater was 1098 $\mu\text{g L}^{-1}$, which was detected in Lanmuchang, Guizhou, China. Even though, δ -
337 MnO₂-DGT can be deployed for about 42 h before reaching the adsorption capacity. Due to the low
338 concentrations of Tl in most of aquatic systems, this capacity of δ -MnO₂-DGT was enough for
339 measurement of Tl.

340 Performance of DGT devices containing δ -MnO₂ binding gels, which had been soaked in 0.01 mol
341 L⁻¹ NaNO₃ solution for 1, 6, 62, 71, 76, 102, 117 d since production, are depicted in Figure 4b. *R* values
342 of δ -MnO₂-DGT were in the range of 1.0 ± 0.1 , implying that storage time of up to 117 d in this study
343 did not affect the characteristics of δ -MnO₂ gels. It needs further experiments to confirm whether the δ -

344 MnO₂ DGT still has a stable and acceptable performance when the δ -MnO₂ gels were stored for a longer
345 time (>117 d). Therefore, δ -MnO₂ gels can be stored in 0.01 mol L⁻¹ NaNO₃ solution at 4°C for at least
346 117 d.

347 **Field Deployments of δ -MnO₂-DGT.** δ -MnO₂-DGT was *in situ* deployed in natural water to verify
348 the robustness of δ -MnO₂-DGT performance in natural aquatic system. Percentages of the Tl(I) and Tl(III)
349 species calculated using the PhreeQC program incorporating the water physical parameters (SI, Table S6)
350 and the concentration of various ions (SI, Table S7) are listed in Table S8. The data suggested that Tl(III)
351 predominated (>98.5% of total dissolved Tl) over Tl(I) in the studied 8 water samples, which was
352 consistent with the study in the Great Lake.^{35,56} Therefore, concentrations of Tl measured by DGT
353 devices deployed in the 8 studied sampling sites were calculated based on Tl(III) and its diffusion
354 coefficient.

355 For Tl, C_{DGT} and total dissolved concentrations, C_{grab}, of grab sampling water with filtration are
356 shown in Figure 5. C_{DGT} was basically between ^{0h}C_{grab} and ^{24h}C_{grab}, or C_{grab} at different random sampling
357 time, except sites 1 and 8, in which C_{DGT} were a few lower than C_{grabs}. Because grab sampling cannot
358 reflect all changes of concentrations of analytes during sampling periods of DGT deployment, it may at
359 least partially account for the lower ratio of C_{DGT} to C_{grab} at sites 1 and 8. Especially for site 8, the junction
360 of Jiangshui River and the Xijiang River brings high flow velocity and ever-changing flow direction,
361 indicating low frequency sampling cannot represent actual changes of concentrations while DGT-
362 measured concentrations reflect the time-averaged concentrations of analytes at the sampling site.

363 ■ CONCLUSIONS

364 In this study, DGT devices equipped with δ -MnO₂ binding gels was newly developed and tested to
365 monitor Tl in water for the first time. H₂C₂O₄ was adopted to elute Tl from the δ -MnO₂ binding gel and

366 obtained high elution efficiency of 1.04 ± 0.06 for Tl(I) and 0.86 ± 0.06 for Tl(III). δ -MnO₂-DGT can
367 exactly measure Tl in solutions in a wide range of pH (4–9) and ionic strength (0.1–200 mmol L⁻¹). Its
368 high capacity of about 27.1 $\mu\text{g Tl cm}^{-2}$ implies that δ -MnO₂-DGT is suitable for long term monitoring of
369 Tl. Although δ -MnO₂ binding gels were stored in 0.01 mol L⁻¹ NaNO₃ solution for up to 117 d here,
370 much longer storage time can be expected judging from the stable performance of δ -MnO₂ binding gels
371 after 117 d storage. Comparison of Chelex-DGT and δ -MnO₂-DGT revealed that the Chelex-DGT was
372 greatly influenced by pH and ionic strength and further proved that newly developed δ -MnO₂-DGT can
373 be used to measure Tl in the environment. Field trial of δ -MnO₂-DGT in a contaminated creek and
374 Jiangshui River near Yunfu Pyrite Mining, Sulphuric Acid Plant, and Qingzhou Cement Plant showed
375 robustness of the DGT method for *in situ* monitoring Tl, indicating that it can be used in many
376 circumstances including Tl contaminated creeks, lakes and rivers, even in the aquatic system with trace
377 level of Tl. Although this study proved that δ -MnO₂-DGT can be used in water with high ionic strength
378 and pH, further validation would be required to test the applicability of the method in estuarine or sea
379 water due to higher concentrations of salts in seawater. The DGT technique can help to monitor the
380 wastewater discharge behavior of factories due to its time-averaged measurement while grab sampling
381 may omit the sudden events. In principle, this newly developed δ -MnO₂-DGT device can be a powerful
382 tool to exactly measure Tl in aquatic system, even in soil and sediment.

383 ■ ASSOCIATED CONTENT

384 Supporting information

385 Preparation of diffusive gel, preparation of Chelex-100 gel, XRD pattern of δ -MnO₂ particles, SEM
386 images of δ -MnO₂ gel, equilibrium constants for Tl species calculation using PhreeQC program,
387 diffusion coefficients of Tl(I) and Tl(III) at 25°C measured by diffusion cell and DGT methods, physical-

388 chemical parameters for water samples collected from different sampling sites, concentrations of various
389 ions in water samples collected from different sampling sites.

390 ■ ACKNOWLEDGEMENTS

391 This work was supported by the National Natural Science Foundation of China (No. 41830753, 41573119,
392 41473124, U161244 and 41771271), Guangzhou Science and Technology Program (No. 201510010225),
393 the Science and Technology Plan of Guangzhou Education Bureau (No. 1201620157), Key Laboratory
394 of Radioactive and Rare Scattered Minerals, Ministry of Land and Resources (No. RRSM-KF2018-04)
395 Major Science and Technology Program for Water Pollution Control and Treatment (No. 2017ZX07302-
396 001), China Scholarship Council (20175087) and Rural Non-point Source Pollution Comprehensive
397 Management Technology Center of Guangdong Province.

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399 Notes

400 The authors declare no competing financial interest.

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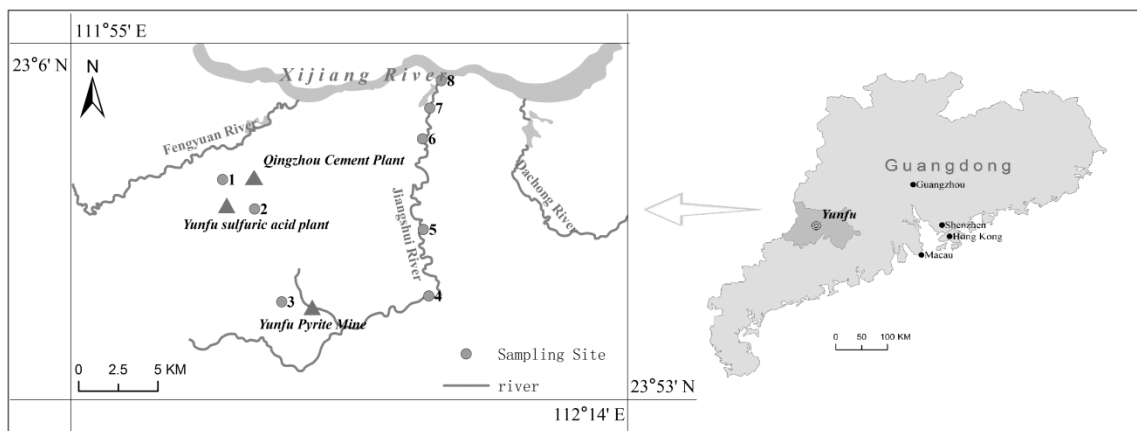
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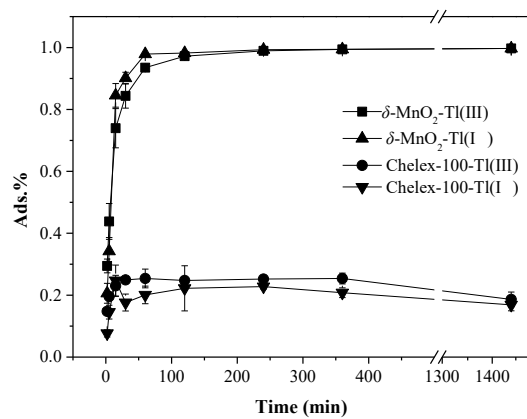
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473 **Figure 1.** Map of sampling sites in Yunfu, Guangdong province, South of China

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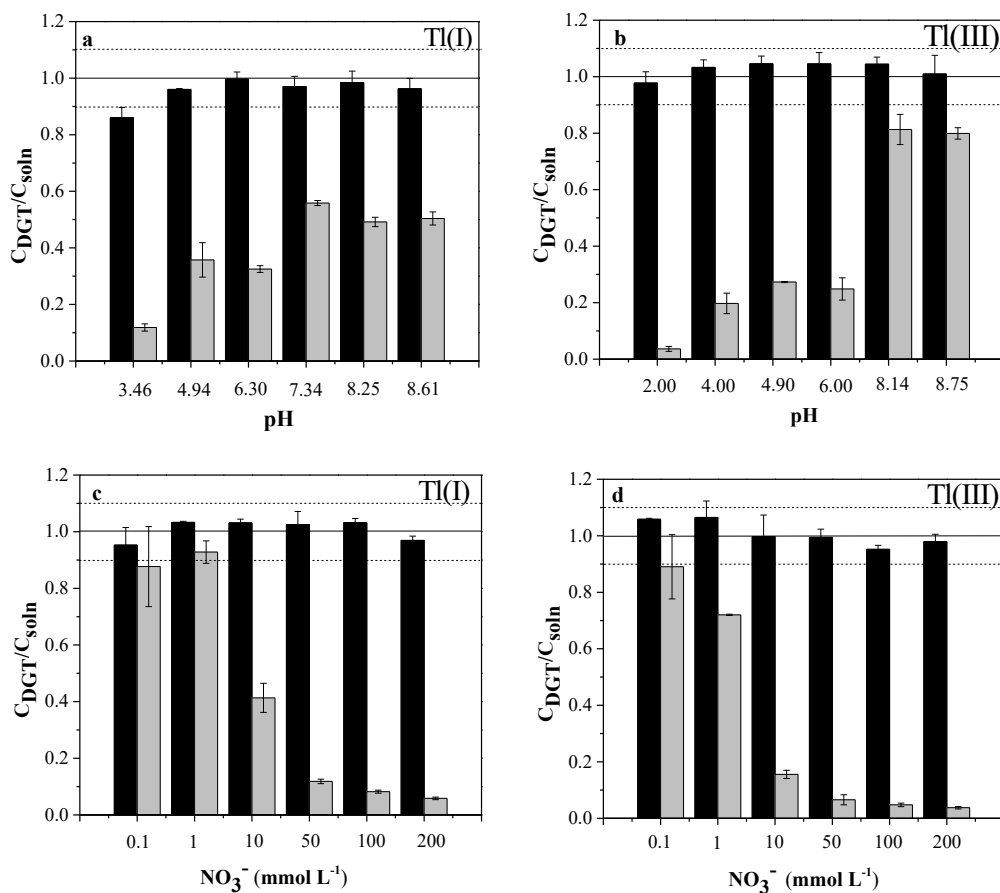


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476 **Figure 2.** Adsorption efficiency of Tl(I) and Tl(III) adsorbed by $\delta\text{-MnO}_2$ gels and Chelex-100 gels in
 477 solutions containing $50 \mu\text{g L}^{-1}$ Tl(I) or Tl(III) and 0.01 mol L^{-1} NaNO_3 at pH 6 and 25°C for different
 478 time from 2 min to 24 h. Error bars represent the standard deviations of replicates ($n = 3$).

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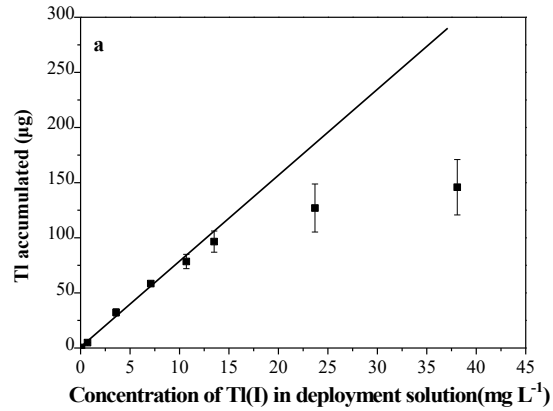
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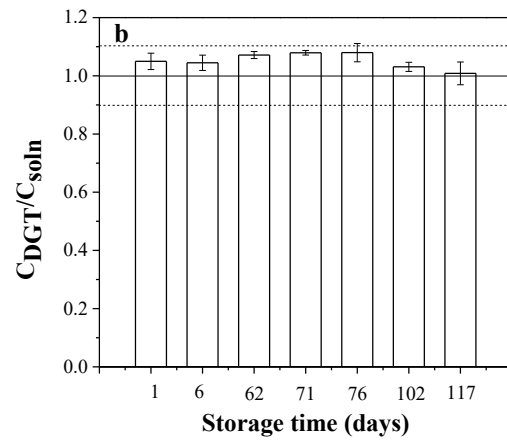
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Figure 3. Effects of pH and ion strength on measurement of δ -MnO₂-DGT (black column) and Chelex-DGT (grey column) for Tl(I) or Tl(III). (a) Devices of Chelex-DGT and δ -MnO₂-DGT soaked in well-stirring solutions containing 30 $\mu\text{g L}^{-1}$ Tl(I) and 0.01 mol L⁻¹ NaNO₃ at pH 3.46–8.61. (b) Devices of Chelex-DGT and δ -MnO₂-DGT soaked in well-stirring solutions containing 30 $\mu\text{g L}^{-1}$ Tl(III) and 0.01 mol L⁻¹ NaNO₃ at pH 2.00–8.75. (c) Devices of Chelex-DGT and δ -MnO₂-DGT soaked in well-stirring solutions containing 40 $\mu\text{g L}^{-1}$ Tl(I) and 0.1–200 mmol L⁻¹ NaNO₃ at pH 5.7. (d) Devices of Chelex-DGT and δ -MnO₂-DGT soaked in well-stirring solutions containing 40 $\mu\text{g L}^{-1}$ Tl(III) and 0.1–200 mmol L⁻¹ NaNO₃ at pH 5.7. Error bars represent the standard deviations of replicates ($n = 3$) and solid and dotted lines show the target C_{DGT}/C_{soln} value (1.0 ± 0.1).

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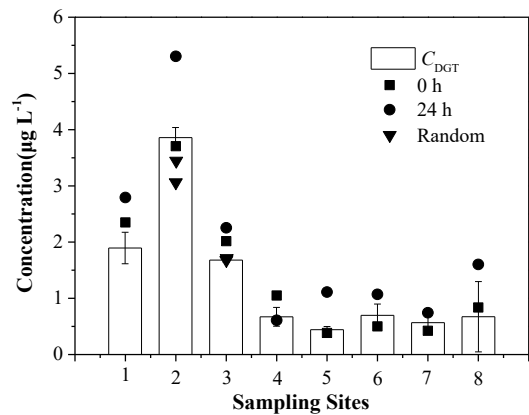
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496 **Figure 4.** (a) Mass of Tl(I) accumulated by δ -MnO₂-DGT deployed in solutions containing 0.1 to 80 mg
497 L⁻¹ Tl(I) and 0.01 mol L⁻¹ NaNO₃ at pH 5.7 for 4 h and solid line represents theoretical mass of Tl
498 accumulation; (b) C_{DGT}/C_{soln} of Tl measured by DGT equipped with δ -MnO₂ gels stored for different
499 times (from 1–117 d) in solutions containing 30 µg L⁻¹ Tl(I) and 0.01 mol L⁻¹ NaNO₃ at pH 5.7 and solid
500 and dotted line show the target value (1.0 ± 0.1). Error bars represent the standard deviations of replicates
501 ($n = 3$).

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Figure 5. Concentrations of Tl in the sampling sites, in

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Yunfu, Guangdong province, China, measured by δ -MnO₂-DGT deployed in the natural water for 24 h

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and grab samplings at 0 h and 24 h of DGT deployment including two more samplings at sites 2 and 3 at

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random time during 24 h. Error bars represent the standard deviations of replicates ($n \geq 3$).

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510 **Table 1.** Elution efficiencies of Tl(I) and Tl(III) bound onto binding gels eluted using different eluents

Binding gels	Eluents	f_e (Tl(I))	f_e Tl(III)
Chelex	1 mol L ⁻¹ HNO ₃	0.85 ± 0.09	0.76 ± 0.05
	2 mol L ⁻¹ HNO ₃	0.99 ± 0.06	0.72 ± 0.15
	3 mol L ⁻¹ HNO ₃	1.05 ± 0.07	0.73 ± 0.10
δ-MnO ₂	2 mol L ⁻¹ HNO ₃	0.06 ± 0.04	0.002 ± 0.001
	3 mol L ⁻¹ HNO ₃	0.17 ± 0.07	0.02 ± 0.08
	1 mol L ⁻¹ H ₂ C ₂ O ₄	1.04 ± 0.06	0.86 ± 0.06
	1 mol L ⁻¹ H ₃ PO ₄	0.008 ± 0.004	0.003 ± 0.003
	1 mol L ⁻¹ NaOH	0.004 ± 0.001	0.0004 ± 0.001

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512 ^a DGT blank concentration were calculated with a 0.8 mm thick diffusive gel, a 0.14 mm thick filter membrane and 2.5 l

513 cm² open area at 25°C for a supposed deployment time of 24 h

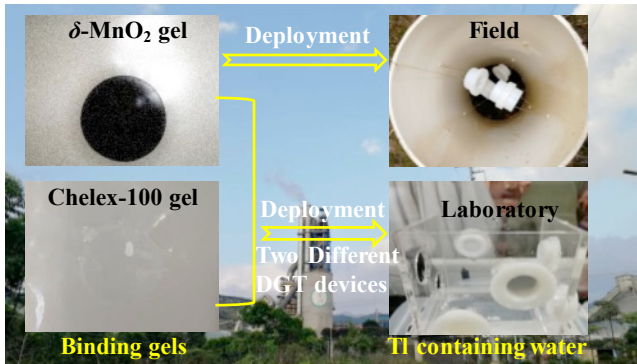
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518 For TOC art only



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