## Supporting information for

# Novel speciation method based on diffusive gradients in thin-films for in situ measurement of Cr<sup>VI</sup> in aquatic systems

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#### Experimental

Synthesis and characteristics of NMDG functionalized resin. NMDG functionalized resin was synthesized following Dambies et al.<sup>1</sup> with minor modification. In brief, NMDG material was dissolved in a mixture of dioxane and Milli-Q water (10:1, v/v). Merrifield resin was placed in dioxane to swell for 1.5 h before the addition of NMDG. The reaction of Merrifield resin (1.0 g) and NMDG (10 g) was carried out in a 250 mL round-bottom flask under reflux with constant stirring for 16 h to obtain the NMDG resin. The product was washed sequentially by Milli-Q water, 1 mol L<sup>-1</sup> NaOH, Milli-Q water, 1 mol L<sup>-1</sup> HNO<sub>3</sub> and Milli-Q water, then dried at 70°C in an oven for 16 h and then characterized by Fourier transform infrared spectroscopy (FIIR) (Nexus 870, Nicolet, USA).

FTIR spectra of the synthesized NMDG resin is shown in Figure S1. The band at 3380 cm<sup>-1</sup> corresponds to the signal of –NH and –OH stretching vibrations. The bands for C-O and C-N stretching, evident at 1082 cm<sup>-1</sup> and 1036 cm<sup>-1</sup>, suggest that N-methyl glucamine was present in the NMDG resin.<sup>2</sup>



The time of preparation of the DGT devices and their cost. There is a standard procedure for preparing the diffusive and binding gels published by Warnken et al. (2006). Following this procedure, it usually takes 2 days to make about 100 pieces of binding and diffusive gels including gel washing with MQ water. These gels can be stored for a long time; at least half a year. The filter membrane, DGT plastic bases and caps are commercially available. Assembling the filter membranes, diffusive gels, binding gels and the plastic holding devices usually only takes about 1 min. There is a commercial company supplying basic DGT equipment at low cost. More information can be found in the website <u>http://www.dgtresearch.com/</u>. Generally, the price is affordable, with a ready-to-use DGT device costing less than 15 US dollars.

**Preparation of synthetic Freshwater.** The composition of the synthetic freshwater followed that given by Langmuir<sup>4</sup> with a little modification and contained: 0.376 mmol L<sup>-1</sup> Ca<sup>2+</sup>, 0.462 mmol L<sup>-1</sup> K<sup>+</sup>, 1.12 mmol L<sup>-1</sup> Na<sup>+</sup>, 0.294 mmol L<sup>-1</sup> Mg<sup>2+</sup>, 0.232 mmol L<sup>-1</sup> Cl<sup>-</sup>, 1.12 mmol L<sup>-1</sup> NO<sub>3</sub><sup>-</sup>, 0.983 mmol L<sup>-1</sup> HCO<sub>3</sub><sup>-</sup> and 0.294 mmol L<sup>-1</sup> SO<sub>4</sub><sup>2-</sup>.

Justification for using NO<sub>3</sub><sup>-</sup> for ionic strength experiment. Indeed there are a lot of anions in aquatic systems. Here our main aim was to investigate the effect of ionic strength. We used NO<sub>3</sub><sup>-</sup> as the representative anion because:

1.  $NO_3^-$  is common in aquatic systems.

2. Compared with other common anions like Cl<sup>-</sup> and  $SO_4^{2^-}$ ,  $NO_3^-$  has the most interference effect on the uptake of Cr(VI) by NMDG resin (Gandhi et al. 2010.), which is the functional material in the binding gel.

3. We also carried on an experiment on the effect of Cl<sup>-</sup> on the performance of NMDG-DGT in measuring Cr<sup>VI</sup>. We found that even when the deployment solution (50  $\mu$ g L<sup>-1</sup> Cr<sup>VI</sup>) contained 100 mM Cl<sup>-</sup>, the NMDG-DGT performed well with an acceptable *R* value, the ratio of of DGT measured to solution concentration, (0.92±0.02), which was also much higher than that (0.68±0.06) when being deployed in 100 mM NO<sub>3</sub><sup>-</sup> solution. We did not directly perform experiments investigating the effect of other potentially competing anions (like SO<sub>4</sub><sup>2-</sup>, PO<sub>4</sub><sup>3-</sup>) on DGT measurements. But synthetic fresh waters, which consisted of 0.232 mmol L<sup>-1</sup> Cl<sup>-</sup>, 1.12 mmol L<sup>-1</sup> NO<sub>3</sub><sup>-</sup>, 0.983 mmol L<sup>-1</sup> HCO<sub>3</sub><sup>-</sup> and 0.294 mmol L<sup>-1</sup> SO<sub>4</sub><sup>2-</sup>, were spiked with both Cr<sup>VI</sup> and Cr<sup>III</sup> and used to deploy NMDG-DGT devices. Good agreement was also obtained between the measured and predicted masses of Cr(VI).

**Collection of groundwater samples.** 5 boreholes were selected in a known abandoned chromate production factory. Each borehole was sufficiently purged ( $3 \times$  well volume) prior to collection of representative samples using 2 L acid-cleaned bottles. The color of the groundwater samples for all boreholes was yellow to orange, indicating high concentrations of Cr<sup>VI</sup>. A 2 L unfiltered sample was taken to laboratory within 6 h, followed by DGT deployment. Triplicate devices were removed at 4 h. Grab samples of the deployment solutions were taken every 2 h and analyzed by the DPC measurement. Parameters regarding groundwater variables (temperature, pH, DOC, and major dissolved elements) are summarized in Table S5.

**DGT theory and calculation.** Diffusive gradients in thin films (DGT) is a passive sampling technique which is based on Fick's first law of diffusion<sup>6</sup>. Analytes diffuse through the well-defined diffusive layer and filter membrane and immediately bind to a binding layer, which results in an effective zero concentration at the diffusive and binding layer interface, forming a linear steady state concentration gradients<sup>7</sup>.



According to Fick's first law, the flux (F) of an analyte through the diffusive gel and filter can be expressed as (Equation S1).

$$F = D \frac{\partial C}{\partial x} = D \frac{(C - C')}{\Delta g}$$
(S1)

W here *D* is the diffusion coefficient of an analyte in the diffusive gel and filter membrane,  $\partial C/\partial x$  is the concentration gradient, *C* is the analyte concentration in the solution, *C'*, the concentration of the analyte at the interface of binding layer and diffusive layer, and  $\Delta g$  is the thickness of the diffusive gel and filter membrane. Before the binding layer reaches saturated, *C'* equals to zero. Then equation S1 becomes S2.

$$F = D \frac{C}{\Delta g}$$
(S2)

Flux, F, can also be expressed as equation S3.

$$F = \frac{M}{A t}$$
(S3)

Where M is mass of the analyte diffusing through an area (*A*) in a given time (t). Combing equation S2 and S3 can get equation S4.

$$C = \frac{M \, \bigtriangleup g}{D \, A \, t} \tag{S4}$$

The mass of elements accumulated in the binding layer can be calculated using equation S5.

$$M = \frac{C_{e} \left( V_{e} + V_{g} \right)}{f_{e}}$$
(S5)

Combining equation S4 and S5, equation S4 is obtained.

$$C = \frac{C_{e} (V_{e} + V_{g}) \Delta g}{D A t f_{e}}$$
(S6)

The concentration of  $Cr^{VI}$  in natural waters can thus be calculated according to equation (S6).

Test of the calculated MDL. To further prove that NMDG-DGT can successfully measure low concentration of  $Cr^{VI}$  in natural waters, synthetic fresh water containing 0.2 µg L<sup>-1</sup> of  $Cr^{VI}$  (10 times the calculated MDL) was prepared. NMDG-DGT samplers were deployed in the water for 12, 24, 48 and 72 h. Good agreement was obtained between the measured and predicted mass of  $Cr^{VI}$  at 24, 48 and 72 h. The accumulated mass of  $Cr^{VI}$  (3.42 ng) for the 12 h deployment was close to (< 2 times) that (1.86 ng) in the gel blank, which accounts for the poorer accuracy.

Table S7. DGT measured concentrations of  $Cr^{VI}$  and their comparison with those in synthetic solutions under ultra-low spiking (0.2 µg L<sup>-1</sup>)

Deployment time (h)	$C_{\text{DGT}}$ (µg L <sup>-1</sup> )	$C_{ m DGT}/C_{ m soln}$
12	$0.16\pm0.015$	$0.78\pm0.07$
24	$0.21\pm0.007$	$1.04\pm0.04$
48	$0.22\pm0.012$	$1.09\pm0.05$
72	$0.20\pm0.001$	$0.99\pm0.01$

Concentration of Cr<sup>VI</sup> was µg/L

The time that the device needs to be deployed to gather enough Cr(VI) to be measurable depends on the concentration of  $Cr^{VI}$  in environment (*C*). In theory, if deployment time is long enough, *C*<sub>e</sub> can be measured accurately by ICP-MS. As long as C<sub>e</sub> is larger than the gel blank, the accuracy of *C* can be obtained. Normally DGT devices were deployed in water for 24, 48 or 72 h, during which time the DGT binding gel can accumulate enough mass of analytes for reliable measurement. Table S2 showed that the concentrations of  $Cr^{VI}$  in Lake Taihu and Jiuxiang River were very low (0.16-0.62 µg L<sup>-1</sup>), but that DGT can measure them accurately after 72 h deployment. However, we also found that DGT can be used to measure  $Cr^{VI}$  even if it is deployed for only 24 h, because DGT can accumulate enough masses of  $Cr^{VI}$  for instrumental analysis in this time.



Figure S1. FTIR spectra of NMDG resin.



**Figure S2.** Diagram of the distribution of sampling sites along the Cr<sup>VI</sup>-contaminated stream. S before the number stands for site.

![](_page_12_Picture_0.jpeg)

**Figure S3.** Photographs of NMDG-DGT devices deployed in the Cr<sup>VI</sup>-contaminated stream mentioned in Figure S2.

![](_page_13_Figure_0.jpeg)

**Figure S4.** Masses of  $Cr^{VI}$  diffused through the diffusive gel versus time in a diffusion cell. Conditions: pH = 7, temperature = 19 °C, ionic strength = 0.01 mol L<sup>-1</sup> NaNO<sub>3</sub>.

![](_page_14_Picture_0.jpeg)

**Figure S5.** Photographs of NMDG-DGT devices deployed in the Cr<sup>VI</sup>-contaminated stream at site 6.

ICP-MS	PerkinElmer Nex-ION 300X
Plasma conditions	
RF power/W	1300
Plasma gas flow/L min <sup>-1</sup>	17
Auxiliary flow/L min <sup>-1</sup>	1.2
Nebulizer gas flow/ L min <sup>-1</sup>	0.85
Mass spectrometer settings	
Ion monitored	<sup>52</sup> Cr
Reaction gas	Ultrapure methane
Reaction gas flow reat/mL min <sup>-1</sup>	0.65
Rejection parameter q	0.65

Table S1. Operation conditions of the DRC-ICP-MS system

Locations	pН	Temp.	Total Cr	Cr <sup>VI</sup>	Fe	Mn	Cl	SO4 <sup>2-</sup>	NO <sub>3</sub> <sup>-</sup>	DOC
		°C	μg /L	μg /L	µg/L	µg/L	mg/L	mg/L	mg/L	mg/L
120°11'26.41"E	7.74	16.8	1.17	0.16	1008	109	52.8	72.3	5.92	9.21
120°11'39.59"E	<u>۹ 07</u>	16.0	0.06	0.20	040	520	61 0	109	2 72	9 62
31°28'34.79"N	8.07	10.9	0.90	0.28	940	55.8	01.8	108	5.75	8.03
120°11'16.66"E 31°26'9.92"N	8.28	17.3	0.98	0.17	737	73.1	50.1	68.7	6.24	11.6
120°11'14.39"E	8.72	17.2	1.05	0.21	1015	83.3	23.5	82.5	4.56	10.3
31°24'40.21"N										
32°6'52.85"N	8.18	18.4	1.68	0.62	386	28.2	34.6	24.2	88.6	16.1
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**Table S2**. Physicochemical properties of natural water in Lake Taihu and Jiuxiang River.

Location	pН	Temp.	Total Cr	Cr <sup>VI</sup>	Fe	Mn	Cl	SO4 <sup>2-</sup>	NO <sub>3</sub> <sup>-</sup>	DOC
		°C	μg/L	μg/L	µg/L	μg/L	mg/L	mg/L	mg/L	mg/L
<b>S</b> 1	8.26	15.9	320	330	237	3.51	12.8	13.6	6.24	7.65
<b>S</b> 2	8.07	15.8	200	203	256	1.24	16.2	14.0	6.18	8.55
<b>S</b> 3	8.35	16.3	102	101	252	0.99	17.0	15.1	11.3	4.25
<b>S</b> 4	7.91	16.6	101	102	321	0.85	17.7	18.6	21.7	6.12
<b>S</b> 5	8.08	16.9	96.3	95.5	286	0.79	15.2	18.3	17.2	5.28
<b>S</b> 6	8.23	17.4	30.8	28.9	179	1.26	14.4	16.5	15.9	3.75
<b>S</b> 7	8.13	17.6	17.4	16.5	147	1.20	14.1	15.6	18.4	5.85

**Table S3**. Physicochemical properties of water in the Cr<sup>VI</sup>-contaminated stream at the sampling sites.

**Table S4.** Elution efficiency ( $f_e$ ) of  $Cr^{VI}$  from NMDG binding gels using nitric acid of different concentrations (n = 12).

HNO <sub>3</sub>	$0.5 \text{ mol } L^{-1}$	$1 \text{ mol } L^{-1}$	$2 \text{ mol } L^{-1}$	$3 \text{ mol } L^{-1}$
$\mathbf{f}_{e}$	$64.7\pm0.032$	$0.71\pm0.014$	$0.72\pm0.015$	$0.72\pm0.019$

Location	pН	Temp.	Total Cr	Cr <sup>VI</sup>	Fe	Mn	Cl	SO4 <sup>2-</sup>	NO <sub>3</sub> <sup>-</sup>	DOC
		°C	mg/L	mg/L	µg/L	μg/L	mg/L	mg/L	mg/L	mg/L
34°44′53.34″E 111°49′32.04″N	7.61	21.4	27.8	20.0	745	1.12	58.7	54.1	24.5	54.2
34°44′54.54″E 111°49′32.04″N	7.76	21.0	132	122	688	3.12	27.4	47.8	14.3	24.6
34°44′56.94″E 111°49′27.06″N	7.69	21.3	316	315	2363	0.99	131	35.1	26.2	25.4
34°44′59.76″E 111°49′26.52″N	7.61	21.2	2.68	2.22	1488	1.05	124	37.5	33.5	13.1
34°44′56.52″E 111°49′24.54″N	7.67	21.2	12.8	12.4	1798	27.1	394	22.3	35.7	11.0

**Table S5.** Physicochemical properties of groundwater at different sampling sites around abandoned chromate production factory.

Site	CDPC	CDGT	$C_{\rm DGT}/C_{\rm DPC}$
<b>S</b> 1	$331\pm67.4$	$325\pm2.1$	$0.96\pm0.16$
S2	$203 \pm 18.4$	$190\pm5.3$	$0.94\pm0.06$
<b>S</b> 3	$100 \pm 2.1$	$85.6\pm3.4$	$0.85\pm0.04$
<b>S</b> 4	$101 \pm 1.1$	$87.8\pm2.1$	$0.86\pm0.03$
S5	$93.5 \pm 1.7$	$85.4\pm2.6$	$0.91\pm0.07$
<b>S</b> 6	$29.0\pm3.1$	$22.1\pm4.0$	$0.76\pm0.13$
S7	$16.5\pm1.0$	$16.5\pm1.2$	$1.00\pm0.06$

**Table S6.** Comparison of DGT measured concentrations ( $\mu$ g L<sup>-1</sup>) of Cr<sup>VI</sup>, C<sub>DGT</sub>, with those in the Cr<sup>VI</sup>-polluted stream water measured by the DPC method, C<sub>DPC</sub>, after active sampling.

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