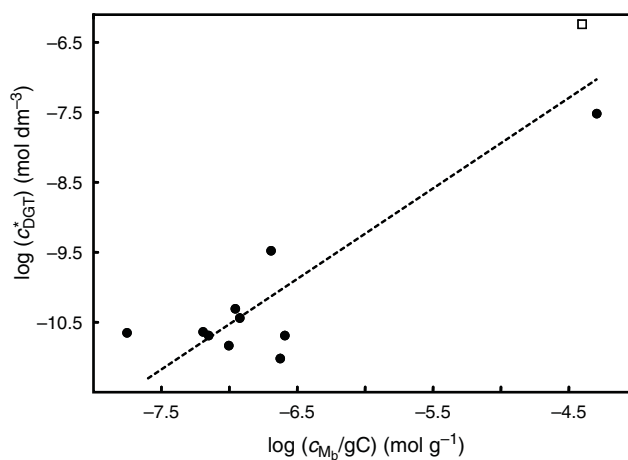
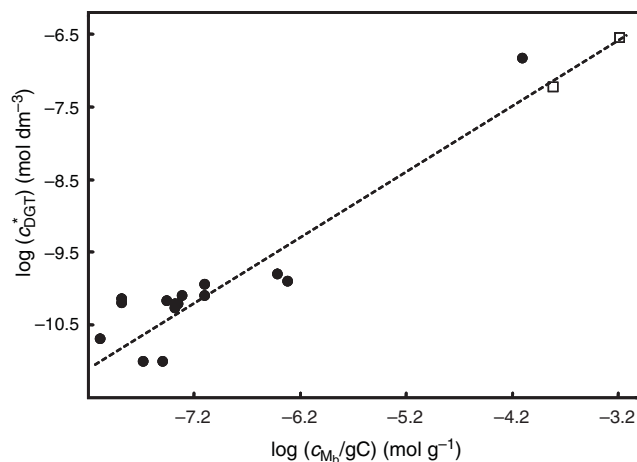


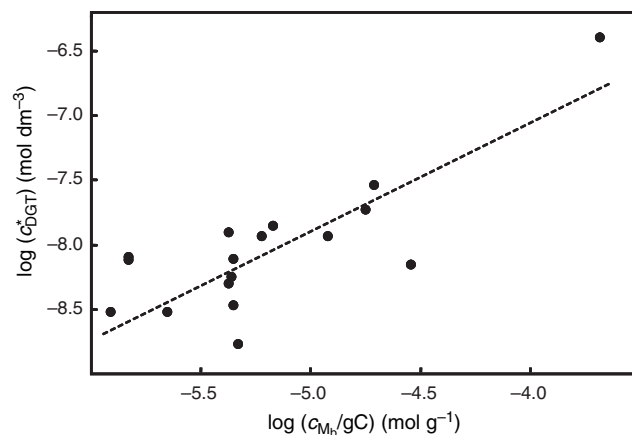
## Accessory publication

**Dynamic DGT speciation analysis and applicability to natural heterogeneous complexes**Raewyn M. Town,<sup>A,C</sup> Parthasarathi Chakraborty<sup>B</sup> and Herman P. van Leeuwen<sup>B</sup><sup>A</sup>Institute for Physics and Chemistry, University of Southern Denmark, Campusvej 55, 5230 Odense, Denmark.<sup>B</sup>Laboratory of Physical Chemistry and Colloid Science, Wageningen University, Dreijenplein 6, 6703 HB Wageningen, the Netherlands.<sup>C</sup>Corresponding author. Email: [rmt@ifk.sdu.dk](mailto:rmt@ifk.sdu.dk)

**Fig. A1.** Concentrations of  $Pb^{II}$  measured by DGT (diffusive gradients in thin film) in natural waters as a function of metal-to-ligand ratio in the sample. Data are shown for unspiked freshwater, pH 7 to 8 ( $\bullet$ )<sup>[35,41,44,59,60]</sup> and isolated humic acid (HA), pH 5.5 ( $\square$ ).<sup>[61]</sup>  $d_g = 8 \times 10^{-4}$  m. The dashed line corresponds to the regression line used to compute  $\Gamma$ .



**Fig. A2.** Concentrations of Cd<sup>II</sup> measured by DGT (diffusive gradients in thin film) in natural waters as a function of metal-to-ligand ratio in the sample. Data are shown for unspiked freshwater (●)<sup>[14,35,36,41,43,44]</sup> and isolated humic substances (□).<sup>[62]</sup> The pH of the waters lies in the range 7 to 8, and  $d_g = 8 \times 10^{-4}$  m. The dashed line corresponds to the regression line used to compute  $\Gamma$ .



**Fig. A3.** Concentrations of Ni<sup>II</sup> measured by DGT (diffusive gradients in thin film) in natural waters as a function of metal-to-ligand ratio in the sample. Data are shown for unspiked freshwater (●).<sup>[14,35,41,42,44,60]</sup> The pH of the waters lies in the range 7 to 8, and  $d_g = 8 \times 10^{-4}$  m. The dashed line corresponds to the regression line used to compute  $\Gamma$ .

**Table A1. Collated DGT (diffusive gradients in thin film) data for freshwaters**

Unless otherwise stated,  $d_g = 8 \times 10^{-3}$  m. For samples, ‘spiked’ denotes the addition of metal to the natural water sample. See *Symbols and abbreviations* in main article for explanation of terms

$c_{M,t}$ nmol dm <sup>-3</sup>	DOC mg dm <sup>-3</sup>	pH	Deployment time	Reported $c_{DGT}$ nmol dm <sup>-3</sup>	Sample	References
Cu <sup>II</sup>						
20	15	7.7 to 8.6	~3 days	2.6 <sup>A</sup>	River Wyre, UK	[14]
486	2	7.8	5 days	263	Meuse river, NL, spiked	[40]
13	4.2	not stated	typically 3 or 7 days	1.9	Theil, Seine river basin, FR	[42]
21	4.2	"	"	4.26	Guerard, Seine river basin, FR	[42]
20	4.2	"	"	3.8	Meaux, Seine river basin, FR	[42]
26	4.2	"	"	7.6	Saint-Maurice, Seine river basin, FR	[42]
25	4.2	"	"	6.2	Chatou, Seine river basin, FR	[42]
34	4.2	"	"	7.3	Andresy, Seine river basin, FR	[42]
472	7.2	7.3	~24 h	118	Savage river, AU	[63]
49.3	3.71	8.7	2 or 3 days	10.7	Lake Greifen, CH	[35]
32.1	3.77	8.7	"	2.1	"	[35]
27.9	3.09	7.5	"	2	"	[35]
27.86	3.5	8.7	"	4.3	"	[35]
19.3	2.95	7.5	"	2.1	"	[35]
27.86	3.36	8.7	"	6.43	"	[35]
17.1	3.09	7.5	"	2.1	"	[35]
30	3.4	8.7	"	8.6	"	[35]
23.6	2.5	7.5	"	5.4	"	[35]
26.2	4.3	8.4	2 days	3.39	Glatt River, CH, spiked	[34]
80.4	4.3	8.4	"	15.3	"	[34]
131	4.3	8.4	"	33.9	"	[34]
192.5	4.3	8.4	"	61	"	[34]
35.4	3.6	7.86	"	21.6	Furtbach River, CH, spiked	[34]
39.8	3.6	7.86	"	28.8	"	[34]
44.25	3.6	7.86	"	27.6	"	[34]
73	3.6	7.86	"	33.6	"	[34]
79.65	3.6	7.86	"	33.6	"	[34]
77.43	3.6	7.86	"	73.2	"	[34]
90.7	3.6	7.86	"	63.6	"	[34]
81.4	3.6	7.86	"	51.6	"	[34]
119.5	3.6	7.86	"	78	"	[34]
8.0	7.5	6.5	48 h	0.39	Loder Creek, AU	[43]
14.2	0.84	6.1	24 h	3.9	Parkwood pond, AU	[36]
19	4.85	7.7 to 8.7	1 to 4 days	3.8	Lake Greifen, CH, 2.5 m	[44]
19	4.85	"	"	4.5	Lake Greifen, CH, 5.0 m	[44]
30	1.9	"	"	17	Furtbach River, CH	[44]
20	15	"	"	2.5	river Wyre, UK	[44]
30	3.96	7.65	1 or 2 weeks	7.15	River Meuse, NL	[60]
40	4.08	7.29	"	11.69	"	[60]
30	2.52	8.03	"	6	River Rhine, NL	[60]
70	1.8	7.0	36 h	22.5	Lake Windermere, UK	[45]
810	12.3	6.8	10 to 15 h	240	unnamed creek, CA, spiked	[46]
1410	12.3	6.8	"	490	"	[46]
400	10.3	6.7	"	80	Duck Lake, CA, spiked	[46]
1490	10.3	6.7	10 to 15 h	590	Duck Lake, CA, spiked	[46]
280	12.4	6.9	"	80	Kalamalka Lake, CA, spiked	[46]

$c_{M,t}$ nmol dm <sup>-3</sup>	DOC mg dm <sup>-3</sup>	pH	Deployment time	Reported $c_{DGT}$ nmol dm <sup>-3</sup>	Sample	References
480	12.4	6.9	"	160	Kalamalka Lake, CA, spiked	[46]
810	12.4	6.9	"	340	"	[46]
1410	12.4	6.9	"	650	"	[46]
400	11	6.7	"	200	Okanagan Lake, CA, spiked	[46]
685	11	6.7	"	280	"	[46]
890	11	6.7	"	410	"	[46]
1530	11	6.7	"	810	"	[46]
241	8	6.8 to 7.3	~24 h	36.2	Woronora River, AU, spiked	[47]
301.5	8	6.8 to 7.3	"	108.6	"	[47]
392	8	6.8 to 7.3	"	162.5	"	[47]
814	8	6.8 to 7.3	"	252.7	"	[47]
121.2	3	6.8 to 7.3	"	53.5	Jock's Creek, AU, spiked	[47]
241.1	3	6.8 to 7.3	"	144.5	"	[47]
489.4	8.4	7.5	~24 h	61.4	East Lake Creek, CA, spiked	[48]
637.3	8.4	7.5	"	122.7	"	[48]
783.6	8.4	7.5	"	153.6	"	[48]
7.4	1.0	8.2	"	2.2	"	[48]
<b>Pb<sup>II</sup></b>						
1.8	15	7.7 to 8.6	~3 days	0.036	River Wyre, UK	[14]
102.3	2	7.8	5 days	29.9	Meuse river, NL, spiked	[41]
0.24	3.71	8.7	2 or 3 days	0.023	Lake Greifen, CH	[35]
0.067	3.77	8.7	"	0.022	"	[35]
0.24	3.4	8.7	"	0.02	"	[35]
0.4	3.96	7.65	1 or 2 weeks	0.0145	River Meuse, NL	[60]
0.6	2.52	8.03	"	0.0096	River Rhine, NL	[60]
1.7	15	7.7 to 8.7	1 to 4 days	0.048	River Wyre, UK	[44]
0.39	1.9	"	"	0.32	Furtbach River, CH	[44]
0.22	4.85	"	"	0.02	Lake Greifen, CH, 2.5 m	[44]
<b>Cd<sup>II</sup></b>						
0.2	15	7.7 to 8.6	~3 days	0.062	River Wyre, UK	[14]
156.6	2	7.8	5 days	148.6	Meuse River, NL, spiked	[60]
0.12	3.71	8.7	2 or 3 days	0.01	Lake Greifen, CH	[35]
0.064	3.09	7.5	"	0.01	"	[35]
0.2	15	7.7 to 8.7	1 to 4 days	0.071	River Wyre, UK	[44]
0.08	1.9	"	"	0.06	Furtbach river, CH	[44]
3.6	7.5	6.5	48 h	0.12	Loder creek, AU	[43]
3.6	9.2	6.1	24 h	0.16	Parkwood pond, AU	[36]
0.15	4.2	not stated	typically 3 or 7 days	0.067	Theil, Seine river basin, FR	[42]
0.173	4.2	"	"	0.053	Guerard, Seine river basin, FR	[42]
0.187	4.2	"	"	0.06	Meaux, Seine river basin, FR	[42]
0.204	4.2	"	"	0.08	Saint-Maurice, Seine river basin, FR	[42]
0.334	4.2	"	"	0.113	Chatou, Seine river basin, FR	[42]
0.334	4.2	"	"	0.08	Andresy, Seine river basin, FR	[42]
<b>Ni<sup>II</sup></b>						
22	15	7.7 to 8.6	~3 days	7.92	River Wyre, UK	[14]
420.7	2	7.8	5 days	398.6	Meuse River, NL, spiked	[60]
20.2	15	7.7 to 8.7	1 to 4 days	7.53	River Wyre, UK	[44]
7	1.9	"	"	2.7	Lake Greifen, CH, 2.5 m	[44]
6	4.85	"	"	3.1	Lake Greifen, CH, 5 m	[44]
18.4	4.2	not stated	typically 3 or 7 days	5.6	Theil, Seine river basin, FR	[42]
17.8	4.2	"	"	5.0	Guerard, Seine river basin, FR	[42]
18.9	4.2	"	"	7.8	Meaux, Seine river basin, FR	[42]
17.8	4.2	"	"	12.2	Saint-Maurice, Seine river basin, FR	[42]

$c_{M,t}$ nmol dm <sup>-3</sup>	DOC mg dm <sup>-3</sup>	pH	Deployment time	Reported $c_{DGT}$ nmol dm <sup>-3</sup>	Sample	References
25.5	4.2	"	"	11.4	Chatou, Seine river basin, FR	[42]
28.1	4.2	"	"	13.9	Andresy, Seine river basin, FR	[42]
70	3.96	7.65	1 or 2 weeks	18.5	River Meuse, NL	[60]
80	4.08	7.29	"	29	"	[60]
30	2.52	8.03	"	11.48	River Rhine, NL	[60]
13.8	3.09	7.5	2 or 3 days	3.4	Lake Greifen, CH	[35]
13.8	2.95	7.5	"	1.7	"	[35]
72.4	2.5	7.5	"	6.9	"	[35]

<sup>A</sup>Average value for  $d_g$  values of 0.16, 0.4, 1.2, and 2.0 mm.

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