Supplementary Material (ESI) for Journal of Environmental Monitoring

Evaluation of the Chemcatcher and DGT passive samplers for monitoring metals with highly fluctuating water concentrations

Ian J. Allan, Jesper Knutsson, Nathalie Guigues, Graham A. Mills, Anne-Marie Fouillac and Richard Greenwood

Supporting information

Further details of the tank trial:

The tank test was set-up for the evaluation of many different monitoring tools and was sized to accommodate the collection of large volumes of water without influencing significantly the conditions inside the vessel.

All parts of the test tank were cleaned and rinsed prior to use in the experiment. Passive sampling devices including Chemcatchers and DGTs were attached to the Teflon carousel with cable ties and the carousel was then fitted into the tank. 220 L of Meuse river water were pumped into the test tank (water adjustment system in Figure S1) at the start of the experiment using a pump and plastic tubing system (previously thoroughly flushed with Meuse river water). The overhead stirrer was then attached and adjusted to a speed of 30 rpm. The system was then left to stabilise overnight prior to spiking with a concentrated multi-metal standard solution. Peaks in concentration were simulated as a series of plateaus. The concentrations of metals in the tank were measured twice per plateau. After the simulation of the first peak of concentration over approximately 48 h, the tank was flushed and contaminated water was replaced by fresh Meuse river water and left to stabilise for period of 24 h before simulating the second peak of concentration.

Spot sampling was performed using the water sampling system shown in Figure S1. One litre samples of water were removed from the test tank and immediately replaced with fresh Meuse river water. This, in addition to the metals reaching equilibrium in

the system, is responsible for the slight decrease in concentration observed for each plateau. Spiking was undertaken following the second measurement for each plateau.

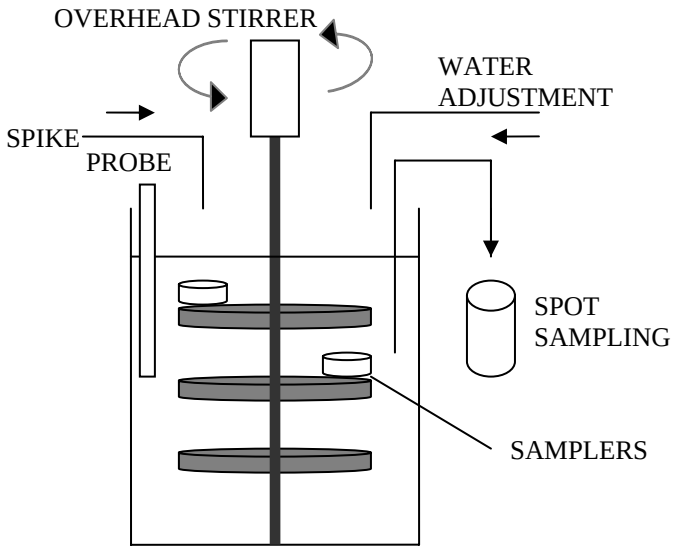

Figure S1. Diagram of the tank test.

The plateaux in concentrations for Cd is shown in Figure S2 with the approximate deployment times for Chemcatcher and DGT samplers highlighted.

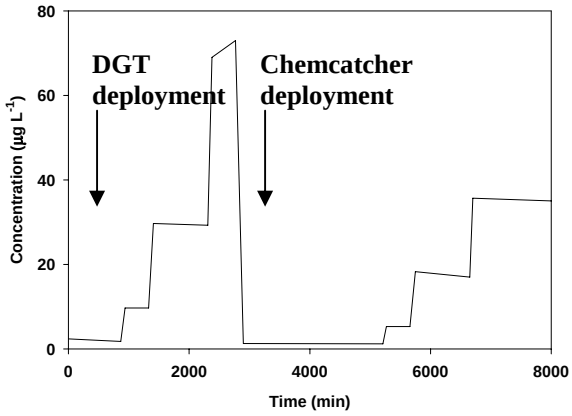

Figure S2. Temporal changes in Cd concentration during the tank trial.

Table S1. Total (unfiltered) metal concentrations determined throughout the experiment.

Time (min)	**Total concentration** (µg L^{-1})				
	Cd	Cu	Ni	Pb	Zn
0	2.4	6.5	3.7	17.9	56.7
870	1.8	4.7	3.5	10.5	45.7
940	9.7	25.0	21.5	19.6	79.0
1330	9.7	25.3	21.6	22.5	77.0
1410	29.7	60.3	44.6	44.9	113.3

2310	29.3	56.3	43	41.5	107.7
2380	69	85.0	57.7	68.7	140.3
2770	73	84.0	58.8	60.9	141.0
2900	1.3	6.0	4.4	9.1	32.0
5210	1.2	6.0	4.4	6.0	22.7
5270	5.3	24.0	13.3	20.3	37.0
5660	5.3	22.3	13.5	12.8	36.7
5750	18.3	40	30.7	22.2	52.0
6650	17	36.7	29.3	14.6	49.0
6700	35.7	54.3	47.9	25.7	53.7
8090	35	49.0	48.2	18.7	50.0

Table S2. Filtered (0.45 µm) metal concentrations determined throughout the experiment.

Time (min)	**Filtered concentration** (µg L^{-1})				
	Cd	Cu	Ni	Pb	Zn
0	1.2	<3	3.2	3.2	36.7
870	1.2	<3	3.3	2.1	20.0
940	9.1	23.0	21.3	6.7	72.3
1330	8.8	21.0	20.8	4.5	63.3
1410	29.3	52.7	44.0	22.5	98.3
2310	28.0	48.0	43.2	15.9	99.0
2380	60.3	77.3	55.6	46.8	131.7
2770	69.7	75.3	57.7	40.8	128.3
2900	0.8	4.0	3.8	2.9	14.7
5210	1.0	5.0	4.1	1.6	15.0
5270	4.9	22.0	13.2	6.4	30.7
5660	4.7	19.0	12.8	3.8	30.3
5750	17.3	34.0	30.1	12.6	42.7
6650	16.3	31.3	30.2	9.0	42.7
6700	35.7	47.7	48.0	22.2	46.3
8090	34.3	43.0	46.0	14.3	45.0

Table S3. Ultrafiltered (5 kDa) metal concentrations determined throughout the experiment (nd: not determined).

Time (min)	**UltraFiltered concentration** (µg L^{-1})				
	Cd	Cu	Ni	Pb	Zn
0	nd	nd	nd	nd	nd
870	1.0	<3	3.5	1.1	37.0
940	Nd	11.0	20.7	2.4	46.0
1330	9.4	11.0	22.0	2.0	47.0
1410	30.0	24.0	41.5	9.8	77.0
2310	33.0	28.0	44.5	6.9	73.0
2380	63.0	34.0	60.9	22.0	89.0
2770	75.0	32.0	48.9	16.8	101.0
2900	0.7	<3	4.0	0.6	12.0
5210	0.9	3.0	3.8	0.5	11.0
5270	nd	nd	nd	nd	nd
5660	nd	nd	nd	nd	nd
5750	21.0	13.0	28.7	4.5	33.0

6650	nd	nd	Nd	nd	Nd
6700	38.0	24.0	48.1	6.4	32.0
8090	nd	nd	Nd	nd	Nd

Speciation modelling undertaken

The Visual MINTEQ software can be found and downloaded free of charge from the Royal Institute of Technology website: (http://www.lwr.kth.se/English/OurSoftware/vminteq/)

Table S4. Average concentration of the principal components of river water and input parameters used in the MINTEQ modelling calculations.

Component	Average concentration (mg L^{-1})
Cl^-	35.4
SO_4^{2-}	40.6
NO_3-N	19.2
NO_2-N	0.3
SiO_2	2.2
Ca^{2+}	63.0
Mg^{2+}	7.3
Na^+	24.0
K^+	3.4
HCO_3^-	195.3

Table S5. Measured TOC values and calculated DOC values for the spot samples used in the MINTEQ calculations.

Spot sample no.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
DOC mg L^{-1}	1.6	1.6	1.7	1.7	1.8	2.2	2.2	2.6	1.9	2.1	2.0	2.2	2.4	2.2	2.7	2.4
TOC mg L^{-1}	2.8	2.7	2.9	3.1	3.1	3.9	3.8	4.5	3.4	3.6	3.6	3.9	4.2	3.8	4.8	4.2

Table S6. Predicted free ion concentrations.

Time (min)	**Predicted free ion concentration** (µg L^{-1})				
	Cd	Cu	Ni	Pb	Zn
0	0.7	0.00	2.7	0.01	29.2
870	0.7	0.00	2.8	0.01	15.2
940	6.8	0.11	19.3	0.04	59.6
1330	6.5	0.08	18.8	0.02	51.9
1410	23.6	1.15	40.4	0.32	82.2
2310	21.8	0.48	39.3	0.13	81.6
2380	49.1	2.14	51.0	0.79	110.1
2770	55.8	1.22	52.5	0.46	106.0
2900	0.4	0.00	3.2	0.01	10.4
5210	0.5	0.00	3.4	0.00	10.4
5270	3.2	0.03	11.5	0.02	23.3

5660	3.1	0.03	11.2	0.01	23.0
5750	12.7	0.13	26.9	0.07	33.1
6650	12.1	0.13	27.2	0.05	33.5
6700	27.1	0.26	43.1	0.15	35.8
8090	26.5	0.26	41.6	0.09	35.2

Table S7. Predicted inorganic metal concentrations.

Time (min)	**Predicted inorganic metal concentration** (μg L^{-1})				
	Cd	Cu	Ni	Pb	Zn
0	0.08	0.00	0.1	0.02	4.0
870	0.08	0.00	0.1	0.01	2.1
940	0.82	0.21	0.9	0.07	8.3
1330	0.78	0.16	0.9	0.04	7.2
1410	2.84	2.17	1.9	0.47	11.4
2310	2.64	0.91	1.9	0.19	11.4
2380	5.95	4.04	2.4	1.16	15.4
2770	6.80	2.30	2.5	0.68	14.9
2900	0.05	0.00	0.2	0.01	1.4
5210	0.06	0.00	0.2	0.01	1.4
5270	0.39	0.06	0.6	0.03	3.2
5660	0.37	0.05	0.5	0.02	3.2
5750	1.55	0.24	1.3	0.10	4.6
6650	1.47	0.24	1.3	0.07	4.7
6700	3.31	0.48	2.1	0.21	5.0
8090	3.22	0.49	2.0	0.13	4.9

Table S8. Predicted fulvic acid complexed metal concentrations.

Time (min)	**Predicted FA-complexed metal concentration** (μg L^{-1})				
	Cd	Cu	Ni	Pb	Zn
0	0.09	0.9	0.12	2.6	0.02
870	0.09	0.9	0.12	1.7	0.01
940	0.42	10.5	0.37	5.4	0.02
1330	0.41	9.6	0.36	3.6	0.02
1410	0.94	22.4	0.51	17.7	0.02
2310	1.14	21.4	0.66	12.7	0.03
2380	1.80	31.8	0.67	36.3	0.03
2770	2.40	32.5	0.85	32.3	0.04
2900	0.08	1.8	0.16	2.3	0.01
5210	0.10	2.2	0.19	1.3	0.01
5270	0.35	10.1	0.37	5.2	0.02
5660	0.33	8.7	0.36	3.1	0.02
5750	0.90	15.5	0.62	10.1	0.02
6650	0.80	14.3	0.57	7.3	0.02
6700	1.65	21.5	0.88	17.8	0.03
8090	1.44	19.4	0.77	11.5	0.02