Chemcatcher™ and DGT passive sampling devices for regulatory monitoring of trace metals in surface waters

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Supporting information

List of Tables and Figures in the supporting information:

1. Characteristics of Meuse river water during the trial

Water temperature was measured continuously throughout the trial. Mean water temperatures are given in Table S1 for each deployment period.

Deployment period	Temperature (°C)	
	Mean	SD
7 days	16.8	1.2
14 days (1)	13.8	0.6
14 days (2)	16.5	1.2
21 days	15.1	1.6
28 days	15.6	1.6

Table S1. Mean water temperature (calculated from continuous measurement) for the various passive sampler exposure periods (SD = standard deviation).

A range of characteristics of the river water was measured during the 28 day field trial (12th April-10th May 2005). On each occasion that spot samples were taken, the characteristics of the water were measured (Table S2). These values were used in the prediction of metal speciation using the Visual MINTEQ software.

Property	Sampling date (2005)											
	April								**May**			
	13th	**15th**	**18th**	**20th**	**25th**	**26th**	**27th**	**29th**	**2nd**	**4th**	**6th**	**9th**
pH	7.90	7.94	7.85	7.87	7.87	7.86	7.87	7.75	7.78	7.69	7.71	7.77
Cl^- mg L^{-1}	36.7	38.0	29.7	38.2	33.9	39.4	34.1	36.7	48.0	32.4	37.2	31.6
SO_4^{2-} mg L^{-1} SO_4	40.9	40.8	37.7	40.2	40.4	41.2	38.6	40.8	43.0	42.1	40.4	34.2
NO_2-N mg L^{-1} NO_2	< 0.01	< 0.01	0.29	< 0.01	< 0.01	0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.67	0.03
NO_3-N mg L^{-1} NO_3	16.6	15.1	14.7	15.5	15.3	15.9	14.6	16.3	16.0	15.6	16.6	15.0
SiO_2 mg L^{-1}	2.8	2.0	2.3	2.5	2.2	2.7	3.8	3.9	3.1	2.7	4.3	5.1
TOC mg L^{-1} C	3.3	2.7	3.2	3.4	2.8	3.7	4.2	3.7	3.2	3.3	3.5	4.3
Ca^{2+} mg L^{-1}	63.1	62.8	55.7	59.5	63.0	60.2	59.4	69.6	68.0	65.7	61.1	50.0
Mg^{2+} mg L^{-1}	7.5	7.4	7.0	7.3	7.9	7.6	7.6	7.5	8.1	7.8	7.5	6.5
Na^+ mg L^{-1}	24.0	25.8	20.1	25.8	22.0	24.8	21.8	23.7	30.8	22.5	23.4	21.6
K^+ mg L^{-1}	3.9	3.3	3.0	3.3	3.2	3.5	3.4	3.5	3.7	3.5	3.3	3.1
Alkalinity mg L^{-1} HCO_3	182	184	168	175	185	175	177	184	195	194	183	153
N total oxide mg L^{-1} NO_3	16.6	15.1	15.1	15.5	15.4	15.9	14.6	16.3	16.0	15.6	17.5	15.0

Table S2. Major components measured in Meuse river water at the twelve spot sampling events during the trial (TOC = total organic carbon).

In addition the main components were measured in the weekly composite samples of river water taken during the trial (Table S3).

	Major components									
Week	Cl^-	SO_4^{2-}	F	NH_4-	NO_2-	NO_3-	PO_4-P	Si	DOC	TOC

				N	N	N				
	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	μg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}
19th April	31.3	38		0.37	0.06	2.60	140	1.14	2	4
26th April	34.3	40	0.4	0.41	0.07	2.61	130	1.49	3	7
3rd May	32.5	41		0.31	0.09	2.42	160	1.42	3	5
10th May	34.2	36	0.42	0.29	0.10	2.31	170	2.63	4	5

Table S3. Major components measured in Meuse river water in the weekly composite samples taken during the trial (TOC = total organic carbon, DOC = dissolved organic carbon).

2. Calculation of time weighted average concentrations for the DGT and Chemcatcher passive samplers

The operation of both samplers is based on Fickian diffusion, but different approaches are used for the calculation of the time weighted average (TWA) concentrations of metals to which the samplers were exposed during the deployment period.

The *Diffusive Gradient in Thin film* (DGT) device has been used extensively for the measurement of TWA concentrations of labile metals and for predicting the speciation of metals in water, and their toxicity to aquatic organisms [1-5]. DGT devices comprise a diffusive layer of polyacrylamide APA2 hydrogel (15 vol % acrylamide and 0.3 vol % agarose-derived cross-linker for the open pore gel) and a Chelex 100 gel layer used for the accumulation of metals. These are housed in a small piston-like plastic holder. A filter can be placed over the gel to provide protection in the field, and this forms part of the diffusive layer. Metal species diffuse across the hydrogel layer of known thickness and accumulate in the Chelex resin receiving phase. Using Fick's first law of diffusion, TWA concentrations (C_{DGT}) may be determined from the mass of metal accumulated (M), the exposure time (t), the surface area of the sampling layer (A), the gel thickness (Δg) and the effective diffusion coefficients (D_e) of metals through the diffusive layer:

$$C_{DGT} = \frac{M \Delta g}{D_e t A} \qquad (1)$$

The area of the sampling surface is 3.14 cm^2, the gel thickness 0.8 mm, and the thickness of the protective filter layer above the hydrogel 0.13 mm. While both types of DGTs used here had the same gel thickness, the pore size (< 1 nm) of the restricted pore gel (RP) was significantly smaller than that (> 5 nm) of the standard open pore (OP) gel. It is assumed that the RP gel allows the diffusion of only free ions and small inorganic and organic complexes, while the OP gel allows the diffusion of larger organic complexes. However, in order for metal bound in complexes to be available for accumulation in the Chelex layer, it is necessary for them to dissociate within the time needed for them to cross the diffusion layer [1]. This implies that a labile fraction of metals is being measured. It is also possible that metal bound to some small colloids will not be accumulated by these samplers [5]. Different diffusion coefficients for metals in the OP and RP gels have been measured in laboratory-based calibration experiments [6] and these need to be included in the calculation of TWA concentrations. Furthermore, in some deployment conditions it may be reasonable to assume that a diffusive boundary layer (average thickness of 0.23 mm in moderately stirred solutions [7, 8]) may be present at the surface of the sampler. It has been shown that metal diffusion coefficients of metals in the filter layer are not significantly different from those in the OP gel [6].

Equation (1) can be reworked to take account of specific metal diffusion coefficients and the thicknesses of the gel, filter and water boundary layers:

$$C_{DGT} = \frac{M\left(\frac{\Delta g}{D_{gel}} + \frac{\Delta f}{D_f} + \frac{d_{DBL}}{D_{DBL}}\right)}{At} \qquad (2)$$

where D_f, D_{gel} and D_{DBL} are the metal diffusion coefficients in the filter, gel and diffusive boundary layer (DBL) respectively; *and* Δf, Δg and d_{DBL} represent thicknesses of the filter, gel and DBL respectively.

Metal-specific diffusion coefficients for the RP and OP hydrogel layers corresponding to the mean temperature of each exposure [7] were used (Table S5). Diffusion coefficients in the filter layer were assumed to be similar to those for the OP gel. The mean water velocity at the deployment site was approximately 0.7 m s^{-1}, and under these conditions it was assumed that a DBL layer would be negligible. Therefore Equation 2 was used without the d_{DBL}/D_{DBL} term.

The Chemcatcher™ passive sampler uses of a common sampler body, with interchangeable diffusion-limiting membranes and receiving phases appropriate for the class of analytes (polar organic, non-polar organic, or metals) being monitored [9-13]. For metals a cellulose acetate diffusion limiting membrane, with an Empore^{TM} chelating disk as the receiving phase.

The approach to calibration of the Chemcatcher™ for metals is the same as that commonly used for samplers for organic pollutants [10, 14, 15]. Laboratory-determined analyte-specific uptake rates are used to estimate TWA concentrations of metals [9]. The rate of diffusion of metal species is influenced by water temperature, hydrodynamics (water turbulence at the surface of the sampler). The latter affects the thickness of the diffusive boundary layer present at the surface of the diffusion membrane. This version of the Chemcatcher™ had a deep cavity in front of the diffusion limiting membrane [11], and so turbulence has an important impact on the thickness of the diffusive boundary layer. Laboratory-based calibration data (analyte specific uptake rates (*Rs*)) obtained for a series of combinations of temperatures and stirring speeds (turbulences) are used to account for variations in environmental conditions.

TWA concentrations measured using the Chemcatcher™ are calculated from the mass of metal accumulated in the chelating disk (*M*), the exposure time (*t*) and selected uptake rates (R_S) [9, 11]:

$$C_{Chemcatcher} = M/R_S t \qquad (3)$$

Based on mean water temperatures and turbulences during the deployment periods, the nearest available laboratory-determined uptake rates (equivalent to a water velocity of 70 cm s^{-1} and water temperature of 18°C) were selected for use in the calculation of TWA concentrations for the Chemcatcher™ (Table S6). Metals sorbed to suspended sediments or large colloids are likely to be selectively excluded by the 0.45 μm cellulose acetate diffusion membrane as are those forming complexes unable to dissociate in the time required for them to pass through the diffusion layers.

3. Diffusion coefficients of metals used for the calculation of TWA concentrations for DGT

Diffusion coefficients of metals were either selected from the DGT Research Handbook or calculated based on mean water temperatures measured throughout the various exposure periods. Values for DGT (OP) were taken from the handbook, and those for DGT (RP) were taken from Wranken *et al*., 2006, and were modified to take into account diffusion across the filter layer.

Exposure	Diffusion coefficients of metals DGT (OP) ($\times 10^{-6}$ cm^2 s^{-1})				
	Cd	Cu	Ni	Pb	Zn

7 day	4.83	4.94	4.57	6.36	4.82
14 day (1)	4.40	4.50	4.17	5.81	4.39
14 day (2)	4.79	4.89	4.53	6.30	4.77
28 day	4.59	4.70	4.35	6.05	4.58

Table S4. Diffusion coefficients of metals for the DGT (OP) hydrogel.

Exposure	Diffusion coefficients of metals in DGT (RP) (× 10^{-6} cm^2 s^{-1})				
	Cd	Cu	Ni	Pb	Zn
7 day	3.16	3.51	3.21	4.59	3.43
14 day (1)	2.88	3.20	2.93	4.19	3.13
14 day (2)	3.13	3.48	3.18	4.54	3.40
28 day	3.01	3.34	3.05	4.37	3.26

Table S5. Diffusion coefficients of metals for the DGT (RP) hydrogel.

4. Uptake rates of metals used for the calculation of TWA concentrations for Chemcatcher™

Exposure Conditions Velocity = 70 cm s^{-1}, Temperature = 18°C	Uptake rates (R_S) of metals for the Chemcatcher™ sampler (mL h^{-1})				
	Cd	Cu	Ni	Pb	Zn
Mean	5.1	4.9	5.7	0.7	5.3
SD	0.62	0.51	0.42	0.09	0.55

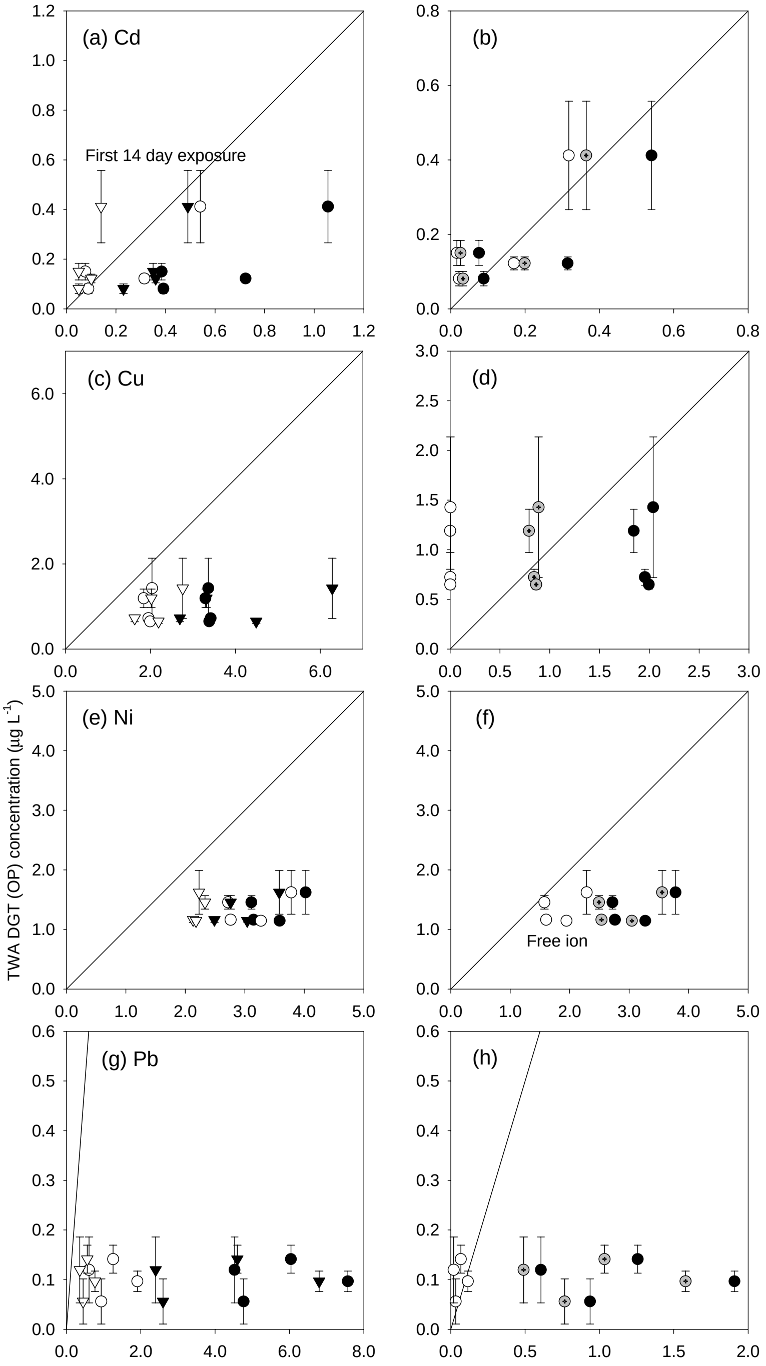
Table S6. Uptake rates of metals for the Chemcatcher passive sampler (SD = standard deviation).

5. Analysis of passive sampler extracts

All extracts were analysed by ICP-MS (Perkin Elmer Elan 6000). Oxide levels and doubly charged ions were below 3 % and the background signal was below 5 cps. After optimisation, the instrument gave at least 3 x 10^5 cps for a 10 ppb indium solution and an RSD < 1 %. Instrument calibration (0.1-500 µg L^{-1}) used an ICP multi-element standard (Merck p.a. quality) and Rhodium (10 ppb) as internal standard. The reagent water was laboratory grade I water prepared from a Milli-Q analytical system using de-ionised feed water.

6. Comparison of passive and spot sampling-based TWA concentration measurements

TWA concentrations were calculated for each metal for each passive sampler exposure period (Figure 1 main text). DGT (OP) based TWA concentrations were compared with concentrations in total and filtered samples based on spot (Team A) and composite water sampling (Team B) (Figure S1: a, c, e, g, i), and with concentrations based on Visual MINTEQ speciation modelling (Figure S1: b, d, f, h, j). Similar plots were constructed for the Chemcatcher™ passive sampler (Figure S2: a, c, e, g, i) and (Figure S2: b, d, f, h, j). On these figures, DGT (Figure S1) and Chemcatcher™ (Figure S2) TWA concentrations are plotted on the y-axis against those from other forms of sampling or speciation calculations on the x-axis, together with a line representing an 1:1 relationship. These comparisons are useful in understanding the fractions of metals being measured by the different monitoring procedures.



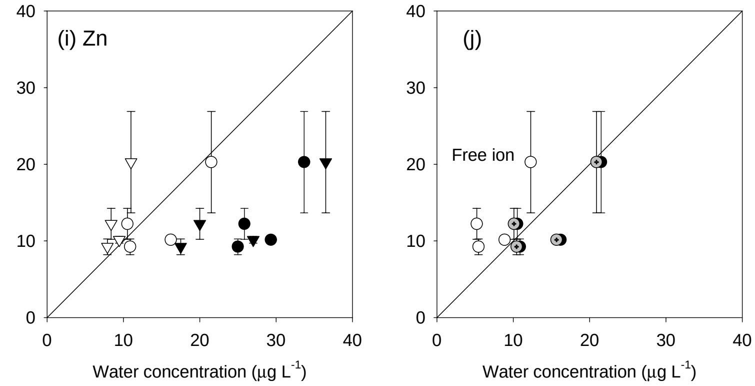
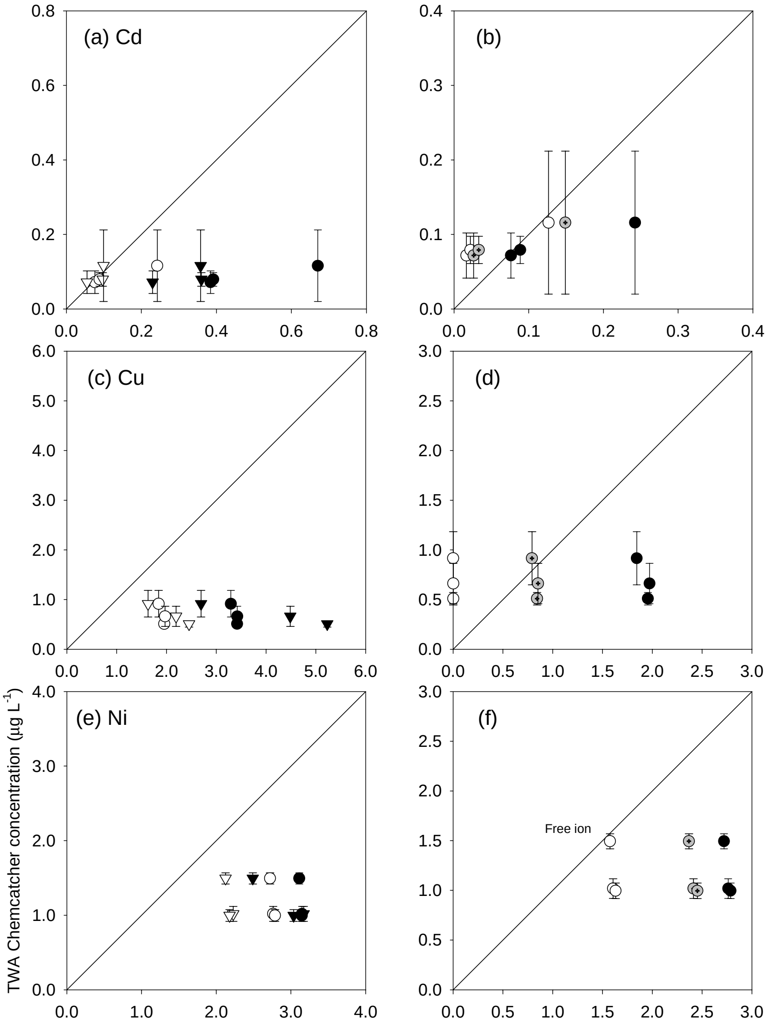


Figure S1. Comparison of time-weighted average concentrations of Cd (a), Cu (c), Ni (e), Pb (g) and Zn (i) obtained using DGT (OP) for exposures of 7, 14 and 28 days, with mean total (●,▼) and 0.45 µm-filtered (○, ▽) metal concentrations measured in spot (Team A) and composite (Team B) water samples; and with concentrations of Cd (b), Cu (d), Ni (f), Pb (h) and Zn (j) obtained using Visual MINTEQ speciation modelling (Key: inorganic- (○),and inorganic + fulvic acid- (⊕) complexed fractions, and filtered fraction (●). Note: the line and error bars represent the 1:1 relationship and standard deviations of the DGT measurement based on triplicate values respectively.



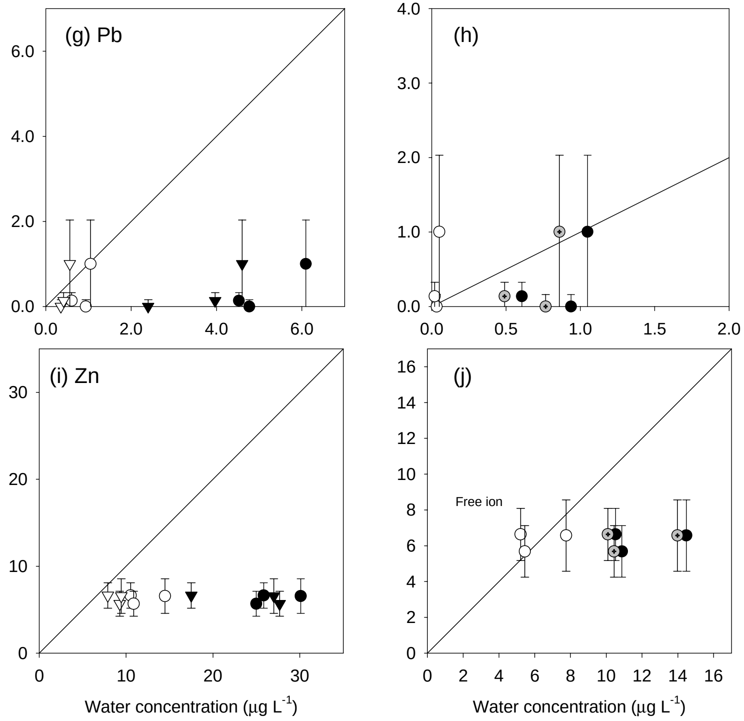


Figure S2. Comparison of time-weighted average concentrations of Cd (a), Cu (c), Ni (e), Pb (g) and Zn (i) obtained using Chemcatcher™ for exposures of 7, 14 and 21 days, with mean total (●,▼) and 0.45 µm-filtered (○, ▽) metal concentrations measured in spot (Team A) and composite (Team B) water samples; and with concentrations of Cd (b), Cu (d), Ni (f), Pb (h) and Zn (j) obtained using Visual MINTEQ speciation modelling (Key: inorganic- (○), and inorganic + fulvic acid- (⊕) complexed fractions, and filtered fraction (●)). Note: the line and error bars represent the 1:1 relationship and standard deviations of the Chemcatcher™ measurement based on triplicate values respectively.

7. Cluster analysis of monitoring data

Cluster analysis (CA) was undertaken (Minitab v14) for Chemcatcher™ and DGT datasets to explore relationships between the various sets of monitoring data. This facilitates the identification of groups or clusters that contain cases with strong association with each other, and with weak association with those in other clusters. Each cluster can therefore be characterized on the basis of its class members. Cases here represent the different methods of measurement of concentrations of metals in water. Descriptor variables were concentrations of Cd, Cu, Ni and Zn in water for the 7, 14, 21 or 28 day exposures. Pb was omitted because of the high uncertainties associated with the passive sampling measurements for this metal. The descriptor variables were standardized to avoid the effects of scale on distance measurements. Euclidean distances and an average linkage method were used to evaluate similarities and dissimilarities.

Key to cases:

1, 2, 3: Chemcatcher™
4: Total (spot sampling Team B)
5: Filtered (composite sampling Team B)
6: Total (spot sampling Team A)
7: Filtered (spot sampling Team A)
8: Free ion (speciation)
9: Inorganic (speciation)
10: Inorganic + Fulvic acid (speciation)

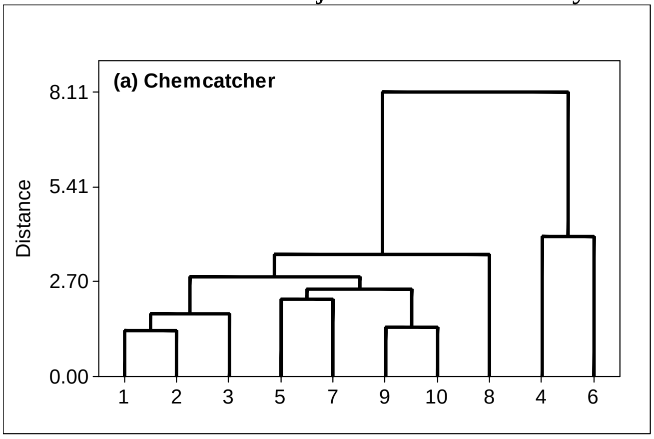


Figure S3. Cluster analysis of the metal fractions measured by spot and passive sampling (Chemcatcher™) techniques and predicted by speciation modeling.

Key to cases:

1, 2, 3: DGT (RP)
4, 5, 6: DGT (OP)
7: Total (composite sampling team B)
8: Filtered (composite sampling team B)
9: Total (spot sampling team A)
10: Filtered (spot sampling team A)
11: Free ion (speciation)
12: Inorganic (speciation)
13: Inorganic + Fulvic acid (speciation)

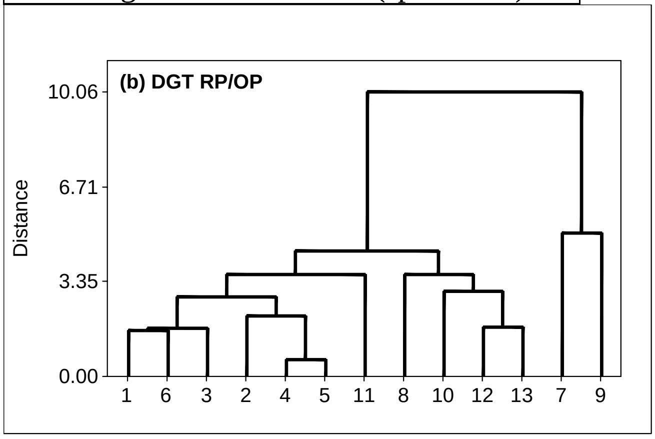


Figure S4. Cluster analysis of the metal fractions measured by spot and passive sampling (DGT) techniques, and those predicted by speciation modeling.

There was a mismatch between some of the deployment periods for Chemcatcher™ and DGT, and when these periods were omitted from the analysis, only a small number of complete cases remained. Therefore separate CAs were undertaken for the Chemcatcher™ and DGT samplers.

With the Chemcatcher™ the methods of determining the concentrations of the various fractions of metals fell into three main clusters, with the free ion prediction based on speciation (Key: 8) falling outside these groupings (Figure S3). Cluster I comprised the Chemcatcher™-based metal concentrations for the three different deployment times (Key: 1, 2, 3), cluster II comprises the filtered fractions based on spot sampling, and the inorganic and inorganic plus fulvic fractions (Key: 5, 7, 9, 10), cluster III comprised the total metal concentrations based on spot sampling by Teams A and B (Key: 4, 6). The most distant cluster (III) comprised the total metal (free, and bound to suspended and dissolved organic matter), and closest clusters are passive sampling and filtered and concentrations predicted by speciation modelling. This is consistent with the idea that the Chemcatcher™ measures the labile metal fraction.

A similar clustering was found for DGT (OP) and DGT (RP) where again three main clusters with the predicted free ion being separate were observed (Figure S4). Cluster I (Key: 1, 6, 3 and 2, 4, 5) comprised passive sampling, Cluster II (Key: 8, 10, 12, 13) filtered fractions based on spot sampling by both teams, and the inorganic and inorganic plus fulvic fractions, and cluster III the total metal concentrations based on spot sampling (Key: 7, 9). The interpretation is similar to that for the Chemcatcher™. The distances between the spot sampling by teams A and B were small.

Overall these CAs provide additional evidence that Chemcatcher™ and DGT measure the labile (biologically relevant) fraction of Cd, Cu, Ni and Zn in water. This is also consistent with previous work comparing the concentrations of metals measured using passive sampling with those determined by other sampling and analytical methods, and speciation models.

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