Electronic Supplementary Material (ESI) for Environmental Science: Processes & Impacts.

Supplementary Information for:

In situ evaluation of DGT techniques for measurement of trace metals in estuarine waters: a comparison of four binding layers with open and restricted diffusive layers

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Experimental

1. Uptake and elution efficiencies for PAMPAA binding layer

Uptake efficiencies for Al, Cd, Co, Cu, Mn, Ni, Pb and Zn were measured by immersing five PAMPAA gel discs in 5 ml of 100 μg L^{-1} of either Al solution (prepared in 0.01 mol L^{-1} $NaNO_3$ at pH 8.30) or mixed analyte solution (prepared in 0.01 mol L^{-1} $NaNO_3$ at pH 6.00). The solutions were gently shaken for 24 h and the gels were removed for analysis. To determine the mass of analytes remaining in the solution, subsamples were taken and analysed by ICP-MS after acidification (2% HNO_3). The total mass of adsorbed metals and consequently uptake efficiencies were calculated by difference. To measure elution efficiencies, the PAMPAA binding layers were immersed in 5 ml of 2 mol L^{-1} HNO_3 for 24 h and the mass of eluted metals determined. The elution efficiency was calculated as the fraction of the total metal that was eluted for each element [1, 2].

2. Assessment of Metsorb acid wash for oxyanion measurements

In addition to the set of DGT-Metsorb deployed for oxyanion measurements, a second set of DGT-Metsorb was deployed in triplicate for measurement of Al alone; these Metsorb binding layers were acid washed in 0.0001 mol L^{-1} HNO_3 prior to elution to increase the elution efficiency of Al [1]. This acid wash process, however, may affect the concentration of other oxyanions on the binding layer, as they may be partially eluted. In this study, we have compared the concentration of Al and oxyanions (As, Sb and V) measured by DGT-Metsorb which were either acid washed or not prior to elution, in order to determine the effect of the acid wash on Metsorb measurements of oxyanions.

Results

1. Uptake and elution efficiencies for PAMPAA binding layer

The determined uptake and elution efficiencies of trace metals for PAMPAA binding layer are provided in Table S2. The uptake efficiencies for Al, Cu and Pb were 89.7 ± 2%, 75.5 ± 1% and 94.99 ± 1% (n= 5), respectively. For all other cations, the results were between 34-55% (n= 5). PAMPAA elution efficiencies (using 2 mol L^{-1} HNO_3) for all cations were between 81 and 97% (n= 5). No elution efficiencies for oxyanions were measured because all the uptake efficiencies were <26%. This discrepancy is not surprising as most of the functional groups of the PAMPAA gel (negatively charged acrylic acid) are likely to chelate cations preferentially (see Section 3.3 in the text).

2. Assessment of Metsorb acid wash for oxyanion measurements

Metsorb binding layers deployed in seawater must be placed in deionised water prior to elution with NaOH [2, 3]. Rinsing with water removes salts (Ca and Mg) associated with the binding layer and prevents the formation of hydroxides and/or carbonates that can interfere with elution. For Al measurements, it has been reported that rinsing the Metsorb binding layers in diluted HNO_3 prior to washing with water increases the elution efficiencies [1]. However, although Al and oxyanions are accumulated simultaneously on the Metsorb binding gel, no study has so far investigated the effect of acid wash procedure on DGT-Metsorb measurements of oxyanions. Figure S1 illustrates the results of a comparison of Al, V, As and Sb concentrations determined using DGT-Metsorb at the study sampling sites, where the binding layers were analysed either with or without the acid wash procedure prior to elution with NaOH. The concentration of Al measured without the acid wash was

significantly ($p < 0.05$) underestimated by 58% and 50% at Runaway Bay Marina and The Spit, respectively; whilst no significant differences ($p > 0.05$) were observed for V, As and Sb concentrations at either site between acid washed and unwashed Metsorb binding layers. It is therefore recommended that the acid pre-wash be used routinely for DGT-Metsorb analyses, which obviates the need to use separate sets of DGT-Metsorb for oxyanion and Al measurements, and enables these to be measured simultaneously using a single set of DGT-Metsorb samplers.

Tables

Table S1: Characteristics of the different types of DGT diffusive and binding layers used in the study.

DGT layers		Monomer type	Cross-linker type	Pore size (nm)	Target analyte	Mechanism of binding
Diffusive layer	**open diffusive layer (ODL)**	acrylamide	agarose derivative	> 5	_	_
	restricted diffusive layer (RDL)	acrylamide	bis-acrylamide	< 1	_	_
Binding layer	**Chelex-100 resin**	incorporated into polyacrylamide	agarose derivative	_	cationic metals	complexation with free ions
	polyacrylamide-polyacrylic acid copolymer (PAMPAA)	derived from polyacrylamide	agarose derivative	_	cationic metals	complexation with free ions
	Metsorb resin	incorporated into polyacrylamide	agarose derivative	_	oxyanionic metals	adsorption of free ions
	Chelex-Metsorb mixed binding layer (MBL)	incorporated into polyacrylamide	agarose derivative	_	cationic and oxyanionic metals	complexation and adsorption

Table S2. Uptake and elution efficiencies of trace metals for PAMPAA binding layer. Data are means ± the standard deviation of the mean (n = 5).

Metal	Uptake efficiency	Elution efficiency
Al	89.70 ± 2.19	96.42 ± 4.85
Mn	34.84 ± 3.09	97.65 ± 10.58
Co	36.59 ± 2.57	92.76 ± 7.18
Ni	38.05 ± 2.64	94.92 ± 9.29
Cu	75.51± 1.23	83.09 ± 3.87
Zn	38.40 ± 3.39	81.05 ± 10.99
Cd	55.84 ± 2.02	85.94 ± 4.60
Pb	94.99 ± 0.194	87.70 ± 5.18

Table S3: Mean concentrations of metals measured by DGT-MBL, DGT-Chelex, DGT-Metsorb and DGT-PAMPAA using open diffusive layer (ODL) and restricted diffusive layer (RDL) at Runaway Bay Marina.

Metal	DGT-ODL				DGT-RDL			
	MBL	Chelex	Metsorb	PAMPAA	MBL	Chelex	Metsorb	PAMPAA
Mn	10.943	8.608	-	-	11.543	8.447	-	-
Co	0.088	0.091	-	-	0.074	0.077	-	-
Ni	0.342	0.336	-	-	0.344	0.300	-	-
Cu	2.897	2.709	-	2.134	1.965	2.004	-	2.016
Zn	3.804	3.375	-	-	3.152	2.740	-	-
Cd	0.033	0.035	-	-	0.031	0.029	-	-
Pb	0.022	0.024	-	0.013	0.022	0.022	-	0.014
Al	7.522	0.493	6.133	3.807	5.880	-	4.491	3.414
V	1.486	-	1.424	-	1.665	-	1.391	-
As	0.805	-	0.865	-	0.705	-	0.894	-
Sb	0.096	-	0.086	-	0.103	-	0.084	-

Table S4: Mean concentrations of metals measured by DGT-MBL, DGT-Chelex, DGT-Metsorb and DGT-PAMPAA using open diffusive layer (ODL) and restricted diffusive layer (RDL) at The Spit.

Metal	DGT-ODL				DGT-RDL			
	MBL	Chelex	Metsorb	PAMPAA	MBL	Chelex	Metsorb	PAMPAA
Mn	12.502	7.683	-	-	11.165	8.558	-	-
Co	0.083	0.071	-	-	0.067	0.061	-	-
Ni	0.209	0.195	-	-	0.189	0.160	-	-
Cu	3.133	3.344	-	2.528	2.261	2.513	-	2.300
Zn	2.502	2.174	-	-	2.062	1.902	-	-
Cd	0.024	0.026	-	-	0.021	0.022	-	-
Pb	0.020	0.019	-	0.013	0.019	0.019	-	0.014
Al	6.501	0.367	4.877	3.555	4.880	-	3.865	3.142
V	1.574	-	1.429	-	1.590	-	1.515	-
As	1.465	-	1.398	-	1.281	-	1.345	-
Sb	0.087	-	0.102	-	0.074	-	0.089	-

Figures

Figure S1. The effect of acid wash on DGT-Metsorb measurements. Solid columns represent concentrations measured using acid washed binding layers and hatched columns represent concentrations measured using unwashed binding layer. Data are mean values and error bars indicate the standard deviation of the mean. Columns with different letter labels indicate significantly different (<0.05) results for DGT measurements.

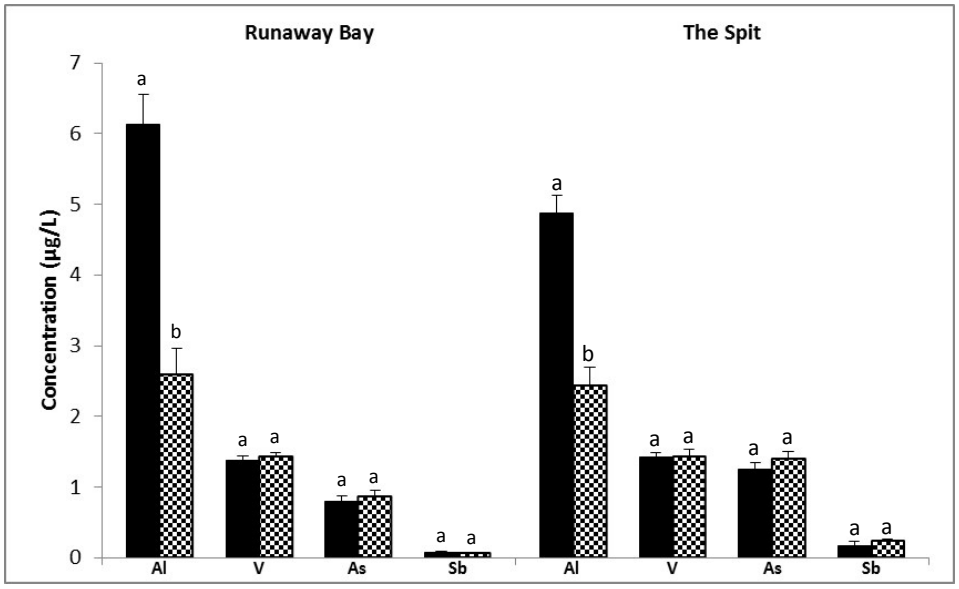


Figure S2. Plots of 1/M (ng^{-1}) versus diffusive layer thickness (Δg, cm) for DGT-MBL deployments at The Spit.

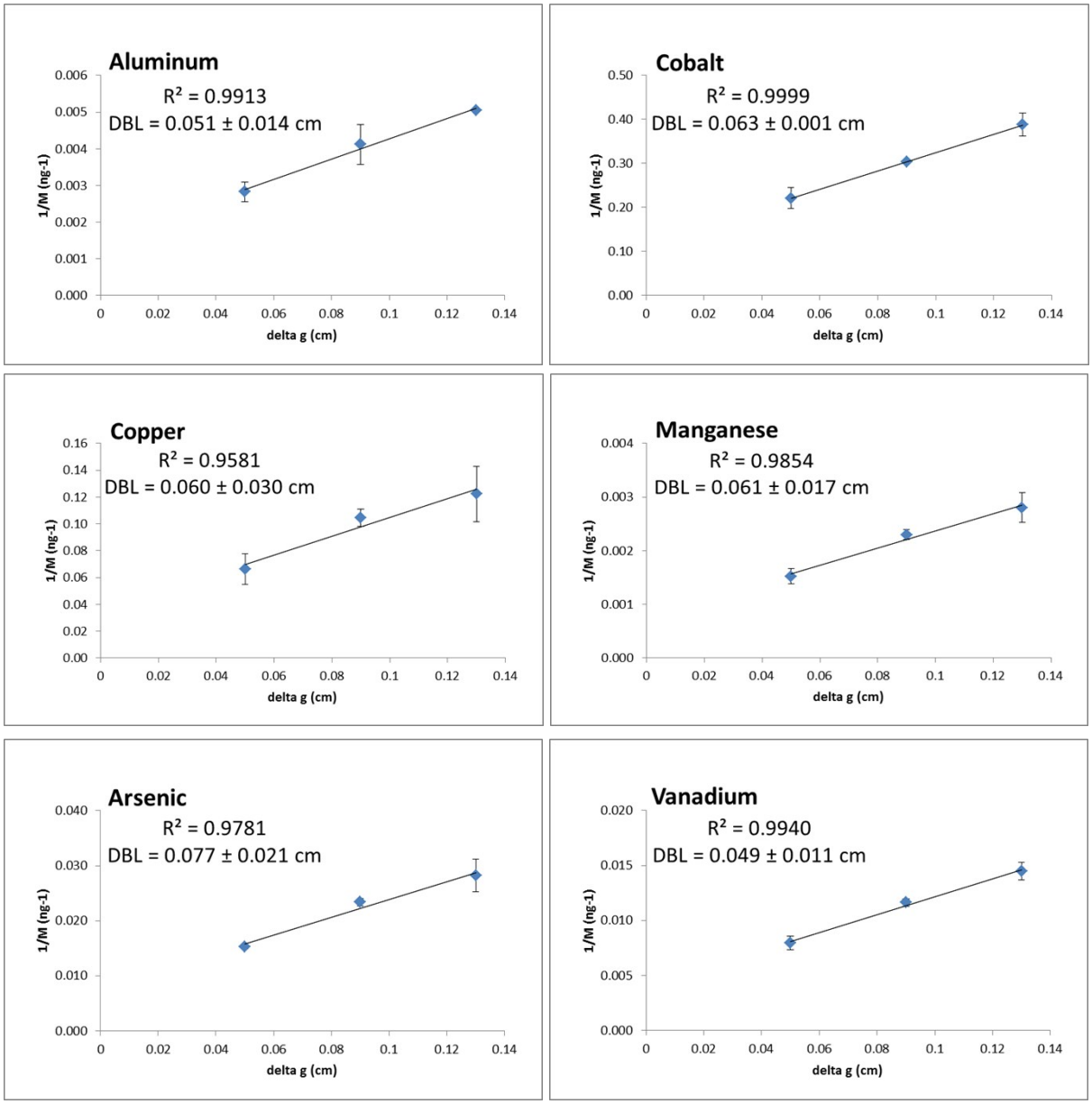
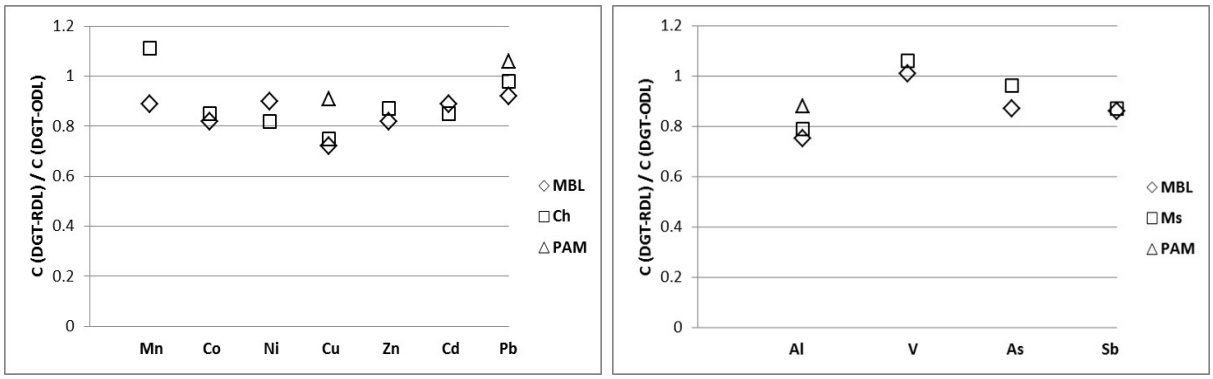


Figure S3. Ratios of DGT measurements for trace metals using different binding layers (MBL= mixed binding layer, Ch= Chelex, PAM = PAMPAA, Ms= Metsorb) with restricted (RDL) and open (ODL) diffusive layers at The Spit.



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3. W. W. Bennett, P. R. Teasdale, J. G. Panther, D. T. Welsh and D. F. Jolley, *Analytical Chemistry*, 2010, **82**, 7401-7407.