Supporting Information for:

Evaluation of the DGT technique for selective measurement of Aluminium and trace metal concentrations in an acid drainage-impacted coastal waterway

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Experimental section

Cleaning of Metsorb binding gel

Metsorb adsorbent was cleaned by soaking 1 g of powder in 50 mL of 1 mol L^{-1} HNO_3 (Baseline) and shaking for 24 h. Following centrifugation for 25 min at 4400 rpm (Eppendorf 5702), the supernatant was discarded and the pellet (adsorbent) was resuspended and re-centrifuged three times using 50 mL of Milli-Q water to remove excess acid. The adsorbent was then soaked in 50 mL of 1 mol L^{-1} NaOH for a further 24 h and was centrifuged as before. To neutralize the basic pH, the adsorbent was subsequently rinsed in 25 mL of Milli-Q water, and the pH of this solution was adjusted to 7.0 using concentrated HNO_3 (Baseline) and pH-indicator strips (MColorpHast™).

Results and discussion

DGT method detection limit (MDL) and diffusive boundary layer (DBL) measurements

Comparison of the detection limits for DGT-MBL with those of DGT-Chelex and DGT-Metsorb shows similar values for Cd, Co, Cu, Pb, As, Sb and V. However, DGT-MBL had higher detection limits for Mn and Ni compared to DGT-Chelex and for Mo compared to DGT-Metsorb. The higher MDL for Zn with Chelex, compared with MBL, suggests that there may be Zn associated with the Chelex-100 resin. Detection limits for all trace metals in this study were similar for DGT samplers employing ODL and RDL, and were well below the relevant ANZECC and ARMCANZ water quality trigger values for 95% protection.

Plots of 1/M (ng^{-1}) versus diffusive layer thickness (Δg, cm) showed relatively good linearity (R^2= 0.8865 - 0.9881) for Cu and As at sampling site 1 (pH 3.29) with an average DBL thickness of 0.160 ± 0.018 cm (Figure S1) calculated for both elements. Excellent linearity (R^2= 0.9430 - 0.9973) was observed for Al, Ni and As at sampling site 2 (pH 5.05) with an average DBL thickness of 0.156 ± 0.013 cm (Figure S2) calculated for these metals. The reciprocal plots also showed excellent linearity (R^2= 0.9701 - 0.9957) for Al, Mn, Co, Ni and As at sampling site 3 (pH 6.28) with the average calculated DBL thickness being 0.118 ± 0.019 cm (Figure S3). Good linearity (R^2= 0.9230 - 0.9840) was also observed for Al, Mn, Co, Ni and As at sampling site 4 (pH 7.81) with the average DBL thickness calculated to be 0.051 ± 0.009 cm (Figure S4). It is worth noting that DBL measurements based on As accumulation were effective at each site.

Table S1. DGT blank masses (ng) and method detection limits (MDL, μg L^{-1}) for the three different binding layers in two acidic drains (sampling sites 1 and 2). Detection limits were calculated using diffusion coefficient of analytes in either open (ODL) or restricted (RDL) diffusive layers from Shiva et al., 2015. Conditions: Δg= 0.09 cm; t= 72 h; A= 3.14 cm^2; T= 23 °C. Data are means for triplicate DGT samplers.

Metal	DGT-MBL			DGT-Chelex			DGT-Metsorb			ANZECC trigger values for fresh waters (μg L^{-1})
	blank	MDL ($_{ODL}$)	MDL ($_{RDL}$)	blank	MDL ($_{ODL}$)	MDL ($_{RDL}$)	blank	MDL ($_{ODL}$)	MDL ($_{RDL}$)	95% protection
Cd	0.035	0.004	0.005	0.078	0.002	0.002	_	_	_	0.2
Co	0.282	0.004	0.005	0.551	0.010	0.013	_	_	_	_
Cu	0.926	0.009	0.012	1.164	0.027	0.035	_	_	_	1.4
Mn	3.379	0.035	0.045	2.014	0.017	0.022	_	_	_	1700
Ni	7.345	0.072	0.101	2.727	0.022	0.031	_	_	_	11
Pb	1.595	0.002	0.003	0.180	0.003	0.004	_	_	_	3.4
Zn	123.5	0.721	0.972	102.8	1.450	1.954	_	_	_	8
Al	140.0	0.604	0.834	53.53	0.220	0.304	94.96	1.481	2.045	55 (pH >6.5) unknown (pH <6.5)
As	0.156	0.001	0.002	_	_	_	0.141	0.002	0.003	24 (As III) 13 (As V)
Mo	2.256	0.056	0.083	_	_	_	0.709	0.015	0.022	_
Sb	0.753	0.005	0.006	_	_	_	0.680	0.008	0.011	_
V	2.107	0.014	0.018	_	_	_	1.671	0.024	0.032	_

Table S2. DGT blank masses (ng) and method detection limits (MDL, µg L^{-1}) for the three different binding layers in Cudgen Lake (site 3). Detection limits were calculated using the diffusion coefficients of the analytes in either open (ODL) or restricted (RDL) diffusive layers from Shiva et al., 2015. Conditions: Δg= 0.09 cm; t= 72 h; A= 3.14 cm^2; T= 26 °C. Data are means for triplicate DGT samplers.

Metal	DGT-MBL			DGT-Chelex			DGT-Metsorb			ANZECC trigger values for fresh waters (µg L^{-1})
	blank	MDL ($_{ODL}$)	MDL ($_{RDL}$)	blank	MDL ($_{ODL}$)	MDL ($_{RDL}$)	blank	MDL ($_{ODL}$)	MDL ($_{RDL}$)	95% protection
Cd	0.035	0.003	0.004	0.078	0.002	0.002	_	_	_	0.2
Co	0.282	0.003	0.004	0.551	0.009	0.011	_	_	_	_
Cu	0.926	0.008	0.010	1.164	0.022	0.029	_	_	_	1.4
Mn	3.379	0.030	0.041	2.014	0.015	0.020	_	_	_	1700
Ni	7.345	0.062	0.081	2.727	0.019	0.025	_	_	_	11
Pb	1.595	0.002	0.003	0.180	0.003	0.004	_	_	_	3.4
Zn	123.5	0.619	0.819	102.8	1.243	1.645	_	_	_	8
Al	140.0	0.410	0.595	53.53	0.150	0.217	94.96	1.006	1.460	55 (pH >6.5) unknown (pH <6.5)
As	0.156	0.001	0.002	_	_	_	0.141	0.002	0.003	24 (As III) 13 (As V)
Mo	2.256	0.056	0.085	_	_	_	0.709	0.015	0.023	_
Sb	0.753	0.005	0.007	_	_	_	0.680	0.008	0.011	_
V	2.107	0.014	0.019	_	_	_	1.671	0.024	0.031	_

Table S3. DGT blank masses (ng) and method detection limits (MDL, μg L^{-1}) for the three different binding layers in Cudgen Creek estuary (sampling site 4). Detection limits were calculated using the diffusion coefficients of the analytes in either open (ODL) or restricted (RDL) diffusive layers from Shiva et al., 2015. Conditions: Δg= 0.09 cm; t= 72 h; A= 3.14 cm^2; T= 27 °C. Data are means for triplicate DGT samplers.

Metal	DGT-MBL			DGT-Chelex			DGT-Metsorb			ANZECC trigger values for marine waters (μg L^{-1})
	blank	MDL ($_{ODL}$)	MDL ($_{RDL}$)	blank	MDL ($_{ODL}$)	MDL ($_{RDL}$)	blank	MDL ($_{ODL}$)	MDL ($_{RDL}$)	95% protection
Cd	0.035	0.003	0.003	0.078	0.002	0.002	_	_	_	5.5
Co	0.282	0.003	0.004	0.551	0.009	0.012	_	_	_	1
Cu	0.926	0.008	0.011	1.164	0.025	0.032	_	_	_	1.3
Mn	3.379	0.033	0.044	2.014	0.017	0.022	_	_	_	_
Ni	7.345	0.068	0.088	2.727	0.021	0.027	_	_	_	70
Pb	1.595	0.002	0.003	0.180	0.003	0.004	_	_	_	4.4
Zn	123.5	0.678	0.806	102.8	1.362	1.621	_	_	_	15
Al	140.0	0.449	0.653	53.53	0.164	0.238	94.96	1.102	1.601	_
As	0.156	0.001	0.002	_	_	_	0.141	0.002	0.003	_
Mo	2.256	0.062	0.094	_	_	_	0.709	0.017	0.025	_
Sb	0.753	0.005	0.007	_	_	_	0.680	0.009	0.012	_
V	2.107	0.015	0.020	_	_	_	1.671	0.026	0.035	100

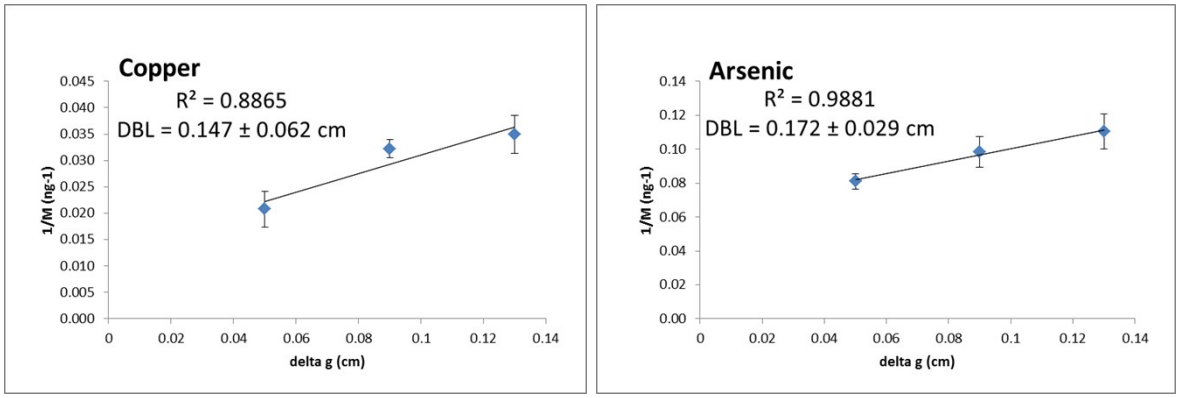

Figure S1: *Plots of 1/M (ng^{-1}) versus diffusive layer thickness (Δg, cm) for DGT-MBL deployments at sampling site 1 (pH 3.29). Data points are mean values (n=3) and error bars indicate the standard deviation of the mean.*

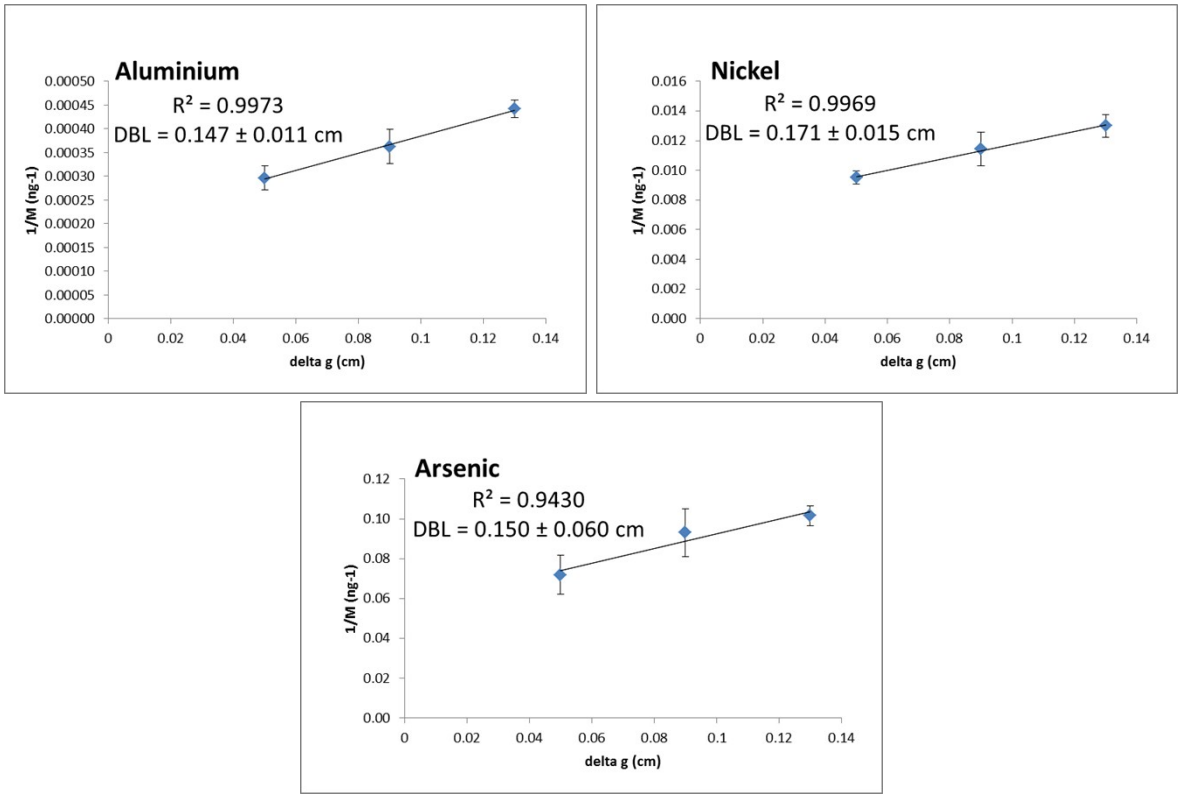

Figure S2: *Plots of 1/M (ng^{-1}) versus diffusive layer thickness (Δg, cm) for DGT-MBL deployments at sampling site 2 (pH 5.05). Data points are mean values (n=3) and error bars indicate the standard deviation of the mean.*

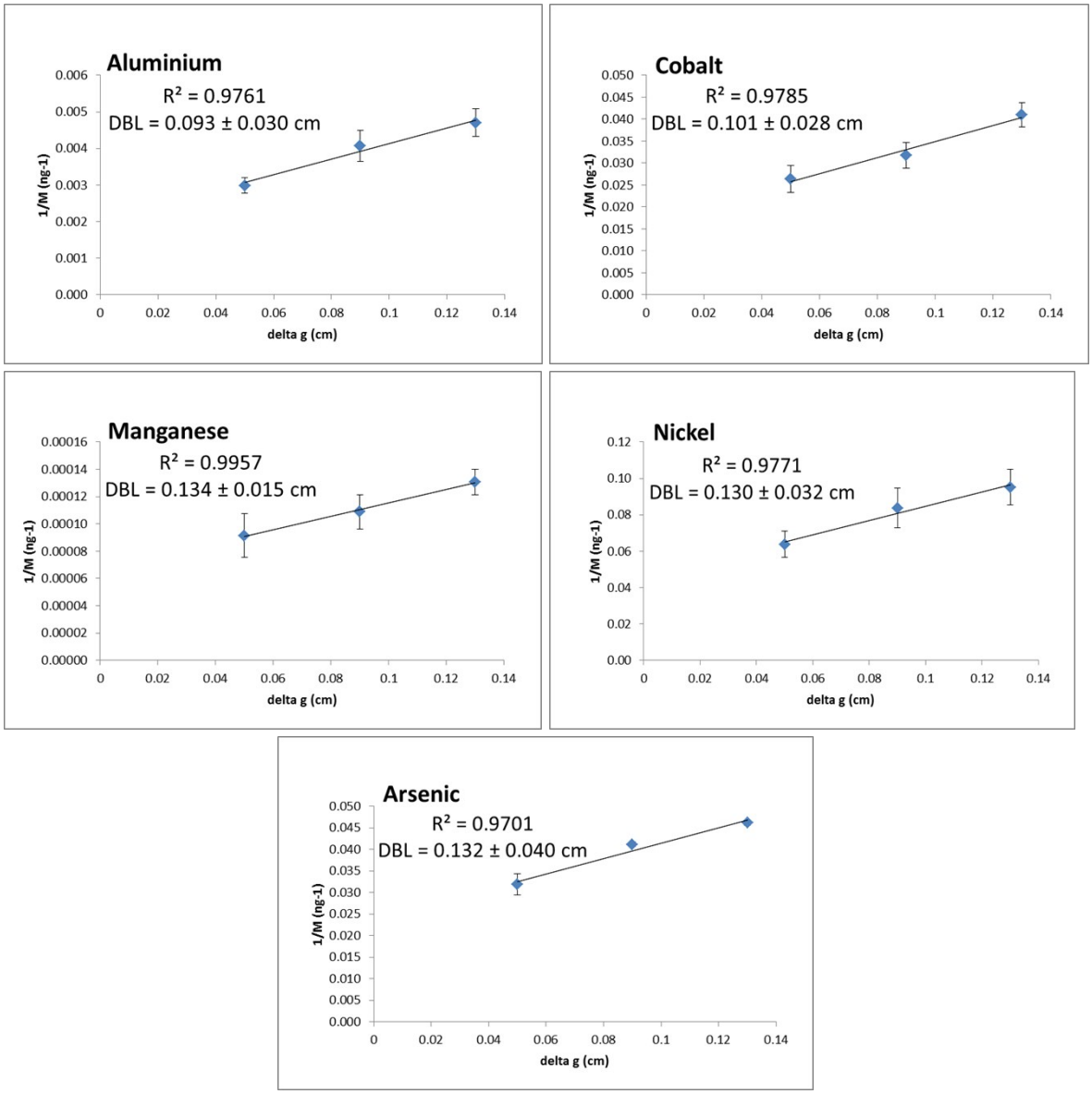

Figure S3. *Plots of 1/M (ng^{-1}) versus diffusive layer thickness (Δg, cm) for DGT-MBL deployments at sampling site 3 (pH 6.28). Data points are mean values (n=3) and error bars indicate the standard deviation of the mean.*

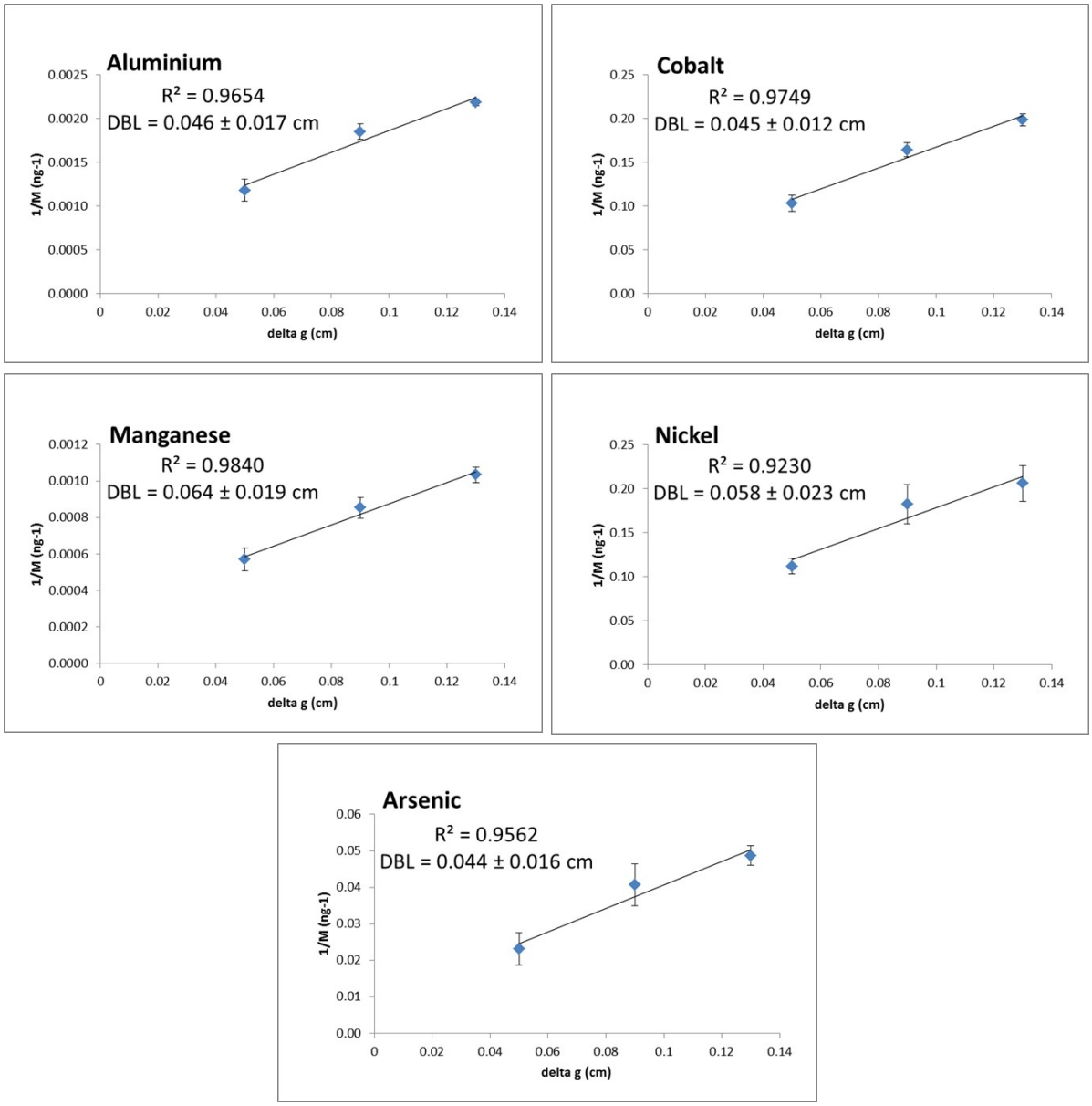

Figure S4. *Plots of 1/M (ng^{-1}) versus diffusive layer thickness (Δg, cm) for DGT-MBL deployments at sampling site 4 (pH 7.81). Data points are mean values (n=3) and error bars indicate the standard deviation of the mean.*

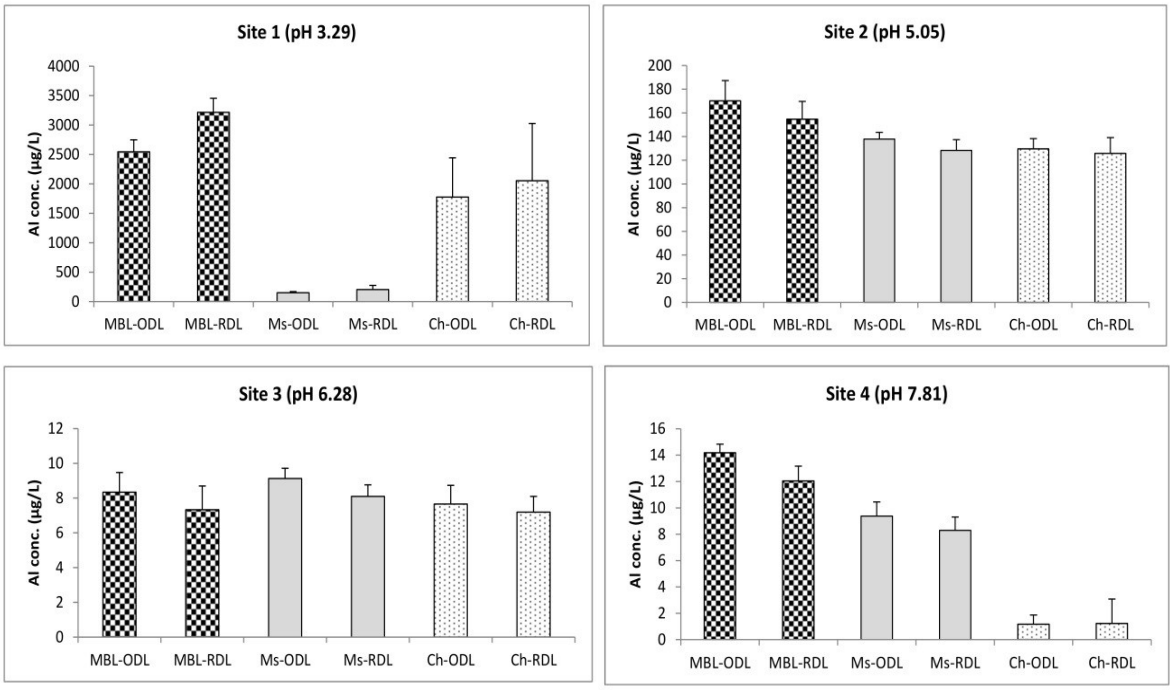

Figure S5. *Labile Al concentrations measured by DGT-MBL, DGT-Metsorb (Ms) and DGT-Chelex (Ch) using open (ODL) and restricted (RDL) diffusive layers in four natural waters with different pH.*

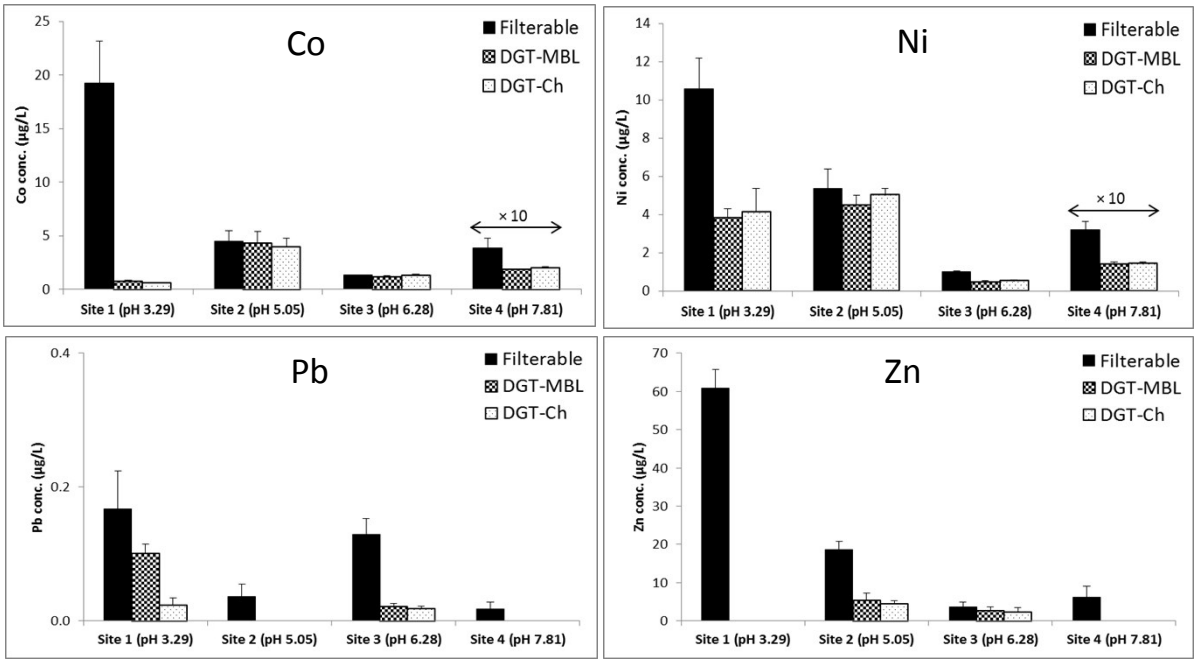

Figure S6. *Comparison of DGT-MBL, DGT-Chelex (Ch) and filterable concentrations for Co, Ni, Pb and Zn in four natural waters with different pH. DGT-measured concentrations are only shown when values were above the determined method detection limits.*

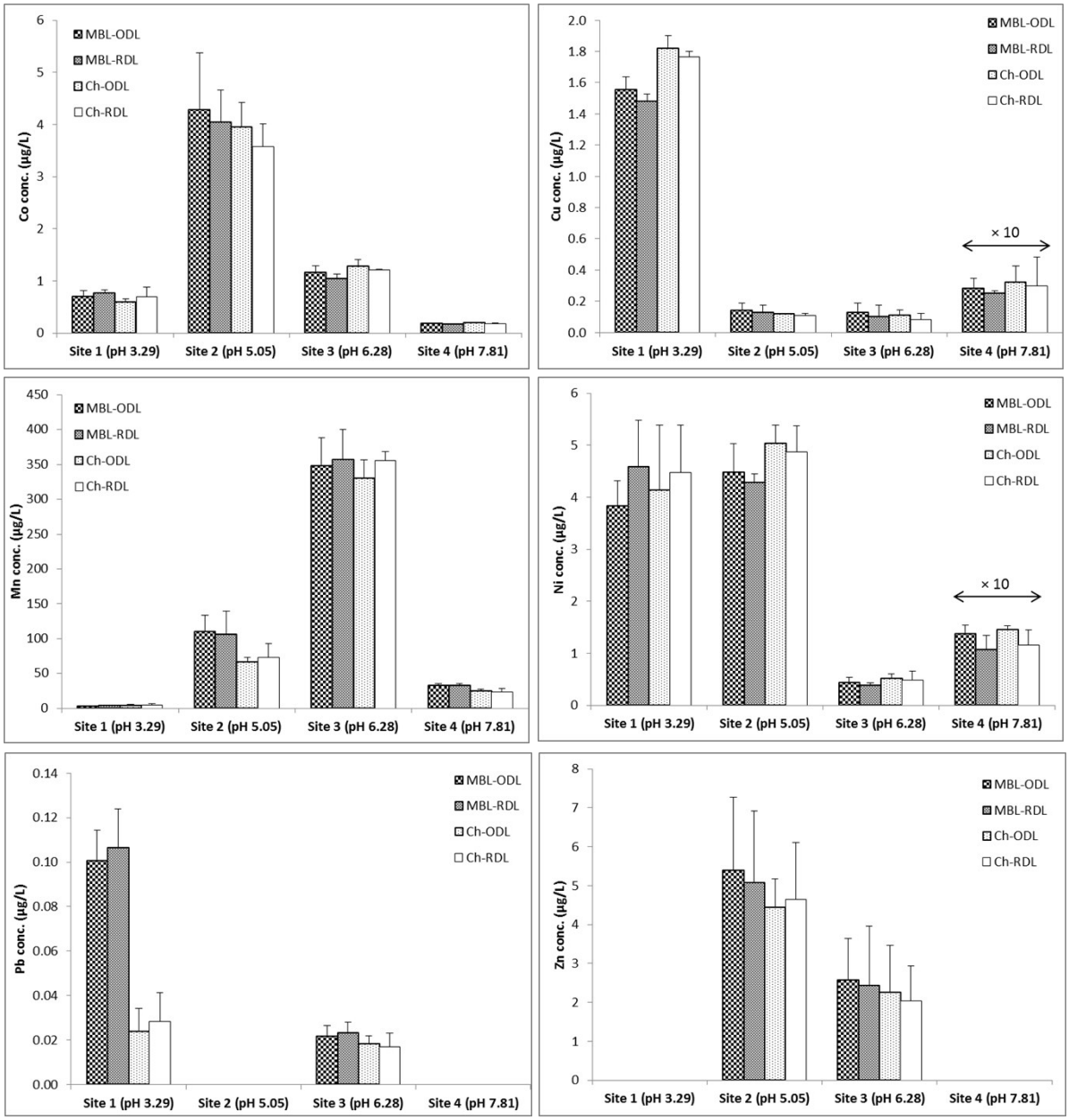

Figure S7: *Labile concentrations of trace metals measured by DGT-MBL and DGT-Chelex (Ch) using restricted (RDL) and open (ODL) diffusive layers in four natural waters with different pH. Concentrations are only shown when values were above the determined method detection limits.*

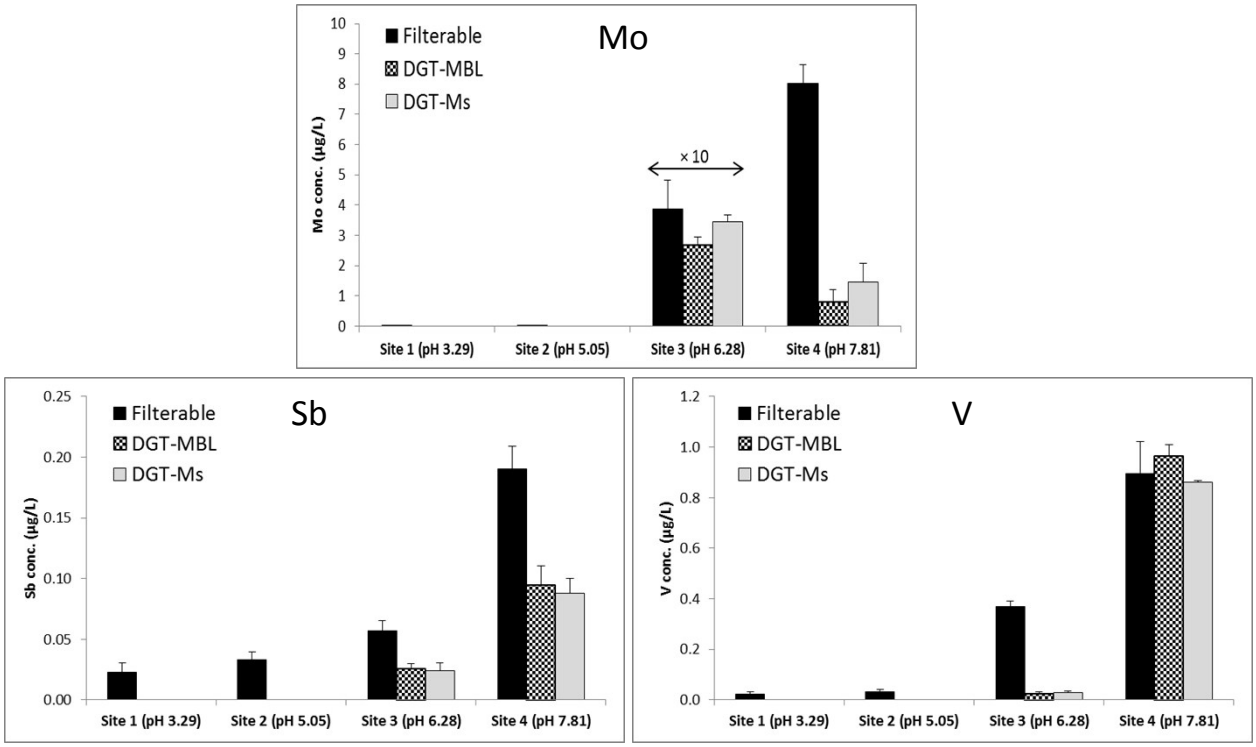

Figure S8: *Comparison of DGT-MBL, DGT-Metsorb (Ms) and filterable concentrations for Mo, Sb and V in four natural waters with different pH. DGT-measured concentrations are only shown when values were above the determined method detection limits.*

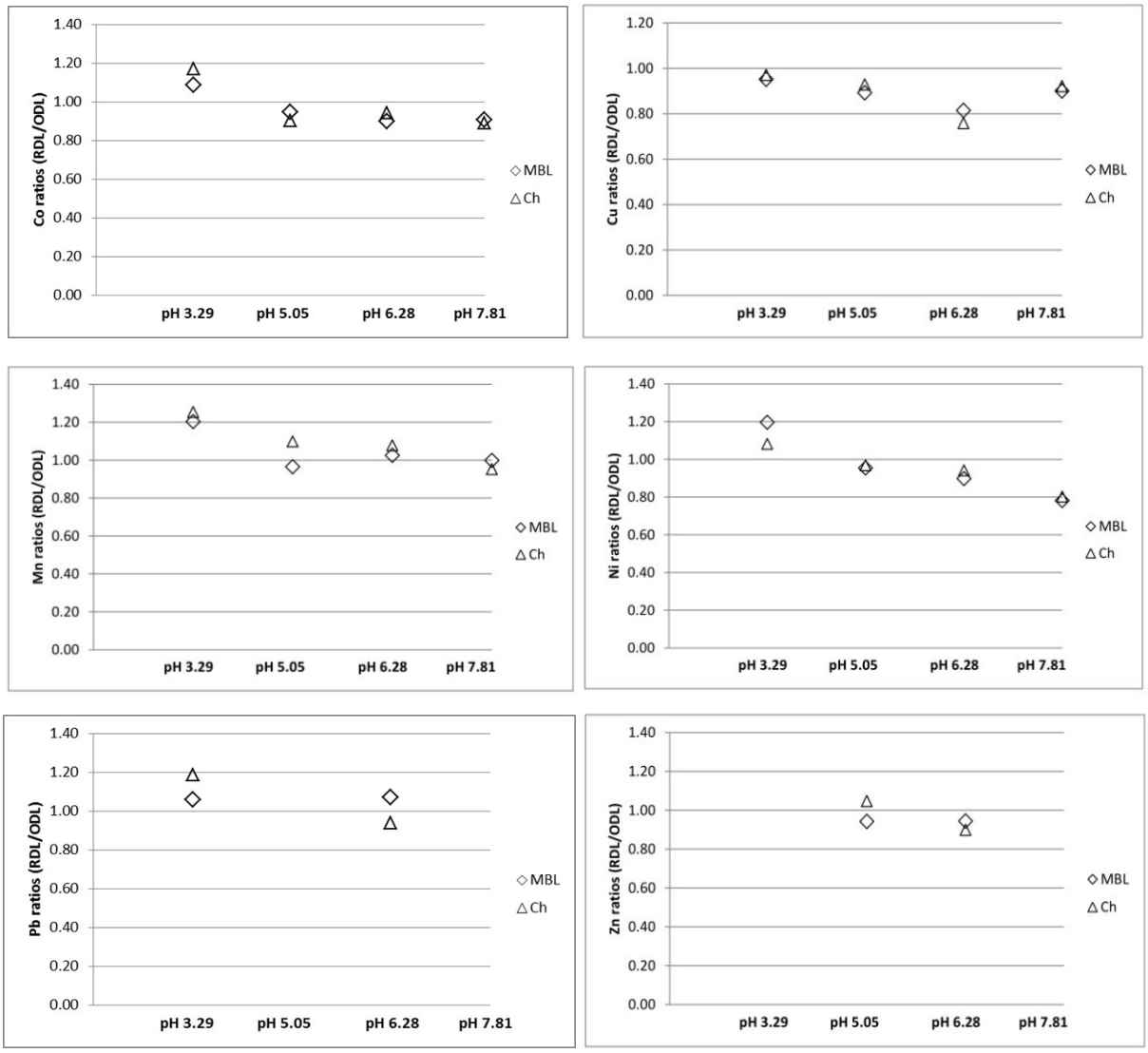

Figure S9: *Ratios of restricted (RDL) to open (ODL) diffusive layer measurements of trace metals by DGT-MBL and DGT-Chelex (Ch) in four natural waters with different pH. Site 1: pH 3.29; Site 2: pH 5.05; Site 3: pH 6.28; Site 4: pH 7.81.*

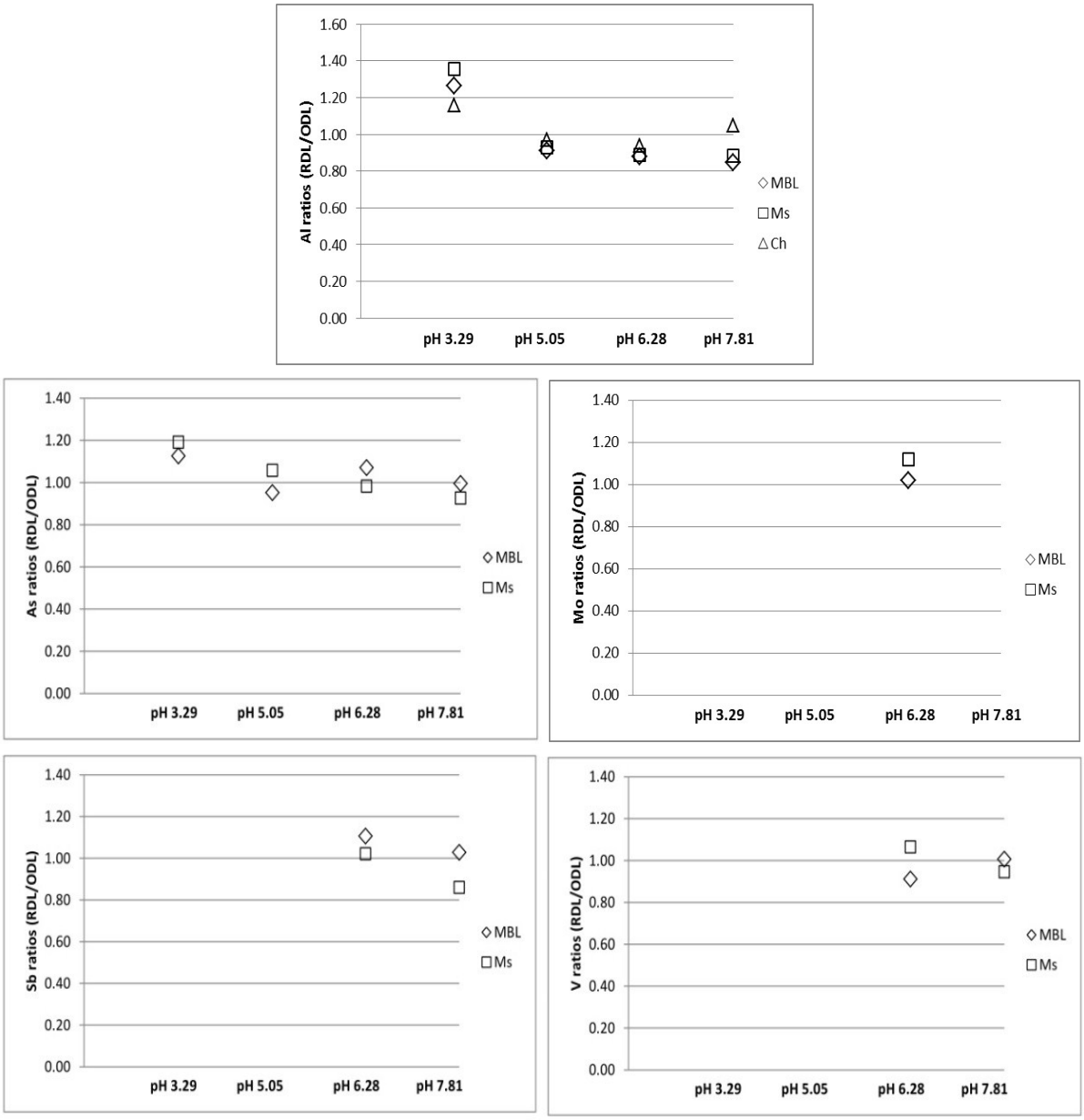

Figure S10: *Ratios of restricted (RDL) to open (ODL) diffusive layer measurements of Al and oxyanions by DGT-MBL, DGT-Metsorb (Ms) and DGT-Chelex (Ch) in four natural waters with different pH. Site 1: pH 3.29; Site 2: pH 5.05; Site 3: pH 6.28; Site 4: pH 7.81.*