

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

Amir Houshang Shiva,¹ Peter R. Teasdale,^{2,3} David T. Welsh¹ and William W. Bennett^{1}*

¹ Environmental Futures Research Institute, Griffith University, Gold Coast campus, QLD 4215, Australia

² Natural and Built Environments Research Centre, School of Natural and Built Environments, University of South Australia, SA 5095, Australia

³ Future Industries Institute, University of South Australia, SA 5095, Australia

*Corresponding Author: w.bennett@griffith.edu.au

Ph: +61 7555 28587

Fax: +61 7555 28067

Abstract

The performance of DGT-Chelex, DGT-Metsorb and DGT-MBL (Chelex-Metsorb mixed binding layer) with open and restricted diffusive layers for trace metal (Al, Cd, Co, Cu, Mn, Ni, Pb, Zn) and oxyanion (As, Mo, Sb, V) measurements, was evaluated in four natural waters with different pH (range 3.29 - 7.81). In moderately acidic (pH \approx 5) and circumneutral (pH \approx 6.3) waters, all three binding layers measured relatively similar concentrations of Al, while in more alkaline waters (pH \approx 8) DGT-MBL measured higher concentrations than the other two binding layers. The measurements of DGT-Chelex and DGT-MBL for Co, Cu, Ni, Pb and Zn, and DGT-Metsorb and DGT-MBL for As, Sb and V were within 82-119% and not statistically different ($p > 0.05$) over the pH range 5 - 8. Mn measurements by DGT-Chelex and DGT-MBL were quite similar (95%) at pH 6.3, while DGT-MBL measured higher concentrations than DGT-Chelex at other pHs. The ratios of measured concentrations with different diffusive layers ($C_{\text{restricted}}/C_{\text{open}}$) were between 0.78 and 1.12 for all binding layers and no statistical differences ($p > 0.05$) were observed, except for Al at pH 7.81 and Cu at pH 6.28. DGT-MBL was comparable to DGT-Chelex for the measurement of most trace metals, and to DGT-Metsorb for the measurement of most oxyanions, over the pH range 5.05 - 7.81. Overall, DGT-MBL is superior to the other tested binding layers because it can simultaneously measure cations and anions, and accurately measure dissolved Al, across the greatest range of environmental conditions.

Key words: Chelex, Metsorb, DGT, open diffusive layer, restricted diffusive layer, metal speciation

1. Introduction

Trace metals in natural waters exist in a wide range of soluble forms including free cations and oxyanions, potentially of more than one oxidation state. Cationic metals also form complexes with dissolved inorganic and organic ligands, which have widely varying lability.¹ Several oxyanions form inorganic polymers and some metals also form organometallic species.² These diverse soluble species can also associate with suspended colloidal and particulate matter.^{3, 4} The relative proportion of each metal species depends on the physicochemical parameters of the water (e.g. pH, alkalinity, ionic strength, salinity, temperature) as well as the analyte concentration, the nature of the ligands present and the propensity of the trace elements and ligands to form stable complexes.⁵ Among these metal species, free ions (including oxyanions) and labile inorganic complexes are assumed to be the most bioavailable forms⁶ that can result in toxic effects.⁷ For instance, dissolved aluminium is known to be toxic to aquatic organisms^{8, 9}, but exhibits complex speciation with cationic forms present at low pH, neutral inorganic complexes at neutral pH and oxyanions at basic pH.¹⁰ Additionally, Al is known to form complexes with natural organic matter, is present in the form of aluminosilicate soil colloids and can associate with various other particles in natural waters.¹⁰

Many chemical and physical methods have been developed to selectively measure trace metal species in natural waters.¹¹⁻¹⁴ The diffusive gradients in thin films (DGT) is a passive sampling technique^{15, 16} that has been widely used in a range of natural and urban waters.^{7, 17-22} DGT measurements are based on the diffusion of trace metal species through a layer of known thickness, followed by accumulation of reactive metal species (free cationic or oxyanionic metals, inorganic complexes and labile organic complexes) on a selective binding material.^{15, 16, 23, 24} The most commonly used diffusive layer is a polyacrylamide hydrogel with a proprietary agarose-based cross-linker, covered with a 0.45 μm pore size filter membrane. The membrane excludes particulate matter while this open diffusive layer (ODL) with a pore size $>5 \text{ nm}$ ¹⁶ is considered to allow diffusion of

free ions and inorganic complexes at about 70-90% of their diffusion coefficients in water.^{25, 26} Diffusion of labile organic complexes will be further retarded based on their size, while very large complexes may be effectively excluded.^{16, 27} A restricted diffusive layer (RDL) composed of a bisacrylamide cross-linked polyacrylamide hydrogel with a smaller pore size (<1 nm) can also be used, which results in free ions being further retarded (40-70% of diffusion coefficients in water)²⁵ and organic complexes being either greatly retarded or excluded.^{28, 29} Therefore, the selectivity of DGT measurements for trace metals varies with the choice of diffusive layer, although the effectiveness of this approach in natural waters has only been evaluated on a preliminary basis.^{17, 28, 30, 31}

DGT binding layers introduce further selectivity through use of a range of materials (usually cast within an open polyacrylamide hydrogel) with varying binding strengths for trace metal species.²³ This binding strength may also effectively vary with changes in solution conditions, such as pH and ionic strength.²⁴ In the absence of competition, free cationic and oxyanionic metals, and labile inorganic complexes should be accumulated quantitatively on the binding layer. Trace metals from organic complexes that are labile over the time it takes to pass through the diffusive layer will also be accumulated quantitatively.²³ Chelex-100 is the most commonly used binding material for measurement of cationic species, having been evaluated in waters with a range of pH.^{16, 24, 32-35} DGT-Chelex has also been used successfully for estimation of Al bioavailability to fish in natural freshwaters at different pH (between 4.8 and 5.9).⁸ Metsorb (a commercially available titanium dioxide-based adsorbent) has been used for measurement of oxyanions^{21, 36, 37}, including anionic Al³⁸, in acidic to slightly basic solutions (4-8.5). A mixed DGT binding layer comprising both Chelex-100 and Metsorb adsorbents has been developed for simultaneous measurement of trace metals and oxyanions over a wide pH (5.03-8.05) and ionic strength (0.001-0.7 mol L⁻¹) range.³⁹ This mixed binding layer (MBL) was further developed for measurement of Al in solutions with acidic (4.01) and basic (8.30) pH.²⁵ The performance of DGT-MBL has also been evaluated in synthetic

freshwater (pH 7.48; conductivity $232 \mu\text{S cm}^{-1}$)³⁹, synthetic seawater (pH 8.02, salinity 32.4)³⁹ and natural seawater (pH 8.02-8.23, salinity 30.70-37.33).³⁰

The aim of this study was to compare selective DGT measurements of cationic metals (Al in acidic waters, Cd, Co, Cu, Mn, Ni, Pb, Zn) and oxyanions (Al in alkaline waters, As, Mo, Sb, V) made with several binding layers (Chelex, Metsorb and the Chelex-Metsorb mixed binding layer) and with both open and restricted diffusive layers in an aquatic system with a wide range of pH and ionic strength conditions. An acid sulphate soil drainage-affected stream, wetland and estuarine system in northern NSW, Australia, afforded a good opportunity to do this and especially focus on aluminium, which is known to leach from acidified soils.¹⁰ Given that many coastal waters in Australia and globally are impacted by acid soils or other sources of acidity^{40, 41}, this was an important opportunity to demonstrate the capability of selective DGT measurements in such systems. This study is also the first application of DGT-MBL (Chelex-Metsorb) in natural freshwaters and provides further information about the capability of this new DGT binding layer for trace metal measurements in aquatic systems.

2. Experimental section

2.1. Description of field sites and study design

Four sites were used for this study (Figure 1) located in the Cudgen Lake catchment in northern New South Wales, Australia, which is subject to acid sulphate soil drainage problems⁴². These sites were selected primarily to ensure a range of pH values but they also represent different waterways. Sites 1 and 2 were located in a modified freshwater stream (Clothiers Creek) with low pH (average 3.29 ± 0.15 and 5.05 ± 0.13 , respectively), flowing through agricultural land and draining into Cudgen Lake. Cudgen Lake (site 3) is a perched tidal lagoon with slightly acidic pH (average 6.28 ± 0.02)

and site 4 was located in the lower Cudgen Creek estuary with slightly basic pH (average 7.81 ± 0.12).

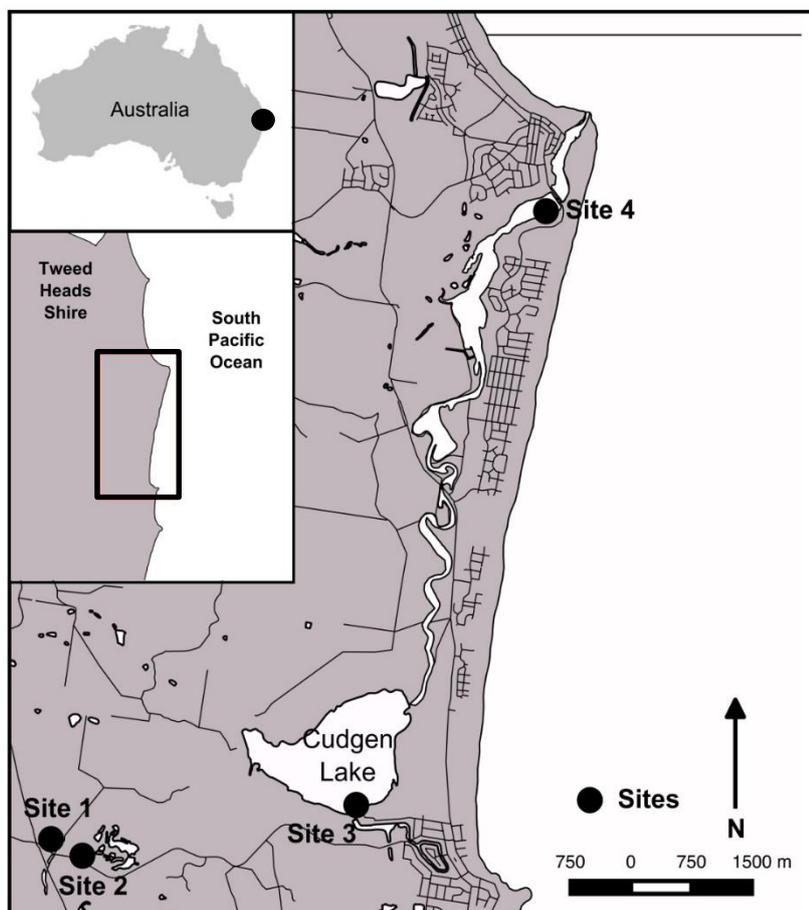


Figure 1. Map of the Cudgen Lake Catchment (New South Wales, Australia) indicating the locations of the four sampling sites.

The field study was conducted over three days, from 16th to 19th March 2015. Water column pH, temperature, dissolved oxygen and conductivity/salinity were monitored daily using a multi-parameter probe (YSI, Professional Plus, USA). Filtered grab water samples (0.45 μm , Millex^(R)-HA, Millipore) were collected daily and immediately acidified (2% v/v with HNO_3) for metal analysis. Details of water column physicochemical parameters at each sampling site are provided in Table 1.

Table 1. Water column physicochemical characteristics and filterable concentrations ($\mu\text{g L}^{-1}$) of trace elements at the four study sites. Data are mean values \pm SD of the daily measurements ($n=3$).

SPC = specific conductance.

<i>Parameter</i>	<i>Site 1</i>	<i>Site 2</i>	<i>Site 3</i>	<i>Site 4</i>
pH	3.29 \pm 0.15	5.05 \pm 0.13	6.28 \pm 0.02	7.81 \pm 0.12
temperature (°C)	23.1 \pm 0.5	23.1 \pm 0.4	25.9 \pm 1.0	26.7 \pm 0.7
SPC ($\mu\text{S cm}^{-1}$)	510 \pm 83	241 \pm 10	824 \pm 80	–
Salinity	–	–	–	27.8 \pm 2.1
dissolved oxygen (% saturation)	32.6 \pm 1.8	17.1 \pm 3.6	70.3 \pm 3.3	80.8 \pm 5.6
Al	5589 \pm 1343	254 \pm 52	113 \pm 7	21.9 \pm 1.4
Cd	0.054 \pm 0.012	< 0.004	< 0.004	0.014 \pm 0.006
Co	19.2 \pm 3.8	4.47 \pm 0.97	1.30 \pm 0.04	0.38 \pm 0.09
Cu	1.60 \pm 0.30	0.27 \pm 0.09	0.36 \pm 0.03	0.21 \pm 0.01
Mn	930 \pm 157	488 \pm 97	376 \pm 9	40.1 \pm 11.1
Ni	10.5 \pm 1.6	5.35 \pm 1.02	1.01 \pm 0.04	0.32 \pm 0.04
Pb	0.16 \pm 0.05	0.036 \pm 0.059	0.13 \pm 0.02	0.015 \pm 0.017
Zn	60.9 \pm 13.7	18.6 \pm 2.0	3.57 \pm 1.40	2.28 \pm 2.91
As	0.62 \pm 0.05	0.69 \pm 0.04	1.83 \pm 0.15	0.91 \pm 0.11
Mo	0.013 \pm 0.005	0.008 \pm 0.004	0.33 \pm 0.09	8.01 \pm 0.64
Sb	0.023 \pm 0.008	0.033 \pm 0.007	0.057 \pm 0.008	0.19 \pm 0.02
V	0.021 \pm 0.011	0.032 \pm 0.008	0.37 \pm 0.02	0.89 \pm 0.12

2.2. General procedures

All equipment including glassware and plasticware were soaked in 10% nitric acid (AR grade, Merck) for at least 24 hours and rinsed with deionised water (Milli-Q Element, Millipore, 18.2 M Ω

cm⁻¹) prior to use. Deionised water was also used to prepare all eluent and reagent solutions. All reagents were AR grade or higher. Preparation and analysis of DGT samplers was done in an ISO class 5 (ISO 14644-1) laminar flow hood within an ISO class 6 clean room, wearing powder free latex gloves (Microtouch Dermaclean, Ansell). Gel casting was performed in a fume hood in a general lab as it involved the use of hazardous chemicals.

2.3. DGT sampler preparation, deployment and elution

2.3.1. Gel preparation

ODL and RDL were prepared according to Shiva *et al.*²⁵, each with a nominal thickness of 0.08 cm. To verify the thickness of the diffusive layers, hydrated ODL and RDL discs (each in triplicate) were selected randomly, a filter membrane placed on one face (as in the DGT application) and the thickness (Δg) measured using digital vernier calipers (Kincrome, 150 mm).⁴³

Chelex binding layers were prepared according to Zhang and Davison¹⁶ using Chelex-100 resin (Sodium form, 200-400 mesh, Bio-Rad). Metsorb binding layers were prepared according to Bennett *et al.*³⁶ using Metsorb Heavy Metal Removal Powder (Graver Technologies, USA). The Metsorb adsorbent was cleaned prior to use, as described in the supporting information (SI), to lower the blank values. The mixed binding layer (MBL) was prepared according to Panther *et al.*³⁹ Gels were rinsed in deionised water for 24 h (with several changes of water) and hydrated binding layers (0.04 cm thick) were stored in deionised water at <4 °C until use.

2.3.2. DGT assembly and elution

DGT samplers were purchased from DGT Research Ltd. (Lancaster, UK) and were assembled as described previously³⁰ using a 0.45 μ m cellulose nitrate filter membrane of thickness 0.01 cm (Millipore). Triplicate DGT-MBL, DGT-Chelex and DGT-Metsorb equipped with both ODL and

RDL were deployed for 72 h (exact time recorded) at each study site. To determine the thickness of the diffusive boundary layer (DBL) at each field site over the deployment period, two additional sets of triplicate DGT-MBL with different thicknesses of ODL (0.04 cm and 0.12 cm) were deployed alongside the standard diffusive layer thickness (0.08 cm).^{44, 45} The calculated DBLs were also applied to DGT-Chelex and DGT-Metsorb measurements.

Following retrieval of the DGT samplers and transport back to the laboratory, the binding layers were removed for elution. Prior to elution, all Metsorb and MBL gels deployed in saline waters (site 4) were rinsed in 5 mL of deionised water for 1 h to dilute the major ions present.⁴⁶ Metsorb binding layers were also immersed in 50 mL of 0.0001 mol L⁻¹ HNO₃ for 1 h to remove adsorbed ions that may interfere with the elution step. This process has been reported to increase Al elution efficiencies³⁸ without interfering with determination of other oxyanions accumulated on the binding gel.³⁰ Chelex and Metsorb binding layers were eluted for 24 h in 1 mL of 1 mol L⁻¹ HNO₃ and 1 mL of 1 mol L⁻¹ NaOH²¹, respectively. The MBL gels were eluted in 1 mL of 1 mol L⁻¹ HNO₃, followed by 1 mL of 1 mol L⁻¹ NaOH, each for 24 h and the eluents were pooled³⁹; prior to elution in NaOH the binding layers were rinsed with deionised water to remove excess acid. For Sb measurements, Metsorb and MBL gels were immersed in 1 mL of 1 mol L⁻¹ NaOH / 1 mol L⁻¹ H₂O₂ for a further 24 h, following initial elution in NaOH and the eluents were pooled.^{21, 39} Chelex, Metsorb and MBL eluents were diluted 10-fold with 2% HNO₃ (Baseline) prior to analysis. Filtered grab samples were analysed without dilution. Due to high concentrations of Al and Mn at sampling site 1, a further dilution (20-fold) was required before analysis.

2.4. Sample analysis and DGT calculations

Elemental analyses were carried out using an inductively coupled plasma-mass spectrometer (ICP-MS, Agilent Technologies, 7900 series) equipped with a collision reaction cell, operated in helium

collision mode. All analytical standards for ICP-MS analysis were prepared in 2% (v/v) ultra-pure HNO₃ (Baseline, Seastar) using a multi-element standard (High Purity Standards). Every 15-20 samples, a 10 µg L⁻¹ quality control standard solution (High Purity Standards) was analysed. Sc, Y, In and Tb were added online as internal standards. In addition, a seawater CRM (CASS-5, National Research Council, Canada) and a freshwater CRM (SLRS-5, National Research Council, Canada) were analyzed as appropriate. All recoveries were in the range of 93-98%.

DGT-labile analyte concentrations (C_{DGT} , µg L⁻¹) were calculated as described previously.¹⁶ The elution efficiencies used in this study (except for Al) were those reported for MBL, Chelex and Metsorb by Panther *et al.*³⁹. For Al measurements by DGT-MBL, an elution of 0.845 (average of efficiencies measured for Chelex and Metsorb by Panther *et al.*³⁸) was used. The diffusion coefficients of all elements in ODL and RDL were obtained from Shiva *et al.*²⁵ using the values at acidic pH (≈ 4) for sites 1 and 2 and the values at neutral pH (≈ 7) for sites 3 and 4. All D_{gel} values were corrected to *in-situ* temperatures using the Stokes-Einstein equation¹⁶ and a value of $0.9 \times D_{gel}$ was used for DGT calculations at site 4 as the medium was seawater.²³ The DBL thickness was calculated as described by Warnken *et al.*⁴⁴ and was included in all C_{DGT} calculations. A value of 3.8 cm² (instead of 3.14 cm²) was used as the effective sampling area in the DGT equation, as previously described.⁴⁴

To monitor for any contamination during preparation, DGT blanks were prepared in the same way as deployed DGT samplers and subjected to all transport and handling procedures (n=3 per sampler type). Method detection limits (MDL, ng) were determined for each element on each binding layer as three times the standard deviation of the measured blank values.^{21, 47} The detection limits were converted to concentration (µg L⁻¹) using the DGT equation¹⁶ and the following parameters: diffusive layer thickness (Δg , 0.09 cm including diffusive layer and filter membrane), deployment time (t, 72 h at 25°C), gel area (A, 3.14 cm²) and diffusion coefficients obtained from Shiva *et al.*²⁵

with either open (D_{ODL}) or restricted (D_{RDL}) diffusive layers. All diffusion coefficients were corrected for pH and temperature.

2.5. Statistical analysis and comparison with water quality guidelines

A one-way ANOVA followed by a Tukey's post-hoc test at a significance level of $p=0.05$ was used to test for statistical differences between Al measurements with DGT-MBL, DGT-Chelex and DGT-Metsorb. For other elements, an independent t-test was used to compare the DGT measurements between binding layers. Independent t-tests were also used to compare DGT_{ODL} and DGT_{RDL} measurements for each binding layer. All DGT labile and filterable concentrations of trace metals were compared to the water quality guidelines determined by the Australian and New Zealand Environment and Conservation Council (ANZECC) and the Agriculture and Resources Management Council of Australia and New Zealand (ARMCANZ)⁴⁸ for the 95% level of ecosystem protection in either freshwaters or marine waters.

3. Results and discussion

3.1. DGT Method detection limit (MDL) and diffusive boundary layer (DBL) measurements

The average DGT blank values and method detection limits (MDL, $\mu\text{g L}^{-1}$) calculated for DGT-MBL, DGT-Chelex and DGT-Metsorb with either ODL or RDL at each sampling site are shown in Tables S1-S3 in the supporting information (SI). Tables are provided separately as different diffusion coefficients (D_{gel}) were used to calculate the detection limits depending on the pH and temperature at each site. The results indicate that most elements (except for Al and Zn) had very low detection limits with each DGT technique ($<0.101 \mu\text{g L}^{-1}$). These findings are in good agreement with

previously published detection limits for DGT-MBL, DGT-Chelex and DGT-Metsorb.^{21, 25, 39, 49} The relatively higher detection limits for Al and Zn ($<2.04 \mu\text{g L}^{-1}$) may be due to the presence of these metals in the Metsorb adsorbent, as has been reported by other investigators.^{30, 47, 50} The detection limits for these two elements, however, are well below the relevant ANZECC and ARMCANZ trigger values⁴⁸ (freshwater trigger values are in Tables S1 and S2 and those for seawater are in Table S3). Additional discussion of MDLs for each element is provided in the SI.

The thickness of the diffusive boundary layer (DBL) is an important factor that should be determined for DGT measurements and has been extensively discussed previously.^{27, 30, 51-53} Plots of $1/M$ versus Δg were used to calculate the thickness of the DBL for each element at each site. Some elements showed non-linear plots, which may indicate that different processes are occurring for certain metals, for instance kinetic limitation of dissociation.²⁹ Therefore, the final DBL thicknesses for each site were calculated based on the average DBLs for individual elements with linear plots, as described previously by Shiva *et al.*³⁰ The average DBLs obtained for each site were as follows: 0.160 ± 0.018 cm for site 1 (Figure S1), 0.156 ± 0.013 cm for site 2 (Figure S2), 0.118 ± 0.019 cm for site 3 (Figure S3) and 0.051 ± 0.009 cm for site 4 (Figure S4). These values were used to correct the DGT concentrations by site as further discussed in the SI.

The calculated DBL thicknesses in our study were in agreement with the range of DBLs reported previously (0.038 – 0.150 cm) by other workers.^{44, 46, 52, 54} Very high DBL thicknesses at sites 1 and 2 indicate that these streams were flowing very slowly during the sampling period; they were more like long, narrow wetlands. Site 3 also had a quite high DBL, because the southern part of Cudgen Lake appeared to be quite stagnant with little tidal influence (supported by the low conductivity and salinity measurements in Table 1). These results are consistent with those described by Warnken *et al.*⁴⁴ who reported high DBL values (0.15 cm) for solutions that were unstirred. The smaller DBLs calculated for site 4 are consistent with substantially faster flow rates as a result of strong tidal influences in the lower estuary.

Turner and co-workers⁵² reported that DBL thickness measurements are not only influenced by water flow rate but also other factors such as suspended solid concentrations and biofouling (for DGT deployments over 7 days). We observed minimal biofouling effect at all sampling sites over the 3-day deployments, which is consistent with the fact that Turner *et al.*⁵² used deployments times double those used in our study.

3.2. Comparison of DGT-MBL, DGT-Chelex, DGT-Metsorb and filterable concentrations for aluminium measurements

Results for Al are of particular importance in acid-drainage affected waters. One of the most significant observations was the extremely high mean concentration of filterable Al at site 1 ($5,589 \mu\text{g L}^{-1}$), which was an order of magnitude above that observed at other sites (Table 1). This site is obviously highly impacted by drainage from acid sulphate soils (pH = 3.29) modified by agricultural practices⁴²; these acidic conditions are known to mobilize Al and other trace metals from soils.^{7, 42, 50} Moreover, the water at this site was highly turbid so this filterable concentration is likely to include colloidal Al. Omanović and co-workers⁴¹ also reported a considerable fraction of Al (68%) present in particulate and colloidal forms in a mining-impacted area with pH ~3. High mean filterable Al concentrations were also observed at site 2 ($254 \mu\text{g L}^{-1}$, pH = 5.05) and site 3 ($113 \mu\text{g L}^{-1}$, pH = 6.28). The mean filterable Al concentration at site 4 was much lower ($21.9 \mu\text{g L}^{-1}$, pH = 7.81, salinity = 27.8) and the waters were much clearer at this site. However, some colloidal forms may still be present, as well as Al complexed with organic matter.¹⁰

Filterable Al concentrations at each field site are compared with the determined DGT-labile (ODL only) concentrations for each binding layer in Figure 2. The DGT-MBL concentrations are the first measurements of Al in freshwaters using this new DGT binding layer. The concentrations measured by DGT-MBL, which was effective at each site, were different to the filterable Al concentrations;

46% at site 1 (pH 3.29), 67% at site 2 (pH 5.05), 7% at site 3 (pH 6.28) and 65% at site 4 (pH 7.81). DGT-Chelex and –Metsorb provided similar results at some sites but otherwise provided useful supporting information on the Al species likely to be present. DGT-Chelex provided a significantly different result to DGT-MBL at site 4 only while DGT-Metsorb did so at sites 1 and 4. These findings are consistent with the results from previous studies^{30, 38}, and are discussed further below.

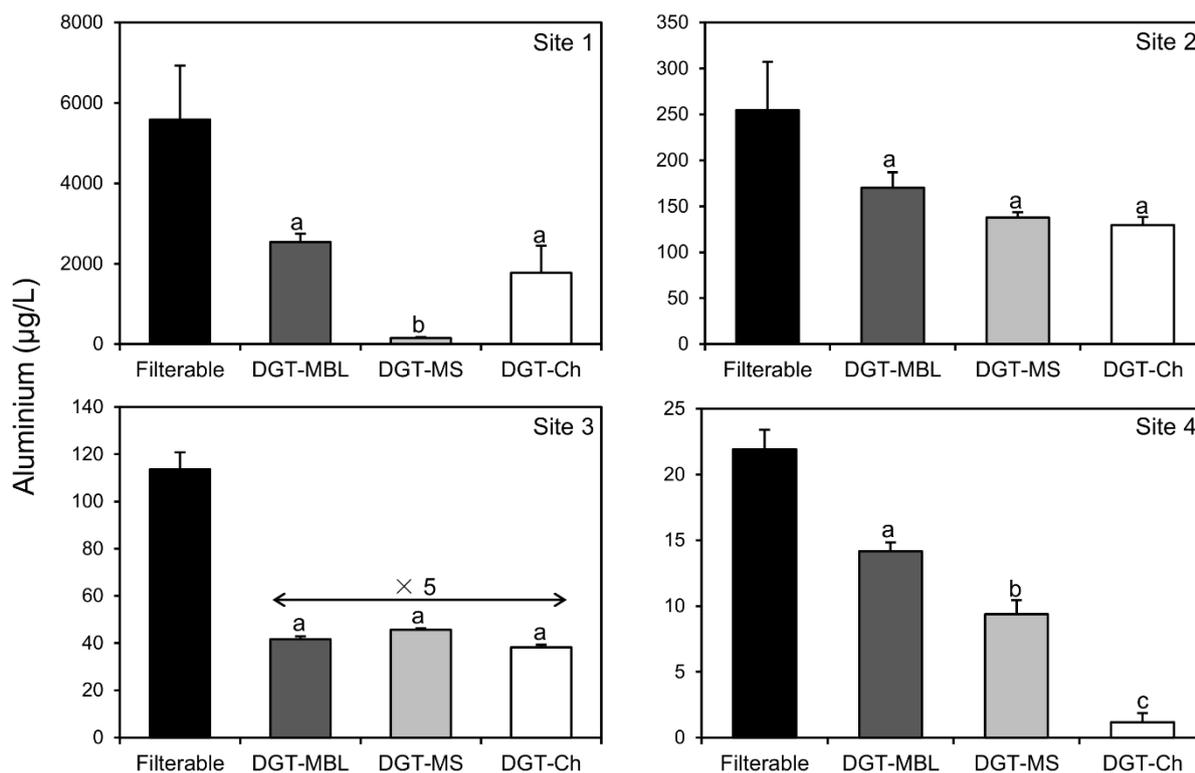


Figure 2. Comparison of DGT-MBL, DGT-Metsorb (Ms), DGT-Chelex (Ch) and filterable concentrations of Al at four sites in the Cudgen Lake catchment with different pH: Site 1= pH 3.29; Site 2 = pH 5.05; Site 3 = pH 6.28; Site 4 = pH 7.81. All DGT-measured concentrations were obtained with an open diffusive layer (ODL).

The high DGT-Chelex (and DGT-MBL) concentrations at sites 1 and 2 suggest a good proportion of Al at these sites is present as soluble cationic Al (Al^{3+} , $\text{Al}(\text{OH})^{2+}$ and $\text{Al}(\text{OH})_2^+$) despite the very high

turbidity. This suggests that competition for surface binding sites by H^+ acted to keep Al in solution. The DGT-Metsorb Al concentration was only 6-9% of that measured using the other binding layers and was statistically different ($p < 0.006$). A likely explanation for the fact that DGT-Metsorb does not function at such low pH is that pH 3.29 is well below the point-of-zero-charge for anatase (5.9)⁵⁵ and therefore Al uptake by Metsorb experiences detrimental competition from H^+ ions. DGT-Metsorb has previously been determined to function well at pH 5.05 and above³⁸.

The highest proportion of DGT-labile Al, as a fraction of filterable Al, was found at site 2 (pH = 5.05), while the lowest was at site 3 (pH = 6.28). At both sites there were no significant differences ($p > 0.05$) in concentrations determined for all three binding layers. DGT-Chelex and DGT-Metsorb measured relatively similar concentrations for Al at pH 5.05 ($C_{\text{Chelex}}/C_{\text{Metsorb}} = 0.94$), and pH 6.28 ($C_{\text{Chelex}}/C_{\text{Metsorb}} = 0.84$), which was in good agreement with the results of a study³⁸ in synthetic freshwater at pH 5.4 and 6.1. The measurements of DGT-MBL were also in good agreement with those of the two other binding layers ($C_{\text{Chelex}}/C_{\text{MBL}}$ and $C_{\text{Metsorb}}/C_{\text{MBL}}$ were in the range of 0.76 - 1.09). Røyset *et al.*⁸ observed that increasing the pH from 4.8 to 5.9 decreased the labile fractions of Al measured by DGT-Chelex, as the proportion of neutral $[Al(OH)_3]$ or organically bound species of Al increased with pH. However, Panther *et al.*³⁸ established that DGT-Metsorb accumulates all soluble forms of free or hydrolysed Al from pH 5.4 to 8.15. Therefore, the most likely reasons for the observed decrease in DGT-labile Al measured by all three binding layers at pH 6.28 are the formation of non-labile organic complexes, formation of colloidal $Al(OH)_{3(s)}$ and/or adsorption of Al to colloids or particles. A high proportion of colloidal Al has also been reported for other natural waters in circumneutral pH.³¹ However, it is also important to note that DGT-labile concentrations are determined using the diffusion coefficient of the free metal ion and hydroxide inorganic complexes (depending upon solution pH), whereas other inorganic complexes and/or labile organic complexes with lower diffusion coefficients may also be measured. This generally makes DGT measurements more selective than filterable grab sample measurements, especially for cationic

metals. This feature of DGT makes the measurement highly operational⁵⁶, but the determinants of this selectivity are very well understood.⁵⁷⁻⁵⁹

The differences between the binding layers became more prominent in the estuarine waters of site 4. DGT-Chelex measured very low concentrations of Al compared to DGT-MBL and DGT-Metsorb (8-12%; $p < 0.001$). In slightly basic waters Al exists predominately as the $\text{Al}(\text{OH})_4^-$ oxyanion,^{10, 38} which is only quantitatively accumulated by binding layers containing Metsorb adsorbent. The results of our study are consistent with those of Panther *et al.*³⁸ who compared DGT-Chelex and DGT-Metsorb for measurement of Al in synthetic freshwater over the pH range of 7.7 to 8.1 and for synthetic seawater (pH 8.15). Other studies have also reported higher Al uptake by DGT-Metsorb compared to DGT-Chelex in estuarine waters³⁰. However, DGT-Metsorb measured Al concentration was only 66% and significantly lower ($p < 0.001$) than that measured by DGT-MBL. A similar result was previously obtained in estuarine waters (pH 8-8.2 and salinity 30-37)³⁰ and it was speculated that Al^{3+} associated with colloids could be accumulated through interaction with the Chelex-100 resin present in the MBL. It is possible that a similar effect occurs with Al^{3+} complexed to organic matter, with a greater range of complexes being labile to DGT-Chelex than to DGT-Metsorb. The fact that a small (non-quantitative) mass of Al is observed to bind to DGT-Chelex supports this possibility. The concentration of Al measured by DGT-MBL, however, was not the sum of that measured by DGT-Metsorb and -Chelex separately, which suggests a possible interactive effect of having both binding agents mixed in a single binding gel layer. Further research is needed to determine the mechanisms responsible for this observed behaviour. Finally, a likely additional factor contributing to the lower accumulation of Al by DGT-Chelex at site 4 is competition from the high concentration of ions in solution. Panther *et al.*³⁸ compared Al measurements of DGT-Chelex and DGT-Metsorb at different ionic strengths and observed lower DGT-Chelex measurements at higher ionic strengths (0.1 and especially 0.7 M NaNO_3), which are comparable with the ranges expected at an estuarine site.

The measured concentrations with RDL and ODL for each binding layer are shown in Figure S5 and the ratios between these measurements in Table 2 and Figure S10. The fact that DGT measurements with RDL consistently provide a higher, although not significantly different, concentration compared with ODL measurements at site 1 is an artefact that will be discussed further in the following section. At site 2 (pH =5.05) there were no significant differences between ODL and RDL measurements for each binding layer, although the ODL measurement was often slightly higher ($C_{\text{RDL}}/C_{\text{ODL}}$ range between 0.91 and 0.97). At site 3 (pH =6.28) there were also no statistical differences ($p > 0.05$) between RDL and ODL measured concentrations for any of the binding layers, although in each case the ODL measurement was slightly higher. This suggests that labile organic complexes were present but only made a minor contribution to ODL measurements ($C_{\text{RDL}}/C_{\text{ODL}}$ range between 0.88 and 0.94). It is in estuarine waters of site 4 where major differences between the binding layers were observed, and significant differences were found between the ODL and RDL measurements. At site 4 a significant difference was observed for DGT-MBL ($C_{\text{RDL}}/C_{\text{ODL}} = 0.85$, $p = 0.047$), although in a previous study³⁰ significant differences between ODL and RDL measurements were observed for both DGT-MBL and –Metsorb in estuarine waters.

Table 2. Ratios of restricted (RDL) to open (ODL) diffusive layer measurements of Al by DGT-MBL, DGT-Metsorb and DGT-Chelex.

	DGT-MBL	DGT-Metsorb	DGT-Chelex
Site 1 (pH 3.29)	1.26	1.35	1.16
Site 2 (pH 5.05)	0.91	0.93	0.97
Site 3 (pH 6.28)	0.88	0.89	0.94
Site 4 (pH 7.81)	0.85	0.88	1.05

3.3. Comparison of DGT-MBL, DGT-Chelex and filterable concentrations for trace metal measurements

DGT-labile concentrations measured by DGT-MBL and DGT-Chelex, and filterable concentrations of cationic trace metals are shown in Figure 3 (for Cu and Mn, which gave the most notable results) and Figure S6 (for Co, Ni, Pb and Zn). Cd DGT measurements were below the method detection limits. These results are discussed by site in order of increasing complexity.

At pH 6.28 (site 3) there was excellent agreement between filterable Mn and both DGT measurements, for which there was no significant difference ($p < 0.05$). This suggests that Mn^{2+} was largely present as free ions, which is consistent with the known speciation of Mn in circumneutral waters.³² This was further supported by comparison between ODL and RDL measurements ($C_{RDL}/C_{ODL} \approx 1$, Figures S7 and S9). At site 3 there was also good agreement between DGT-MBL and -Chelex for all other cationic metals (Co, Cu, Ni, Pb and Zn) with no statistical differences observed. For Co and Zn, the DGT-labile and filterable concentrations showed quite good agreement ($C_{DGT}/C_{filterable}$ ratios of 0.78 to 0.98) and the C_{RDL}/C_{ODL} ratios of 0.90 to 0.94 for both metals, suggest that organic complexes made minor contributions (Figures S6, S7 and S9). However, the filterable concentrations were substantially higher for other metals (Cu, Ni and Pb) at site 3, suggesting the presence of non-labile complexes or colloids⁵⁶, particularly for Cu, where the ratio of C_{RDL}/C_{ODL} measurements was between 0.76 and 0.81.

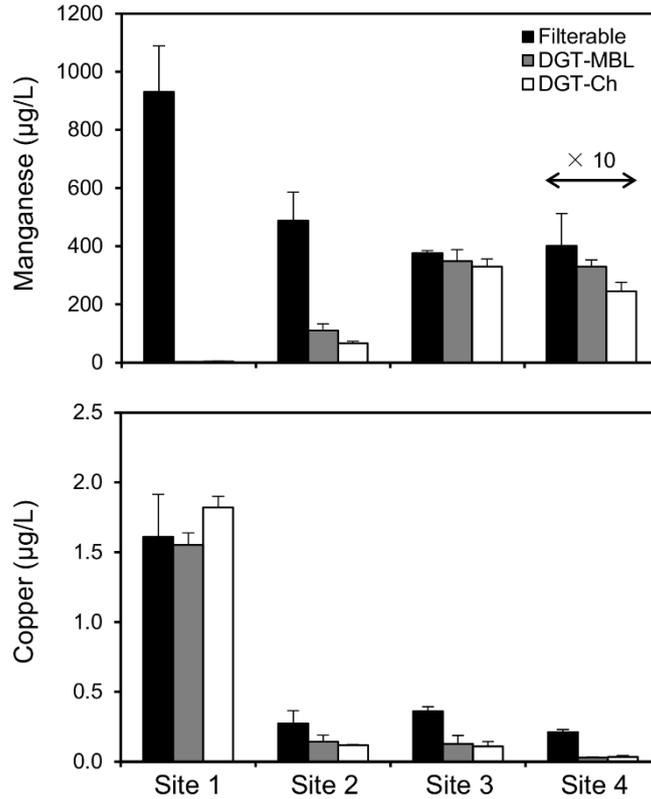


Figure 3. Comparison of DGT-MBL, DGT-Chelex (Ch) and filterable concentrations for Mn and Cu at four sites in the Cudgen Lake catchment with different pH: Site 1 = pH 3.29; Site 2 = pH 5.05; Site 3 = pH 6.28; Site 4 = pH 7.81. DGT-measured concentrations are only shown when values were above the determined method detection limits.

At the estuarine site 4 (pH 7.81) there was reasonable agreement between filterable Mn and DGT-MBL measurements, as has been observed previously in estuarine waters³⁰, and is consistent with the dominance of free Mn^{2+} in coastal waters^{20, 29}. There were significant differences between DGT-MBL and -Chelex measurements ($C_{Chelex}/C_{MBL} = 0.74$, $p = 0.019$) as observed previously for this element in estuarine waters.³⁰ A likely explanation is adsorption of Mn^{2+} by TiO_2 to some extent (either by direct sorption or by precipitation as MnO_2 (Mn (IV) oxide). This observation also supports the findings of other researchers that DGT-Chelex measurements of Mn in seawater or

lower estuarine waters may not be quantitative over deployment times longer than 24 h, as a consequence of competition between major cations and Mn^{2+} ions.^{39, 60} There was good agreement between DGT-MBL and -Chelex for other cations that were above the detection limits (Co, Cu and Ni). The DGT-labile concentrations were lower than the filterable concentrations, as observed previously in estuarine waters⁶¹, indicating the presence of non-labile complexes and/or colloids (Figures S7 and S9).

At site 2 (pH 5.05) the DGT measurements were only 14-23% of the filterable Mn concentrations. Previous studies have reported good agreement between DGT-Chelex and filterable Mn in natural freshwaters at pH 4.7.³² The difference here might reflect a higher proportion of colloidal material present at this site, which would contribute to filterable Mn but not to DGT measurements. There were also significant differences between Mn concentrations measured by DGT-MBL and -Chelex ($C_{\text{Chelex}}/C_{\text{MBL}}=0.60$, $p=0.035$), suggesting that the Metsorb adsorbent may be capable of adsorbing Mn^{2+} under conditions where Chelex can not. Measurements of other cationic metals (Co, Cu, Ni and Zn) were not significantly different between binding layer types at site 2. Filterable Co and Ni were also very similar to the DGT measurements, while filterable Cu and Zn were considerably higher.

Trace metal concentrations measured using ODL and RDL at site 2 (Figure S7) were similar, with $C_{\text{RDL}}/C_{\text{ODL}}$ ratios of ≈ 1 for Mn, Ni, Zn and ≈ 0.9 for Co and Cu (Figure S9). Balistrieri and co-workers⁷ previously reported $C_{\text{RDL}}/C_{\text{ODL}}$ ratios of 0.97-1.01 for Cd, Cu, Ni and Zn in fresh waters with pH ≈ 5 , and concluded that almost all the dissolved metal species were present in inorganic forms. The results from this study suggest that DGT measurements with ODL and RDL may distinguish between fractions of metal species in waters in which labile organic complexes are present, with the results varying somewhat with solution pH, salinity, and the organic matter pools present. However, these measurements cannot be simply interpreted as measuring total labile 'organic + inorganic' and 'inorganic' species under field conditions, and other barriers for metal diffusion may be required, such as dialysis membranes.⁶² This does not mean that the differences in

selectivity between ODL and RDL will not prove to be useful for some waterways, such as those rich in humics.

The concentration of filterable Mn at site 1 (pH 3.29) was almost double that at the other sites, indicating high inputs of Mn from acid sulphate soil runoff, as discussed in section 3.2. DGT-measured concentrations at this site were <1% of the measured filterable Mn concentration (Figure 3), which confirms that DGT-Chelex and DGT-MBL are incapable of measuring Mn at pH below 4.³⁴ This is due to competition from H^+ and/or other trace metals, which are abundant in acidic waters.⁴² Other cations such as Co^{2+} and Zn^{2+} were also observed to have similar non-quantitative responses at site 1, with $C_{DGT}/C_{filterable}$ of less than 0.04 (Figure S6). The DGT-labile Ni and Pb concentrations also did not agree with the filterable concentrations but gave relatively better results. However, there was excellent agreement between the filterable Cu and DGT measurements using both binding layers (Figure 3). Other studies also have noted that Chelex-100 inefficiently binds most metal cations below pH 4, but is quantitative for Cu at pH values as low as 2.²⁴ The C_{RDL}/C_{ODL} ratio for Cu was ≈ 1 which suggests that Cu was present at this site primarily as the free ion (Figures S7 and S9).

These non-quantitative DGT measurements also explain the observation of C_{RDL}/C_{ODL} ratios >1 (Al, Co, Mn, Ni and Pb) for DGT-Chelex and -MBL at site 1 (Figure S9). As the accumulated mass are determined by competition rather than accumulation according to the DGT equation (and were therefore quite similar), using different diffusion coefficient values for RDL and ODL measurements inflated the RDL concentrations (as the diffusion coefficients are lower²⁵).

Measured trace metal concentrations determined with either DGT measurements or on filtered water samples were compared to the ANZECC and ARMCANZ water quality guidelines⁴⁸ to assess the ecological and environmental health at each field site, as reported by other investigators.⁵⁰ The trigger values for the 95% level of ecosystem protection in freshwaters (sites 1-3) and marine waters

(site 4) are provided in Table S2 and Table S3, respectively, where such data exist. Results showed that DGT-labile and filterable concentrations of Cu, Mn, Ni, Pb and Zn were well below the trigger values at sites 2, 3 (freshwater) and 4 (marine). At site 1, filterable Cu and Ni, were marginally above the guidelines, while the concentrations of filterable Zn greatly (8 times) exceeded the water quality trigger value. Due to the likelihood of DGT-measured trace metal concentrations, other than Cu, being significantly underestimated at site 1, only the DGT-labile Cu concentration was compared with guidelines, with this value being marginally above the guidelines. For Al, there is a lack of information about trigger values in marine waters and also in freshwaters with pH <6.5; therefore it was not possible to compare the measurements of Al at any of the field sites in the current study with the ANZECC and ARMCANZ water quality guidelines. However, it should be noted that Clothiers Creek has recently been subject to remediation processes due to high concentrations of Al and Fe that are present.⁶³

3.4. Comparison of DGT-MBL, DGT-Metsorb and filterable concentrations for oxyanion measurements

Filterable, DGT-MBL and DGT-Metsorb concentrations of oxyanions (As, Mo, Sb and V) at the four study sites are shown in Figure 4 (As) and Figure S8 (Mo, Sb and V). These results represent the first measurements of oxyanions using DGT-MBL in natural freshwaters. As these elements are redox-active, it is also worth noting that dissolved oxygen concentrations varied considerably between the four sites; sites 1 and 2 had very low concentrations (32.6 and 17.1 % saturation, respectively), indicating a substantial oxygen demand at these sites, while higher oxygen concentrations were measured at sites 3 and 4 (70.3 and 80.8 % saturation, respectively). However, DGT-Metsorb, and thereby DGT-MBL, are known to provide quantitative measurements of both oxidized and reduced As and Sb species^{36, 64}, although the diffusion coefficients of the oxidized ions²⁵ were used for all the

DGT calculations, which would tend to result in the total calculated concentrations being slightly overestimated, if substantial concentrations of the reduced species were present. However, this result was not observed for any of the oxyanions.

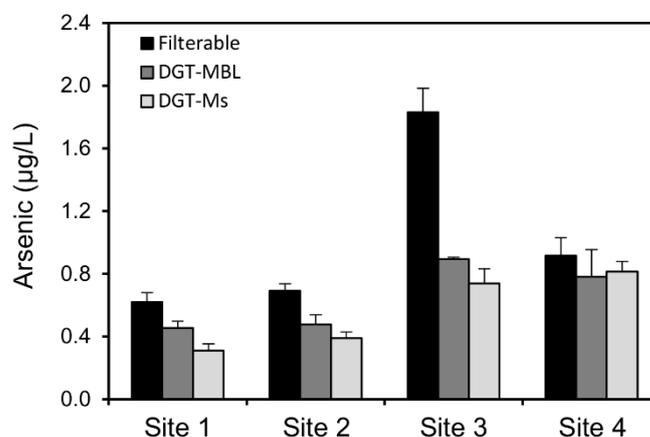


Figure 4. Comparison of DGT-MBL, DGT-Metsorb (Ms) and filterable concentrations for As at four sites in the Cudgen Lake catchment with different pH: Site 1 = pH 3.29; Site 2 = pH 5.05; Site 3 = pH 6.28; Site 4 = pH 7.81.

The highest filterable concentrations for Mo, Sb and V were observed in Cudgen Creek estuary (site 4, pH 7.81). Seawater is known to have dissolved Mo, Sb, V and As at about or higher than these concentrations⁶⁵, which is likely to be a source of these elements to both the estuary and Cudgen Lake (site 3); even though Site 3 was not strongly influenced by tides Cudgen lake is a tidal lagoon. Very low concentrations of Mo, Sb and V were observed at sites 1 and 2, which suggest that these elements are not associated with agricultural run-off or drainage from acid sulphate soils. DGT-measured and filterable concentrations for As were different at all the sampling sites, but especially so at site 3 (Figure 4). This elevated concentration might be due to the presence of organo-arsenic species in these circumneutral waters; however, the concentration was well below the guideline trigger value.⁴⁸

There was excellent agreement between filterable concentrations and DGT-MBL and -Metsorb measurements of As and V at site 4 (Figures 4 and S8), with no statistical differences determined; $C_{\text{DGT}}/C_{\text{filterable}}$ ratios were between 0.85 and 1.08, and $C_{\text{Metsorb}}/C_{\text{MBL}}$ ratios were 1.04 for As and 0.89 for V. Determination of Mo by both DGT techniques was unsuccessful at this site, as observed previously in synthetic saline waters.²¹ There were no statistical difference between the Sb concentrations measured by the two DGT techniques ($C_{\text{Metsorb}}/C_{\text{MBL}} = 0.93$). However, the DGT-determined Sb concentrations were about half of the filterable Sb concentrations measured, indicating the presence of non-labile Sb species. These results generally support the findings of other studies of oxyanion measurements in estuarine waters.³⁰

Similar results were also observed for As, Sb and V at site 3, with the DGT measurements showing no statistical differences, but accounting for only about half of the filterable concentration for As and Sb, and <10% for V (Figures 4 and S8). Whereas, for Mo, the DGT techniques were relatively similar to the filterable concentrations. Overall, these results suggest that at this site As, Sb and V were largely present as non-labile species, whereas the speciation of Mo was dominated by DGT-labile species. Additionally, although the DGT measurements of As, Sb and V using both binding layers were not statistically different, DGT-Metsorb measured higher concentrations than DGT-MBL for Mo. This observation is consistent with the results obtained for Mo in synthetic freshwater³⁹ and needs further investigation.

At sites 1 and 2 DGT-labile Mo, Sb or V were below the method detection limits and only As was measurable. At site 2, DGT-MBL and -Metsorb As measurements were 69% and 56%, respectively, of filterable As concentration, with no statistical differences ($C_{\text{Metsorb}}/C_{\text{MBL}} = 0.82$, $p = 0.105$). Whereas, at site 1, DGT-MBL and -Metsorb measurements were significantly different ($C_{\text{Metsorb}}/C_{\text{MBL}} = 0.68$, $p = 0.013$) and accounted 74% and 50%, respectively, of filterable As concentration. This is the first time that a significant difference has been observed for DGT-labile As measurements determined by MBL and Metsorb techniques, and this observation requires further

investigation in other waters with a low pH. The C_{RDL}/C_{ODL} ratios for all measurable oxyanion species were close to 1 at all sites (Figure S10) which is as expected given that oxyanions do not associate with humic matter.

4. Conclusion

This study is the first field application of DGT-MBL in freshwaters and has demonstrated excellent performance of this mixed binding layer across a range of pH and conductivities. DGT-MBL was comparable with DGT-Chelex for the measurement of most trace metals and with DGT-Metsorb for the measurement of most oxyanions over the pH range 5.05 - 7.81.

The study clearly demonstrates that DGT-Metsorb and DGT-Chelex should not be used for Al measurements in very acidic (pH \approx 3.5) or basic (pH \approx 8) waters, respectively, as these binding layers cannot quantitatively accumulate the Al species present. The DGT-MBL can be used in a much wider range of conditions and generally measured a greater range of Al species, especially in estuarine waters. A similar observation was made for the measurement of Mn.

There was lack of additional selectivity using RDL over ODL for most elements, except for Al and Cu at particular sites, suggesting that the majority of metal species in these natural waters were present in DGT-labile forms and/or that organic complexes excluded by the RDL relative to ODL tended to not be DGT-labile.

Overall this study has provided a more detailed investigation of the capability of DGT-MBL for the simultaneous measurement of a wide range of trace metals and oxyanions in natural and acid-impacted waters. DGT-MBL (Chelex and Metsorb) is recommended where the measurement of both cations and anions is desired, and/or where aluminium is an element of interest.

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