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Environmental Impact Statement:

The diffusive gradients in thin films (DGT) is a highly effective technique for selectively measuring trace metals concentrations in natural waters, providing information on the environmental health of waterways and understanding key processes. DGT is a monitoring tool for which the selectivity can be modified by use of different components, especially the diffusive and binding layers. In this study, we have evaluated DGT measurements of trace metals using four binding layers and two diffusive layers in waters adjacent to an urbanised coast. The choice of DGT measurements with differing selectivity will be important for future studies.

**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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24 **Abstract**

25 Four different DGT binding layers were used to make selective measurements of trace metals
26 in coastal waters within The Broadwater (Gold Coast, Queensland). Chelex and PAMPAA
27 (polyacrylamide-polyacrylic acid) binding layers were used to measure cations (Cd, Co, Cu,
28 Mn, Ni, Pb, Zn), and Metsorb was used to measure anions (Al, As, Mo, Sb, V, W). A mixed
29 binding layer (MBL) containing both Chelex and Metsorb was used to measure each of the
30 trace metals and determine diffusive boundary layer (DBL) thicknesses. DGT measurements
31 that were not corrected for the DBL thickness (0.049-0.087) were underestimated by 70% on
32 average. Good agreement was observed between DGT-MBL and DGT-Chelex for
33 measurement of Cd, Co, Cu, Ni, Pb and Zn, and between DGT-MBL and DGT-Metsorb for
34 As, Sb and V. DGT-MBL measured significantly higher concentrations for Mn (compared
35 with DGT-Chelex) and Al (compared with DGT-Metsorb). DGT-Chelex measured only 6-
36 8% of Al species measured by either DGT-MBL or DGT-Metsorb. DGT-PAMPAA
37 measurements of Cu, Pb and Al were lower than those of either DGT-MBL or DGT-Chelex
38 varying from 74-81% for Cu to 54-70% for Pb and 51-55% for anionic $\text{Al}(\text{OH})_4^-$, suggesting
39 that this binding layer may make more selective measurements. All measured trace metal
40 concentrations were well below ANZECC water quality guidelines, except for Cu which was
41 2 to 10 times higher than trigger values. Each of the DGT techniques was deployed using
42 both open and restricted diffusive layers (ODL and RDL). Most trace metal measurements
43 were not significantly different with ODL and RDL for all binding layers. However,
44 concentrations of Cu ($C_{\text{RDL}}/C_{\text{ODL}} = 0.68\text{-}0.75$) and Al ($C_{\text{RDL}}/C_{\text{ODL}} = 0.73\text{-}0.79$) were
45 significantly different with DGT-MBL, DGT-Chelex and DGT-Metsorb.

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47 *Key words:* diffusive gradients in a thin film, Chelex, Metsorb, mixed binding layer,
48 polyacrylamide-polyacrylic acid, diffusive boundary layer.

1. Introduction

Trace metals are one of the major contaminants of concern in many coastal and estuarine waters as a result of inputs from anthropogenic sources ^{1, 2}. Elevated concentrations of essential (e.g. Cu, Mn, Ni and Zn) and non-essential (e.g. Cd, Pb and As) trace metals can have detrimental impacts on the environment and may cause toxicity to aquatic organisms ³. Trace metals often exhibit complex speciation in seawater with the free metal cations or oxyanions, especially, and labile inorganic/organic complexes considered to be bioavailable through environmental exposure ⁴. Therefore, in order to assess environmental health and potential biological impacts of trace metals, there is a need for methods that are able to make selective measurements of the most bioavailable metal species.

The diffusive gradients in thin films (DGT) technique is a passive sampler that measures the free ions and labile inorganic/organic complexes in water, sediment and soil ⁵⁻⁷, allowing inferences to be made on metal bioavailability and toxicity ^{6, 8, 9}. DGT techniques are based on the diffusional transport of analytes across a layer of known thickness (diffusive layer) and their accumulation on a binding layer, which is usually a resin or metal oxide material embedded in a polyacrylamide hydrogel ¹⁰. Depending on the target analyte, various binding materials with differing selectivity have been used for metal cations or oxyanions. Chelex-100 has been the most commonly used binding material for measurement of trace metals ¹¹⁻¹³ and is suitable for coastal waters ¹⁴⁻¹⁷. Polyacrylamide-polyacrylic acid (PAMPAA) is another type of binding layer for measurement of metal species, which is prepared from the polyacrylamide hydrogels, typically used for diffusive layers, through a hydrolysis reaction in an alkaline solution ¹⁸. This binding layer has been validated for Cu and Cd measurements in the laboratory and compared with DGT-Chelex and other novel DGT binding layers in natural waters ^{18, 19}. On the other hand, several binding materials have been used for oxyanion

species including zirconium oxide^{20, 21}, mercaptopropyl-silica²², ferrihydrite^{23, 24} and Metsorb^{25, 26} (a commercially available titanium dioxide-based resin).

Binding materials have also been combined to allow simultaneous measurement of cationic and oxyanionic metal species by DGT. A mixture of Chelex-100 and zirconium oxide has been used to measure phosphorous and iron²⁷. Mason *et al.*²⁸ and Huynh *et al.*²⁹ combined Chelex-100 and ferrihydrite for measurement of Mn, Cu, Zn, Cd, Pb, As, Mo and P in water and soils. Recently, Panther *et al.*³⁰ developed a Chelex-Metsorb mixed binding layer (MBL) for simultaneous measurement of a wide range of cations and oxyanions (Cd, Co, Cu, Mn, Ni, Pb, Zn, As, Mo, Sb, V, W) in water. Additionally, Shiva *et al.*³¹ evaluated the capability of DGT-MBL for measurement of Al at different pH, based on the findings of other study³² that DGT-Chelex and DGT-Metsorb accurately measure Al only in weakly acidic and slightly basic waters, respectively. Although the previous study³⁰ has evaluated the capability of DGT-MBL in synthetic freshwater and seawater, the performance of this binding layer has not yet been evaluated in natural waters.

DGT techniques are therefore able to make selective measurements of trace metals in natural waters, either by using binding layers with differing selectivity²² or by using diffusive layers (polyacrylamide hydrogels) with differing pore sizes³³. It has been demonstrated that the smaller pore size and greater tortuosity of the restricted diffusive layers (RDL) results in retarded diffusion of trace metals compared to the open diffusive layers (ODL) that have normally been used with DGT^{31, 34}. Therefore, DGT techniques employing a RDL will exclude or diffusionally retard the organic complexes, and preferentially measure smaller species such as free metals and inorganic complexes, compared to the same DGT techniques employing ODL³³. Since these smaller species are considered to be the most bioavailable⁴, measurements with RDL may better represent the bioavailable metal concentrations in the environment. The performance of DGT as a speciation tool has been evaluated by

comparison with other speciation techniques for selective measurement of trace metals³⁵⁻³⁷; however, none of these investigations have evaluated DGT measurements with different binding and diffusive layers in coastal waters.

The purpose of this study was to systematically evaluate the selectivity of DGT measurements using several DGT binding layers selective for trace metals and/or oxyanions combined with ODL and RDL in coastal waters. Chelex, Metsorb, mixed Chelex-Metsorb and PAMPAA binding layers were used, with particular interest on evaluating the performance of the mixed binding layer (MBL) in natural saline waters. Further characterization of the PAMPAA binding layer was done, measuring uptake and elution efficiencies for aluminium and cationic metals. All DGT measurements were compared with filterable metal concentrations at two estuarine sites within The Broadwater, Gold Coast City, Queensland.

2. Experimental section

2.1. General procedures

All equipment, including DGT devices, were soaked in 10% nitric acid (AR grade, Merck) for at least 24 hours and were rinsed with deionised water (Milli-Q Element, Millipore, >18.2 Mohms cm⁻¹) prior to use. Deionised water also was used for preparing the reagent solutions and for processing all samples. All preparation and experiments were done in an ISO class 5 (ISO 14644-1) laminar flow hood within an ISO class 6 (ISO 14644-1) clean room. Powder free latex gloves (Microtouch Dermaclean, Ansell) were used. Diffusive and binding layers were cast in a fume hood.

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121 **2.2. Preparation of hydrogels and DGT samplers**

122 *2.2.1. Diffusive layers*

123 ODL (>5nm pore size) and RDL (<1nm pore size) with nominal thickness of 0.08 cm were
124 prepared according to Shiva *et al.* ³¹. Further information on the characteristics of the
125 different diffusive layers is provided in Table S1 in the Supplementary Information (SI).
126 Triplicate hydrated open and restricted diffusive layers were selected randomly, overlain with
127 a filter membrane on one face (as in the DGT application) and the combined thickness of gel
128 and membrane was measured using digital vernier calipers (Kincrome, 150mm) ³⁸.

129 *2.2.2. Binding layers*

130 Chelex binding layers were prepared according to Zhang and Davison ¹¹ using 2 g of dry
131 Chelex-100 (sodium form, 200-400 mesh, Bio-Rad) per 10 ml stock solution. Metsorb
132 binding layers were prepared according to Bennett *et al.* ²⁵ using 1 g of cleaned Metsorb
133 (Graver Technologies, USA) per 10 ml stock solution. The process for cleaning the Metsorb
134 adsorbent has been described elsewhere ³². The mixed Chelex-Metsorb binding layers (MBL)
135 were prepared according to Panther *et al.* ³⁰. Briefly, 2 g of dry Chelex-100 and 1 g of
136 cleaned Metsorb were mixed thoroughly and added to every 10 ml of acrylamide gel stock
137 solution. 60 µl of ammonium persulphate (10%) and 20 µl of TEMED were added while the
138 solution was vigorously stirred. The solution was immediately cast between glass plates
139 (separated by a 0.025 cm thick plastic spacer) and polymerised for 1 h at 45°C. The gels were
140 rinsed in deionised water for 24 h (changed three times) and hydrated binding layers (0.04 cm
141 thick) were stored in deionised water at <4°C.

142 PAMPAA binding layers were prepared according to Li *et al.* ¹⁸. Briefly, polyacrylamide
143 hydrogel sheets were placed at 80°C for 5 h within sealed flasks containing 40 ml of 10%

(w/v) NaOH. The hydrolysis reaction that occurs results in amide groups within the polyacrylamide gel being converted into carboxylic acid groups. However, as the ammonia produced by this reaction is trapped within the sealed flask the reaction cannot proceed to completion, resulting in an equilibrium and formation of the PAMPAA copolymer. Following hydration for 24 h in deionised water, the gels were placed in 0.1 M HNO₃ for a further 24 h to remove unreacted alkali and ammonia, and then stored in 0.1 M NaNO₃ at <4°C to remove stickiness. Further information on the characteristics of the different binding layers used in this study is provided in Table S1 in the Supplementary Information (SI).

2.2.3. Assembly of DGT samplers

DGT water samplers were purchased from DGT Research Ltd. (Lancaster, UK) and were assembled as described previously¹¹ using a 0.45 µm cellulose nitrate filter membrane of thickness 0.01 cm (Millipore). Briefly, the binding layers were placed on the piston of the DGT sampler, overlain with the diffusive layer and filter, and finally the sampler cap was pressed over the piston. The assembled samplers were fitted into ports within rectangular Perspex plates (up to 12 samplers per plate) and stored at <4°C in double plastic bags with a few drops of deionised water in the outer bag to ensure a humid environment.

2.3. DGT deployment and DBL calculations

DGT deployments were performed at two sites in The Broadwater, a coastal lagoon on the Gold Coast, southeast Queensland, connected to the Pacific Ocean by the Seaway (Figure 1). The first site was The Spit, a popular boat anchorage in a well flushed area on the seaward side of the Broadwater, immediately south of the Seaway. The second site was within Runaway Bay Marina, on the landward side of the Broadwater, north of the Seaway.

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167 Runaway Bay Marina has a hardstand and also receives urban stormwater from the
168 surrounding urban area. These sites were selected as they have different influences and have
169 previously been reported to have measurable concentrations of filterable trace metals ^{14, 15}.

170 Three replicates of each DGT type (DGT-MBL, DGT-Chelex, DGT-Metsorb and DGT-
171 PAMPAA) with ODL and three replicates with RDL were deployed from 18th to 21st
172 November 2013 at each site for approximately 72 h (exact time recorded). An additional set
173 of triplicate acid-washed DGT-Metsorb were also deployed for Al measurements ³². pH,
174 salinity and temperature were monitored in situ every day using a Mettler-Toledo pH meter
175 (FiveGo, FG2) and a TPS conductivity-TDS meter (model MC-84). The respective values for
176 average pH, salinity and temperature were 8.02±0.05, 37.33±0.25 and 25.5±0.72 °C at
177 Runaway Bay Marina, and 8.23±0.10, 30.70±1.57 and 26.5±0.89 °C at The Spit. Filtered
178 (0.45 µm, Millex^(R)-HA, Millipore) grab water samples were collected daily, acidified (pH
179 <2) immediately and stored at <4°C.

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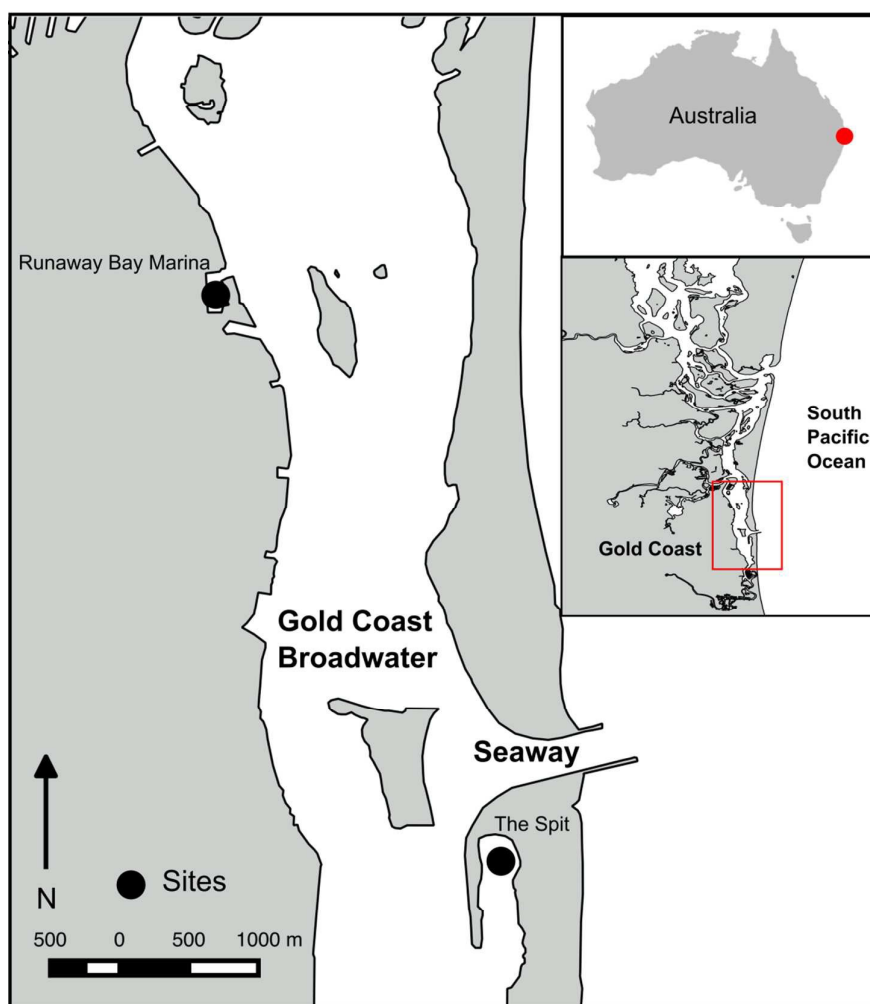


Figure 1. Map of the Broadwater (Gold Coast, Queensland, Australia) showing the location of The Spit anchorage and Runaway Bay Marina.

To measure the thickness of the diffusive boundary layer (DBL), a quiescent layer of water that forms at the interface of DGT samplers and bulk water, two additional sets of triplicate DGT-MBL with ODL thicknesses of 0.04 and 0.12 cm were deployed at each site³⁹. The average DBLs determined were applied to all DGT-Chelex, DGT-Metsorb and DGT-PAMPAA measurements (see Section 2.4).

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191 **2.4. Sample analysis and DGT calculations**

192 Following removal of the binding layers from the DGT samplers, Metsorb and MBL gels
193 were rinsed in 5 ml of deionised water for 1 h to remove the salts present in the gel, which
194 can interfere with the elution procedure^{32, 40}. The additional set of DGT-Metsorb used for Al
195 measurements, was immersed in 50 ml of 0.0001 mol L⁻¹ HNO₃ for 1 h, prior to rinsing with
196 deionised water. This process has been reported to increase the elution efficiency for Al³². In
197 this study, we also investigated the effect of an acid wash on DGT-Metsorb measurements for
198 oxyanions, as Al and oxyanions accumulate on the Metsorb gel at the same time (see
199 Supplementary Information).

200 The elements retained by binding layers were eluted using different eluents. Chelex and
201 PAMPAA binding layers were eluted for 24 h in 1 ml of 1 mol L⁻¹ HNO₃ (Baseline) and 5 ml
202 of 2 mol L⁻¹ HNO₃ (Baseline)¹⁸, respectively. MBL gels were eluted in 1 ml of 1 mol L⁻¹
203 HNO₃ (Baseline) for 24 h, rinsed with deionised water to remove excess acid and then eluted
204 in 1 ml of 1 mol L⁻¹ NaOH, for a further 24 h³⁰. Then, to elute Sb, the MBL gels were
205 immersed in 1 ml of 1 mol L⁻¹ NaOH / 1 mol L⁻¹ H₂O₂ for another 24 h³⁰. These eluents were
206 combined before analysis. Metsorb binding layers were eluted in 1 ml of 1 mol L⁻¹ NaOH for
207 24 h, and then for elution of Sb, the gels were immersed in 1 ml of 1 mol L⁻¹ NaOH / 1 mol
208 L⁻¹ H₂O₂ for another 24 h⁴⁰. The eluents for Chelex, Metsorb and MBL were diluted 10-fold
209 (using 2% HNO₃, Baseline), and for PAMPAA diluted 2-fold prior to analysis. 0.45 µm
210 filtered grab samples were diluted 20-fold with 2% HNO₃ prior to analysis.

211 All elemental analyses were carried out using an inductively coupled plasma mass
212 spectrometer (ICP-MS, Agilent 7500a). Analytical standards for ICP-MS analysis were
213 prepared in 2% (v/v) HNO₃ (Baseline) using a multi-element standard (High Purity
214 Standards). A quality control blank (QCB) followed by a 10 µg L⁻¹ quality control (QC, High

Purity Standards) were run every 15-20 samples to ensure there was no change in ICP-MS sensitivity. Sc, Y and In were added to each sample as internal standard (100 $\mu\text{g L}^{-1}$, High Purity Standards) to account for any instrument drift and all recoveries were in the range of 91-102%.

The accumulated mass of each analyte (M , ng) on each binding layer was calculated from analyte concentration in the eluent (C_e) using equation 1¹¹; where V_e is the volume of the eluent, V_{gel} is the volume of the gel (0.2 ml) and f_e is the elution efficiency for the element.

$$M = \frac{C_e(V_e + V_{\text{gel}})}{f_e} \quad (\text{Eq. 1})$$

The elution efficiencies used in this study (except for Al) were those reported for MBL, Chelex and Metsorb by Panther *et al.*³⁰. For Al, the elution efficiencies measured for Chelex and Metsorb binding layers by Panther *et al.*³² were used and an elution factor of 0.845 (average of Chelex and Metsorb) was utilized for MBL. For the PAMPAA binding layer, a separate experiment was carried out to determine uptake and elution efficiencies for the complete range of cations and Al (see Table S2, supplementary information). The results showed that only Al, Cu and Pb have reasonable uptake efficiencies (ranged 75.51 to 94.99%), and therefore only these three elements and Cd (which has been more thoroughly evaluated previously¹⁸) were selected for comparison with other binding layer.

The DGT-measured concentrations (C_{DGT} , $\mu\text{g L}^{-1}$) were determined using equation 2¹¹; where D_{gel} ($\text{cm}^2 \text{s}^{-1}$) represents the diffusion coefficient of analytes through the diffusive layer (Δg , cm) and DBL (δ , cm), t (s) is the deployment time, and A (cm^2), is the area of the gel exposed to the water. Diffusion coefficients of all the analytes in both open and restricted diffusive layers (D_{gel}) were obtained from Shiva *et al.*³¹, corrected for temperature using the Stokes-Einstein equation¹¹, and values of $0.9 \times D_{\text{gel}}$ were used as the medium was seawater⁵.

$$C_{DGT} = \frac{M(\Delta g + \delta)}{D_{gel}At} \quad (\text{Eq. 2})$$

The thickness of the DBL (δ) was calculated as described by Warnken *et al.*³⁹ using equation 3; where, D_w represents the diffusion coefficient of analytes in the water⁴¹. A plot of $1/M$ (ng^{-1}) accumulated by the binding layer versus the diffusive layer thickness (Δg , cm) is a straight line with a slope (m) of $1/(D_{gel}C_{DGT}At)$ and an intercept (b) of $\delta/(D_wC_{DGT}At)$. Therefore, the DBL thickness can be calculated using equation 4³⁹.

$$\frac{1}{M} = \frac{\Delta g}{D_{gel}C_{DGT}At} + \frac{\delta}{D_wC_{DGT}At} \quad (\text{Eq. 3})$$

$$\delta = \frac{b}{m} \left(\frac{D_w}{D_{gel}} \right) \quad (\text{Eq. 4})$$

Since the DBL thickness is incorporated into all DGT calculations, a value of 3.8 cm^2 (instead of 3.14 cm^2) was used as the effective sampling area (A) in the DGT equation (see Warnken *et al.*³⁹ for more information on the determination of this value).

2.5. DGT blanks and method detection limits (MDL)

To monitor for any contamination during synthesis, DGT blanks were prepared in the same way as the deployed DGT samplers and subjected to all procedures except for deployment in the water; however the blanks were transported to the field and exposed to the air for several minutes to detect contamination associated with dust or handling. Blanks were conducted in triplicate for each DGT type and mass measurements were calculated using equation 1. The average blank mass was subtracted from the accumulated mass for each analyte to obtain corrected mass values (ng). A set of triplicate filtration blanks were also collected in the field with daily grab samples using deionised water.

Method detection limits (MDL, ng) were calculated for each element for the Chelex, Metsorb, MBL and PAMPAA binding layers as three times the standard deviation of the blanks^{28, 40}. The detection limits were converted to concentrations ($\mu\text{g L}^{-1}$) using the DGT equation with the diffusion thickness, Δg of 0.09 cm (diffusive layer and filter membrane), deployment time, t of 72 h, an available gel area, A of 3.14 cm² and diffusion coefficients obtained from Shiva *et al.*³¹ for open (D_{ODL}) and restricted (D_{RDL}) diffusive layers corrected for temperature.

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267 2.6. Statistical analysis and interpretation of metal risks to the environmental

A one-way ANOVA followed by a Tukey's post-hoc test at a significance level of 0.05 was used to determine the statistical differences between DGT-MBL, DGT-Chelex, DGT-Metsorb and DGT-PAMPAA measurements of each element at each site. Measurements for each DGT type with ODL and RDL were compared using an independent t-test. All filterable and DGT-measured concentrations of metals were compared to the water quality guidelines determined by the Australian and New Zealand Environment and Conservation Council (ANZECC)⁴² for the 95% level of ecosystem protection in marine waters to assess the ecological risks of metals to the Gold Coast Broadwater.

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277 3. Results and discussion

278 3.1. DGT blanks and method detection limits (MDL)

Table 1 shows the method detection limits (MDL, $\mu\text{g L}^{-1}$) calculated for DGT-MBL, DGT-Chelex, DGT-Metsorb and DGT-PAMPAA with both ODL and RDL. To lower the blank

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values, Metsorb adsorbents were cleaned with 1 mol L⁻¹ HNO₃ and 1 mol L⁻¹ NaOH prior to use³² as higher detection limits have been reported for Mn, Ni, Cu, Zn and V when using unwashed Metsorb³⁰. All detection limits in our study (except for Al and Zn) were below 0.112 µg L⁻¹ and in most cases ≤ 0.045 µg L⁻¹, indicating low-level contamination of binding layers. The estimated detection limits in our study are in line with previously reported values for DGT-MBL³⁰, DGT-Chelex^{30, 43}, DGT-Metsorb^{25, 40}, DGT-PAMPAA¹⁹. Values were quite similar for ODL and RDL, and were all considerably below the ANZECC water quality guidelines for each trace metal⁴². Relatively high detection limits for Al and Zn have also been reported by other investigators^{17, 28} and may be due to the presence of these elements in the Metsorb adsorbent; however, the calculated MDLs are generally acceptable for these elements. Theoretically, DGT detection limits can be lowered by increasing the deployment time.

Table1. DGT method detection limits (MDL, $\mu\text{g L}^{-1}$) for different binding layers using diffusion coefficients for analytes in either open diffusive layer (ODL) or restricted diffusive layer (RDL) measured by Shiva *et al.*³¹. Conditions: $\Delta g = 0.09$ cm; $t = 72$ h; $A = 3.14$ cm²; $T = 26$ °C. The MDLs are compared to the ANZECC trigger values for marine waters ($\mu\text{g L}^{-1}$); 95% level of species protection.

Metal	DGT-MBL		DGT-Chelex		DGT-Metsorb		DGT-PAMPAA		ANZECC trigger values for marine waters
	MDL _{ODL}	MDL _{RDL}	MDL _{ODL}	MDL _{RDL}	MDL _{ODL}	MDL _{RDL}	MDL _{ODL}	MDL _{RDL}	95% protection
Cd	0.010	0.013	0.005	0.006	—	—	0.016	0.022	5.5
Co	0.035	0.045	0.002	0.003	—	—	—	—	1
Cu	0.087	0.112	0.022	0.028	—	—	0.015	0.020	1.3
Mn	0.023	0.030	0.010	0.013	—	—	—	—	—
Ni	0.062	0.081	0.025	0.032	—	—	—	—	70
Pb	0.008	0.010	0.008	0.011	—	—	0.013	0.018	4.4
Zn	2.05	2.71	1.83	2.42	—	—	—	—	15
Al	0.461	0.672	0.177	0.257	1.32	1.93	0.323	0.470	—
As	0.014	0.020	—	—	0.011	0.016	—	—	—
Mo	0.001	0.002	—	—	0.003	0.004	—	—	—
Sb	0.004	0.006	—	—	0.004	0.006	—	—	—
V	0.028	0.037	—	—	0.018	0.023	—	—	100
W	0.020	0.029	—	—	0.027	0.039	—	—	—

3.2. Diffusive Boundary Layer (DBL) measurements

To accurately determine dissolved analyte concentrations using DGT techniques, it is important that the total diffusive path-length (Δg plus DBL) is known^{39, 44}. In order to determine the DBL at the sampling sites, DGT-MBL samplers with varying diffusive layer thicknesses (0.05, 0.09 and 0.13 cm, including filter membrane) were deployed in triplicate. Regression lines from plots of $1/M$ vs Δg were used to calculate the thickness of the DBL for each element (Eq. 4). Good linearity ($R^2 = 0.9761 - 0.9974$) was observed for Al, Co, Cu, Mn, As and V at Runaway Bay Marina with an average DBL thickness of 0.065 ± 0.014 cm

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determined (Figure 2). This average DBL thickness was quite similar for cations (0.065±0.017 cm) and oxyanions (0.064±0.010 cm), and is in excellent agreement with previously reported DBL thicknesses at the same locations (0.072 cm³², 0.067 cm²⁵ and 0.068 cm²⁶). Good linearity ($R^2 = 0.9581 - 0.9999$) was also observed for Al, Co, Cu, Mn, As and V at The Spit with an average DBL thickness of 0.060 ± 0.010 cm determined (Figure S2, Supplementary Information). This average DBL was also very similar for cations (0.059±0.005 cm) and oxyanions (0.063±0.019 cm). While varying DBL values for different cationic metals have been previously shown to reflect kinetic effects related to the lability of organic complexes^{6, 45, 46}, the relatively low standard deviations for the DBL thicknesses and the similarity between cations and oxyanions, indicates that such kinetic effects were not important in this study. Therefore, the average DBL thickness was used to determine the concentrations for all trace metals in this study. These DBL values are higher than those that have been reported in rivers previously⁴⁷, but this is consistent with the fact that water movement at these coastal sites will largely be due to tidal exchange, which will produce both strong currents and virtually no current at different times over the tidal cycle.

The effect of the DBL was investigated by comparing DGT measurements, with each binding layer, with and without correction for the DBL thickness. The DGT concentrations for all metals at Runaway Bay Marina and The Spit, when the DBL was not corrected for, were 70% and 73%, respectively, of the values obtained when the DBL was corrected for. This highlights the degree of underestimation associated with not accounting for the DBL. Example results for Al are shown in Table 2, which allow comparison of the differences in concentrations when corrected for the DBL thickness. These results are described in more detail in Section 3.4.

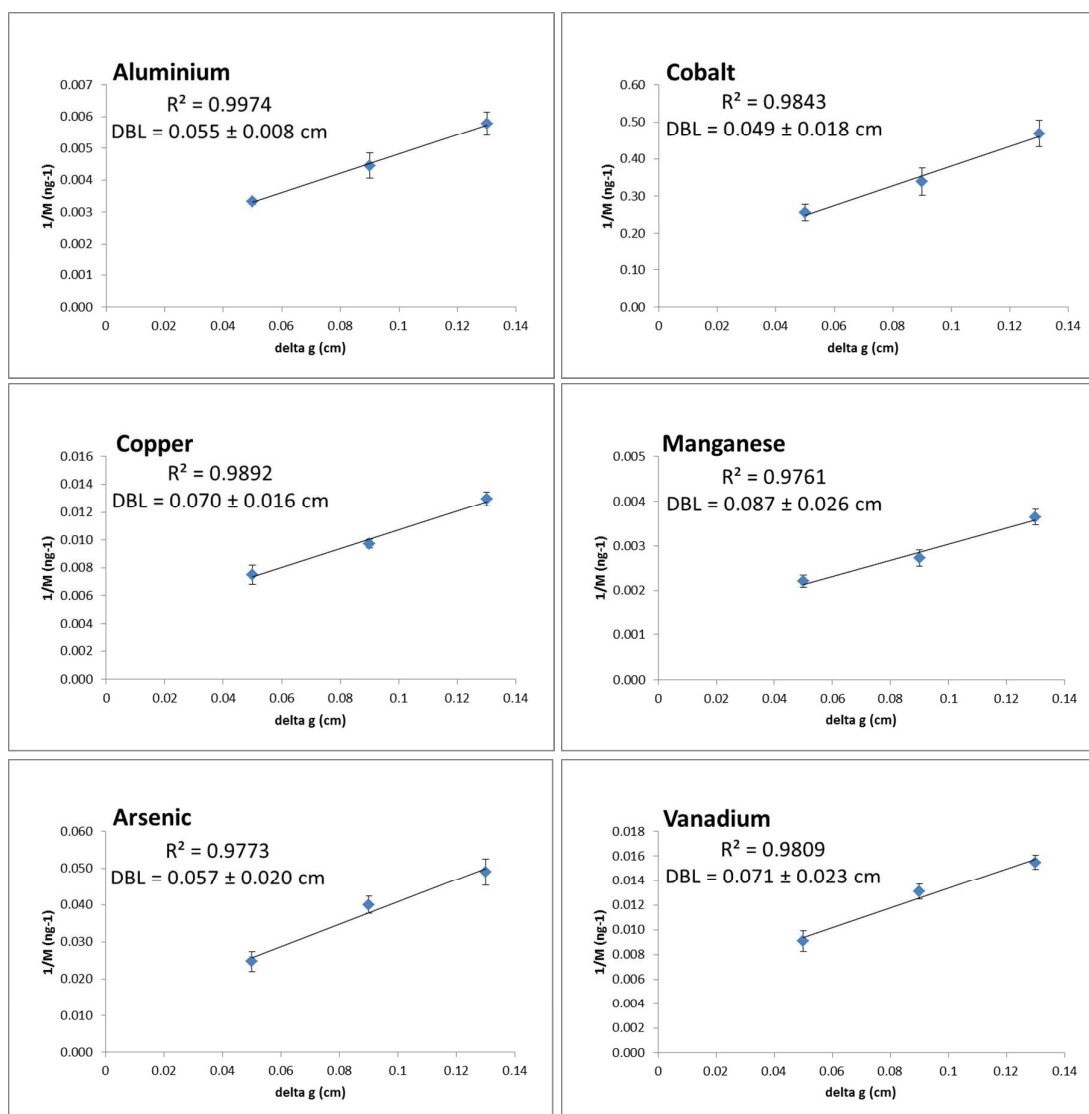


Figure 2. Plots of $1/M$ (ng^{-1}) versus diffusive layer thickness (Δg , cm) for DGT-MBL deployments at Runaway Bay Marina. Data points are mean values ($n=3$) and error bars indicate the standard deviation of the means.

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Table 2. Effect of the DBL on DGT concentrations of aluminium at Runaway Bay Marina and The Spit determined for each DGT type (MBL, Metsorb, Chelex, PAMPAA). Data are mean values \pm standard deviation of the mean.

Field Site	Binding layers	Measured Al with DBL (μgL^{-1})	Measured Al without DBL (μgL^{-1})	$C_{\text{without DBL}} / C_{\text{DBL}}$
Runaway Bay Marina	DGT-MBL	7.52 ± 0.22	5.29 ± 0.16	0.70
	DGT-Metsorb	6.13 ± 0.42	4.31 ± 0.29	
	DGT-Chelex	0.49 ± 0.08	0.35 ± 0.05	
	DGT-PAMPAA	3.81 ± 0.67	2.68 ± 0.47	
The Spit	DGT-MBL	6.50 ± 0.45	4.72 ± 0.33	0.73
	DGT-Metsorb	4.88 ± 0.25	3.54 ± 0.18	
	DGT-Chelex	0.37 ± 0.11	0.27 ± 0.08	
	DGT-PAMPAA	3.56 ± 0.42	2.58 ± 0.30	

3.3. Comparison of DGT-labile and filterable concentrations for cationic metals

DGT-labile concentrations for cations (Cd, Co, Cu, Mn, Ni, Pb, Zn) measured by DGT-MBL and DGT-Chelex, and the mean filterable concentrations over 3 days at Runaway Bay Marina and The Spit are summarised in Figure 3. DGT-PAMPAA measurements for Cu and Pb are also in Figure 3. Mean concentrations of filterable metals, collected over the course of the DGT deployments, were substantially greater than the DGT labile concentrations measured by all DGT binding layers for all cations at both sampling sites, with the exception of Mn by DGT-MBL. The DGT-labile concentrations represented only 24-41% of Cd, 12-26% of Co, 17-24% of Cu, 27-41% of Ni, 17-37% of Pb and 23-31% of Zn filterable concentrations

measured at the field sites. This observation suggests the majority of these metals existed as colloids and/or non-labile complexes which are not measured by DGT^{35, 48}.

Natural waters typically contain a wide range of complexes with different diffusion and dissociation rates. Organic complexes can dominate the speciation of many cationic metals, and the fact that DGT-labile concentrations are >10% of the filterable concentrations implies that a sizeable fraction of organic complexes are measurable. Most inorganic complexes are considered to be labile to DGT measurements, although there are some inorganic complexes that need longer times than the duration of the DGT deployments to dissociate, and are therefore non-labile^{46, 49} (see reviews by Davison and Zhang⁶, and Galceran and Puy⁴⁵, for more details). Since non-labile complexes have a low bioavailability via exposure, the DGT-labile concentrations are considered to better represent bioavailable fractions of metals than filterable concentrations in natural waters. However, it should be noted that the measured DGT-labile concentrations use the diffusion coefficients of the free metal ions, even though labile inorganic and/or organic complexes may dominate the metal speciation; this is an aspect of DGT measurements that are highly operational, especially for cationic metals. In this study, all the DGT measured metal concentrations were calculated based on the diffusion coefficients of the respective free metal ions measured by Shiva *et al.*³¹ in open or restricted diffusive gels, as appropriate; due to their larger size, organic metal complexes have lower diffusion coefficients than free metal ions and consequently these species contribute less to DGT-measured concentrations than highly labile smaller species (free metal ions and inorganic complexes). DGT measured concentrations using ODL and RDL are compared in section 3.5, as use of RDL is operationally considered to exclude or further diminish the contribution of organic complexes.

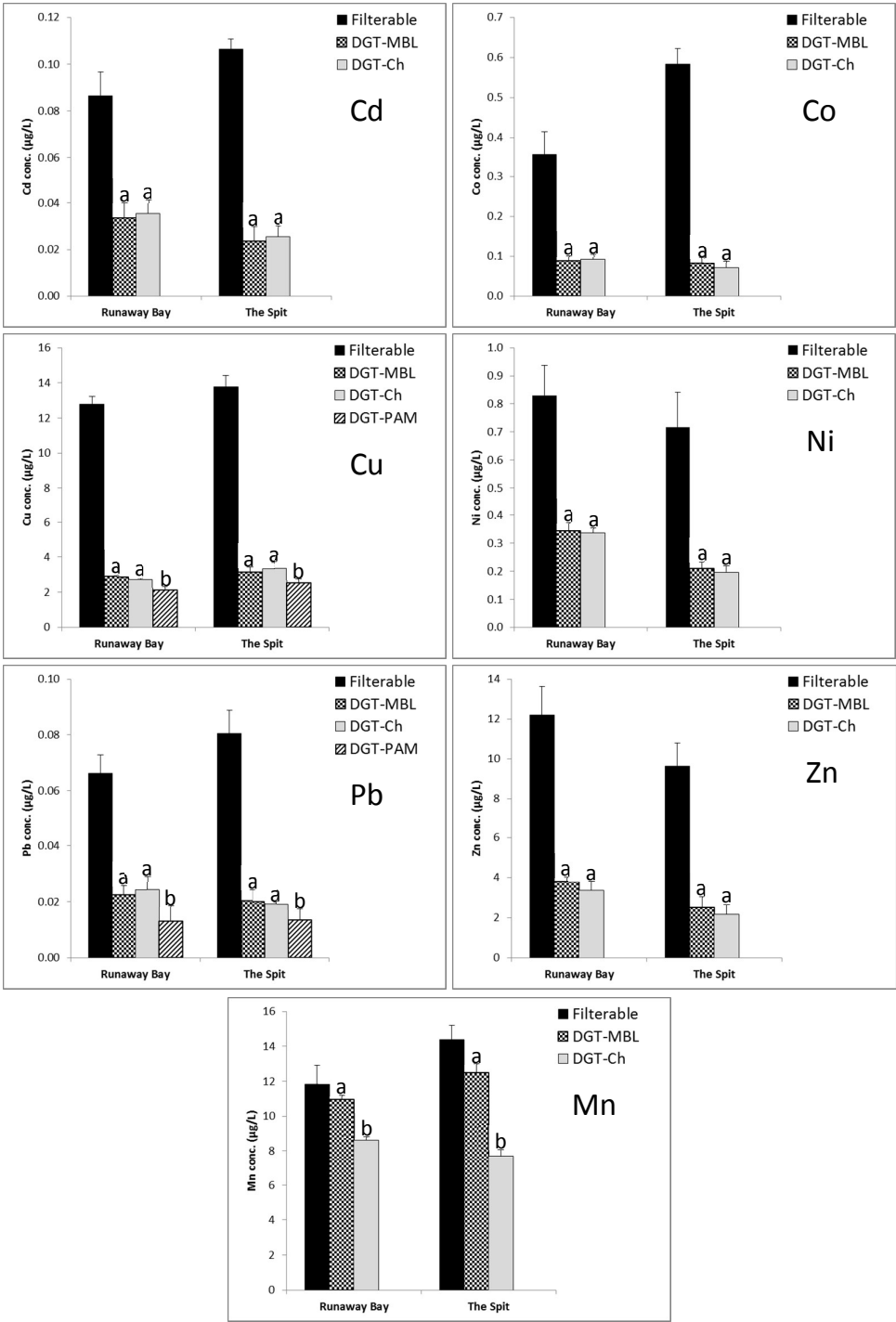


Figure 3. Comparison of labile concentrations for cations determined using DGTs with open diffusive layers and different binding layers (MBL, Chelex, PAMPAA) at two estuarine sampling sites. Columns with different letter labels indicate significantly different (<0.05) results for DGT measurements.

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392 Although the Gold Coast Broadwater is an important coastal lagoon in southeast Queensland,
393 the number of studies conducted on the environmental health of this estuary is limited ¹⁴. To
394 assess the risk of metals to the health of the environment at each of the field sites, all DGT
395 measured and filterable trace metal concentrations were compared to the ANZECC water
396 quality guidelines ⁴² for the 95% level of ecosystem protection in marine waters, where such
397 data exist (Table 1). Results indicated that Cd, Co, Ni and Pb concentrations with all
398 measurement techniques were well below trigger values at both sites. Concentration of Zn
399 measured by the DGT techniques were also well below the guidelines, however, filterable
400 concentrations of Zn were only marginally below the trigger values. Cu had concentrations
401 above the guidelines at both sampling sites with all measurement methods (approximately 10
402 times higher for grab measurements and 2 times higher for DGT measurements). Dunn *et al.*
403 ¹⁴ also reported Cu concentrations above the ANZECC guidelines at different locations
404 within the Broadwater, indicating anthropogenic inputs of Cu in the urban waterways of the
405 Broadwater. These inputs are likely due to the presence of a large number of boats, used for
406 recreational activities that use Cu-based antifouling paints ^{15,50}.

407 There were no significant differences ($p > 0.05$) between concentrations measured by DGT-
408 MBL (C_{MBL}) and DGT-Chelex (C_{Chelex}) for Cd, Co, Cu, Ni, Pb and Zn at both sampling
409 locations; $C_{\text{MBL}}/C_{\text{Chelex}}$ values ranged from 0.92 to 1.16 for all elements at both sampling
410 sites. These results indicate that DGT-Chelex and DGT-MBL measured similar ranges of
411 metal species. Panther *et al.* ³⁰ reported a similar correspondence between measurements of
412 cationic metals by DGT-Chelex and DGT-MBL during laboratory deployments in synthetic
413 seawater. Concentrations for DGT-PAMPAA were also determined for Cd, Cu and Pb,
414 although Cd was below the detection limit (Figure 3). DGT-PAMPAA measured
415 concentrations represented only 17-18% and 17-20% of the filterable concentrations of Cu

and Pb, respectively. C_{PAMPAA} concentrations were between 74 and 81% for Cu, and 54 and 70% for Pb of those of C_{Chelex} and C_{MBL} at both sites with significant differences ($p < 0.05$; values between 0.001 and 0.047). These data are in accordance with the results obtained by Li *et al.*¹⁹, where DGT-PAMPAA and DGT-Chelex were compared in coastal waters for Cd and Cu. The stability constant of Cu is reported to be higher for Chelex than for PAMPAA¹⁹, and it is therefore possible that DGT-PAMPAA measures a more selective fraction of Cu species (e.g. weaker labile complexes). Lehto *et al.*⁵¹ have discussed the effect of the stability constant of binding sites and metal-ligand complex lability on DGT metal uptake using numerical models. This is a potentially interesting result that warrants further investigation, but DGT-PAMPAA needs to be more thoroughly validated for a range of cations, especially in seawater, to ensure that the lower concentrations measured are not due to the effects of competition.

The relationship of filterable, DGT-Chelex and DGT-MBL data for Mn were different to those of other cations. Independent t-tests revealed that there was no statistical difference ($p > 0.05$) between C_{MBL} and $C_{\text{filterable}}$ at both sites, while C_{Chelex} and $C_{\text{filterable}}$ were significantly different ($p < 0.05$; values between 0.014 and 0.026). $C_{\text{DGT}}/C_{\text{filterable}}$ ratios of 0.87-0.93 were observed for DGT-MBL and 0.53-0.73 for DGT-Chelex. Ratios close to 1, especially for DGT-MBL, is not surprising as Mn tends not to readily form organic complexes and the dominant species in seawater is Mn^{2+} with some hydr(oxide) forms likely to be present as neutral species or as colloids^{52, 53}. DGT-MBL measured significantly different ($p < 0.001$) and considerably higher Mn concentrations compared to DGT-Chelex ($C_{\text{MBL}}/C_{\text{Chelex}} = 1.27$ and 1.63 at Runaway Bay Marina and The Spit, respectively). This difference in the Mn concentrations measured by DGT-MBL and DGT-Chelex will be due to Metsorb accumulating a species that Chelex does not. However, this explanation is unlikely based on the known speciation of Mn in seawater which is dominated by free metal ions⁵³; the

possibility of neutral or colloidal species binding to the MBL is discussed further in Section 3.5 using the DGT measurements with RDL. Alternatively, previous research^{30, 54} has observed underestimation of Mn in seawater with DGT-Chelex with deployment times >24 h, and proposed that this may be due to competition by Mg^{2+} and Ca^{2+} , which are present at high concentrations in seawater. Therefore, another explanation for the higher concentration measured by DGT-MBL is that Metsorb also binds Mn^{2+} quite strongly and with less interference from Mg^{2+} and Ca^{2+} . It is not possible to consider the relative contributions of the Chelex and Metsorb to MBL measurements of Mn without separate DGT-Metsorb measurements; however the DGT-MBL technique measurements appear to largely overcome the known limitations of DGT-Chelex for Mn.

3.4. Comparison of DGT-labile and filterable concentrations for oxyanionic metals

DGT-MBL and DGT-Metsorb labile concentrations of oxidized As, Sb and V, along with filterable concentrations of Sb and V, measured at Runaway Bay Marina and The Spit are summarised in Figure 4. Filterable concentrations could not be measured for As in seawater by ICP-MS due to the spectral interference with polyatomic $ArCl$ (m/z 75)⁵⁵, whereas these interferences are effectively diluted by the DGT measurements. Mo and W concentrations were below the method detection limits of DGT-MBL and DGT-Metsorb at both sampling sites. Additionally, DGT-Metsorb has been reported to be incapable of measuring Mo in synthetic seawater due to the competition between major anions and Mo ions⁴⁰. DGT measured concentrations for Sb and V were generally more similar to the mean filterable concentrations than observed with cations, as 61-79% of total filterable Sb, and 70-98% of total filterable V in both estuarine waters was DGT labile. This is consistent with these elements having a simpler speciation than cationic metals in seawater^{56, 57}; the difference in

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concentrations may be due to the presence of these elements adsorbed onto colloids in the filterable samples. DGT-MBL and DGT-Metsorb measured concentrations were consistent for As, Sb and V with no significant differences ($p > 0.05$) recorded and all ratios of $C_{\text{MBL}}/C_{\text{Metsorb}}$ in the range of 0.85 to 1.12. These results support those of Panther *et al.*³⁰, who recorded no significant differences in the concentrations of As, Sb and V determined by DGT-Metsorb and DGT-MBL in synthetic seawater, and further validate the use of DGT-MBL for measurement of these oxidized oxyanion species in natural seawaters.

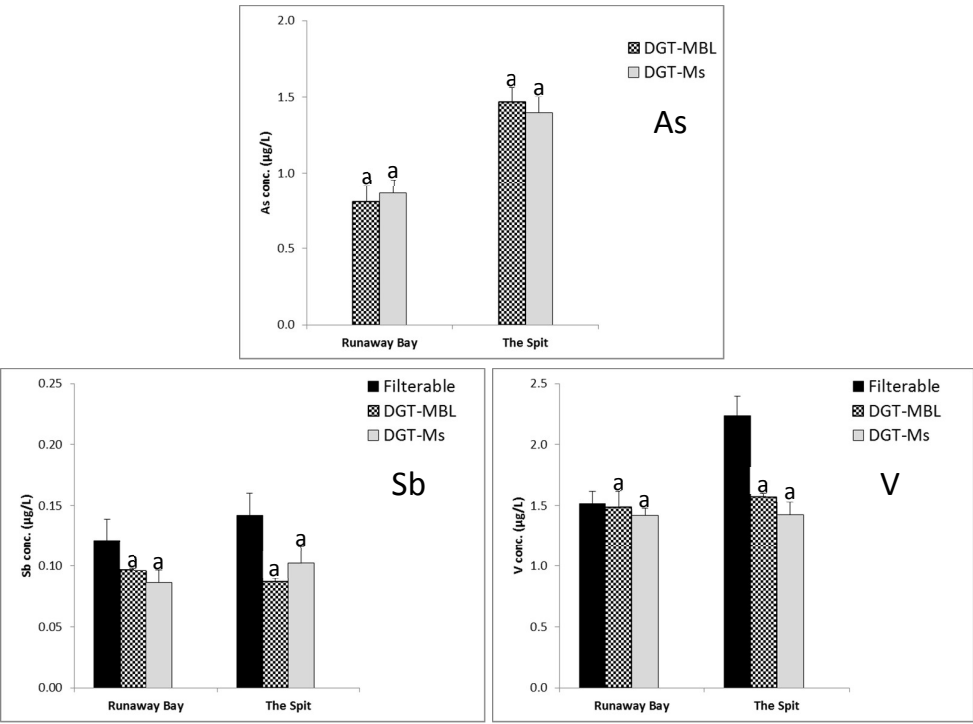


Figure 4. Comparison of labile concentrations for oxyanions determined using DGTs with open diffusive layer and two binding layers (MBL and Metsorb) at two estuarine sampling sites. Columns with same letter labels indicate no significantly different (<0.05) results for DGT measurements.

Filterable and DGT-labile concentrations of Al measured by DGT-MBL, DGT-Metsorb, DGT-PAMPAA and DGT-Chelex at Runaway Bay Marina and The Spit are shown in Figure 5. Filterable Al concentrations were higher than all of the DGT labile concentrations ($C_{\text{DGT}}/C_{\text{filterable}}$ ranged from 0.03 to 0.05 for Chelex, and 0.30 to 0.55 for the other binding layers, although DGT-MBL measured up to 70% of the filterable at Runaway Bay Marina). Al is known to associate with colloids and natural dissolved organic matter in natural waters⁵⁸, which would explain the higher filterable concentrations.

However, the dominant soluble form of Al in waters at pH >8 is $\text{Al}(\text{OH})_4^-$ (aq), which makes interpretation of the various DGT measurements interesting, as they all measured significantly different concentrations at both sites. DGT-MBL measured significantly ($p \leq 0.036$) higher concentrations of Al compared to DGT-Metsorb at both sampling sites, with ratios of $C_{\text{MBL}}/C_{\text{Ms}}$ between 1.23 and 1.33, even though DGT-Metsorb had previously been shown to accurately determine Al in synthetic seawater³². DGT-Chelex measurements were very low (6% of DGT-MBL) and significantly different ($p < 0.001$) from the measurements of other DGT binding layers, consistent with the fact that Chelex-100 is a cation exchange resin and therefore not expected to work for Al in seawater³², where the dominant species is $\text{Al}(\text{OH})_4^-$ (aq). The slight DGT-Chelex response may be due to the uptake of Al^{3+} and labile organic complexes, or due to a partial uptake of the dissociated anionic and minor neutral species. The DGT-MBL measurement, however, does not appear to be simply the sum of the DGT-Chelex and DGT-Metsorb measurements. DGT-PAMPAA measured significantly lower ($p = 0.002$ at Runaway Bay Marina and $p = 0.031$ at The Spit) concentrations of Al compared to DGT-Metsorb ($C_{\text{PAMPAA}}/C_{\text{Ms}}$ 0.62 and 0.73 at Runaway Bay Marina and The Spit, respectively). Although this DGT technique has not been validated for Al, the large difference with DGT-Chelex and relatively high uptake efficiency of PAMPAA for Al (Table

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S2) indicates that this technique merits further investigation and validation in various waters, especially seawater, using a range of Al species.

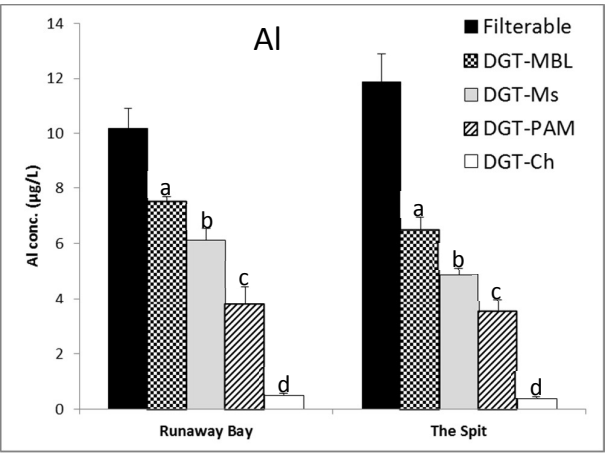


Figure 5. Comparison of labile concentrations for Al determined using DGTs with open diffusive layer and different binding layers (MBL, Metsorb, PAMPAA and Chelex) at two estuarine sampling sites. Columns with different letter labels indicate significantly different (<0.05) results for DGT measurements.

3.5. Further evaluation of the speciation of trace metals using DGT techniques

The DGT measurements using various binding layers described previously in this study used open diffusive layers (ODL). This section discusses the additional insights into selective DGT measurements of metals available by using restricted diffusive layers (RDL), something that has not been done often in natural waters. The pore sizes of ODL and RDL are different and the application of DGTs with both diffusive layer types at the same time has been reported to be useful for discriminating between organic and inorganic species of analytes in laboratory studies³³. The measured concentrations were used to determine the ratio of

520 C_{RDL}/C_{ODL} for each analyte and DGT binding type. The results are summarised in Figure 6
521 for Runaway Bay Marina and Figure S3 (Supplementary Information) for The Spit, and the
522 full range of data is provided in Tables S3 and S4 (Supplementary Information) for
523 comparison.

524 The data for Runaway Bay Marina (Figure 6) indicate that C_{RDL}/C_{ODL} values for several
525 metals (Mn, Ni, Pb, V, As, Sb) were within the range of 0.9-1.1 for all binding layers,
526 suggesting that these metals do not have substantial labile organic complexes in this coastal
527 water and the majority of the analyte masses accumulated by the DGTs were due to the
528 binding of free ions and very small labile complexes^{52, 59}. Similar outcomes were observed
529 for Mn, Pb, V and As at The Spit (Figure S3). Co, Zn and Cd at Runaway Bay Marine
530 (Figure 6) and Co, Ni, Zn, Cd and Sb at The Spit (Figure S3) had ratios in the range 0.8-0.9,
531 perhaps signifying that labile organic complexes were contributing slightly more to the DGT
532 measurements with ODL for these metals.

533 Our results are in general agreement with those of the other DGT studies in natural waters,
534 where ratios of C_{RDL}/C_{ODL} ranged from 0.6 to 1.1 for a wide range of cations³⁵ and were
535 between 0.80 and 0.89 for Cu and Ni⁶⁰. While the situation in the field is more complex than
536 for laboratory studies, these interpretations seem reasonable and are generally consistent with
537 what is known about the speciation of these metals in coastal waters, although variation in
538 measurements should also be considered to be a factor in some instances (e.g. Sb at The
539 Spit). Furthermore, the differences between these ratios (standard deviations not shown) for
540 different binding layers were not significant ($p > 0.05$) for any of these metals, indicating that
541 the DGT_{RDL} measurements with the various binding layers were also equivalent.

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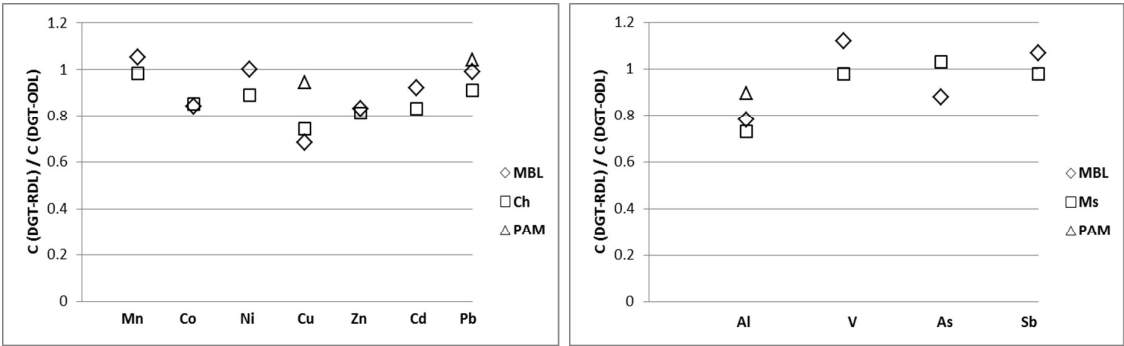


Figure 6. Ratios of DGT measurements for trace metals using different binding layers (MBL= mixed binding layer, Ch= Chelex, PAM= PAMPAA, Ms= Metsorb) with restricted (RDL) and open (ODL) diffusive layers at Runaway Bay Marina.

Significant differences ($p < 0.05$; values between 0.001 and 0.037) were only observed between RDL and ODL concentrations for Cu measured by DGT-Chelex and DGT-MBL (C_{RDL}/C_{ODL} ratio of 0.68-0.75), and Al measured by DGT-Metsorb and DGT-MBL (C_{RDL}/C_{ODL} ratio of 0.73-0.79) (Figure 7). These observations suggest that DGT measurements of Al and Cu in coastal waters using ODL include some labile organic species that are excluded or significantly retarded when using RDL. While Cu is well known to bind to organic matter in coastal waters^{48, 61}, these observations may provide new insights into speciation of Al in coastal waters, especially as determined by DGT. The greater complexity of results for Al with the various binding and diffusive layers suggests that species in addition to (or perhaps even instead of) organic complexes may be contributing to some measurements, such as colloids³⁵. For instance, the Chelex present in MBL may solubilize lattice or counterion Al^{3+} ions from very fine aluminosilicates that pass through the diffusive layers. These will then hydrolyse to $Al(OH)_4^-$ at the pH of these coastal waters and bind to Metsorb in the MBL. The relationship between DGT-Chelex, DGT-Metsorb and DGT-MBL measurements of Al with the different diffusive layers therefore requires further evaluation.

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3 563 In contrast, there were no significant differences ($p > 0.05$) in the ODL and RDL
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5 564 concentrations of Cu and Al measured by DGT-PAMPAA, with C_{RDL}/C_{ODL} ratios being
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7 565 between 0.91-0.94 for Cu and 0.88-0.90 for Al. This demonstrates that the
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9 566 exclusion/retardation of organic/inorganic complexes by RDL, which significantly influenced
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11 567 the Cu and Al concentrations measured by the other DGT binding layers, had no significant
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13 568 effect on the measurements of DGT-PAMPAA, although the ODL measurements of
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15 569 PAMPAA were slightly higher than RDL for both metals. Furthermore, there were no
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17 570 differences between the RDL measurements for Cu with DGT-MBL and DGT-Chelex and
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19 571 either of the DGT-PAMPAA measurements. This suggests that DGT-PAMPAA may largely
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21 572 measure free ions or inorganic complexes of Cu; therefore perhaps PAMPAA binding layer
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23 573 provides a more selective measurement, with only highly labile Cu complexes being
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25 574 measured, as suggested previously¹⁹. The DGT-PAMPAA technique is therefore worth
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27 575 investigating further as a measure of bioavailable Cu in particular.
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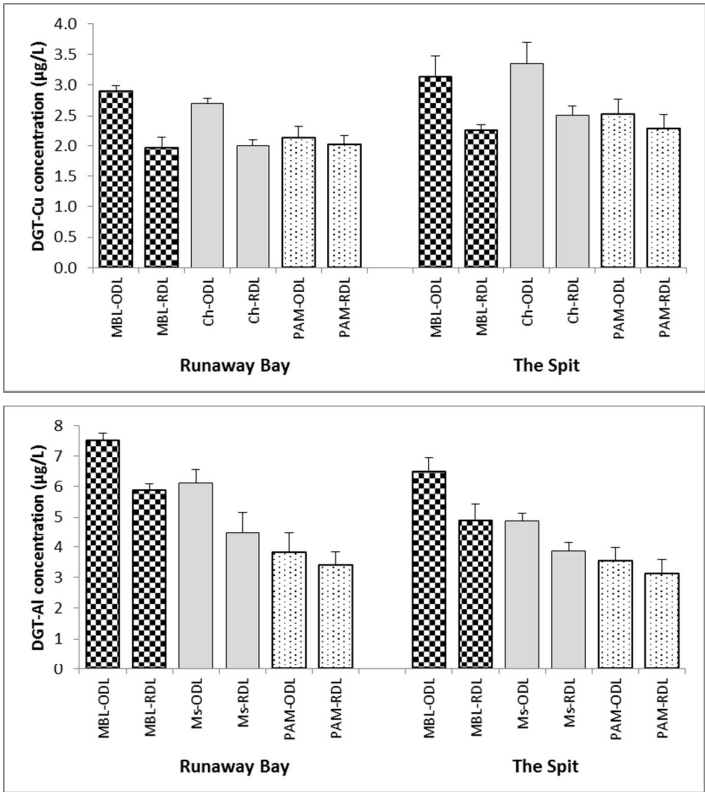


Figure 7. Labile concentrations of Cu and Al measured by DGT-MBL, DGT-Chelex (Ch), DGT-Metsorb (Ms) and DGT-PAMPAA (PAM) with open (ODL) and restricted (RDL) diffusive layers.

4. Conclusion

It is of great importance to evaluate any new DGT binding layer in saline waters, which is one of the most difficult and challenging matrixes in the environment. This complex matrix is characterised by the presence of high concentrations of potentially competing ions and natural ligands, both of which can interfere with DGT measurements. This study provides the first evaluation of DGT-MBL (Chelex-Metsorb) in natural seawaters for simultaneous measurement of cations and oxyanions. The results obtained were also compared with three other DGT types (DGT-Chelex, DGT-Metsorb and DGT-PAMPAA).

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3 593 The concentrations obtained for DGT-MBL agreed very well with DGT-Chelex for cationic
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5 594 trace metals (Cd, Co, Cu, Ni, Pb and Zn), and with DGT-Metsorb for oxyanionic metals (As,
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7 595 Sb and V), as reported by Panther *et al.*³⁰ for laboratory evaluations in synthetic seawater.
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9 596 This consistency between binding layers was observed regardless of the diffusive layer used.
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11 597 However, significant differences were observed between DGT-MBL and DGT-Chelex for
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13 598 Mn, with the most likely explanation being that use of MBL overcomes the known
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15 599 limitations of DGT-Chelex for Mn. The fact that DGT-MBL measurements were very close
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17 600 to the filterable Mn concentrations supports this interpretation. Al also gave different results
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19 601 between DGT-MBL and other binding layers (see below). Overall, these findings validate use
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21 602 of the DGT-MBL technique in natural saline waters and confirm that the DGT-MBL method
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23 603 provides a more versatile alternative to DGT-Chelex and DGT-Metsorb due to its ability to
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25 604 simultaneously measure both cationic and anionic trace metal species using a single sampler.
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27 605 DGT-PAMPAA, measured lower concentrations of Al, Cu and Pb compared to DGT-MBL
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29 606 and DGT-Chelex. We propose that DGT-PAMPAA may have the capability to measure
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31 607 selectively the fraction of metals that are not bound to other organic/inorganic complexes,
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33 608 especially for Cu. Since carboxylic acid functional groups play a significant role for metal
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35 609 complexation in PAMPAA binding layers¹⁸, and these functional groups are often present at
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37 610 sites of biological uptake, it might be useful to compare DGT-PAMPAA measurements with
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39 611 metal bioaccumulation in future studies to determine whether it provides better information
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41 612 on metal bioavailability in the environment, compared to other DGT techniques.
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48 613 This study also investigated the capability of DGT techniques as a speciation tool in coastal
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50 614 waters by using different binding and diffusive layers to vary the selectivity of measurements.
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52 615 The overall results suggest that although the use of DGT samplers with a restricted diffusive
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54 616 layer (DGT_{RDL}) will theoretically result in accumulation of mostly free ions and inorganic
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56 617 complexes, the situation is more complicated with in situ deployments. The ratio of RDL to
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618 ODL measurements was effectively 1 for Mn, Pb, V and As at both sites, indicating the
619 presence of no labile organic ligands. Cd, Co and Zn had ratios of 0.8-0.9 at both sites
620 suggesting that labile organic ligands were present and contributing to the DGT measurement
621 with ODL. The results for Ni and Sb varied with ratios of about 1 at Runaway Bay Marine
622 and ratios of 0.8-0.9 at The Spit. A ratio of about 0.7 between RDL and ODL measurements
623 was found for Cu using DGT-MBL and DGT-Chelex, and Al using DGT-MBL and DGT-
624 Metsorb, which indicates that labile organic complexes make a substantial contribution to
625 ODL measurements of these metals. These results were generally consistent with what is
626 known about the speciation of these metals in coastal waters and therefore do not contradict
627 the previous operational observations that DGT measurements using RDL are mostly of free
628 metals and inorganic complexes, while measurements using ODL can also include labile
629 organic complexes.

630 A ratio of about 1 was obtained between ODL and RDL measurements of DGT-PAMPAA
631 for Cu though, with the concentrations similar to the RDL measurements for the other
632 binding layers. This suggests that DGT-PAMPAA measures only inorganic complexes and
633 free Cu, which would be an important finding and needs to be investigated further. The
634 results for Al were also very interesting with significant differences observed between
635 measurements with MBL, Metsorb, PAMPAA and Chelex binding layers, with
636 concentrations decreasing in this order, and often between ODL and RDL also. These results
637 indicate that selective Al measurements by DGT are very complex and require further
638 detailed investigation.

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Acknowledgements

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