

DGT Measurement of Dissolved Aluminium Species in Waters: Comparing Chelex-100 and Titanium Dioxide-Based Adsorbents

*Jared G. Panther, William W. Bennett, Peter R. Teasdale, * David T. Welsh and Huijun Zhao*

Environmental Futures Centre, Griffith University, Gold Coast campus, QLD 4222, Australia

*Corresponding Author: p.teasdale@griffith.edu.au

Abstract

Aluminium is acutely toxic and elevated concentrations of dissolved Al can have detrimental effects on both terrestrial and aquatic ecosystems. Robust analytical methods that can determine environmentally relevant Al fractions accurately and efficiently are required by the environmental monitoring community. A simple, robust passive sampling method, the diffusive gradients in thin films (DGT) technique, was evaluated for the measurement of dissolved Al species in freshwater and marine water using either Chelex-100 or Metsorb (a titanium dioxide-based binding agent) as the adsorbent. Mass vs. time DGT deployments at pH 5.05 (Al^{3+} and $\text{Al}(\text{OH})^{2+}$ dominate) and 8.35 ($\text{Al}(\text{OH})_4^-$ dominates) demonstrated linear uptake of Al ($R^2 = 0.989$ and 0.988 , respectively) for Metsorb. Similar deployments of Chelex-DGT showed linear uptake at pH 5.05 ($R^2 = 0.994$), however, at pH 8.35 the mass of Al accumulated was 40-70% lower than predicted, suggesting that Chelex-100 is not suitable for Al measurements at high pH. The Metsorb-DGT measurement was independent of pH (5.0-8.5) and ionic strength (0.001-0.7 mol L⁻¹ NaNO₃), whereas the Chelex-DGT measurement was only independent of ionic strength at pH 5.0. At pH 8.4, increasing ionic strength led to considerable underestimation (up to 67%) of Al concentration. Deployments of Metsorb-DGT (up to 4 days) in synthetic freshwater (pH range 5.4-8.1) and synthetic seawater (pH 8.15) resulted in linear mass uptakes and the concentration measured by DGT agreed well with solution concentrations. Conversely, deployment of Chelex-DGT in synthetic seawater and freshwater (pH ≥ 7.7 $\text{Al}(\text{OH})_4^-$ dominant species) resulted in a decrease in accumulated mass with increasing deployment time. *In situ* field evaluations in fresh, estuarine and marine waters confirmed that Metsorb-DGT was more accurate than Chelex-DGT for the measurement of dissolved Al in typical environmental waters.

Introduction

The mining, refining and fabrication of aluminium (Al) often produce point sources of primary Al pollution.⁽¹⁾ However, Al is also a major component of natural soil minerals that can be mobilised as a secondary pollutant by anthropogenic acidification processes.⁽²⁻⁴⁾ Acidification of surface waters and soils is a serious environmental problem that has led to widespread, harmful ecological effects in both Europe and North America,⁽⁵⁻⁷⁾ and is of increasing concern in many parts of China.⁽⁸⁻¹⁰⁾ The mobilisation of Al resulting from acidification can have detrimental effects on both terrestrial and aquatic ecosystems.⁽²⁻⁴⁾

The environmental impact of Al is governed by its speciation rather than the total element concentration.^(3, 11) The monomeric forms of dissolved Al present at low pH (e.g. Al^{3+} , $\text{Al}(\text{OH})^{2+}$ and $\text{Al}(\text{OH})_2^+$)^(1, 3, 4, 11) are considered toxic, whereas, complexation of dissolved Al species by organic matter has been shown to ameliorate toxicity.^(3, 4, 12-14) The toxicity of $\text{Al}(\text{OH})_4^-$, the dominant Al species present in alkaline waters,^(1, 3, 4, 11) remains unclear and evidence has been presented that both supports and rejects toxic effects.^(4, 15-19) Generally, $\text{Al}(\text{OH})_4^-$ is considered less toxic than the monomeric forms of Al.^(4, 17) In the pH range 6.0-7.5, Al is relatively insoluble and is most commonly present as gibbsite ($\text{Al}(\text{OH})_3(\text{s})$), but many other mineral phases can also form.^(1, 3)

Analytical methods that are capable of determining environmentally relevant Al fractions (e.g. bioavailable or toxic fractions), rather than total Al, are highly desirable. Although there are established protocols for collection and storage of natural waters, it is often difficult to maintain the original sample composition prior to speciation analysis of Al in the laboratory.^(11, 20) Using on-site or *in situ* speciation techniques lessens sample handling and eliminates the need for sample storage, reducing the risk of contamination and alleviating problems associated with preservation and storage of samples.^(1, 20) The *in situ* diffusive gradients in thin film (DGT) technique^(21, 22) is one such option that has been utilized to measure Al in soils and natural waters.⁽²³⁻³⁰⁾

The DGT technique is a time-integrated, passive sampling method that utilizes an adsorbent, immobilized in a polyacrylamide gel (i.e. binding gel), to selectively accumulate labile species from water, soil or sediment.^(21, 22) The DGT binding gel is separated from the sampling solution by a well-defined gel layer (diffusive layer) that controls the overall rate of mass transport from the bulk solution to the binding gel. Both gels are housed within a plastic device (collectively called a DGT sampler). The DGT sampler is deployed for times typically ranging from 1 to 4 days. During the sampling period, analyte species diffuse from the bulk solution through the diffuse layer and are accumulated by the binding gel. After the deployment time, the analyte is extracted from the binding gel and measured, allowing the time-averaged concentration of analyte in the bulk solution to be calculated using the DGT equation.⁽²²⁾

Chelex-100 has been the binding phase of choice for accumulating divalent and trivalent cations,^(22, 30, 31) whereas ferrihydrite and, more recently, zirconium oxide and titanium dioxide-based (Metsorb) binding phases have been employed for determining oxyanionic species.⁽³²⁻⁴²⁾ DGT has been extensively appraised for many analytes over broad pH and ionic strength ranges that encompass those encountered in most natural waters, however, a complete laboratory evaluation of DGT for the measurement of Al has never been undertaken. Nevertheless, DGT has been used frequently for measuring labile Al species in laboratory solutions and *in situ*.⁽²³⁻³¹⁾ Much of the DGT development for Al has been driven by specific research interests and, as a result, has narrowly focused on answering immediate research questions rather than providing a general evaluation of the technique. Sondergaard⁽²⁶⁾ utilized Chelex-DGT for the measurement of Al in waters affected by acid mine drainage and, as a consequence, evaluated DGT response over a relatively narrow pH range (2.5-4.5). In another specific study carried out by Garmo and co-workers,⁽³¹⁾ Chelex-DGT was evaluated for a range of metals (including Al) in acidic surface waters between pH 4.7 and 5.9. To date, the performance of DGT for measuring Al above pH 5.9 has not been systematically studied. In fact, there have been no laboratory evaluations for DGT measurement of Al above pH 7.0 or in high ionic strength

matrices such as seawater. Despite this, Chelex-DGT has been used to measure Al in both freshwater and seawater above pH 7.0.^(27, 29, 30)

The current study is an evaluation of DGT for the measurement of dissolved Al in water, with a focus on extending the range of conditions in which the Chelex-DGT method for measurement of Al has been characterised, and to evaluate the Metsorb binding layer for the DGT measurement of Al. Metsorb-DGT has proven to be a useful *in situ* tool for the measurement of As, Se and P oxyanion species in both freshwater and seawater.⁽³⁵⁻³⁷⁾ A series of laboratory experiments were carried out initially to evaluate the Chelex- and Metsorb-DGT techniques over pH (4.0-8.5) and ionic strength (0.001-0.7 mol L⁻¹ NaNO₃) ranges typical of natural waters. This was followed by time-series investigations of the performance of both DGT binding layers in synthetic freshwater and seawater, and a field evaluation at freshwater, estuarine and marine sites.

Experimental

Reagents, materials and solutions. Deionised water (Milli-Q Element) was used to prepare all solutions. A 1000 mg L⁻¹ Al stock solution was prepared by dissolving Al(NO₃)₃·9H₂O in 2% (v/v) HNO₃ (Baseline, High Purity Standards). All experimental components were acid-cleaned in 10% (v/v) HNO₃ (AR grade, Merck) for at least 24 h and rinsed thoroughly with deionised water prior to use.

Gel preparation. Procedures for the preparation of diffusive gels were similar to that described previously.⁽²²⁾ Metsorb (Graver Technologies, DE, USA) binding gels were prepared according to Bennett *et al.*⁽³⁵⁾ The DGT capacity of the Metsorb binding gel for P and As has been reported to be 1.19 µmol/DGT sampler⁽³⁷⁾ and 1.09 µmol/DGT sampler,⁽⁴²⁾ respectively. Chelex-100 (Bio-Rad, 200-400 mesh, sodium form) binding gels were prepared according to Zhang and Davison⁽²²⁾ using 2 g of dry adsorbent per 10 mL of gel solution. Further details are provided in the supporting information (SI). The Metsorb binding agent was cleaned prior to use to lower the Al blank value (see SI).

Aluminium solution preparation. Aluminium solutions were carefully prepared to prevent formation of insoluble $\text{Al}(\text{OH})_{3(s)}$. A 10 mg L^{-1} unacidified Al standard, prepared daily via dilution of a 1000 mg L^{-1} Al stock solution, was used to spike all experimental solutions. Solution pH was adjusted using dilute HNO_3 or NaOH . Prior to immersion of DGT binding gels or deployment of DGT samplers, the experimental solutions were left to equilibrate for 72 h.

DGT deployment. DGT samplers were supplied by DGT Research Ltd. and were assembled as described previously.⁽²²⁾ A $0.45 \mu\text{m}$ cellulose nitrate membrane filter (Millipore) was used to protect the diffusive gel and was pre-cleaned as detailed previously.⁽³⁶⁾ For laboratory experiments, DGT samplers were deployed in polyethylene containers in 2-7 L of well-mixed solution. The pH, temperature and, if required, conductivity/salinity of the deployment solution were monitored daily. Samples of the experimental solution were removed at the beginning of each experiment and when DGT samplers were retrieved. Samples were filtered ($0.22 \mu\text{m}$), acidified to 2% (v/v) HNO_3 and stored at $<4^\circ\text{C}$ in the dark until analyzed.

Elution. Chelex-100 binding gels were eluted in 1 mL of 1 mol L^{-1} HNO_3 for 24 h (elution efficiency = $84 \pm 5\%$) and Metsorb binding gels were eluted in 1.5 mL of 1 mol L^{-1} NaOH for 24 h (elution efficiency = $85 \pm 3\%$). For synthetic seawater experiments and field deployments, the Metsorb binding gels were rinsed in 50 mL of 0.001 mol L^{-1} HNO_3 for 1 h (to remove salts associated with the binding gel) followed by 5 mL of deionised water for 1 h, prior to elution with NaOH .

Calculation of the DGT concentration. The DGT-measured concentration (C_{DGT} , ng mL^{-1}) of Al in solution was calculated using eq 1:⁽²²⁾

$$C_{\text{DGT}} = \frac{M\Delta g}{DtA} \quad (1)$$

where M (ng) is the mass of Al diffused through the diffusive layer of thickness, Δg (cm), after sampling time, t (s), and D ($\text{cm}^2 \text{s}^{-1}$) and A (cm^2) are the diffusion coefficient of Al and the area of the sampling window exposed to solution, respectively. The effective diffusion coefficient of Al was measured at pH 5.15 and 8.35 using DGT samplers and determined to be $(4.36 \pm 0.40) \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ and $(5.38 \pm 0.38) \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, respectively, at 25 °C. For seawater and high ionic strength ($0.7 \text{ mol L}^{-1} \text{ NaNO}_3$) deployments a value of $0.9 \times D$ was used.⁽²¹⁾

Sample analysis. Aluminium measurements were performed using an inductively coupled plasma mass spectrometer (ICP-MS, Agilent 7500a). All ICP-MS samples and standards were prepared in a 2% (v/v) HNO_3 matrix. Quality control standards at $10 \mu\text{g L}^{-1}$ were analyzed every 20-30 samples. Scandium was added to all samples (final concentration of $10 \mu\text{g L}^{-1}$) as an internal standard to account for instrument drift.

Speciation calculations. Visual MINTEQ ver. 3.0. was used for all speciation calculations, using the default database constants and assuming amorphous $\text{Al}(\text{OH})_{3(\text{s})}$ was the dominant solid phase.

Laboratory evaluation. *Uptake and elution efficiencies.* Uptake and elution efficiencies were measured by immersing Chelex-100 and Metsorb binding gel discs (4.91 cm^2) in 4.5 mL solutions (prepared in $0.01 \text{ mol L}^{-1} \text{ NaNO}_3/0.005 \text{ mol L}^{-1}$ sodium acetate at pH 4.8 or $0.01 \text{ mol L}^{-1} \text{ NaNO}_3/0.005 \text{ mol L}^{-1} \text{ NaHCO}_3$ at pH 8.4) ranging in Al concentration from 20 to $200 \mu\text{g L}^{-1}$; this was carried out in triplicate for each binding gel at each Al concentration. After 24 h the gels were removed, eluted and analyzed. Samples of the uptake solutions were also analyzed (after acidification) to determine the mass of Al remaining in solution. The mass of adsorbed Al, and thereby the uptake and elution

efficiencies of Al were calculated by difference. Elution efficiencies were also measured in the same manner for Metsorb gels immersed in synthetic seawater containing Al. Synthetic seawater was prepared according to Grasshoff *et al.*⁽⁴³⁾ and was spiked with 100 $\mu\text{g L}^{-1}$ Al; pH was adjusted to 8.30.

Time-series Accumulation. The accumulation of Al by Chelex-DGT and Metsorb-DGT was evaluated at pH 5.05 (0.002 mol L⁻¹ NaNO₃/0.0005 mol L⁻¹ sodium acetate) and pH 8.35 (0.002 mol L⁻¹ NaNO₃/0.0005 mol L⁻¹ NaHCO₃) for 8 to 97 h in a 20 $\mu\text{g L}^{-1}$ Al solution.

pH and Ionic Strength. Chelex-DGT and Metsorb-DGT samplers were deployed in Al solutions (50 $\mu\text{g L}^{-1}$) of varying pH (4.0-8.5; 0.002 mol L⁻¹ NaNO₃) for 9-10 h; solutions at pH 4, 5 and 6 were buffered with 0.0005 mol L⁻¹ sodium acetate and solutions at pH 7.5, 8 and 8.5 were buffered with 0.0005 mol L⁻¹ NaHCO₃. The effect of ionic strength was investigated by deploying DGT samplers in Al solutions (50 $\mu\text{g L}^{-1}$) of varying ionic strength (0.01-0.7 mol L⁻¹ NaNO₃) at pH 5.0 (0.0005 mol L⁻¹ sodium acetate) and pH 8.4 (0.0005 mol L⁻¹ NaHCO₃) for 9-10 h.

Synthetic Freshwater and Synthetic Seawater. DGT samplers were deployed in synthetic freshwater (at pH 5.4, 6.1, 7.7, 7.9 and 8.1) and synthetic seawater (pH 8.15) for four days to evaluate the performance of the binding gels. The composition of the synthetic freshwater was similar to that described by Langmuir⁽⁴⁴⁾ and contained either 10 $\mu\text{g L}^{-1}$ Al (for pH 5.4 and 6.1) or 20 $\mu\text{g L}^{-1}$ Al (for pH 7.7, 7.9 and 8.1). The synthetic seawater was prepared according to Grasshoff *et al.*⁽⁴³⁾ and contained 20 $\mu\text{g L}^{-1}$ Al. Composition of the synthetic waters is given in the SI.

Field Evaluation. DGT samplers were deployed at three field sites in Queensland, Australia. A freshwater river (Coomera River, Oxenford), a tidal estuary (Jabiru Island) and a large marina (Runaway Bay Marina) located on the Gold Coast Broadwater, a coastal lagoon. Nine Metsorb-DGT samplers containing varying diffusive layer thicknesses ($\Delta g = 0.05$ cm, 0.09 cm, 0.13 cm; all deployed in triplicate) and three Chelex-DGT samplers ($\Delta g = 0.09$ cm), were deployed at each site 30 cm

beneath the water surface for four days. Temperature, pH and conductivity/salinity were measured daily on-site, and 0.45 µm filtered grab samples were collected daily, along with unfiltered samples for total Al measurements. These water samples were stored at <4 °C in the dark until analyzed. Grab samples were acidified to 2% HNO₃ after filtration. At the completion of the deployment, DGT samplers were rinsed thoroughly on-site with deionised water, placed in acid-washed plastic bags and stored at <4°C until elution.

The thickness (δ) of the solution diffusive boundary layer (DBL) and the concentration of Al in solution was calculated according to Warnken *et al.*⁽⁴⁵⁾ using eq 2. When the thickness of the DBL was incorporated into the DGT calculations, a value of 3.80 cm² was used for the sampling area, A .⁽⁴⁵⁾

$$\frac{1}{M} = \frac{\Delta g}{DC_{\text{DGT}} At} + \frac{\delta}{DC_{\text{DGT}} At} \quad (2)$$

Results and Discussion

Uptake and Elution Efficiencies. At pH 4.8, the uptake efficiencies were >98% (n=21) for both Chelex-100 and Metsorb, and at pH 8.4 the corresponding uptake efficiencies were 85±5% (n=21) and 95±3% (n=42), respectively, over the mass range investigated (90-900 ng Al taken up). The Chelex-100 elution efficiency using 1 mol L⁻¹ HNO₃ was 84±3% (n=42) and the Metsorb elution efficiency using 1 mol L⁻¹ NaOH was 86±4% (n=63).

Elution efficiencies were also determined for Metsorb gels immersed in synthetic seawater spiked with Al. It has been reported that direct elution (with 1 mol L⁻¹ NaOH) of Metsorb gels that have been exposed to seawater results in significantly lower elution efficiencies.⁽³⁶⁾ This effect was attributed to the precipitation of Mg and Ca hydroxides and/or carbonates upon elution, encapsulating the binding agent and preventing elution of the analyte. Panther *et al.*⁽³⁶⁾ utilized a pre-elution wash step to improve phosphate recovery from 48% (without washing) to 85% (with washing). In the present work, the

elution efficiency for unwashed Metsorb gels that had been loaded with Al in synthetic seawater was $20\pm 6\%$ ($n=5$) (Table S1). However, when the same pre-elution wash procedure as detailed in Panther *et al.*⁽³⁶⁾ (gel washed in 5 mL of water for 1 h followed by elution in 1 mol L^{-1} NaOH) was followed an elution efficiency of only $52\pm 4\%$ ($n=5$) was achieved prompting alternative pre-elution washing procedures to be investigated (Table S1). Optimum elution efficiency ($85\pm 6\%$; $n=5$) was obtained when the Metsorb binding gels were washed in 50 mL of $0.0001 \text{ mol L}^{-1}$ HNO₃ for 1 h followed by 5 mL of water for 1 h.

Time-series Accumulation at pH 5.05. The mass of Al accumulated by DGT increased linearly for both Metsorb ($R^2=0.9894$) and Chelex-100 ($R^2=0.9944$) and the accumulated mass was in good agreement with the predicted mass of Al (dashed line in Figure 1). The relative standard deviations (RSDs) for triplicate DGT deployments were generally $<15\%$ and $<10\%$ for Metsorb and Chelex-100, respectively. Based on the data presented in Figure 1, the effective diffusion coefficients of Al through the polyacrylamide diffusive gel at pH 5.05 were $4.51\pm 0.31 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ and $4.20\pm 0.25 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ (corrected to 25°C)⁽²²⁾ for the Metsorb- and Chelex-DGT samplers, respectively. The good agreement between the two diffusion coefficients allowed an average value ($4.36\pm 0.40 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$) to be calculated. This value agrees quite well with those reported by others ($4.65\text{-}5.10 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ at 25°C).^(24, 31) At pH 5.05, the major Al species predicted in the experimental solution (modelled using Visual Minteq) were Al³⁺ (43% of total Al), Al(OH)²⁺ (38%) and Al(OH)₂⁺ (18%), and hence, the diffusion coefficient calculated in the present work is an effective diffusion coefficient.

Time-series Accumulation at pH 8.35. Figure 1b shows the time-series uptake of Al by Metsorb-DGT and Chelex-DGT at pH 8.35. Even though the mass of Al accumulated by Metsorb-DGT increases linearly with time ($R^2=0.9883$), the accumulated mass was 10-30% greater than the predicted accumulated mass (dotted line in Figure 1b). Hence, the effective diffusion coefficient of Al calculated

from the Metsorb data is $(5.38 \pm 0.38) \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ at 25 °C, which is 20% higher than that calculated at pH 5.05. The discrepancy in Al diffusion coefficients measured at pH 5.05 and 8.35 is probably due to differences in the degree of hydration of the Al species. The extent of hydration depends on the size of the ion and charge density.⁽⁴⁶⁾ Furthermore, cations tend to be more strongly hydrated than anions due to high positive charge density and stronger interactions with the negatively polarised oxygen of water;⁽⁴⁶⁾ ions with larger hydration spheres tend to diffuse more slowly.⁽⁴⁷⁾ At pH 8.35, Al will predominately be present as the negatively charged $\text{Al}(\text{OH})_4^-$ species which should be less strongly hydrated than the +3 and +2 charged species present at pH 5.05 (Al^{3+} and $\text{Al}(\text{OH})^{2+}$). Thus, the size of the diffusing Al species at pH 8.35 can be expected to be smaller than the sizes of the diffusing Al species at pH 5.05, producing a comparatively higher Al diffusion coefficient at pH 8.35.

The Chelex-DGT data at pH 8.35 (Figure 1b) shows that the mass of Al accumulated is 40-70% lower than the mass of Al accumulated by Metsorb-DGT; the exception is for the 8 h deployment in which the mass of Al accumulated by Metsorb-DGT and Chelex-DGT agree within 15%. These results clearly show that Chelex-DGT is not operating as expected at pH 8.35 for deployment times >8 h and that the use of Chelex-DGT to measure Al in solution at pH values in which the dominant Al species is negatively charged ($\text{Al}(\text{OH})_4^-$) requires further investigation.

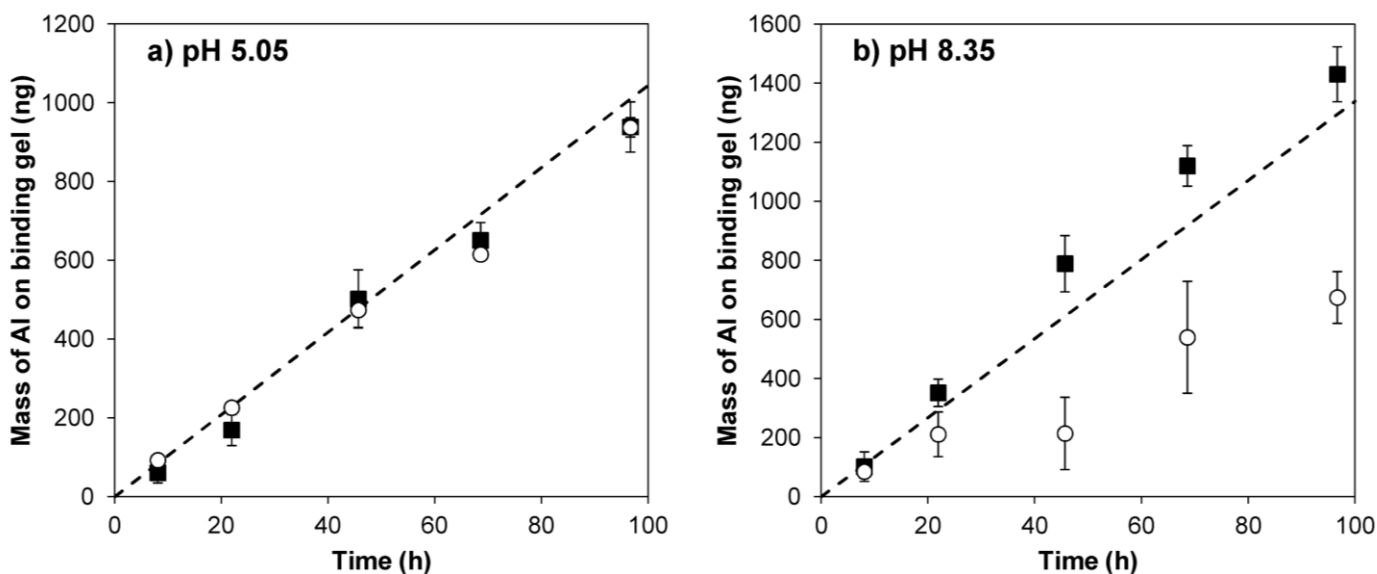


Figure 1: Mass of Al accumulated by Metsorb-DGT (■) and Chelex-DGT (○) samplers at a) pH 5.05 and b) pH 8.35, as a function of time ($20 \mu\text{g L}^{-1}$ Al in 0.002 mol L^{-1} NaNO_3). The dashed line represents the predicted accumulated mass of Al calculated using the DGT equation and $D = 4.75 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ ($25 \text{ }^\circ\text{C}$).⁽³¹⁾ The uncertainty associated with each point in this and subsequent figures represents the S.D. of the mean ($n = 3$).

Effect of pH. The concentration of Al determined by Chelex-DGT agreed well with the dissolved Al concentration over the pH range 4.0-8.0 ($C_{\text{DGT}}/C_{\text{Sol}} = 0.99-1.18$; Figure S1). At pH 8.5 the fraction of Al measured by Chelex-DGT was appreciably less than 1 ($C_{\text{DGT}}/C_{\text{Sol}} = 0.63$). This is further evidence to support the notion that Chelex-DGT is incapable of quantitatively measuring Al at $\text{pH} > 8.0$ where negatively charged $\text{Al}(\text{OH})_4^-$ is the dominant species.

The concentration of Al determined by Metsorb-DGT between pH 5.0 and 8.5 is in good agreement with the dissolved Al concentration ($C_{\text{DGT}}/C_{\text{Sol}} = 0.95-1.1$). At pH 4.01, $C_{\text{DGT}}/C_{\text{Sol}}$ was 0.70 ± 0.03 indicating lower uptake of Al by Metsorb. The point of zero charge of titanium dioxide (the active binding groups of Metsorb) has been estimated to be between pH 5.5-6.5,^(48, 49) and it is likely that uptake of positively charged Al species (Al^{3+} and $\text{Al}(\text{OH})^{2+}$) by Metsorb will be diminished at pH

4.0 due to the positive character of the adsorbent. Adsorption of positively charged Al species and other cations onto titanium dioxide has been reported to be reduced at $\text{pH} < 5$.^(50, 51)

At pH 4.01 and 5.02 the Al species are soluble as indicated by good agreement between the amount of Al added and the amount of Al measured after 0.22 μm filtration. At pH 6.05, Al precipitated out of solution, presumably as amorphous $\text{Al}(\text{OH})_{3(\text{s})}$, and the concentration of Al measured in solution ($3.5 \mu\text{g L}^{-1}$) was only 7% of the total Al added. Good agreement between the concentration of Al measured by both DGT methods at pH 6.05, and also with the concentration of Al measured directly in solution, shows that only the dissolved Al fraction is DGT reactive and that the colloidal or particulate fraction of Al does not contribute to the DGT measurement.

Effect of Ionic Strength. The concentration of Al measured by Metsorb-DGT showed good agreement with the solution concentration over the ionic strength range investigated ($0.001\text{-}0.7 \text{ mol L}^{-1} \text{ NaNO}_3$) at both pH 5.0 and 8.4 (Table 1), indicating that the measurement of Al by Metsorb-DGT is independent of ionic strength. For Chelex-DGT at pH 5.0, $C_{\text{DGT}}/C_{\text{Sol}}$ ratios between 0.85-1.07 were obtained across the ionic strength range. However, at pH 8.4, $C_{\text{DGT}}/C_{\text{Sol}}$ decreased as ionic strength increased. For these short deployment times ($\sim 10 \text{ h}$) at pH 8.4 (where $\text{Al}(\text{OH})_4^-$ accounts for $>99.9\%$ of total dissolved Al forms), ionic strength significantly affects the uptake of Al by Chelex-DGT. These results clearly demonstrate that the measurement of Al by Chelex-DGT is critically dependent on both pH and ionic strength and that the Chelex-DGT method may not be applicable to all natural waters, especially seawater, for the measurement of Al.

Table 1: Effect of ionic strength on measurement of Al by Metsorb DGT and Chelex-DGT at pH 5.0 and 8.4.

pH	Ionic Strength		
	(mol L ⁻¹ NaNO ₃)	$C_{DGT-Metsorb}/C_{Sol}$	$C_{DGT-Chelex}/C_{Sol}$
5.00 ± 0.10	0.001	1.05 ± 0.07	0.98 ± 0.04
	0.01	1.06 ± 0.06	1.07 ± 0.06
	0.1	0.96 ± 0.09	0.85 ± 0.17
	0.7	1.05 ± 0.08	1.05 ± 0.15
8.40 ± 0.05	0.001	0.97 ± 0.10	0.83 ± 0.04
	0.01	1.05 ± 0.13	0.76 ± 0.16
	0.1	1.00 ± 0.03	0.62 ± 0.06
	0.7	1.12 ± 0.06	0.24 ± 0.11

*Uncertainties associated with C_{DGT}/C_{Sol} values are derived from replicate DGT and grab sample measurements.

Deployment of DGT in Synthetic Freshwater and Synthetic Seawater. Metsorb-DGT and Chelex-DGT were deployed in synthetic freshwaters at pH 5.4, 6.1, 7.7, 7.9 and 8.1 for up to four days (Figure 2). Predicted Al speciation in the synthetic freshwaters is shown in Table 2. Over the entire pH range investigated, the mass of Al accumulated by Metsorb-DGT agreed well with the predicted mass (see Figure 2a-e) and the Metsorb-DGT concentrations were in good agreement with grab sample concentrations (C_{DGT}/C_{Sol} ratios between 0.87-1.09; see Table 3). These results show that Metsorb-DGT is capable of measuring all Al species (Al^{3+} , $Al(OH)^{2+}$, $Al(OH)_2^+$, $Al(OH)_3(aq)$ and $Al(OH)_4^-$) present in the synthetic freshwater in the pH range 5.4-8.1. It should be noted that there is a slight underestimation of the Al concentration at pH 5.4 (13% at $t=72$ h; 12% at $t=98$ h), however, the authors consider this to be acceptable for a field-based analytical method. Similarly, at pH 5.4 and 6.1 for Chelex-DGT, good agreement was obtained between the predicted and accumulated Al mass (Figure 2a-b) with C_{DGT}/C_{Sol} ratios ranging from 1.00-1.23 (Table S3). These results indicate quantitative uptake of Al in synthetic freshwater at $pH \leq 6.1$ and are in good agreement with those of Garmo and co-

workers⁽³¹⁾ who also found quantitative uptake of Al by Chelex-DGT over a 72 h sampling period between pH 4.7 and 5.9.

However, in the present study, Chelex-DGT did not operate as expected at pH 7.7, 7.9 and 8.1 with C_{DGT}/C_{Sol} ratios significantly less than 1.0 (Table S3 and Figure 2c-d). In fact, the mass of Al accumulated by DGT decreased with deployment time, indicating possible replacement of Al on the Chelex-100 binding gel by major cations and/or anions in solution. At pH 8.1, the mass of Al accumulated by Chelex-DGT samplers deployed for 72 and 98 h was lower than the mass of Al associated with the blank DGT value, again suggesting replacement of Al on the adsorbent by other ions in solution. Other researchers have reported non-quantitative uptake of Al at high pH when using Chelex-100.⁽⁵²⁻⁵⁴⁾ Riley and Taylor⁽⁵²⁾, Kozuh *et al.*⁽⁵³⁾ and Pesavento *et al.*⁽⁵⁴⁾ all reported low or no uptake of Al ($Al(OH)_4^-$) by Chelex-100 above pH 7.5. Furthermore, a previous DGT study reported that Chelex-DGT measurements were 80% of the actual Al concentration at pH 7.0, which was attributed to the formation of insoluble $Al(OH)_3(s)$ species.⁽²³⁾ However, it is entirely possible that the lower than predicted uptake was also due to the presence of a small amount of $Al(OH)_4^-$ in solution, which was not accumulated by Chelex-DGT.

It is interesting to note that although the ionic strength (0.002 mol L^{-1} total ions) of the synthetic freshwaters were similar to the experiment illustrated in Figure 1b (pH 8.35; $0.002 \text{ mol L}^{-1} \text{ NaNO}_3$), it is apparent that the Chelex-DGT method is underestimating the Al concentration to a greater extent in the synthetic freshwater compared to the NaNO_3 solution over similar time scales and total Al concentrations. For example, at pH 8.35 in $0.002 \text{ mol L}^{-1} \text{ NaNO}_3$, $C_{DGT-Chelex}/C_{Sol}$ ranged from 0.78-0.49, whereas for the synthetic freshwater at pH 7.9 and 8.1, $C_{DGT-Chelex}/C_{Sol}$ ranged from 0.59-0.05 and 0.04-0, respectively. This is further evidence that major ions in the synthetic freshwater (e.g. Ca^{2+} , Mg^{2+} , Cl^- , SO_4^{2-}), that are not present in the simple NaNO_3 matrix, may be affecting uptake of Al by Chelex-DGT.

It is clear from the data presented in Figure 2 and Table S3 that both pH and deployment time influence the measurement of Al by Chelex-DGT; increasing pH and deployment time results in a decrease in the C_{DGT}/C_{Sol} ratio. Generally, these results indicate that both Metsorb-DGT and Chelex-DGT can be used to quantitatively measure Al in acidic freshwaters between pH 5.4 and 6.1, but only Metsorb-DGT is able to accurately measure Al in freshwaters above pH 7.7 where the dominating Al species is $Al(OH)_4^-$. DGT samplers were also deployed in synthetic seawater (salinity= 36.2 ± 0.8) at pH 8.15 for up to four days (Figure S2). Good agreement was obtained between the concentration of Al measured by Metsorb-DGT and that measured directly in solution, as reflected by C_{DGT}/C_{Sol} ratios in the range 0.96-1.13. However, for Chelex-DGT, the mass of Al measured on the adsorbent after 24, 48, 72 and 96 h was less than the mass of Al on a blank Chelex-100 binding gel.

It should be noted that in some cases meaningful data has been obtained when using Chelex-DGT to measure dissolved Al in natural waters above pH 7.0.^(29, 30) Sherwood and co-workers^(29, 30) measured DGT-labile concentrations of Al, amongst other metals, from a deep sea tailings outfall, however the pH of these waters are not clearly stated and it is possible that the DGT samplers were exposed to low pH water dominated by the tailings, thus, influencing uptake of Al by the Chelex resin. In another study, Warnken *et al.*⁽³⁰⁾ showed that above pH 7.0 DGT-measured Al concentrations were much less than dissolved concentrations for some, but not all, freshwaters investigated. This discrepancy could not be explained by slower diffusion of organically complexed Al (speciation calculated using WHAM program) and was attributed to either an underestimation of the calculated fraction of complexed Al (as a result of lower $Al(OH)_{3(s)}$ solubility than predicted) or the presence of colloidal Al. The data of Warnken *et al.*⁽³⁰⁾ are also consistent with lower uptake of dissolved Al, especially $Al(OH)_4^-$, by Chelex-DGT at high pH, as observed in the current study.

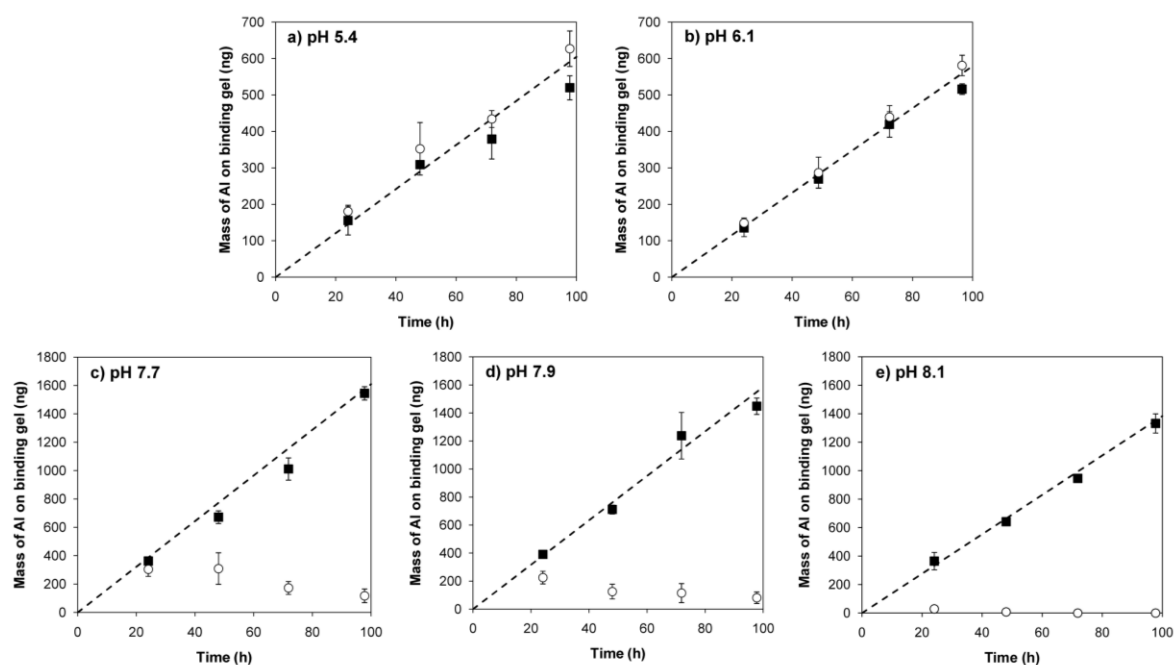


Figure 2: Mass of Al accumulated by Metsorb-DGT (■) and Chelex-DGT (○) samplers deployed in synthetic freshwater at a) pH 5.4, b) pH 6.5, c) pH 7.7, d) pH 7.9, and e) pH 8.1, as a function of time. The dashed line represents the predicted accumulated mass of Al calculated using the DGT equation and $D = 4.36 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ at pH 5.4 and 6.1 or $5.38 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ at pH 7.7, 7.9 and 8.1. Conductivity of freshwaters was $206 \pm 11 \mu\text{S cm}^{-1}$.

Table 2: Al speciation in synthetic freshwaters as predicted by Visual Minteq

<i>% of Al Species Present in Synthetic Freshwater</i>						
<i>Al concentration</i> ($\mu\text{g L}^{-1}$)	<i>pH</i>	Al^{3+}	$Al(OH)^{2+}$	$Al(OH)_2^+$	$Al(OH)_3(aq)$	$Al(OH)_4^-$
10.7	5.4	18.7	36.8	40.2	3.9	0.4
10.2	6.1	0.9	9.2	50.2	24.1	15.6
22.6	7.7	-	-	0.2	3.70	96.1
22.4	7.9	-	-	0.1	2.4	97.5
20.3	8.1	-	-	-	1.5	98.5

Table 3: C_{DGT}/C_{Sol} values for Metsorb-DGT and Chelex-DGT (in parentheses) samplers deployed in synthetic freshwaters (pH 5.4-8.1). Uncertainties have been omitted for clarity but were generally within 15% of the C_{DGT}/C_{Sol} value .

<i>pH</i>	Time (h)			
	24	48	72	98
5.4	1.06 (1.23)	1.06 (1.14)	0.87 (1.00)	0.88 (1.06)
6.1	0.97 (1.07)	0.95 (1.02)	1.00 (1.05)	0.92 (1.04)
7.7	0.94 (0.79)	0.87 (0.40)	0.87 (0.15)	0.98 (0.07)
7.9	1.02 (0.59)	0.93 (0.17)	1.07 (0.06)	0.93 (0.05)
8.1	1.09 (0.04)	0.97 (0.01)	0.95 (<0.01)	0.98 (<0.01)

Field Evaluation. Measurement of Al by DGT was evaluated *in situ* at three field sites: Coomera River (freshwater), Jabiru Island (marine) and Runaway Bay Marina (marine). Metsorb-DGT samplers were deployed with varying diffusive layer thicknesses ($\Delta g = 0.05$ cm, 0.09 cm, 0.13 cm) so that the DBL could be estimated, whereas Chelex-DGT samplers were deployed with a single diffusive layer thickness ($\Delta g = 0.09$ cm).

The $1/\text{mass}$ (ng^{-1}) versus Δg (cm) plots for Metsorb-DGT (Figure 3) show good linearity ($R^2 = 0.9788-0.9995$), allowing accurate calculation of both Al concentration and DBL thickness (δ). The $C_{DGT-Metsorb}$ values for Runaway Bay Marina and Jabiru Island are in reasonable agreement with the average $0.45 \mu\text{m}$ filtered measurements obtained from grab samples ($C_{Sol(0.45 \mu\text{m})}$) as shown in Table 3. The small underestimation of the Al concentration by DGT may be due to Al associated with sub- $0.45 \mu\text{m}$ colloids which are not DGT reactive, or a result of complexation of Al by organic matter which would slow diffusion of Al to the binding layer. For Runaway Bay Marina and Jabiru Island, $C_{Sol(0.45}$

μm) was 62% and 70% of the total Al measurement, indicating that a significant amount of Al was bound to particulate material $>0.45 \mu\text{m}$ in size. The deployment of Chelex-DGT at both Runaway Bay Marina and Jabiru Island resulted in lower Al masses than blank DGT samplers, as observed for deployments in artificial seawater, again indicating that ions present in the seawater were able to displace bound Al. For the freshwater Coomera River, $C_{\text{Sol}(0.45 \mu\text{m})}$ was 24% of the total Al measurement, again indicating a substantial fraction of Al is associated with particulate material $>0.45 \mu\text{m}$. The $C_{\text{DGT-Metsorb}}$ value was 58% of $C_{\text{Sol}(0.45 \mu\text{m})}$, demonstrating that a significant fraction of dissolved Al is associated with sub- $0.45 \mu\text{m}$ colloids that are not DGT reactive and/or significant complexation of Al by organic matter. The concentration of Al measured by Chelex-DGT was only 36% of the Metsorb-DGT value and the RSD was 35%. The Chelex-DGT technique performed marginally better for the freshwater field deployment ($C_{\text{DGT-Chelex}}/C_{\text{DGT-Metsorb}} = 0.36$; $t=4$ days) than the corresponding synthetic freshwater deployment at pH 7.7 in the laboratory ($C_{\text{DGT-Chelex}}/C_{\text{DGT-Metsorb}} = 0.08$; $t=4$ days). The pH of the freshwater Coomera River was 7.47 ± 0.14 , which is ~ 0.2 pH units below the synthetic freshwater. This work has shown that the uptake of Al by Chelex-DGT is critically dependent upon pH and it is possible that the higher uptake of Al by Chelex-DGT observed for the Coomera River site is a result of the lower pH. However, Chelex-DGT still significantly underestimated the dissolved concentration of Al for this site.

The thickness of the DBLs for Runaway Bay Marina, Jabiru Island and Coomera River were 0.072 ± 0.006 cm, 0.052 ± 0.016 cm and 0.011 ± 0.002 cm, respectively. The flow of water at Coomera River was substantially faster than at both Jabiru Island and Runaway Bay Marina as reflected by the smaller DBL calculated for this site. The DBL calculated for Runaway Bay Marina (0.072 ± 0.006 cm) was in excellent agreement with previously calculated DGT DBLs at the same location (0.068 ± 0.006 cm⁽³⁶⁾ and 0.067 ± 0.007 cm⁽³⁵⁾). If the DBL was not accounted for then the concentration of Al measured by the Metsorb-DGT at Runaway Bay Marina, Jabiru Island and Coomera River would have been underestimated by 33%, 37% and 10%, respectively. As expected, the degree of underestimation

of analyte concentration is more pronounced for those sites that have larger DBLs (Runaway Bay Marina and Jabiru Island) than the site with a smaller DBL (Coomera River).

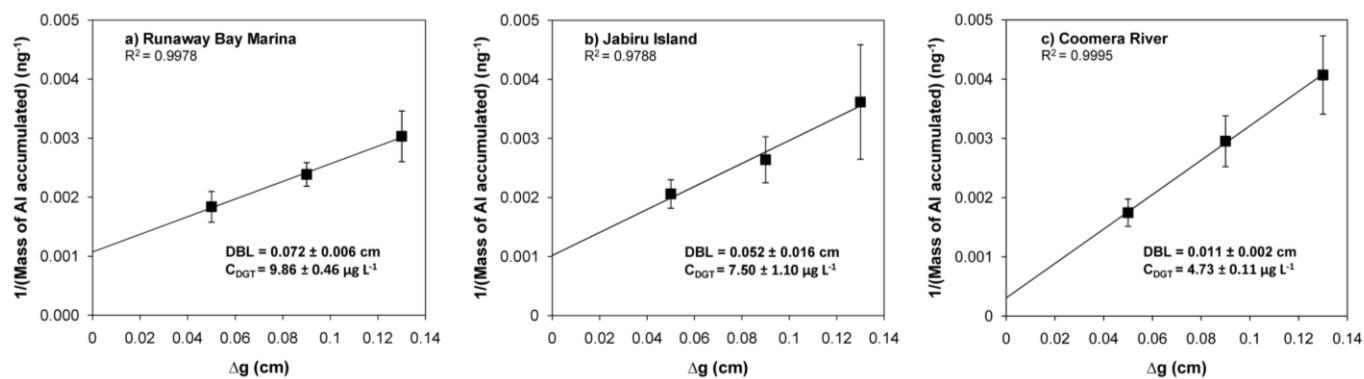


Figure 3: Plot of $1/\text{Mass of Al}$ (ng^{-1}) accumulated by Metsorb-DGT versus diffusive layer thickness (Δg ; cm) for a) Runaway Bay Marina, b) Jabiru Island and c) Coomera River.

Table 3. Physical Parameters and Comparison of Al concentrations ($\mu\text{g L}^{-1}$) for Runaway Bay Marina, Jabiru Island and Coomera River Field DGT Deployments

	Runaway Bay Marina	Jabiru Island	Coomera River
pH	8.04 ± 0.06	8.01 ± 0.03	7.47 ± 0.14
Salinity	31.0 ± 0.2	30.0 ± 1.4	-
Conductivity ($\mu\text{S cm}^{-1}$)	-	-	200 ± 4
Temperature ($^{\circ}\text{C}$)	28.6 ± 0.5	30.0 ± 1.4	26.0 ± 1.9
$C_{\text{Sol (UF)}}^{\text{a}}$	18.1 ± 4.2	11.8 ± 2.3	33.5 ± 6.2
$C_{\text{Sol (0.45 } \mu\text{m)}}^{\text{b}}$	11.2 ± 0.8	8.3 ± 0.6	8.1 ± 1.5
$C_{\text{DGT-Metsorb}}^{\text{c}}$	9.9 ± 0.5	7.5 ± 1.1	4.7 ± 0.1
$C_{\text{DGT-Metsorb}}/C_{\text{Sol}}^{\text{d}}$	0.88 ± 0.08	0.91 ± 0.07	0.91 ± 0.07
$C_{\text{DGT-Chelex}}^{\text{e}}$	-	-	1.7 ± 0.6

^a Average Al concentration from unfiltered grab samples.

^b Average Al concentration from 0.45 μm filtered grab samples.

^c Calculated from eq. 4 using slope of plots from Figure 3 and $A = 3.80 \text{ cm}^2$.

^d $C_{\text{DGT-Metsorb}}/C_{\text{Sol (0.45 } \mu\text{m)}}$

^e Calculated from eq 1 using $A = 3.80 \text{ cm}^2$ and the calculated DBL.

General evaluation of Metsorb-DGT and Chelex-DGT. This is the first time that the utility of the DGT technique for the measurement of Al in both freshwater and in seawater has been comprehensively investigated. The speciation of Al in solution is complex with often large changes in speciation occurring with only a small change in solution pH. To understand the measurement of Al species by the DGT technique a wide range of conditions were employed resulting in one of the most comprehensive DGT validations ever undertaken.

The Chelex-DGT and Metsorb-DGT methods proved to be useful *in situ* sampling methods for the determination of dissolved Al in synthetic freshwaters at $\text{pH} \leq 6.1$ and therefore show promise as analytical tools for monitoring Al in waters affected by acidic deposition. Metsorb-DGT was also

shown to accurately measure dissolved Al in freshwaters above pH 7.7 and in seawater where the predominant Al species is predicted to be Al(OH)_4^- . Conversely, Chelex-DGT considerably underestimated the dissolved Al concentration in freshwaters above pH 7.5 and in seawater to such a degree that the utility of Chelex-DGT as a monitoring tool for Al should seriously be reassessed.

Although Al(OH)_4^- is considered to be much less toxic than the monomeric forms of Al present at low pH, the indirect toxicity of Al(OH)_4^- to fish has been recognised.^(4, 13) Water pH within the gill microenvironment can be substantially lower than that in the bulk solution, causing essentially non-toxic Al(OH)_4^- to polymerize and precipitate on the gill surface, causing respiratory dysfunction.^(3, 4) Analytical techniques that are able to accurately measure Al at high pH (e.g. Metsorb-DGT method) would be useful for determining the potentially toxic pool of Al in alkaline waters and assessing risk to aquatic animals and plants.

This study has shown the importance of a comprehensive laboratory evaluation of new and existing DGT techniques prior to their application in the field. The Chelex-DGT technique has been used for monitoring Al *in situ* without a detailed laboratory investigation and this study has highlighted some of the issues that may be encountered if prior evaluation is not carried out carefully. As stated earlier, the authors appreciate that Chelex-DGT has been used by researchers to measure Al in freshwaters and seawater above pH 7.0 and in some cases meaningful data has been obtained. Further research will be carried out to ascertain the effects that major anions and cations have on the Chelex-DGT and Metsorb-DGT measurement. High concentrations of iron (Fe) can also be found in waters affected by acidification processes.^(55, 56) Consequently, Fe may compete with Al for binding sites on the Metsorb binding gel leading to saturation of the adsorbent, resulting in non-theoretical uptake of Al by Metsorb-DGT. Further work will investigate Fe as a possible interfering species for the uptake of Al by Metsorb-DGT. Furthermore, the capacity of each adsorbent to bind Al at high and low pH will be examined and experiments will be carried out to assess the utility of Metsorb-DGT to measure labile Al in waters where complexation of Al by organic and inorganic ligands is significant.

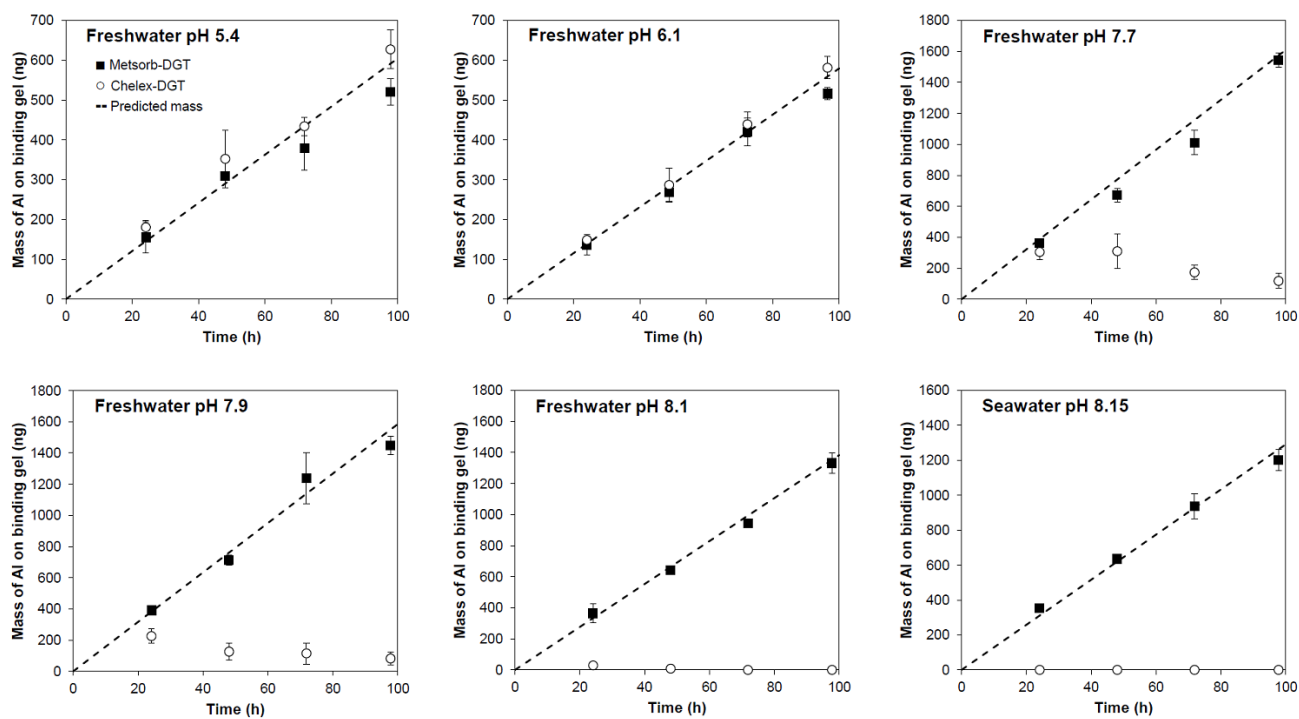
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Supporting Information Available

This information is available free of charge via the Internet at <http://pubs.acs.org>.

TOC Art



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