

**Determining time-weighted average concentrations of nitrate and
ammonium in freshwaters using DGT with ion exchange membrane-based
binding layers**

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Table S1. The recipe of synthetic freshwater in 8 L (pH = 7.20 ± 0.05 and conductivity = 0.23 mS cm^{-1}).

Synthetic freshwater with different ionic strengths were prepared by proportionally changing the concentrations of ions (e.g. $0.080 \text{ mS cm}^{-1} = \frac{2}{5}$ the amount of the ions in the new recipe, $0.40 \text{ mS cm}^{-1} =$ approximately $2 \times$ the amount). Finally, the concentration of HCO_3^- was $<2 \text{ mmol L}^{-1}$ to maintain the pH (7.0 ± 0.5).

Chemicals	Concentration (mmol L^{-1})
$\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$	0.375
Na_2SO_4	0.115
KCl	0.058
NaCl	0.229
$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$	0.294
HCO_3^-	0.983

AMI and CMI membranes had high uptake and elution efficiencies for NO₃-N and NH₄-N, respectively.

Table S2. Comparison of the uptake and elution efficiencies for binding membranes and hydrogels.

Binding agents	AMI	A520E ¹	CMI	PrCH ²
Uptake efficiency (%)	96.7 ± 3.3	98.7 ± 1.4	94.8 ± 2.3	92.5 ± 5.1
Elution efficiency (%)	77.6 ± 6.1	82.7 ± 4.2	89.9 ± 4.6	87.2 ± 5.3

The ratios of $C_{\text{AMI-DGT}}/C_{\text{SOLN}}$ and $C_{\text{CMI-DGT}}/C_{\text{SOLN}}$ were between 0.87 and 1.06, suggesting that the binding layer membranes produced similar results to the resin binding gels.

Table S3. Comparison of the uptake of binding membranes and hydrogels for different pH.

pH	$C_{\text{AMI-DGT}}/C_{\text{SOLN}}$	$C_{\text{A520E-DGT}}/C_{\text{SOLN}}$	$C_{\text{CMI-DGT}}/C_{\text{SOLN}}$	$C_{\text{PrCH-DGT}}/C_{\text{SOLN}}$
3.5	0.87 ± 0.02	0.94 ± 0.04	0.89 ± 0.07	1.02 ± 0.06
5	0.91 ± 0.06	0.92 ± 0.11	0.95 ± 0.07	0.95 ± 0.08
7	1.01 ± 0.03	1.00 ± 0.02	0.91 ± 0.03	0.99 ± 0.05
8.5	0.93 ± 0.06	0.89 ± 0.03	0.90 ± 0.03	1.06 ± 0.03

Similar NH₄⁺ diffusion coefficients were found in CMI-DGT and PrCH-DGT.² Mass of accumulated NH₄-N on CMI-DGT decreased with increasing conductivity (Figure S3). High diffusion coefficient of NH₄⁺ was found at low ionic strength (conductivity) and decreased with increasing conductivity (Figure S2).

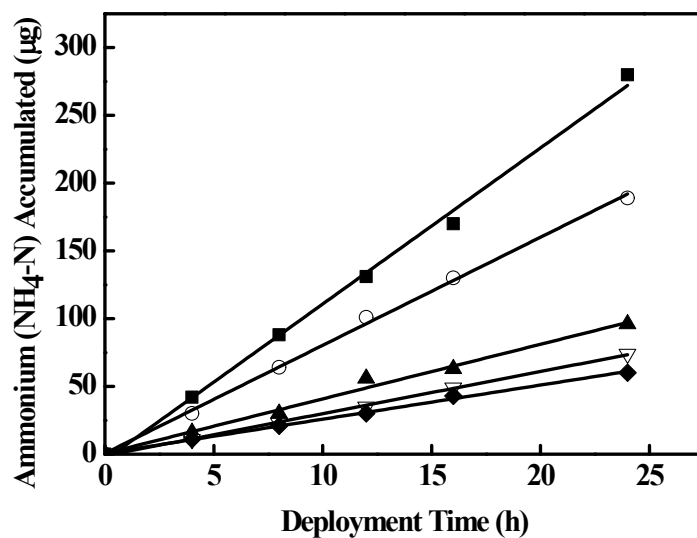


Figure S1. Mass of $\text{NH}_4\text{-N}$ accumulated by CMI-DGT over 24 h at various ionic strength solutions. The solid line is a regression line. Experimental conditions: $\text{NH}_4\text{-N} = 1.5 \pm 0.21 \text{ mg L}^{-1}$; conductivity = $0.0855 \pm 0.001 \text{ mS cm}^{-1}$ (○), $0.203 \pm 0.029 \text{ mS cm}^{-1}$ (∞); $0.469 \pm 0.019 \text{ mS cm}^{-1}$ (◻); $0.683 \pm 0.016 \text{ mS cm}^{-1}$ (♦); $1.0 \pm 0.023 \text{ mS cm}^{-1}$ (⊕).

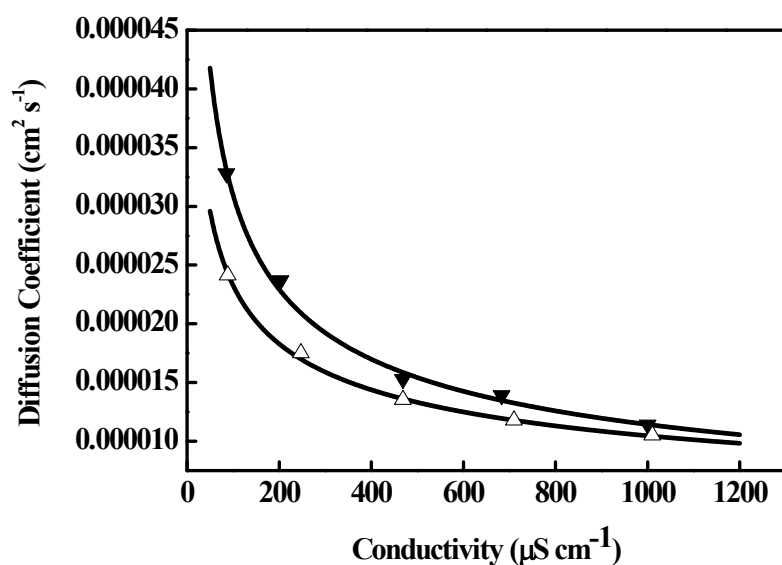


Figure S2. Relationship between the diffusion coefficient of $\text{NH}_4\text{-N}$ and conductivity for CMI-DGT (\square) and PrCH-DGT (\triangle) using an agarose diffusive layer. Data were modified according to the Stokes-Einstein equation to 25 °C. $\text{pH} = 7.07 \pm 0.44$. The trend line for the exponential relationship between diffusion coefficient (D) and conductivity for CMI-DGT was $R^2 = 0.9979$, $D = 0.000115 \text{ Conductivity}^{-0.346833}$ and PrCH-DGT was $R^2 = 0.9918$, $D = 0.000227 \text{ Conductivity}^{-0.432705}$.

Table S4. The corresponding D values of CMI-DGT and PrCH for NH_4^+ at different conductivity (0.0001, 0.001 and 0.01 mol L^{-1} NaCl).

Conductivity ($\mu\text{S cm}^{-1}$)	22	141	1108
D values (10^{-5})			
CMI	3.93	2.07	1.01
PrCH	5.96	2.67	1.09

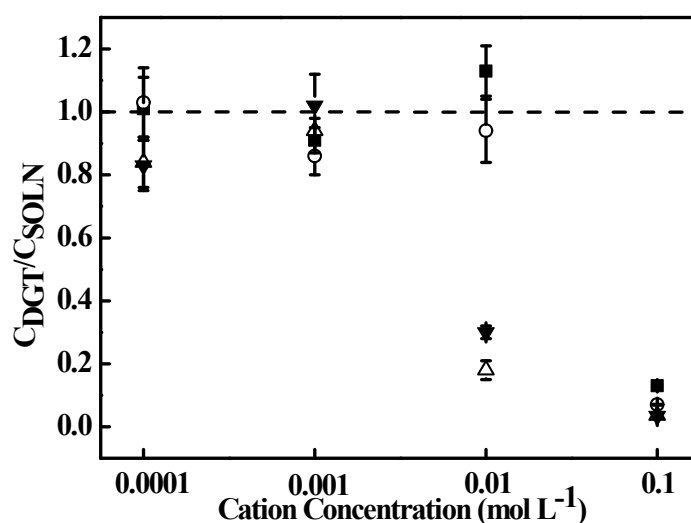


Figure S3. Effects of different concentrations of Na⁺ (○), K⁺ (△), Ca²⁺ (□) and Mg²⁺ (◇) on NH₄-N uptake by CMI-DGT. Data are mean values (n = 3) ± 1 standard deviation. Experimental conditions: NH₄-N concentration = 1.5 ± 0.1 mg L⁻¹; time = 24 h; pH = 7.0 ± 0.37 for 0.0001 - 0.1 mol L⁻¹ Na⁺, K⁺, 0.0001 - 0.001 Ca²⁺ and Mg²⁺, pH = 5.9 ± 0.28 for 0.01 - 0.1 mol L⁻¹ Ca²⁺ and Mg²⁺.

$C_{DGT}:C_{SOLN}$ for NH₄-N was between 0.84 and 1.03 at 0.0001 - 0.001 mol L⁻¹ of Na⁺, K⁺, Ca²⁺ and Mg²⁺. $C_{DGT}:C_{SOLN}$ was 1.13 and 0.94 at 0.01 mol L⁻¹ Na⁺ and K⁺, respectively. As the ionic strength increased, the $C_{DGT}:C_{SOLN}$ ratio for NH₄-N tended to decrease in the presence of all cations. At 0.01 mol L⁻¹ Ca²⁺ and Mg²⁺, $C_{DGT}:C_{SOLN}$ ratio was only 0.18 and 0.30, respectively. CMI-DGT was not quantitative at 0.1 mol L⁻¹ for any of the cations.

Membrane DGTs have high binding capacities for $\text{NO}_3\text{-N}$ ($921 \pm 88 \mu\text{g}$) and $\text{NH}_4\text{-N}$ ($3512 \pm 51 \mu\text{g}$).

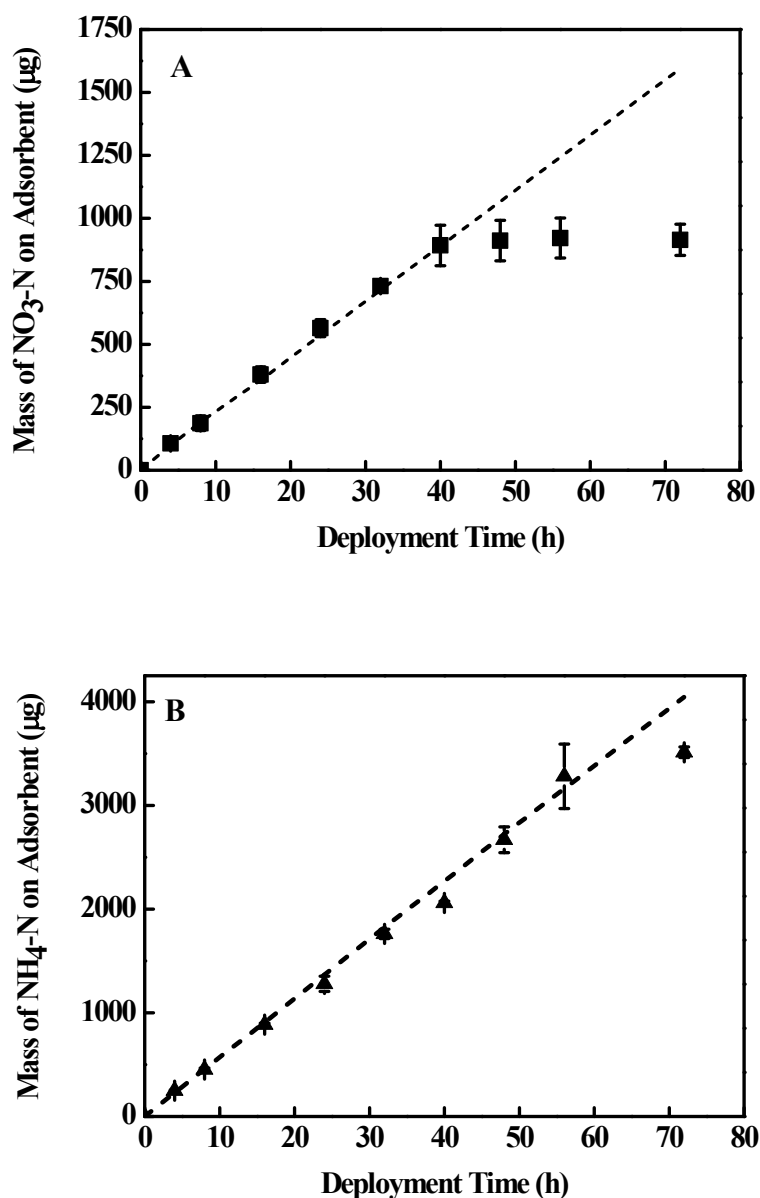


Figure S4. (A) Binding capacity of AMI-DGT (\bullet) for $\text{NO}_3\text{-N}$ and (B) CMI-DGT (\blacksquare) for $\text{NH}_4\text{-N}$. Data are mean values ($n = 3$) ± 1 standard deviation. Experimental conditions: (A) initial $\text{NO}_3\text{-N} = 13.6 \text{ mg L}^{-1}$, final $\text{NO}_3\text{-N} = 12.3 \mu\text{g L}^{-1}$; temperature = $24.1 \pm 0.5 \text{ }^\circ\text{C}$; (B) initial $\text{NH}_4\text{-N} = 33.1 \text{ mg L}^{-1}$, final $\text{NH}_4\text{-N} = 30.6 \text{ mg L}^{-1}$; temperature = $23.5 \pm 0.4 \text{ }^\circ\text{C}$; both conductivities are between $0.41 - 0.45 \text{ mS cm}^{-1}$ and volumes are 8 L .

Table S5. Trigger values based on Queensland Water Quality Guidelines.

Ecosystem type	NO _x -N (µg L ⁻¹)	NH ₄ -N (µg L ⁻¹)	PO ₄ -P (µg L ⁻¹)
Upland stream	40	10	15
Lowland stream	60	20	20
Freshwater lakes/ reservoirs	10	10	5

Table S6. NO₃-N concentrations (µg L⁻¹) at Loders Creek: C_{SOLN} , $C_{\text{A520E-DGT}}$ and $C_{\text{AMI-DGT}}$.

Concentrations are presented as mean values ($n = 3$) \pm 1 standard deviation.

Time	C_{SOLN}	$C_{\text{AMI-DGT}}$	$C_{\text{A520E-DGT}}$	$C_{\text{AMI-DGT}}:C_{\text{A520E-DGT}}$
8 - 11 Dec	320.4 \pm 205.0	404.1 \pm 17.3	410.3 \pm 6.0	0.98 \pm 0.04
11 - 14 Dec	303.4 \pm 74.9	268.5 \pm 7.4	285.6 \pm 1.6	0.94 \pm 0.03
14 - 17 Dec	180.7 \pm 43.3	178.5 \pm 2.9	184.4 \pm 2.1	0.97 \pm 0.01

Table S7. NH₄-N concentrations (µg L⁻¹) at Loders Creek: C_{SOLN} , $C_{\text{PrCH-DGT}}$ and $C_{\text{CMI-DGT}}$.

Concentrations are presented as mean values ($n = 3$) \pm 1 standard deviation.

Time	C_{SOLN}	$C_{\text{CMI-DGT}}$	$C_{\text{PrCH-DGT}}$	$C_{\text{CMI-DGT}}:C_{\text{PrCH-DGT}}$
8 - 11 Dec	167.5 \pm 70.6	217.0 \pm 12.4	238.0 \pm 13.0	0.91 \pm 0.08
11 - 14 Dec	217.2 \pm 68.0	192.3 \pm 0.7	229.6 \pm 25.9	0.85 \pm 0.09
14 - 17 Dec	269.1 \pm 119.1	279.8 \pm 20.7	309.9 \pm 6.9	0.90 \pm 0.07

Table S8. NO₃-N concentrations (µg L⁻¹) at Saltwater Creek: C_{SOLN}, C_{A520E-DGT} and C_{AMI-DGT}. Concentrations are presented as mean values (n = 3) ± 1 standard deviation.

Time	C _{SOLN}	C _{AMI-DGT}	C _{A520E-DGT}	C _{AMI-DGT} :C _{A520E-DGT}
27 - 30 Jan	209.6 ± 58.5	256.8 ± 5.1	257.4 ± 8.0	1.06 ± 0.04
31 Jan - 2 Feb	136.2 ± 19.9	159.2 ± 15.7	150.9 ± 9.5	1.06 ± 0.06
2 - 5 Feb	181.4 ± 32.7	184.3 ± 17.6	176.2 ± 16.2	1.10 ± 0.24

Table S9. NH₄-N concentrations (µg L⁻¹) at Saltwater Creek: C_{SOLN}, C_{PrCH-DGT} and C_{CMI-DGT}. Concentrations are presented as mean values (n = 3) ± 1 standard deviation.

Time	C _{SOLN}	C _{CMI-DGT}	C _{PrCH-DGT}	C _{CMI-DGT} :C _{PrCH-DGT}
27 - 30 Jan	22.7 ± 5.4	20.8 ± 3.3	20.2 ± 1.3	1.11 ± 0.15
31 Jan - 2 Feb	17.0 ± 4.7	15.2 ± 0.2	13.7 ± 1.3	1.11 ± 0.09
2 - 5 Feb	15.2 ± 5.6	16.5 ± 1.9	14.1 ± 1.6	1.21 ± 0.09

References

1. J. Huang, W. W. Bennett, P. R. Teasdale, S. Gardiner and D. T. Welsh, *Anal. Chim. Acta.*, 2016, **923**, 74-81.
2. J. Huang, W. W. Bennett, D. T. Welsh, T. Li and P. R. Teasdale, *Anal. Chim. Acta.*, 2016, **904**, 83-91.