“Diffusive Gradients in Thin Films” Techniques Provide Representative Time-Weighted Average Measurements of Inorganic Nutrients in Dynamic Freshwater Systems

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S Supporting Information

ABSTRACT: Nutrient concentrations in freshwater are highly variable over time, with changes driven by weather events, anthropogenic sources, modifications to catchment hydrology or habitats, and internal biogeochemical processes. Measuring infrequently collected grab samples is unlikely to adequately represent nutrient concentrations in such dynamic systems. In contrast, in situ passive sampling techniques, such as the “diffusive gradients in thin films” (DGT) technique, provide time-weighted average analyte concentrations over the entire deployment time. A pair of recently developed DGT techniques for nitrate (A520E-DGT) and ammonium (PrCH-DGT), as well as the Metsorb-DGT technique for phosphate, were used to monitor inorganic nutrients in different freshwater systems (i.e., streams and wetlands) with a range of environmental values and that were affected by different catchment types. Measurements of grab samples collected frequently (1–2 times daily, 8–10 a.m. and 2–4 p.m.) showed that concentrations of $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ changed dramatically in most of the studied freshwater systems over short time scales, while there were only relatively small fluctuations in $\text{PO}_4\text{-P}$. The DGT measurements were highly representative in comparison with the average nutrient concentrations obtained from daily grab samples over short-term (24 h) and long-term (72 h) deployments. The ratios of DGT-labile concentrations to the average concentrations from grab samples were between 1.00 and 1.12 over the studied deployment periods. The results of this study confirmed that DGT measurements provided a reliable and robust method for monitoring $\text{NH}_4\text{-N}$, $\text{NO}_3\text{-N}$, and $\text{PO}_4\text{-P}$ in a diverse range of dynamic freshwater systems.

INTRODUCTION

Nitrogen ($\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$) and phosphorus ($\text{PO}_4\text{-P}$) are the primary nutrients that determine the productivity of aquatic ecosystems. However, due to human activities such as the widespread use of fertilizer,^{27,45} release of treated and untreated sewage⁶ or industrial effluent,¹⁸ and increased use of specific household products,⁵ nutrient concentrations in aquatic environments have increased dramatically over the last few decades.^{19,24} Excess nutrient loadings to rivers, lakes, bays, and estuaries have led to eutrophication, the associated problems of phytoplankton and algal blooms, and subsequent episodes of water column hypoxia or anoxia when these blooms collapse and decompose.^{4,24} The ecological health of natural waters, particularly freshwater, has become a global concern and many countries have developed guidelines to protect against the effects of eutrophication.^{1,7,17,38} Liu et al. (2012) modeled past and future dissolved inorganic nitrogen (DIN: $\text{NH}_4\text{-N}$, $\text{NO}_3\text{-N}$, and $\text{NO}_2\text{-N}$) and phosphorus ($\text{PO}_4\text{-P}$) in the world's major rivers. Their results indicated that the number of rivers polluted by DIN and $\text{PO}_4\text{-P}$ had increased by 33% and 25%, respectively, from 1970 to 2000 and predicted that DIN and $\text{PO}_4\text{-P}$ would increase by a further 38% and 77%, respectively, by 2050. These circumstances clearly demonstrate the need to

establish sophisticated monitoring programs for DIN and $\text{PO}_4\text{-P}$ using accurate and representative measurements.

Nutrient loads in rivers and estuaries can vary significantly across a wide range of temporal and spatial scales. To assess the quality of water sources and the likelihood of eutrophication, nutrient loads (estimated as the product of concentrations and water flow)⁸ have to be determined. However, dissolved inorganic nutrient concentrations can differ spatially due to natural differences in climate,⁴² habitats, catchment geology, and hydrology; anthropogenic factors such as habitat clearing and agriculture;³⁷ modifications to catchment hydrology;⁹ and the presence of point sources such as wastewater treatment plants.²⁸ Additionally, nutrient concentrations can also change considerably over time due to events such as stormwater runoff,¹² effluent release, daily shifts in biological productivity from net photosynthesis to respiration,^{14,41} and major N-cycling processes such as ammonification, nitrification, and denitrification.²⁶ This variability over time provides challenges to interpreting the results of monitoring as it may occur on a

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scale that obscures regional differences.¹⁰ Consequently, the widespread use of infrequent grab-sampling methods for monitoring purposes is unlikely to be representative of nutrient concentrations within aquatic systems and may entirely miss high-concentration pulses.^{29,35} Autosampler stations are now used to obtain and preserve more frequent grab samples (for instance, to characterize changes in concentrations over a hydrograph),²⁰ but these are very expensive and tend to be used at a small number of strategic locations. Therefore, there is a clear need for complementary and less expensive methods, such as passive samplers,³⁹ to determine representative nutrient concentrations in freshwater systems.

In situ passive sampling techniques provide a time-weighted average concentration over the deployment time, which varies from days to many weeks depending on the analyte.¹⁶ Because this time-integrated measurement responds to all concentration changes during deployment and integrates temporal environmental variability, it provides a more-representative measurement of solute concentrations compared to grab sampling.² Moreover, as analyte species are continuously accumulated within the passive sampling device and eluted into a small volume, the concentration in the measured extract will usually be higher than grab-sample concentrations, reducing the uncertainty of analytical determination and improving detection limits.²⁵

The “diffusive gradients in thin films” (DGT) technique is a well-established passive sampling technique that relies on diffusion of analytes through a gel layer of known thickness before accumulation on a layer containing an analyte specific binding agent. The DGT technique has previously been used to measure concentrations of various contaminants, including trace metal ions,^{31,43} dissolved sulfide,^{30,36} and oxyanions such as P, As, V, and Sb.^{3,32,33} Several DGT techniques have been developed for the determination of $\text{PO}_4\text{-P}$,^{13,44} including Metsorb-DGT,³⁴ which utilizes a titanium dioxide-based binding agent. Recently, DGT techniques for the measurement of nitrate (A520E-DGT)²¹ and ammonium (PrCH-DGT)²² in freshwaters have been developed, which use ion exchange resins as binding agents. This study focuses on evaluating the capability of these three DGT techniques to measure representative dissolved inorganic nitrogen and phosphorus concentrations in seven dynamic freshwater systems, including streams and wetlands with diverse environmental values¹¹ and different catchment types, on the Gold Coast, Queensland, Australia (Table S1).

■ EXPERIMENTAL SECTION

Description of Study Locations. A total of seven freshwater sites within five urban waterways on the Gold Coast, Queensland, were used for this study. These included Saltwater Creek (stream and wetland), Loders Creek (stream), Gold Coast Regional Botanic Gardens (wetland), Currumbin Creek (stream and wetland), and Worongary Creek (stream).

Saltwater Creek is a microtidal stream with an urbanised and modified freshwater catchment.¹⁵ The stream is approximately 17 km long, 13.5% of which flows through suburban areas. An artificial pond, constructed as a sediment retention basin during the clearing and building stage of an estate adjacent to Saltwater Creek, which receives local stormwater runoff, was also used in this study. The pond is used for flood storage for Saltwater Creek during the wet season. Loders Creek is a microtidal stream with a total catchment area of approximately 10 km², which is dominated by light industry and well-established

residential areas. The freshwater section of Loders Creek has been highly modified to manage stormwater, but the northern tributary still has a natural channel. Therefore, the northern tributary of Loders Creek was selected for this study. Previous studies have reported very high concentrations of $\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$ at this site.^{21,22} The Botanic Gardens is bordered by a golf club and a large residential area and contains a series of artificial ponds, dense with lilies and algae, which receive stormwater runoff from the surrounding areas and the gardens. Previous measurements at this site have found high $\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$ concentrations. Worongary Creek is the northern tributary in the Mudgeeraba Creek catchment and is surrounded by a golf club and urban and rural residential areas. Currumbin Creek is a microtidal stream, which is approximately 24 km long, flowing from Mount Cougal National Park to Currumbin Alley. The stream sampling site was located downstream of the National Park in peri-urban Currumbin Valley with mostly acreage properties and small-scale agriculture. The wetland in this system is a pond where the stream channel widens close to the uppermost part of the estuary and is surrounded by acreage properties.

Field Study Design and Methods. During the study period, pH, temperature, conductivity, and dissolved oxygen were recorded at least twice daily at each site, at a water depth of approximately 30 cm, using a calibrated combination meter (YSI ProPlus Multiparameter). Rainfall conditions (every 2 h) for each deployment were obtained from the Australian Bureau of Meteorology (BOM) (www.bom.gov.au).

DGT samplers for each analyte were deployed at the same water depth mentioned above in triplicate ($n = 3$) for 24 h at four of the seven field sites (Saltwater Creek wetland, Loders Creek, Botanic Gardens, and Currumbin Creek stream) and for 72 h at all seven field sites. The selected field sites for 24 h deployment include two wetlands and two stream sites to ensure a variety of water flow rates. DGT samplers of each type were also deployed in triplicate ($n = 3$) for periods of approximately 3 days over 9 consecutive days at Currumbin Creek. DGT samplers with diffusive layer thicknesses (Δg) of 0.09 and 0.13 cm were selected for the experiments of DGT concentrations (C_{DGT}) of dissolved inorganic nutrients over 24 h (short-term) and 72 h (long-term) deployments, respectively. The diffusive layer thickness of 0.13 cm was used for longer DGT deployments for $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ in anticipation that this would decrease the effects of competing ions.^{21,22} The diffusive layer thickness of 0.09 cm was selected for $\text{PO}_4\text{-P}$ as previous work demonstrated that Metsorb-DGT can accurately measure $\text{PO}_4\text{-P}$ in freshwaters with even very high ion concentrations.³⁴ A deployment apparatus was designed, consisting of a plastic plate with holes to house the samplers and a backing plate to hold them in place, to deploy up to 12 DGT samplers at a time. The apparatus was anchored to a plastic pipe inserted into sediment so that the windows of the DGT probes faced the direction of water flow. Upon removal, the DGT samplers were rinsed briefly with deionized water, placed in plastic bags with 1–2 mL of deionized water, and stored at 4 °C until analysis. Samplers for $\text{NO}_3\text{-N}$ or $\text{PO}_4\text{-P}$ with varying diffusive gel layer thicknesses (Δg) of 0.05, 0.09, and 0.13 cm (all deployed in triplicate) were deployed to allow the calculation of the diffusive boundary layer thickness (DBL).^{40,44} Field blank DGTs for each analyte were done in triplicate ($n = 3$) by exposing the laboratory blank DGTs in the open air in the field for 30 s. The field blanks were then placed in sealed plastic bags and stored at 4 °C until analysis. All of the

field measurements were blank corrected. Limits of detection of PrCH-DGT, A520E-DGT, and Metsorb-DGT for $\text{NH}_4\text{-N}$, $\text{NO}_3\text{-N}$ and $\text{PO}_4\text{-P}$ were 8.70, 11.6, and $2.12 \mu\text{g L}^{-1}$, respectively, based on a 24 h deployment and a diffusive layer thickness of 0.09 cm; and 5.02, 5.59, and $0.71 \mu\text{g L}^{-1}$, respectively, based on a 72 h deployment and a diffusive layer thickness of 0.13 cm.

Grab water samples were collected in triplicate 1–2 times daily (8–10 a.m. and 2–4 p.m.) at each site to determine inorganic nutrient concentrations over the deployment periods. Syringes (50 mL) were rinsed two to three times with the site water before collecting the grab samples. Water samples were immediately filtered through $0.45 \mu\text{m}$ pore-size membrane filters (PVDF, Millipore), stored in 50 mL conical centrifuge tubes (polypropylene, Sigma-Aldrich Australia), and kept cool until being frozen upon return to the laboratory.

General Experimental. Deionized water (Milli-Q Advantage A10, $18.2 \text{ M}\Omega \text{ cm}^{-1}$) was used to prepare all solutions and rinse all containers and materials used in this study. All chemicals were analytical reagent grade or equivalent. Ion exchange resins PrCH and A520E, and Metsorb (titanium dioxide) powder were provided by the Purolite Company and Graver Technologies, respectively. Ultrapure agarose (Life Technologies) and acrylamide (Bio-Rad) were used to prepare agarose and polyacrylamide diffusive and binding layers. Containers used to collect samples and for the preparation and storage of solutions, and the glass plates used for preparing gels, and DGT components were acid-cleaned in 10% (v/v) HCl (AR grade, Merck) for at least 24 h and rinsed thoroughly with deionized water prior to use.

DGT Preparation. Polyacrylamide diffusive layers for $\text{NO}_3\text{-N}$ and $\text{PO}_4\text{-P}$ DGT samplers were prepared as described previously³⁴ and stored in $0.001 \text{ mol L}^{-1} \text{ NaCl}$ ²¹ and $0.01 \text{ mol L}^{-1} \text{ NaNO}_3$,³⁴ respectively, after washing two to three times in deionized water. Ultrapure agarose (Life Technologies) diffusive layers for $\text{NH}_4\text{-N}$ were prepared as described previously and stored in $0.001 \text{ mol L}^{-1} \text{ NaCl}$ solution.²² PrCH, A520E, and Metsorb binding layers for $\text{NH}_4\text{-N}$, $\text{NO}_3\text{-N}$, and $\text{PO}_4\text{-P}$, respectively, were prepared as described previously.^{3,21,22} All binding layers were washed two to three times and stored in deionized water prior to use.

Polysulfone filter membranes ($0.45 \mu\text{m}$; VWR Australia) were selected for PrCH-DGT and A520E-DGT, as polysulfone membranes do not contain any nitrogen, which could be a potential source of contamination. Membranes were soaked in deionized water for 24 h and washed in 5% (v/v) HCl for another 24 h, rinsed with deionized water, and stored in $0.001 \text{ mol L}^{-1} \text{ NaCl}$ solution. Cellulose nitrate membranes ($0.45 \mu\text{m}$; Whatman) were used for Metsorb-DGT samplers as described previously.³⁴ They were prepared in the same manner but washed in 5% (v/v) HNO_3 for 24 h, rinsed with deionized water, and stored in $0.01 \text{ mol L}^{-1} \text{ NaNO}_3$ solution.³⁴

DGT sampler moldings (DGT Research Ltd.) were acid-washed (10% HCl AR grade) and rinsed in deionized water (two to three times) before assembly. DGT samplers were assembled as described previously.^{21,22,34} The probes were stored in sealed plastic bags with 1–2 mL of deionized water prior to deployment.

Sample Analysis. PrCH and A520E binding gels were eluted in 2 mL of $2 \text{ mol L}^{-1} \text{ NaCl}$ for 24 h,^{21,22} and Metsorb binding gels were eluted in 1.5 mL of $1 \text{ mol L}^{-1} \text{ NaOH}$ for 24 h.³⁴ Eluates were diluted 5–10 times with deionized water to meet the acceptable concentration range of the analytical

method. Prior to analysis, the pH of the Metsorb binding layer eluates were adjusted to a circumneutral pH using dilute HCl.

$\text{NH}_4\text{-N}$, $\text{NO}_3\text{-N}$, and $\text{PO}_4\text{-P}$ concentrations in eluates and filtered grab water samples were measured according to colorimetric standard methods for the examination of water from American Public Health Association (APHA) 4500- NH_3H , 4500- $\text{NO}_3\text{-F}$, and 4500-P G using a Seal AA3 segmented flow analyzer. For $\text{NH}_4\text{-N}$ analysis, complexing reagent, salicylate reagent and dichloroisocyanuric acid (DIC) are applied. For $\text{NO}_3\text{-N}$ analysis, a cadmium column is used to reduce $\text{NO}_3\text{-N}$ to $\text{NO}_2\text{-N}$, and color reagent and ammonium chloride buffer reagent are also used. For $\text{PO}_4\text{-P}$ analysis, ammonium molybdate reagent and ascorbic acid are applied. Calibration standards from 0 to $380 \mu\text{g L}^{-1} \text{ NH}_4\text{-N}$, $\text{NO}_3\text{-N}$, and $\text{PO}_4\text{-P}$ were prepared from $1000 \text{ mg L}^{-1} \text{ NH}_4\text{Cl}$, NaNO_3 , and KH_2PO_4 certified standard solutions (Merck). Ammonium sulfate ($(\text{NH}_4)_2\text{SO}_4$) (AR, Merck), potassium nitrate (KNO_3) (AR, Chem Supply), and potassium phosphate (KH_2PO_4) (AR, Chem Supply) were used to prepare quality control standards (at $50 \mu\text{g L}^{-1}$), which were analyzed frequently throughout each analytical run. Recoveries of quality control standards were typically between 95–110%. The results from quality control standards were used to correct for any observed instrument drift. The instrument detection limits, calculated as three times the standard deviation of the blanks, were $2.3 \mu\text{g L}^{-1}$ for $\text{NH}_4\text{-N}$, $0.59 \mu\text{g L}^{-1}$ for $\text{NO}_3\text{-N}$, and $0.66 \mu\text{g L}^{-1}$ for $\text{PO}_4\text{-P}$, respectively ($n = 10$).

DGT-measured concentrations (C_{DGT} : ng mL^{-1} ; converted to $\mu\text{g L}^{-1}$) of nutrients were calculated using the DGT eq (eq 1):⁴³

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

where M is the mass of $\text{NH}_4\text{-N}$, $\text{NO}_3\text{-N}$, or $\text{PO}_4\text{-P}$ bound to the adsorbent (ng) corrected with the appropriate elution efficiency,^{21,22,34} Δg is the diffusive layer thickness, D is the diffusion coefficient of inorganic nutrient ion through the diffusive layer ($\text{cm}^2 \text{ s}^{-1}$), A is the area of the probe exposed to solution (3.14 cm^2), and t is the deployment time (s). Values of D for $\text{NO}_3\text{-N}$, $\text{NH}_4\text{-N}$, and $\text{PO}_4\text{-P}$ were obtained from Huang et al. (2016a and 2016b) and Panther et al. (2010), respectively. The value of D for $\text{NH}_4\text{-N}$ was adjusted for the conductivity of the site water according to Huang et al. (2016b).²² Independent t tests were used to compare the triplicate DGT measurements and average concentrations obtained from daily grab samples.

Additionally, the deployment of DGT samplers with different diffusive gel layer thicknesses allowed the thickness (δ) of the diffusive boundary layer (DBL) to be calculated at each field site:⁴⁴

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

A plot of $1/M$ versus Δg is a straight line with a slope (m) of $1/(DC_{\text{DGT}}At)$ and intercept (b) of $\delta/(DC_{\text{DGT}}At)$. Therefore, δ (eq 3) and C_{DGT} (eq 4) can be calculated.

$$\delta = \frac{b}{m} \quad (3)$$

$$C_{\text{DGT}} = \left(\frac{1}{mDA t} \right) \quad (4)$$

Figure 1. Changes in pH (A), temperature (B), conductivity (C), and dissolved oxygen (D) at each field site for multiple sampling times ($n = 7$) at SC (Saltwater Creek; deployment time: June 15–18, 2015); SCP (Saltwater Creek pond; June 15–18, 2015); LC (Loders Creek; June 22–25, 2015); BG (Botanic Gardens; June 22–25, 2015); WC (Worongary Creek; June 29–July 2, 2015); CC (Currumbin Creek; July 6–9, 2015); CCW (Currumbin Creek wetland; July 6–9, 2015). Each point represents the individual measurements of the parameter over the DGT deployment period.

Figure 2. Mean values of $\text{NH}_4\text{-N}$ (■), $\text{NO}_3\text{-N}$ (●), and $\text{PO}_4\text{-P}$ (▼) in grab samples at Saltwater Creek pond (A), Loders Creek (B), Worongary Creek (C), and Currumbin Creek wetland (D). Bars indicate rainfall.

When the thickness of the DBL was included in the DGT calculations, a value of 3.8 cm^2 was used for the sampling area, A , as the effective sampling window has a larger diameter (2.20 cm) than the geometric diameter of the exposure window (2.00 cm), which results in lateral diffusion of solutes within the diffusive gel (see Warnken et al. for more information).⁴⁰

RESULTS AND DISCUSSION

Variability of Physicochemical Parameters. Physicochemical data at each site during the study period are presented in Figure 1, with the mean, standard deviation, and relative standard deviation (RSD) of each parameter at each site given

in Table S2. The average pH (Figure 1A) at the study sites ranged from 6.61 (Worongary Creek) to 7.47 (Saltwater Creek stream), indicating circumneutral pH conditions at all sites. The Saltwater Creek wetland was the most variable with a pH range of 6.53 to 7.47 and an RSD of 3.5%. Mean temperatures at the sites (Figure 1B) ranged between 14.4°C (Currumbin Creek) and 19.3°C (Saltwater Creek wetland). The greatest variations in temperature were observed at Saltwater and Currumbin Creek wetlands (6.7% and 6.8% RSD, respectively). Conductivity data is shown in Figure 1C. The two sites with the highest average conductivity (0.636 mS cm^{-1} at Loders Creek and 0.655 mS cm^{-1} at Saltwater Creek stream) also had the

most variable conductivity (22.3% and 13.1% RSD, respectively). This may be because these sites are impacted most by stormwater runoff due to the high proportion of impermeable surfaces and small block sizes in both catchments. Figure S1 shows the impacts of rainfall on the conductivity at Saltwater Creek and Saltwater Creek wetland. The conductivities at Saltwater Creek and Saltwater Creek wetland decreased during rainy days from June 15 to 17 (5 to 18 mm), and after the rain stopped, the conductivities at both sites increased back to 0.613 and 0.488 mS cm⁻¹, respectively. The two lowest average conductivities were at the two Currumbin Creek sites (0.109 and 0.145 mS cm⁻¹), which are clearly influenced by drainage from a large pristine national park and a lowland catchment with a much lower proportion of impermeable surfaces. Most importantly, all conductivities were less than 1 mS cm⁻¹, which is the recommended maximum for use of the NO₃-N and NH₄-N DGT techniques.^{21,22}

Dissolved oxygen saturation (%) (Figure 1D) also varied considerably between sites, with mean values ranging from 49% (Saltwater Creek stream) to 103% (Currumbin Creek stream). All sites, except Currumbin Creek stream had an average DO below the Queensland Water Quality Guidelines lower value of 85% in lowland streams and 90% in freshwater lakes. Within-site variability was also high, with some sites exhibiting large relative changes (>50%) in dissolved oxygen over the relatively short study period, with Loders Creek having an RSD of 24.2% and the Currumbin Creek wetland 18.4% (Table S2 and S3). The generally under-saturated dissolved oxygen concentrations indicate that all the sites, with the exception of Currumbin Creek, were net heterotrophic. Whereas the short-term variability is likely related to the degree of biological productivity, changes in water flow (reoxygenation) and elevated oxygen demands, possibly linked to labile (low C:N easily degradable) organic matter inputs.

Grab-Sample Measurements. The measurements of NO₃-N, NH₄-N, and PO₄-P in frequently collected grab samples ($n = 7$ over ~3 days) from the seven study sites (Figures 2 and S3) were largely made for the purposes of characterizing the variability in the diverse waterways and for comparison with the DGT measurements of the same nutrients over the same periods.

The grab sample measurements demonstrated that PO₄-P was the least variable nutrient, but concentrations were observed to increase after sustained moderate rainfall at the two Saltwater Creek sites (Figures 2A and S3A). The concentrations of DIN species were both more variable with rainfall, with NO₃-N increasing substantially after rainfall at the two Saltwater Creek sites. A similar increase was not observed at Worongary Creek (Figure 2C), however, likely because grab samples were not collected during the actual rainfall event and the catchment of Worongary Creek is less urbanized, which may limit both the volume of runoff and the NO₃-N load during rainfall events. This suggests that stormwater runoff is a major source of NO₃-N, at least in Saltwater Creek, as has already been confirmed in the estuarine section of this waterway.¹⁵ NH₄-N also responded to rainfall but in a less-consistent manner than NO₃-N, sometimes increasing immediately or after a lag period, and sometimes decreasing. Ammonification (mineralization of organic nitrogen by heterotrophic bacteria) is a major source of NH₄-N within aquatic ecosystems.^{14,26,41} Rainfall events may have multiple effects, such as flushing NH₄-N accumulated in the water column during periods of low flow out of a system, resulting in

lower concentrations; increasing the input of NH₄-N-rich runoff into a system, resulting in higher concentrations; and transporting labile organic matter into or out of a system, resulting in changes to NH₄-N regeneration rates.^{12,23} Therefore, it is not unexpected that rainfall events had differing influences on NH₄-N concentrations in the studied systems, given the diversity of water-body types and catchment conditions investigated.

The very high concentrations of NH₄-N (>1500 µg L⁻¹) and NO₃-N (>400 µg L⁻¹) within Loders Creek (Figure 2B) were unable to be explained by runoff from a recent rainfall event. They could be the result of intensive organic nitrogen turnover and partial nitrification of the regenerated NH₄-N or suggestive of an anthropogenic source, such as light-industry. The Loders Creek catchment is dominated by light-industry and NH₃ is commonly used as an industrial bleach or disinfectant.

Substantial daily differences were also observed for DIN concentrations at two of the wetland sites (Currumbin Creek and the Botanic Gardens; Figures 2D and S3B) during periods when rainfall was absent or very minor. At Currumbin Creek wetland (Figure S2C), the average values of NH₄-N, especially, and NO₃-N collected in the early morning (50–100 and 35–50 µg L⁻¹, respectively) were much higher than those collected in the afternoon (10–30 and 20–30 µg L⁻¹, respectively). Similar changes were also observed at the Botanic Gardens wetland, although NO₃-N was less dynamic over the latter measurements. These fluctuations in DIN concentrations in these wetlands are most likely to be due to diurnal shifts in the balance between autotrophic and heterotrophic processes in the wetlands.^{26,41} During the night, heterotrophic respiration in the sediment would dominate and the NH₄-N produced by ammonification would efflux to and accumulate in the water column. Additionally, partial nitrification of the effluxing NH₄-N during transport would lead to production and efflux of NO₃-N, which would also accumulate in the overlying water,¹⁴ whereas, over the course of the day, photosynthesis by benthic microalgae, rooted macrophytes, their epiphytes, and phytoplankton will occur, and the photoassimilation of DIN (especially NH₄-N) into the primary producer biomass would both limit nutrient efflux from the sediment and consume the nutrients that had accumulated in the water overnight.^{26,41} The Saltwater Creek wetland seemed to be influenced more by rainfall associated runoff over the study period, but some changes in NH₄-N concentrations after the rainfall event toward the end of the monitoring period are also consistent with diel changes in internal biogeochemical cycling playing a role in regulating water column DIN concentrations.

Comparison of DGT Measurements with Grab Sample Concentrations. Short-term (24 h, $\Delta g = 0.09$ cm) deployments were carried out at four sites (Saltwater Creek pond, Loders Creek, Botanic Gardens, and Currumbin Creek stream) and long-term (72 h, $\Delta g = 0.13$ cm) deployments at all seven sites. C_{DGT} -to- C_{SOLN} ratios for each deployment are used to compare the concentrations obtained with each DGT method, with C_{SOLN} calculated as the average of all grab sample concentrations determined over the DGT deployment period and C_{DGT} as the average of the three replicate DGTs. Limits of detection of PrCH-DGT, AS20E-DGT, and Metsorb-DGT for NH₄-N, NO₃-N, and PO₄-P measurements were 8.70, 11.6, and 2.12 µg L⁻¹, respectively, based on 24 h deployment with a 0.09 cm diffusive layer thickness, and 5.02, 5.59, and 0.71 µg L⁻¹, respectively, based on 72 h of deployment with a 0.13 cm

Figure 3. Ratio of C_{DGT} and C_{SOLN} of $\text{NH}_4\text{-N}$ (A), $\text{NO}_3\text{-N}$ (B), and $\text{PO}_4\text{-P}$ (C) at each field site for 24 h (○) deployments at four field sites (SCP, LC, BG, and CC) and 72 h (■) deployments at all field sites. SC, Saltwater Creek; SCP, Saltwater Creek pond; LC, Loders Creek; BG, Botanic Gardens; WC, Worongary Creek; CC, Currumbin Creek; and CCW, Currumbin Creek wetland. SC did not contain the ratio of C_{DGT} and C_{SOLN} for $\text{NH}_4\text{-N}$ because the field data was below the detection limit.

diffusive layer thickness. $\text{NH}_4\text{-N}$ concentrations from 72 h deployments at Saltwater Creek were below the limit of detection. As the Saltwater Creek stream site had a high average conductivity of 0.655 mS cm^{-1} , the 72 h deployment time may have resulted in competition from major cations, leading to an underestimation, although the average grab-sample concentrations for this deployment ($7.01 \mu\text{g L}^{-1}$) are only marginally higher than the LOD ($5.01 \mu\text{g L}^{-1}$). DBL corrections were made for DGT calculations at all sites, as outlined in Tables S5–S7. All of the field results were blank corrected.

Previous studies^{21,22} have demonstrated the importance of measuring the DBL thickness and using it to correct the measured DGT concentration. The thicknesses of DBLs were calculated from the slope and y-intercept of the plots according to previous studies.^{40,44} Figure S2 shows DBL plots have good linearity ($R^2 > 0.94$) with relative standard deviations less than 20%. The results demonstrated that the DBL (0.036–0.101 cm) can have a significant impact on DGT measurements (Tables S4). C_{DGT} values calculated with the DBL correction included agree better with the average values of grab samples collected over the same deployment time in many instances, while C_{DGT} values calculated without the DBL included tended to underestimate concentrations (Tables S5 – S7).

C_{DGT} -to- C_{SOLN} ratios for $\text{NH}_4\text{-N}$, $\text{NO}_3\text{-N}$, and $\text{PO}_4\text{-P}$ were between 0.86–2.1, 0.87–1.4, and 0.64–1.2, respectively, across all sites (Figure 3), but most (21 out of 33) were within 0.8–1.2 (a range selected to indicate acceptable agreement between methods). Independent t tests were used to analyze the DGT results and various grab sample measurements. This analysis indicated that there were no significant difference ($\alpha > 0.05$) between the DGT results and the average values from grab samples in most of the field sites, which demonstrates that the DGT techniques provided accurate time-weighted average concentrations of dissolved inorganic nutrients in these diverse systems.

However, exceptions were observed ($p < 0.05$) for four measurements, in which the DGTs determined higher

concentrations of $\text{NH}_4\text{-N}$ ($C_{\text{DGT}}/C_{\text{SOLN}}$ of between 1.6 and 2.2) and $\text{NO}_3\text{-N}$ ($C_{\text{DGT}}/C_{\text{SOLN}}$ of between 1.3 and 1.5) compared with average values of grab samples at the Botanic Gardens and Currumbin Creek wetland sites. This is not unexpected because these two sites experienced dramatic changes in grab-sample concentrations at different times of day, and it would be expected that the night time concentrations of DIN would generally be higher than those during the day (see the discussion in the [Grab-Sample Measurements](#) section). Therefore, the DGT measurements may have more-effectively measured the average DIN concentrations than the grab samples, which were collected only during the daytime. The other two exceptions were lower C_{DGT} -to- C_{SOLN} ratios for $\text{PO}_4\text{-P}$ at Loders Creek (0.86, $p = 0.043$) and Currumbin Creek (0.65, $p < 0.01$). While only minor variation was observed in the grab sample $\text{PO}_4\text{-P}$ concentrations at both sites (RSD < 10%), this does not mean that lower concentrations did not occur at other times between grab sample collection.

Although the measurements were not significantly different, high C_{DGT} -to- C_{SOLN} ratios of $\text{NH}_4\text{-N}$ were observed at Currumbin Creek (≈ 1.4 for both deployments) and $\text{NO}_3\text{-N}$ at Saltwater Creek (≈ 1.4 for 72 h deployments). The DGT measurements of $\text{NO}_3\text{-N}$ would have better captured the effect of the period of extended moderate rainfall that occurred during the Saltwater Creek deployment (Figure 2A) than did grab samples, as there were some large changes in $\text{NO}_3\text{-N}$ concentrations between adjacent grab samples, and it is unlikely that the grab sample times were coincident with the peaks or troughs in $\text{NO}_3\text{-N}$ concentration over the rainfall event or that the changes in concentration were linear between the sampling points. The $\text{NH}_4\text{-N}$ concentrations measured in grab samples in Currumbin Creek also appear to be subject to diurnal variations (RSD > 25%), similar to those observed in the Currumbin Creek wetland, which would lead to the daytime collected grab samples underestimating the actual average concentration (see discussion in the [Grab-Sample Measure-](#)

Figure 4. Changes in $\text{NH}_4\text{-N}$, $\text{NO}_3\text{-N}$, and $\text{PO}_4\text{-P}$ concentration measured in grab samples (●) and DGT values (dark gray line) for $\text{NH}_4\text{-N}$ (A), $\text{NO}_3\text{-N}$ (B), and $\text{PO}_4\text{-P}$ (C) at Currumbin Creek from February 25 to March 6, 2015. Data are mean values ($n = 3$) ± 1 standard deviation. The columns represent the rainfall (mm) during the deployment.

ments). Therefore, each of these differences can be related to the lower representativeness of the grab sample measurements, compared to the time-weighted DGT measurements. Overall, the DGT techniques gave “recoveries” of $112 \pm 20\%$, $105 \pm 17\%$, and $102 \pm 12\%$ of average values of grab samples for $\text{NH}_4\text{-N}$, $\text{NO}_3\text{-N}$, and $\text{PO}_4\text{-P}$, respectively, at those field sites and can therefore be considered to provide accurate measurements, but corrections for the DBL were necessary to obtain that level of accuracy.^{21,22,34}

This study has shown the high variability of nutrient concentrations over time in natural waters and the limitations of monitoring nutrients using infrequent grab samples. The grab samples only provide a snapshot of the nutrient concentrations at each sampling time, with no information provided between samples. Therefore, infrequent grab samples are less representative of nutrient concentrations within a waterway and likely to miss periodic increases in concentration due to a variety of events. DGT techniques are able to capture the changes associated with these events as they integrate all changes in nutrient concentrations over the deployment period. However, grab samples do provide valuable information on short-term variability within dynamic waterways, provided that they are frequent enough to capture this variability. In this regard, the two methods are highly complementary. A study in which high-frequency grab samples, collected every 3 h for 24 h for instance, compared with DGT measurements made over 24 h or over day and night periods would allow an even more detailed assessment of the accuracy and precision of these DGT techniques.

Time Series Deployment at Currumbin Creek.

Consecutive 72 h DGT deployments were completed at Currumbin Creek stream over a period of 9 days (Figure 4). DGT results were blank and DBL-corrected. Grab samples for DIN and $\text{PO}_4\text{-P}$ were also collected daily over these periods, including when the DGTs were deployed and collected, and rainfall data was obtained from BOM. In most instances the

DGT measurements were intermediate between the grab sample concentrations over the same period. There were multiple rainfall events (3.1–24.9 mm) 2 days before the deployments commenced, which resulted in relatively high nutrient concentrations during the first deployment day. Nutrient concentrations were quite variable in Currumbin Creek. $\text{NH}_4\text{-N}$ concentrations measured in grab samples were $30 \mu\text{g L}^{-1}$ on 25th February and increased to $43 \mu\text{g L}^{-1}$ on 26th February after a minor rainfall event (≈ 5 mm). Thereafter, $\text{NH}_4\text{-N}$ concentrations declined and fluctuated around $20 \mu\text{g L}^{-1}$ until the end of the sampling period, although they increased slightly ($28 \mu\text{g L}^{-1}$) during a heavy rainfall (45 mm) event. $\text{NO}_3\text{-N}$ concentrations in the grab water samples decreased from $170 \mu\text{g L}^{-1}$ on February 25 and 26 to about $100 \mu\text{g L}^{-1}$ on February 27 and then increased to $150 \mu\text{g L}^{-1}$ on February 28 with the heavy rainfall. $\text{NO}_3\text{-N}$ concentrations then declined steadily from $100 \mu\text{g L}^{-1}$ on March 1 to $53 \mu\text{g L}^{-1}$ on March 6. Changes in $\text{PO}_4\text{-P}$ concentrations in grab samples were similar to $\text{NH}_4\text{-N}$, responding to rainfall in a similar manner, which had not been observed in the previous fieldwork. $\text{PO}_4\text{-P}$ concentrations were $10 \mu\text{g L}^{-1}$ on February 25 and increased to $15 \mu\text{g L}^{-1}$ on February 26. Subsequently, $\text{PO}_4\text{-P}$ concentrations declined to $\sim 6 \mu\text{g L}^{-1}$ before increasing with the heavy rainfall and fluctuating around $8\text{--}10 \mu\text{g L}^{-1}$ until the end of the sampling period.

Comparison of the mean concentrations showed that the DGTs provided similar concentrations compared with the average values of grab samples over each deployment period (Table S8). Independent *t* tests showed that only two DGT results ($\text{NH}_4\text{-N}$ from March 3 to 6 and $\text{PO}_4\text{-P}$ from February 28 to March 3) were significantly different to the average grab sample ($p < 0.05$) concentrations for the same periods; although the DGT results were still quite similar, the grab samples had a low standard deviation for these deployments. These differences are also apparent in Figure 4. On the basis of the comparisons in the Time Series Deployment at Currumbin

Creek section and previous studies,^{21,22} in which DGTs have been demonstrated to provide highly representative measurements, it is probable that there were changes in nutrient concentrations that were not accurately captured by the daily grab samples. For instance, the heavy rainfall event on 28th February could readily have produced a higher peak $\text{PO}_4\text{-P}$ concentration than was measured with the grab samples. Additionally, given the diurnal changes in $\text{NH}_4\text{-N}$ observed, particularly at the wetland sites (Figure 2C and S3B), lower or higher $\text{NH}_4\text{-N}$ concentrations may have been present at different times of the day to when these grab samples were collected, especially as all the grab samples were collected in the morning. Other circumstances can also readily be foreseen, especially over longer deployment times, in which the DGT measurements would be quite different to average concentrations in daily grab samples, as it is highly unlikely that the grab sampling times would coincide with the maxima or minima in the nutrient concentrations or those changes in nutrient concentrations would be linear. These observations reinforce the limitations of monitoring nutrients using infrequent grab samples, as is done routinely with monthly environmental monitoring. Only regular samples collected using autosamplers would be able to provide data with a similar degree of accuracy and representativeness as the DGT techniques utilized in this study.

DGT techniques for $\text{NH}_4\text{-N}$, $\text{NO}_3\text{-N}$, and $\text{PO}_4\text{-N}$ were evaluated at seven freshwater sites (stream or wetland) with a range of water-quality conditions (pH, temperature, conductivity, and dissolved oxygen) and catchment features, and at one site over a time series deployment. Quite different nutrient concentrations and processes were observed at each of the sites. As was expected, $\text{PO}_4\text{-P}$ was the least-variable nutrient, although rainfall events often led to an increase in concentration. $\text{NH}_4\text{-N}$ concentrations were affected unpredictably by rainfall, but strong diurnal cycling was apparent in productive wetland sites. $\text{NO}_3\text{-N}$ almost always increased with rainfall events and diurnal cycling was also observed at wetland sites. This study has clearly demonstrated that the in situ DGT techniques provide time-weighted average concentrations that are highly representative of the inorganic nutrient concentrations in dynamic waters over both 24 and 72 h deployment times. The significant differences that were observed could be explained by the grab-sampling frequencies being insufficient to obtain a representative average result. Therefore, DGT techniques are very suitable to being used for monitoring purposes to determine accurate and representative nutrient concentrations and loads in a wide range of freshwater systems. More importantly, DGT techniques will be able to provide a powerful tool to monitor and understand the dynamic changes in nutrient concentrations that can occur in freshwater ecosystems.

■ ASSOCIATED CONTENT

■ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.6b02949.

Experimental details of the preparation of Metsorb binding layers and variability of physicochemical parameters. Figures showing the influence of rainfall, the plot of the reciprocal mass on DIP, grab samples, information about field sites, characterization of each

field site, DO data, DBL thickness data, and concentrations of various compounds at each site. (PDF)

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

- (1) Australian and New Zealand Environment and Conservation Council. *Australian and New Zealand Guidelines for Fresh and Marine Water Quality*; ANZECC/Agriculture and Resource Management Council of Australia and New Zealand: Canberra, Australia, 2000.
- (2) Apte, S.; Batley, G.; Maher, W. Monitoring of Trace Metals and Metalloids in Natural Waters. In *Environmental Monitoring Handbook*; Burden, F.; McKelvie, I.; Forstner, U.; Guenther, A., Eds.; McGraw-Hill: New York, 2002.
- (3) Bennett, W. W.; Teasdale, P. R.; Panther, J. G.; Welsh, D. T.; Jolley, D. F. New Diffusive Gradients in a Thin Film Technique for Measuring Inorganic Arsenic and Selenium(IV) Using a Titanium Dioxide Based Adsorbent. *Anal. Chem.* **2010**, *82* (17), 7401–7407.
- (4) Bhatnagar, A.; Sillanpaa, M. A review of emerging adsorbents for nitrate removal from water. *Chem. Eng. J.* **2011**, *168* (2), 493–504.
- (5) Braga, E. S.; Bonetti, C. V. D. H.; Burone, L.; Bonetti Filho, J. Eutrophication and Bacterial Pollution Caused by Industrial and Domestic Wastes at the Baixada Santista Estuarine System – Brazil. *Mar. Pollut. Bull.* **2000**, *40* (2), 165–173.
- (6) Carlson, J. C.; Anderson, J. C.; Low, J. E.; Cardinal, P.; MacKenzie, S. D.; Beattie, S. A.; Challis, J. K.; Bennett, R. J.; Meronek, S. S.; Wilks, R. P. A.; Buhay, W. M.; Wong, C. S.; Hanson, M. L. Presence and hazards of nutrients and emerging organic micro-pollutants from sewage lagoon discharges into Dead Horse Creek, Manitoba, Canada. *Sci. Total Environ.* **2013**, *445–446*, 64–78.
- (7) CCME. *Canadian Water Quality Guidelines for the Protection of Aquatic Life*; Canadian Council of Ministers of the Environment: Winnipeg, Canada, 2007.
- (8) Cohn, T. A.; Caulder, D. L.; Gilroy, E. J.; Zynjuk, L. D.; Summers, R. M. The validity of a simple statistical model for estimating fluvial constituent loads: an empirical study involving nutrient loads in Chesapeake Bay. *Water Resour. Res.* **1992**, *28* (9), 2353–2363.
- (9) Davies, P. L.; Eyre, B. D. Estuarine modification of nutrient and sediment exports to the Great Barrier Reef Marine Park from the Daintree and Annan River catchments. *Mar. Pollut. Bull.* **2005**, *51* (1–4), 174–185.
- (10) de Jonge, V. N. Importance of temporal and spatial scales in applying biological and physical process knowledge in coastal management, an example for the Ems estuary. *Cont. Shelf Res.* **2000**, *20* (12–13), 1655–1686.
- (11) DERM. *Environmental Protection (Water) Policy 2009*; Department of Environment and Resource Management, Queensland Government: Queensland, Australia, 2010.
- (12) Dillon, K. S.; Chanton, J. P. Nutrient transformations between rainfall and stormwater runoff in an urbanized coastal environment: Sarasota Bay Florida. *Limnol. Oceanogr.* **2005**, *50*, 62–69.

- (13) Ding, S.; Xu, D.; Sun, Q.; Yin, H.; Zhang, C. Measurement of Dissolved Reactive Phosphorus Using the Diffusive Gradients in Thin Films Technique with a High-Capacity Binding Phase. *Environ. Sci. Technol.* **2010**, *44* (21), 8169–8174.
- (14) Dunn, R. J.; Welsh, D. T.; Jordan, M. A.; Waltham, N. J.; Lemckert, C. J.; Teasdale, P. R. Benthic metabolism and nitrogen dynamics in a sub-tropical coastal lagoon: microphytobenthos stimulate nitrification and nitrate reduction through photosynthetic oxygen evolution. *Estuarine, Coastal Shelf Sci.* **2012**, *113*, 272–282.
- (15) Dunn, R. J. K.; Robertson, D.; Teasdale, P. R.; Waltham, N. J.; Welsh, D. T. Benthic metabolism and nitrogen dynamics in an urbanised tidal creek: Domination of DNRA over denitrification as a nitrate reduction pathway. *Estuarine, Coastal Shelf Sci.* **2013**, *131*, 271–281.
- (16) Dunn, R. J. K.; Teasdale, P. R.; Warnken, J.; Jordan, M. A.; Arthur, J. M. Evaluation of the in situ, time-integrated DGT technique by monitoring changes in heavy metal concentrations in estuarine waters. *Environ. Pollut.* **2007**, *148* (1), 213–220.
- (17) EU. Directive 2006/44/EC of the European Parliament and of the Council on the Quality of Fresh Waters Needing Protection or Improvement in Order to Support Fish Life; *Official Journal of the European Union*; EU: Brussels, Belgium, 2006; pp 20–31.
- (18) Gibson, R. N.; Atkinson, R. J. A.; Gordon, J. D. M.; Hughes, R. N. Anthropogenic nutrient enrichment and blooms of harmful phytoplankton. *Oceanography and Marine Biology-An Annual Review* **2012**, *50*, 65–126.
- (19) Harrison, J. A.; Seitzinger, S. P.; Bouwman, A. F.; Caraco, N. F.; Beusen, A. H. W.; Vörösmarty, C. J. Dissolved inorganic phosphorus export to the coastal zone: results from a spatially explicit, global model. *Global. Biogeochem. Cy.* **2005**, *19*, 1–13.
- (20) Hateley, L. R.; Ellis, R.; Shaw, M.; Waters, D.; Carroll, C. *Modelling Reductions of Pollutant Loads Due to Improved Management Practices in the Great Barrier Reef Catchments - Wet Tropics NRM Region*; Technical Report; Queensland Department of Natural Resources and Mines: Cairns, Australia, 2014; Vol. 3.
- (21) Huang, J.; Bennett, W. W.; Teasdale, P. R.; Gardiner, S.; Welsh, D. T. Development and evaluation of a diffusive gradients in thin films technique for measuring nitrate in freshwaters. *Anal. Chim. Acta* **2016**, *923*, 74–81.
- (22) Huang, J.; Bennett, W. W.; Welsh, D. T.; Li, T.; Teasdale, P. R. Development and evaluation of a diffusive gradients in a thin film technique for measuring ammonium in freshwaters. *Anal. Chim. Acta* **2016**, *904*, 83–91.
- (23) Liu, A.; Egodawatta, P.; Guan, Y.; Goonetilleke, A. Influence of rainfall and catchment characteristics on urban stormwater quality. *Sci. Total Environ.* **2013**, *444* (0), 255–262.
- (24) Liu, C.; Kroeze, C.; Hoekstra, A. Y.; Gerbens-Leenes, W. Past and future trends in grey water footprints of anthropogenic nitrogen and phosphorus inputs to major world rivers. *Ecol. Indic.* **2012**, *18*, 42–49.
- (25) Montero, N.; Belzunce-Segarra, M. J.; Gonzalez, J. L.; Larreta, J.; Franco, J. Evaluation of diffusive gradients in thin-films (DGTs) as a monitoring tool for the assessment of the chemical status of transitional waters within the Water Framework Directive. *Mar. Pollut. Bull.* **2012**, *64* (1), 31–39.
- (26) Nizzoli, D.; Welsh, D. T.; Longhi, D.; Viaroli, P. Influence of *Potamogeton pectinatus* on benthic metabolism, nutrient fluxes and denitrification in a freshwater littoral sediment in an agricultural landscape: N assimilation versus N removal. *Hydrobiologia* **2014**, *737*, 183–200.
- (27) Nolan, B. T.; Hitt, K. J. Vulnerability of Shallow Groundwater and Drinking-Water Wells to Nitrate in the United States. *Environ. Sci. Technol.* **2006**, *40* (24), 7834–7840.
- (28) Nyberg, U.; Andersson, B.; Aspegren, H. Experiences with on-line measurements at a wastewater treatment plant for extended nitrogen removal. *Water Sci. Technol.* **1996**, *33* (1), 175–182.
- (29) Ouyang, Y. Estimation of shallow groundwater discharge and nutrient load into a river. *Ecol. Eng.* **2012**, *38* (1), 101–104.
- (30) Pagès, A.; Welsh, D. T.; Robertson, D.; Panther, J. G.; Schäfer, J.; Tomlinson, R. B.; Teasdale, P. R. Diurnal shifts in co-distributions of sulfide and iron(II) and profiles of phosphate and ammonium in the rhizosphere of *Zostera capricorni*. *Estuarine, Coastal Shelf Sci.* **2012**, *115*, 282–290.
- (31) Panther, J. G.; Bennett, W. W.; Welsh, D. T.; Teasdale, P. R. Simultaneous Measurement of Trace Metal and Oxyanion Concentrations in Water using Diffusive Gradients in Thin Films with a Chelex–Metsorb Mixed Binding Layer. *Anal. Chem.* **2014**, *86*, 427–434.
- (32) Panther, J. G.; Stewart, R. R.; Teasdale, P. R.; Bennett, W. W.; Welsh, D. T.; Zhao, H. Titanium dioxide-based DGT for measuring dissolved As(V), V(V), Sb(V), Mo(VI) and W(VI) in water. *Talanta* **2013**, *105*, 80–86.
- (33) Panther, J. G.; Teasdale, P. R.; Bennett, W. W.; Welsh, D. T.; Zhao, H. Comparing dissolved reactive phosphorus measured by DGT with ferrihydrite and titanium dioxide adsorbents: Anionic interferences, adsorbent capacity and deployment time. *Anal. Chim. Acta* **2011**, *698* (1–2), 20–26.
- (34) Panther, J. G.; Teasdale, P. R.; Bennett, W. W.; Welsh, D. T.; Zhao, H. J. Titanium Dioxide-Based DGT Technique for In Situ Measurement of Dissolved Reactive Phosphorus in Fresh and Marine Waters. *Environ. Sci. Technol.* **2010**, *44* (24), 9419–9424.
- (35) Taylor, G. D.; Fletcher, T. D.; Wong, T. H. F.; Breen, P. F.; Duncan, H. P. Nitrogen composition in urban runoff—implications for stormwater management. *Water Res.* **2005**, *39* (10), 1982–1989.
- (36) Teasdale, P. R.; Hayward, S.; Davison, W. In situ, high-resolution measurement of dissolved sulfide using diffusive gradients in thin films with computer-imaging densitometry. *Anal. Chem.* **1999**, *71* (11), 2186–2191.
- (37) Thorburn, P. J.; Wilkinson, S. N.; Silburn, D. M. Water quality in agricultural lands draining to the Great Barrier Reef: A review of causes, management and priorities. *Agric., Ecosyst. Environ.* **2013**, *180*, 4–20.
- (38) U.S. EPA *Update of Ambient Water Quality Criteria for Ammonia*; U.S. Environmental Protection Agency Office of Water: Washington, DC, 1999.
- (39) Vrana, B.; Allan, I. J.; Greenwood, R.; Mills, G. A.; Dominiak, E.; Svensson, K.; Knutsson, J.; Morrison, G. Passive sampling techniques for monitoring pollutants in water. *TrAC, Trends Anal. Chem.* **2005**, *24* (10), 845–868.
- (40) Warnken, K. W.; Zhang, H.; Davison, W. Accuracy of the diffusive gradients in thin-films technique: Diffusive boundary layer and effective sampling area considerations. *Anal. Chem.* **2006**, *78* (11), 3780–3787.
- (41) Welsh, D. T.; Bartoli, M.; Nizzoli, D.; Castaldelli, G.; Riou, S. A.; Viaroli, P. Denitrification, nitrogen fixation, community primary productivity and inorganic-N and oxygen fluxes in an intertidal *Zostera noltii* meadow. *Mar. Ecol.: Prog. Ser.* **2000**, *208*, 65–77.
- (42) Wu, J.; Malmström, M. E. Nutrient loadings from urban catchments under climate change scenarios: Case studies in Stockholm, Sweden. *Sci. Total Environ.* **2015**, *518–519*, 393–406.
- (43) Zhang, H.; Davison, W. In situ speciation measurements of trace components in natural-waters using thin-film gels. *Nature* **1994**, *367* (6463), 546–548.
- (44) Zhang, H.; Davison, W.; Gadi, R.; Kobayashi, T. In situ measurement of dissolved phosphorus in natural waters using DGT. *Anal. Chim. Acta* **1998**, *370* (1), 29–38.
- (45) Zhu, M.; Zhu, G.; Li, W.; Zhang, Y.; Zhao, L.; Gu, Z. Estimation of the algal-available phosphorus pool in sediments of a large, shallow eutrophic lake (Taihu, China) using profiled SMT fractional analysis. *Environ. Pollut.* **2013**, *173*, 216–223.