



## Development and evaluation of a diffusive gradients in a thin film technique for measuring ammonium in freshwaters



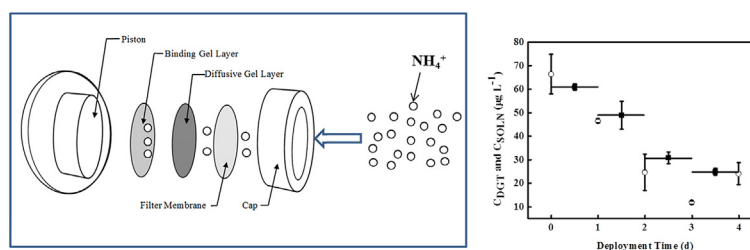
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### HIGHLIGHTS

- A new DGT technique, using Microlite PrCH, was developed and evaluated for monitoring  $\text{NH}_4\text{-N}$  in freshwaters.
- PrCH-DGT is suitable for a wide range of pH conditions (3.5–8.5) and ionic strengths (up to  $0.012 \text{ mol L}^{-1}$  NaCl).
- PrCH-DGT showed a good linear uptake for  $\text{NH}_4\text{-N}$  over 72 h in synthetic freshwater.
- During field deployments  $C_{\text{DGT}}$  values with DBL matched well with the average grab sample values.

### GRAPHICAL ABSTRACT



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### ABSTRACT

A new diffusive gradients in a thin film (DGT) technique, using Microlite PrCH cation exchange resin, was developed and evaluated for measuring  $\text{NH}_4\text{-N}$  in freshwaters. Microlite PrCH had high uptake (>92.5%) and elution efficiencies (87.2% using  $2 \text{ mol L}^{-1}$  NaCl). Mass vs. time validation experiments over 24 h demonstrated excellent linearity ( $R^2 \geq 0.996$ ). PrCH-DGT binding layers had an extremely high intrinsic binding capacity for  $\text{NH}_4\text{-N}$  (~3000  $\mu\text{g}$ ).  $\text{NH}_4\text{-N}$  uptake was quantitative over pH ranges 3.5–8.5 and ionic strength (up to  $0.012 \text{ mol L}^{-1}$  as NaCl) typical of freshwater systems. Several cations ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ ) were found to compete with  $\text{NH}_4\text{-N}$  for uptake by PrCH-DGT, but  $\text{NH}_4\text{-N}$  uptake was quantitative over concentration ranges typical of freshwater (up to  $0.012 \text{ mol L}^{-1}$   $\text{Na}^+$ ,  $0.006 \text{ mol L}^{-1}$   $\text{K}^+$ ,  $0.003 \text{ mol L}^{-1}$   $\text{Ca}^{2+}$  and  $0.004 \text{ mol L}^{-1}$   $\text{Mg}^{2+}$ ). Effective diffusion coefficients determined from mass vs. time experiments changed non-linearly with electrical conductivity. Field deployments of DGT samplers with varying diffusive layer thicknesses validated the use of the technique *in situ*, allowed deployment times to be manipulated with respect to  $\text{NH}_4\text{-N}$  concentration, and enable the calculation of the diffusive boundary layer thickness. Daily grab sample  $\text{NH}_4\text{-N}$  concentrations were observed to vary considerably independent of major rainfall events, but good agreements were obtained between PrCH-DGT values and mean grab sample measurements of  $\text{NH}_4\text{-N}$  ( $C_{\text{DGT}}:C_{\text{SOLN}}$  0.83–1.3). Reproducibility of DGT measurements in the field was good (relative standard deviation < 11%). Limit of detection was  $0.63 \mu\text{g L}^{-1}$  (equivalent to  $0.045 \mu\text{mol L}^{-1}$ ) based on 24 h deployments.

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### 1. Introduction

Significant nitrogen pollution has been reported in water bodies [1–3] worldwide and elevated nutrient loadings in estuaries, rivers

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and lakes are one of the major concerns in water quality management [4]. Dissolved inorganic nitrogen (DIN) species, including ammonium ( $\text{NH}_4\text{-N}$ ) and nitrate are highly bioavailable and often present in high concentrations [5]. Anthropogenic loads of DIN not only come from the widespread use of fertilizers, but also from stormwater run-off [6,7], organic wastewater [8] and treated effluent [9]. High nutrient loads can stimulate nuisance algal growth in receiving surface waters, which may lead to hypoxia or anoxia zones, and highly undesirable changes in ecosystem structure and function [10].

$\text{NH}_4\text{-N}$  is present as either ammonium ( $\text{NH}_4^+$ ) or its conjugate base, ammonia ( $\text{NH}_3$ ), with the speciation highly dependent upon pH, and to a lesser extent temperature and salinity [11]. In most natural waters of near neutral pH, ammonium is the dominant species.  $\text{NH}_4\text{-N}$  is the principle form of DIN generated by the remineralisation of organic matter in both the water column and sediment, and is the preferred nitrogen source for the growth of most plants [12,13]. Due to the significant ecological impacts of  $\text{NH}_4\text{-N}$  there is a need to monitor concentrations to assess the ecological status of water bodies and estimate nutrient loads to downstream ecosystems, this is often a regulatory requirement. Queensland Water Quality Guideline value for  $\text{NH}_4\text{-N}$  to protect freshwater ecosystems is about  $20 \mu\text{g L}^{-1}$  at lowland rivers [14]. Ammonia can be toxic to fish and other aquatic fauna with the degree of toxicity varying significantly between species and with life stage [15]. Because ammonia toxicity is not of major relevance to humans, no drinking water guidelines have been established by the World Health Organization [16].

In most countries, monitoring of ammonium concentrations in water bodies and load estimate calculations are based on grab samples, which only provide a snapshot of the nutrient concentrations at the moment of sampling [17,18]. These sampling frequencies are generally insufficient to capture the dynamic behaviour of water quality as the samples are only collected every week or month [19]. Furthermore, differences in climate [20], land use [21], water flow, the influence of N-cycling processes (e.g. nitrification and denitrification), and seasonal and diurnal shifts between net autotrophy (production) and heterotrophy [22–24] can significantly affect  $\text{NH}_4\text{-N}$  concentration in natural waters. Consequently, intermittent grab samples, often collected at a fixed period of the day are unlikely to be representative of shifting  $\text{NH}_4\text{-N}$  conditions within water systems. It is therefore important to develop more representative monitoring techniques for  $\text{NH}_4\text{-N}$ . An alternative approach is the use of *in situ* passive sampling techniques that allow determination of time-averaged concentration measurements over environmentally relevant time-scales [25].

The diffusive gradients in a thin film (DGT) technique is a time-integrated, passive sampling technique, commonly used to measure concentrations of elemental contaminants in water. DGT probes consist of a protective covering filter membrane, a diffusive layer of known thickness and a binding layer incorporating an analyte specific binding agent, such as Chelex-100 for heavy metals [26], ferrihydrite and Metsorb ( $\text{TiO}_2$ ) for oxyanions [27,28] including phosphate [29,30] and As [31]. Analytes in the bulk solution diffuse across the filter membrane and diffusive layer and are accumulated at the surface of the binding layer [32]. A time-weighted average analyte concentration in the solution is calculated from the mass of the analyte accumulated on the binding agent over a known deployment time using the DGT equation [32,33], which is derived from Fick's First Law of Diffusion [26,32].

To develop a DGT technique for  $\text{NH}_4\text{-N}$ , a suitably selective binding material is required. Some cation exchange resins, such as Purolite C 160 MBH and Dowex 50w-x8 have reportedly removed  $\text{NH}_4\text{-N}$  from aquatic systems over a range of pH and cation concentrations [34,35]. These results, however, also showed that the

resins shrink or swell with changes in solution pH or cation concentrations which affects the effective intra-particle diffusivity of the resin [34,35], subsequently making them inappropriate for a diffusion based sensor like DGT. Microlite PrCH is a cation exchange resin which incorporates sulfonic acid functional groups attached to a styrene-divinylbenzene matrix that does not shrink or swell. Sun et al. [36] have recently described a DGT technique for  $\text{NH}_4\text{-N}$  using a zeolite material cast within polyacrylamide hydrogel as the binding layer.

In this study a series of laboratory and field experiments were performed to evaluate Microlite PrCH as a DGT binding agent for  $\text{NH}_4\text{-N}$ , including determination of uptake and elution efficiencies, evaluation of linear accumulation of mass over time, the effect of ionic strength on the  $\text{NH}_4\text{-N}$  diffusion coefficient, and the effect of varying pH and ionic strength on uptake. Potential interferences from major cations ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ ) present in natural waters were evaluated over a range of ionic concentrations. An interesting effect of diffusive layer thickness was observed and characterized with this DGT technique. The performance of PrCH-DGT over extended deployments in the field was compared with grab sample measurements permitting determination of the diffusive boundary layer thickness.

## 2. Material and methods

### 2.1. Reagents, materials and solutions

All standards, samples and cleaning solutions were prepared in deionised water (Milli-Q Element 18 M $\Omega$ ). All chemicals were analytical reagent grade or higher. PrCH cation exchange resin (Purolite Company) and ultrapure agarose (Life Technologies) were used to prepare PrCH binding layers and diffusive layers.  $\text{NH}_4\text{-N}$  solutions were prepared from standard solutions of  $1000 \text{ mg L}^{-1}$  as  $\text{NH}_4\text{Cl}$  (Merck). All plastic containers used for experimental work, the preparation and storage of solutions, glass plates used for preparing diffusive and binding layers, and all DGT components were acid-washed in 10% (v/v) HCl (AR grade, Merck) for at least 24 h and thoroughly rinsed with deionised water prior to use.

### 2.2. Preparation of diffusive and binding layers

All diffusive and binding layers were prepared using agarose [37] in place of the polyacrylamide hydrogels typically used for DGT, as preliminary studies found that the amide functional groups in these layers interfered with the measurement of  $\text{NH}_4\text{-N}$ . Diffusive layers were prepared by dissolving 2.5% (w/v) ultrapure agarose (Life Technologies) in boiling water until completely dissolved. The solution was pipetted into moulds, consisting of two acid washed glass plates clipped together and separated by a 0.04, 0.08 and 0.12 cm thick spacer, respectively for different diffusive layer thicknesses. These layers were heated to  $95^\circ\text{C}$  to avoid premature setting of the layer. The layers were allowed to set for 45 min at room temperature and upon removal from the moulds, washed 2–3 times in deionised water then stored in  $0.001 \text{ mol L}^{-1}$  NaCl solution.

PrCH binding layers were prepared in the same manner as the diffusive layers except that 2.5 g of PrCH was added and mixed into 6 mL of agarose solution prior to casting. The glass plates used for casting were separated by a 0.075 cm thick spacer ( $3 \times 0.025$  cm plastic spacer) to improve the strength of the binding layers. The PrCH binding layers were set for 45 min at room temperature and upon removal from the moulds, the layers were washed several times before being stored in deionised water.

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