



A modified DGT technique for the simultaneous measurement of dissolved inorganic nitrogen and phosphorus in freshwaters



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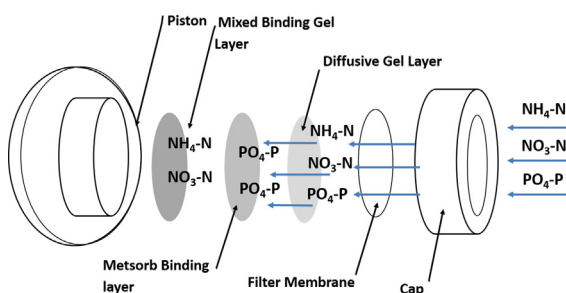
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HIGHLIGHTS

- A modified DGT technique to measure dissolved inorganic nitrogen and phosphorus (INP-DGT) was evaluated.
- INP-DGT provided representative measurements of $\text{NH}_4\text{-N}$, $\text{NO}_3\text{-N}$ and $\text{PO}_4\text{-P}$ for various deployment times.
- Enables cost-effective monitoring of time-weighted average concentrations of dissolved nutrients.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 13 April 2017

Received in revised form

20 July 2017

Accepted 16 August 2017

Available online 26 August 2017

Keywords:

Diffusive gradients in thin films

Nitrate

Ammonium

Passive sampler

Diffusion coefficient

Diffusive boundary layer

ABSTRACT

A modified diffusive gradients in thin films (DGT) technique uses both a mixed binding layer (PrCH and A520E resins for $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$, respectively) and multiple binding layers (Metsorb binding layer for $\text{PO}_4\text{-P}$ overlying the mixed binding layer) for the simultaneous measurement of dissolved inorganic nitrogen (nitrate and ammonium) and phosphate in freshwater (INP-DGT). High uptake and elution efficiencies were determined for a mixed (PrCH/A520E) binding gel for dissolved inorganic nitrogen and an agarose-based Metsorb binding layer for $\text{PO}_4\text{-P}$. Diffusion coefficients (D) obtained from DGT time-series experiments (conductivity $180 \mu\text{S cm}^{-1}$) for $\text{NH}_4\text{-N}$, $\text{NO}_3\text{-N}$ and $\text{PO}_4\text{-P}$ agreed well with those measured using individual DGT techniques in previous studies, but were characterised over a wider range of ionic strengths here. D for $\text{NO}_3\text{-N}$ and $\text{PO}_4\text{-P}$ were constant over a range of ionic strengths (between 100 and $800 \mu\text{S cm}^{-1}$) while the diffusion coefficient for $\text{NH}_4\text{-N}$ decreased with increasing ionic strength, as reported previously. The measurement of $\text{NH}_4\text{-N}$, $\text{NO}_3\text{-N}$ and $\text{PO}_4\text{-P}$ using the INP-DGT was independent of pH (3.5–8.5) and quantitative over varying ionic strength ranges (up to 0.004 mol L^{-1} NaCl for $\text{NH}_4\text{-N}$, up to 0.014 mol L^{-1} NaCl for $\text{NO}_3\text{-N}$ and over 0.1 mol L^{-1} NaCl for $\text{PO}_4\text{-P}$) for a 24 h deployment time. Performance of INP-DGT in synthetic freshwaters with differing conductivity indicated the three nutrients were affected differently, with $\text{NH}_4\text{-N}$ measurements being most sensitive. Representative performance was determined for $\text{NO}_3\text{-N}$ ($90\text{--}330 \mu\text{S cm}^{-1}$) and $\text{PO}_4\text{-P}$ (all tested conductivities) over a 72 h deployment period and for $\text{NH}_4\text{-N}$ ($<330 \mu\text{S cm}^{-1}$) over a 24 h deployment period. Field validations showed that the ratios of INP-DGT concentrations to the average concentrations from grab samples were generally between 0.80 and 1.13 over 24 and 48 h deployment periods. To ensure the representative performance of INP-DGT for all three nutrients, the conductivity should not exceed

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400 $\mu\text{S cm}^{-1}$ and deployment times should be no longer than 24 h. The results of this study have demonstrated that INP-DGT could provide a cost-effective monitoring technique for measuring time-weighted average concentrations of dissolved inorganic nutrients in many freshwaters.

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1. Introduction

Water quality issues deriving from nitrogen and phosphorus pollution have been reported in many water bodies globally [1,2], and nutrient loadings to aquatic systems are one of the primary concerns in water quality management [3–5]. High concentrations of dissolved inorganic nitrogen (DIN) and phosphate are known to stimulate algal growth in water bodies and elevated nutrient loads to receiving waters, which have led to eutrophication, phytoplankton and algal blooms, and ultimately contribute to water column hypoxia/anoxia and the formation of so called “dead zones” [6]. Repeated algal blooms can cause undesirable changes in ecosystem structure and function [7]. Due to the significant impacts readily bioavailable nutrients can have on the environment, there is a need to monitor their concentrations to assess the ecological status of water bodies and to estimate nutrient loads.

Passive sampling methods are *in situ* techniques that determine time-weighted average analyte concentrations over varying deployment periods [8–11]. Compared to conventional grab-sampling methods, passive sampling techniques can reduce the frequency of measurements [9,10,12], and provide a more representative measurement of variations in analyte concentrations [9,10,13]. The diffusive gradients in thin films (DGT) technique is a well-established passive sampling technique that has been used to measure concentrations of trace metals (e.g. Cu, Zn, Ni, Pb, Co etc.) [12,14–17], sulfide [18], oxyanions (e.g. As, Se, V etc.) [15,19,20], using a variety of selective materials (binding layers). In recent years, DGT methods have also been developed to measure inorganic nutrients, including Metsorb, ferrihydrite and Zr oxide binding layers for $\text{PO}_4\text{-P}$ [21–23], PrCH and zeolite binding layers for $\text{NH}_4\text{-N}$ [24,25], A520E and SIR-100-HP binding layers for $\text{NO}_3\text{-N}$ [26,27]. However, each of these DGT techniques is specific for only one nutrient and three different DGT types have to be prepared, deployed and individually analysed. There is potential to combine these approaches into a single DGT measurement for dissolved inorganic nutrients.

Use of multi-layer DGTs (i.e. separate binding layers stacked sequentially within the sampler) and mixed binding layers (i.e. a single binding layer containing a mixture of binding agents) have been used to simultaneously determining several key analytes in natural water, sediment and soil [28]. Motelica-Heino et al. developed a combined DGT device with AgI and Chelex-100 binding layers for the simultaneous measurement of sulfide and metals in sediment [29] and Stockdale et al. utilised a AgI and ferrihydrite multiple binding layer DGT for the quantitative analysis of $\text{PO}_4\text{-P}$, V, As and sulfide in freshwater sediment [30]. Mason et al. developed a DGT technique with a mixed binding layer of Chelex-100 and ferrihydrite for the measurement of $\text{PO}_4\text{-P}$, Mn, Cu, Mo, Zn, and Cd [31] in natural waters and Trang et al. applied the same type of mixed binding layer to measure As, Cd, Cu, Pb and Zn [32] in mining impacted water and soil. Xu et al. also developed a mixed Chelex-100 and Zr-oxide binding layer to measure $\text{PO}_4\text{-P}$ and Fe (II) in aquatic systems [33]. Panther et al. developed a Chelex-100 and Metsorb mixed binding layer for simultaneous measurement of cationic (Mn, Co, Ni, Cu, Cd and Pb) and oxyanionic (V, As, Mo, Sb, W and $\text{PO}_4\text{-P}$) trace element concentrations in natural water [34].

Recently, Shiva et al. extended the use of this technique for the measurement of Al in estuarine waters [15,35]. Compared to the use of single-analyte DGT techniques, DGT techniques with multiple and mixed binding layers have the advantage of reducing the materials and time required for preparation, deployment and analysis. However, using mixed binding layers can potentially reduce the intrinsic binding capacity for the individual analytes and thereby increase competition between analytes and major ions compared with single analyte DGTs.

The aim of this study was to develop a new DGT technique with i) a mixed-binding layer for the measurement of dissolved inorganic nitrogen (DIN) species ($\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$) and ii) a second binding layer for $\text{PO}_4\text{-P}$, resulting in a single DGT method for the simultaneous measurement of dissolved inorganic nitrogen and phosphorus (INP-DGT) in freshwaters. A series of laboratory and field experiments were conducted to characterize the performance of the INP-DGT technique, including determining the uptake and elution efficiencies of DIN and Metsorb binding gel layers, evaluating the diffusion coefficients of $\text{NH}_4\text{-N}$, $\text{NO}_3\text{-N}$ and $\text{PO}_4\text{-P}$ using time-series DGT deployments, and measuring the capacity of INP-DGT for the three analytes. The effects of various pH, ionic strengths and hydrogel materials on the DGT uptake were also assessed. The performance of the new DGT technique was validated, by measuring $\text{NH}_4\text{-N}$, $\text{NO}_3\text{-N}$ and $\text{PO}_4\text{-P}$ over three day deployments in synthetic freshwaters with different ionic strengths and at two field sites, through comparison with grab sample concentrations.

2. Material and methods

2.1. General experimental details

All solutions and reagents were prepared using deionised water (Milli-Q Advantage A10, 18.2 $\text{M}\Omega\text{ cm}^{-1}$). Ammonium, nitrate and phosphate solutions were prepared from certified standard solutions (1000 mg L^{-1} as NH_4Cl , NaNO_3 and KH_2PO_4) (Certipur, Merck). Ion exchange resins for DIN (PrCH for $\text{NH}_4\text{-N}$ and A520E for $\text{NO}_3\text{-N}$), and agglomerated nanocrystalline titanium dioxide (Metsorb) for $\text{PO}_4\text{-P}$ were obtained from Purolite Company and Graver Technologies, respectively. Ultrapure agarose (Life Technologies) was used to prepare agarose diffusive layers, and acrylamide (Bio-Rad) and agarose-derived crosslinker (DGT research) were used to prepare polyacrylamide diffusive layers. All plastic containers used for experimental work and preparation and storage of solutions, DGT sampler components and glass plates used for casting gel layers were cleaned in 10% (v/v) HCl (AR grade, Merck) for at least 24 h and rinsed thoroughly with deionised water prior to use.

2.2. DGT procedures

Preparation of diffusive and binding layers. Polyacrylamide contains amide functional groups that could be a potential source of error for $\text{NH}_4\text{-N}$ determinations by DGT. Therefore, in order to eliminate this potential source of error, all diffusive and binding gel layers for the INP-DGT were prepared with agarose.

Agarose diffusive layers for PrCH- and INP-DGT were prepared

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