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Simultaneous sampling of dissolved orthophosphate and ammonium in freshwaters using diffusive gradients in thin films with a mixed binding phase

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ABSTRACT

A new diffusive gradients in thin films (DGT) technique with a micro-sized biochar-zeolite-zirconium oxide mixed binding phase is described for simultaneous sampling of dissolved orthophosphate and ammonium in freshwaters. The performance of mixed binding layer (MBL) DGT technique was characterized by evaluation of the following parameters: (1) the adsorption efficiency of phosphate and ammonium by the mixed binding phase, (2) the elution efficiency, (3) the time-series accumulation, and (4) the influences of pH, coexisting cations and DOC on DGT uptake. The mixed binding phase had high uptake for both phosphate and ammonium. The accumulated analyte mass increased linearly with time over 48 h (Δg = 1.3 mm) and 84 h (Δg = 1.9 mm), respectively. Simultaneous sampling of phosphate and ammonium using MBL-DGT was consistent over the 10–80 mg C L^{-1} DOC concentration range and the 3–8 pH range for a 24 h deployment. The coexisting cations (Na^+, K^+, Mg^{2+}, and Ca^{2+}) were found to compete with the ammonium accumulation by MBL-DGT, but ammonium accumulation was consistent over concentration ranges typically found in most freshwaters (up to 0.01 mol L^{-1} Na^+, 0.001 mol L^{-1} K^+, 0.01 mol L^{-1} Mg^{2+}, 0.03 mol L^{-1} Ca^{2+}). The MBL-DGT method also performed predictably in natural freshwaters containing different concentrations of metal ions and dissolved organic carbon. The results of this project have demonstrated that this new DGT method can offer a more cost-efficient method for simultaneously determining time-weighted average concentrations of ammonium and dissolved orthophosphate in most freshwaters, but inefficiently in high salinity waters because of its extremely high concentration of competing cations.

1. Introduction

Nitrogen and phosphorus are well known to be the two most essential nutrients for the growth of hydrophilous plants and have significant implications for ecosystem function [1]. Increased nutrients loading can stimulate algae blooms in water bodies, which may lead to oxygen depletion, toxin release and clogging of fish gills [2,3]. In natural waters, the principle form of phosphorus is the dissolved orthophosphate species (PO_4^{3-}, HPO_4^{2-}, $H_2PO_4^-$), which is readily available to algae and hydrophytes (bioavailable) [4]. Among the inorganic nitrogen, ammonia nitrogen is the primary form of polluting species in waters, which can be oxidized to nitrate by strictly chemolithotrophic bacteria and cause the reduction of dissolved oxygen [5]. Ammonia nitrogen is comprised of ammonium (NH_4^+–N) and its conjugate base, ammonia (NH_3), with the speciation is highly temperature sensitive and pH-dependent [6]. Ammonium is the dominant species in most surface waters because of its near neutral pH. Therefore, simultaneous sampling of dissolved orthophosphate and ammonium is critical for understanding eutrophication process and assessing the ecological status of natural waters.

Passive sampling methods have been extensively applied for measuring both inorganic and organic pollutants. These monitoring techniques offer some advantages over traditional grab sampling methods, which allows for in situ long-term monitoring and obtaining time-weighted average concentrations [7,8]. In many cases, analyte measurement requires a sample to be grabbed on spot site, filtered or preserved, transported and stored [9–11]. Due to the processes such as particle adsorption, microbial uptake, and precipitation, analyte speciation and concentration may be changed. Passive sampling methods can minimize the above problems, avoid repeated spot sampling, and

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Abbreviations: DGT, the diffusive gradients in thin films technique; SEM, scanning electron microscope; MBL, mixed binding layer; MBL-DGT, the diffusive gradients in thin films technique based on mixed binding layer

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require low energy and low cost [12]. Therefore, dissolved orthophosphate and ammonium are preferable sampled by in situ passive techniques to diminish sample handling and obtain good representative data.

Among the wide range of passive sampling techniques, the diffusive gradients in thin films(DGT) technique has been extensively used for sampling metals, oxyanions, nutrients and several organic pollutants [13–16]. DGT is an in situ time-integrated, passive sampling technique. DGT probe, usually a special plastic device, consists of a filter membrane (supporting and protecting gels), a diffusive gel (controlling flux of the pollutant), and a binding gel (accumulating the pollutant) [11,17,18]. There have been some applications of DGT measurement for dissolved orthophosphate and ammonium. It has been reported that ferrihydrite [19], titanium dioxide (Metsorb) [20] and amorphous zirconium hydroxide (Zr-oxide) [21,22] binding phases were developed for phosphorus measurement. Metsorb and Zr-oxide were used extensively for sampling dissolved phosphorus in water, soil and sediment, because of their high accumulating capacity. Two kinds of ammonium DGT applications were reported in 2015, using a Microlite PrCH resin [23] and a zeolite adsorbent [24], respectively. The binding capacity of PrCH resin and zeolite for ammonium can be interfered by coexisting cations, which limits the applications of these two DGT methods during long-term deployment. Thus, a new high-capacity adsorbent for ammonium is required. Typically, if the concentrations of both phosphate and ammonium are to be determined using DGT, separate samplers utilizing different adsorbents are deployed. However, few of DGT technique employing a mixed binding phase containing high-capacity adsorbents for simultaneously sampling dissolved orthophosphate and ammonium has been reported.

In this study, micro-sized biochar, zeolite and zirconium hydroxide is introduced as a new mixed binding layer (MBL) for simultaneous DGT sampling of dissolved orthophosphate and ammonium in waters. Biochar, a charcoal mesoporous material produced from biomass, has shown a high capacity for binding ammonium [25]. Based on previous research, zeolite [26]and zirconium hydroxide [27] were widely utilized for selective adsorption of ammonium and phosphate, respectively. The following series of laboratory experiments were performed to validate the MBL-DGT technique: measuring elution efficiency, determining phosphate and ammonium accumulation over time for 5 days, estimating the influence of pH and dissolved organic carbon, evaluating the potential interferences from various coexisting cations (Na^+, K^+, Mg^{2+}, and Ca^{2+}). The MBL-DGT devices were deployed in synthetic freshwater and natural river waters for simultaneously sampling dissolved orthophosphate and ammonium.

2. Experimental procedures

2.1. General experimental details

All chemicals used in this study were of analytical reagent grade or higher and purchased from Sinopharm Chemical Reagent Co. Ltd., unless stated otherwise. All samples and solutions were prepared with deionized water. Corncob sample was collected from Liuxi Village, Shenyang, China. Micro-sized natural zeolite powder (10–15 μm, Shunxin Mineral Processing Co. Ltd., China) was used to prepare the mixed binding agents. Ammonium solutions were prepared from the N stock solution of 1000 mg L^{-1} as NH_4Cl (GR grade, 99.8% purity, Aladdin). Phosphate solutions were prepared from the P stock solution of 1000 mg L^{-1} as KH_2PO_4 (GR grade, 99.8% purity, Aladdin). Plastic containers and all DGT components were acid-cleaned in 10% (v/v) HNO_3 (AR grade, 65–68%, J&K) for 12 h and washed with deionized water. All tests were implemented under ammonia-free conditions.

2.2. Preparation of diffusive and mixed binding gels

Diffusive gels were made by dissolving 2.5% (w/v) agarose powder (Biorad) in boiling water until the gel solution was transparent. Then, the gel solution was pipetted into pre-warmed molds separated by a certain thick spacer. The gels were allowed to set at room temperature for 1 h, cut into discs of ~ 1.8 cm diameter and stored in 0.001 mol L^{-1} NaCl solution. The diffusion coefficients of $H_2PO_4^-$ and NH_4^+ through the diffusive gel at 25 °C were found to be 6.05×10^{-6} [19] and 17.1×10^{-6} cm^2 s^{-1} [23], respectively.

The dried clean corncob was crushed, sieved to a size of < 0.6 mm and heated at 600 °C under N_2 flow for 1 h in a pipe furnace [25]. The corncob biochar was then modified by immersing in a 6 mol L^{-1} solution of HNO_3 for 8 h and washed three times using deionized water. After that, the biochar was soaked in 1 mol L^{-1} NaOH solution for 24 h and washed several times with deionized water until at a pH of 7–8. The modified biochar was oven dried, gently crushed and sieved into a size of < 48 μm. Scanning electron microscope (SEM) images were recorded by a high resolution field emission SEM (SU8000, Hitachi, Japan). N_2 adsorption-desorption isotherm of corncob bicohar was recorded on a Micromeritics ASAP 2020 apparatus at 77 K. The BET model was utilized to calculate the BET surface area. The BJH model was used to calculate the pore-size distribution.

Zr-oxide was precipitated from zirconium oxychloride with ammonia water following published procedures [21,28]. Mixed binding gels were made with biochar, zeolite, zirconium hydroxide and agarose. Firstly, 5 mL 3% (w/v) agarose solution was prepared. Then, 5 mL slurry solution (made with 0.3 g biochar, 0.9 g zeolite and 1.2 g Zr-oxide powder added into 10 mL deionized water) was added to the warm gel solution. The mixture solution was pipetted into pre-warmed molds separated by a 0.8 mm thick spacer. This mixture was set at room temperature for 1 h, cut into discs of ~ 1.8 cm diameter and stored in 0.1 mol L^{-1} NaOH solution to remove impurities such as unreacted substance and substances adsorbed on the surface. Before use, the binding gels were rinsed thoroughly with deionized water until the pH reached 7. Each gel disc contained approximately 8 mg biochar, 24 mg zeolite, and 32 mg Zr-oxide.

2.3. MBL-DGT sampler assembly

Nitrocellulose membrane (0.45 μm, Millipore) of 0.1 mm thickness was pretreated as mentioned previously. A DGT sampler was established using a nitrocellulose membrane overlying an agarose gel (Φ = 1.8 cm, Δg = 1.3 mm /1.9 mm) and a mixed binding gel. The combined thickness of nitrocellulose membrane and agarose gel was calculated in all DGT equation.

2.4. Uptake and elution

In order to determine the uptake of ammonium and phosphate by the mixed binding gel discs, triplicate discs were soaked in 20 mL solutions of ammonium and phosphate ranging from 0.5 to 150 mg L^{-1} at pH 6.2 (0.001 mol L^{-1} NaCl). These static adsorption procedures were implemented for 12 h at room temperature. Moreover, the accumulation ability for ammonium and phosphate of the mixed binding gel was compared to other binding gels made from biochar, zeolite, zirconium oxide, biochar-zeolite, biochar-zirconium oxide and zeolite-zirconium oxide by soaking in 20 mL solution of 2.5 mg L^{-1}. Then, water samples were taken to determine the phosphate concentrations before and after discs immersion by the molybdenum blue method [29]. Ammonium concentrations in the solutions before and after discs immersion were measured using the indophenol-blue method [30]. The details about the determination methods of phosphate and ammonium were available in Supporting information(SI).

The harvested mixed binding gels were immersed in 10 mL solutions of 0.2, 0.6 or 1.0 mol L^{-1} NaOH with a matrix of 0.2 mol L^{-1} KCl solution for 8 h. The elution efficiency f_e was calculated according to the ratio between the eluted analyte mass and the decreased analyte mass in the bulk solution.