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Development of a passive sampler based on a polymer inclusion membrane for total ammonia monitoring in freshwaters

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Abstract A passive sampler for determining the time-weighted average total ammonia (i.e. molecular ammonia and the ammonium cation) concentration (C_{TWA}) in freshwaters, which incorporated a polymer inclusion membrane (PIM) as a semi-permeable barrier separating the aqueous source solution from the receiving solution (i.e. 0.8 mol L^{-1} HCl), was developed for the first time. The PIM was composed of dinonylnaphthalene sulfonic acid (DNNS) as a carrier, poly (vinyl chloride) (PVC) as a base polymer and 1-tetradecanol as a modifier. Its optimal composition was found to be 35 wt% commercial DNNS, 55 wt% PVC and 10 wt% 1-tetradecanol. The effect of environmental variables such as the water matrix, pH and temperature were also studied using synthetic freshwaters. The passive sampler was calibrated under laboratory conditions using synthetic freshwaters and exhibited a linear response within the concentration range 0.59 - 2.8 mg L^{-1} NH_4^+ (0.46 - 2.1 mg N L^{-1}) at 20 °C. The performance of the sampler was further investigated under field conditions over 7 days. A strong correlation between spot sampling and passive sampling was achieved, thus providing a proof-of-concept for the passive sampler for reliably measuring the C_{TWA} of total ammonia in freshwaters, which can be used as an indicator in tracking sources of faecal contamination in stormwater drains.

Keywords Passive sampling; Polymer inclusion membranes (PIMs); Dinonylnaphthalene sulfonic acid (DNNS); Total ammonia; Freshwater; Faecal contamination.

Introduction

Effective monitoring of pollutants in waterways is challenging from both a sampling and analytical point of view. Several procedures are involved resulting in a complex, time-consuming and expensive process. Most monitoring programmes involve the collection of discrete water samples, also known as ‘spot’ sampling, however, in aquatic environments where the chemical concentration typically fluctuates over time (e.g. urban stormwater drains), intermittent pollution events are likely to be missed. Increasing the frequency of spot sampling will increase the likelihood of detecting pollution events, although this is often limited by substantial time or cost implications. To help address these problems, passive sampling approaches have been increasingly being adopted [1,2]. These approaches involve the use of sampling devices that allow the pollutants of interest to be collected into their receiving phases, *on site*, and over an extended period of time (i.e. day(s) or weeks). The time-weighted average concentration (C_{TWA}) of the pollutant of interest in the source solution during that period can be determined on the basis of the relationship between the concentration of the target pollutant in the source solution (i.e. aquatic environment) and its amount accumulated in the receiving phase within the sampling period [2,3]. These sampling devices are not only more efficient in detecting pollution events, but they also simplify the overall analytical process by combining sampling, pollutant separation, accumulation and preservation in one step.

Different types of passive samplers have been developed for environmental water quality monitoring over the last three decades [2]. Amongst the most commonly used are semi-permeable membrane devices (SPMDs) [4], polar organic chemical integrative samplers (POCISs) [5], diffusion gradient in thin-films (DGT) [6] and Chemcatcher samplers [7], covering a wide range of organic and inorganic compounds (e.g. herbicides, polycyclic aromatic hydrocarbons, heavy metals) [8,9]. However, to the best of our knowledge, no passive sampler has been developed for ammonia monitoring in water.

Ammonia is an important micronutrient as it plays a fundamental role in the nitrogen cycle, although at mg L^{-1} levels it is toxic to a range of aquatic life [10,11]. Elevated concentrations of ammonia in freshwater environments are usually caused by human activities (e.g. sewage leaks, septic tank discharges, detergents) which can lead to major impacts to the ecological health of waterways as well as pose a public health risk for aquatic recreation where pollution sources are often associated with sewage contamination. Accordingly, ammonia is frequently included as an indicator of water quality in freshwater and marine environmental monitoring programs [12]. In this context, the present research proposes a passive sampler to measure the C_{TWA} of total ammonia (i.e. molecular ammonia and the ammonium cation) based on the use of a polymer inclusion membrane (PIM) as a semi-permeable barrier. This novel type of passive sampler has been introduced recently and applied for Zn(II) monitoring in urban freshwaters using a PIM with di-2-(ethylhexyl) phosphoric acid (D2EHPA) as the extractant [13]. PIMs are flexible polymeric materials, optically transparent, homogenous, robust, and generally composed of a base polymer and an extractant [14,15]. The base polymer gives the structure and mechanical strength to the membrane while the extractant (often referred to as membrane carrier) is responsible for binding the target analyte and for its transport across the PIM as a carrier-analyte adduct (e.g. complex or ion-pair). In some cases plasticizers and modifiers can also be added to the PIM composition to improve membrane flexibility and solubility of the extracted carrier-analyte adducts in the membrane. These membranes allow both extraction and back-extraction of the analyte to occur simultaneously on either side of the membrane [16]. Hence, when applied as a semi-permeable barrier in a passive sampler, the PIM separates the aquatic environment (i.e. source phase) from the receiving phase which contains a suitable stripping reagent (e.g. mineral acid), which means that the concentration of the analyte accumulated into the receiving solution can be measured directly, thus further simplifying the analytical process. With a number of passive samplers currently used (e.g. Chemcatcher and DGT) chemical analysis can take place only after the stripping of the pollutant(s) from the solid receiving phase of the sampler. Another advantage of using PIMs in passive sampling is based on their versatility, since the membrane composition can be tailored to the pollutant of interest. In the present work, a PIM composed of dinonylnaphthalene sulfonic acid as an extractant, poly (vinyl chloride) as a base polymer and 1-tetradecanol as a modifier, which had been studied previously [17], was used as a semi-permeable barrier to develop the first PIM-based passive sampler to monitor total ammonia in freshwaters with the aim of identifying faecal contamination sources in urban stormwater drains.

Experimental

Reagents and solutions

Dinonylnaphthalene sulfonic acid (DNNS) (King Industries, 50 wt% in 2-butoxyethanol), high molecular weight poly(vinyl) chloride (PVC) (Aldrich), 1-tetradecanol (Aldrich) and tetrahydrofuran (THF) without a stabilizer (VWR, Australia) were used as received in the preparation of the PIMs.

Stock solutions containing 10 g L^{-1} and 100 g L^{-1} NH_4^+ were prepared by dissolving ammonium chloride (BDH, Australia), previously dried at 100 °C for at least 2 h, in deionized water. Working standard solutions were obtained by dilution of the 100 mg L^{-1} NH_4^+ stock solution with deionized water or 0.8 mol L^{-1} M HCl solution to match the acidity of the samples to be analyzed (i.e. source or receiving solutions).

Synthetic freshwaters were prepared by appropriate dilution of the following stock solutions: sodium chloride (Chem-supply, Australia) containing 20 g L^{-1} Na, potassium chloride (Chem-supply, Australia) or potassium hydrogen carbonate (Ajax, Australia) containing 15 g L^{-1} K, magnesium sulfate heptahydrate (Chem-supply, Australia) containing 30 g L^{-1} Mg and calcium nitrate tetrahydrate (Chem-supply, Australia) containing 40 g L^{-1} Ca.

The HCl solutions (0.2 - 0.8 mol L^{-1}), used as the receiving solutions in the passive sampler, were prepared by appropriate dilution of concentrated HCl solution (32%, RCI Labscan, Thailand) and subsequently standardized against sodium tetraborate (Chem-supply, Australia).

In the gas-diffusion flow injection analysis (GD-FIA) system, 2.0 mol L^{-1} NaOH (Chem-supply, Australia) was used as the donor stream and an acid-base indicator solution was used as the acceptor stream, prepared by 50 times dilution of a stock solution of 0.5 g L^{-1} of cresol red (Aldrich) and 1.5 g L^{-1} of thymol blue (Sigma-Aldrich). The absorbance of the working acid-base indicator solution at 590 nm was adjusted to read between 0.12 and 0.20 by the addition of 0.1 mol L^{-1} NaOH, which was set to zero on the spectrophotometer (Biochrom Libra S12, UK) [18].

Deionized water (resistivity > 18 MΩ cm, Millipore, Synergy 185, France) was used for the preparation of all solutions and all chemicals were analytical-reagent grade.

Total ammonia determination

In the pH range of freshwaters, the predominant ammonia species is the ammonium ion (NH_4^+) although small amounts of molecular ammonia (NH_3) might also be present [19]. Though the sum of both ammonia and ammonium is usually referred to as 'total ammonia', the term 'ammonium' will be used to express total ammonia throughout this manuscript for brevity and concentrations will be expressed in mg L^{-1} of NH_4^+.

The concentration of total ammonia in the source and receiving solutions during the passive sampling experiments in the absence of interferences, were determined by a GD-FIA system with a limit of detection of 0.61 mg L^{-1} [17]. In the presence of interferences (i.e. analysis of synthetic or natural freshwaters) higher sensitivity was required and samples were analyzed using the same GD-FIA system but with a gas-diffusion unit with a larger gas-diffusion membrane area which incorporated 12 cm donor and acceptor channels with a zig zag configuration instead of the 6.5 cm straight channels in the original system. Under these conditions, the limit of detection of the modified GD-FIA system was 0.013 mg L^{-1}.

The concentration of total ammonia in spot samples collected from a creek in Park Orchards, Melbourne, Australia were determined by ALS Global, Australia, using the indophenol blue method [20]. All samples were filtered after collection using a syringe filter (Millipore, PES membrane, 0.45 μm) and were frozen until sent to the laboratory for analysis.

Instrumentation

A TPS smartChem-Lab Multi-Parameter Laboratory Analyzer (Australia) was used to measure the pH of the source solutions. The ionic strength of the source solutions composed of ammonium chloride only was adjusted using a solution of potassium chloride in order to achieve a final ionic strength of approximately 0.2 mol L^{-1}.

Passive sampling experiments performed at temperatures below room temperature (i.e. 15 and 20 °C) were carried out inside a commercial refrigeration cabinet (Clegg, Australia) regulated by an E5CN OMRON temperature controller. The temperature of the source solutions was measured using a digital temperature probe (U-Lab Instruments, display resolution < 0.5 °C).

Freshwaters collected from a stormwater drain and a creek in Frankston and Park Orchards (Melbourne, Australia), respectively, as well as receiving solutions from the samplers deployed in a creek in Park Orchards, were analysed by inductively coupled plasma optical emission spectrometry (ICP-OES; Varian Vista Pro Axial, Varian, Australia) under the following conditions: power 1.3 kW, plasma flow 18 L min^{-1}, auxiliary flow 1.5 L min^{-1}, nebuliser flow 0.75 L min^{-1}. Measurements were conducted in quintuplicate at the following nm wavelengths: 396.2 (Al), 189.0 (As), 393.4 (Ca), 230.8 (Co), 284.3 (Cr), 327.4 (Cu), 238.2 (Fe), 766.5 (K), 280.3 (Mg), 589.6 (Na) and 231.6 (Ni).

Membrane preparation

Each PIM (320 mg) was prepared by dissolving commercial DNNS, 1-tetradecanol and PVC in 5 mL of THF and the solution was then poured into a glass ring (73 mm in diameter), positioned on a glass plate, which was covered with filter paper and a watch glass to allow slow evaporation of the solvent over a period of 24 h. These conditions ensured the manufacturing of homogeneous and transparent PIMs with oil free surfaces and an average thickness of 40 ± 7 μm.

A maximum of four circular membrane segments of 25 mm in diameter each (20.9 ± 0.9 mg, *n*=15) were cut from the center of each casted membrane and used as the semi-permeable barrier in the passive samplers. All membrane compositions are presented in mass percentages (wt%).

Passive sampler

A passive sampler, using a D2EHPA-based PIM as the semi-permeable barrier, has been developed previously in our laboratory to measure the C_{TWA} of Zn(II) [13]. This passive sampler consisted of a Teflon block with a well to accommodate the receiving solution (10 mL). The PIM was attached to the sampler using Teflon and stainless steel washers which were screwed to a stainless steel structure in order to seal the well. With the aim of making the passive sampler lighter, easier to assemble and cheaper, we have redesigned it and materials, such as Teflon and stainless steel, have been replaced by glass and plastic (Fig. 1).

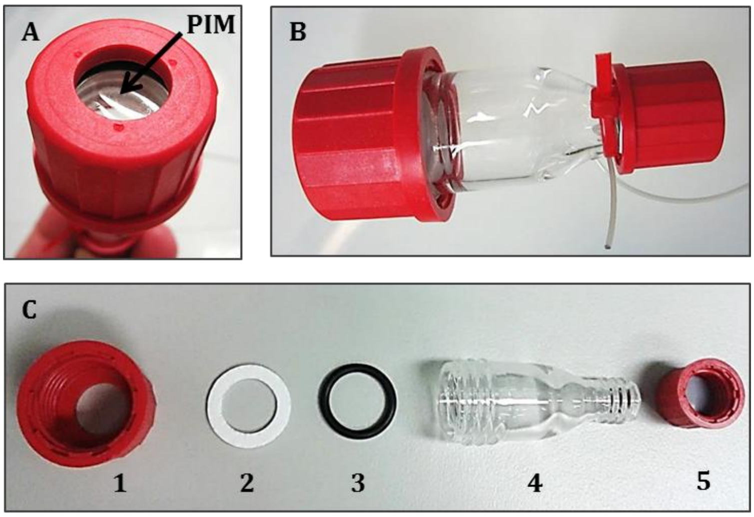

Figure 1 Photographic images of the PIM-based passive sampler used in the present study. **A**, Screw cap with aperture accommodating the PIM. **B**, Assembled passive sampler. **C**, Components of the passive sampler: (1) cap with aperture; (2) Teflon washer; (3) rubber o-ring; (4) glass vessel with screw threads on the ends; (5) screw cap.

The redesigned passive sampler consists of a glass vessel with screw threads on each end (Fig. 1C-4), two screw caps (Fig. 1C-1, 25 mm with aperture; Fig. 1C-5, 14 mm with no aperture), a Teflon washer (Fig. 1C-2) and a rubber o-ring (Fig. 1C-3). The glass vessel consists of two screw thread glass tubes (Lenz Laborglas, Germany) with different diameters (24 and 14 mm) joined together to create a 5.4 cm long bottle shaped container with a capacity to accommodate 10 mL of solution. The smaller opening is used to sample the receiving solution and the larger opening to expose the membrane to the source solution. The PIM is placed between a Teflon washer (1.5 mm thick, 24 mm O.D., 16 mm I.D., Gasketech) and a rubber o-ring (No 13, L.W. Gemmell, Australia). A 25 mm diameter circular membrane was used, although only a 15 mm diameter of this was exposed to the source solution (contact surface area of 177 mm^2) (Fig. 1A). Several layers of Teflon tape were wound around the glass threads before screwing on the caps to prevent leakage.

Passive sampling experiments

The passive samplers were assembled by incorporating a DNNS-based PIM and 10 mL of receiving solution (Fig. 1B). For laboratory passive sampling experiments, three samplers were placed inside a plastic container comprising 10 L of source solution, with the PIM side facing downwards. A polypropylene test tube rack (Kartell, 24 place, 30 mm diameter) was also positioned inside the plastic container in order to maintain the position and orientation of the passive samplers. To promote the circulation of the source solution to imitate water flow in aquatic systems such as creeks, an underwater fish tank pump (AQUAP333L Watermaster, White International, Australia) was attached to one of the inside walls of the plastic container. The source solution was prepared by weighing 10 L of deionized water (digital precision scale balance, Breville, model BSK200), and transferring it into the plastic container, followed by the addition of the appropriate volume of stock solution containing the required cation(s) (before this addition, the same volume of deionized water was removed from the plastic container in order to keep the water volume of 10 L constant). The composition of the source solutions used in the different passive sampling experiments is described in Table 1.

Table 1 Composition and characterization of the source solutions (SS) used in the laboratory passive sampling experiments.

Cations / Salts	SSa	SSb	SSc	SSd
NH_4^+ / NH_4Cl (mg L^{-1} NH_4^+)	1 or 3 0.515-2.46*	1	1.5	1.5 0.587-2.75*
Na^+ / NaCl (mg L^{-1} Na)	-	186	100	200
Ca^{2+} / $Ca(NO_3)_2$ (mg L^{-1} Ca)	-	-	25	40
Mg^{2+} / $MgSO_4$ (mg L^{-1} Mg)	-	-	15	30
K^+ / KCl^a or $KHCO_3^b$ (mg L^{-1} K)	-	-	5	15
pH (*n*=4)	6.5±0.3	4.7±0.8	4.8±0.5^a/7.8±0.1^b	4.7±0.8^a/7.8±0.0^b
EC (µS cm^{-1}) (*n*=4)	-	1018±21	810±19^a/797±10^b	1513±33^a/1494±15^b
Water hardness (mg L^{-1} $CaCO_3$)	-	-	124 (Hard)	223 (Very Hard)

* Concentration range for the calibration curve.

EC, electrical conductivity

"a" and "b" refer to solutions containing either KCl or $KHCO_3$, respectively.

In the preliminary experiments, such as those for determining the optimal membrane composition, optimization of the receiving solution concentration and calibration of the passive samplers in the absence of interferences, a source solution containing only ammonium (i.e. Table 1, SSa) was used. In these experiments, the source solution was replaced every two days in order to keep its ammonium concentration and pH constant. For all other passive sampling experiments (i.e. the study of the effect of the environmental variables and the calibration curve in the presence of interferences), synthetic freshwater spiked with ammonium was used as the source solution (i.e. Table 1, SSb, SSc and SSd). The pH of the synthetic freshwaters was adjusted by using either KCl or $KHCO_3^-$, respectively (Table 1, SSc and SSd).

A sampling period of 7 days was selected with future freshwater field applications in mind, where it was considered desirable to be able to monitor the freshwater during both weekdays and weekends. Within the 7 days, both the source and receiving solutions were sampled (3.00 mL and 0.500 mL, respectively) at pre-determined periods of time and the total ammonium concentration was determined by GD-FIA. Each sample removed was replaced with the same volume of original solution and dilution was taken into account when processing the data. To monitor the pH of the source solutions, 5.00 mL samples was collected at pre-determined periods of time and replaced with the original solution.

In the field, passive samplers were attached to a floating structure via their sampling ports. The structure consisted of a baseless metallic cage coated with plastic (21 cm length, 10 cm width, and 6 cm depth) with a mesh size of 14 mm approximately. After inserting the sampling port of each sampler in one of the holes of the cage, the small cap was screwed on in order to seal the passive sampler and attach it firmly to the meshed structure. Two polystyrene blocks were placed on the top of the structure (one on each side) and fixed with cable ties. This approach allowed the structure containing the passive samplers to float, ensuring that the passive samplers' caps containing the PIMs were facing downwards throughout the period of deployment, thus guaranteeing that both source and receiving solutions were in contact with the membrane.

Results and discussion

PIM extraction and transport of ammonium

The ability of membranes containing DNNS, an acidic extractant with cation-exchange properties, to extract ammonium has been studied recently [17]. In a passive sampling system where the DNNS-based PIM separates the source solution from the receiving solution, both the extraction and back-extraction processes occur simultaneously, allowing ammonium to be transported and accumulated into the receiving solution as shown schematically in Fig. 2.

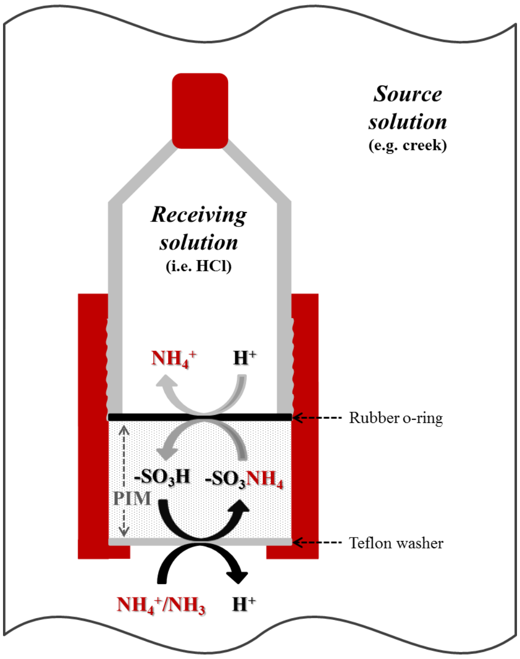

Figure 2 Cross section of a passive sampler (amplified membrane thickness) with a schematic representation of the transport mechanism for total ammonia across the DNNS-based PIM. Black solid arrows illustrate the extraction process. Grey solid arrows illustrate the back-extraction process.

The ammonium ion present in the source solution can replace the hydrogen ion of a DNNS sulfonic acid group (-SO_3H) and form an ion-pair in the PIM with the DNNS anion (Fig. 2, black solid arrows). Molecular ammonia, present as a small fraction of total ammonia in most freshwaters, can be protonated by the hydrogen ions of the sulfonic acid groups of DNNS molecules and also form ion-pairs in the PIM with the corresponding DNNS anions (Fig. 2, black solid arrows). The ammonium-DNNS ion-pairs formed at the PIM/source solution interface diffuse towards the PIM/receiving solution interface along the corresponding concentration gradient. At the membrane/receiving solution interface, the extracted ammonium is stripped into the acidic receiving solution (Fig. 2, grey solid arrows) thus regenerating the original DNNS molecules which diffuse back to the PIM/source solution interface. This mass transport is known as facilitated transport [15,16]. The acidity of the receiving solution, determined by its H^+ concentration which is much higher than that of the source solution, is thus the driving force for the facilitated ammonium transport across the PIM and ammonium will be continuously accumulated in the receiving solution as long as the acidity of the receiving solution is higher than that of the source solution.

Influence of the membrane composition

A previous study in our laboratory on DNNS-based membranes [17] using both PVC and cellulose triacetate (CTA) as the base polymers and 1-tetradecanol as a modifier, demonstrated that PIMs could be produced with properties that showed potential for the extraction and transport of ammonium. In the present application, where acidic receiving solutions were used, PVC was chosen as the base polymer instead of CTA which could undergo acid hydrolysis [14].

In order to determine the optimal concentration of commercial DNNS in the PVC-based membrane to achieve the best transport and accumulation of ammonium in the passive sampler, an initial passive sampling experiment was carried out using 0.8 mol L^{-1} HCl receiving solution and 3 mg L^{-1} ammonium source solution (Table 1, SSa). The amount of modifier in the membrane was kept constant (i.e. 10% 1-tetradecanol) and the amount of PVC was decreased as the amount of DNNS was increased. The effect of the DNNS concentration in the PIM on the accumulation of ammonium in the receiving solution over a 7-day period is depicted in Fig. 3.

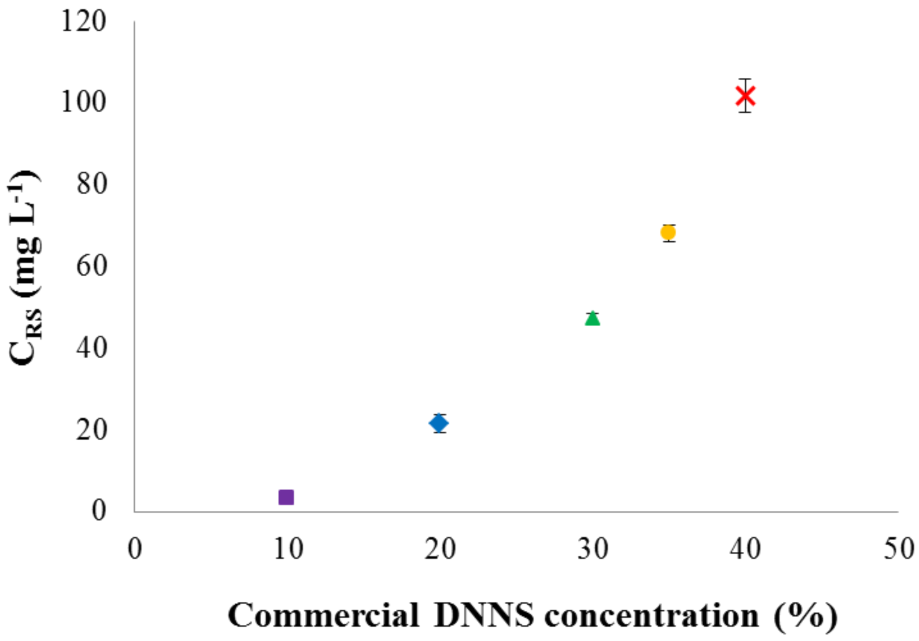

Figure 3 Concentration of ammonium in the receiving solution (C_{RS}) versus the concentration of commercial DNNS in the membrane. Membrane compositions: (■) 10% DNNS, 10% 1-tetradecanol, 80% PVC; (◆) 20% DNNS, 10% 1-tetradecanol, 70% PVC; (▲) 30% DNNS, 10% 1-tetradecanol, 60% PVC; (●) 35% DNNS, 10% 1-tetradecanol, 55% PVC; (×) 40% DNNS, 10% 1-tetradecanol, 50% PVC. Source solution, 10 L of 2.84 ± 0.12 mg L^{-1} NH_4^+; receiving solution, 10.0 mL of 0.8 mol L^{-1} HCl solution, sampling period, 7 days; temperature, 23 °C. Experiments were carried out in triplicate and the error bars are shown.

The concentration of ammonium in the receiving solution (C_{RS}) after 7 days of contact time with the source solution increased exponentially by increasing the concentration of DNNS in the membrane. Although the membrane composed of 40% commercial DNNS, 10% 1-tetradecanol and 50% PVC gave the highest accumulation, PIMs of this composition can suffer from poor stability [17]. Thus, as a compromise between membrane stability and maximum pre-concentration, the membrane containing 35% commercial DNNS, 10% 1-tetradecanol and 55% PVC was chosen for further studies. Under the experimental conditions described above, the mass loss of this membrane after 7 days of exposure was not significant (i.e. 4.4±0.5%, calculated by weighing the membrane before placing it in the sampler and after the 7 days of exposure to both the source and receiving solutions).

Optimization of the concentration of the receiving solution

Because the concentration of the receiving solution plays an important role in the transport of ammonium across the membrane and the accumulation of ammonium in the receiving solution, it ultimately determines the accumulation capacity of the sampler. Hence, the effect of the concentration of HCl in the receiving solution was studied at room temperature within the range 0.2 - 0.8 mol L^{-1} using a source solution containing only ammonium (Table 1, SSa). After a 2-day sampling period, statistical differences were found at the 95% confidence level between the average ammonium concentration (n=3) of receiving solutions with 0.2 and 0.6 mol L^{-1} HCl as well as with 0.2 and 0.8 mol L^{-1} HCl (Student's t test: $30.8 > 4.31$ and $27.0 > 5.32$, respectively). The accumulation of ammonium in the 0.2 mol L^{-1} HCl receiving solution was significantly lower than that for the other two concentrations studied, showing that this concentration was insufficient to ensure efficient transport and accumulation of ammonium. On the other hand, after either 2 or 7 days of sampling, no statistical differences were found between the average concentration of ammonium (n=3) present in the receiving solution for 0.6 and 0.8 mol L^{-1} HCl (Student's t test: $3.80 < 6.65$ and $5.60 < 10.9$, respectively). In order to guarantee that the HCl concentration is high enough, even in the presence of more complex source solutions, 0.8 mol L^{-1} was selected as the optimum HCl receiving solution concentration.

Calibration of the passive sampler in the absence of interferences

In order to be able to calculate the C_{TWA} of ammonium using the PIM-based passive sampler, it is essential to calibrate it under known conditions and correlate the concentration obtained in the receiving solution after a particular sampling period with the average concentration found in the sampled medium, i.e. source solution. A source solution containing only ammonium was used initially to calibrate the passive sampler (Fig. 4).

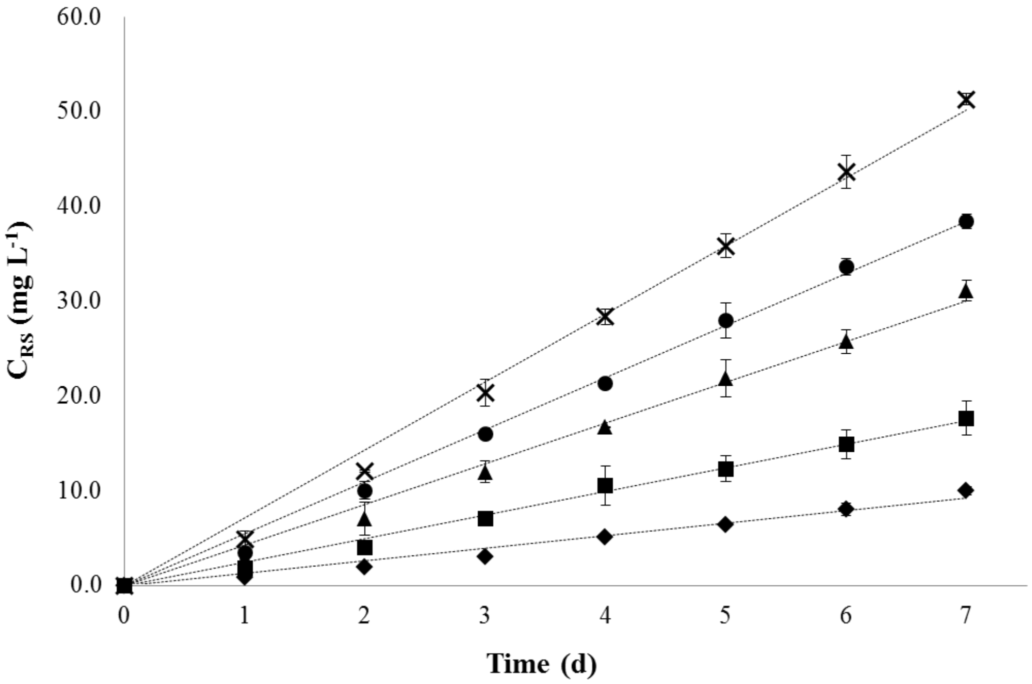

Figure 4 Transient concentration of ammonium in the receiving solution (C_{RS}) versus sampling time for the following source solutions: (◆) 0.51 ± 0.03, (■) 0.98 ± 0.02, (▲) 1.54 ± 0.06, (●) 2.00 ± 0.02, and (✕) 2.46 ± 0.03 mg L^{-1} NH_4^+. Source solution volume, 10 L; receiving solution, 10.0 mL of 0.8 mol L^{-1} HCl solution; PIM composition, 35% commercial DNNS, 10% 1-tetradecanol, 55% PVC; temperature, 23 °C. Triplicate measurements were made and error bars are shown.

Fig. 4 shows a linear rate of ammonium transfer from the source to the receiving solution at five different concentrations. A linear calibration curve of the ammonium passive sampler was obtained at ammonium concentrations in the source solution of up to 2.5 mg L^{-1} (C_{RS} = 20.1 C_{SS}, R^2 = 0.990) for a 7-day sampling period.

Effect of the water matrix and temperature

The water matrix is one of the environmental factors expected to affect the PIM-based passive sampler's performance. Since DNNS is a cation-exchanger, it is anticipated that other cations present in the sampled medium (i.e. source solution) will also be transported across the membrane along with ammonium and, such competition is likely to affect the overall ammonium trans-membrane transport rate. The 4 major cations present in freshwaters are Na^+, Ca^{2+}, Mg^{2+} and K^+, and they typically exist in higher concentrations than ammonium [21]. In this context, Fig. 5 illustrates the effect of three different matrix compositions on the ammonium transient concentration in the receiving solution, the slope of which is indicative of the overall trans-membrane ammonium transfer rate: 1 mg L^{-1} ammonium only (Table 1, SSa), 1 mg L^{-1} ammonium and 186 mg L^{-1} Na^+ (Table 1, SSb) and freshwater collected from a stormwater drain (Frankston, Melbourne, Australia) spiked with 1 mg L^{-1} ammonium. The concentration of NaCl in source solution SSb was adjusted to achieve an electrical conductivity (EC) similar to that of the spiked freshwater (i.e. 992 µS cm^{-1}). It should be pointed out that in addition to Na^+ (128 mg L^{-1}) the spiked freshwater also contained other cations such as Ca^{2+} (22.3 mg L^{-1}), Mg^{2+} (21.7 mg L^{-1}) and K^+ (5.47 mg L^{-1}).

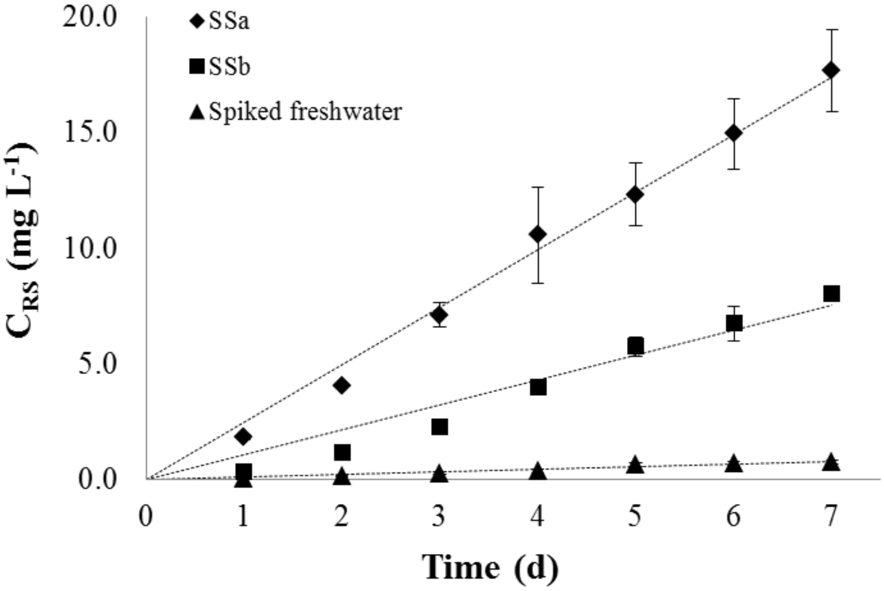

Figure 5 Transient concentration of ammonium in the receiving solution (C_{RS}) versus sampling time for the following source solutions: (◆) SSa (0.98 ± 0.02 mg L^{-1} NH_4^+), (■) SSb (0.98 ± 0.04 mg L^{-1} NH_4^+; EC, 1018 ± 21 µS cm^{-1}), (▲) Spiked freshwater (0.91 ± 0.01 mg L^{-1} NH_4^+; EC, 986 ± 3 µS cm^{-1}). Source solution volume, 10 L; receiving solution, 10.0 mL of 0.8 mol L^{-1} HCl solution; PIM composition, 35% commercial DNNS, 10% 1-tetradecanol, 55% PVC; temperature, 24 °C. Triplicate measurements were made and error bars are shown.

The presence of Na^+ in a higher concentration than that of ammonium clearly affected the transport rate of ammonium since the enrichment factor after 7 days decreased from 18 (calculated as C_{RS}/C_{SSa}) to 8.4 (calculated as C_{RS}/C_{SSb}) (Fig. 5). The enrichment factor in the sampler exposed to the spiked with ammonium freshwater was even lower (i.e. 0.83, calculated as $C_{RS}/C_{SS\ \text{spiked freshwater}}$), demonstrating that the presence of other cations significantly reduced ammonium uptake, to a point where the concentration of ammonium present in the receiving solution after 7 days was lower than that in the source solution. The absence of any pre-concentration would be an issue if ultra-trace levels of ammonium were to be monitored, however, the ammonium concentration in most freshwaters is normally within the range 0.03 – 17.5 mg L^{-1} NH_4^+ [22] which can easily be measured directly by both conventional batch (e.g. Berthelot method) and flow-through (e.g. GD-FIA) analytical method [19]. Thus, the PIM-based passive sampler can still be used to monitor ammonium in freshwater even when its concentration in the receiver solution is lower than its concentration in the source solution.

The greater variability in the results for source solution SSa (Fig. 5) can be attributed to performance variability of the GD-FIA system used in measuring the ammonium concentration in the receiving solution.

It is neither practical nor realistic to collect several liters of a freshwater sample and transport it to the laboratory for calibration purposes every time a different aquatic system is to be monitored. Thus, synthetic freshwaters were prepared to examine the effect of the freshwater matrix on the ammonium uptake with the aim to determine if calibration using spiked synthetic freshwater solutions as calibration standards was feasible. Because the main interferences affecting the newly developed PIM-based passive sampler were cations, synthetic freshwaters containing the 4 major cations usually present in natural freshwaters (i.e. Na^+, Ca^{2+}, Mg^{2+} and K^+) were prepared and their compositions are shown in Table 1 (i.e. SSc and SSd). Moreover, in order to mimic the composition of natural freshwaters as closely as possible, parameters including EC, water hardness and pH were used to characterize the water matrix, and the salts used contained the main anions present in freshwaters (i.e. Cl^-, SO_4^{2-}, NO_3^- and HCO_3^-) [21].

The effect of the matrix composition (Table 1, SSc and SSd) on the uptake of ammonium by the PIM-based passive sampler is depicted in Fig. 6.

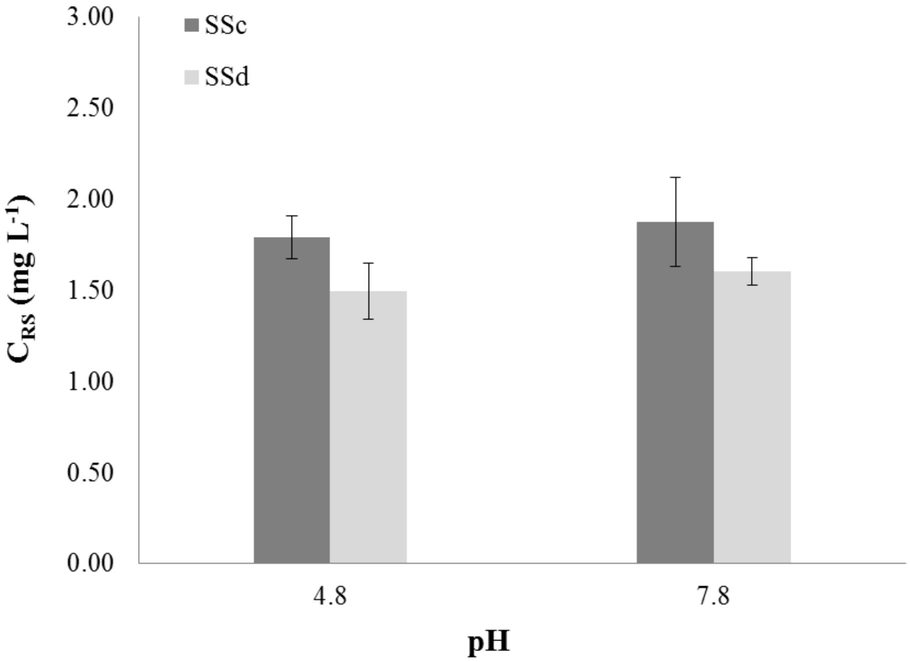

Figure 6 Effect of the freshwater matrix and pH on the concentration of ammonium transported into the receiving solution (C_{RS}). Dark grey bars, SSc with 1.5 mg L^{-1} NH_4^+. Light grey bars, SSd with 1.5 mg L^{-1} NH_4^+. The full compositions of SSc and SSd are outlined in Table 1. Source solution volume, 10 L; receiving solution, 10.0 mL of 0.8 mol L^{-1} HCl solution; PIM composition, 35% commercial DNNS, 10% 1-tetradecanol, 55% PVC; sampling period, 7 days; temperature, 24 °C. Triplicate measurements were made and error bars are shown.

The amount of ammonium found in the receiving solution when samplers were exposed to source solution SSc (hard water with EC around 800 μS cm^{-1}) was 16.8 and 14.4% higher than the average value measured when samplers were exposed to source solution SSd (very hard water with EC around 1500 μS cm^{-1}), at pH 4.8 and 7.8, respectively. These results are consistent with the findings shown in Fig. 5 which illustrate the fact that as the complexity of the matrix increases, the transport rate of ammonium across the membrane decreases. However, for the two freshwater matrices studied (i.e. SSc and SSd), the difference in the transport rates is not so significant as to impede the application of the newly developed PIM-based passive sampler for monitoring freshwaters to assess their ammonium contamination levels rather than for conducting highly accurate concentration measurements.

With regard to the effect of pH on the ammonium concentration in the receiving solution, no statistically significant differences according to the Student's t test were found at the 95% confidence level between the

C_{RS} values (after 7 days, *n*=3) at pH 4.8 and 7.8 for both SSc (0.08 < 0.219) and SSd (0.110 < 0.143). The fact that pH does not affect the ammonium uptake of the PIM-based passive sampler can be explained by the presence of only a small amount of molecular ammonia at the pH values studied, i.e. at 24 °C the percentage molar fractions of molecular ammonia in solutions at pH 4.8 and 7.8 are 0.005 and 3.2%, respectively [23].

Temperature is another environmental factor known to affect diffusion rate [2] and its influence on the PIM-based passive sampler was studied using source solution SSd (Table1).

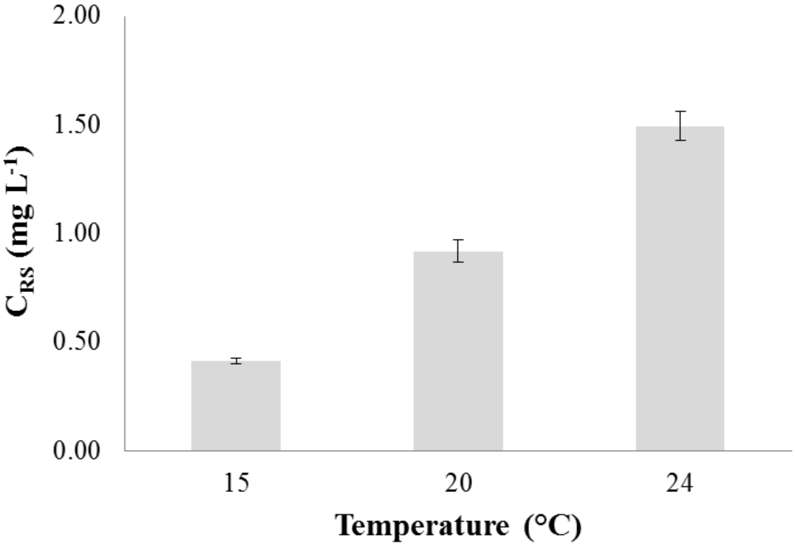

Figure 7 Effect of the temperature on the concentration of ammonium in the receiving solution (C_{RS}). Source solution (SSd, Table 1), 1.5 mg L^{-1} NH_4^+; source solution volume, 10 L; receiving solution, 10.0 mL of 0.8 mol L^{-1} HCl solution; PIM composition, 35% commercial DNNS, 10% 1-tetradecanol, 55% PVC; sampling period, 7 days; pH, 7.8. Triplicate measurements were made and error bars are shown.

The ammonium uptake of the passive sampler decreased linearly with a decrease in the temperature of the source solution (C_{RS} = 0.120 Temperature – 1.41, R^2 = 0.990). This means that, when deployed in the field, the temperature of the freshwater source should be measured and the laboratory calibration should be made at the same temperature, or the calibration data should be corrected using the temperature relationship derived under laboratory conditions (Fig. 7).

Calibration of the passive sampler using synthetic freshwater standards and a field application

The results described above demonstrate that calibration of the passive sampler with standards in deionized water for field applications is not suitable because the ammonium uptake of the sampler is significantly affected by the water matrix. We also demonstrated that the use of synthetic freshwater calibration standards was expected to limit the matrix effect in field measurement. Thus, the newly developed PIM-based passive sampler was calibrated with synthetic freshwater ammonium standards (Table 1, SSd) and deployed in a creek located in Park Orchards, Melbourne, Australia. Synthetic freshwater SSd (Table 1) was used because it matched more closely the matrix of the creek freshwater (Table 2) than the other synthetic freshwater compositions (Table 1).

Table 2 Concentrations of metals and ammonium in creek freshwater in Park Orchards, Melbourne (C_{SS}) and in the receiving solution (C_{RS}) of the PIM-based passive sampler after a 7-day sampling period (*n*=2) in the same creek. Except for ammonium, the measurements were carried out by ICP-OES (LOD, limit of detection).

Metals and ammonium	C_{SS} (mg L^{-1})	C_{RS} (mg L^{-1})
Na	183 ± 58	32 ± 4
Ca	42.8 ± 8.6	56.7 ± 1.3
Mg	29.3 ± 5.6	26.6 ± 2.2
K	16.2 ± 2.0	7.9 ± 0.2
NH_4^+	1.97 ± 0.39*	1.18 ± 0.08**
Fe	0.310 ± 0.199	0.204 ± 0.019
Al	0.268 ± 0.091	0.095 ± 0.065
Cu	0.0276 ± 0.0066	0.0361 ± 0.0045
As	< LOD	< LOD
Co	< LOD	< LOD
Cr	< LOD	< LOD
Ni	< LOD	< LOD

* Determined by ALS Global, Australia; ** Determined by GD-FIA

A linear calibration curve was obtained between 0.587 and 2.75 mg L^{-1} NH_4^+ ($C_{RS} = 0.618\ C_{SS}$, $R^2 = 0.998$) for a 7-day sampling period under the following conditions: EC, 1474 ± 5 µS cm^{-1}; pH, 7.6 ± 0.2; temperature, 20 °C.

To test the performance of the ammonium PIM-based passive sampler, two samplers were deployed in Park Orchards creek (Melbourne, Australia) for a period of 7 days while spot samples were collected on a daily basis. Fig. 8 shows the transient ammonium profile obtained by using spot sampling and the C_{TWA} of ammonium determined on the basis of the 2 passive samplers and the calibration curve prepared in synthetic freshwater standards (i.e. $C_{TWA} = C_{RS}/0.618$).

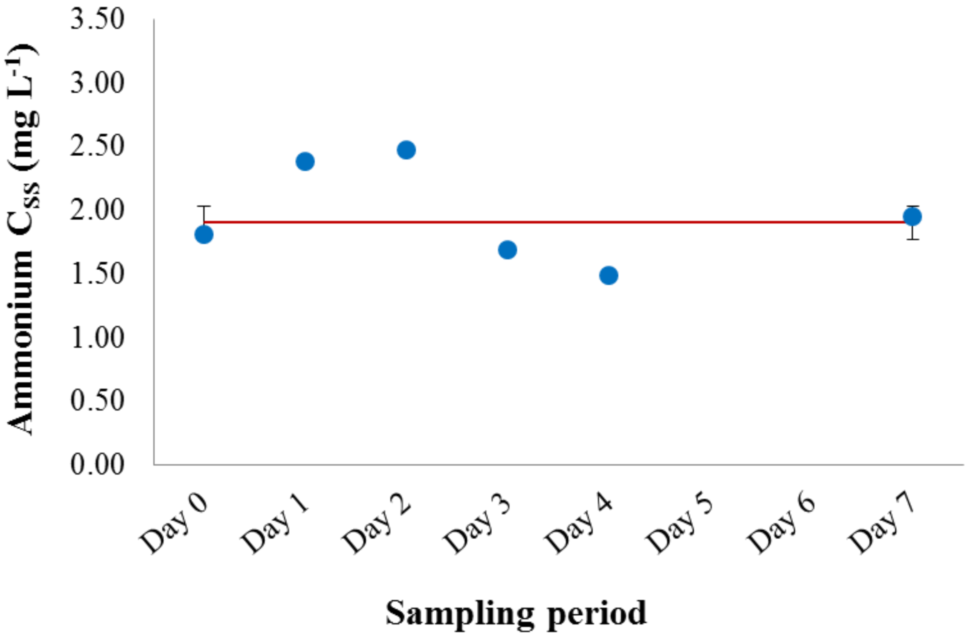

Figure 8 Ammonium concentration in Park Orchards creek (C_{SS}) obtained by spot sampling (●) versus C_{TWA} determined by passive sampling (*n*=2) (——). Environmental conditions: EC, 1185 ± 326; pH, 7.7 ± 0.1; temperature, 20 °C. Passive sampling conditions: receiving solution, 10.0 mL of 0.8 mol L^{-1} HCl solution; PIM composition, 35% commercial DNNS, 10% 1-tetradecanol, 55% PVC.

No statistically significant difference was found at the 95% confidence level (Student's t test: $0.06 < 0.29$) between the average concentration of ammonium of the six spot samples (1.97 ± 0.39 mg L^{-1}) and the mean C_{TWA} of the two passive samplers (1.91 ± 0.13 mg L^{-1}). The good agreement between the two sampling methods, despite the fact that other cations were also transported into the receiving solution of the passive sampler (Table 2), provided a proof-of-concept for the applicability of the newly developed PIM-based passive sampler for the determination of the C_{TWA} of ammonium in freshwaters. Moreover, after 7 days of exposure to the creek freshwater, there was no sign of biofouling which was most likely due to the fact that the PIM employed had a hughly acidic surface that restricted biofilm growth.

Conclusions

The first PIM-based passive sampler for the determination of the time-weighted average concentration of total ammonia in freshwaters was developed and calibrated. This novel passive sampler was designed to be small, cheap, robust and reusable. It was demonstrated that a polymer inclusion membrane of composition 35 % commercial DNNS, 10 % 1-tetradecanol and 55 % PVC could be used as a suitable semi-permeable barrier in the sampler to transport both molecular ammonia and the ammonium cation to an acidic receiving solution (0.8 mol L^{-1} HCl). The newly developed passive sampler is expected to simplify the monitoring of total ammonia in freshwaters since the receiving solution can be analysed directly (i.e. without the usual sample pretreatment steps required in the processing of the solid receiving phases of DGT and Chemcatcher samplers) and even *on site* if necessary and no special measures are required for preservation of the receiving solution due to its high acidity. It can also be considered as an environmentally friendly device since it does not incorporate organic solvents like POCIS.

The water matrix and temperature were found to affect the ammonium uptake of the sampler, but these effects were successfully mitigated by calibration using synthetic freshwater standards at the same temperature as the aquatic system. The effect of pH was studied within the range usually found in freshwaters and it was shown to have no influence on the transport rate of ammonium across the membrane.

The newly developed passive sampler was tested in a freshwater creek in Park Orchards, Melbourne, Australia and a strong correlation between spot and passive sampling was observed. Also, after a period of 7 days of sampling, the passive sampler did not show any sign of biofouling which could be explained by the high acidity of the PIM surface.

Underwater pumps were used in the laboratory calibration experiments to mimic the flow pattern in the creek where passive sampling was conducted. However, recent research conducted in our laboratory has demonstrated that flow effects on passive sampling results can be minimized by utilizing a passive sampler with a stagnant liquid layer between the aquatic system and its PIM [24].

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Compliance with ethical standards

Conflict of interest The authors have declared no conflict of interest.

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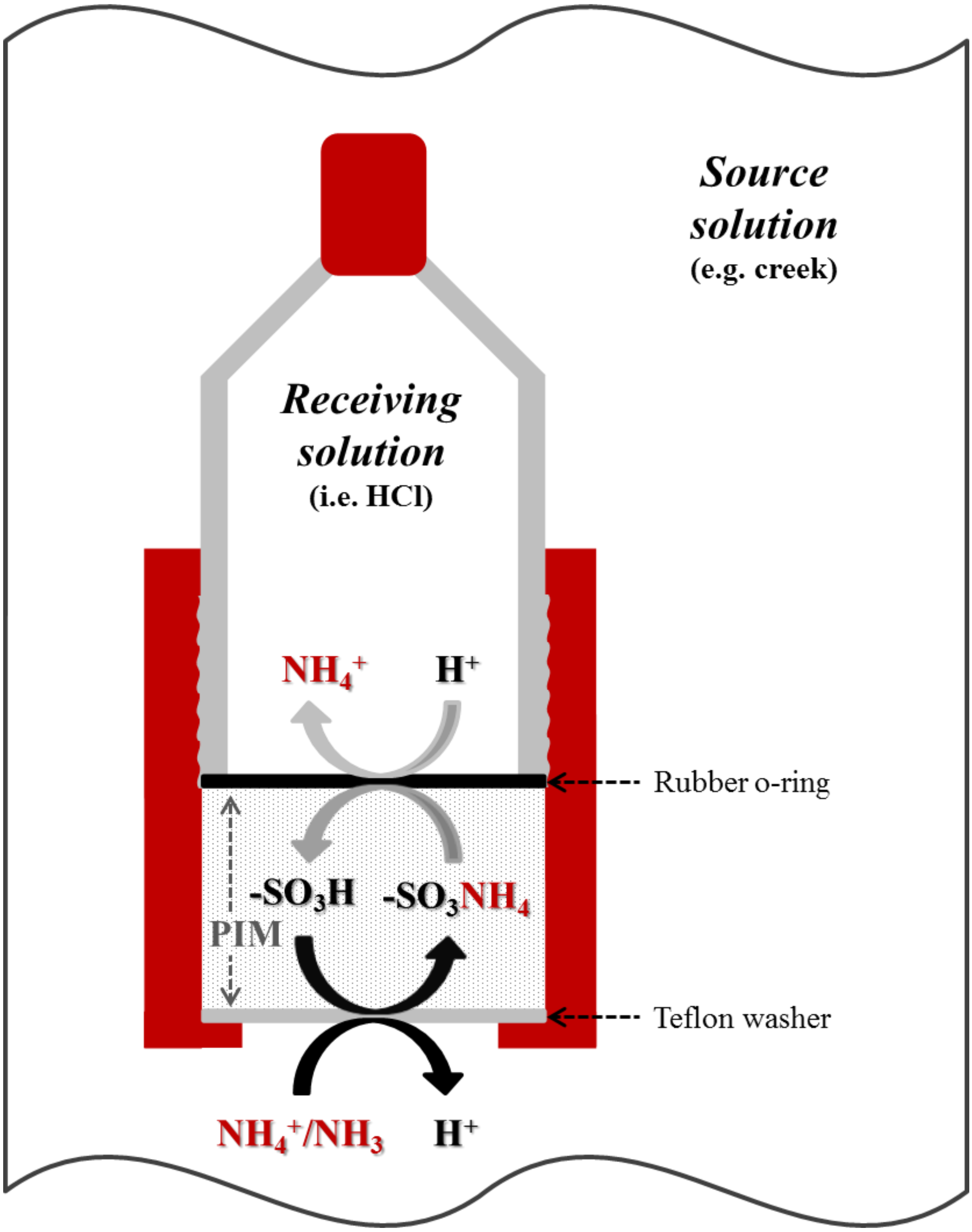
Source solution
(e.g. creek)
Receiving solution
(i.e. HCl)
NH_4^+
H^+
Rubber o-ring
$-SO_3H$
$-SO_3NH_4$
PIM
Teflon washer
NH_4^+/NH_3
H^+