



Development of a polymer inclusion membrane-based passive sampler for monitoring of sulfamethoxazole in natural waters. Minimizing the effect of the flow pattern of the aquatic system



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ABSTRACT

Antibiotics are commonly used pharmaceuticals for both human and veterinary purposes. Wastewater treatment plants (WWTPs) are not designed to completely remove these compounds from their influents. Thus, some antibiotics are being continuously discharged in the environment and subsequently found in diverse natural waters. Sulfamethoxazole (SMX) is one of the most frequently detected antibiotics in WWTP effluents and environmental waters. It exerts harmful effects on living organisms and therefore, there is a need to monitor its presence in aquatic systems. This study focused on the development of a passive sampler incorporating a polymer inclusion membrane (PIM) with Aliquat 336 as the extracting agent/membrane carrier for the monitoring of SMX in aquatic systems. Different PIM compositions were tested and the PIM composed of 30 wt.% cellulose triacetate (CTA), 26 wt.% Aliquat 336 and 44 wt.% of the plasticizer 2-nitrophenyl octyl ether (NPOE) provided the best SMX permeation from natural waters to a 2 mol L⁻¹ NaCl receiving solution. It was demonstrated that the flow pattern of the source solution influenced significantly the performance of a sampler with traditional design. The flow pattern of aquatic systems cannot be controlled and this potentially endangers the reliability of passive sampling data collected in these systems. A passive sampler with a new design is proposed which has been found to minimize the influence of the flow pattern of the aquatic medium being monitored.

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1. Introduction

Antibiotics are widely used pharmaceuticals for agricultural industries and for health care purposes, thus high amounts of these compounds are continuously manufactured and consumed worldwide. Antibiotics are then released into natural water bodies through several pathways (e.g., wastewater treatment plant effluents, leaching from soils, or industrial wastes, among others) [1]. Lately, a number of studies have revealed that the concentrations of antibiotics in different environmental waters (e.g., surface water, ground water, wastewater) vary in the range from ng L⁻¹ to µg L⁻¹ [2]. Because of their continuous release and their constant presence in the environment, these compounds are considered as “pseudopersistent” contaminants [3].

Sulfamethoxazole (SMX) is a low reactive antibiotic that belongs to the family of sulfonamides and is among one of the most frequently detected antibiotics in streams and groundwater [1]. Its high frequency of detection and relative persistence in aquatic systems indicates that it poses a potential risk to the ecosystem balance, as it exhibits biotoxicity

for some fish and algae [4]. A number of studies have demonstrated that the elimination of SMX through sewage treatment is incomplete. Residual SMX with concentrations varying from 0.01 to 2.0 µg L⁻¹ has been detected in municipal sewage treatment plant effluents and levels from 30 to nearly 500 ng L⁻¹ have been observed in surface waters [4, 5]. Hence, in order to identify the presence, fate and behavior of SMX in aquatic environments it is important to conduct continuous monitoring studies. However, currently, most of the published studies on antibiotics monitoring are based on discrete grab sampling with subsequent solid-phase extraction (SPE) of the antibiotics followed by their determination by liquid chromatography–tandem mass spectrometry [2,6, 7]. This procedure relies on multiple analytical steps that result in a lengthy and costly analysis, and tends to increase the magnitude of the experimental errors [8–10]. Furthermore, due to the usually ultra-trace level of these compounds in environmental waters, large sample volumes are often required, thus increasing the presence of interfering substances [11–13]. Moreover, discrete grab sampling provides results that are only representative of the concentration of antibiotics at the physical location and time of sampling and therefore it is not suitable for detecting episodic discharges of antibiotics into the environment [14,15]. To overcome these issues, techniques providing time-

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weighted average (TWA) concentrations of the antibiotics are recommended.

Passive sampling is an analytical technique involving the exposure of sampling devices for extended periods of time (from days to weeks) within the aquatic system of interest to provide TWA concentration data. In most cases, the sampling process is based on diffusion of the species of interest across a hydrophilic or hydrophobic barrier, usually a porous membrane, into a receiving phase [16]. It integrates in a single step analyte separation from the water matrix thus eliminating or minimizing interferences and its preconcentration in the sampler's receiving phase [14,17]. Passive sampling of organic species is often conducted by polar organic chemical integrative samplers (POCIS), which consist of a sorbent positioned between two microporous membranes. Another approach utilizes diffusion gradient thin films (DGT) where the analytes diffuse through a stagnant water boundary layer and a diffusion layer that comprises a filter membrane and hydrogel which separates the solid receiving phase from the aquatic system. Chen et al. [18] evaluated for the first time the performance of DGTs under laboratory conditions, involving the use of ultrapure water, for the monitoring of the antibiotic SMX and they observed an increase in the SMX uptake over time. The passive sampler was applied to the monitoring of SMX in a UK river over a two week period. For both POCIS and DGT based passive sampling, it is necessary to elute the organic species accumulated in the solid sorbent with a suitable organic solvent prior to their determination, similarly as described above for the SPE step [14,17].

The complex and time-consuming extraction procedure can be omitted if semi-permeable membrane devices (SPMDs) incorporating a polymer inclusion membrane (PIM) as the semi-permeable barrier and a suitable aqueous solution as the receiving phase are used instead. PIMs are advanced liquid extracting membranes that are composed of a base polymer, providing mechanical strength, an extractant (carrier), which is immobilized within the chains of the base polymer and is responsible for the extraction and transport of the analytes across the membrane, and, in some cases, a plasticizer, which provides elasticity to the membrane [19,20]. Once the analyte is extracted into the PIM it is transported to the receiving phase where it is back-extracted and the carrier is released to bind another analyte molecule/ion. Subsequently, the target analyte can be directly measured in the receiving solution at the end of the passive sampling period.

Currently, the above described passive sampling methodology based on PIMs has only been described by Almeida et al. [14] for the sampling of Zn(II). To the best of our knowledge there is no study based on this alternative passive sampling methodology for the monitoring of organic compounds.

The goal of passive sampling is to provide TWA concentrations that are representative of the original concentration levels of the compounds of interest in the aquatic environment. This is primarily dependent on the passive sampler calibration, which is usually carried out under controlled laboratory conditions [21]. Hence, prior to the use of passive samplers in the field it is important to develop an adequate calibration methodology.

This paper describes the development of the first PIM-based passive sampler for SMX in environmental waters incorporating Aliquat 336 as the membrane carrier. Its performance as a function of the compositions of the membrane and the source and receiving solutions, the passive sampler design, and the flow pattern of the source solution was studied.

2. Materials and methods

2.1. Solution preparation

All chemicals were of analytical reagent grade and used as received. Deionized water (18.2 MΩ cm, Millipore, France) was used for the preparation of all solutions.

SMX was purchased from Sigma Aldrich. A 250 mg L⁻¹ stock solution was prepared in methanol. Working solutions were prepared

daily by appropriate dilution of the stock solution with environmental waters (groundwater, river water, and wastewater) or deionized water. Sodium chloride (Sigma Aldrich) was used to prepare the receiving solution.

The PIM components: Aliquat 336, cellulose triacetate (CTA), poly(vinyl chloride) (PVC), and 2-nitrophenyl octyl ether (NPOE, 99%), were purchased from Sigma Aldrich. Chloroform (Panreac, Spain) was used for dissolving CTA whereas tetrahydrofuran (THF) (Panreac, Spain) was used for dissolving PVC.

Liquid chromatography grade methanol was obtained from Carlo Erba (Sabadell, Spain) and Gillman S.A. (Australia) and formic acid was purchased from Sigma Aldrich.

2.2. Membrane preparation

PIMs with four different compositions (M1: 30% CTA + 26% Aliquat 336 + 44% NPOE; M2: 30% CTA + 44% Aliquat 336 + 26% NPOE; M3: 30% PVC + 26% Aliquat 336 + 44% NPOE; M4: 30% PVC + 44% Aliquat 336 + 26% NPOE) were prepared following the procedures described by Garcia-Rodríguez et al. [22]. It should be noted that all PIM compositions are quoted in mass percentages. Once all the membrane components were completely dissolved in THF for the PVC-based PIMs and in chloroform for the CTA-based PIMs, the resulting solution was poured into a flat bottom glass Petri dish which was set horizontally and covered loosely. The solvent was allowed to evaporate over 24–48 h at room temperature, and the resulting film was then carefully peeled off the bottom of the Petri dish. Initially 200 mg of the base polymer were used in the preparation of both the PVC and CTA-based membranes. However, unlike the CTA-based PIMs which were found to be sufficiently mechanically strong, the PVC-based membranes exhibited poorer mechanical stability and appeared sticky. To overcome mechanical stability issues thicker PVC-based PIMs were prepared by increasing the amount of PVC per membrane from 200 to 400 mg. Circular segments were cut from the centre of the membranes to ensure uniform thickness (i.e., M1: 94 ± 5 μm; M2: 87 ± 5 μm; M3: 145 ± 5 μm; and M4: 125 ± 5 μm) and placed in the proposed membrane-based device.

2.3. Passive sampling configurations

2.3.1. Effect of the chemical parameters on SMX enrichment in the receiving solution

The passive sampler and passive sampling configuration used in this study are similar to those used earlier by us [22] and are shown in Fig. 1(a) and 1(b), respectively.

The PIM-based passive sampler, which contained 4 mL of NaCl receiving solution, was partially submerged in 120 mL of mechanically stirred source solution (100 μg L⁻¹ SMX in deionized water or environmental water). All experiments were conducted in triplicate or duplicate at an ambient temperature of 22 ± 1 °C.

Samples (200 μL each) were taken from both the source and receiving solutions at fixed time periods and replaced with the same volume of the corresponding original solutions.

The SMX enrichment factor (EF) of the PIM-based passive sampler was calculated by Eq. (1).

$$EF = \frac{[SMX]_{r,t}}{[SMX]_{s,0}} \quad (1)$$

where [SMX]_{r,t} is the transient SMX concentration in the receiving solution and [SMX]_{s,0} is its initial concentration in the source solution.

The chemical parameters varied in these experiments were the membrane composition (type of base polymer, i.e., PVC or CTA) and the concentrations of the carrier (Aliquat 336) and plasticizer (NPOE), the concentration of NaCl in the receiving solution, the concentration of SMX in the source solution and the source solution matrix.

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