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Selection of performance reference compound (PRC) for passive sampling of pharmaceutical residues in an effluent dominated river

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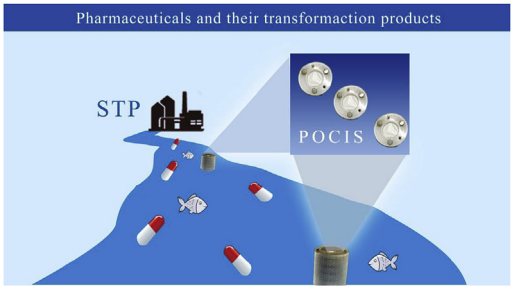
HIGHLIGHTS

- Pharmaceuticals and their transformation products were monitored in a river using POCIS.
- Antipyrine-d_3 was successfully tested as a PRC.
- POCIS with a PRC correction was used for measuring attenuation of the target compounds.

GRAPHICAL ABSTRACT



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ABSTRACT

A passive sampling device, a polar organic chemical integrative sampler (POCIS), was used to monitor 13 pharmaceuticals and 8 transformation products in upstream and downstream wastewater treatment plant effluent. A POCIS laboratory calibration study was performed to determine uptake behavior and the effect of water flow on the sampling rate. Most compounds showed a linear accumulation, and the sampling rate values ranged from 0.031 to 0.559 L/day. The developed POCIS samplers were used in field experiments in a wastewater-impacted river. Using the calculated sampling rates, the time-weighted average concentration values were measured by three different approaches: (1) laboratory calibration sampling rates (2) performance reference compound (PRC) correction sampling rates and (3) field calibration sampling rates. Nine deuterated compounds (acetaminophen-d_3, antipyrine-d_3, sulfamethoxazole-d_4, carbamazepine-d_{10}, diclofenac acid-d_4, clofibric acid-d_4, bezafibrate-d_6, ibuprofen-d_3 and naproxen-d_3) were studied as PRCs. Antipyrine-d_3 was successfully tested as a PRC for sulfamethoxazole, ibuprofen, 2-hydroxy ibuprofen, diclofenac acid, 4-hydroxydiclofenac acid, carbamazepin, carbamazepin 10,11-epoxide, sulfadiazine, 1-naphthol, antipyrine, naproxen and 4-chlorobenzoic acid. Finally, the POCIS was used to monitor target compounds in river water and measure their attenuation. For most compounds, the POCIS attenuation results were not significantly different from those of the spot samples, which demonstrated that a POCIS with a PRC correction can determine the attenuation of organic micropollutants in rivers.

1. Introduction

As a result of improving living standards and growing populations, the contamination of aquatic environments has become a

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serious global issue (Gros et al., 2007; Rivera-Utrilla et al., 2013). Pharmaceuticals are one of the main contributors to water contamination, and increasing concentrations of these contaminants in aquatic environments may threaten human health and destroy the balance of ecosystems (Rivera-Utrilla et al., 2013; Liu et al., 2013). Conventional chemical and biological wastewater treatment processes often cannot completely remove pharmaceuticals (Gros et al., 2007). Therefore, pharmaceuticals and their transformation products (TPs) are emitted from wastewater treatment plants (WWTP) into the receiving aquatic systems and can undergo further transformations (Boxall et al., 2012; Hass et al., 2012; Fono et al., 2006). To assess the environmental and public health risks of pharmaceutical residues, the main source must be identified, and the most biologically active compounds in water resources must be monitored.

Traditionally, monitoring of organic micropollutants in water is based on spot sampling, but this method provides only a snapshot of the concentration at a specific time, fluctuations in the concentration level over time and sudden pollution events cannot be monitored (Iparraguirre et al., 2017; Ibrahim et al., 2013). This problem can be solved by increasing the frequency of the sampling, which is time consuming and costly (Vallejo et al., 2013). Moreover, the pretreatment of water samples can be complicated, and changes may occur in the biological activity during storage of the water samples. An alternative is a passive sampling method, which has become an increasingly significant tool in global pollution monitoring schemes and is being added to water sampling protocols (Novic et al., 2017). Depending on the polarity of the studied compound, different types of passive samplers should be used (Ahrens et al., 2015; Moschet et al., 2015; Hoque et al., 2014). A polar organic chemical integrative sampler (POCIS), has been designed to monitor polar organic pollutants, such as polar pesticides, pharmaceuticals and personal care products, in aquatic environments (Ibrahim et al., 2013; Zenobio et al., 2015). A POCIS consists of a solid sorbent phase between two microporous polyether sulfone (PES) membranes, which allow dissolved contaminants to pass through to the sorbent. Passive sampling relies on the transport of a pollutant from the sampled matrix to a receiving phase within a sampling device. A passive sampler can be used to estimate the time-weighted average (TWA) concentration and total load of contaminants in aquatic environments over a specific period. However, for this technique to be successful, the sampling rate (R_S) of each pollutant in the sampler must be known.

Generally, the R_S is obtained via a laboratory calibration, but the R_S obtained in a laboratory may significantly vary due to different laboratory conditions. Furthermore, the environmental conditions encountered by a POCIS cannot always be simulated in laboratory calibration studies, and laboratory generated R_S values may not be representative of the actual values under different environmental conditions. The biggest challenge facing the use of POCIS is the lack of a correction method for field environmental conditions (e.g., water flow rate, temperature, and pH) that affect the uptake process. To overcome this issue, performance reference compounds (PRCs) have been proposed to account for the effects of field exposure conditions on R_S values. PRCs do not occur in the environment and are spiked into samplers prior to exposure. If their dissipation follows first-order kinetics, which is analogous to the uptake, they can be used to estimate the actual R_S of selected contaminants in the field. Huckins et al. (2002a) proposed the use of PRCs to determine the effects of the field condition on the R_S of hydrophobic semipermeable membrane devices (SPMD), and they discovered that the PRCs can estimate R_S values for field SPMD that are within 2-fold of the directly measured values. Although PRCs have been successfully applied with hydrophobic passive samplers, their use in polar passive samplers is lacking because appropriate PRCs have not been established (Vallejo et al., 2013). One main reason is that the isotropic exchange is not always assured for PRCs and analytes. After all, the uptake process in POCIS is driven by adsorption and not partitioning.

In this study, a POCIS was studied for sampling 13 pharmaceuticals and 8 TPs. Different PRCs and R_S values were used to correct the differences between the environment of laboratory calibration and the field sampling of upstream and downstream WWTP effluent. The results were used to evaluate whether POCISs are suitable for determining the attenuation of pharmaceuticals and their TPs in rivers.

2. Materials and methods

2.1. Chemical reagents and materials

Details on all the reagents are provided in the Supporting Information. The physicochemical properties of all the target compounds are shown in Table S1.

The pharmaceutical version of the POCIS consists of 200 mg of Oasis HLB sorbent (Waters, USA) sandwiched between two PES membranes (0.1 μm pore size, 47 mm diameter, Yi Bo Filter Company, China) that are clamped between two homemade plexiglass flanges. The POCIS and PES membranes were cleaned with methanol and ultrapure water before use. The prepared POCISs were packed in aluminum foil to prevent cross contamination and stored at −20 °C before deployment.

2.2. POCIS laboratory calibration

The POCIS sorbent was spiked with the PRCs before the calibration. The HLB sorbent (200 mg) was spiked with 1 μg/g of nine different deuterated compounds, acetaminophen-d_3 (ACE-d_3), antipyrine-d_3 (ATP-d_3), sulfamethoxazole-d_4 (SMZ-d_4), carbamazepine-d_{10} (CBZ-d_{10}), diclofenac acid-d_4 (DCF-d_4), clofibric acid-d_4 (CA-d_4), bezafibrate-d_6 (BZB-d_6), ibuprofen-d_3 (IPF-d_3), and naproxen-d_3 (NPX-d_3), to evaluate the applicability of these compounds as PRCs. The PRCs were spiked according to Vallejo et al. (2013), 30 μL of a solution containing 100 mg/L of the deuterated compounds was added to 25 mL of methanol, and after homogenization, the solution was added to the sorbent. This mixture was stirred overnight, and the solvent was evaporated to near dryness under a continuous nitrogen stream. The sorbent was then dried at 50 °C for 3 h. The final sorbent was used to prepare the exposed POCIS and blanks (200 mg per POCIS).

A static renewal calibration was used as the POCIS laboratory calibration. The experiment was conducted in a 2 L beaker at ambient temperature (20 °C). A magnetic stirrer (Shanghai Sile Instrument Company, China) was used to mix the water. The experiments were conducted under three different stirring conditions, 150 rpm, 300 rpm and 600 rpm. A stock mixture containing all the target analytes in methanol was added to the beaker, and a final, constant concentration of 100 ng/L was obtained. Each POCIS was vertically suspended in the water (pH = 7) in each exposure vessel, and 12 POCISs were exposed to the 4 beakers. To maintain constant analyte concentrations, the test water was removed every 24 h. All beakers were covered with aluminum foil to reduce light exposure and minimize analyte volatilization. Three POCISs and 200 mL of water were removed after 4, 7, 10 and 14 days.

2.3. POCIS field deployment experiment

Field deployment experiments were performed at Yunliang (YL) River (Nanjing, China), which is affected by the eastern city WWTP. The sampling sites were located upstream of the WWTP (E1, E: