Talanta 120 (2014) 30–33

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Short communication

A simple recirculating flow system for the calibration of polar organic chemical integrative samplers (POCIS): Effect of flow rate on different water pollutants

Marina Di Carro, Luca Bono, Emanuele Magi *

Department of Chemistry and Industrial Chemistry, University of Genoa, Via Dodecaneso 31, 16146 Genoa, Italy

ARTICLE INFO

Article history:
Received 8 September 2013
Received in revised form
27 November 2013
Accepted 30 November 2013
Available online 6 December 2013

Keywords:
Water monitoring
Polar organic chemical integrative sampler (POCIS)
Polar organic micropollutant
Sampling rate
Time-Weighted Average concentration (TWA)

ABSTRACT

A calibration system for POCIS was developed and used to calculate the sampling rates of eight analytes belonging to pesticides, non-steroidal anti-inflammatory drugs and perfluorinated compounds: atrazine, propazine, terbutylazine, diclofenac, ibuprofen, ketoprofen, perfluorooctanoic acid and perfluorooctanesulfonate. Experiments with a linear velocity of 2.0, 5.1, 10.2 and 15.3 cm/s were carried out for 96 h using two different analyte concentrations. POCIS extracts were analyzed by liquid chromatography–tandem mass spectrometry (LC–MS/MS), using multiple reaction monitoring to maximize sensitivity. Results highlighted that the calculated sampling rates are rather constant at the considered concentrations and flow rates. Obtained values of sampling rates were then employed to calculate Time-Weighted Average concentration of the analytes in river and drinking waters.

1. Introduction

In the last few years, a rapid increase in the use of passive sampling for the monitoring of micropollutants in different water matrices has occurred [1], especially of the Polar Organic Chemical Integrative Sampler (POCIS) that was designed to sample and concentrate hydrophilic contaminants [2]. It contains a sorbent phase sandwiched between two microporous polyethersulfone (PES) membranes: chemicals diffuse from the water through the membrane and adsorb onto the sorbent phase. POCIS can provide Time-Weighted Average (TWA) concentration of contaminants in water if the sampling rates (R_s) are known [2]. Sampling rates are specific for each compound and depend on the experimental site conditions; they represent the quantity of water cleared by the sampler per time unit. Some papers [3,4] use R_s calculated by other authors: even if not accurate, the obtained values can give a rough estimation of the analyte average concentration in the studied water matrix. Sampling rates can be obtained with a calibration experiment by measuring both the analyte concentration in water and in the POCIS and applying the following equation [2]:

$$C_s = C_W R_s t / M_s \tag{1}$$

where C_s and C_W are the concentrations of the compound in the POCIS sorbent (ng/g) and in the water (ng/L), respectively, t is the sampling period (days) and M_s is the mass of the sorbent in the POCIS (g). Recently, two other methods for R_s calculation have been proposed in the literature: the use of only the analyte concentration in water after the POCIS exposure [5] or the slope of the concentration decrease in water over the exposure time [6,7]. Both methods appear to overestimate the R_s values, so the use of Eq. (1) has been recommended for the calculation of sampling rates in recent reviews [8,9].

Sampling rates can be calculated either at the specific sampling site or in the lab. The in-situ calibration takes into account the peculiar site environmental conditions (water flow, temperature and biofouling) [10,11], but it is costly and time consuming. The most used approach [9] so far has employed in-lab static calibration [12] or static renewal calibration [13], with a closed system in which the contaminants are spiked only at the beginning of the experiment or at constant time intervals, respectively. Another in-lab method involves continuous flow calibration system [14,15], which allows a careful setting of the main variables which are characteristic of the sampling site.

In our previous works [3,16–18] POCIS were used to sample and preconcentrate endocrine disrupting compounds in different water matrices: drinking water, surface water and wastewater. In these papers we used R_s obtained by other authors to calculate a rough estimation of the levels of the considered pollutants in water. In this work a custom made calibration system was used to

---

* Corresponding author. Tel.: +39 010 3536187; fax: +39 010 3536190.
E-mail address: emanuele.magi@unige.it (E. Magi).

0039-9140/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.talanta.2013.11.088

calculate the sampling rates of eight analytes (atrazine, propazine, terbutylazine, diclofenac, ibuprofen, ketoprofen, perfluorooctanoic acid and perfluorooctanesulfonate) belonging to three different classes of pollutants: pesticides, non-steroidal anti-inflammatory drugs (NSAIDs) and perfluorinated compounds. Different linear flow rates, between 2 and 15.3 cm/s, and two analyte concentrations were tested to evaluate their possible influence on R_s. The obtained data are herein discussed and compared to the literature; TWA concentrations measured with calibrated POCIS exposed in river and drinking water are also presented.

2. Experimental

2.1. Chemicals

Standards of pesticides (atrazine, atrazine-d_5, propazine and terbutylazine), NSAIDs (diclofenac, ibuprofen and ketoprofen) and perfluorinated compounds (perfluorooctanoic acid – PFOA- and perfluorooctanesulfonate – PFOS) were obtained from Sigma Aldrich (Milan, Italy). Methanol, acetic acid, formic acid and acetonitrile were purchased from Merck (Milan, Italy). All solvents were of analytical or chromatographic grade. Water was purified by a Milli-Q system (Millipore, Watford, Hertfordshire, UK).

Stock solutions of individual standards were prepared by dissolving each compound in CH_3OH at a concentration of 1000 μg/l. Individual standards and a standard mixture containing the analytes (100 ng/l) were prepared in CH_3OH. The working solution at different concentration levels were prepared by dilution using Milli-Q water. All standards and working solutions were stored in the dark at −20 °C.

2.2. Recirculating flow system

The recirculating flow system was developed in our laboratories (Fig. 1) and consisted of a pump, a 5 L tank that was shielded from ambient light and a POCIS container in which up to four samplers could be deployed parallel to the water flow. All parts of the system were of stainless steel. The hydraulic circuit included a flowmeter, a flow regulator and a bypass that could be adjusted to obtain flow ranges between 200 and 2000 L/h; the bypass could be also used to exclude the POCIS container from the flow path. The total volume of the system was 7 L. The exposure system was placed in a temperature-controlled room; the water temperature inside the system was kept constant at 18 °C by means of a water coil.

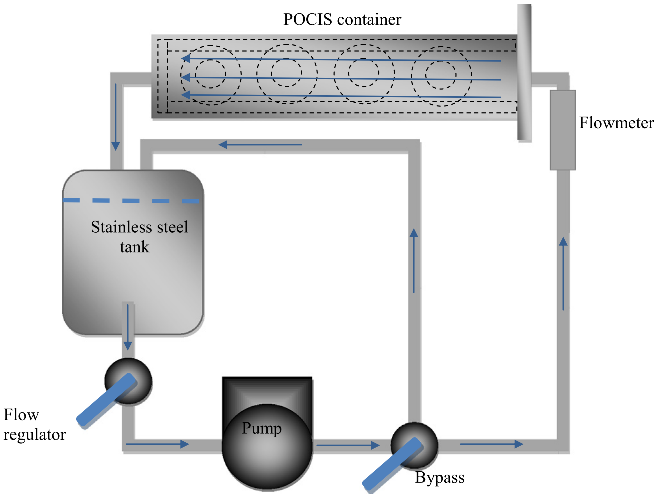

Fig. 1. Scheme of the custom made recirculating flow system employed for the calibration of POCIS.

Before the first use of the exposure system, several washing cycles were made with tap water and a 10% v/v solution of CH_3OH in tap water. A blank experiment was carried out with two POCIS which were exposed to 7 L of tap water flowing into the circuit for 30 h. The samplers were then retrieved, dismantled and processed according to Section 2.5; no signal was present at the retention times of the analytes in the resulting LC–MS/MS chromatogram.

2.3. POCIS

POCIS samplers were assembled in our laboratories in accordance with the characteristics of the commercial ones (mass of the sorbent phase 200 mg and 45.8 cm^2 as sampler surface area). PES membranes (0.1 μm pore size) and HLB sorbent phase were purchased from Pall Italia (Buccinasco, Italy) and Waters (Vimodrone, Italy), respectively. PES membranes were washed before use in a H_2O/CH_3OH solution (80:20 v/v) for 24 h and then with CH_3OH for 24 h. After drying in a laminar hood, the membrane-sorbent-membrane layers were compressed between two stainless-steel support rings held together with three thumbscrews and stored frozen at −20 °C.

2.4. POCIS exposure and R_s calculation

To investigate the possible adsorption of the analyte by the exposure system, a preliminary experiment was carried out twice filling the recirculating flow system with 7 L of tap water; no passive sampler was inserted into the POCIS container. Small aliquots of water (200 μl) were collected after 2 and 16 h and analyzed by LC–MS/MS as blanks. Immediately afterwards, a solution containing the eight analytes was spiked into the tank to obtain a final concentration of 3 ng/mL of each chemical; the system was operating at 1000 L/h. After 15 min and 2, 4, 20, 23 and 28 h, small aliquots of water solution were sampled from the tank and analyzed in LC–MS/MS. The concentration of the analytes did not show any significant decrease, indicating that the exposure system was suitable to study the sampling rates.

To calculate R_s for the eight analytes, different experiments with 200, 500, 1000 or 1500 L/h (corresponding to a linear velocity of 2.0, 5.1, 10.2 and 15.3 cm/s, respectively) were carried out for 96 h. Water flow rate values were chosen in this range because they are similar to those found in many environments [19]. The circuit was filled with 7 L of tap water and after 30 min a small aliquot of water was sampled and analyzed by LC–MS/MS as blank. Immediately afterwards, the chemical mixture with the analytes at 0.2 or 1.0 ng/mL was spiked into the water tank. The water into the circuit was replaced with freshly fortified tap water after 48 h (same concentration). In each experiment two POCIS were deployed in the POCIS container. Twice a day a small aliquot of water was sampled from the tank to check the residual concentration in the recirculating flow system. After the exposure, samplers were retrieved, rinsed with Milli-Q water, wrapped in aluminum foil and stored frozen at −20 °C.

A solution containing the same concentration of analytes was kept in the same room and was analyzed at regular intervals of time to check the analyte stability in time and exclude their degradation.

An application experiment was carried out deploying three POCIS in the river Arno for two weeks, while three other samplers were put in a 20 L-tank in which the drinking water of the city of Firenze was flowing continuously; both flow rates were estimated to be in the studied range (8–15 cm/s).