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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

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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]:

$$C_s = C_w R_s t / M_s \quad (1)$$

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

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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

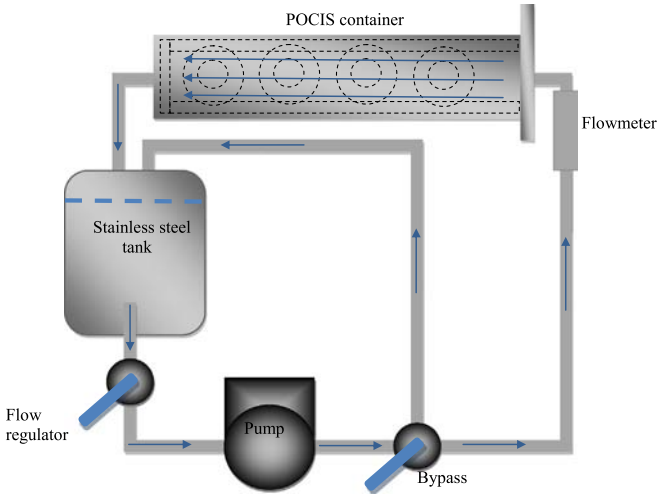

Fig. 1. Scheme of the custom made recirculating flow system employed for the calibration of POCIS.

inside the system was kept constant at 18 °C by means of a water coil.

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).

2.5. Analyte extraction

Prior to processing, the samplers were thawed and rinsed with Milli-Q water. Each POCIS was dismantled and the sorbent was transferred by means of Milli-Q water into a 1 cm i.d. glass syringe cartridge fitted with a Teflon frit and glass wool. The sorbent phase was eluted with 50 mL of acetone. The eluate was then collected in a flask, reduced to dryness in a rotary evaporator and redissolved in 1 mL of methanol; this solution was diluted 100 times for the LC–MS/MS analyses. Atrazine-d_5 was spiked into the POCIS sorbents prior to extraction to compensate for the mass loss during the sample preparation and the matrix effects during LC–MS/MS analysis; its recovery ranged from 92% to 96%.

2.6. Liquid chromatography

Chromatographic separations were performed by an Agilent Liquid Chromatograph Series 1200 SL consisting of a binary HPLC pump, an online vacuum degasser, an automatic sampler ALS and a thermostatted compartment with a Hypersil Gold Aq column (3×30 mm, particle size 1.9 μm), purchased by Thermo Scientific (San Jose, CA, USA).

Separation of perfluorinated compounds and non-steroidal anti-inflammatory drugs was carried out maintaining the column at 60 °C. A 10 μL aliquot of sample extract was injected and eluted with a flow rate of 0.2 mL/min in isocratic separation with 50% Milli-Q water containing 0.1% of acetic acid and 50% acetonitrile.

Separation of pesticides was carried out at 25 °C: an aliquot of 1 μL of sample extract was injected and eluted off the column with a flow rate of 0.45 mL/min in isocratic separation with 55% Milli-Q water containing 0.05% of formic acid and 45% acetonitrile with 0.05% of formic acid.

2.7. Tandem mass spectrometry

LC–MS/MS analyses were performed with an Agilent 6430 MSD triple-quadrupole mass spectrometer (Agilent Technologies, Santa Clara, CA, USA) with an API-electrospray source used both in positive and negative mode. MassHunter software was used for data acquisition and processing. Nitrogen was employed as desolvation and nebulizer gas. Final MS source parameters were optimized to a source temperature of 350 °C, a nebulizer gas of 35 psi and a desolvation gas of 10 L/min. Capillary voltage was set at −3000 V for the analyses of perfluorinated compounds and NSAIDs and at +1500 V for pesticides determination.

2.8. Quantitative analysis

Quantitation of analytes was achieved running MS in multiple reaction monitoring mode (MRM) to maximize sensitivity. Two different transitions were chosen for each compound: the first and more abundant was used for the quantitation and the second for confirmation of the results. Quantitative analyses were performed by means of the internal standard method for pesticides. The internal standard concentration (Atrazine-d_5) was maintained constant at 1 ng/mL, while the analyte concentrations were 0.1, 0.5, 1, 10, 50 and 100 ng/mL. External standard calibration was used for NSAIDs and perfluorinated compounds: each point of the respective calibration curves (0.1, 1, 5, 10 and 15 ng/mL) was the mean of three replicates. All analytes showed good linearity (R^2 between 0.9945 and 0.9997).

3. Results and discussion

In this work the sampling rates of the eight selected analytes were calculated using four different flow rates (2.0, 5.1, 10.2 and 15.3 cm/s) at two concentration levels (0.2 and 1.0 ng/mL) and introducing experimental data in the Eq. (1), already cited in the Section 1, valid for the linear (or kinetic) regime.

Analyte sampling rates, obtained in all the different experimental conditions, are shown in Table 1: calculated R_s are reported as the mean deriving from the two exposed POCIS with their relative percent difference. Obtained values do not show apparently any correlation with the flow rates or the concentrations. Table 2 summarizes the average values of the sampling rates with the standard deviations of the whole analytical procedure.

For all the considered compounds, the R_s values obtained spiking the water in the calibration system were rather similar: in fact, their overall standard deviation (including the whole analytical procedure) did not exceed 18% for pesticides, 21% for perfluorinated compounds and 28% for NSAIDs. In our opinion, this variability is not significant, suggesting that the sampling rates of the selected analytes can be considered constant in the

Table 2
.Calculated values of sampling rates (value obtained from the average of all experimental conditions, with the standard deviations of the whole analytical procedure) and analyte Time-Weighted Average concentration in river and tap water (passive samplers exposed for two weeks).

Analyte	Average R_s (L/day)	TWA in river water (ng/L)	TWA in tap water (ng/L)
Atrazine	0.200 ± 0.027	4.10	2.43
Propazine	0.190 ± 0.034	3.12	2.46
Terbutylazine	0.159 ± 0.028	57.84	6.12
Diclofenac	0.058 ± 0.015	0.25	0.22
Ibuprofen	0.075 ± 0.020	0.67	0.20
Ketoprofen	0.066 ± 0.018	0.11	< LOD
Perfluorooctanoic	0.211 ± 0.043	0.17	0.08
Perfluorooctanesulfonate	0.065 ± 0.014	0.34	0.19

Table 1
.Calculated values of sampling rates for the analytes (reported as mean of two POCIS ± Relative Percent Difference, RPD) in the different experimental conditions of the calibration system.

Flow rate (cm/s)	Spiked concentration (ng/mL)	Atrazine R_s (L/day) ± RPD (%)	Propazine R_s (L/day) ± RPD (%)	Terbutylazine R_s (L/day) ± RPD (%)	Diclofenac R_s (L/day) ± RPD (%)	Ibuprofen R_s (L/day) ± RPD (%)	Ketoprofen R_s (L/day) ± RPD (%)	PFOA R_s (L/day) ± RPD (%)	PFOS R_s (L/day) ± RPD (%)
2.0	0.2	0.232 ± 27	0.233 ± 24	0.195 ± 8%	0.069 ± 35	0.048 ± 35	0.080 ± 20	0.157 ± 31	0.069 ± 12
2.0	1.0	0.199 ± 13	0.194 ± 14	0.167 ± 18	0.064 ± 32	0.108 ± 5	0.064 ± 32	0.241 ± 3	0.074 ± 7
5.1	0.2	0.189 ± 5	0.177 ± 10	0.135 ± 9	0.055 ± 33	0.070 ± 34	0.080 ± 23	0.215 ± 29	0.057 ± 17
5.1	1.0	0.200 ± 29	0.194 ± 27	0.151 ± 27	0.059 ± 29	0.086 ± 24	0.072 ± 33	0.234 ± 20	0.059 ± 28
10.2	0.2	0.188 ± 27	0.148 ± 29	0.134 ± 23	0.065 ± 32	0.064 ± 22	0.073 ± 29	0.233 ± 21	0.061 ± 19
10.2	1.0	0.194 ± 9	0.184 ± 26	0.156 ± 31	0.056 ± 35	0.080 ± 4	0.041 ± 24	0.253 ± 9	0.055 ± 33
15.3	0.2	0.196 ± 16	0.187 ± 27	0.153 ± 29	0.053 ± 13	0.080 ± 29	0.069 ± 2	0.202 ± 12	0.071 ± 17
15.3	1.0	0.202 ± 22	0.203 ± 5	0.184 ± 5	0.054 ± 33	0.065 ± 32	0.047 ± 12	0.158 ± 27	0.073 ± 31

experimental range of the flow rate (2.0–15.3 cm/s). Few authors studied the possible variation of the sampling rate with water flow rate: Li et al. found that the POCIS uptake of some contaminants (pharmaceutical, personal care products and endocrine-disrupting compounds) showed a relatively slight increase (less than twofold) in a sewage effluent flowed at rates between 2.6 and 37 cm/s [20].

Besides, Harman et al. [8], reviewing the different sampling rates obtained by various research groups, remarked the difficulty of their comparison, especially because sometimes experimental conditions are not reported in detail; for instance a nine-fold increase in R_s was observed as a maximum for different compounds, changing from static to stirred conditions [2].

Although it is very difficult to compare these values with sampling rates reported in the literature, considering data summarized in the two previously cited reviews [8,9], the R_s calculated for pesticides and NSAIDs fall in the reported range; in particular the R_s of atrazine, which was probably calibrated in the largest number of studies, is very similar to 0.25 ± 0.03 L/day, calculated by Harman [8] as a mean value of the different sampling rates obtained in the literature for this compound.

An application experiment was carried out using the average sampling rates obtained with the calibration, to assess the TWA concentration of the eight selected analytes in Arno river water and in the drinking water of the city of Firenze. TWA concentration in water was calculated for each analyte as C_w from Eq. (1), knowing C_s, M_s, t and the sampling rate previously obtained. Results are reported in Table 2 as mean values of TWA.

In river water all analytes were detected: data show low levels of NSAIDs and perfluorinated compounds and relatively higher concentration of pesticides, especially terbutylazine which was one order of magnitude higher than atrazine and propazine. The calculated TWA of these three pesticides are in good agreement with the respective concentration levels detected in the river Arno [21] by the Tuscan Regional Environmental Agency (ARPAT); this supports the calibration approach proposed in the present work.

In tap water, as expected, concentrations were lower; all analytes were detected except ketoprofen, which was below LOD. The concentration of terbutylazine was slightly higher than the other pesticides, while NSAIDs and perfluorinated compounds levels were very low.

4. Conclusions

The sampling rates of eight contaminants belonging to different chemical classes (pesticides, NSAIDs and perfluorinated compounds) were calculated at two concentration levels by means of a custom made recirculating flow system; different flow rates, similar to those found in many environments, were tested.

Results at both concentration levels highlighted that R_s values do not show a noticeable dependence upon flow rates between 2 and 15.3 cm/s. Although preliminary, our results indicate that after a rather simple calibration, POCIS can provide a first estimation of the TWA concentration of common water pollutants, thus offering a useful and inexpensive tool for the intensive monitoring of various water bodies.

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