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Combining passive sampling and tandem mass spectrometry for the determination of pharmaceuticals and other emerging pollutants in drinking water

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ABSTRACT

Passive sampling and liquid chromatography-tandem mass spectrometry can be profitably employed to detect emerging contaminants in waters at very low concentration levels. In this work, two types of Polar Organic Chemical Integrative Sampler (POCIS) were subjected to calibration at two different temperatures to calculate the sampling rates of eight emerging pollutants (five pharmaceuticals, two perfluorinated compounds and caffeine). Results obtained changing the temperature from +5 to +25 °C showed a limited influence on the sampling rate values for all the selected analytes. Preliminary evaluations on storage life-time of POCIS devices were also taken into account.

After calibration, samplers were deployed in the inlet and the outlet of two drinking water treatment plants in Northwestern Italy, for two and four weeks; the extracts were then analyzed by means of LC-MS/MS in multiple reaction monitoring mode, which provided high sensitivity and allowed the detection of the selected compounds at the low ng L^{-1} level. Three analytes were measured in both treatment plants: the two perfluorinated compounds, in the range 2.93–13.42 ng L^{-1}, and caffeine, in the range 0.07–0.93 ng L^{-1}.

1. Introduction

In recent years, environmental studies have partially shifted their attention from classical pollutants to the so-called "emerging contaminants". These substances have been detected in the environment, and in particular in waters, at very low concentrations (ng L^{-1} to μg L^{-1} levels) [1–2]; nonetheless their presence should not be neglected, due to the unknown effects of long-term exposition. In fact, even though their low environmental concentrations are usually considered non-harmful for humans, the contemporaneous presence of many pollutants could cause unpredicted synergistic effects [3].

Very sensitive methodologies are therefore required to detect emerging contaminants: the choice of the appropriate preconcentration methods and analytical technique is crucial to obtain satisfactory results [4–5]. A successful approach can be represented by the combination of passive sampling with sensitive analytical techniques such as HPLC-MS. Passive sampling presents the remarkable advantage of combining sampling and preconcentration in one step; in fact, samplers are usually deployed for a certain period of time in order to accumulate contaminants, whose levels would be otherwise difficult to detect by spot sampling. The Polar Organic Chemical Integrative Sampler (POCIS), first introduced in 2004 [6], contains a sorbent phase sandwiched between two membranes and, once exposed in water, is able to sample and concentrate hydrophilic contaminants. Since POCIS are usually deployed for periods of time up to several weeks, they are able to pre-concentrate analytes from a large volume of water. Moreover, the continuous sampling allows to take into account episodic events that are not easily identified by classical spot sampling [7].

As a result of prolonged exposition, POCIS provides the time-weighted average (TWA) concentration of a compound, derived from the fluctuations of contamination levels [6]. In fact, the amount of chemicals found in the sorbent phase after deployment is correlated with their concentration in water, mediated over time, and it depends on the sampling rate (R_s), i.e. the volume of water that the POCIS is able to "clear" from a specific compound in a time unit, according to the following equation [8]:

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

where C_s and C_w are the concentrations of the compound in the POCIS sorbent (ng g^{-1}) and in water (ng L^{-1}), respectively, R_s is the specific sampling kinetic constant, known as sampling rate (L day^{-1}), t is the exposure time (days) and M_s is the mass of the sorbent in the POCIS (g).

To calculate TWA concentrations, the sampling rates of the analytes must be determined through calibration experiments; this is a crucial

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step and can be performed in situ or in the laboratory [9–10]. In situ calibration enables to obtain specific R_s for a determined site, and takes into account the physico-chemical conditions of the site itself (water temperature and flow, ionic strength, biofouling, pH…), but is costly and time consuming [11–12]. Laboratory calibration is the most common method because of its simplicity; experiments can be performed using either a static approach or a recirculating flow system [13–14].

TWA concentrations obtained can only provide semi-quantitative values of water contamination, nonetheless passive samplers are powerful tools to perform screening studies and to monitor sites for long periods in a much easier and more economical way than spot sampling.

The aim of this work was to use POCIS and tandem mass spectrometry for the determination of some emerging contaminants in drinking water, performing the calibration of passive samplers in different conditions. In fact, calibration was carried out comparing POCIS assembled in our laboratory to commercial samplers, at different working temperatures. The obtained R_s values were then employed to calculate the TWA concentrations in two case studies. The chemicals chosen were five anti-inflammatory drugs (ibuprofen, naproxen, diclofenac, ketoprofen and mefenamic acid), two perfluoroalkyl compounds (perfluorooctanoic acid and perfluorooctane sulfonate) and caffeine, considered a tracer of anthropic contamination.

2. Experimental

2.1. Standard and reagents

Diclofenac (DIC), ketoprofen (KET), mefenamic acid (MEF), naproxen (NAP), ibuprofen (IBU), ketoprofen-d3 (KET-d3), perfluorooctanoic acid (PFOA), perfluorooctanesulfonate (PFOS) and Caffeine (CAF) were obtained from Sigma-Aldrich (Milan, Italy). All standards were of high purity grade (>97%). Methanol (MeOH), acetonitrile (ACN) and acetic acid were obtained from Merck (Darmstadt, Germany). All solvents were of analytical or chromatographic grade. Water was purified by Milli-Q system (Millipore, Watford, Hertfordshire, UK).

Stock solutions of nonsteroidal anti-inflammatory drugs (NSAIDs) and caffeine were prepared by dissolving each compound in CH_3OH at a concentration of 2000 ng mL^{-1}. Working solutions of NSAIDs, perfluorinated compounds and caffeine were prepared at a concentrations of 200 ng mL^{-1} by subsequent dilution of the stock solution in MQ water. Both stock and working solutions were stored at −20 °C. The working solutions at different concentration levels were prepared by dilution using Milli-Q water.

2.2. LC-MS/MS analysis

Analyses were performed on an Agilent Liquid Chromatograph Series 1200SL (consisting of a binary HPLC pump, an online vacuum degasser, an automatic sampler ALS and a thermostatted column compartment and a DAD detector) coupled to an Agilent 6430 MSD triple-quadrupole mass spectrometer (Agilent Technologies, Santa Clara, CA, USA) with an Electrospray source. Separation of the analytes was carried out by means of a Hypersil Gold Aq column (3 × 30 mm, particle size 1.9 μm), purchased by Thermo Scientific (San Jose, CA, USA), at 60 °C. An isocratic elution with 50% Milli-Q water containing 0.1% of acetic acid and 50% acetonitrile was performed with a flow rate of 0.2 mL min^{-1} and injection volume 10 μL, allowing the separation of compounds within 10 min. Negative ionization was used to analyze NSAIDs, PFOA and PFOS compounds, while positive ionization was employed for caffeine investigation. ESI conditions for both kinds of ionization were: drying gas flow (N_2) 10 L min^{-1}, capillary potential ± 3000 V, nebulizer pressure 35 psi and drying gas temperature 350 °C. Mass calibration for MS experiments was performed by infusion of ESI Tuning Mixture (Agilent Technologies, Palo Alto, CA, USA).

MassHunter software was used for data acquisition and processing.

Quantitation of the analytes was achieved using polarity switching MS in multiple reaction monitoring mode (MRM) to maximize sensitivity. Two different transitions were chosen for each compound on the basis of literature data [15–16]: the first and more abundant was used for the quantitation and the second for confirmation of the results. In Table 1 chemical formulas, retention times and MRM transitions are reported for the considered compounds.

Quantitative analysis was performed by means of the internal standard method. The internal standard concentration (Ketoprofen-d_3) was maintained constant at 25 ng mL^{-1}, while the analyte concentrations were 2, 5, 10, 15 and 30 ng mL^{-1}. Each point of the respective calibration curves was the mean of three replicates. All analytes showed good linearity (R^2 between 0.992 and 0.999).

Limits of detection and quantitation (calculated as a signal to noise ratio of 3 and 10, respectively) were slightly different for each analyte; in particular perfluorinated compounds provided the highest analytical response with a limit of detection of 0.15 ng mL^{-1} and a limit of quantitation of 0.50 ng mL^{-1}. Nonetheless, for practical reasons, the lowest point of the calibration curve (2 ng mL^{-1}) was considered as the limit of quantitation for all of the compounds.

2.3. Passive samplers

Commercial POCIS with HLB (hydrophilic-lipophilic balance) phase were supplied by Environmental Sampling Technologies (St. Joseph, USA). Home-made POCIS were assembled using HLB sorbent phase (60 μm particle size), purchased from Sigma-Aldrich (Milan, Italy), and 0.1 μm pore size polyethersulfone (PES) membranes (Pall Italia, Buccinasco, Italy), with the same characteristics of the commercial ones (200 mg as mass of the sorbent phase and 45.8 cm^2 as sampler surface area). PES membranes were washed before assembling 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.

Both commercial and assembled POCIS samplers were used for static calibration at two different temperatures: room temperature (RT, +25 °C) and +5 °C. The samplers were deployed in triplicate, as described in the section "POCIS calibration"; upon retrieval, the samplers were rinsed with Milli-Q water, wrapped in aluminum foil and stored frozen at −20 °C.

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 Teflon frit and glass wool. The sorbent was dried for 30 min under vacuum. Prior to extraction, 50 μL of a 1000 ng mL^{-1} solution of ketoprofen-d3 were added into the sequestering phase, which was subsequently eluted with 50 mL of acetone. The eluate was collected in a flask, reduced to dryness in a rotary evaporator and redissolved in 1 mL of methanol; this solution was diluted 1:1 with Milli-Q for the LC-MS/MS analyses of real samples, while, during calibration experiments, it was diluted 1:100 with a water - methanol mixture 50:50.

2.4. POCIS calibration

The R_s calibration experiments were performed for both commercial and home-made POCIS at two different temperatures, +5 °C and +25 °C. A 1.8 mL mixture containing 22.5 μg of each analyte was spiked into a clean 5 L-capacity beaker containing 4.5 L of tap water. The mixture was allowed to equilibrate for about 30 min at a stirring rate of 1300 rpm using a F30 magnetic stirrer (Falc Instruments s.r.l., Italy), resulting in a nominal concentration of 5 μg L^{-1} of each compound. For each experiment, three POCIS were suspended in the spiked solution and the beaker was covered with aluminum foil. The calibration at +5 °C was performed in a fridge. Both experiments were conducted for 72 h under stirring at 1300 rpm.

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