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RESEARCH ARTICLE

Short-term stability assessment for the analysis of emerging contaminants in seawater

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Abstract

This paper describes the stability study performed in seawater and seawater extracts (spiked at ~ 200 ng/L) for 23 emerging contaminants. Four different alternatives were tested at six different times (0, 3, 10, 17, 24 and 31 days): (i) seawater at 4 °C, (ii) mixed-mode solid-phase extraction cartridge (Bond Elute Plexa and Strata X-AW) stored at − 20 °C, (iii) polyethersulfone hollow fibre stored at − 20 °C and (iv) methanol extracts once the samples were extracted from PES hollow fibre and stored at − 20 °C. Moreover, the integrity of the supporting polymeric phases was studied by Raman, optical microscopy, differential scanning calorimetric and thermogravimetric analysis. As may be expected, seawater samples showed the lowest stability (losses between 21 and 99%) while methanol extract provides stable results (losses < 30%) over the tested period. In the case of solid-phase cartridges, the stability profile showed an average loss of 7% while, in polyethersulfone hollow fibres, losses up to 58% were observed. Finally, we were able to relate the lower efficiency of polyethersulfone fibres with the wettability of this material based on the thermogravimetric analysis.

Keywords Mixed-mode solid-phase cartridges · Polyethersulfone hollow fibres · Polymer characterisation · Seawater · Short-term stability · Marine environment

Introduction

The analysis of the so-called emerging contaminants, i.e. the potentially hazardous compounds that are not under any environmental regulation (Postigo and Barceló 2015), is facing a number of methodological challenges. Among them, we can highlight the design of proper extraction and preconcentration procedures allowing the screening of the widest variety of compounds in a single run, and the strategies to assure the integrity of the samples up to the analysis, since most of the compounds considered are bioactive and their lack of stability can hamper all the analytical efforts (Baker and Kasprzyk-Hordern 2011a; Fedorova et al. 2014; Petrovic 2014).

Regarding the last point, we tend to assume the integrity of the analytes during the sampling step while the storage of the samples should assure their stability, as pointed recently (AMCTB No 65 2015). The increasing interest for the analysis of contaminants of emerging concern, the extended use of passive sampling methods (Miège et al. 2015) and the management requirements when a large number of samples are being processed have opened the discussion about the stability of the samples as well as the best approaches to assure their preservation. In this sense, we can highlight the review for pharmaceuticals in natural waters by Mompelat et al. (2013), the analysis of illicit drugs in sewers and wastewaters by McCall et al. (2016) or the analysis of antibiotics in purified water samples by Llorca et al. (2014).

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Concerning the passive sampling methods and its increasing use (Miège et al. 2015), new sampling methodologies such as semipermeable membrane devices (Sultana et al. 2017), Chemcatcher (Kaserzon et al. 2014; Vermeirssen et al. 2012) and polar organic chemical integrative samplers (POCIS) (Iparraguirre et al. 2017; Mijangos et al. 2018) allow the direct analysis from water matrices avoiding, to some extent, the stability issues. However, issues such as the preservation of compounds in different sorbents during the passive sampling may also arise, as pointed by Carlson et al. (2013).

As pointed before, labile analytes such as pharmaceuticals and pesticides are bioactive and hence may undergo different chemical, physical and biological processes from the sampling up to the analysis (Fatta-Kassinos et al. 2011). Thus, depending on stability, quantifying a compound that has been released several hours previously may, in fact, lead to a significant underestimation of the actual amount of residue present. As a consequence, the procedures and strategies to collect and handle the samples are usually guided by the compliance to the existing regulations or to the proper laboratory procedures (Baker and Kasprzyk-Hordern 2011a; Mompelat et al. 2013). Typically, the factors studied are the influence of suspended solids (Baker and Kasprzyk-Hordern 2011a); the addition of a preserving agent (González-Mariño et al. 2010; Llorca et al. 2014); and the storage conditions (temperature, pH and time) (Baker and Kasprzyk-Hordern 2011a; Mompelat et al. 2013).

One of the options is the use of solid-phase extraction (SPE) cartridges (González-Mariño et al. 2010; Petrović and Barceló 2000; Turiel et al. 2004) because we gain the extraction of the analytes and we save a lot of space in the labs. On the other hand, the growing interest for passive samplers such as POCIS (Carlson et al. 2013) can provide simplified procedures to sampling and storing but we lack the knowledge regarding the sorptive features on the different polymers.

Therefore, the aim of this work was the evaluation of the stability of 23 organic contaminants (21 emerging compounds and 2 priority contaminants) during 1 month and under different preservation procedures. For this purpose, four different storage conditions were tested: (i) seawater samples stored at 4 °C, (ii) preconcentration of spiked seawater in a SPE cartridge with a mixture of Bond Elute Plexa and Strata X-AW sorbents (commonly used as passive sampler sorbents (Fauvelle et al. 2012; Kaserzon et al. 2012, Kaserzon et al. 2014; Mijangos et al. 2018) and stored at −20 °C, (iii) preconcentration in PES hollow fibres (disposable polymeric materials used in microextraction techniques (Bizkarguenaga et al. 2015; Blanco-Zubiaguirre et al. 2014; Mijangos et al. 2017) and stored at −20 °C and, finally, (iv) the storage of methanol extracts (obtained from seawater preconcentration in PES fibres) at −20 °C. The target analytes include herbicides, hormones, lifestyle products (stimulants and artificial sweeteners), personal care products, phytoestrogens, industrial chemicals (corrosion inhibitor and perfluoroalkyl substances) and pharmaceuticals (dihydrofolate reductase inhibitor, fluoroquionolones, sulfonamides, dihydrofolate reductase inhibitor (DHFR inhibitor), tricyclic antidepressants, antihypertensives, anti-inflammatories, β-blocker cardiovascular drugs, lipid regulators, angiotensin II receptor antagonists (ARA-IIs) and anticonvulsant psychiatric drug). Additionally, supporting polymeric phases' (PES, Plexa and Strata X-AW) integrity was also evaluated by means of Raman spectroscopy, optical microscopy and differential scanning calorimetric and thermogravimetrical analysis.

Material and methods

Reagents and materials

The selection of the target pollutants was carried out taking into account their presence and relevance on the environment (Brack et al. 2017; Busch et al. 2016; Tousova et al. 2017). According to these criteria, 23 organic pollutants with urban, rural and industrial use were selected, which cover a wide variety of physicochemical properties as shown in Table 1, including their chemical structure and some physicochemical parameters.

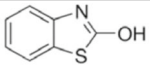
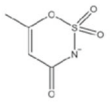
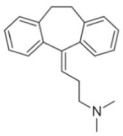
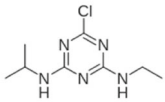
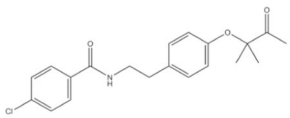
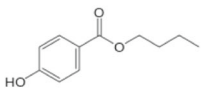
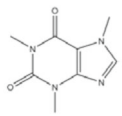
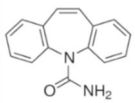
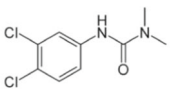
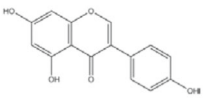
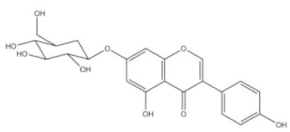
2-Hydroxybenzothiazole (OBT), amitriptyline hydrochloride, butylparaben, caffeine, carbamazepine, lineal perfluorooctane sulfonic acid (PFOS), imipramine hydrochloride, lineal nonafluorobutanesulfonic acid (PFBS), progesterone and sulfadiazine were purchased from Sigma-Aldrich (St. Louis, MO, USA). Atrazine, diuron, norfloxacin hydrochloride, sulfamethoxazole and trimethoprim were acquired from Fluka (Buchs, Switzerland). Acesulfame potassium was supplied by Supelco (Bellefonte, PA, USA), and ketoprofen, bezafibrate and propranolol were acquired from MP biomedicals (Illkirch Cedex, France). Genistein and genistin were purchased from Extrasynthese (Lyon, France), perfluorooctanesulfonamide (PFOSA) from Dr. Ehrenstofer (Augsburg, Germany) and irbesartan from Sanofi (Paris, France). The purity of all the target analytes was higher than 95%.

Individual stock standard solutions were dissolved on a weight basis in methanol (MeOH, UHPLC-MS MeOH, Scharlab, Barcelona, Spain) in order to prepare approximately 1000–2500 mg/L solutions. However, the addition of 100 μL sodium hydroxide 1 M (NaOH, 98%, Panreac, Barcelona, Spain) was necessary for the proper dissolution of fluoroquinolone antibiotics as described by Gros et al. (2013). One hundred milligrams per litre dilutions were prepared in MeOH

every month, and dilutions at lower concentrations containing all analytes were prepared daily in MeOH: Milli-Q (30:70, *v:v*). All the chemical standard solutions were stored at − 20 °C.

The most relevant characteristics and suppliers of the polymers evaluated in the present work are listed in Table 2. Empty SPE tubes (6 mL) and polypropylene (PP) frites were purchased from Supelco. PES hollow fibre agitation was carried out using 150-mL glass vessels provided by ServiQuimia (Tarragona, Spain) in a 15-position magnetic stirrer (Gerstel, Mülheim an der Ruhr, Germany). Desorption was made in 1.5-mL Eppendorf tubes purchased from Eppendorf (Berzdorf, Germany) using a Digital Ultrasonic Cleaner (2500 mL, USB Axtor by Lovango, Barcelona, Spain). Ethylenediaminetetraacetic acid sodium salt (Na_2EDTA, 99.0–101.1%, Panreac), formic acid (HCOOH ≥ 98%, Scharlau, Barcelona, Spain), ammonia (25% as NH_3, Panreac) and sodium chloride (NaCl, > 99.8%, Merck) were used for matrix modification and elution step. MeOH (HPLC grade, 99.9%) was supplied by LabScan (Dublin, Ireland).

Table 1 Family, name (abbreviation), CAS number, structure and some physicochemical parameters of the target analytes

Analyte Family	CAS	Structure	Mw (g/mol)	pKa[a]	log $_{Kow}$[a]	Log D[a] (pH=2; pH=10)	Solubility[a] (mg/L)
2-hydroxybenzothiazole (OBT) *Corrosion inhibitor*	934-34-9		151.2	6.4	2.5	2.5; 0.9	$2.4 \cdot 10^3$
Acesulfame *Artificial sweetener*	55589-62-3		163.1	3.0	-0.6	-0.6; -1.5	$9.1 \cdot 10^8$
Amitriptyline *Tricyclic antidepressant*	50-48-6		277.4	9.8	4.8	2.5	0.8
Atrazine *Herbicide*	1912-24-9		215.7	3.2; 14.5	2.2	2.2	214.1
Bezafibrate *Lipid-regulating*	41859-67-0		361.8	-0.8; 3.8	4.0	0.7	$1.2 \cdot 10^3$
Butylparaben *Personal care product*	94-26-8		194.2	8.5	3.0	3.0	207
Caffeine *Stimulant*	58-08-2		194.2	-1.1	-0.6	-0.6	$1.6 \cdot 10^3$
Carbamazepine *Anticonvulsant*	298-46-4		236.3	16.0	2.8	2.8	17.6
Diuron *Herbicide*	330-54-1		233.1	13.2	2.5	2.5	150
Genistein Phytoestrogen	446-72-0		270.2	6.6; 8.1; 9.0	3.1	2.12	257
Genistin Phytoestrogen	529-59-9		432.3	7.3; 9.0; 12.2	0.8	0.4	$1.4 \cdot 10^3$

[a] Values reported in the Free Data Base www.chemicalize.org (21.02.2017)

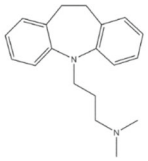
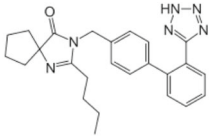
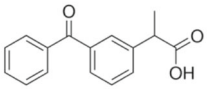
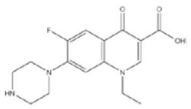
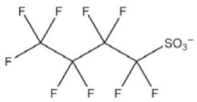
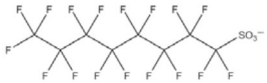
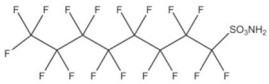
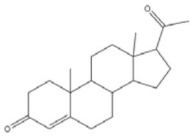
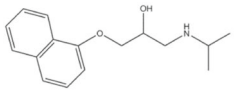
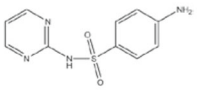
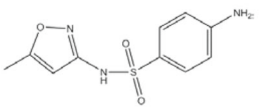
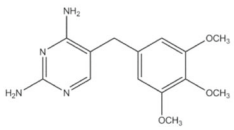
Imipramine *Tricyclic antidepressant*	50-49-7		208.4	9.2	4.3	2.5	$1.0 \cdot 10^3$
Irbesartan *ARA-II*	138402-116		428.5	4.1; 5.8	5.4	4.2	0.06
Ketoprofen *Antiinflammatory*	22071-15-4		254.3	3.9	3.6	0.4	120
Norfloxacin *Fluoroquinolone antibiotics*	70458-96-7		319.3	5.8	-0.9	-0.9	$1.2 \cdot 10^8$
Nonafluorobutanesulfonic acid (PFBS) *PFAS*	29420-49-3		338.2	-3.0	2.6	0.2	$8.4 \cdot 10^4$
Perfluorooctane sulfonic acid (PFOS) *PFAS*	1763-23-1		500.1	-3.3	5.4	3.0	520
Perfluorooctanesulfonamide (PFOSA) *PFAS*	754-91-6		499.1	3.4	4.8	3.9	-
Progesterone *Hormone*	57-83-0		214.5	-4.8	4.2	4.2	$5 \cdot 10^3$
Propranolol *ß-Blocker*	525-66-6		259.3	9.7; 14.1	2.6	0.4	228
Sulfadiazine Sulphonamide antibiotics	68-35-9		250.3	2.0; 7.0	0.4	-0.1	$8.0 \cdot 10^4$
Sulfamethoxazole Sulphonamide antibiotics	723-46-4		253.3	2.0; 6.2	0.8	0.0	$3.9 \cdot 10^4$
Trimethoprim *DHFR inhibitor antibiotics*	738-70-5		292.3	7.2	1.3	1.1	$2.33 \cdot 10^3$

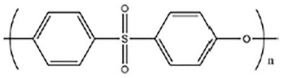
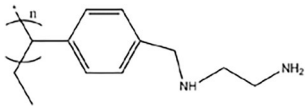
Table 1 (continued)

The extracts were evaporated using a Turbovap LV Evaporator (Zymark, Hopkinton, USA) under a gentle stream of nitrogen (> 99.999% of purity) supplied by Messer (Tarragona, Spain). The extracts were filtered through PP filters (0.22 μm, 13 mm, Phenomenex, California, USA). Milli-Q (< 0.05 μS/cm, Milli-Q, Millipore) water and UHPLC-MS MeOH (Optima, Scharlau, Barcelona, Spain) were used as mobile phase eluents and HCOOH (Optima, Fischer Scientific, Geel, Belgium) for mobile phase modification. High-purity nitrogen gas (> 99.999%) supplied by Messer was used as collision gas, and nitrogen gas (99.999%) provided by AIR Liquid (Madrid, Spain) was used as both nebuliser and drying gas.

Stability tests

The removal of suspended particulates from water samples may avoid further degradation or losses of analytes through

Table 2 Main characteristics of the materials evaluated

Polymer	Supplier	Chemical structure	Mode of action	Characteristics
Polyethersulfone (PES)	Membrane GmbH		Reverse phase	Hollow fibre, external diameter 0.7 mm Porosity 87%
Bond Elute Plexa (Plexa)	Agilent	Hydrophilic styrene divinylbenzene[a]	Reverse phase	Bulk, particle size 45 μm Pore size 160 Å
Strata X-AW	Phenomenex		Weak anion mixed mode	Bulk, particle size: 30 μm Pore size 85 Å

[a] Chemical structure not provided by the manufacturer

their adsorption onto the solid particles, but the retention of these analytes in the filters should be also thoroughly considered (Baker and Kasprzyk-Hordern 2011a; Petrovic 2014). In this sense, unfiltered seawater samples were collected in 2-L clear-PP bottles as previously described by Llorca et al. (2014) from the Plentzia Marine Station (PiE-UPV/EHU, Basque Country, Northern Spain) and used for the stability experiments. Furthermore, some physicochemical parameters (temperature, dissolved oxygen, pH, redox potential, conductivity and salinity, see Table S1 in online resource) of the seawater were monitored with a multiparametric probe (EXO 2, YSI, USA).

The experiments were carried out spiking the seawater (100 mL) with a mixture of the 23 analytes at a final concentration of ~ 200 ng/L each one. In parallel to the spiked samples, a non-spiked control sample (blank) was also processed in duplicate alongside each of the stability tests and at the same conditions. The experiments were performed in triplicate for each preservation mode at 6 different sampling times (after 0, 3, 10, 17, 24 and 31 days), and all the samples were analysed at the same day by LC–MS/MS (Mijangos et al. 2017) (see "Liquid chromatography–tandem mass spectrometry analysis").

In the case of preservation mode (i), 100 mL of unfiltered seawater were stored at 4 °C in the pre-cleaned PP bottles. In the case of mode (ii), 200 mg SPE cartridges (a 1:1 mixture of Strata X-AW and Plexa, as the sorbent composition used for passive sampler previously published (Mijangos et al. 2018)) were prepared from 100 mL spiked seawater samples. SPE cartridges were sequentially conditioned with 5 mL of MeOH and 5 mL of ultrapure water. Then, the water sample (100 mL) was percolated through the cartridge assisted by a vacuum pump at ca. 5 mL/min.

In the case of mode (iii), 4 pre-cleaned PES hollow fibres of 4 cm (final weight of approx. 50 mg) were used, according to the previously published work (Mijangos et al. 2017). First of all, the fibres were cut using a sharp blade and conditioned by soaking overnight in MeOH and air dried. Two aliquots of 120 mL of spiked seawater (dual extraction) were directly poured into 150-mL extraction vessels, and NaCl and Na_2EDTA were added to achieve final concentrations of 30% (*w*/*v*) and 0.1% (*w*/*w*), respectively. The pH of each aliquot was fixed at pH = 2 and pH = 10, and finally, hollow fibres and a magnetic stirrer were also added. Thereafter, vessels were closed and extraction was performed at room temperature (RT) and at 800 rpm overnight (14 h). Once the sorption step was over, the polymers were removed and rinsed with Milli-Q water in order to eliminate salt residues, and, finally, dried with a clean tissue and stored in an air-tight freezer bag at − 20 °C.

Finally, in the case of mode (iv), PES fibres were used following the extraction procedure described before, and once the extraction was accomplished, the fibres were introduced into a 1.5-mL Eppendorf tube containing 1 mL of MeOH and soaked for 32 min in an ultrasound bath and then, the methanolic extracts were stored in Eppendorf tubes at − 20 °C.

To run the analysis (18 aliquots per preservation mode), water samples (mode (i)) were extracted by SPE cartridges according to the previously published work (Mijangos et al. 2017). In the case of mode (ii), the cartridges were washed with 6 mL of ultrapure water, vacuum dried and eluted with 6 mL of 2.5% (*v*/*v*) ammonia solution in methanol followed by 6 mL of methanol (Mijangos et al. 2018). PES fibres used in modes (iii) and (iv) were extracted using the procedure described before. All the extraction solutions from modes (i–iv) were always evaporated to dryness under a gentle stream of nitrogen at 35 °C and reconstituted in 200 μL of MeOH:Milli-Q (30:70, *v*:*v*). Finally, the reconstituted extracts were filtered through a 0.2 μm PP filter before the LC–MS/MS analysis.

The target analyte stability was calculated according to Eq. (1), and a 100% result represents a lack of analyte losses or degradation:

$$\text{Recovery}\ (\%) = 100 \times \frac{A^{i}_{x,sp} - A^{i}_{x,nsp}}{A^{0}_{x,sp} - A^{0}_{x,nsp}} \quad (1)$$

where $A^{i}_{x,\mathrm{sp}}$ and $A^{i}_{x,\mathrm{nsp}}$ correspond to the chromatographic peak areas of analyte *x* from the spiked (sp) and non-spiked (nsp) samples, respectively, at time *i*, and $A^{0}_{x,\mathrm{sp}}$ and $A^{0}_{x,\mathrm{nsp}}$ are the corresponding peak areas at day 0. A significant (mean)

loss of 30% in the recovery of the analytes was chosen to point out the lack of stability during a given storage preservation mode and time, since the precision attributable to an analytical method, expressed as RSD (inter-day precision), must be ≤ 30% according to the European Commission decision 2002/657/EC (Commission E 2002).

Characterisation of sorptive materials

PES, Plexa and Strata X-AW were individually examined prior to and after storage at − 20 °C and RT for a month. The surface and the cross section of the polymer materials were examined by a Nikon SMZ800 stereomicroscope coupled to a NIKON DS-RI1 at × 40 magnifications. Chemical characterisation of the sorptive materials was assured by means of Raman spectroscopy. They were analysed using a portable Renishaw RA 100 Raman spectrometer (Renishaw, Gloucestershire, UK) using either the 785 nm or the 514 nm excitation laser. Measured scans were accumulated during 50 s at 100% of the maximum power of the used laser. The homogeneity of the PES hollow fibre was tested by acquiring longitudinally ten Raman spectra per fibre (one measurement per 1.5 mm). The software used to collect and process the Raman spectra was BWspec4 and Omnic (Nicolet, Madison, WI, USA).

The wettability and thermal stability of the polymeric materials were studied by differential scanning calorimeter (DSC) by a Mettler Toledo Differential Scanning Calorimeter instrument (model DSC822). Ten milligrams of each polymeric material was subjected to 5 sequential heating/cooling cycles: the first 4 were done consecutively and the 5th run was performed after having the polymer 1 h out of the measuring chamber (nitrogen ambient). Temperature range was from 0 to 200 °C, and the scanning rate was of 20 °C/min. Furthermore, a thermogravimetric analysis (TGA) was performed in a Mettler Toledo TGA/SDTA 851 system. Ten milligrams of solid-phase samples was kept during 30 min at 20 °C prior to the measurement and then heated from 20 to 800 °C. The scanning rate was 10 °C/min, and all measurements were carried out under nitrogen atmosphere.

Liquid chromatography–tandem mass spectrometry analysis

An Agilent 1260 series HPLC chromatograph equipped with a degasser, binary pump, autosampler and a column oven coupled to an Agilent 6430 triple quadrupole (QqQ) mass spectrometer with electrospray ionisation (ESI) source (Palo Alto, CA, USA) was employed. For analyte separation, a Kinetex F5 100 Å core-shell (2.1 mm × 100 mm, 2.6 μm) column coupled to a Kinetex F5 pre-column (2.1 mm × 4.6 mm, 2.6 μm from Phenomenex (Torrance, CA, USA) was used. The column temperature and the injection volume were set to 35 °C and 5 μL, respectively. The separation of the target analytes was carried out at a flow rate of 0.3 mL/min. Under optimised conditions [25], a binary mixture consisting of water:MeOH (95:5, *v*:*v*) (phase A) and MeOH:water (95:5, *v*:*v*) (phase B), both containing 0.1% of HCOOH, was used for gradient separation of target analytes. The gradient profile started with 30% B, and it was increased to 50% in 4 min and maintained for 12 min. Then, it was increased to 90% B and it was kept constant for 10 min. Initial gradient conditions (30% B) were then recovered in 6 min and held constant for another 10 min (post-run step). ESI was carried out using a N_2 flow rate of 12 L/min, a capillary voltage of 3500 V, a nebuliser pressure of 45 psi and a source temperature of 350 °C. Quantification was performed in the selected reaction monitoring (SRM) acquisition mode by recording the two most intense transitions for each analyte (the most sensitive was chosen as the quantifier and the second one as qualifier) when it was possible. Both, negative and positive voltages, according to the target analytes, were simultaneously applied in a single injection. Optimum parameter values for each target compound are summarised in Table S2 in Online Resource. Instrumental operations, data acquisition and peak integration were performed with the MassHunter Workstation Software (v B.06.00, Agilent Technologies).

Results and discussions

Quality control

Some physicochemical parameters (temperature, dissolved oxygen, pH, redox potential, conductivity and salinity) of the seawater were measured along the experiment (see Table S1 in Online Resource). Temperature, pH and salinity were constant with average values of 13.6 ± 0.2 °C, 0.4 ± 0.2 and 33.7 ± 0.2 psμ, respectively, and the redox potential values (144 ± 25 mV) showed an RSD of 18%.

Furthermore, the analytical figures of merit in real spiked seawater samples ($n = 3$, 100 ng/L) of both the previously published PES-LC-MS/MS (Mijangos et al. 2017) methodology and in the case of SPE-LC-MS/MS method are summarised in Table S2 in Online Resource. The quantification of the target analytes in real seawater was carried out using an external calibration together with surrogate corrections approach for SPE, while, in the case of PES method, a procedural calibration with Milli-Q using isotopically labelled analogues as surrogates was used. In this sense, process efficiency, apparent recovery (recovery after correction with the corresponding surrogate included in Table S2) and method quantification limits (MQLs) were determined. MQLs were calculated using the Eq. (2) (Baker and Kasprzyk-Hordern 2011b; Huntscha et al. 2012; Kasprzyk-Hordern et al. 2008).

$$MQL = \frac{LOQ \times 1000}{PE\ (\%) \times CF} \quad (2)$$

where LOQ (ng/mL) is the instrumental quantification limit (included in Table S2 in Online Resource), PE (%) is the process efficiency of the analyte in the corresponding matrix (see Table S2) and CF is the analyte concentration factor according to the developed procedures.

Additionally, during the sample treatment, control samples (samples spiked at known concentration level, $n = 3$) and procedural blanks ($n = 3$) were analysed periodically every 12–15 samples. RSDs in the range of 3–30% were obtained for all the analytes, and concentrations lower than their MQLs were obtained in the case of blanks for the target compounds.

Characterisation of sorptive materials

The polymers used in the present study (Plexa, Strata X-AW and PES) were characterised chemically and thermally before and after being stored at − 20 °C and RT for a month. Good-quality Raman spectra (see Fig. S1 for the PES hollow fibre as example) and microscopy surface images (see Fig. S2 **a-l**) were obtained for all the sorptive phases before and after storing, and no differences were observed at the two temperatures.

However, when the thermal degradation was studied by running a TGA curve, in the case of PES hollow fibre, the thermal characteristics obtained from TGA and first-derived thermogravimetric (DTG) curves (seen in Fig. 1a, b) showed difference between the polymers without storage and after low-temperature storage. When the fibres were kept at RT, a significant weight loss temperature was observed at 550 °C and attributed to the decomposition of polymer main chain (Cao et al. 2011; Guan et al. 2005; Sharma and Bijwe 2012). When PES fibres were kept at − 20 °C for 1 month, an additional sharp weight (35% of the total mass) can be seen at 100 °C and this loss can be related to the desorption of water. These results are in total agreement with published data (Cao et al. 2011; Guan et al. 2005; Sharma and Bijwe 2012) where it was observed that water can be bonded through the sulfonic groups of polyethersulfone polymers. Plexa and Strata X-AW did not show any significant changes (see Fig. 1c–d) in thermal behaviour; the weight loss origin from water content was <5% in both cases.

Finally, the wettability of these polymers was studied by running DSC analysis in a sequential way. As shown in Fig. 2a, PES hollow fibres showed two signals in its thermogram: a broad peak around 100 °C, due to the desorption of water molecules present in the polymers (Cao et al. 2011; Sharma and Bijwe 2012) and a glass transition temperature (Tg) at 230 °C, which is in agreement with the values reported in the literature for pure PES (Bolong et al. 2009; Cao et al. 2011; Prieto et al. 2012; Sharma and Bijwe 2012). Regarding the wettability, the removal of water content of the PES fibre was achieved after running the scan several times (runs 1–4 in Fig. 2a) since the humidity peak was significantly smoothed at every scan. Furthermore, the observed increase of the glass transition temperature is a consequence of the plastification induced by the humidity that lowers Tg. Finally, once the fibre was released from the inert gas chamber of the DSC for an hour (run 5 in Fig. 2a), the broad peak corresponding to the humidity increased again suggesting that the PES hollow fibre can re-adsorb water. Thus, PES hollow fibre has the ability to re-uptake water from the air even after being totally dried (Guan et al. 2005). On the contrary, the signals of Plexa and Strata X-AW (see Fig. 2 b and c, respectively) remain constant after getting dried. These results suggest that the polymers chosen (PLEXA, Strata X-AW and PES hollow fibre) have a good thermal and chemical stability; however, the hydrophobicity of the PES hollow fibre, closely linked to the chemical structure of the polymer, may be an issue.

Stability test

The variation of the concentrations of all the analytes along the storage time in the four modes studied in this work is shown in Fig. 3a–d. As mentioned before (see "Characterisation of sorptive materials"), the storage procedure assures the stability when the losses along the storage time are below 30%.

In the case of procedure (i), three profiles were observed, as shown in Fig. 3a: a declining profile (78% of the studied analytes), an increasing profile and constant concentrations throughout the experimental period. After 31 days, statistically significant losses (within 20–45% at a p level < 0.05 in the analysis of variance) were observed for atrazine, bezafibrate, butylparaben, caffeine, diuron, ketoprofen, norfloxacin, OBT, propranolol, sulfadiazine, sulfamethoxazole and trimethoprim, whereas amitriptyline, imipramine, genistein, genistin, irbesartan and progesterone reduced quantitatively (> 99%) their initial concentrations in just 3 days. These behaviours could be attributed to the chemical structure and reactivity of the studied analytes. With regard to pharmaceutical-like compounds, numerous studies have reported the lack of stability in aqueous samples (Baker and Kasprzyk-Hordern 2011a; Fedorova et al. 2014; Llorca et al. 2014; Mompelat et al. 2013). Baker et al. (Baker and Kasprzyk-Hordern 2011a) described a thorough verification of methodologies commonly used for the storage of aqueous samples and for the analysis of pharmaceuticals and illicit drugs, and observed that antidepressant showed a poor stability with a recovery decreased of 61% after 72 h in unfiltered wastewater samples. Turiel et al. (2004) studied the degradation of fluoroquinolones under different storage conditions (time, light and temperature) for 2 weeks, and the analyte losses were mainly attributed to photolysis (after 2 weeks, a loss of 50% of the initial concentration was observed).

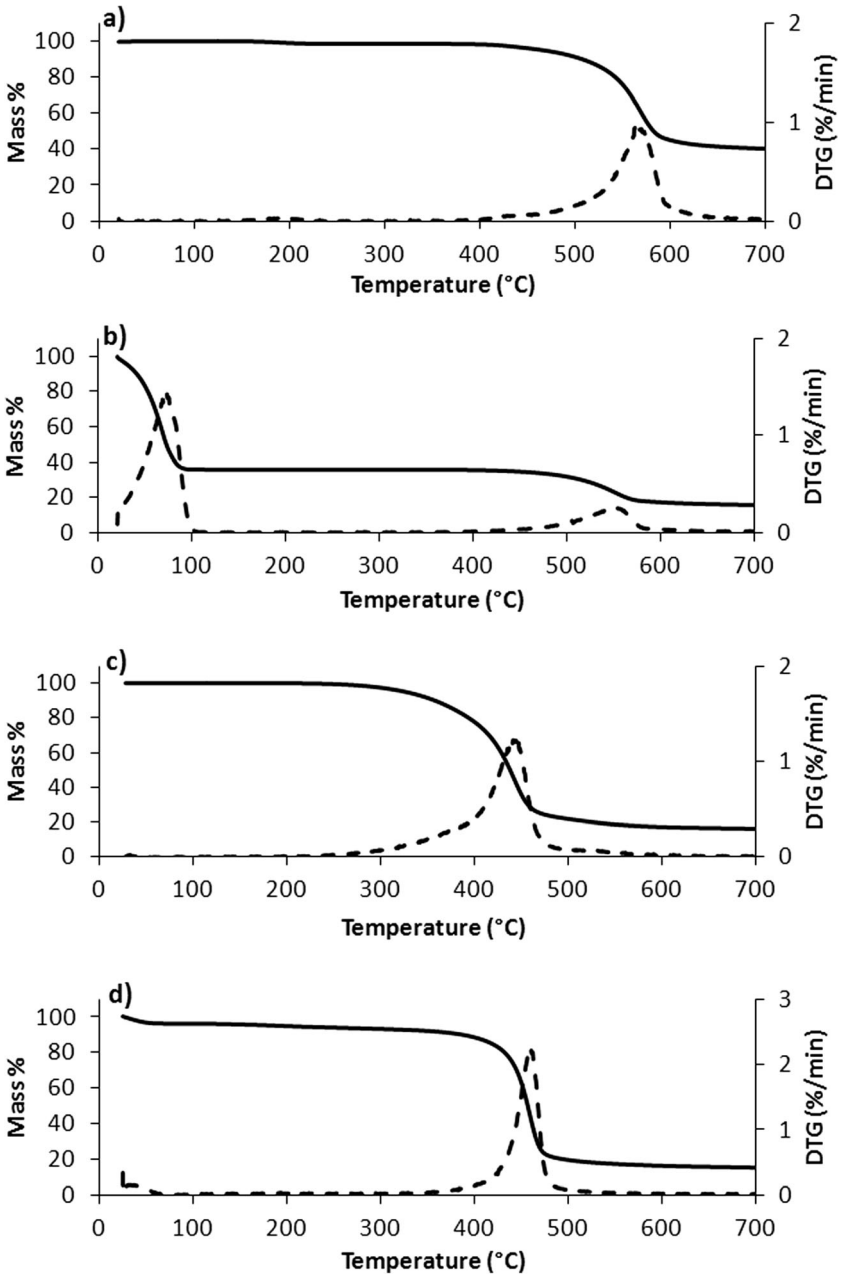


Fig. 1 Thermogravimetric (TGA) curve (left axis, line) and first derivate thermogravimetric (DTG, right axis, dots) of the studied polymers before and after storage at − 20 °C for 1 month: **a** PES hollow fibre before storage; **b** PES hollow fibre after storage; **c** PLEXA after storage; **d** Strata X-AW after storage

The increasing profile (up to 146%) was detected in the case of PFOS accompanied by a parallel signal decrease (up to 42%) of its parent compound PFOSA. Similar degradation pathway of PFOSA precursor into the stable PFOS end-product has been reported in the literature (Buck et al. 2011; Zhang et al. 2017). Finally, only acesulfame, carbamazepine and PFBS remain constant during the 31-day evaluation (p level > 0.05, according to the analysis of variance, ANOVA). These results are in good agreement with those of Van Stempvoort et al. (2011), which compared refrigerated and frozen environmental samples for the stability of artificial sweeteners (acesulfame, cyclamate, saccharin, sucralose) over a storage time of 13 months and found acesulfame was stable during this period. Due to their high stability in aquatic media, acesulfame and carbamazepine compounds have been proposed as tracers of human wastewater contamination in environmental samples (Huntscha et al. 2012; Jekel et al. 2015; Lange et al. 2012; Mawhinney et al. 2011).

In the case of the SPE cartridges, the average loss of all compounds after 31 days of storage was 7% with a maximum loss of 24% for OBT (see Fig. 3b). Therefore, the short-term preservation of extracted samples in SPE cartridges in the freezer (− 20 °C) is a good approach. The advantages of using SPE cartridges for these purposes have been previously described in several works (Baker and Kasprzyk-Hordern 2011a; Fedorova et al. 2014; Mompelat et al. 2013).

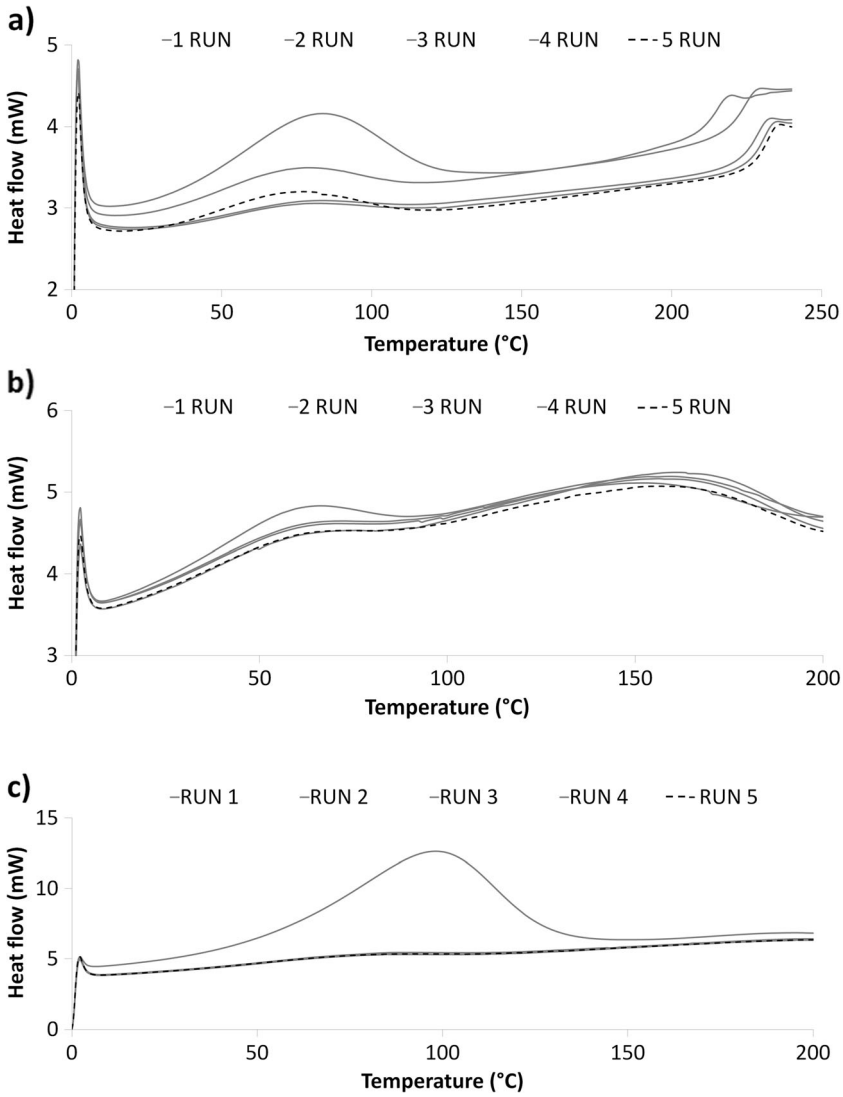


Fig. 2 Sequential differential scanning calorimetric (DSC) carried out for the three studied polymers after storing at − 20 °C for 1 month: **a** PES hollow fibre, **b** Plexa and **c** Strata X-AW. First four measurements (continuous line) were run sequentially (heating/cooling cycles) but the 5th run (dots) was performed after having each polymer 1 h out of the measuring chamber (nitrogen inert gas ambient)

On the contrary, though a close stability pattern would have been expected in PES hollow fibres, the stability profiles obtained in PES were quite different from those obtained onto SPE cartridges (see Fig. 3 b and c for SPE and PES, respectively). PES hollow fibres showed remarkable losses in analyte concentrations after 31 days for acesulfame (45% remaining after 31 days), caffeine (65%), genistein (42%), genistin (60%), norfloxacin (50%), OBT (45%), PFBS (65%), sulfadiazine (43%) and sulfamethoxazole (53%). In contrast to the well-known stability onto SPE cartridges (C_{18} and/or HLB) (Llorca et al. 2014; McCall et al. 2016; Mompelat et al. 2013), there is no published data on stability tests for PES polymer material, even though it is highly used in POCIS as the supporting membrane (Carlson et al. 2013; Posada-Ureta et al. 2017; Vermeirssen et al. 2012) and in sorptive microextraction methods (Bizkarguenaga et al. 2015; Blanco-Zubiaguirre et al. 2014; Prieto et al. 2012; Ros et al. 2015).

Finally, as can be seen in Fig. 3d, all the analyte concentrations (< 7 0%) remain stable up to 31 days in the MeOH extracts allowing the accurate estimation of the concentrations of the target compounds in environmental matrices.

Regarding the four different modes evaluated and in the case of some of the studied compounds, only carbamazepine remained constant regardless of the preservation mode after 31 days. Remarkable losses onto PES hollow fibres were observed in compounds such as acesulfame (55%) and PFBS (35%) that showed a high stability in water (91–108% and 87–102%, respectively). The stability of the phytoestrogens, OBT, fluoroquinolones and sulphonamides was rather low onto PES hollow fibres (42–60% remaining concentrations after 31 days) as well as in seawater. In contrast, amitriptyline, butylparaben, imipramine, irbesartan, progesterone and PFOSA were significantly more stable onto PES hollow fibres (losses < 20%) compared with seawater (losses up to 99%).

The patterns observed in the PES hollow fibre might not be related to the degradation of those compounds in the polymer

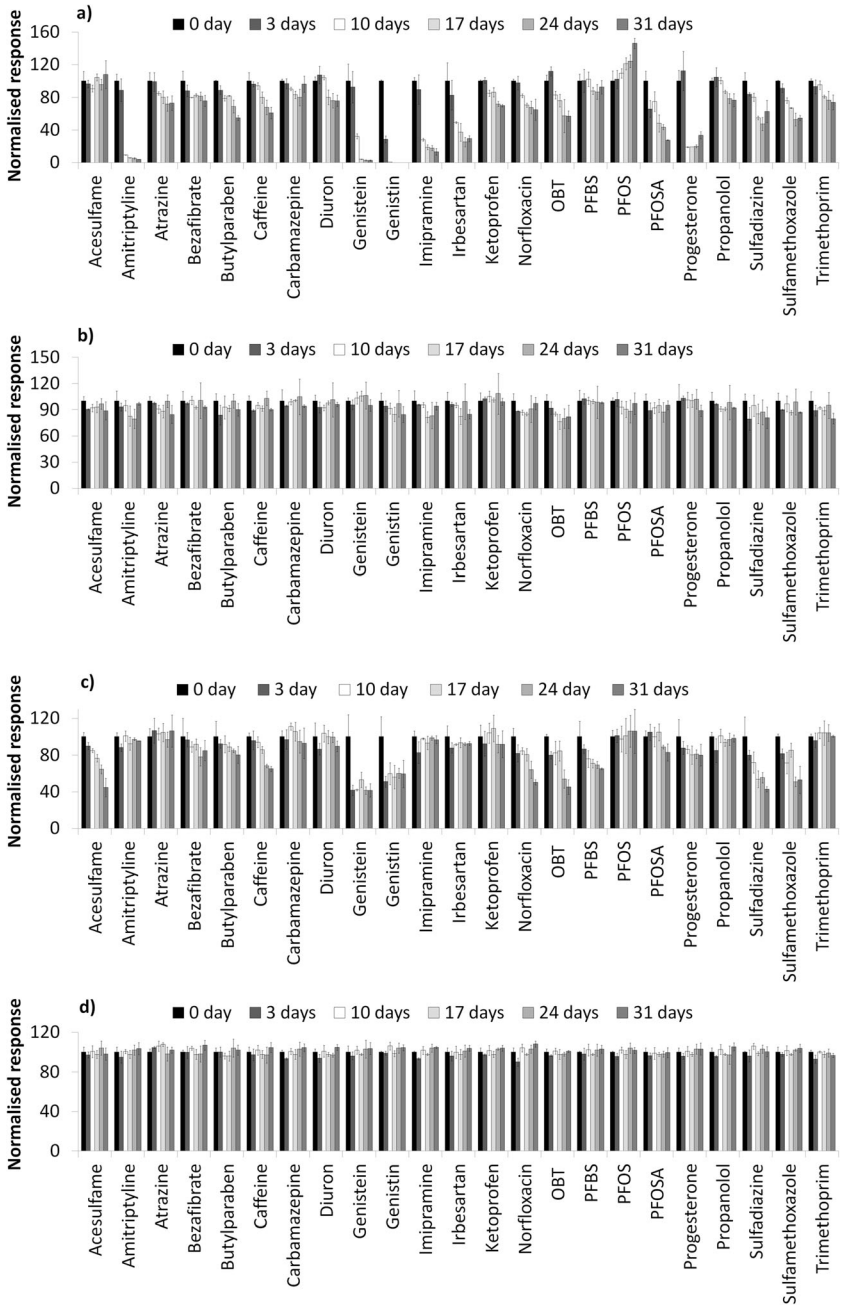


Fig. 3 Relative recovery percentage of each analyte at 6 times (0, 3, 10, 17, 24 and 31 days) preserved at **a** raw seawater at 4 °C, **b** SPE cartridges at − 20 °C, **c** PES hollow fibres stored at − 20 °C and **d** 100% methanol extracts stored at − 20 °C

but to the presence of the low amount of water observed in the previous section that may help to solubilise and to lose some analytes such as genistein, genistin, OBT, PFOSA, sulfadiazine or sulfamethoxazole as it happens to a similar extent in water (see the solubility values collected in Table 1).

Conclusions

According to the results obtained in this work, the best way to assure the stability of the water samples containing polar or slightly polar emerging contaminants is either to keep the MeOH extracts after being extracted the samples by SPE or any other procedure or to keep the extracted samples in SPE cartridges. Both procedures assure a high recovery of a wide amount of contaminants typically found in aquatic media for a short-term period. This way, the management of the sample analysis can be effectively carried out. Furthermore, PLEXA, Strata X-AW and PES hollow fibre showed a good thermal and chemical stability to be used as potential solid phases but the wettability of the PES fibres has been linked to the lack of stability of a number of compounds. A deeper study of the

polymeric materials showed that the losses observed in PES hollow fibres were related to the capability of the polymer to re-absorb water, which might degrade biotically some analytes or redissolve them due to their high water solubility.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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