Ultra-high-performance liquid chromatography–tandem mass spectrometry for determining the presence of eleven personal care products in surface and wastewaters

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ABSTRACT

Personal care products (PCPs) are widely used emerging contaminants which can cause adverse environmental effects. This paper reports the development and validation of a method based on solid-phase extraction (SPE) and ultra-high-performance liquid chromatography–electrospray ionisation–tandem mass spectrometry (UHPLC–(ESI)MS–MS) for simultaneously determining eleven PCPs: 4 preservatives (methylparaben; ethylparaben; benzylparaben; propylparaben); 2 antimicrobial agents (triclocarban and triclosan) and 5 UV filters (2,4-dihydroxybenzophenone; 2,2-dihydroxy-4-methoxybenzophenone; benzophenone-3; octocrylene and octyldimethyl-*p*-aminobenzoic acid) in environmental waters in only 9 run minutes of chromatographic separation. The SPE was carried out with two polymeric cartridges (Oasis HLB and Bond Elut Plexa). The recoveries obtained with Bond Elut Plexa were between 69% and 101% for 500 mL of river waters, with the exception of octyldimethyl-*p*-aminobenzoic acid (46%). Limits of detection for 500 mL of river water were in the range of 1–5 ng/L. Oasis HLB was chosen for wastewater samples with recoveries between 38% and 92% (250 mL of effluents) and 36–89% (100 mL of influents). In both wastewater samples, octyldimethyl-*p*-aminobenzoic acid and methylparaben showed the lowest recoveries (20% and 27%). The method revealed benzophenone-3 as having the highest concentration levels (7 ng/L) in river waters. Most of PCPs determined were found in influent waters being methylparaben and propylparaben the ones found at highest concentration with values of 5613 and 1945 ng/L, respectively. In effluent waters, significant lower levels of some PCPs were found, being benzophenone-3 the one found at the highest concentration (100 ng/L).

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1. Introduction

Public interest in pharmaceuticals and ingredients of personal care products (PCPs) entering the environment has recently been increasing because research has shown they reach detectable and potentially harmful concentrations. PCPs, included in the so-called emerging contaminants, comprise diverse chemical substances such as fragrances, lotions, cosmetics, sunscreen agents and others [1–3]. The interest in these kinds of compounds focuses on their pronounced microbial and algal toxicity and potential for fostering resistance [4] and on the fact that some PCPs (e.g., parabens, UV filters) have been suspected of being endocrine-disrupting compounds [5,6]. The main pathway through which PCPs enter the aquatic environment is from household waters that are released by sewage treatment plants (STPs) [7]. They have been found in effluent wastewaters at levels of a few μg/L [8] because conventional STPs are not designed to completely remove these pollutants.

Several studies about the treatment and effective removal of personal care products have been published in recent years [9–11]. One of the most studied PCPs is triclosan because it is used as an antimicrobial agent in a large number of medical and personal-hygiene products. Although it is reported that primary treatments only remove triclosan in a 32% [12], ozonation appeared to be an effective technique for enhancing its removal [13].

A preconcentration step is needed before determining PCPs by chromatographic techniques because of the low concentration levels in the samples (ng/L and low μg/L). Some studies using solid-phase microextraction (SPME) [14,15] and stir bar sorptive extraction (SBSE) [16,17] have determined some PCPs in waters. However, solid-phase extraction (SPE) is the preferred technique for preconcentrating PCPs due to the excellent capabilities of the sorbents such as Oasis HLB [18,19], Oasis MCX [8] or Strata X [7] to retain these compounds.

Some methods for determining PCPs include gas chromatography coupled to mass spectrometry (GC–MS) [4,16,20] and tandem mass spectrometry (GC–MS–MS) [21], but these are limited to those compound classes that are volatile or can be derivatized. Over the past 20 years, the sensitivity, specificity and reliability

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of liquid chromatography have advanced dramatically with liquid chromatography–mass spectrometry (LC–MS) and LC–MS–MS. The recently developed ultra-high-performance liquid chromatography (UHPLC), which uses analytical columns packed with 1.8 μm particles, offers increased speed and improved sensitivity, selectivity and specificity compared to conventional HPLC analysis [22]. Not only does UHPLC offer very low chromatographic times but it also has a better resolution and narrow peaks that help prevent the analytes from coeluting with the interferences and this can lessen the matrix effects [23]. The advances in analytical instrumentation have made it possible to confirm the presence of a compound at very low levels using liquid chromatography coupled to mass spectrometry [8]. Nowadays, the triple quadrupole (QqQ) is very common and useful tool for high sensitivity target analysis. Monitoring two transitions between precursor and product ions working with multiple reaction monitoring mode (MRM) it is possible to confirm and quantify the presence of PCPs in waters at very low ng/L [19,24]. For example, Rodil et al. [19] used a QqQ to determine nine UV filters in waters and after an SPE step, they found LODs between 7 and 46 ng/L.

The goal of this paper was to develop and to validate a rapid method to determine eleven PCPs from different families in river and wastewaters. The rapid and sensitive techniques SPE/UHPLC–MS–MS allowed us to determine in a unique analysis: UV filters, preservatives and antimicrobial agents.

2. Experimental

2.1. Reagents and standards

We purchased 2-phenylbenzimidazole-5-sulfonic acid (PMDSA); methylparaben (MPB); ethylparaben (EPB); benzylparaben (BPB); propylparaben (PPB); 2,4-dihydroxybenzophenone (DHB); 2,2-dihydroxy-4-methoxybenzophenone (DHMB); benzophenone-3 (BP-3); triclocarban (TCC); triclosan (TCS); octocrylene (OC) and octyldimethyl-*p*-aminobenzoic acid (OD-PABA) from Sigma–Aldrich Chemie (Steinheim, Germany).

Stock solutions of individual standards were prepared by dissolving each compound in methanol at a concentration of 1000 mg/L and then storing it at 4 °C. Fresh stock solutions were prepared each 6 months. A mix of all compounds in water at a concentration of 50 mg/L was prepared weekly. Working solutions were prepared daily by diluting the previous solution with water.

Ultra-pure water was obtained using a Milli-Q water purification system (Millipore, Bedford, MA, EEUU); acetonitrile and methanol were HPLC grade from SDS (Peypin, France); and nitrogen was from Carburos Metálicos (Tarragona, Spain). Hydrochloric acid (HCl), sodium hydroxide (NaOH) and acetic acid from Prolabo (Bois, France) were used to adjust the pH of the sample and the mobile phase.

2.2. Sample collection

All samples were collected from Catalonia (NE Spain). The river water samples were collected from the Ebro River and Llobregat River. The wastewater samples were collected from the influent and effluent of two domestic sewage treatment plants (STPs) in two cities on the coast, with populations of about 120,000 habitants. All samples were collected by using pre-cleaned amber glass bottles acidified to pH 3 (HCl) and stored at 4 °C until analysis.

2.3. Sample extraction

Before the extraction, the sample was filtered using a 0.45-μm nylon filter (Whatman, Maidstone, UK). The cartridges used for the SPE procedure were 500 mg Oasis HLB (Waters, Milford, MA, USA)

and 200 mg Bond Elut Plexa (Varian, Middelburg, The Netherlands). They were connected to a manifold (Teknokroma, Barcelona, Spain) and a pump as a vacuum source.

Both cartridges, Oasis HLB and Bond Elut Plexa, were conditioned with 5 mL of MeOH and 2 mL of Milli-Q water. Sample volumes of 100 mL (influent), 250 mL (effluent) and 500 mL (river water) were extracted. River water samples were extracted with Bond Elut Plexa and sewage samples (influent and effluent) were extracted with Oasis HLB cartridges. The samples were passed through the cartridge at a flow rate of 10–15 mL/min. Then there was a clean-up step using 15% MeOH in 5 mL water solution, and afterwards the cartridge was dried for 5 min. The retained analytes were first eluted with 5 mL of MeOH and, after a completely drying, 5 mL of DCM were passed through the cartridge. Extracts were reduced under a gentle flow of N_2 gas to approximately 3–4 mL. The final extracts were diluted to 5 mL with Milli-Q water. After being filtered through 0.45 μm syringe filters (Scharlab, Barcelona, Spain), 50 μL of this solution was injected into the chromatographic system.

2.4. UHPLC–(ESI)MS–MS

Ultra-high-performance liquid chromatography–electrospray ionisation–tandem mass spectrometry, in both positive and negative modes, was used to determine the target compounds. The chromatographic instrument was an HP 1200 liquid chromatographic system coupled to a triple quadrupole mass spectrometer from Agilent Technologies (Waldbronn, Germany) with an ESI interface, an automatic injector, a degasser, a quaternary pump and a column oven. The chromatographic column was a Zorbax Eclipse XDB C18 (4.6 mm × 50 mm) with a 1.8 μm particle size (Agilent Technologies, Waldbronn, Germany), and the volume injected was 50 μL. The mobile phase flow rate was 0.6 mL/min and the column temperature was kept at 50 °C.

A binary mobile phase with a gradient elution was used. Solvent A was Milli-Q water with acetic acid (pH 2.8) and solvent B was methanol. The gradient was performed as follows: 60% B increased to 100% B in 6 min, constant for 4 min and then decreased to 60% B in 3 min. The UHPLC allowed for powerful separation of the target analytes within 9 min run time.
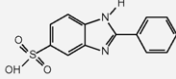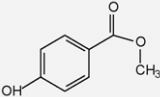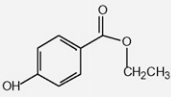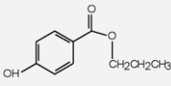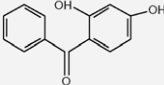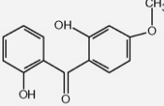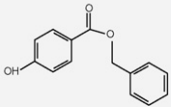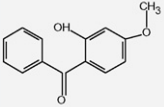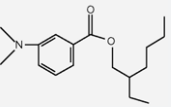
In order to achieve sensitive and selective detection of analytes, the (ESI)MS–MS parameters were optimized by injection of each compound. Analyses were performed in the MRM mode either in the negative or positive ionisation mode to allow the simultaneous determination of all the compounds. Nitrogen was used as collision gas. Optimized MS–MS parameters were as follows: a N_2 flow rate of 12 L/min, a spray potential of 4000 V, a nebulizer pressure of 45 psi (N_2) and a source temperature of 350 °C. As Table 1 shows, the cone voltage was between 80 and 200 V for all the compounds, with the exception of TCS with only 18 V. Collision energies between 5 and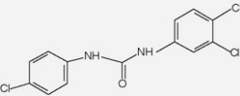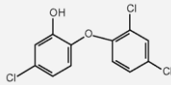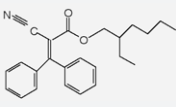 30 V were optimized for each analyte and the best values are shown in Table 1. The retention time and two MRM transitions (Table 1) were compared to confirm the presence of the compounds.

3. Results and discussion

3.1. UHPLC–MS–MS analysis

Methanol and acetonitrile were initially evaluated for the chromatographic separation but methanol was selected because a better peak shape was obtained. MRM transitions were determined for each compound by injection of the standards into the MS–MS. Upon ionisation, all the compounds produced precursor ions that were fragmented into one or more product ions. The product ion

Table 1
Retention time, MRM conditions and proposed product ion for the determination of PCPs.

Analyte	Structure	t_R (min)	Precursor ion	Transition	Proposed product ion	Cone voltage (V)	Collision energy (V)
PMDSA		1.2	$[M+H]^+$	275 > 194	$[M-H-SO_3]^+$	200	30
				275 > 211	$[M-H-SO_2]^+$	200	25
MPB		1.5	$[M-H]^-$	151 > 92	$[C_6H_4O]^-$	80	15
				151 > 136	$[M-H-CH_3]^-$	80	5
EPB		1.9	$[M-H]^-$	165 > 136	$[M-H-CH_2CH_3]^-$	100	15
				165 > 92	$[C_6H_4O]^-$	100	5
PPB		2.5	$[M-H]^-$	179 > 92	$[C_6H_4O]^-$	100	15
				179 > 136	$[M-H-CH_2CH_2CH_3]^-$	100	5
DHB		2.9	$[M-H]^-$	213 > 135	$[M-H-C_6H_5]^-$	130	5
				213 > 169	$[M-H-CH_3CHO]^-$	130	15
DHMB		3.5	$[M-H]^-$	243 > 93	$[C_6H_5O]^-$	80	15
				243 > 123	$[C_7H_7O_2]^-$	80	5
BPB		3.5	$[M-H]^-$	227 > 92	$[C_6H_4O]^-$	100	15
				227 > 136	$[M-H-C_7H_7]^-$	100	5
BP-3		4.8	$[M+H]^+$	229 > 151	$[M+H-C_6H_6]^+$	130	15
				229 > 105	$[C_7H_5O]^+$	130	15
TCC		5.7	$[M-H]^-$	313 > 160	$[C_6H_4NCl_2]^-$	130	5
				316 > 126	$[M-H-C_7H_5NOCl_2]^-$	130	15
TCS		5.9	$[M-H]^-$	287 > 35	$[Cl]^-$	18	8
				289 > 35	$[Cl]^-$	18	8
OC		7.5	$[M+Na]^+$	384 > 272	$[M+Na-C_8H_{16}]^+$	130	5
				384 > 228	$[M+Na-C_8H_{16}-CN-H_2O]^+$	130	5
OD-PABA		8.4	$[M+H]^+$	278 > 151	$[M+H-C_8H_{16}-H_2O]^+$	100	15
				278 > 166	$[M+H-C_8H_{16}]^+$	100	15

spectra from the molecular ions of selected compounds are easily interpretable, and the main fragmentation pathways are displayed in Table 1. For each compound, two characteristic fragmentations of $[M-H]^-$ or $[M+H]^+$ were monitored, with the exception of OC, whose precursor ion was $[M+Na]^+$. The first and most abundant transition was used for quantification and the second one was used for qualification. For example, DHB and BP-3 are both UV filters with similar chemical structure which showed similar fragment ions after losing the benzene group. Thus, we could see the ion m/z 151 for BP-3 and m/z 135 for DHB. The same reasoning is given for the fragment ion $[C_6H_5O]^-$ seen in the spectrum of DHMB which has a phenol group sensitive to be lost for giving the main ion m/z 93. Table 1 also indicates that all the parabens (methyl, ethyl, propyl and benzyl) showed a fragment ion of (m/z 92) in the mass spectrum. All these parabens have a similar structure and they easily lost a methyl, ethyl, propyl and benzyl, respectively, to give the second ion. Only ethylparaben showed the transition $[M-H-CH_2CH_3]^-$ as the most abundant, whereas in the other parabens $[C_6H_4O]^-$ was the most abundant fragment.

The TCS showed parents ion at m/z 287 and m/z 289. Both parent ions gave the same transition, leading to the chloride ion m/z 35. The cone voltage used to fragment the molecule was also much lower than it was for the other compounds. It was seen that only 18 V were enough because higher voltages decreased the response. As can be seen in Table 1, there is only one compound (OC) which showed an adduct with Na$^+$ at m/z 384 corresponding to $[M+Na]^+$. OC and OD-PABA showed similar fragment ions and both compounds lost a fragment of C_8H_{16}. Their mass spectrum also showed the second ion (in relative abundance) due to the loss of a H_2O molecule (m/z 151) in OD-PABA, and the loss of CN$^-$ group and the molecule of H_2O (m/z 228) in OC.

Since the signal intensity of individual ions generally decreases as the number of ions being simultaneous scanned increases, time segments were monitored so that some of the analytes were monitored within specific small time windows according to their chromatographic separation. Six time windows were used in both positive (+) and negative (−) polarities as follows: (+) 0–1.3 min (PMDSA), (−) 1.3–2.3 min (MPB, EPB, PPB), (−) 2.3–4.5 min (DHB, DHMB, BPB), (+) 4.5–5.5 min (BP-3), (−) 5.5–7 (TCC, TCS), and (+) 7–13 (OC, OD-PABA). As can be seen, the UHPLC allowed a chromatographic separation of the twelve initial compounds in six time windows of only 9 min.

The UHPLC–MS–MS chromatographic procedure in MRM had an excellent linear range of 0.05–500 μg/L (MPB) and 0.1–500 μg/L for the rest, except DHMB, TCS, OC and OD-PABA, which had a linear range between 0.5 and 500 μg/L, after injection of standards in Milli-Q water ($r^2 > 0.996$) regarding all the compounds. A chromatogram of a standard of 200 ng/L was included as supplementary data. The detection limits calculated as the concentration which give a response corresponding a signal-to-noise ratio of 3:1, were as low as 20 ng/L for MPB and 50 ng/L for all the compounds except for DHMB, TCS, OC and OD-PABA with a LOD of 200 ng/L. The limit of quantification (LOQ), considered as the lowest concentration that can be quantified, was determined as the lowest point in the calibration curve.

3.2. Ion suppression study

It is well known that a critical aspect in quantitative analysis with ESI is the occurrence of ion suppression which may lead to a significant difference in the response of an analyte in a sample compared to a pure standard solution [25,26]. Different strategies have been proposed to minimise this effect, such as sample dilution or using internal and labelled standards [18,27], although these strategies are not useful in all cases. From our previous experience [28], we knew that ion suppression could be a big challenge. There-

Table 2
Study of the signal suppression effects. Values shown correspond to the recoveries.

Analyte	Test 1[a]			Test 2[b]		
	River	Effluent	Influent	River	Effluent	Influent
PMDSA	<10%	<10%	<10%	14	<10%	<10%
EPB	15	17	15	60	32	43
MPB	4	6	4	32	26	24
BPB	55	31	28	85	78	91
DHMB	58	34	34	86	76	91
DHB	66	40	49	90	89	98
PPB	37	38	43	78	81	89
BP-3	90	42	40	84	59	81
TCC	96	73	31	108	109	121
TCS	92	61	65	105	106	109
OC	40	20	9	45	40	43
OD-PABA	82	72	34	75	78	90

RSD ($n = 3$) <10%.
[a] Test 1: Evaporation until dryness and dissolution at 1 mL.
[b] Test 2: Evaporation until 3–4 mL and dissolution at 5 mL.

fore, to ensure the extraction procedure, we decided to study this effect to check the behaviour of our compounds in real samples. Because of our previous studies [25], we chose Oasis HLB as sorbent and a volume for each sample according to its complexity: 500 mL of river water, 250 mL of effluent and 100 mL of influent sewage water. After passing the samples through the cartridge, we tested the extracts in two ways to study also the action of the evaporation step with N_2 in the effect of ion suppression. In Test 1 we evaporated the extract to dryness and reconstituted it with 5% MeOH in 1 mL of water, and in Test 2 we evaporated the extract down to 3–4 mL and diluted it with water back up to 5 mL, with a consequent less complex matrix. Both reconstituted extracts were spiked to a final concentration of 20 μg/L and the signal was compared with pure water standards. Simultaneously, the losses caused by evaporating with N_2 were evaluated with a standard in Milli-Q water and this gave satisfactory results which ruled out problems with the evaporation process. The results (%R) of both tests are shown in Table 2 and they were conclusive in helping us to decide not to evaporate until dryness. Despite increasing the LODs, the SPE process become faster because we avoided the arduous task of evaporating to dryness. As can be seen in Table 2, the differences between recoveries in Test 1 and Test 2 were higher in sewage water (influent and effluent) because of the complexity of this matrix. Although we tried to avoid this effect in the evaporation step some compounds still showed a high ion suppression (>50%) such as PMDSA, EPB, MPB, and OC. Signal suppression of MPB and EPB due to the ESI has been reported to be 48–69% in river water [8]. Therefore, we decided to assume this effect in MPB, EPB and OC. However, at this point, PMDSA was eliminated from the study because it showed the highest ion suppression effect (86–95%) in Test 2, which is in keeping with its short retention time and probable coelution with other polar components of the matrix.

3.3. Optimization of the extraction procedure

Two different sorbents were tested to determine whether they could extract eleven PCPs in only one step. Oasis HLB and Bond Elut Plexa are both polymeric sorbents with a polar group in their structure. This property made them very suitable for extracting the selected compounds. Oasis HLB was chosen because of its demonstrated ability to retain polar compounds [25,29] thanks to a pyrrolidone group in its structure. Bond Elut Plexa, which has recently become commercially available, has a hydroxylated ligand on the surface and a narrower particle size distribution. We wanted to study the behaviour of this new sorbent, which initially seemed to have an advantage over Oasis HLB for some of our compounds. The efficiency of both sorbents was checked after the

optimization of some parameters using, initially, 100 mL of Milli-Q water spiked at 1 μg/L. The sample pH was studied to ensure that it had the most suitable conditions for retaining all the analytes. The eluted extract was evaporated until 3–4 mL and reconstituted to 5 mL as was discussed in Section 3.2. We could see that BP-3 was not retained in the Oasis HLB cartridge when the sample pH was in neutral conditions and it only showed a recovery of 36%. Similar behaviour was seen for DHB with recoveries of only 33%, meanwhile in acidified samples all the compounds showed recoveries higher than 67%. Therefore, samples were acidified to pH 3 prior to the extraction. Although 5 mL of MeOH were checked as elution solvent, we tried to improve the lowest recoveries of some compounds such as BP-3 (67%). Therefore, after drying the cartridge, 5 mL of DCM were added to elute the most apolar compounds and this led to a significant improvement in BP-3 recovery (99%). As the purpose of this study was to analyze very complex matrices, a clean-up step of 15% MeOH in 5 mL of water solution was added before eluting the analytes, without significant losses in the recoveries. Sample volume was increased from 100 to 1000 mL to decrease the LOQs. When the sample volume was 1000 mL of Milli-Q water, the recoveries with Oasis HLB were between 77% and 101% for all the compounds, except for OC (56%). When the same study was done with Bond Elut Plexa the recoveries were even higher. Although the sorbent mass was less than half (200 mg), the recoveries were between 90% and 102%, and even OC showed increased recovery (76%).

We compared both cartridges to check the influence of the matrix in real samples (river and sewage water) and reduced the volume of the samples as the complexity of the matrix increased. For Oasis HLB, the recoveries from 500 mL of river sample were between 39% and 101%, except for MPB (25%) and EPB (22%). Therefore, we tried to improve the recoveries of these two parabens. When we did the same study with Bond Elut Plexa we realized that the recoveries of most of the analytes were higher, as can be seen in Table 3 (46–101%), particularly for MPB and EPB (88%). Both sorbents have a hydrophobic group in their structure but the different characteristics previously mentioned gives to Bond Elut Plexa more efficiency at retaining the compounds. Therefore, we chose Bond Elut Plexa to analyze river water.

However, there were no significant differences in the results when we compared the effect of both sorbents in sewage waters (250 mL of effluent water and 100 mL of influent water). The results showed that both sorbents gave acceptable recoveries of the compounds. When deciding which sorbent was best for the most complex matrix, we realized that the velocity of charge

in the Bond Elut Plexa cartridge was slower than in the Oasis HLB cartridge. The reason was that the particle size was different in both sorbents (60 μm for Oasis HLB and 45 μm for Bond Elut Plexa). Because it is very important to optimize the extraction procedure time, we decided to choose the Oasis HLB to extract sewage, although it is worth emphasizing that both sorbents were suitable for our compounds and the choice was only made because of the velocity in the extraction procedure. The recoveries for 250 mL of effluent and 100 mL of influent water were 56–92% and 39–89%, respectively, except for EPB, MPB and OC, which gave values between 20% and 38% in both cases (Table 3). A possible explanation for the low recovery of these compounds could be the fact that the matrix effect is higher in those compounds which appear at the beginning of the chromatogram.

3.4. Method validation

When a sample of river water was analyzed, we only found PPB. Therefore, this signal was subtracted from the signal found in the spiked samples. The calibration curves were obtained by the whole method developed. Linear range was tested between 3 and 5000 ng/L for MPB and between 5 and 5000 ng/L for the rest of the compounds following the method developed. The precision of the method was evaluated by preparing a set of samples fortified with the analytes at levels of 100 ng/L. The repeatability ($n = 3$) and reproducibility between days ($n = 3$) gave results that were lower than 12% and 18% (%RSD), respectively. The LODs, calculated as previously explained, were as low as 1 ng/L for all the compounds except for BP-3 and DHMB (2 ng/L), TCS, TCC and OD-PABA (3 ng/L), and OC (4 ng/L). Limits of quantification (LOQs) were calculated as the lowest point in the calibration curve and this was 5 ng/L for all the compounds, except for MPB (3 ng/L).

Because of the presence of these PCPs in the sewage samples analyzed, we were unable to use the whole method to obtain a calibration curve in order to determine concentrations in sewage water. Therefore, the concentrations in real samples were achieved using calibration curves by injection of the standard solutions and applying the corresponding recoveries. Recoveries were checked at lower concentration (200 ng/L for influent and 100 ng/L for effluent) and results were similar to those included in Table 3. Sewage water samples were spiked at low levels in order to determine the LOD as the concentration which give a response of signal-to-noise of 3. However, when the compounds were present in real samples, the LODs were estimated from calibration curves and the corresponding recoveries. The LODs in 250 mL of effluent waters were 3 ng/L for all the compounds except, 5 ng/L (DHMB) and 10 ng/L (TCS, TCC, OC, OD-PABA). LOQs were those which gave an instrumental response corresponding to the lowest point of the calibration curve. The LOQs were 5 ng/L for MPB, EPB, BPB, DHB, PPB and BP-3 and 20 ng/L for the rest of the compounds. The LODs in 100 mL of influent waters were 5 ng/L (MPB, EPB, BPB, DHB, PPB and BP-3), 10 ng/L (DHMB) and 20 ng/L for the rest. The LOQs were 10 ng/L for all the compounds except DHMB, TCC, TCS, OC and OD-PABA with 50 ng/L.

3.5. Application to environmental samples

The SPE/UHPLC–MS–MS method was used to determine the presence of eleven PCPs in three kinds of matrices (river water, effluent and influent wastewater). As expected, the levels found in river waters were considerably lower than in wastewater because the sewage waters become diluted when they are released into the environment [30]. MPB, DHB, PPB, and TCC were found in the Ebro and Llobregat rivers at levels lower than the limit of quantification. BP-3 was only found in the Ebro River and its concentration

Table 3
Recoveries and relative standard deviations (%RSD, $n = 4$) of selected compounds in different kinds of water.

| Compound	Influent STP[a]		Effluent STP[a]		River water[b]	
	%R^c	%RSD	%R^d	%RSD	%R^e	%RSD
EPB	36	3	38	12	88	9
MPB	27	3	20	12	88	11
BPB	89	2	70	2	94	2
DHMB	78	1	70	2	97	2
DHB	86	2	64	7	97	6
PPB	79	2	61	5	101	1
BP-3	59	1	56	5	70	11
TCC	39	11	67	10	69	7
TCS	85	14	92	1	89	7
OC	27	9	20	1	46	13
OD-PABA	59	5	71	7	69	6

[a] Extraction with Oasis HLB.
[b] Extraction with Bond Elut Plexa.
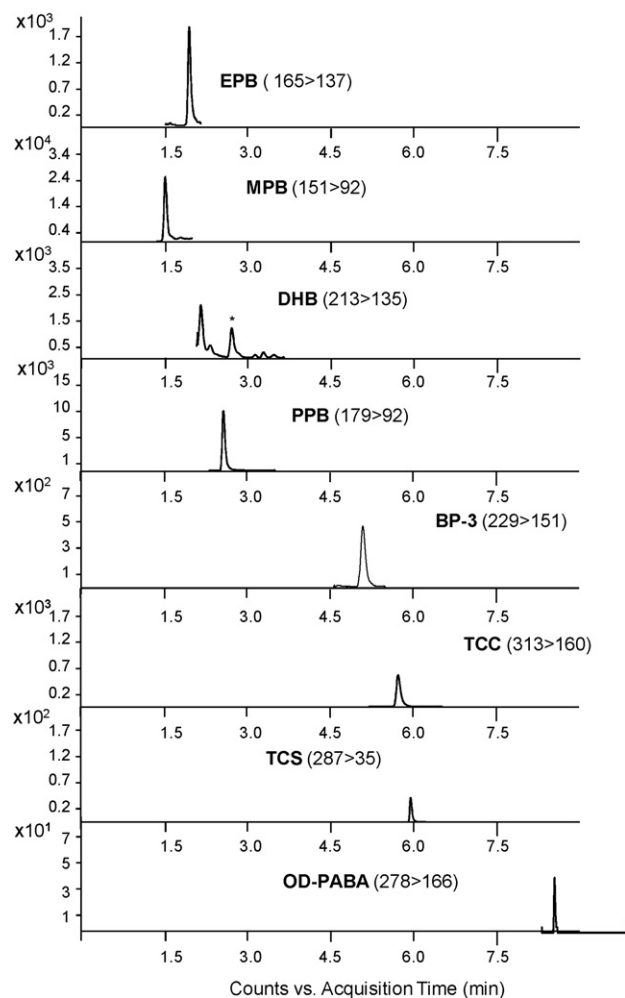[c] 100 mL spiked at 5 μg/L.
[d] 250 mL spiked at 2 μg/L.
[e] 500 mL spiked at 1 μg/L.
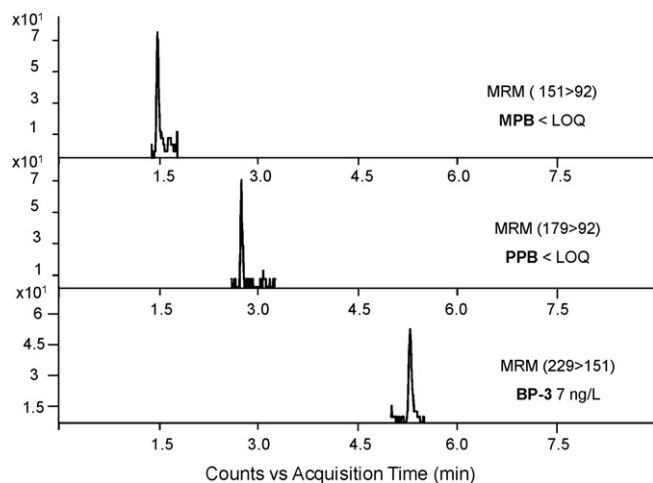
Fig. 1. MRM chromatograms of a sample from the Ebro River. For conditions see the text.

was 7 ng/L. Although TCS had been found in lake and river waters in previous studies at low ng/L [7,16], none sample of both rivers showed TCS. Fig. 1 shows the MRM chromatogram of a sample from the Ebro River which also shows MPB and PPB at values <LOQ.

To study the presence of PCPs in waters from sewage treatment plants, wastewater samples were taken during three periods of the year between the 2007 and 2008. The results in these samples are presented in Table 4. As can be seen in Table 4, EPB, MPB and PPB were the commonest compounds in the influent waters. The samples correspond to three different seasonal sets and showed some differences in the levels of these analytes. For example, concentrations of EPB were found in influent waters ranging from 625 to 196 ng/L. The range for MPB was from 4427 to 1658 ng/L and for PPB was from 1945 to 77 ng/L. The highest values for EPB, MPB and PPB were in the samples taken in spring (Table 4), whereas the lowest values came from the samples taken in winter (Table 4). An example of a spring sample can be seen in Fig. 2. Another important difference between the different sets of samples is the concentration of UV filters. For example, BP-3 was found in the three sets and its concentration was the highest in May (286 ng/L) and decreased to 11 ng/L in January. This agrees with the results reported by Rodil et al. [19] where the highest value of BP-3 (168 ng/L) in raw water was in July. Other UV filters found in our study were DHB (47 ng/L and 155 ng/L) and OD-PABA which was found only in one sample at 103 ng/L. The sampling area is very tourist area with warm temperatures, and this could probably be the reason why some UV filters appeared in influent waters of spring and summer. Although this is not an exhaustive study into the removal of PCPs by STP, it is shown that the tendency was for the STP process to eliminate PCPs. This statement was clearly confirmed when the high concen-

Table 4
Concentrations of PCPs in wastewater samples (influent and effluent) in ng/L ($n = 3$).

Compound	May 2007		September 2007		January 2008	
	Influent	Effluent	Influent	Effluent	Influent	Effluent
EPB	625	<LOD	498	<LOD	196	48
MPB	4427	<LOD	5613	<LOD	1658	<LOQ
BPB	<LOD	<LOD	<LOD	<LOD	<LOD	<LOQ
DHB	155	<LOD	47	<LOD	<LOD	11
PPB	1945	24	1002	39	77	<LOD
BP-3	286	20	61	100	11	<LOD
TCC	362	<LOD	21	<LOD	<LOD	<LOD
TCS	87	<LOD	22	<LOD	<LOD	<LOD
OD-PABA	103	<LOD	<LOD	<LOD	<LOD	<LOD

RSD < 15%.

Fig. 2. MRM chromatograms of a sample from STP influent water in May 2007. For conditions see the text.

trations of parabens in influents were greatly reduced in effluents. One of the most commonly used PCPs is TCS and there are several studies [20,21] which show its presence in wastewater samples. For example, Kanda et al. [20] found levels of 3100 ng/L in influent sewage, although in the present study only 87 ng/L were detected in an influent sample. TCS is reported to be well removed during sewage treatment for activated sludge plants with measured removal rates of 95–98% [12,31] and this should ensure that no trace levels were found in effluents. This agreed with our study and no positive results for TCS and TCC were found during the effluent sampling.

4. Conclusion

A rapid method based on a SPE/UHPLC–MS–MS with triple quadrupole was developed to determine a group of emerging contaminants. These compounds were eleven representative PCPs including UV filters, parabens and antimicrobial agents. The new approach described in this paper is to determine several families of PCPs together in the same short analysis in different water matrices (river and wastewater). For the SPE, two cartridges (Oasis HLB and Bond Elut Plexa) were selected to study the extraction efficiency in the different matrices. Bond Elut Plexa was selected to extract river water because it gave the best recoveries for all the compounds. Meanwhile, Oasis HLB was chosen to extract wastewater because of its rapid extraction rate. The extract was only slightly evaporated

to avoid preconcentrating the interferences that affect the ESI. Most of the compounds showed good recoveries for river waters and acceptable recoveries for STP waters. The UHPLC allowed a chromatographic separation of all the compounds to be obtained in only 9 min. The method has been proven to be linear, with LOQs in the low ng/L levels and highly selective using MRM mode. The results showed the presence of some of these compounds in river waters at very low ng/L. The highest concentrations found in influents were for MPB and PPB, (included in several commercial personal care products) with values between 77 and 5613 ng/L. Meanwhile BP-3 showed the highest concentration in effluents (100 ng/L) and river water (7 ng/L).

Acknowledgements

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.chroma.2009.08.039.

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