

Occurrence, fate and risk assessment of personal care products in river-groundwater interface

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Abstract

This work presents the occurrence and fate of selected personal care products (PCPs) in the urban river-groundwater interface. To this end, urban river and groundwater samples were collected in Sant Adrià del Besòs (NE of Spain) and a total of 16 PCPs were analyzed including benzophenone derivatives, camphor derivatives, *p*-aminobenzoic acid derivatives, triazoles and parabens in three different campaigns (from May 2010 to July 2014). These compounds reach the aquifer through the recharge of Besòs River that receives large amounts of effluents from waste water treatment plants. Results shown that most of compounds were not or barely detected (maximum concentrations around 200 ng/L) in groundwater samples during the different sampling campaigns. Only two triazoles, namely benzotriazole (BZT) and methyl benzotriazol (MeBZT) were found at high concentrations in groundwater samples (maximum concentration around 2000 ng/L). The fate of PCPs in the aquifer was assessed using mixing analysis considering the seasonal variability of the Besòs River. Overall, measured groundwater concentrations were significantly much lower than those estimated by the mixing of the river water. This observation suggested that most of the PCPs are naturally removed when river water infiltrates the aquifer. However, some compounds were more persistent in the aquifer. These compounds were in descending order: the triazoles BZT and MeBZT followed by the camphor derivative 4MBC and the paraben MePB. The measured concentrations allowed us to assess the environmental risk posed by the selected UV-filters and parabens in the river and groundwater samples. Hazard Quotients (HQs) for different aquatic species were calculated in order to characterise the ecotoxicity potential of the studied compounds in the river-groundwater interface. HQ values were always below 1 indicating that at the concentrations observed in the surface or aquifer water of Besòs River these compounds pose no risk to the selected aquatic organisms.

Keywords: Personal care products, UV filters, parabens, polluted river, urban groundwater, field study

1. Introduction

Personal care products (PCPs) are a group of organic chemicals added at different products widely used in daily human life (lotions, toothpaste, cosmetics and even food). When used, PCPs may be absorbed by the body and excreted or washed off after their application (Tolls and Berger, 2009). They and their metabolites end up in wastewater treatment plants (WWTPs) (Rodil et al., 2008), where are partially eliminated and retained in the sludge, but an important fraction of them may be released into the aquatic environment through the effluents (Molins-Delgado, 2015a). Even though pollutants are commonly present at low concentration levels, the concern about the adverse effects of a chronic exposure to them is rising. The main concern relies on the documented capability of these contaminants to act as endocrine disruptors being able to interfere with the reproductive system and the normal development of living organisms (Molins-Delgado, 2015a).

UV filters also known as sunscreen agents, constitute a heterogeneous group of chemicals used to protect humans and goods against the harmful effects of UV solar radiation. They are extensively used in a wide variety of personal care products such as lotions, shampoos or sunscreens. They are also used as additives in polymeric materials that have to be protected from sunlight-initiated disruption, in pharmaceutical products and in other industrial goods (Gago-Ferrero et al., 2013a). UV filters have achieved high popularity since their protective role against photoaging, photocarcinogenesis and photoimmunosuppression promoted by UV sun radiation was demonstrated. Because of it, UV filters have been increasingly used.

These compounds were classified as emerging environmental pollutants some years ago (Richardson, 2004), but yet there is a lack of knowledge about their occurrence, fate and effects on the aquatic ecosystems. These emerging pollutants are considered as pseudo-persistent because they are continuously introduced into the aquatic environment through two pathways: direct inputs as consequence of recreational water activities and mainly, indirect inputs from WWTPs as a result of the domestic use of PCPs, as well as industrial waste (Gago-Ferrero et al., 2013a). Residues of more

polar organic UV filters have been found in all kind of water matrices including tap water (Díaz-Cruz et al., 2012). Because of the high lipophilicity and poor biodegradability of many of them, they end up in sewage sludge during wastewater treatment (Gago-Ferrero et al., 2011a), and accumulate in sediments (Barón et al., 2013; Gago-Ferrero et al., 2011b), and in biota (Buser et al., 2006; Fent et al., 2010, Gago-Ferrero et al., 2013b; Gago-Ferrero et al., 2015). It has been suggested that biomagnification may occur through the food web (Fent et al., 2010). These findings are of concern because it is known that UV filters such as benzophenone 3 (BP3), benzophenone 4 (BP4) and ethylhexyl-methoxycinnamate (EHMC) are able to alter the transcription profile in fish, with the possibility of altering genes related with the production of sexual hormones (Blüthgen et al., 2012, Zucchi et al., 2011a and 2011b). Moreover, when UV filters were investigated in tissues of paired mother-fetus franciscana (*Pontoporia blainvillei*) and Guiana (*Sotalia guianensis*) dolphins from Brazilian coastal waters, the comparison of UVF concentrations in maternal tissues (blubber 105 ± 155 , and muscle $2,175 \pm 3,720$ ng/g lw) and fetal tissues (blubber 125 ± 115 , and muscle $2,490 \pm 4,120$ ng/g lw) showed up to 10 times higher load in fetuses than in their mothers (Alonso et al., 2015).

Parabens are widely used in a wide range of goods because of their effectiveness as antibacterial and fungicidal against a wide range of microorganisms, its low production cost, their lack of smell and taste and their stability in a wide pH range (Molins-Delgado, 2015a). A few number of studies have reported levels in WWTPs and surface water, obtaining generally lower concentrations in effluent water (Jonkers et al., 2010; Lee et al., 2005; Loraine and Pettigrove, 2006). These compounds have been also detected in sewage sludge, in sediments (Liao et al., 2013), and in biota (Ramaswamy et al., 2011). Moreover, a very recent study on UV filters and parabens documented the presence of these compounds in human placenta, suggesting their perinatal mother-foetus transfer (Valle-Sistac et al., 2016). There is an increasing evidence that they might be endocrine disruptors (Regueiro et al., 2009), despite they are extensively used worldwide.

The main potential sources of groundwater contamination by anthropogenic pollutants are storage tanks, septic systems, uncontrolled hazardous waste, landfills, chemical spills and rain run-off. In regard to groundwater bodies, a recent study addressed the contamination of urban groundwater by UV filters (Jurado et al., 2014). UV filters were detected at low but measurable concentrations in the urban groundwater below Barcelona city (Spain). The concentrations of UV filters in the aquifer were lower than those expected from simple mixing of the different recharge sources which suggested their removal from urban groundwater under different redox conditions. The presence of PCPs has been also reported in the groundwater bodies of UK (Stuart et al., 2011 and 2014), Spain (Cabeza et al., 2012), Switzerland (Kahle et al., 2009), Germany (Reh et al., 2013), USA (Barnes et al., 2008), China (Peng et al. 2014) and Australia (Liu et al., 2011).

To sum up, there are few studies on the occurrence of PCPs in urban groundwater. The objective was to determine the presence of UV filters and parabens in groundwater but also in river water and to assess their fate in the river-groundwater interface using mixing analysis. The samples were collected from the urban aquifer in the low part of the Besòs River catchment and from the main Besòs River. We selected this study area for the following reasons: (1) the interaction between river-groundwater is well characterized (Tubau et al., 2014; Jurado et al., 2015) and (2) previous studies have reported the occurrence of different micro-pollutants such as illicit drugs (Jurado et al., 2012), pharmaceuticals (López-Serna et al., 2013) and UV Filters (Jurado et al., 2014).

2. Materials and methods

2.1 Site description

The Besòs River Delta, with a catchment area of 1038 km², is located near Barcelona in the north east of Spain at the foot of the southern slope of the Catalan Coastal mountain range (Figure 1A). The study area corresponds to the lower part of the catchment and is placed in the town of Sant Adrià del Besòs where there is the underground parking area at the Plaça de la Vila site (Figure 1B and C).

The average yearly temperature and rainfall are 15 °C and 600 mm/year, respectively. The Besòs River is a good example of a Mediterranean fluvial system with very irregular flow patterns which are controlled by the seasonal rainfall events. Generally, these events are different from one year to another and within the year from a season to another. The average base flow is 4 m³/s at the Santa Coloma gauging station (located 2.5 km upstream from Plaça de la Vila site, Figure 1A) but the flow has reached up to 100 m³/s during torrential rains. The Besòs River flow is dramatically reduced during summer (dry season), when it comes basically from the effluents of the WWTPs, being on average around 2 m³/s. The Besòs River flows in a heavily industrialized area in the lower part of the catchment and, therefore, its water is a mixture of different sources such as raw and treated sewage waters from more than 20 WWTPs, rainfall and industrial waters.

The aquifers of the Besòs River Delta are formed within Quaternary sediments that rest discordantly on top of Palaeozoic (slates and granites) and Pliocene (gray marls) materials. The hydrogeological units that constitute the study area from the bottom to the top are: (1) the main aquifer, which is constituted by sands (2) silt wedge that is an aquitard formed by clays and silts and (3) the shallow aquifer, which is an unconfined aquifer made up by sands and gravels.

Most of groundwater extracted between the river and the parking area is mainly recharge water from the Besòs River, which is hydraulically connected to the shallow aquifer (i.e. river water is directly recharged to the saturated zone). Other sources include leaks from water supply and sewage water pipes network, infiltration from rainfall and city runoff (Vázquez-Suñé et al., 2010). However, they represented less than 10% of the total resident water of this aquifer (Jurado et al., 2013). Groundwater flows from the river to the parking area due to an uninterrupted pumping of 150 l/s to avoid seepage problems (Fig. 1C). This results in a very dynamic aquifer system with short residence times ranging from three weeks to one month from the river to the underground car park at Plaça de la Vila (Jurado et al., 2015). Besides, groundwater has a reducing character because redox processes

such as aerobic respiration and denitrification occurred when the aquifer is infiltrated by river water (Jurado et al., 2015).

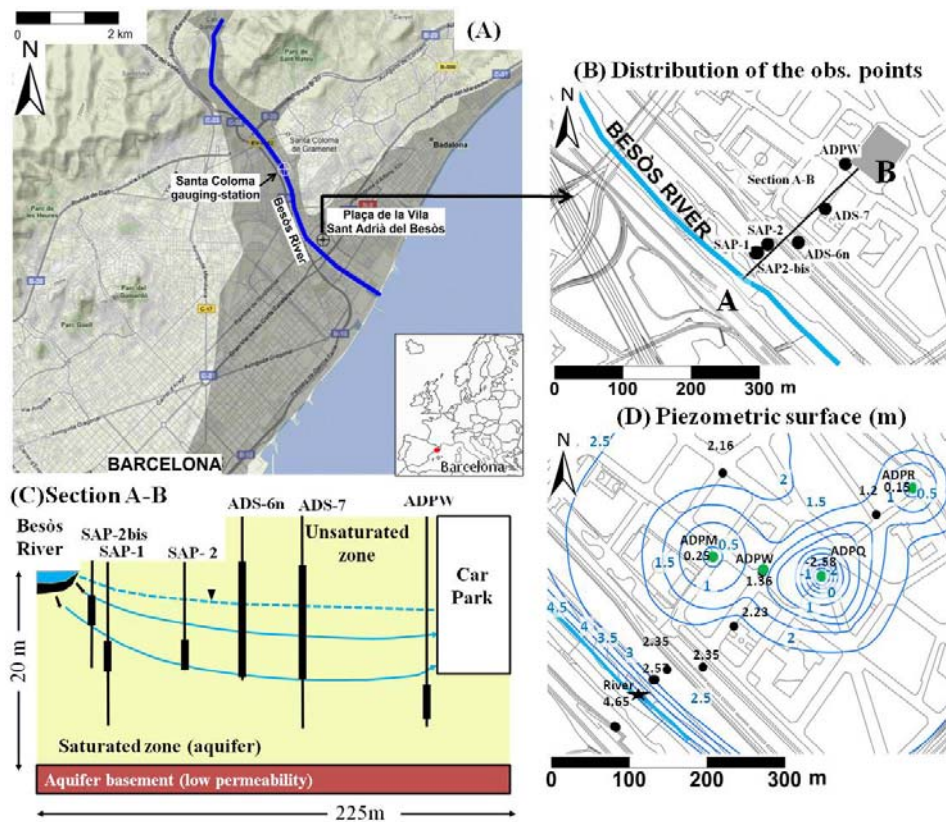


Figure 1. (a) Location of the study area, (b) spatial distribution of the observation points, (c) schematic description of the hydrogeological conceptual model (section A-B) and screen depths of the observation points and (d) piezometric surface where wells ADPQ, ADPM and ADPR are pumping (Figure modified from Jurado et al. (2015)).

A detailed monitoring system, which consists of 4 pumping wells (ADPM, ADPQ, ADPR and ADPW) and 16 piezometers were designed to control the aforementioned seepage problems in the parking lot. There are three of these wells (ADPM, ADPQ and ADPR) that are continuously pumping leading to groundwater levels up to -2.5 m (Figure 1D). We have taken advantage of this system to collect groundwater samples from the shallow aquifer. The observation points included in this study were: the piezometers called SAPs, located close to the river, the piezometers ADS-6n and ADS-7 and the pumping well ADPW. Their screen depth intervals are 9.5-11.5 m for SAP-1 and SAP-2, 4.5-6.5 m for SAP-2b and 3-15 m for ADS-6n and ADS-7 (Figure 1B and 1C).

2.2 Sampling

Groundwater samples were collected from a total of 6 observation points distributed between Besòs River and the parking area (Figure 1B and 1C) during three sampling campaigns carried out in May 2010 (C1), December 2013 (C2) and July 2014 (C3). Additionally, one sample from the Besòs River was collected in each campaign. All the observation points were purged and samples collected after removing three well volumes or once field parameters had stabilized. The physico-chemical parameters such as temperature ($^{\circ}\text{C}$), pH, electrical conductivity (EC, $\mu\text{S}/\text{cm}$) and dissolved oxygen (mg/L) were measured in situ inside a closed flow cell to avoid contact with air. Samples were collected after stabilization of field parameters wearing gloves to avoid their contamination, stored in a field refrigerator and shipped to the laboratory.

Groundwater samples for general chemistry analysis were analyzed at two different laboratories and they were treated or not in the field based on the laboratory requirements. The samples from the first sampling campaign (May 2010) were analyzed at laboratory of the ATLL (Aigües Ter-Llobregat) in Barcelona and were treated in the laboratory facilities. The rest of the samples (December 2013 and July 2014) were analyzed at the IDAEA-CSIC laboratory which required filtration through a $0.22\ \mu\text{m}$ nylon filter for anion and cation analysis. For cation determination, samples were further acidified with 1 mL of 20% nitric acid for preservation. In these campaigns, total alkalinity was determined in the field by acid-base titration using the Aquamerck Alkalinity Test.

For the analysis of the PCPs (UV filters and parabens), samples were vacuum filtered at the IDAEA laboratory through $1\ \mu\text{m}$ glass fiber filters, followed by $0.45\ \mu\text{m}$ nylon membrane filters, and stored in the dark at $-20\ ^{\circ}\text{C}$ until analysis.

2.3. Standards and Reagents

BP3, BP1, 4-hydroxybenzophenone (4HB), BP4, 4DHB and Et-PABA were purchased from Sigma–Aldrich (Steinheim, Germany), 4MBC was supplied by Dr. Ehrenstorfer (Augsburg, Germany); and benzophenone-2 (BP2) and 2,2'-dihydroxy-4-methoxybenzophenone (DHMB) by Merck (Darmstadt, Germany). The isotopically labelled compounds 2-hydroxy-4-methoxy-

2',3',4',5',6'-d₅ (BP3-d₅) and 3-(4-methylbenzylidene-d₄) camphor, used as internal standards, were obtained from CDN isotopes (Quebec, Canada). All these standards were of >99%purity. Benzotriazole UV blockers and parabens were included in the study for the two last campaigns.

Methanol (MeOH), acetonitrile (ACN) and HPLC grade water (Lichrosolv), as well as formic acid (98% purity) were provided by Merck. N₂ and Ar purchased from Air Liquide (Barcelona, Spain) were of 99.995% purity. Glass fiber filters and nylon membrane filters were obtained from Whatman International Ltd (Maidstone, England).

The individual stock standard solutions as well as the isotopically labelled internal stock standard solutions were prepared on a weight basis in MeOH and stored in the dark at -20 °C. Working solutions were prepared daily by appropriate dilution of the standard solutions. In the Table S1 from the Supplementary Material, the structures and CAS numbers of the analyzed compounds are listed.

2.4 Analytical methods

2.4.1. Sample Pre-treatment

In order to extract, purify and pre-concentrate the samples for their further chromatographic separation, an automated on-line SPE-HPLC instrument SymbiosisTM Pico from Spark Holland (Emmen, The Netherlands) was used. On-line SPE pre-concentration of all filtered samples, aqueous standard solutions and blanks were performed by loading 5 mL of the corresponding solutions through a PLRP-s SPE cartridge. Then, the trapped analytes were eluted to the HPLC column through the mobile phase. An extended description of the method can be found elsewhere (Gago-Ferrero et al., 2013a).

2.4.2. HPLC-MS/MS analysis

A 4000 Q TRAPTM MS/MS system from Applied Biosystems-Sciex (Foster City, Ca, USA) was used to perform the mass spectrometry detection. The chromatographic separation was achieved on a Hibar Purosher® STAR® HR R-18 (50 mm x 2.0 mm, 5 µm) from Merck.

For those analyses under positive ionization (PI) mode, the mobile phase consisted of a mixture of HPLC grade water and ACN (both with 0.1% formic acid). In the negative ionization (NI) mode, the mobile phase consisted of HPLC grade water and ACN both containing 5 mM of ammonium acetate.

MS/MS detection was conducted in both modes with electrospray ionization (ESI) under selected reaction monitoring (SRM) mode. In order to enhance method sensitivity and selectivity, two transitions were monitored per analyte. The most abundant and the second most abundant transitions were used for quantification and confirmation, respectively.

For the PI mode, general conditions were as follows: capillary voltage, 5000 V; source temperature, 700 °C; curtain gas, 30 psi; ion source gas 1, 50 psi; ion source gas 2, 60 psi; entrance potential, 10V. For the NI mode they were as follows: capillary voltage, -4000 V; source temperature, 500 °C; curtain gas, 20 psi; ion source gas 1, 50 psi; ion source gas 2, 60 psi; entrance potential, -10V (Gago-Ferrero et al., 2013a). In Table S2 from the Supplementary Material the experimental HPLC-MS/MS conditions relative to the analysis of the target analytes in samples are compiled.

2.5 Assessment of the fate of the personal care products in the aquifer

The methodology to assess the fate of PCPs in the aquifer consisted of the following two steps: (1) identification of the potential recharge sources and selection of the appropriate tracers and (2) evaluation of the mixing ratios in groundwater recharge by means of multivariate statistical analysis. The code used was the MIX code (Carrera et al., 2004). Briefly, this methodology allows quantifying the proportion in which the different sources contributed to the total recharge of the aquifer (mixing ratios) in the case of uncertain end-members (recharge sources), using the concentration of mixed samples (groundwater samples) to reduce uncertainty. Mixing ratios are evaluated assuming that the samples are a mixture of the recharge sources in an unknown proportion. In the step 2, mixing ratios are evaluated using major and minor ions and some redox indicators previously used (Tubau et al., 2014). Finally, the fate of PCPs can be assessed by means of the evaluated mixing ratios and their concentration in the recharge sources. With this approach is possible to quantify the depletion/release

of a given compound in the river-groundwater interface. The concentration of the conservative tracers in a mixture is obtained by a linear combination of the recharge sources. However, when deviations from the ideal mixing line exist they may be due to some chemical processes that are depleting a given compound from the aquifer (Jurado et al., 2013). The following references can be consulted for further details on the use of this code: Vázquez-Suñé et al. (2010), Jurado et al. (2013 and 2015) and Tubau et al. (2015).

3. Results

Table 1(a to c) lists the concentrations found for the selected PCPs in each sampling campaign (C1-C3). It is important to comment that the triazoles and parabens were not analyzed in C1. There were detected 11 out of the 16 compounds investigated. At least one compound was detected in the samples from Besòs River Delta area.

Regarding groundwater samples, the most frequently detected compounds and at the highest concentrations were BZT and MeBZT during C2 and C3. BP4, 4MBC, MePB, PrPB and DMBZT have been also measured, but at lower concentrations. The rest of the target compounds were not quantified or detected in any of the samples (Table 1a, b and c). The highest groundwater concentrations and the largest number of detected PCPs were observed in C3 (Table 1c). In contrast, the smaller number of PCPs were found in C2.

Data from the Besòs River shows high levels of BZT, MeBZT and BP4, especially at C2, where these compounds reach concentrations near to 1000 ng/L. This might be because of the amount of WWTP effluents discharged in this river. The two polar triazoles are widely used in detergents as anticorrosive agent, for instance in products for dishwashing machines and as sun blockers in many daily use products and materials. Furthermore, they are known to be only partially removed in the WWTPs (Molins-Delgado et al., 2015b). As regards BP4, it is a compound in continuous growth

within the UV filters group. This chemical is water-soluble (0.65 g/L at 25 °C) with a strong acidic character ($pK_a < 1$) and is increasingly used as a consequence of population's preferences for lighter textures (aqueous based) in personal care and hygiene products. BP4 is a quite hydrophilic UV filter ($\log K_{ow} = 0.88$), which may be an additional factor driving their occurrence in the river water as is not expected to be accumulated in the soil. As regards MePB and PrPB parabens occurrence in the river water, despite their quite efficient removal in WWTPs (Molins-Delgado et al, 2016) can be easily explained because of they are the most common compounds used as preservative in cosmetics, pharmaceuticals and hygiene products, not to mention beverages and food. Overall, they are additives in more than 15.000 products.

Table 1 Concentration (ng/L) of UV filters and parabens in surface and groundwater of the Besòs River Delta (a) First sampling campaign (C1), (b) Second sampling campaign and (c) Third sampling campaign. nd: Not detected, na: Not applicable, <LOQ: Not quantifiable

Table 1a. First sampling campaign (May 2010, C1).

Sample	BP1	BP2	BP3	BP4	4HB	4DHB	DHMB	Et-PABA	4MBC
River	<LOQ	nd	34	nd	nd	<LOQ	nd	nd	<LOQ
SAP-2bis	<LOQ	nd	<LOQ	nd	nd	nd	nd	nd	<LOQ
SAP-1	nd	nd	nd	<LOQ	nd	nd	nd	nd	nd
SAP-2	na	na	na	na	na	na	na	na	na
ADS-6n	nd	nd	nd	nd	nd	nd	nd	nd	<LOQ
ADS-7	nd	nd	<LOQ	nd	nd	nd	nd	nd	nd
ADPW	nd	nd	nd	nd	nd	nd	nd	nd	<LOQ

Table 1b. Second sampling campaign (December 2013, C2).

Sample	BP1	BP3	BP4	4DHB	Et-PABA	4MBC	BZT	MeBZT	DMBZT	MePB	PrPB	BuPB	BePB
River	nd	58	1160	nd	nd	<LOQ	965	1340	<LOQ	nd	nd	nd	nd
SAP-2bis	nd	nd	nd	nd	nd	<LOQ	1500	1790	nd	nd	nd	nd	nd
SAP-1	nd	nd	nd	nd	nd	<LOQ	818	662	nd	nd	nd	nd	nd
SAP-2	nd	nd	nd	nd	nd	30	626	559	nd	nd	nd	nd	nd
ADS-6n	nd	nd	nd	nd	nd	nd	1300	1980	nd	nd	nd	nd	nd
ADS-7	na	na	na	na	na	na	na	na	na	na	na	na	na
ADPW	nd	nd	nd	nd	nd	<LOQ	1080	1260	nd	nd	nd	nd	nd

Table 1c. Third sampling campaign (July 2014, C3).

Sample	BP1	BP3	BP4	4DHB	Et-PABA	4MBC	BZT	MeBZT	DMBZT	MePB	PrPB	BuPB	BePB
River	<LOQ	24.9	nd	nd	nd	nd	744	622	61.1	102	73.3	nd	nd
SAP-2bis	nd	<LOQ	nd	nd	nd	42.3	1280	970	nd	194	61.9	nd	nd
SAP-1	nd	nd	nd	nd	nd	72	495	267	nd	<LOQ	nd	nd	nd
SAP-2	<LOQ	<LOQ	nd	nd	nd	73.1	748	414	59.7	nd	nd	nd	nd
ADS-6n	<LOQ	<LOQ	nd	<LOQ	nd	42.3	1350	918	nd	38.9	nd	nd	nd
ADS-7	nd	<LOQ	34.4	nd	nd	nd	1030	827	nd	45.3	nd	nd	nd
ADPW	nd	<LOQ	nd	nd	<LOQ	<LOQ	1270	358	nd	nd	nd	nd	nd

4. Discussion

4.1. Personal care products in the recharge sources

4.1.1. Seasonal evolution of Besòs River recharge in the aquifer

As mentioned before, up to five different recharge sources have been identified in the study area but Besòs River is by far the largest contributor to groundwater recharge, representing the 90% (Jurado et al., 2013). Consequently, it has been the only aquifer recharge source that we have taken into account. However, it is necessary to consider the seasonal variability of the river because groundwater samples were collected from May 2010 to July 2014. According to Tubau et al. (2014), three end-members are needed to explain seasonal variability of river water: Two from the dry season (D1 and D2) and one from the wet season (W1). The former corresponded to concentrated water related to dry periods and the latter represented diluted waters corresponding to wet periods when heavy but short events of rain occurs. The difference between the two dry end-members is mainly the concentration of nitrogen species nitrate and ammonium. For the sake of simplicity, the tracers used to quantify groundwater recharge are those included in Tubau et al. (2014).

The spatial distribution of the average mixing ratios accounting for the 3 sampling campaigns is illustrated in Figure 2. The river water recharge in the aquifer has not presented significant variations in the three different sampling campaigns because the contribution to groundwater from the wet and

dry river end-members has been practically constant. The wet end-member percentage varies from 40.4% (C1) to 44.1% (C3) whilst this of dry end-members ranges from 55.9% (C3) to 59.6% (C1). On average, the dry end-member D2 is the largest contributor to groundwater recharge, representing the 52.6%, followed by the wet end-member (42.7%, W1). The remaining 4.7% corresponds to the dry end-member D1. Despite its low contribution to groundwater recharge, this end-member is necessary to explain the most reducing conditions (low or null levels of nitrate and high concentrations of ammonium) in the aquifer at observation points SAP-2bis and ADS6-n. The dry end-member D1 represents, on average, the 15% and the 6% of the groundwater recharge at SAP-2bis and ADS6-n, respectively (Figure 2). Comparing the average groundwater recharge evaluated in previous studies (Tubau et al., 2014), the contribution of the wet-member W1 has been much more significant in this study than in the previous one (42.7% versus 26%, respectively). This difference can be explained by short but intense rainfall events that occurred in the Besòs River Delta, represented by the wet river end-member, when groundwater samples were collected.

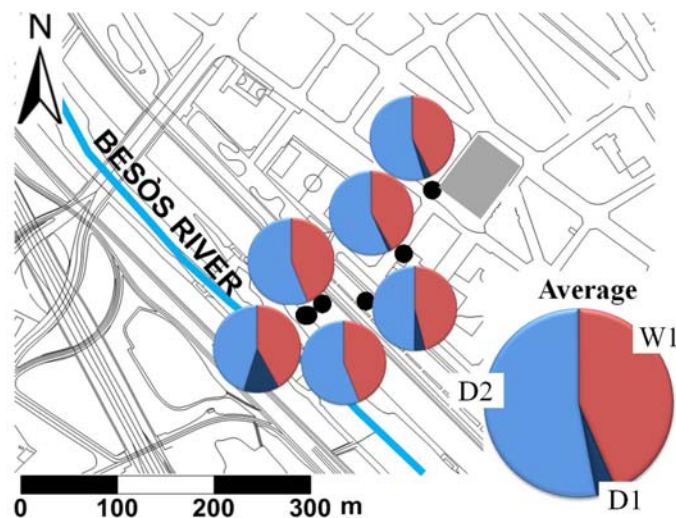


Figure 2. Average mixing ratios evaluated at the observation points accounting for the 3 river end-members

4.1.2 Concentration of personal care products in the recharge sources

A bibliographic research on the occurrence of the PCPs in some of the aforementioned recharge sources such as rivers and WWTPs effluents was carried out given that only 3 samples from the Besòs River were analyzed and we doubt that they might not be representative because of the river

flow regime. As commented before, this regime is characterized to be highly variable and, therefore, the PCPs concentration can fluctuate significantly (dilution effect). With this survey we can assess (1) if the range of concentrations observed in the river water samples are representative or not and (2) the fate of these PCPs in the studied aquifer.

Table 2 shows the concentrations of PCPs in Besòs River and treated waste water reported in the literature. The highest ones correspond to the triazoles BZT and MeBZT, ranging from 1080 to 2855.6 ng/L and 925 to 5004 ng/L, respectively at the Besòs River. Benzophenone derivatives concentrations varied considerably. Some of them, such as BP1, BP3 and 4HB, are detected at maximal concentrations near to 50 ng/L or detected below the limit of quantification (4DHB). The concentrations of the compounds 4MBC and Et-PABA have been reported at concentrations lower than 40 ng/L. Parabens have never been studied in the Besòs River before.

These PCPs mainly reach rivers through the WWTPs discharges (Table 2, WWTPs effluents). Triazoles were the most ubiquitous and abundant compounds in the WWTPs effluents. Overall, MeBZT has been detected at higher concentrations than BZT, with maximum values of 4411.7 ng/L and 1469.2 ng/L, respectively. Recently, Molins-Delgado et al. (2015b) evaluated the removal of these compounds in several WWTPs located in the Besòs River catchment (LLA, SRS, MDV, MON, BES and GRA). These authors concluded that these contaminants are quite recalcitrant, with removal rates in the range from 39% to 76% for BZT and from non-removal to 57% for MeBZT. Other studies have also confirmed the ubiquity of the benzophenones BP-1, BP-3 and BP-4 at relevant levels in sewage effluent, especially for BP-4 with maximum concentration of 1080 ng/L. As benzotriazoles, BP-4 is barely removed at WWTPs, ranging from non-removal to 49% (Molins-Delgado et al., 2016). The remaining compounds are seldom or not detected. For instance, all the parabens have removal efficiencies close to 100% and, not surprisingly, they are observed below their corresponding limit of quantification in WWTPs effluents (Molins-Delgado et al., 2016).

Table 2. Occurrence of PCPs in (1) Besòs River and (2) wastewater treatment plants (WWTPs) effluents located in the Besòs River catchment. LOD = limit of detection; LOQ = limit of quantification; nd = non detected. References: ¹ Martins Ferreira (2014), ² Jover et al. (2009), ³ Molins-Delgado et al. (2016) and ⁴ Molins-Delgado et al. (2015b).

Location	Analyte	Concentrations (ng/L)	
		River water	WWTPs effluents
Besòs River Catchment	Benzophenone derivatives		
	BP1	31.2-48.2 ¹	211.2 ¹
	BP3	20.9-52.2 ¹	217.8 ¹
	BP4	-	136-1080 ³
	4HB	10.1-12.1 ¹	<LOQ ¹
	4DHB	<LOQ ¹	<LOQ ¹
	Camphor derivatives		
	4MBC	<LOQ-13.1 ¹	21 ¹
	p-aminobenzoic acid derivatives		
	Et-PABA	27.2-38.6 ¹	35.8 ¹
	Triazoles		
	BZT	1080-2855.6 ^{1,2}	214.1-1469.2 ⁴
	MeBZT	925-5004 ^{1,2}	1482.4-4411.7 ⁴
	Parabens		
	BePB	-	<LOQ ³
	BuPB	-	<LOQ ³
	PrPB	-	<LOQ ³
MePB	-	<LOQ ³	

As shown in Table 2, concentrations of PCPs in river water are, on average, of the same order of magnitude than WWTP effluents for most of the compounds. Exceptions are for the compounds BP1 and BP3 in the Besòs River where river water concentrations are lower than those found in WWTP effluents. It is also important to comment that the maximum concentration found for MeBZT at Besòs River has been higher than those detected in WWTP effluents (being 5004 ng/L and 4411.7 ng/L, respectively). The bibliographic research has been useful to corroborate that PCPs' concentrations in the Besòs River are of the same order of magnitude than those previously reported in literature for detected compounds (BP3, BP4, BZT and MeBZT) accounting for the 3 sampling campaigns (Table 1-2). According to the literature, the remaining compounds have been not detected or observed at low concentrations.

Finally, the concentration of the target PCPs in the three river end-members (D1, D2 and W1) was evaluated (Table 3). To this end, we calculated the concentration of PCPs in these river end-members with the river flow using a dilution factor (f) that is calculated as follows:

$$f = \frac{Q_s}{Q_{em}} \quad (1)$$

where Q_s is the flow rate on the sampling day and Q_{em} is the flow rate of the aforementioned end-members (Jurado et al., 2012).

Table 3. Concentrations of PCPs (ng/L) in the recharge sources used in the mixing analysis.

River end-members	BP1	BP3	4MBC	BZT	MeBZT	MePb
D1	20.2	40.4	40.4	1715.6	2018.4	121.1
D2	26.4	52.7	52.7	2241.1	2636.6	158.2
W1	3.3	6.6	6.6	278.6	327.8	19.7

4.2. Assessment of the fate of the personal care products in the aquifer

Once the river recharge was quantified and the levels of PCPs in the three river end-member determined, it was possible to assess the fate of PCPs in the aquifer. Figure 3 plots the measured and estimated concentrations for the selected PCPs during the three sampling campaigns. It is important to note that only the most commonly detected compounds (BZT, MeBZT, 4MBC, MePB, BP1 and BP3) are included in this figure. Overall, most of the compounds were seldom detected or observed at low concentrations in the river and groundwater samples accounting for all the sampling campaigns (C1 to C3). This is the case of UV filters 4DHB, 4HB and DHMB, BP4, Et-PABA, the parabens BePB, BuPB and PrPB and the triazole DMBZT. These PCPs are efficiently removed in the WWTPs of the Besòs River catchment (Table 2) and, therefore, they have not been measured at significant concentrations in the river during the three sampling campaigns (maximum was 73.3 ng/L for PrPB in C3). An exception occurred with BP4 in C2, determined at 1160 ng/L at Besòs River. These observations suggest that: (1) these PCPs hardly reach groundwater environment because of their high removal rates in WWTPs or (2) they are naturally removed in the aquifer. In fact, Figure 3

shows a drastic reduction (blue arrow) in the aquifer concentrations. Estimated concentrations for a given PCP are in the same variation range at the 3 sampling campaigns because of evaluated mixing ratios were similar among them. When measured and estimated concentrations of the selected PCPs are compared, it can be observed that the samples do not fit the ideal mixing line 1:1. Measured concentrations for most of the PCPs are lower than the estimated ones. This finding is in good agreement with the fact that most PCPs are susceptible to undergo natural attenuation processes that depleted them from the aquifer because they could not be explained by mixing of the Besòs River end-members (W1, D1 and D2). The processes that might affect the removal of these compounds in the aquifer are redox processes such as aerobic respiration and denitrification that occur when river water infiltrates the aquifer (Jurado et al., 2015). This observation is supported by the nitrate and dissolved oxygen concentrations at River Besòs, which can reach concentrations up to 15 mg/L and 10 mg/L, respectively. In contrast, measured concentrations of these tracers are drastically reduced to null or low levels in the aquifer (on average, 4.7 mg/L and 0.7 mg/L for nitrate and dissolved oxygen, respectively). Other processes might involve adsorption onto organic components of the soil or suspended organic particulate matter. However, some of them such as the triazoles BZT and MeBZT (C2 and C3), the camphor derivative 4MBC (C1, C2 and C3) and the paraben MePB (C3) were persistent under the redox conditions of the aquifer because they have been only partially removed. The removal rate (RR) of these PCPs from the aquifer for other process rather than river water mixing (i.e. redox processes) can be evaluated using Eq. (2),

$$RR (\%) = 100 \times \frac{C_e - C_m}{C_e} \quad (2)$$

where C_e is the estimated concentration by MIX code and C_m is the measured concentration at each sampling site. Note that C_e represents the concentration explained by river water mixing. The RR varied from one compound to another and during the different sampling campaigns. The most persistent compound was BZT with average RR of 38% at C2 and 24% at C3, representing an

average concentrations of 524 ng/L at C2 and 329 ng/L at C3. MeBZT has also been found to be quite persistent with average *RR* being 49% (779 ng/L) at C2 and 61% at C3 (971 ng/L). Regarding the average *RR* of 4MBC, they were in descending order: 83% (27 ng/L) at C1, 62% (20 ng/L) at C3 and 58% (18 ng/L) at C2. Finally, MePB was completely removed at C2 and the average *RR* for MePB at C3 was of 82% (78 ng/L). It is important to highlight that there were some observation points where measured concentrations were higher than the corresponding ones (Figure 3). This suggests that the pollutants' concentrations at the river (recharge sources) could be higher than those used in mixing calculations. In fact, groundwater samples present higher concentrations than those found in the river at some sampling sites for a few compounds such as BZT, MeBZT, or MePB (Table 1). These points are not included to estimate the average *RR*.

To summarise, based on the data collected during the three sampling campaigns, most of the PCPs were barely detected in groundwater samples of the Besòs Delta aquifer, except BZT, MeBZT, 4MBC and MePB. PCPs aquifer concentrations were much lower than those evaluated by the Besòs River water mixing. This suggests that PCPs may undergo some natural attenuation processes that occurred when river water infiltrates the aquifer. However, BZT, MeBZT, 4MBC and MePB appeared to be less affected than other PCPs by the removal processes occurring at the reducing conditions of the aquifer because they were not completely removed. This points out that further research on the seasonal variability of PCPs is needed to better understand the key factors driving their fate in aquifer ecosystems.

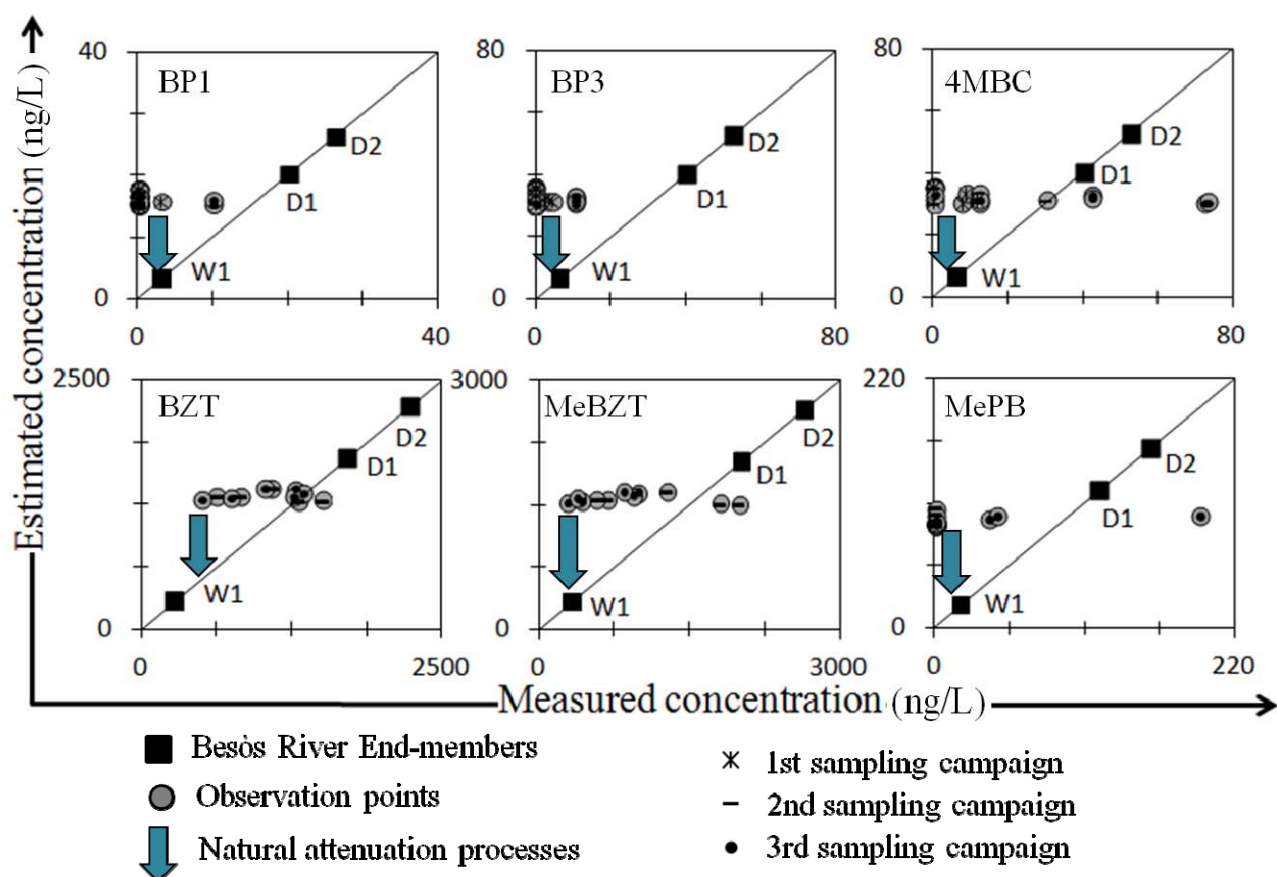


Figure 3. Measured concentrations of PCPs (ng/L) at the aquifer versus the concentrations estimated from the end-members (squares) for each sampling campaign (C1, C2 and C3). Note that for most PCPs measured concentrations are much lower than expected from river water mixing.

4.3. Environmental risk assessment

A risk assessment was conducted for the target PCPs with the available short- and long-term toxicity data and the environmental concentrations determined using hazard quotients (HQs). HQs were calculated following the EMEA guidelines (EMEA, 2006), which are the ratio between exposure concentration and the toxicological benchmark concentration causing adverse effects. HQs above 1 indicate potential toxic effects, whereas HQs below 0.5 denotes scenarios with minimal associated risk (Molins-Delgado et al., 2015b). Furthermore, as generally mixtures of compounds occur, cumulative HQs were calculated as the addition of HQs for each compound where more than one was measured. In order to set up the worst case scenario, exposure concentrations were the maximum values measured, whereas the toxicity data used were the lowest reported in the literature. As these

ecotoxicological parameters are quite limited, calculations were subjected to their availability. The estimated HQ corresponded to the aquatic species *Vibrio fischeri*, *Daphnia magna*, *Raphidocelis subcapitata*, *Ceriodaphnia dubia* and *Pimephales promelas*. The complete data set of estimated HQs and cumulative HQs is listed in Table S3 of the Supplementary Material.

Results showed that individual HQs for groundwater were in the range of $2.26E-4$ – $9.0E-2$ (in ADS-6n for *P. promelas* and MeBZT) and for the river from $1.62E-4$ to $6.09E-2$ (for *P. promelas* and MeBZT), far below any potential hazard. Cumulative HQs proved also the low risk posed by these contaminants at current concentrations. The highest cumulative ratio corresponded to ADS-6n with a value of 0.11 for *P. promelas*.

Summarizing, HQ values calculated were always below 0.12, indicating that the occurrence of target PCPs at the concentrations observed in this aquifer do not constitute any threat to the selected species.

5. Conclusions

The following conclusions may be drawn from this study:

- The occurrence of UV filters and parabens was studied in the surface water and in the groundwater of the Besòs River. Eleven compounds were detected, three of them at very low levels precluding their quantification (Et-PABA, 4DHB and BP1). Maximum concentrations were as high as 1980 ng/L for MeBZT and 1500 ng/L for BZT in the groundwater collected from ADS-6n and SAP-2bis sampling sites, respectively. In the surface water of the river, up to nine compounds were simultaneous detected. The higher concentrations corresponded to the second campaign and were as follows MeBZT > BP4 > BZT.
- The potential source of contamination in the aquifer is the polluted Besòs River that receives effluents from several WWTPs along its catchment.

- The assessment of the PCPs in the aquifer has been done considering the seasonal evolution of the river water recharge. PCP aquifer concentrations have been lower than those expected for simple mixing of the Besòs River during all sampling campaigns. This suggests significant removal of PCPs under the reducing conditions of groundwater when aquifer is infiltrated by river water.
- Natural attenuation appears to play a major role in the removal of PCPs from the aquifer to different extents since some of these compounds (BZT, MeBZT, 4MBC and MePB) have not been completely removed. This observation suggests that further research is needed to identify the key factors driving the fate of PCPs in the aquifer.
- The potential environmental risk posed by the selected UV filters and parabens has been evaluated in the river-groundwater interface resulting in no hazard for the species assayed because of the concentrations measured in groundwater were far below those causing toxic effects.

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Appendix A. Supplementary material. Supplementary data associated with this article can be found in the online version.

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