Personal care products reconnaissance in EVROTAS river (Greece): Water-sediment partition and bioaccumulation in fish

M. Silvia Díaz-Cruz a,⁎, Daniel Molins-Delgado a, M. Pau Serra-Roig a, Eleni Kalogianni b, Nikolaos Th. Skoulikidis b, Damià Barceló a,c

a Department of Environmental Chemistry, Institute of Environmental Assessment and Water Research of the Spanish Council for Scientific Research IDAEA-CSIC, C/Jordi Girona 18-26, 08034 Barcelona, Spain
b Hellenic Centre for Marine Research, Institute of Marine Biological Resources and Inland Waters, 46.7 km Athens-Sounio Ave., Anavyssos 19013, Greece
c Catalan Institute for Water Research (ICRA), Parc Científic i Tecnològic de la Universitat de Girona, C/Emili Grañut, 101 Edifici H2O, 17003 Girona, Spain

HIGHLIGHTS
• First determination of 20 personal care product in Evrotas River (Greece)
• High levels of UV filters adsorbed onto the river sediments
• High bioaccumulation potential of methyl benzotriazole in Squalius keadicus tissues
• Eventual ecological risk for BP3 and ODPABA, but generally no hazard

GRAPHICAL ABSTRACT

ABSTRACT
Twenty-six common ingredients of personal care products (PCPs) in water, sediment and fish from the Evrotas River (Greece) were investigated. Water sample analysis revealed the occurrence of twenty PCPs at concentrations ranging from 2.8 to 2031.0 ng l⁻¹, the maximum corresponding to the endocrine disrupting UV filter benzophenone 3 (BP3). In sediment samples, six compounds were found to be adsorbed, the highest concentration being that of 4-methylbenzylidene camphor (4MBC, 1400.4 ng g⁻¹ dw). Evrotas cyprinid fish (Squalius keadicus) showed a high accumulation potential for these chemicals, 100% detection frequency with maximum concentration that of benzophenone 2 (BP2, 41.9 ng g⁻¹ dw). These data allowed estimating the distribution coefficients (DCs-w) and the bioaccumulation factors (BAFs) of the pollutants investigated. Calculated rates revealed that benzophenone 1 (BP1), 4-hydroxybenzophenone (4HB) and ethyl-4-(dimethyl-amino)benzoate (EtPABA) have a strong tendency to adsorb onto the sediments, showing high DCs-w, i.e. 8.2E + 4 l g⁻¹, 6.7E + 4 l g⁻¹ and 5.7E + 3 l g⁻¹, respectively. BAFs were only estimated for 5-methyl benzotriazole (MeBT), the compound having paired data from fish and water. The obtained values (range 2.0E + 2 l g⁻¹–3.8E + 3 l g⁻¹), indicated MeBT’s strong bioaccumulation. Risk assessment of the investigated compounds for
1. Introduction

Ingredients in personal care products (PCPs) are diverse and can reach high proportions of the product. Many of these ingredients have already been considered as endocrine disrupting compounds (Kunz et al., 2006). These chemicals are currently a matter of concern due to their extensive use, environmental ubiquity, pseudo-persistence and potential ecotoxicity in aquatic ecosystems (Molins-Delgado et al., 2015). This has led, for the first time, to the inclusion of one UV filter, ethylhexyl methoxycinnamate (EHMC), for assessment within the framework of EU-water monitoring according to the Directive 2013/39/EU (Directive EU, 2013) that amended Directive 2000/60/EC (Directive EU, 2000, WFD) regarding priority chemicals in the field of water policy. EHMC was included in the Wash List in 2015 (Wash List, 2015). This document lists a number of contaminants that, being toxic, might be appropriate for prioritization but for which there is a gap of knowledge on their occurrence at European Union level. However, in the last amendment of this document, (Commission Implementing Decision (EU), 2018/840 of 5 June 2018) EHMC has been excluded arguing that there is limited reported data on the occurrence of EHMC in sediments to perform a conclusive analysis for the monitoring of EHMC in this specific matrix. Hence, the Commission is investigating whether Member States could monitor it in sediment in a reliable and comparable manner.

The quantification of the occurrence and partition coefficients of chemical pollutants in water, sediment and biota is a critical step in defining the level of pollutants in the aquatic ecosystems and their potential impact on environmental quality. So far, several studies have reported the occurrence of PCPs residues in drinking water, freshwater, seawater and groundwater (Fent et al., 2010; Balmer et al., 2005, Weiss and Reemtsma, 2005, Villa et al., 2012, Rodil et al., 2012, Díaz-Cruz et al., 2012, Chased et al., 2012; Serra-Roig et al., 2016). However, few studies have demonstrated the presence of these pollutants in sediments and suspended particulate matter (Gago-Ferrero et al., 2011; Barón et al., 2013; Liao et al., 2013; Mizukawa et al., 2017). The accumulation of such substances in living organisms, both local biota and humans, has also been reported (Fent et al., 2010, Buser et al., 2006, León et al., 2010, Schlumpf et al., 2010, Vela-Soria et al., 2011, Gago-Ferrero et al., 2015, Valle-Sistac et al., 2016, Molins-Delgado et al., 2018a). PCPs are indirectly released through wastewater treatment plant (WWTP) effluents as a consequence of their inefficient removal, and also directly during aquatic recreational activities (Molins-Delgado et al., 2015). It has been shown, for example, that an increase in PCPs concentration in the environment is observed during the tourist season (Mandaric et al., 2017).

The ecotoxic effects attributed to these compounds have been described in a number of studies. Increased vitellogenin synthesis for Oryzias latipes (Sapozhnikova et al., 2005) and for Paralichthys californicus (Schlenk et al., 2005) exposed to wastewaters and sediments containing BP3 has been reported. The BP3 metabolite BP1 and OC cause increased vitellogenin production in Pimephales promelas (Kunz et al., 2006), while 4MBC was found to be estrogenic in Oryzias californicus (Schlenk et al., 2005) exposed to wastewaters and sediments. In vivo assays with OC have been described for BP3, OC and ODPABA both in in vitro and in vivo assays with Danio rerio (Schreurs et al., 2002; Blüthgen, 2014). Also, BP3 causes coral-ceil bleeding, DNA damage, deformity and mortality at environmental level, specifically at 62 ng 1−1 (Downs et al., 2016). Benzophenone-type UV-Fs inhibited embryonic development of algae and sea urchin at concentrations similar to those toxic for coral (10 ng ml−1) (Downs et al., 2016). BP3 also affects the thyroid and the sex hormone system of mice (Calafat et al., 2008), while in rats BP3, 4DHB, OD-PABA and 4MBC have been found to possess estrogenic activity (Schlecht et al., 2004; Durrer et al., 2005). Transformation products can be even more toxic than the parent compounds, as is the case of BP2 (Schlenk et al., 2005; Downs et al., 2014). In women, the estrogenicity displayed by benzophenone-type UV filters was associated to endometriosis (Kunisue et al., 2012). These estrogenic effects are visible at quite low concentrations (EC50: 2.042·10−4–4.456·10−7 mol L−1), which might be the result of additive toxic effects (Kunz and Fent, 2006).

So far, scarce data is currently available on the ecotoxicity of benzotriazoles; they have been ranged as toxic to aquatic organisms and slightly toxic to humans (Breedveld et al., 2002; Hem et al., 2003). As regards the polycyclic musk fragrances, tonalide and celestolide both caused toxic effects in some organisms through inhibition of xenobiotic resistance transporters (Luckenbach and Epel, 2005). Likewise, reproductive toxicity was reported for the springtail Folsomia candida and the earthworm Eisenia fetida exposed to tonalide (ECB, 2008).

As in the rest of the European countries, monitoring programmes in Greece do not include the survey of PCPs residues. Thus, occurrence data for PCPs in rivers of this country are lacking. In the light of the current concern on the prevalence of these pollutants in the aquatic environment, the main objective of the current study was to provide occurrence data of target PCPs in water, sediment and biota across the Evrotas River (Southern Greece). The reported data will contribute to gaining a reliable picture of the distribution of such compounds in European rivers for a proper risk evaluation and for the potential inclusion of PCPs in future monitoring programmes, leading to the amendment of current Directives and/or to the development of new regulations as regards water policy.

The dominant anthropogenic pressure in the Evrotas River Basin is overexploitation of water resources for field irrigation that leads, in late summer–early autumn, to the partial desiccation of the river, similarly to other Mediterranean rivers (Gasith and Resh, 1999; Skoulidakis et al., 2011). In the Evrotas basin there is also diffuse agrochemical pollution and pollution from the effluent of the Sparta WWTP (Lampou et al., 2015). By conducting our study during two consecutive summers with different precipitation levels that resulted to a variation in summer discharge (higher in 2015 compared to 2014), we also assessed the occurrence and spatial distribution of PCP contaminants at different levels of water scarcity in an intermittent river.

2. Experimental

2.1. Chemicals and materials

The target PCPs analyzed in this study were: benzophenone 1 (BP1, 99% purity), benzophenone-2 (BP2, 97%), benzophenone 3 (BP3, 98%), benzophenone 8 (BP8, 98%), 4-hydroxybenzophenone (4HB, 98%), 4,4′-di-hydroxybenzophenone (4DHB, 99%), 4-methylbenzylidene camphor (4MBC, 98%), ethyl-4-(dimethyl-amino)benzoate (EtPABA, 98%), 2-ethylhexyl 4-((dimethyl-amino)benzoate (ODPABA, 98%), 2-ethylhexyl 2-cyano-3,3-diphenylacrylate (OC, 97%), ethylhexyl methoxycinnamate (EHMC, 98%) and 1H-benzotriazole (1HTB 99%), and were supplied by Merck (Darmstadt, Germany).

2-(2-Benzotriazol-2-yl)-p-cresol (UVP, 98%) and 5,6-dimethyl-1H-benzotriazole (DMEBT, 99%) and 2-(2H-benzotriazole-2-yl)-4-methyl-
6-(2-propyl)phenol (AllylBZT, 99%) used as internal standard (IS) for UVP, methyl paraben (MPB, 99%), ethyl paraben (EPB, 99%) and benzyl paraben (BPB, 99%) were obtained from Sigma–Aldrich (Steinheim, Germany).

5-Methyl benzotriazole (MeBT, 99%) and 2-(5-tert-butyl-2-hydroxyphenyl)benzotriazole (TBHPBT, 98%), 2-tert-butyl-6-(5-chlor-2H-benzotriazol-2-yl)-4-methylphenol (bumetrizole, UV326, 98%), 2,4-di-tert-butyl-6-(5-chlor-2H-benzotriazol-2-yl)phenol (UV327, 98%), 2-(5-benzotriazol-2-yl)-4,6-di-tert-pentylphenol (UV328), 2-(5-chlor-2H-benzotriazol-2-yl)-4-{1,1,3,3-tetramethylbutyl}phenol (octrizole, UV329, 98%) and celestolide (98%) were supplied by TCI (Zwijndrecht, Belgium). Tonalide (technical) and galaxolide (technical) were from LGC standards (Teddington, Middlesex, UK).

BP3-d5, 1HBT-d4 and 4MBC-d4, used as IS (98% D), were purchased from CDN isotopes (Quebec, Canada). Tonalide (6-acetyl)-d3 (99%) used as IS, was supplied by Dr. Ehrenstorfer (Augsburg, Germany).

Tables S1 and 2S list the name, abbreviation, CAS number and Log Kow of the target compounds and the IS, respectively.

The solvents water (HPLC gradient grade), methanol (MeOH, (Ultra) gradient HPLC grade), acetonitrile (ACN, (Ultra) gradient HPLC grade), ethyl acetate (EtAc, for organic residue analysis grade), and dichloromethane (DCM, for organic residue analysis grade) were purchased by J.T. Backer (Deventer, The Netherlands), and the formic acid (for organic residue analysis grade) from Merck. The 99% purity nitrogen needed to evaporate the extracts was supplied by Air Liquide (Barcelona, Spain). PURADISC syringe filters and 1 μm glass fiber filters and 0.45 μm nylon filters were provided by Whatman International Ltd. (Maidstone, UK).

On–line solid phase extraction (SPE) PLRP-s cartridges (Waters) and off-line Isolute C18 SPE columns were used for sample extraction. Stock solutions of individual standards were prepared in MeOH and stored in the dark at −20 °C. Working mixture standard solutions were freshly prepared at the time of analysis.

2.2. Quality assurance and quality control

Background contamination in the laboratory is known to be potentially an issue in the analysis of UV filters at environmentally significant levels. Thus, in order to avoid this, all glassware used in this study was previously washed and heated overnight at 380 °C, and further sequentially rinsed with ACN, MeOH and HPLC grade water. Furthermore, gloves were worn during sample handling and preparation; furthermore, only previously unopened packages of solvents, and other supplies were used. All solutions prepared (standards and samples) were always covered with aluminium foil and stored in the dark to avoid photodegradation.

In every batch of samples analyzed, a procedural blank, a control standards mixture solution (to check for instrumental drift in response factors), and two pure MeOH blanks (indicators of instrument contamination) were measured.

2.3. Evrotas river basin and sampling sites

The Evrotas River drains a mid-altitude, large (2418 km²) Mediterranean basin, located at the South-eastern Peloponnese (Southern Greece, Fig. 1). The climate, discharge and precipitation of the basin follow a predictable seasonal pattern, similar to other Mediterranean rivers, with hot and dry summers and cool, wet winters. Average annual temperature is 16 °C and mean annual precipitation is 803 mm. The Evrotas basin is representative of a large fraction of Greek territory drained by intermittent rivers (exceeding 40%, Skoulikidis et al., 2017). The vast majority of the river basin is covered by natural and semi-natural areas accounting for 61% of the total river basin, followed by agricultural areas that cover 38%, while urban areas account for 1%. The dominant pressures in Evrotas derive mainly from agricultural activities and include overexploitation of water resources for irrigation, disposal of...
agro-industrial wastes (mainly from olive oil mills), and agrochemical pollution and hydromorphological modifications. Overexploitations of groundwater aquifers and water abstraction from surface waters have led to a dramatic long-term discharge reduction, as well as to the artificial desiccation of large parts of the Evrotas main stem and tributaries, particularly during dry years (Skoulidakis et al., 2011). In addition, the river receives the effluents of the WWTP of the city of Sparta (Fig. 1), while villages are served by traditional permeable and impermeable cesspools. As a result of desiccation and pollution, massive fish deaths occur in summer and the three native range-restricted endemic fish species of the Evrotas River, and especially the raphophilic Evrotas chub Squaleus keadicus, are threatened (Vardakas et al., 2017; Kalogianni et al., 2017).

During the current study, samplings were conducted at four reaches on the main channel of the Evrotas River, targeting for different levels of water stress and water quality degradation. The two more upstream reaches, i.e. Uskó (sampling sites 1 and 2, Fig. 1) and Dskól (sites 3 and 4, Fig. 1) are relatively undisturbed and typologically similar. However, while Uskó is located in a perennial section of the Evrotas, Dskól located 1.2 km downstream, is an intermittent reach, drying out partially during late summer due to natural and artificial desiccation. In addition, Dskól is located immediately downstream from the confluence of the Kolliniatiako stream, receiving the effluents of the small community of Kollinaí (Fig. 1). The other two sampling reaches, i.e. Vivári (sites 5 and 6, Fig. 1) and WWTP (sites 7 and 8, Fig. 1) are located in the middle section of the Evrotas River with a wider active channel and higher discharge than the upstream ones; the spring-fed Vivári is a perennial reach, with some pollution from agriculture and animal husbandry, while the WWTP reach, located 20 km downstream, dries out in periods of extreme drought and is heavily impacted by pollutants, as it receives diffuse pollution from agriculture and, notably, point source pollution from the Sparta WWTP and from illegal cesspool waste dumping.

2.4. Sample collection

Evrotas samplings were conducted during two campaigns, in mid-June 2014 (C1) and in late July 2015 (C2). Water and sediment samples were collected during both campaigns, whereas fish were sampled in C2. In 2014, water and sediment samples were obtained from two sites at each reach (inflow and outflow, 1.5–4 km apart); in 2015, water samples were again obtained from the two sites of each reach, while sediment and fish samples were obtained from one site per reach.

2.4.1. Water sampling protocol

During the two Evrotas campaigns, composite water samples were obtained from the four sampling reaches, at the inflow and outflow of each reach in order to assess the chemical fate of the target pollutants, and their attenuation. To determine the travel time between the inflow and the outflow of each reach, the Lagrangian approach (Writer et al., 2011) was applied using sodium chloride as tracer, tested at stretches of 100, 200 and 300 m. The rationale was to track a parcel of water as it gets in and out of a river reach, defined by a travel time (τ). The Lagrangian approach is the most rigorous method for linking hydrology and biogeochemical processes. In the case of the four Evrotas reaches, travel time (τ) between inflow and outflow varied from 85 to 140 min between the reaches. More specifically, during sampling at the inflow of each reach, the composite sample integrated a time period of τ/4, i.e. 3 water samples were obtained within a period of τ/4, centered at t = 0, and mixed to obtain a composite sample; sampling at the output of each reach, integrated a time period of τ/2, i.e. 5 samples were obtained within a period of τ/2, centered at t = 0 + τ and mixed to obtain a composite sample. After sampling, water samples collected in amber glass bottles from the eight sampling points (inflows and outflows of the four reaches) were frozen at −20 °C, packed on dry ice and shipped to the laboratory. Once in CSIC, samples were kept frozen until analysis.

2.4.2. Sediment sampling protocol

Sediment sampling followed the recommendations laid on the guidance document on chemical monitoring of sediment and biota under the Directive 2000/60/EC (Directive EU, 2000, WFD). From each location, 3 to 8 kg of the uppermost sediment layer (10 cm) were collected in a bucket. For most reaches, 3 kg of sediment was adequate. All samples were sieved using 2 mm mesh sieve after collection, to remove large detritus and benthic organisms. In order to minimise the potential for disturbance of the water-sediment equilibrium, wet sieving was performed at the sampling point with ambient (river) water. Fractions <2 mm were afterwards shipped to the CSIC lab. Sample aliquots were transferred in appropriate containers covered by a layer of the corresponding river water.

2.4.3. Biota sampling protocol

Biota sampling followed the recommendations of the guidance document on chemical monitoring of sediment and biota from the Directive 2000/60/EC (Directive EU, 2000, WFD) as did for sediments. Five to ten fish specimens of the Evrotas chub Squaleus keadicus were collected from each sampling reach (a total of four samples), euthanized in ice water and kept at 4 °C until frozen. Shipment to CSIC was done by transport on dry ice. Upon arrival, samples were kept at −20 °C until analysis.

2.5. Sample pretreatment and analysis

For water analysis, we applied an on-line solid phase extraction followed by high performance liquid chromatography coupled to tandem mass spectrometry method (SPE-HPLC-MS/MS) developed by Gago-Ferrero et al. (2013a). On-line SPE was carried out using a Symbiosis TM Pico from Spark Holland (Emmen, The Netherlands) ending in a high-performance liquid chromatograph coupled to a 4000 QTRAP hybrid quadrupole-linear ion trap mass spectrometer (Applied Biosystems, Foster City, CA, USA) with a turbo ion spray source. The target PCPs were eluted from the column into the chromatograph with the LC-mobile phase, which consisted of a mixture of HPLC grade water and ACN, both 0.1% formic acid. The separation was achieved using a Híbar Purospher® STAR® HR R-18 ec. (50 mm × 2.0 mm, 5 μm) LC-column from Merck. Positive electrospray ionization (ESI+) and selected reaction monitoring (SRM) modes were selected for the MS/MS detection. Prior to the analysis, an aliquot of a standard mixture containing all IS was added to the extracts for further isotope dilution-based quantification. The limits of quantification (LOQs) of the method applied are summarized in Table 3S of the SM.

For sediments analysis, the fraction ~63 μm was analyzed. This portion was obtained by wet sieving of the <2 mm sediment’s fraction. In this case, PCPs were determined according to the method by Gago-Ferrero et al. (2011), using frozen-dried and homogenized sediment samples. The target analytes were extracted by pressurized liquid extraction (PLE) in an ASE-350 Accelerated Solvent Extractor (Thermo Fisher Scientifics). The resulting extracts (22 ml approx.) were brought to 25 ml with MeOH and aliquots of 2 ml were then filtered, using a 0.45 μm nylon syringe filter into LC-vials. The vial contents were evaporated in a nitrogen stream and finally reconstituted with 1 ml of the IS solution. The analyses of the sediment extracts were carried out by HPLC-MS/MS, following the same method to that for the water samples, but disabling the on-line configuration. Other instrumental parameters were the same as those used for water analysis. The LOQs of the method applied are summarized in Table 3S of the SM.

For fish, whole frozen specimens were pulverized in a mixer, stored in PE sampling vessels and kept frozen until further analysis. The biota samples were analyzed based on the method by Gago-Ferrero et al. (2013b). Lyophilised and homogenized fish samples spiked with the isotopically labeled surrogate standard, BP-13C, were extracted using the same PLE instrument as for sediment analysis. However, in this case in order to perform an extended purification able to remove fat and proteins, both in-cell purification and off-line SPE of the extracts
were applied. The final elution of the analytes from the SPE columns was performed with 7 ml of the mixture AcEt:DCM (1:1 v/v) and 2 ml of DCM. The extracts were then evaporated until dryness with nitrogen, and the residue reconstituted in 1 ml ACN containing the IS. The HPLC-MS/MS analyses of the fish extracts were performed as those of the sediments. The LOQs of the method applied are summarized in Table 3S of the SM.

2.6. PCPs sediment-water distribution

Once released into the aquatic environment, contaminants can be adsorbed onto suspended particulate matter and sediments, depending on their water solubility and binding affinity to particles. The sediment-water partitioning informs us on the tendency of organic pollutants to be dissolved in the water column or retained in sediments and suspended matter, which plays a main role in the uptake and accumulation of chemical pollutants in aquatic organisms (Thomann et al., 1992). Higher sediment concentration, with respect to those in the water media, may lead to the predominant transfer of the chemicals from the sediments through the benthic food web into organisms of a higher level in the trophic chain, whereas lower concentration in sediments favors uptake both directly from the water through the gills and indirectly via dietary transfer through the pelagic food web.

The extent of partitioning of organic chemical pollutants between sediment and water in an aquatic medium is expressed in terms of distribution coefficients (DCs-w), which are defined as the ratio between the concentration of the contaminant adsorbed onto the sediment and its concentration in the surrounding water. Adsorbed pollutants are hydrophobic, and thus it is expected that their concentration will increase as the organic fraction of the sediment increases. Therefore, the concentration of a chemical in the sediment is usually expressed on an organic carbon basis (i.e. normalized by the total organic carbon (TOC) of the sediment). In the present study, we determined the TOC of every sediment sample and normalized the PCPs concentrations accordingly.

2.7. PCPs bioaccumulation in fish

Aquatic organisms are continuously exposed to the contaminants emitted into the environment. Depending on their physicochemical properties, such as Kow and pKa, these substances may enter the exposed aquatic organisms through the respiratory system, dermal contact or through dietary uptake, and accumulate in the tissues. This may result in a higher concentration of substances within the exposed organism than in its surrounding medium. The bioaccumulation factor (BAF) of a substance is defined as the ratio between the concentration of the substance in an organism and its concentration in the surrounding medium. The level to which a chemical is bioaccumulated in fish depends on the rate and mode of uptake i.e. through inhalation (gills), ingestion, contact (skin), and on its metabolization and elimination rate. In the present study, BAFs in fish were calculated as the ratio between the individual PCP concentration in the fish and its concentration in the surrounding water. Lipophilic compounds are prone to accumulate in fatty tissues, thus in the estimation of the BAFs, the concentration of the contaminant in the organism is expressed on a lipid weight basis.

3. Results

3.1. PCPs in water

3.1.1. Occurrence

Out of the 26 target PCPs, 20 were found in the Evrotas water samples. The concentrations of the various compounds were determined by the HPLC-MS/MS method described above and are presented in Fig. 2 (also see Fig. 2S). The UV Fs BP3 and EtPABA, and the UV blocker 4MeBT were the most frequently detected (in 88% of the samples collected). The relatively high concentrations measured ranged from 0.2 (LOD) to 2031.0 ng l$^{-1}$ for BP3, from nd to 955.8 ng l$^{-1}$ for EtPABA, and from nd to 784.7 ng l$^{-1}$ for 4MeBZT. Three metabolites of BP3 were also detected, i.e. BP1, 4HB and 4DHB. Among them, 4DHB was the most frequently observed (in 50% of the samples), from nd to 50.8 ng l$^{-1}$, however the highest concentration detected (123.0 ng l$^{-1}$) was of BP1 (38% frequency). The lowest detection frequency was found for the metabolite 4HB, which was detected only in four out of the total of 16 water samples collected in both campaigns, at 50.0 ng l$^{-1}$ maximum concentration. 4MBC was present in more than half of the samples (56%) with a concentration of 63.7 ng l$^{-1}$, whereas ODPA was measured (38%) at lower concentrations, with a maximum value of 25.1 ng l$^{-1}$. The paraben preservatives and the sunscreens BP2, OC and EHMC were not detected. Finally, fragrances tonalide and celestolide were present in six samples and galaxolide in two out of the total of 16 water samples analyzed, at low concentrations, in the range of nd to 35.8 ng l$^{-1}$.

3.1.2. Temporal and spatial distribution

Quite different results were obtained between the two sampling campaigns, as higher substance diversity and concentration levels were detected in water samples obtained during C1, that was characterized by lower discharge compared to C2. Twenty compounds were detected in C1 samples, almost triple those detected in C2 (seven compounds). Total PCPs load in C1 samples was 3104.8 ng l$^{-1}$, whereas in C2 samples this was 94.3 ng l$^{-1}$. However, in both campaigns UV Fs were the major overall pollution contributors, followed by UV Bs, and with much less input from fragrances, as shown in Fig. 3. In C1, BP3 was the major pollutant as it was ubiquitous and had the highest concentration. 4DHB, 4MBC and UV328 were also present in all the C1 samples; EtPABA and 4MeBT were the ubiquitous compounds in C2 samples. Differences were found as regards contamination attenuation at low and high discharges. While the WW-out water samples (collected at the outflow of the WWTP reach) from C1 (at lower discharge) were characterized by a decrease in the total load of UV Fs, UV Bs and fragrances (see Fig. 4, left panel), in those from C2 (at higher discharge, Fig. 4, right panel) a discrete reduction in overall contamination was observed. However, in both sampling campaigns an increase of concentration was observed for BP3, whereas the concentration of 4DHB decreased.

The most polluted sites were DS-In for C1 and Vi-In for C2. DS-In samples in C1 had the highest diversity of compounds detected, up to 18, i.e. all the detected compounds with the exception of DMeBT and galaxolide. The total load of PCPs residues in that location was 5598.1 ng l$^{-1}$, the highest in the study. At C2 samples in contrast, in that site, only EtPABA and MeBT were determined and those at low concentrations (total load of 13.9 ng l$^{-1}$). In C2, WW-In was the site with the highest diversity of compounds, with seven chemicals detected, while the maximum PCPs load was detected in Vi-In.

3.2. PCPs in sediments

3.2.1. Occurrence and temporal distribution

In sediments, few compounds were determined, but at very high levels during C2 at higher discharge. In C1 sediment samples, OC was ubiquitous and the only PCP detected (range 0.1 to 0.7 ng g$^{-1}$ dw). Though the presence of BP3, BP8, 4HB and 4DHB was confirmed by MS/MS, their concentrations were below their respective LOQs and thus could not be quantitatively determined. In contrast to water samples, sediment samples from C2 (at higher discharge) showed higher concentration levels and a higher variety of PCP residues relatively to those of C1, as evident in Fig. 5 (C2 sediment sample concentrations). BP1 was determined in 100% of the C2 samples with a range of 30.5–185.1 ng g$^{-1}$ dw. 4MBC was detected in three out of the four C2 sediment samples. This compound was found to be the major contributor to the overall load of PCPs, with 408.8, 902.7 and 1400.4 ng g$^{-1}$ dw.
Fig. 2. PCPs concentrations (ng l\(^{-1}\)) in the water phase of Evrotas River for the two sampling campaigns, C1 (a) and C2 (b).

Fig. 3. Cumulative loads (ng l\(^{-1}\)) of PCPs in the water phase of Evrotas River for the two sampling campaigns, C1 (a) and C2 (b).
concentration values at the three samples detected. 4HB was observed in half of the samples, and BP3 and EtPABA were detected in one sample at low concentrations. The rest of the investigated PCPs were not detected in any sample, with only UV Fs being observed.

3.2.2. Spatial distribution

From the eight sediment samples collected in C1, WW-In was the most polluted sample, with OC concentration of 0.7 ng g\(^{-1}\) dw. A quite high attenuation of OC level was achieved, with the sediment collected from WW-Out in C1 showing a concentration 3-folds below that measured at WW-In. In C2 (at higher discharge) up to five compounds were detected, all at very high concentrations. The highest total load of UV filters in sediments corresponded to that measured in DS-In, namely 1804.4 ng g\(^{-1}\) dw. As mentioned above, this location was also the more polluted in C1.

3.2.3. Sediment-water distribution

The DCs-w could only be calculated for those compounds present in both environmental compartments i.e. in the same pair water/sediment. Therefore, DCw-s could be estimated only in four samples of C2 for BP1, 4HB and EtPABA. For all of them, ratios \(>1\) g\(^{-1}\) were obtained. Mean DCw-s values followed the order BP1 > 4HB > EtPABA; i.e. \(8.2E+1\) g\(^{-1}\), \(6.7E+1\) g\(^{-1}\) and \(5.7E+3\) g\(^{-1}\), respectively. These high partition ratios indicate that these compounds tend to be adsorbed strongly onto the sediments, despite the fact they are dissolved, to some extent, in the water column.

3.3. Bioaccumulation in fish

3.3.1. Occurrence and spatial distribution

Fish of the cyprinid species \(S.\) \(keadicus\) were collected only during campaign C2. BP2 and MeBT were detected in all the fish samples, ranging from 11.8 to 41.9 ng g\(^{-1}\) dw and from 3.5 to 6.2 ng g\(^{-1}\) dw, respectively for the two substances. BP3 was detected in 50% of the fish samples at low concentrations (<LOQ – 1.8 ng g\(^{-1}\) dw), whereas EtPABA was detected in the WW-In fish sample only, but at very low levels that could not be quantitatively determined. The more polluted fish samples were from DS-In, which is in line with the results from water and sediments, with a total PCPs load in the corresponding fish sample of 47 ng g\(^{-1}\) dw.

3.3.2. Bioaccumulation factor

On the basis of the results obtained, and as in the case of the DCw-s estimation, BAFs could be calculated only for MeBT (see Table 4S). For all the analyzed fish samples, BAF > 1 were obtained and ranged from \(2E+2\) g\(^{-1}\) to \(3.7E+3\) g\(^{-1}\), indicating the strong tendency of this UV B to be accumulated in fish tissues.
3.4. Environmental risk assessment

In order to place into a risk context, the monitoring data generated in this study, an evaluation of the risk posed by the occurrence of the detected PCPs to the environment was conducted, through the assessment of the hazard quotients (HQs) in the water from Evrotas River. HQs were calculated following the EMEA guidelines (EMEA, 2006).

Fig. 1S shows the HQs estimated for the fish *Pimephales promelas* (96 h bioassay) and for the microorganisms *Raphidocelis subcapitata*, *Daphnia magna* and *Ceriodaphnia dubia* (48 h) and *Vibrio fischeri* (30 min). The lack of ecotoxicity data impeded a broader assessment, and thus it was only possible to calculate HQs for those contaminants with available EC50 values.

According to the HQs estimated, BP3 at DS-In displayed high risk (HQ > 1) and ODPABA medium risk (1 > HQ > 0.5) to the freshwater planktonic crustacean *D. magna* and the freshwater microalga *R. subcapitata*, respectively in C1. For the rest of the PCPs, the estimated risk was minimal (0.5 > HQ).

Cumulative HQs were also calculated considering additive toxicity for the present PCPs in every sample. The additive effects considered led to the same results (Fig. 2S). These findings indicate the relevance of assessing the potential ecological risk posed by the PCPs for aquatic ecosystems, not only on the basis of their concentrations in environmental matrices but also on the basis of their ecotoxicity (Kosma et al., 2014).

4. Discussion

The results of the current study show differences in both the diversity and concentration of PCPs from the two sampling campaigns that were characterized by different discharges (see Fig. 2; C1 mean discharge 1.06 m³/s and Feb-July precipitation 236.4 mm, C2 mean discharge 1.22 m³/s Feb-July precipitation 437.3 mm). Lower PCPs concentrations were observed in C2 water samples (at higher discharge) probably as a result of dilution. This dilution effect could have been also the reason why the less concentrated compounds in C1, fragrances and parabens (indicated as other in Fig. 4) could not be detected in C2.

The PCPs concentration profiles shown in Fig. 4, indicate that natural attenuation of these compounds, while being transported in the water along the four reaches considered in the study, appears to be random, with no clear trend observed. For instance, while total PCP load from DS-In to DS-out decreased in C1, in the second campaign total load of UV Fs increased, but in contrast, the total load of UV Bs decreased. We can speculate that unregulated/illegal discharges locally might be an additional point source of the target compounds. Moreover, the travel time along each Evrotas reach length (1.7 to 4 km) were likely shorter (range 1 h 25 min to 3.5 h) than the required time for accomplishment of transformation processes (normally 3–5 h). UV Fs and UV Bs transformation appears to be a complex process, barely addressed to date. Gago-Ferrero et al. (2012) investigated the degradation processes of BP3 and BP1 by both fungal treatment and photodegradation. The results showed very efficient fungal degradation of 99% for both UV Fs in 24 h, whereas the photo-exposure upon 24 h of simulated sunlight irradiation was very inefficient, especially for BP3, which remained unaltered (Gago-Ferrero et al., 2012). In another study, the same fungus *T. versicolor* appeared to completely degrade 4MBC in 22 h of treatment. However, full elimination of its metabolites was not achieved even after 21 day of treatment (Badia-Fabregat et al., 2012). Under the light of these findings, travel time in our study appears to have been too short in order to allow natural media attenuation, at least for BP3, BP1 and 4MBC.

Regarding the distribution of our target compounds such as the extremely high total loads of PCPs observed in DS-In water samples during C1 (see Fig. 3) could be possibly explained by the fact that this site is heavily impacted by drought, which leads to a concentration effect of pollutants. Furthermore, as mentioned earlier, this reach receives the effluents of the neighboring Kollinai village (350 inhabitants) and thus the high PCPs load in C1 could be attributed to possibly a temporary high release of pollutants (this is also supported by the fact that in C2 this site had a low water pollution load). During C2 at higher discharge, sites WW-In and WW-Out, as well as Vi-In were the most polluted sites, with the proximity of the Sparta city and the release of the effluent of its municipal WWTP into the river, together with the diffuse pollution load these sites receive, considerably increasing the concentration level of some PCPs, particularly BP3 and derivatives. In conclusion, when considering PCP loads at high discharge these were mainly found in water samples at the section below the effluent of the Sparta WWTP (sites WW-In and WW-Out) and, to a lesser degree, to the Vivari reach, at the more populated middle section of the Evrotas basin.

Regarding sediments, from all substances tested, only OC was determined in a small number of samples during the first campaign. Its occurrence in sediments but not in the water column is, however, expected due to its hydrophobicity (log Kow 7.5) and low water solubility (0.004 mg l⁻¹ at 25 °C). In the second campaign (at higher discharge) five compounds were found to be adsorbed on the sediments i.e. BP1, BP3, 4HB, 4MBC and EtPABA that were already detected in water. 4MBC was predominant along the river basin, but it was not found at the area below the WWTP likely due to its low solubility in water (0.005 mg l⁻¹ at 25 °C) and high log Kow, 4.95, being retained in the sediments (Molins-Delgado et al., 2017). In connection with the water results, in DS-in, the water sample contained EtPABA and 4MeBT, which are of similar polarity, log Kow 1.86 and 1.89, respectively, and high solubility in water, 131 and 5 mg l⁻¹ (25 °C), respectively. In the DS-in sediments, the four more hydrophobic (log Kow > 3) and less soluble compounds (solubility from 0.005 to 0.4 mg l⁻¹ at 25 °C) where adsorbed.

High concentrations of BP2 were determined in fish, with the highest concentration in the sample from DS-In, in agreement with the high total pollution observed in water samples from this site in C1 and sediments in C2. Though its polarity indicates a low tendency to bioaccumulate, its structural symmetry and relatively small size would favor its penetration through the tissues. Special attention should be paid to this finding, as BP2 is known to strongly alter thyroid axis in rats and humans (Schmutzler et al., 2007) and to cause the development of endometriosis in women (Kunisue et al., 2012). Another interesting outcome was the ubiquitous accumulation of 4MeBT in all the fish samples analyzed. This compound is water soluble (5 mg l⁻¹ at 25 °C) and polar (log Kow 1.89), however its high acidic dissociation constants (pKa 8.7, the most basic substance within the benzotriazole USVs family), prevents its anionic form in solution at the pH of the river water (pH range in 2014 7.9–8.2; in 2015 7–7.6), and thus it is prone to be adsorbed/bioaccumulated.

5. Comparison with previous studies

Reported values of PCPs residues in the aquatic environment in Greece are currently absent, with related research limited to WWTP effluents (e.g. Kosma et al., 2010; Stamatis and Konstantinou, 2013). However, there are a number of monitoring studies in other countries that include PCPs in different environmental matrices. In order to properly compare the results obtained in our survey on water, sediment and fish from the Evrotas River, we considered here only those published works dealing with the determination of PCPs in water, sediment and fish solely from riverine systems (marine or underground environments excluded). The considered works are listed in Table 1.

5.1. River water

The detected levels in the Evrotas River water are generally lower than those measured in river water in other countries (see Table 1). Fragrances levels in USA (Chased et al., 2012) and Italy (Villa et al., 2012),
for instance, reach values of up to 1000 ng l$^{-1}$, whereas in our study the maximum value was 35.8 ng l$^{-1}$. A similar trend was observed for UV Bs, with a maximum concentration of 784.7 ng l$^{-1}$, whereas much higher values have been reported in the literature (Weiss and Reemtsma, 2005; Serra-Roig et al., 2016), in the range 0.05–1000 ng l$^{-1}$. Concerning the preservatives, no paraben has been reported in river water (Serra-Roig et al., 2016) in line with our results. In contrast, the Evrotas water samples were much more contaminated with UV Fs residues (up to 2031 ng l$^{-1}$ were measured), in comparison to the concentrations reported elsewhere in the literature, which are in the range of 0.1–603 ng l$^{-1}$ (Balmer et al., 2005; Fent et al., 2010; Rodil et al., 2012; Serra-Roig et al., 2016).

In the Evrotas sediments, only UV Fs were found to accumulate. UV Fs have been reported in the range of nd–2.96 and nd–54.4 ng g$^{-1}$ dw in Chile and Colombia, respectively (Barón et al., 2013) and ranging from nd to 23 ng g$^{-1}$ dw in Spain (Gago-Ferrero et al., 2015). In Brazil higher concentrations of UVFs and UVBs were detected in river sediments from Iguazu River and its tributaries. In this case, 1HBt and OC were prevalent, with concentrations in the range of nd – 630 and nd – 322.2 ng g$^{-1}$, respectively. The other 10 target sunscreen agents have also quite frequently been detected (range 4.6 to 166.8 ng g$^{-1}$), with the exception of ODPA, TBHPBT, and MeBT, whose concentrations were below their respective limits of quantification or were not detected.

However, our results are more similar to those observed along the Ebro river basin (Spain, Gago-Ferrero et al., 2011). In that study, a widespread occurrence of OC was observed, reaching concentrations of up to 2400 ng g$^{-1}$ dw, the highest reported so far in the literature. ODPA and BP3 have also been frequently detected (60–65%) in the Ebro, but at lower concentrations (4.4–27 ng g$^{-1}$ dw) compared to Evrotas. BP3, one of the degradation products of BP3, was also measured at low levels (12–21 ng g$^{-1}$ dw).

Finally, in the current study, we did not observe preservative residues, despite parabens being prone to adsorb on sediments, as it has been reported in river sediments from Korea, Japan and USA (Liao et al., 2013) at the low ng g$^{-1}$ dw range.

### 5.3. Fish

In the current study, we monitored the exposure of the endemic Evrotas chub S. keadicus to the target compounds As there are no studies available in the literature on this particular Greek endemic species occurring only in the Evrotas basin, we compared bioaccumulation rates reported on other freshwater fish species, such as Barbos barbus, Leuciscus cephasalus, Salmo trutta, Anguilla anguilla, Luciobarbus graellsii, Cyprinus carpio, Silurus glanis and Luciobarbus sclateri (Buser et al., 2006; Fent et al., 2010; Gago-Ferrero et al., 2015). Bioconcentration is expressed in lipid weight or dry weight basis, and there usually is not enough information in the relevant studies to calculate the concentrations in the same units, a fact that hinders comparisons among results. Considering that these compounds have been found in other than lipophilic tissues (gills and muscle), as documented for the marine species Mugil liza from Brazil (Molins-Delgado et al., 2018b) in the current study we decided to express bioconcentration in dry weight basis. Reported values using this unit for diverse fish species in Iberian rivers in Spain (Gago-Ferrero et al., 2015) were around 5-fold higher than those measured in the Evrotas fish, with maximum values of 241.70 and 41.9 ng g$^{-1}$ dw, respectively. Regardless of the units, the highly lipophilic UVFs EHMC and OC were the most frequently found in the Iberian study, and BP3 and 4MBC were determined to a lower extent in all the species analyzed. In our study, BP3 was only detected at one site at low concentrations, while the UV Fs BP2 and MeBT were ubiquitous in the individuals analyzed in all the catchment reaches.
6. Conclusions

The results of the current study confirmed the ubiquity of PCs in the intermittent Evrotas River (Greece) and complement the existing literature data related to the occurrence of PCs residues in the aquatic ecosystems of Europe. The survey conducted at four Evrotas reaches, allowed us to assess the distribution of twenty PCs residues, with the Mediterranean flow regime of the river resulting in pollutant dilution at higher discharge. The proximity of urban areas, illegal dumping of wastes and the effluents from the local WWTP were the main factors responsible for the PCs contamination observed, with no clear natural attenuation. More lipophilic PCs tended to sorb onto sediments and/or to accumulate in the tissues of the target fish species. Among the twenty-six PCs analyzed, the endocrine disruptors BP3 in water, 4MBC in sediments and BP2 in fish where the most prevalent. No environmental risk is posed for the species assayed by the PCs detected in Evrotas, with the exception of BP3 and ODPABA, as at lower discharge, concentrations were higher leading to higher risk for BP3 towards D. magna and medium risk for ODPABA towards R. subcapitata. This indicates that these two UV Fs are potentially hazardous to the aquatic biota and thus should be included in future monitoring surveys.

Acknowledgements

This study has been supported by the EU project GLOBAQUA (FP7–ENV-2013, GA 603629) and by the Generalitat de Catalunya (Water and Soil Quality Unit 2017-SGR-1404).

Competing interests

The authors have no competing interests to declare.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2018.10.008.

References

Badia-Fabregat, M., Rodríguez-Rodríguez, C.E., Gago-Ferrero, P., Olivares, A., Pila, B., Diaz-Cruz, M.S., Vicent, T., Barceló, D., Glória Caminal, G., 2012. Degradation of UV screen agents benzophenone-3 in residents of the United States: National Health and Science Total Environ. 416, 253

-2013. Effects of UV Filters (Benzophenones and Octocrylene) and Mifepristone on Aquatic Biota. Sci. Total Environ. 518, 518–525.

Gago-Ferrero, P., Díaz-Cruz, M.S., Barceló, D., 2011. Fast pressurized liquid extraction with in-cell purification and analysis by liquid chromatography tandem mass spectrometry for the determination of UV Filters and their degradation products in sediments. Anal. Bioanal. Chem. 400, 2195–2204.

Gago-Ferrero, P., Badia-Fabregat, M., Olivares, A., Pila, B., Blanquez, P., Vicent, T., Caminal, G., 2012. Occurrence of some organic UV Filters in wastewaters and the ef-

fects on aquatic ecosystems in Switzerland. Environ. Pollut. 158 (5), 1817–1824.

Gago-Ferrero, P., Diaz-Cruz, M.S., Barceló, D., 2013a. Fully automated determination of nine ultraviolet filters and transformation products in natural waters and wastewaters by on-line solid phase extraction-liquid chromatography-tandem mass spectrometry. J. Chromatogr. A 1249, 106–116.

Gago-Ferrero, P., Diaz-Cruz, M.S., Barceló, D., 2013b. Multi-residue method for trace level determination of UV Filters in fish based on pressurized liquid extraction and liquid chromatography-quadrupole-linear ion trap mass spectrometry. J. Chromatogr. A 1286, 93–101.

Gago-Ferrero, P., Diaz-Cruz, M.S., Barceló, D., 2015. UV Filters bioaccumulation in fish from Iberian river basins. Sci. Total Environ. 518, 518–525.

Kosma, C.L., Lambropoulou, D.A., Albanis, T.A., 2010. Occurrence and removal of PPCPs in municipal and hospital wastewater in Greece. J. Hazard. Mater. 179, 804–817.

Kosma, C.L., Lambropoulou, D.A., Albanis, T.A., 2014. Investigation of PPCPs in wastewater treatment plants in Greece: occurrence, removal and environmental risk assessment. Sci. Total Environ. 466, 467–476.

Kunisue, T., Chen, Z., Buck Louis, G.M., Sundaram, R., Hediger, M.L., Sun, L., Kannan, K., 2012. Urinary concentrations of benzophenone-type UV Filters in U.S. women and their association with endometriosis. Environ. Sci. Technol. 46 (8), 4632–4632.

Kunz, P.Y., Fent, K., 2006. Estrogenic activity of UV Filters mixtures. Toxicol. Appl. Pharmacol. 217, 86–99.

Kunz, P.Y., Galicia, H.F., Fent, K., 2006. Comparison of in vitro and in vivo estrogenic activity of UV Filters in fish. Toxicol. Sci. 90, 349–361.

Lampou, A., Skoulikidis, N., Papadoulakis, V., Vardakas, L., 2015. Evaluation of the waters’ condition in the final receiver of the wastewater treatment plant in municipality of Sparta. Proceedings of the 11th Panhellenic Symposium on Oceanography and Fish-
Care Products in the Aquatic Environment. Series Title: The Handbook of Environmental Chemistry. Springer International Publishing Series ISBN: 1867-979X. ISSN: 1616-864X.

Molins-Delgado, D., Tavora, J., Díaz-Cruz, M.S., Barceló, D. 2017. UV filters and UV blockers in urban aquatic ecosystems: the footprint of daily use products. Sci. Total Environ. 601–602, 975–986.

Molins-Delgado, D., Olmo-Campos, M.M., Valeta-Juan, G., Pleguezuelos-Hernández, V., Barceló, D., Díaz-Cruz, M.S., 2018a. Determination of UV filters in human breast milk using turbulent flow chromatography and babies’ daily intake estimation. Environ. Res. 161, 532–539.

Molins-Delgado, D., Muñoz, R., Nogueira, S., Alonso, M.B., Paulo Torres, J., Malin, O., Ziedl, R.L., Hauser-Davis, R.A., Eljarrat, E., Barceló, D., Díaz-Cruz, M.S., 2018b. Occurrence of organic UV filters and metabolites in lebranche mullet (Mugil liza) from a southeastern tropical coast in Brazil. Sci. Total Environ. 618, 451–459.

Rodil, R., Quintana, J., Concha-Grana, E., López-Mahía, P., Muniategui-Lorenzo, S., Prada-Rodríguez, D., 2012. Emerging pollutants in sewage, surface and drinking water in Galicia (NW Spain). Chemosphere 86 (10), 1040–1049.

Sapozhnikova, Y., Schlenk, D., McElroy, A., Snyder, S., 2005. Estrogenic activity measurement in wastewater using in vitro and in vivo methods. Tech. Aquat. Toxicol. 2, 56670–56678.

Schlecht, C., Clammer, H., Jarry, H., Wuttke, W., 2004. Effects of estradiol, benzophenone-2 and benzophenone-3 on the expression pattern of the estrogen receptors (ER) alpha and beta, the estrogen receptor-related receptor 1 (ERR1) and the aryl hydrocarbon receptor (AhR) in adult ovariectomized rats. Toxicology 205, 123–130.

Schlenk, D., Sapozhnikova, Y., Irwin, M., 2005. In vivo bioassay-guided fractionation of marine sediment extracts from the Southern California Bight, USA, for estrogenic activity. Environ. Toxicol. Chem. 24, 2820–2826.

Schlumpf, M., Kypl, K., Wittassek, M., Angerer, J., 2010. Exposure patterns of UV filters, fragrances, parabens, phthalates, organochlor pesticides, PBDEs, and PCBs in human milk-correlation of UV filters with use of cosmetics. Chemosphere 81, 1171–1183.

Schnitzler, C., Racinski, A., Kühle, J., et al., 2007. The UV filter benzophenone 2 interferes with the thyroid hormone axis in rats and is a potent in vitro inhibitor of human recombinant thyroid peroxidase. Endocrinology 148 (6), 2835–2844.

Schreurs, R., Lasser, P., Seinen, W., Van der Burg, B., 2002. Estrogenic activity of UV filters determined by an in vitro reporter gene assay and an in vivo transgenic zebrafish assay. Arch. Toxicol. 76, 257–261.

Serra-Roig, M., Jurado, A., Díaz-Cruz, M.S., Vázquez-Suñé, E., Pujades, E., Barceló, D., 2016. Occurrence, fate and risk assessment of personal care products in river–groundwater interface. Sci. Total Environ. 568, 829–837.

Skoulikidis, N., Vardakas, L., Karasuazska, I., Economou, A.N., Dimitriou, E., Zogaris, S., 2011. Assessing water stress in Mediterranean lotic systems: insights from an artificially intermittent river in Greece. Aquat. Sci. 73, 581–597.

Skoulikidis, N.Th., Sabater, S., Darty, T., Moraís, M., Buffagni, A., Dörfinger, G., Zogaris, S., Sánchez-Montoya, M.M., Bonada, N., Kalogianni, E., Rosado, J., Vardakas, L., De Girolamo, A.M., Tockner, K., 2017. Non-perennial Mediterranean rivers in Europe: status, pressures, and challenges for research and management. Sci. Total Environ. 577, 1–18.

Stamatis, N.K., Konstantinou, L.K., 2013. Occurrence and removal of emerging pharmaceuticals, personal care products and caffeine tracer in municipal sewage treatment plant in Western Greece. J. Environ. Sci. Health A 48, 800–813.

Thomann, R.V., Connelly, J.P., Parkerton, T.F., 1992. An equilibrium model of organic chemical accumulation in aquatic food webs with sediment interaction. Environ. Toxicol. Chem. 11, 615–629.

Valle-Sistac, J., Molins-Delgado, D., Díaz, M., Ibáñez, L., Barceló, D., Díaz-Cruz, M.S., 2016. Determination of parabens and benzophenone-type UV filters in human placenta: first description of the existence of benzyl paraben and benzophenone-4. Environ. Int. 88, 243–249.

Vardakas, L., Kalogianni, E., Economou, A.N., Koutsikos, N., Skoulikidis, N.T., 2017. Mass mortalities and population recovery of an endemic fish assemblage in an intermittent river reach during drying and rewetting. Fundam. Appl. Limnol. 190 (4), 331–347.

Vela-Soria, F., Jiménez-Díaz, L., Rodríguez-Gómez, R., Zafra-Gómez, A., Ballesteros, O., Navalón, A., Vilchez, J.L., Fernández, M.F., Olea, N., 2011. Determination of benzoic nitrates in human placental tissue samples by liquid chromatography–tandem mass spectrometry. Talanta 85, 1848–1855.

Villa, S., Assi, L., Ippolito, A., Bonfanti, P., Finizia, A., 2012. First evidence of the occurrence of polycyclic synthetic musk fragrances in surface water systems in Italy: spatial and temporal trends in the Molgara River (Lombardia Region, Northern Italy). Sci. Total Environ. 416, 137–141.

Watch List, 2015. Commission Implementing Decision (EU) 2015/495 of 20 March 2015 Establishing a Watch List of Substances for Union-wide Monitoring in the Field of Water Policy Pursuant to Directive 2008/105/EC of the European Parliament and of the Council.

Weiss, S., Reentsma, T., 2005. Determination of benzotriazole corrosion inhibitors from aqueous environmental samples by liquid chromatography-electrospray ionisation tandem mass spectrometry. Talanta 67, 7420–7426.