1   **Environmental Risks Associated with Legacy and Emerging Contaminants at European Aquaculture**
2   **Areas**

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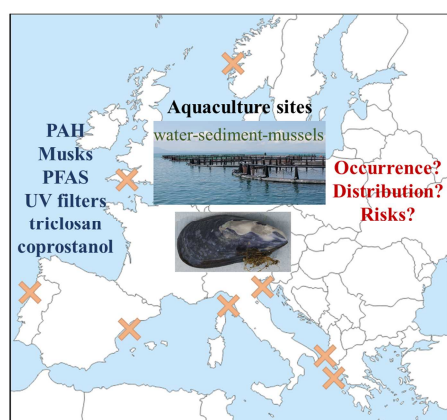20   Portugal
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27   **Graphical abstract:**

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29

30   **Abstract (214 words - max 300)**

31 The contamination of marine ecosystems by emerging contaminants such as personal care products
32 or perfluoroalkyl substances is of increasing concern. This work assessed the concentrations of
33 selected contaminants of emerging concern in European aquaculture areas, to evaluate their co-
34 variation with legacy contaminants (polycyclic aromatic hydrocarbons) and faecal biomarkers, and
35 estimate the risks associated with their occurrence. The 9 study sites were selected in 7 European
36 countries to be representative of the aquaculture activities of their region: 4 sites in the Atlantic
37 Ocean and 5 in the Mediterranean Sea. Musks, UV filters, preservatives, perfluoroalkyl substances
38 and polycyclic aromatic hydrocarbons were detected in at least one of the sites with regional
39 differences. While personal care products appear to be the main component of the water
40 contamination, polycyclic aromatic hydrocarbons were mostly found in sediments. As expected,
41 generally higher levels of personal care products were found in sewage impacted sites, urbanised
42 coasts and estuaries. The risk assessment for water and sediment revealed a potential risk for the
43 local aquatic environment from both legacy and emerging contaminants, with a significant
44 contribution of the UV filter octocrylene. Despite marginal contributions of perfluoroalkyl substances
45 to the total concentrations, PFOS (perfluorooctane sulfonate) aqueous concentrations combined to
46 its low ecotoxicity thresholds produced significant hazard quotients indicating a potential risk to the
47 ecosystems.

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51 **Highlights**

52 - 59 emerging and legacy contaminants investigated in 9 European aquaculture areas

53 - Levels of personal care products were higher in sewage impacted zones

54 - Hazard quotients revealed potential environmental risks from PAHs, PFAS and UV filters

55

56 **Keywords**

57 Aquaculture, legacy and emerging contaminants, personal care products, perfluoroalkyl substances

58

59 **1. Introduction**

60 The conservation and sustainable use of the oceans, seas and marine resources is a worldwide
61 concern identified as one of the 17 goals of the UN 2030 agenda for sustainable development. In
62 2016, the products of aquaculture and fisheries accounted for about 17 % of the global population's
63 intake of animal protein and offered means of sustainable livelihoods to 10-12 % of the world
64 population (FAO, 2016). Despite their ecological role as nursery habitats for many marine fish
65 species and their socio-economic value, coastal and estuarine environments are threatened by the
66 presence of human-produced chemicals originating from industrial, domestic and agricultural
67 applications. There are about 100,000 chemicals traded in Europe, of which about 30,000 have a
68 production volume higher than 1 t/y and have been on the market for more than 20 years.
69 Monitoring strategies for marine environments have essentially focused on the so-called legacy
70 contaminants such as organochlorine pesticides or polychlorinated biphenyls of industrial and agro-

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71 industrial origins, and polycyclic aromatic hydrocarbons (PAHs) of petrogenic and pyrolytic origins.
72 Water pollution is identified as one of the main environmental concerns of European citizens
73 (Eurobarometer, European Union, 2017), and chemicals from industrial waste are generally
74 perceived as the main cause of marine environmental contamination (Jacobs et al., 2015). However,
75 daily use chemicals such as cosmetic additives, intended for domestic, personal and hygiene use, are
76 released to the marine environment. Among fragrance compounds, galaxolide, tonalide and lilial are
77 produced or imported up to 10,000 tons per year in the EU (Table S1) and are found in coastal
78 waters (Andresen et al., 2007; Sumner et al., 2010). Tonalide and lilial are currently under extensive
79 evaluation in the EU over concerns of potential endocrine disrupting effects and high aggregated
80 tonnage (tonalide), carcinogenic and mutagenic reprotoxic suspicions (CMR), and consumer and
81 wide dispersive use (lilial). UV filters are highly produced or imported chemicals (Table S1) and have
82 been found in coastal waters, sediment and biota (Baron et al., 2013; Cunha et al., 2015; Picot Groz
83 et al., 2014). Other PCPs such as triclosan, parabens and insect repellents have raised concerns over
84 their environmental ubiquity and potential ecotoxicity (Díaz-Cruz and Barceló, 2009; Merel and
85 Snyder, 2016; Pintado-Herrera et al., 2017a). Perfluoroalkyl substances (PFAS) are also considered as
86 emerging contaminants, despite being first synthesised in the 1950's. Their surfactant and thermal
87 properties generated multiple industrial and domestic applications, such as fire-fighting foams,
88 lubricants, surfactants, pesticides, and coating additives. The unintentional releases and day-to-day
89 usages of PFAS have caused a ubiquitous contamination of ecosystems (Munoz et al., 2017a).

90 The objectives of this work were to evaluate the levels of impregnation of emerging contaminants in
91 European aquaculture areas, evaluate their co-variation with legacy contaminants (PAHs) and faecal
92 biomarkers, and estimate the risks associated with these contaminants.

93

94 2. Materials and methods

95 2.1 Sites and sampling

96 The sites of study were selected in 7 European countries in order to be representative of the
97 aquaculture activities throughout their region. Four sites are on the Atlantic Ocean and 5 in the
98 Mediterranean Sea. Full details on the sampling locations and parameters are given in Table S2,
99 Figure S1 and further information is available in a joint study on flame retardants (Aznar-Alemany et
100 al., 2018). Water (n=27), sediment (n=24) and mussel (n=17) were sampled between May and June
101 2016, and physico-chemical parameters were measured in-situ. Glass and PET bottles were used for
102 water samples, and aluminium trays for sediment and biota samples. The samples were transported
103 frozen and further stored in a freezer at -24 °C until analysis.

104 In Portugal, the mouth of the Aveiro lagoon was selected for study. Aquaculture (oysters, mussels),
105 tourism and a major harbour are the main activities of the area. The treated sewage of the whole
106 Aveiro region (325,700 population equivalent) is collected and discharged 3.3 km offshore.
107 Treatment and collection of wastewater effluents have been reported as only partial (Rada et al.,
108 2016). The three points were close to the coast, within 700 m of each other.

109 In the UK, the site is situated in the Exe estuary (south coast). Bed mussels are the main species
110 harvested. The estuary drains an estimated 300,000 inhabitants, including the city of Exeter. The
111 sampling points were in areas of commercial mussel collection, with UKS1 close to the mouth
112 estuary, 500 m from UKS2 and 2 km from UKS3, upstream in the estuary. Note that the main Exeter
113 sewage treatment plant (152,749 population-equivalent) is situated 8 km upstream.

114   Two sites on the same stretch of water were selected in Norway, a salmon farm and a bivalve
115   (mainly scallops) farm situated in the Bergen fjord, over 25 km away from Bergen. The area is not
116   densely populated, with no major pollution sources identified.

117   In Spain, the site is situated in the Ebro delta, in a semi enclosed salt water lagoon on the
118   Mediterranean coast. Longline mussels are the main species harvested. The potential pressures
119   identified relate to agriculture (rice), fishing and tourism, and to the potential pollution of the Ebro
120   catchment area. The sampling was made along the mussel lines, with point SPS1 in more open
121   water. Note that the point SPS2 is situated within 500 m of a treated waste water outfall, serving a
122   16,046-population equivalent. The points SPS1 and SPS2 are 150 m and 500 m away, respectively.

123   In Italy, the fish farm site was selected in the northern Tyrrhenian Sea, being 1.5 km offshore and
124   away from two small towns (about 40,000 inhabitants combined). The other Italian site, the Goro
125   lagoon, is situated in the northern Adriatic Sea and produces essentially clams and mussels. The local
126   town of Goro has a 3,582 population-equivalent sewage treatment plant and the lagoon receives the
127   waters of the Po River, draining the North of Italy. The point ITS1 is situated in more open waters,
128   with ITS2 and ITS3 about 2 km inside the lagoon.

129   A fish farm of North-West Greece, on the Adriatic Sea, was selected. The area has a very small
130   population (nearest town of 600 inhabitants 10 km away), with no industrial or town sewage
131   discharge, but a dozen fish farms on a 10 km stretch of coast. The point GRF1 is the closest to the
132   coast, whereas GRF3 is about 200 m offshore.

133   In Albania, the site was in the Butrint lagoon, a semi enclosed water body in a rural area of low
134   population. The lagoon is one of the 2 major mussel farming areas of the country. In 2015, the
135   nearest town of Ksamil (about 3,000 inhabitants) was reported to have septic tanks only for waste
136   water treatment (Kumar, 2015).

137   Solvent-cleaned aluminium or combusted glass containers were used to collect and store the
138   samples. They were sent frozen to the analytical laboratories by courier delivery and stored at –
139   24 °C. Sediments and mussels were freeze-dried in the analytical laboratory. Several whole mussels
140   were collected from each point and the edible content was combined and homogenised after freeze-
141   drying.

142

143   **2.2 Chemicals and reagents**

144   The selected analytes were 19 personal care products [PCPs] (tonalide, galaxolide, galaxolidone,
145   cashmeran, lilial, celestolide, phantolide, musk xylene, musk ketone, traseolide, oxybenzone,
146   octocrylene, homosalate, ethylhexylmethoxycinnamate [EHMC], 4-methyl benzylidene camphor [4-
147   MBC], triclosan, methyl paraben, propyl paraben, and N, N-diethyl-meta-toluamide [DEET]), 2 sterols
148   (coprostanol and cholesterol), 16 PAHs (naphthalene, acenaphthylene, acenaphtene, fluorene,
149   phenanthrene, anthracene, fluoranthene, pyrene, benz[*a*]anthracene, chrysene,
150   benzo[*k* + *f*]fluoranthene, benzo[*a*]pyrene, indeno[*1,2,3-c,d*]pyrene, benzo[*ghi*]perylene, and
151   dibenz[ah]anthracene) and 24 perfluoroalkyl substances (PFPA, PFHxA, PFHpA, PFOA, PFNA, PFDA,
152   PFUdA, PFDoA, PFTrA, PFTeA, PFBS, PFHxS, PFOS, PFDS, PFDoS, PFOSA, 6:2 F53B, 4:2 F53B, FOSAA,
153   me-FOSAA, et-FOSAA, 4:2 FTS, 6:2 FTS, and 8:2 FTS). 12 labelled molecules were used as internal
154   standards (Table S3)

155 All chemicals, standards and internal standards were of the highest purity commercially available
156 and purchased from QMX Laboratories (UK), Sigma-Aldrich (UK) or LGC Standards (UK). Solvents
157 were of HPLC grade and provided by Rathburn Chemicals Ltd., Walkerburn, UK. Copper powder was
158 purchased from Sigma-Aldrich (UK) and activated by using HCl 10 %. Ultra-pure water was produced
159 on-site using a Millipore Milli-Q system (specific resistivity of 18.2 MΩ cm - 25 °C).

160

161 **2.3 Extraction and analysis**

162 2.3.1 PCPs and PAHs

163 PCPs and PAHs were quantified in water and sediment (University of Plymouth, UK). Water samples
164 were defrosted overnight and spiked with the internal standard mixture. Unfiltered samples (700
165 mL) were loaded onto a pre-conditioned (5 mL methanol) and pre-equilibrated (5 mL ultrapure
166 water) Oasis HLB 200 mg cartridge (Waters, UK), at a flow rate kept at 5-10 mL/min. After loading,
167 the sorbent was washed with 5 mL of ultrapure water and dried under vacuum for 30 min. The
168 elution was performed by sequential percolation of: (1) 3 mL ethyl acetate, (2) 3 mL of ethyl
169 acetate/dichloromethane 1:1, and (3) 3 mL of dichloromethane (DCM). The eluate was evaporated
170 to near dryness under a gentle stream of nitrogen and reconstituted in 300 µL of ethyl acetate.

171 Sediment samples were freeze dried for approximately 3 days and stored in the dark at room
172 temperature. 2 g of sediment was accurately weighed, transferred to a 40-mL glass vial and spiked
173 with the internal standard mixture. The analytes were extracted by ultrasonication assisted
174 extraction with 3 times 10 mL of DCM/acetonitrile (1:1, v:v) for 3 times 10 min in a sonication bath.
175 The extracts were centrifuged for 5 min at 2,500 rpm to collect the supernatants and combined.
176 Elemental sulphur was removed by adding approximately 1 g of activated copper powder to the
177 extracts. After nitrogen evaporation down to 200 µL, 30 mL of water was added, and the extracts
178 were purified by SPE on HLB cartridges following the water extraction protocol.

179 A 100 µL aliquot of the extracts was analysed by GC-MSD (1 µL injected splitless) operated in SIM
180 mode and another 50 µL was derivatised with 20 µL BSTFA + TMCS, 99:1 (Sigma-Aldrich, UK), for 60
181 min at 70 °C to form the trimethylsilyl derivatives of: methyl paraben, propyl paraben, homosalate,
182 triclosan, oxybenzone, coprostanol and cholesterol, before analysis by GC-MSD operated in SIM
183 mode (ions in Table S3)

184

185 2.3.2 PFAS

186 PFAS were screened in water, sediment and mussels (NIVA, Norway). Internal standards were added
187 to the water sample (1 L) before extraction using a HLB solid phase extraction cartridge (Waters).
188 The analytes were eluted of the HLB with methanol. The methanol extract was evaporated under
189 nitrogen and resolved in 60/40 acetonitrile and 2.6 mM ammonium acetate (aq).

190 Sediment and biota samples were homogenized and 2 g aliquots taken. Internal standards were
191 added and the samples were shaken and sonicated for 1 hour with acetonitrile (4 mL) and then
192 centrifuged for 5 min at 3,500 rpm. The solvent was decanted off and the procedure was repeated,
193 and the two extracts were combined. One mL of the extract was diluted with 0.5 mL 5.2 mM
194 ammonium acetate (aq) and 75 µL acetic acid (cons) before active coal was added. After mixing, the
195 sample was finally centrifuged with a 0.2 µm nylon Spin-X filter (Costar).

196   PFAS analyses were performed on a UPLC-HRMS system. Separation was achieved on an Acquity BEH
197   C8 column (100 x 2 mm x 1.7 μm) with water (5.2 mM ammonium acetate) and acetonitrile mobile
198   phases using a gradient elution program over a period of 8 minutes with a flow rate of 0.5 ml/min.
199   The MS parameters are shown in Table S4.

200

201   **2.4 QA/QC**

202   Appropriate procedural and instrumental blanks were analysed within each set of analyses. For
203   compounds measured in the procedural blanks, the limits of detection and quantification were
204   calculated as 3 and 10 times, respectively, the variability of the blank average concentration (n=5).

205   In all investigated sites, the water concentrations of methyl and propyl parabens showed a
206   decreasing pattern from the 1st sampling spot to the 3rd sampling spot. This systematic behaviour
207   seemed unrelated to the actual water contamination levels when compared to the other
208   determinants and was attributed to a progressive decontamination of the sampling material during
209   sampling operations. It is noteworthy that the sampling was performed by 6 different sampling
210   teams using their own sampling material and that none of the sampling, procedural and
211   instrumental blanks revealed contamination by parabens. No contamination issues were
212   encountered in sediment.

213   Recoveries were calculated on fortified water and sediment samples (n=5) and were for PCPs and
214   PAHs 82-124 % and 80-131 % for water and sediment, respectively, and, for PFAS, 44-124 and 79-
215   103 % (Tables S2 and S3). In addition, NIST-1941b reference sediment was analysed for PAHs in
216   sediment and indicated good agreement and precision (Figure S2).

217   Analysis of the sediment total organic content was performed using an Elemental Microanalysis
218   EA1110 CHN analyser after acidification of the sediment aliquots with HCl (10 %).

219

220   **2.5 Risk assessment**

221   The concentration of contaminants measured during this survey in water and sediment (MEC) were
222   compared with threshold values to assess potential risks to the environment, following previously
223   published methodologies (Langford et al., 2015; Pintado-Herrera et al., 2017b). Predicted no effect
224   concentrations (PNEC) were used for the set of emerging contaminants when available and
225   environmental quality standards (EQS) were used for the PAHs and selected PFAS (Table S5). Hazard
226   quotients (HQ) were calculated as the ratio of the MEC to the PNEC or EQS.

227

228   **3. Results and discussions**

229   **3.1 Occurrence in water**

230   The sum of the PCPs, PAHs and PFAS is given per site in Figure 1a and Table 1.

231   3.1.1 Musks and fragrances

232   The polycyclic musk galaxolide was the most concentrated fragrance with concentrations of 5.7-6.1
233   ng/L in the Italian Goro lagoon, 5.2-10.8 ng/L in the British Exe estuary, 17-99 ng/L in the Albanian
234   lagoon and 92 ng/L in one spot of the Ebro delta site. Galaxolide's main transformation product, the

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235 lactone derivative galaxolidone, was found at generally higher levels (ratio 2:1), with matching
236 geographical trends, and up to 196 ng/L in the Ebro delta. Galaxolide sources are associated with
237 treated or partially treated waste waters and galaxolidone can be formed during waste water
238 treatment and after discharge into the environment (Lange et al., 2015). Our results suggest a
239 sewage origin, as the contaminated spot of the Ebro delta is within 500 m of a treated waste water
240 outfall and the British Exe estuary site is situated 8 km downstream of the Exeter city main waste
241 water treatment plant. The site in the Italian Goro lagoon does not appear to be in a very populated
242 area but receives the waters of the densely populated Po basin, of known historical pollution from
243 municipal wastewater discharges (Casatta et al., 2015; European Commission, 2016). Conversely, the
244 Norwegian and Greek sites, in areas of low population density, indicated limited to no
245 galaxolide/galaxolidone contamination. In the Albanian lagoon, the higher values can relate to the
246 absence of wastewater treatment in the local town (Kumar, 2015). The concentrations of galaxolide
247 reported in our study are similar to those found in British coastal waters in 2007 (Sumner et al.,
248 2010) but higher than those found in the German bight (< 5 ng/L) in the early 1990's, reported in one
249 of the first observation of musks in marine waters (Bester et al., 1998). As the nitro-musks were
250 partially phased out for persistence and toxicity, increase in the use of galaxolide as a replacement
251 compound over the past 30 years most likely accounts for this increase.

252 Within the exception of tonalide, found in one sample at 12 ng/L and matching a galaxolide
253 contaminated spot (SPS2), the other polycyclic musks celestolide, phantolide and traseolide were
254 not detected, in agreement with their lower reported use and previous reports in coastal waters
255 (Aminot et al., 2017; Sumner et al., 2010). Among nitro-musks, only musk ketone was measured at
256 low levels (<6 ng/L) in the samples also showing higher galaxolide concentrations. Nitro musks were
257 banned or substituted with polycyclic musks in the 1980's and their lower concentrations match
258 previous studies in coastal waters. Lilial, a less widely reported aromatic aldehyde fragrance, was not
259 found in any of the studied sites despite its widespread use in cosmetics (1,000 – 10,000 tonnes per
260 year in REACH; (Celeiro et al., 2015). Rapid degradation through wastewater treatment and after
261 discharge can explain our results, as it is documented as readily biodegradable according to OECD
262 criteria in the REACH chemicals database.

263

264 3.1.2 Preservatives and insect repellents

265 As previously discussed, methyl and propyl parabens results were discarded following the evidence
266 of a ubiquitous contamination occurring during sampling.

267 The antiseptic compound triclosan was quantified in 10 samples, at concentrations below 2 ng/L.
268 The highest values were found in the waters from the urbanised Exe estuary in the UK (0.4 - 1.3
269 ng/L) and close to the sewage treatment plant outfall in the Ebro delta (1.9 ng/L). In previous
270 studies, low ng/L were also measured in the Hudson river estuary (Wilson et al., 2009) whilst 1-2
271 order of magnitude higher concentrations (27-314 ng/L) were found in estuarine waters from the
272 south of Spain (Pintado-Herrera et al., 2014). With concerns over its endocrine disrupting potential
273 and its broad-spectrum antibacterial activity that has led to restrictions on its use in cosmetics in EU
274 from the beginning of 2017, under ten tonnes of triclosan per year are currently
275 imported/manufactured in the European Union (REACH). Its occurrence in sewage-impacted coastal
276 zones needs to be documented in the coming years to evaluate the environmental impact of such
277 policies.

278 The insect repellent DEET was detected in 17 out of the 27 water samples and was quantified
279 between the limit of quantification (LQ 1 ng/L) and 12.5 ng/L, confirming its reported ubiquity
280 (Merel and Snyder, 2016). Similarly to fragrance compounds, findings occurred mostly in the sewage
281 impacted spots (the British estuary Exe and one sampling location of the Spanish Ebro delta),
282 consistent with its application as a skin product and further wash-off in waste waters. In the Ebro
283 delta in particular, a high use of DEET is likely, being an area known for substantial populations of
284 mosquitoes growing in the rice fields.

285

286 3.1.3 UV filters

287 Four of the 5 monitored UV filters were found in water samples. Octocrylene had the highest
288 concentrations (median 19 ng/L), followed by homosalate (median 13 ng/L), EHMC (median 9 ng/L)
289 and 4-MBC (median 2 ng/L). Octocrylene was ubiquitous from 1.2 ng/L to 509 ng/L. The Spanish Ebro
290 delta site indicated a similar contamination profile compared to other sewage related markers, with
291 the SPS2 spot (303 ng/L) exhibiting concentrations 8 times higher than the other spots of this site.
292 The levels in the Aveiro lagoon in Portugal, ranging from 27 to 46 ng/L, were comparable to those
293 encountered in the north Italian fish-farming site (19 to 77 ng/L) and in the north Greek fish farming
294 site (24-87 ng/L). The concentrations measured in the Butrint lagoon (Albania) spanned a wider
295 range, from 19 to 509 ng/L, with no clear geographical distribution but in agreement with galaxolide
296 findings. In the Exe estuary (UK), the Norwegian fjord and the Goro lagoon (Italy), octocrylene
297 concentrations were notably lower: 4.3, 9.8 and 4.2 ng/L, respectively. EHMC and homosalate
298 showed generally similar geographical distributions to octocrylene. The camphor-based compound
299 4-MBC had lower levels and was quantified only in the Aveiro lagoon site (Portugal) and in the
300 sewage-impacted Ebro delta spot, at concentrations in the low ng/L. Interestingly, the UV filters
301 contamination hot spots do not necessarily match those of other sewage markers, in particular in
302 the Exe estuary (UK) and Goro lagoon (Italy). Previous studies have successfully correlated UV filter
303 concentrations and touristic recreational activities (Langford and Thomas, 2008; Mandaric et al.,
304 2017; Picot-Groz et al., 2018). The littoral of the Po delta is a preserved natural area where tourism is
305 limited. The south coast of the UK is a popular touristic destination in summer but the early sampling
306 period (mid-June) was likely in a period of lower sunscreen product use. Conversely, the higher
307 touristic season at the same period of time in milder southern European countries could account for
308 the higher concentrations observed in Spain, Portugal and Greece.

309

310 3.1.4 Sewage biomarker

311 Coprostanol, a sterol produced in mammalian digestive systems, is a useful marker of faecal
312 contamination for tracing sewage inputs (Readman et al., 2005; Tolosa et al., 2014). Water
313 concentrations ranged from below the limit of detection (LD) to 250 ng/L in the British estuary.
314 Waters of the Norwegian fjord (bivalves and fish culture), the Albanian lagoon (mussels) and of the
315 Italian fish farming site exhibited negligible concentrations, attributed to the lower population of the
316 studied areas or the higher distance to the shore. In the Ebro delta (Spain), the concentration at the
317 site close to the sewage discharge (SPS2 - 46 ng/L) was more than 10 times higher than those 1 to 4
318 km further (SPS1 and SPS3, respectively), indicating its situation in the plume. In the Exe estuary, the
319 concentrations were found to decrease gradually from the site UKS3 to UKS1, i.e. from the middle
320 estuary to more open seas (250 to 134 ng/L). In the Aveiro lagoon (Portugal), the concentrations
321 ranged from 12 to 33 ng/L, suggesting incomplete collection of the sewage in the offshore

322 discharging collector. Coprostanol was found in the Greek site at values between 35 and 59 ng/L,
323 indicating possible contamination by faecal material in the surrounding waters.

324

325 3.1.5 Polycyclic aromatic hydrocarbons

326 PAHs were almost only detected in the Exe estuary (UK), with values ranging from 22 to 46 ng/L as a
327 sum of the 16 PAHs. Their decreasing distribution from the inside of the estuary towards more open
328 waters is in agreement with the turbidity distribution, proxy for suspended solid concentrations (see
329 Table S2). The particulate fraction most likely accounts for these results, as PAHs are hydrophobic
330 compounds. The marginal values (0.6-1.2 ng/L as the sum of the PAHs) measured in the Aveiro
331 lagoon (Portugal) can relate to the surrounding harbour and industrial area. High sum of the PAHs in
332 Spanish samples is due to the light naphthalene and acenaphthylene, attributed to a local oil spill.

333

334 3.1.6 Perfluoroalkyl substances

335 Out of the 24 monitored PFAS, 7 legacy PFAS were found at least once above their LD (between 0.1
336 and 0.4 ng/L depending on the compounds) with total concentrations as high as 25-30 ng/L in the
337 Goro lagoon in the Po delta. In this site, PFBS was the dominant compound (17-19 ng/L) followed by
338 PFPA and PFOA (both at 3-4 ng/L), whilst PFHxA, PFHpA, PFHxS and PFOS were in the low ng/L.
339 Alternative PFAS such as 6:2 FTS, FOSAA or the PFOS replacement 6:2 F53B were not found in any
340 sample. The Exe estuary (UK) and the sewage-impacted spot in the Ebro delta had summed
341 concentrations of 4-8 and 1.6 ng/L, respectively. PFOS was the dominant compound in the Exe
342 estuary (UK) and had notable levels in the Goro lagoon (Italy), Aveiro lagoon (Portugal) and
343 Norwegian fjord fish farm site.

344 The molecular profile observed in the water was generally in good agreement with previous reports,
345 with a predominance of short to medium perfluoroalkyl chain-length compounds such as PFHxA,
346 PFOA, PFBS and PFOS (Pignotti et al., 2017). Unusually high level of PFBS in the water such as those
347 measured consistently in the Po delta (16-21 times higher than PFOS in all 3 samples) have been
348 previously attributed to local industrial point sources, such as in the Rhine River (Kwadijk et al.,
349 2010) or in Shanghai surface waters (Sun et al., 2018). The higher turbidity measured in the British
350 Exe estuary and the high affinity of PFOS to suspended particles (Munoz et al., 2017b) accounted for
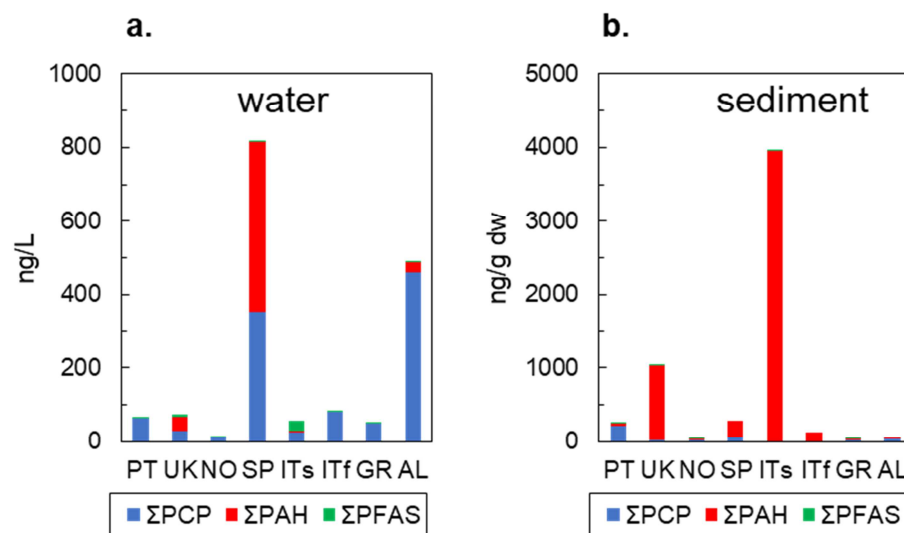351 the relative prevalence of PFOS in this hydrosystem.

352

353

354 Figure 1. Water and sediment concentrations of PCPs, PAHs and PFAS (average of the site 3 sampling
355 spots).

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357

Musks	LD ng/L	LQ ng/L	PTS1	PTS2	PTS3	UKS1	UKS2	UKS3	NOF1	NOF2	NOF3	NOS1	NOS2	NOS3	SPS1	SPS2	SPS3	ITS1	ITS2	ITS3	ITF1	ITF2	ITF3	GRF1	GRF2	GRF3	ALS1	ALS2	ALS3
galaxolide	1.1	3.7	<LD	<LD	<LD	10.8	<LQ	5.2	<LQ	<LD	<LQ	<LD	<LD	<LD	<LD	92.0	<LD	6.1	5.8	5.7	<LD	4.2	<LQ	<LQ	<LQ	<LD	16.7	<LD	98.9
galaxolidone	0.2	0.7	3.6	9.3	6.3	8.0	9.8	7.1	0.8	<LD	<LD	<LD	<LD	<LD	1.5	196.2	1.0	11.6	11.4	12.5	0.8	1.3	1.0	2.0	1.9	1.6	3.9	<LD	13.6
tonalide	1.2	3.8	<LD	<LQ	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	12.0	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LQ
celestolide	0.1	0.2	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LQ
phantolide	0.1	0.2	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD
traseolide	0.1	0.4	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD
musk xylene	0.9	2.7	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD
musk ketone	0.1	0.4	0.5	0.4	0.4	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	6.2	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	0.9	<LD	3.3
lilial	2.0	6.7	<LD	<LD	<LD	<LQ	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	8.8	<LD	24.1	<LD	<LD	<LD	<LQ	<LD	<LD	<LD	<LD	<LD	<LD	<LD	114.9
UV filters																													
homosalate	1.9	6.4	12.5	<LQ	<LQ	<LQ	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	18.2	14.1	7.3	<LD	<LD	<LD	<LD	<LQ	<LQ	<LD	<LQ	<LQ	10.5	<LD	14.9
oxybenzone	6.0	19.8	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD
EHMC	0.4	1.4	11.8	3.6	3.4	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	1.6	<LD	<LD	<LD	<LD	49.4	8.6	24.2	9.3	<LD	<LD	125.9	6.0	17.6
4MBC	0.3	1.0	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	2.2	<LD	1.1	4.4	2.3	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD
octocrylene	0.2	0.7	45.8	29.1	27.4	4.3	4.8	3.8	3.3	4.7	4.3	42.2	1.6	2.3	38.4	303.5	46.0	1.2	7.7	3.5	77.5	18.6	53.7	23.8	86.6	10.4	509.0	18.5	107.0
Other PCPs																													
methyl paraben	*0.5*	*1.6*	*21.6*	*12.8*	*5.9*	*9.7*	*5.4*	*<LQ*	*476.3*	*287.0*	*49.8*	*86.6*	*62.4*	*38.3*	*28.5*	*11.4*	*3.4*	*<LD*	*<LQ*	*<LD*	*<LQ*	*<LQ*	*1.6*	*1.6*	*1.7*	*1.6*	*18.4*	*4.7*	*7.9*
propyl paraben	*0.3*	*0.9*	*<LQ*	*1.4*	*<LQ*	*6.6*	*3.1*	*2.4*	*1.6*	*0.9*	*<LQ*	*2.2*	*<LD*	*<LQ*	*8.3*	*4.1*	*1.9*	*1.0*	*<LQ*	*<LD*	*2.0*	*1.3*	*0.9*	*3.8*	*3.3*	*2.4*	*14.3*	*4.6*	*4.1*
triclosan	0.1	0.4	1.3	1.0	1.8	0.9	1.3	0.4	<LD	<LD	<LD	<LD	<LD	<LD	<LD	1.9	<LD	<LQ	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	0.5	0.7	0.4
DEET	0.3	1.0	<LQ	1.2	<LQ	7.8	9.2	10.8	<LQ	<LQ	<LD	<LD	<LD	<LD	<LQ	12.5	<LD	2.2	1.7	2.2	<LQ	<LQ	<LQ	<LD	<LD	<LD	<LD	<LD	3.7
ΣPCPs	-	-	75.6	44.6	39.3	31.8	25.0	27.4	4.2	4.7	4.3	42.2	1.6	2.3	66.9	642.4	78.4	22.2	31.1	26.2	127.7	32.6	78.9	35.1	88.6	12.0	667.4	25.3	374.4
Faecal biomarkers																													
coprostanol	0.5	1.6	11.7	29.4	33.0	134.2	170.1	250.0	2.2	2.4	<LD	5.6	<LD	1.9	3.1	46.2	4.0	13.1	11.1	10.1	3.4	<LD	<LD	59.0	37.9	35.2	2.0	1.6	6.4
cholesterol	14.6	48.1	6543.6	4987.9	5240.6	4301.5	6382.0	6735.3	2175.9	2116.5	2691.0	6692.6	1122.8	2250.5	3300.3	9394.0	5544.2	3918.5	3773.1	2474.7	1477.6	3782.9	816.9	4581.3	7425.3	4322.7	5246.5	2946.4	7792.2
Polycyclic Aromatic Hydrocarbons																													
naphthalene	14.9	49.6	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	65.5	<LD	229.1	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD
acenaphthylene	0.2	0.7	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	240.1	12.0	636.9	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD
acenaphthene	1.2	3.8	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LQ	<LQ	15.3	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD
fluorene	0.6	2.0	<LD	<LD	<LD	<LQ	<LD	<LQ	<LD	<LD	<LQ	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LQ
phenanthrene	0.8	2.8	<LD	<LQ	<LD	<LQ	<LD	<LQ	<LD	<LD	<LD	<LD	<LD	<LD	<LQ	<LD	<LQ	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	5.6	3.1
anthracene	0.1	0.3	<LD	<LQ	<LQ	0.7	0.9	0.8	<LD	<LD	<LD	<LD	<LD	<LQ	0.4	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	0.5	<LQ
fluoranthene	0.1	0.2	0.2	0.7	0.3	2.4	3.8	4.1	<LQ	<LD	<LD	<LD	<LD	<LQ	0.3	<LQ	<LD	0.5	<LQ	<LD	<LQ	<LD	<LQ	<LQ	<LD	<LQ	<LQ	18.9	0.5
pyrene	0.1	0.2	0.3	0.4	0.4	1.9	3.6	3.8	<LD	<LD	<LD	<LD	<LD	<LD	<LQ	<LQ	<LD	0.5	<LQ	<LD	<LQ	<LD	<LD	<LD	<LD	<LD	<LD	5.8	0.5
Benz[a]anthracene	0.1	0.3	<LD	<LD	<LD	1.0	1.9	2.2	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD
chrysene	0.0	0.1	0.2	0.1	0.1	0.9	1.8	2.0	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	0.1	0.1	<LQ	<LD	<LD	<LD	<LD	<LD	<LD	<LD	4.9	0.1
Benzo[b]fluoranthene	0.0	0.1	<LD	<LD	<LD	3.7	8.0	7.4	<LD	<LD	<LD	<LD	<LD	<LD	0.2	0.1	<LD	<LD	<LD	<LD	<LQ	<LD	<LD	<LD	<LD	<LD	<LD	5.4	0.2
Benzo[k]fluoranthene	0.1	0.2	<LD	<LD	<LD	1.4	3.1	3.3	<LD	<LD	<LD	<LD	<LD	<LD	<LQ	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	1.5	<LD
Benzo[a]pyrene	0.0	0.1	<LQ	<LQ	<LQ	2.3	4.6	5.0	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	0.3	<LD
indeno[1,2,3-c,d]pyrene	0.2	0.5	<LD	<LD	<LD	3.5	6.5	8.1	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	0.7	<LD
Dibenz[a,h]anthracene	0.2	0.7	<LD	<LD	<LD	0.6	0.9	1.2	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LQ
Benzo[ghi]perylene	0.3	1.0	<LQ	<LD	<LD	3.7	5.8	8.4	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LQ	<LD
ΣPAHs	-	-	0.6	1.2	0.8	22.1	40.9	46.4	-	-	-	-	-	-	306.4	12.1	881.4	1.1	0.1	-	-	-	-	-	-	-	-	-	43.6	4.3
Perfluoroalkyl substances																													
PFPA	0.1	0.4	<LD	<LD	<LD	<LD	0.9	0.9	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	3.5	3.1	4	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD
PFHxA	0.1	0.4	<LD	<LD	<LD	<LD	0.4	0.4	<LD	<LD	<LD	<LD	<LD	<LD	<LD	0.4	<LD	1.3	1.1	1.3	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD
PFHpA	0.1	0.4	<LD	<LD	<LD	<LD	0.4	0.4	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	0.7	0.6	0.7	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD
PFOA	0.1	0.4	<LD	<LD	<LD	<LD	0.9	0.8	<LD	0.5	<LD	0.5	1.7	<LD	0.6	0.6	0.8	3.8	2.9	3.3	<LD	<LD	1	<LD	<LD	<LD	<LD	<LD	<LD
PFNA	0.1	0.4	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD
PFDA	0.1	0.4	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD
PFUdA	0.1	0.4	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD
PFDoA	0.1	0.4	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD
PFTrA	0.1	0.4	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD
PFTeA	0.1	0.4	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD
PFBS	0.1	0.2	<0.1	<0.1	<0.1	<0.1	0.3	0.3	0.1	0.1	0.2	0.2	0.1	0.1	0.1	0.2	0.2	17.4	16.5	19	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.4	0.3	0.4

PFHxS	0.1	0.2	<LD	<LD	<LD	<LD	0.3	0.2	<LD	<LD	<LD	<LD	<LD	<LD	<LD	0.1	<LD	0.3	0.3	0.3	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD
PFOS	0.1	0.2	0.1	0.3	0.4	4.3	5.2	0.9	0.1	0.1	0.1	0.3	0.2	0.2	0.1	0.3	0.1	1.1	0.8	1.2	0.1	<LD	0.1	0.1	0.1	0.1	<LD	<LD	0.1
PFDS	0.1	0.2	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD
PFDoS	0.1	0.2	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD
PFOSA	0.1	0.2	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD
6:2 F53B	0.1	0.3	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD
4:2 F53B	0.1	0.3	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD
FOSAA	0.1	0.3	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD
me-FOSAA	0.1	0.3	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD
et-FOSAA	0.1	0.3	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD
4:2 FTS	0.1	0.3	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD
6:2 FTS	0.1	0.3	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD
8:2 FTS	0.1	0.3	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD
ΣPFAS	-	-	0.1	0.3	0.4	4.3	8.4	3.9	0.2	0.7	0.3	1	2	0.3	0.8	1.6	1.1	28.1	25.3	29.8	0.1	-	1.1	0.1	0.1	0.1	0.4	0.3	0.5

Table 1. PCPs, PAHs and PFAS in water (ng/L). For methyl and propyl paraben: refer to the discussion in the QA/QC section of material and methods. The sums of the PCPs exclude parabens.

3.2 Occurrence in sediment

The sum of the PCPs, PAHs and PFAS is given per site in Figure 1b and Table S6.

3.2.1 Musks and fragrance

Galaxolide was detected in 18 of the 24 sediments, with quantifiable levels in the Aveiro lagoon (4-8.5 ng/g dw) and in one Norwegian fjord sediment sample (4.6 ng/g dw). With lower LD/LQ, its degradation product galaxolidone was detected in 23 out of 24 samples at levels between 0.9 and 16.3 ng/g dw. The Aveiro lagoon also showed the highest galaxolidone, whilst the Goro lagoon, the Exe estuary, the Ebro delta and the Norwegian fjord had low ng/g dw levels. Among other musks, tonalide had detectable but not quantifiable levels in 15 sampling spots and phantolide was found at 0.6-0.8 ng/g dw in the Ebro delta (Spain) and Exe estuary (UK). This geographical distribution is in agreement with the higher sewage pressure in the Po delta and Exe estuary, as observed in water samples. Among other fragrances, only musk ketone was detected below LOQ in Aveiro lagoon (Portugal) and in one of the Goro lagoon (Po delta, Italy) sites.

3.2.2 Preservatives and insect repellents

The parabens were not found above quantification levels in any sample. Triclosan was detected in 9 samples from sites with other sewage related markers (Ebro delta, Exe estuary, Goro lagoon, Aveiro lagoon), and was quantified at 2 ng/g dw in one sample of the Exe estuary and one of the Goro lagoon. In a previous study of Goro lagoon, similar concentrations of triclosan (1.1 – 2.0 ng/g dw) were found in the fine fraction (< 63 μm) of sediments sampled in 2010 (Casatta et al., 2015). The insect repellent DEET was quantified in the Aveiro lagoon at concentration between 0.9 and 2 ng/g dw and in the sewage impacted spot of the Ebro delta at 4.4 ng/g dw, where the DEET water concentration was also the highest.

3.2.3 UV filters

Among UV filters, octocrylene was found with the highest concentrations, with up to 128 ng/g dw in the Ebro delta sediment collected 500 m from the sewage outfall whilst the other spots had levels one order of magnitude lower (12-15 ng/g dw). Concentrations in the Aveiro lagoon were between 12 and 34 ng/g dw, with the lower concentrations at the spot of low organic carbon percentage. Octocrylene was also measured in one sediment from the Butrint lagoon in Albania at 39 ng/g dw and in one sediment of the North Greek fish farm close to the shore facilities, at 24 ng/g dw, consistent with the higher water concentration. Lower levels of octocrylene (13 ng/g dw) were found in the Exe estuary (UK), with one positive detection in the sediment sample of highest organic carbon percentage (inside of the estuary). Its presence in this northern and less touristic area is attributed to the use of octocrylene not only in sunscreens but in numerous cosmetic products such as hair spray or face creams (Díaz-Cruz and

Barceló, 2009; Jamey et al., 2012). In recent years, octocrylene has emerged as a new persistent and bioaccumulative pollutant, with measurements in coastal areas in water, sediment and biota (Amine et al., 2012; Gago-Ferrero et al., 2013; Langford et al., 2015; Picot Groz et al., 2014), whilst its toxicity is still largely unknown.

Oxybenzone was quantified in 2 samples from the Aveiro lagoon (7 ng/g dw) and from the Ebro delta (11 ng/g dw), 4-MBC was found in 2 samples of the Aveiro lagoon (2.9-3.4 ng/g dw), EHMC and homosalate in the Aveiro lagoon (10-27 and 109-168 ng/g dw, respectively) and in one sample of the Norwegian fjord fish farm (3 and 19 ng/g dw, respectively). In previous work, EHMC was detected in sediments from the fjord of Oslo between 8.5 and 19.6 ng/g dw and in sediments from the Lebanese coast at 9 ng/g dw, whilst oxybenzone was not detected in sediments from Oslo fjord (Amine et al., 2012; Langford et al., 2015).

The Aveiro lagoon appears to be a hot spot of UV filter contamination in sediments essentially, most likely with regards to its touristic activity. The collection and discharge of Aveiro's sewage 3.3 km offshore was realised in the past years. This would reduce the water contamination rapidly, but sediment contamination, if not irreversible, can be much slower (Belles et al., 2017; Mizukawa et al., 2017), so the levels measured here probably reflect contamination from past inputs.

3.2.4 Sewage biomarker

Coprostanol was detected in 20 out of 24 sediments, at concentrations from 32 ng/g dw (LQ) to 4,300 ng/g dw. The fish farm in Greece had the highest values, consistently with our findings in the water. In the Ebro delta, the concentrations were between 61 and 280 ng/g dw, with the spot situated nearby the sewage outfall having the lowest value. This is likely related to the nature of the sediment, i.e. visibly sandier and with a lower organic carbon content (Table S2). After normalisation of the sediment concentration by its organic carbon percentage, the concentration distribution of this site followed the one observed for water, with a notably higher impact of faecal matter near the sewage discharge point. In the Exe estuary (UK), the sediment coprostanol concentrations spanned 2 orders of magnitude, with up to 1,300 ng/g dw in the higher estuary and below LD in the site near the estuary mouth. This latter sample was very sandy, with a low organic carbon percentage of 0.02 %. There were similar discrepancies in the sediment organic carbon of the Goro lagoon (Italy), where the most open-water spot showed no quantifiable amounts of coprostanol. In the Aveiro lagoon, coprostanol concentrations were relatively low, between 140 and 167 ng/g dw and in agreement with the values found in a previous study on faecal sterols in the area (Rada et al., 2016).

Negligible amounts of coprostanol in the Butrint lagoon (Albania) and in the Norwegian fjord sediments reflected the absence of sewage contamination, with only one sediment sample having high organic carbon (9 %, NOS3) showed low quantifiable coprostanol (38 ng/g dw).

The coprostanol to cholesterol ratio is commonly used to evaluate threshold levels of contamination in sediments, where coprostanol/cholesterol values >0.2 are considered sewage contaminated sediments and values >1 are considered highly contaminated (Readman et al.,

2005). In our study, all values are <0.15, apart from 2 sediments from the Greek fish farm, with values of 0.26 and 0.28. According to these criteria, the 9 European aquaculture areas studied have low to moderate faecal matter contamination.

3.2.5 Polycyclic aromatic hydrocarbons

The PAHs levels indicated very contrasting contamination between sites. The Ebro delta and the Goro lagoon had moderate contamination, with total PAHs of 173-281 and 114-188 ng/g dw, respectively (note that in each site a sample of much lower organic carbon content had non-detectable PAHs levels). The Exe estuary (UK) and the Italian fish farm site of the North Tyrrhenian Sea exhibited higher concentrations of the summed PAHs, up to an order of magnitude higher, of 457-1,463 and 1,272-5,539 ng/g dw, respectively, while the other sites had marginal contamination levels, i.e. below 50 ng/g dw. These discrepancies do not apparently relate to the nature of the sediment as they remained after normalisation to the organic carbon percentage. In both the Exe estuary and the Italian fish farm sites, 4-ring PAHs were predominant, but the lower-to-higher molecular weight PAHs ratio (sum of the 2-3 ring PAHs divided by the sum of the 4-6 ring PAHs) indicated a higher proportion of lower molecular weight PAHs in the Italian sediment. The PAHs isomer molecular ratios were not dissimilar between samples and suggested mainly combustion-derived PAHs at both sites. PAHs are historical hydrophobic pollutants, widely dispersed in the environment, resulting from the combustion of coal, wood, oil, etc. Mainly formed in urban and industrial environments, they bind to suspended particles and are washed off to the coast through rivers. Their occurrence in the Exe estuary is attributed mainly to the discharges and runoff from the upstream city of Exeter, together with the high suspended particle concentrations of these estuarine waters. The origin of the high PAHs load in the Italian fish farm sample remains unknown.

3.2.6 Perfluoroalkyl substances

Among the 24 monitored compounds, only PFOS (legacy) and 6:2FTS (emerging) were found at low levels, 0.05-0.14 and 0.4-1.8 ng/g dw, respectively. In good agreement with the water findings, PFOS was quantified in the Goro lagoon (Italy), the Exe estuary (UK), the Aveiro lagoon (Portugal) and the Norwegian fjord fish farm. It is worth noting that the Norwegian shellfish farm, located in the same water body within less than 1 km had no detectable PFOS in sediment and also lower levels in water. Further research would be required to investigate if fish farming, through the nets, cages or feed, can introduce PFAS in the environment. The emerging PFAS compound 6:2 FTS was found in 2 Portuguese and one Greek sediment, with no evident factors to account for it.

3.3 Perfluoroalkyl substances in mussels

In the mussel tissues, only 2 of the 24 monitored PFAS were found at least once (Table S7). The legacy PFAS compound PFOS was measured at 0.14 – 0.18 ng/g dw in the mussels of the 3 sites

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of the Po delta. Trace levels of PFOSA (0.1 – 0.3 ng/g dw) were also measured in the mussels of the Po delta, of the British Exe estuary and of the Norwegian coast. Despite the evidence of a higher contamination of the Po delta waters, no PFBS or perfluoroalkyl carboxylates were found in the mussel tissues. Similarly, although predominant in the waters of the British Exe estuary, PFOS was not found above detection limits. The low bioaccumulation potential of mussels for PFAS has been identified in previous work (Gómez et al., 2011). Only PFOS was found above detection limits in a recent monitoring study of the French coast bivalves (Munschy et al., 2013) and the levels of the sites selected in our study are in agreement with the low range of their reported concentrations. PFOSA, a precursor of PFOS, was also measured in bivalves of a temperate estuary at concentrations slightly higher, 0.45–0.85 ng/g dw (Munoz et al., 2017a). The authors suggested that the lower metabolic capacity of filter-feeding bivalves for PFOSA could explain its incomplete conversion to PFOS and its bioaccumulation in the tissues.

3.4 Environmental risk assessment

Hazard quotients (HQ) are given in Figure 2 and Table S8. PFOS, octocrylene, benzo[*a*]pyrene, benzo[*ghi*]perylene and fluoranthene had a HQ >1 in respectively 12, 12, 4, 3 and 1 waters of the 27 sites when considering annual average quality standards (AA-EQS). PFOS low EQS was based on evidence for biomagnification to consider toxicity to predators through secondary poisoning and to human health via consumption of fishery products. The long-term toxicity of the UV filter octocrylene to aquatic invertebrates observed at relatively low levels (NOEC of 2.66 µg/L on daphnia reproduction - octocrylene registration dossier, ECHA 2019) was used to extrapolate a marine PNEC of 27 ng/L using an assessment factor of 100. The derivation of the low AA-EQS for benzo(ghi)perylene relates to its reprotoxicity on a species of zooplankton and a further assessment factor of 100.

In sediment, benzo[*ghi*]perylene, benzo[*a*]pyrene, anthracene, EHMC, homosalate and oxybenzone had a HQ >1 in respectively 6, 4, 4, 3, 3 and 2 sediments of the 24 studied sites. The low PNEC for the UV filters EHMC and homosalate are derived from a toxicity study on snails (Kaiser et al., 2012) and QSAR studies (Pintado-Herrera et al., 2017b). In the case of oxybenzone, PNEC for both water and sediment are strict due to an assessment factor (uncertainty factor) of 10,000, associated with an EC50-72h of the test substance to a species of microalgae of 0.67 mg/L. There are no EQS or PNEC available for PFOS in sediment, quantified in 6 sediment samples. Another 2 musks (galaxolide and musk ketone), 2 UV filters (4-MBC and EHMC), 2 PAHs (naphthalene and benzo[*b*]pyrene) and the PFAS PFOA were found to have a HQ between 0.1 and 1 in at least one water sample.

Assuming an additive model, the HQ in water of all compounds were summed in each site to allow for their comparison (Figure S3). When considering their contribution to the total HQ, PAHs, PFOS and the UV filter octocrylene appear to be responsible for virtually all environmental risks. The UK estuarine site showed the highest risk (HQ between 48 and 75), with PAHs and PFAS accounting for 56 and 44 % of the total HQ, respectively, followed by a site in Albania (HQ of 19) and the site situated downstream of a domestic effluent discharge in the Ebro delta (HQ of 14), where the UV filter octocrylene contributed for 99.5 % and 79 % of the total HQ,

respectively. In the Po delta, PFOS accounted for 99 % of the total HQ, between 6 and 9. The lack of information available on the environmental effects of other PCPs can explain their lower contribution to the risk, as further evidence for biomagnification for example would have a strong influence on the EQS (PFOS case). This simple approach also does not account for potential synergistic interactions between chemicals, known to occur for as little as 3 constituents (Molins-Delgado et al., 2016; Moore et al., 2018).

The potential risk for the local aquatic environment from both legacy (PAHs) and emerging contaminants (PFOS, UV filters) raises concerns over the sustainable use of coastal areas for aquaculture. Our results indicate that exposure to harmful chemicals is higher on sites set on anthropised coastlines. In addition to threatening the ecosystems, compounds such as PFOS, musks or UV filters can accumulate in the farmed species (Cunha et al., 2015; Munschy et al., 2013) and threaten food safety (Justino et al., 2016). Interestingly, the occurrence of contaminants originating from domestic use confirms that coastal pollution is not restricted to industrial activities, the usual public perception of marine environmental contamination (Jacobs et al., 2015).
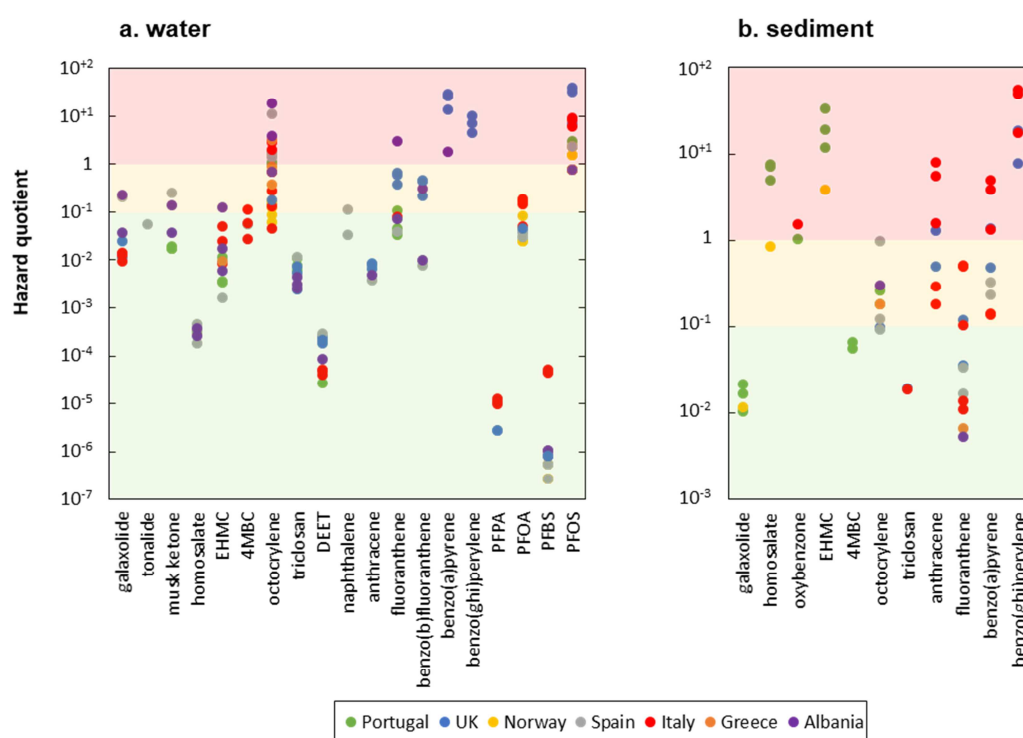
Figure 2. Hazard quotients of the detected compounds for which PNEC or EQS were available.

4 Conclusions

Compounds from personal care products, polycyclic aromatic hydrocarbons and perfluoroalkyl substances, were detected in the 27 sites investigated in 7 European countries. PCPs appear to be the main component of the water contamination in most sites, with marginal contributions from PFAS. Generally higher levels of PCPs were found in the sewage impacted sites, as showed by the co-varying coprostanol concentrations. UV filters appear to have higher concentrations in the southern European sites in comparison to the UK and Norway sites, in connection with coastal tourism. PAHs were the main component of the sediment contamination in most sites, in particular in the British and Italian sites. The Aveiro lagoon in Portugal appears to be a hot spot of UV filter contamination in sediment, most likely with regards to its tourist load. Sediment contamination does not necessarily pose a threat to marine organisms but as an integrative environmental compartment, it reflects the hydrophobic contamination to which biota is exposed.

The risk assessment for water and sediment indicated a potential risk for the local aquatic environment from both legacy (PAHs) and emerging (PFOS, UV filter octocrylene) contaminants. The implications for the ecosystem and the aquaculture activities would require further investigation. This risk assessment was based on EQS and PNEC values, available in the literature for less than a third of the investigated compounds. These ecotoxicological thresholds can be determined by *in-silico* approaches using large uncertainty factors (typically 10,000) and undergo regular revisions accounting for new scientific evidences, which can drastically change the hazard quotients determined here (e.g. case of PFOS potential for biomagnification). Future research should focus on the refinement of these thresholds, especially in the context of complex mixtures.

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