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

3

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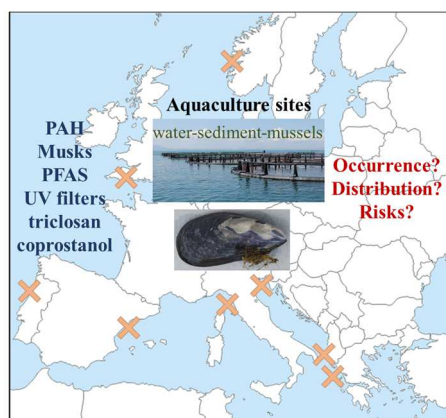
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31 **Abstract (214 words - max 300)**

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

49

50

51

52 **Highlights**

- 53 - 59 **contaminants of legacy and emerging concern** searched in 9 European aquaculture areas
- 54 - Levels of personal care products were higher in sewage impacted zones
- 55 - Hazard quotients revealed potential environmental risks from PAHs, PFAS and UV filters

56

57 **Keywords**

58 Aquaculture, **contaminants of legacy and emerging concern**, personal care products, per- and
59 polyfluoroalkyl substances

60

61 **1. Introduction**

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

72 agro-industrial origins, and polycyclic aromatic hydrocarbons (PAHs) of petrogenic and pyrolytic
73 origins. Water pollution is identified as one of the main environmental concerns of European citizens
74 (Eurobarometer, European Union, 2017), and chemicals from industrial waste are generally
75 perceived as the main cause of marine environmental contamination (Jacobs et al., 2015). However,
76 daily use chemicals such as **additives of personal care products (PCPs)**, are released to the marine
77 environment. Among fragrance compounds, galaxolide, tonalide and lilyal are produced or imported
78 up to 10,000 tons per year in the EU (Table S1) and are found in coastal waters (Andresen et al.,
79 2007; Sumner et al., 2010). UV filters are highly produced or imported chemicals (Table S1) and have
80 been found in coastal waters, sediment and biota (Baron et al., 2013; Cunha et al., 2015; Picot Groz
81 et al., 2014). **Other PCPs such as triclosan, parabens and insect repellents have raised concerns over
82 their environmental ubiquity and potential ecotoxicity as endocrine disruptors (Díaz-Cruz and
83 Barceló, 2009; Merel and Snyder, 2016; Pintado-Herrera et al., 2017a). Contamination of triclosan
84 and paraben in coastal areas and in particular aquaculture shellfish was found in South-East China,
85 most likely originating from pharmaceuticals, foodstuffs, and PCPs via wastewater discharges (Lu et
86 al., 2019). Per- and polyfluoroalkyl substances (PFASs) are also considered as **contaminants of
87 emerging concern**, despite being first synthesised in the **late 1940's**. Their surfactant and thermal
88 properties generated multiple industrial and domestic applications, such as fire-fighting foams,
89 lubricants, surfactants, pesticides, and coating additives. The unintentional releases and day-to-day
90 usages of PFAS have caused a ubiquitous contamination of ecosystems (Munoz et al., 2017a).
91 **Perfluorooctane sulfonate (PFOS) and long-chain perfluorocarboxylic acids (PFCAs) were found in
92 coastal marine shellfish (Munsch et al., 2019), which is of high concern since diet and particularly
93 seafood are major sources of PFAS in humans (Haug et al., 2010).****

94 **The aim of this work was to assess the quality of environments used to farm various seafood, with a
95 focus on wastewater derived contaminants of emerging concern originating from the surrounding
96 environments. The specific objectives were to: (1) evaluate the levels of impregnation of
97 contaminants of emerging concern in European aquaculture areas, (2) evaluate their co-variation
98 with legacy contaminants (PAHs) and faecal biomarkers, and (3) estimate the environmental risks
99 associated with these contaminants.**

100

101 **2. Materials and methods**

102 **2.1 Sites and sampling**

103 The sites of study were selected in 7 European countries in order to be representative of the
104 aquaculture activities throughout their region. Four sites are on the Atlantic Ocean and 5 in the
105 Mediterranean Sea, **and 3 spots were sampled in each site**. Full details on the sampling locations and
106 parameters are given in Table S2, Figure S1 and further information is available in a joint study on
107 flame retardants (Aznar-Alemany et al., 2018). Water (n=27), sediment (n=24) and mussel (n=17)
108 were sampled between May and June 2016, and physico-chemical parameters were measured in-
109 situ. **Water grab samples were preferred to integrative sampling for which no consensus method is
110 yet available for most of the contaminants of emerging concern targeted**. Glass and PET bottles were
111 used for water samples, and aluminium trays for sediment and biota samples. The samples were
112 transported frozen and further stored in a freezer at -24 °C until analysis.

113 In Portugal, the mouth of the Aveiro lagoon was selected for study. Aquaculture (oysters, mussels),
114 tourism and a major harbour are the main activities of the area. The treated sewage of the whole
115 Aveiro region (325,700 population equivalent) is collected and discharged 3.3 km offshore.

116 Treatment and collection of wastewater effluents have been reported as only partial (Rada et al.,
117 2016). The three points were close to the coast, within 700 m of each other.

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

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

126 In Spain, the site is situated in the Ebro delta, in a semi enclosed salt water lagoon on the
127 Mediterranean coast. Longline mussels are the main species harvested. The potential pressures
128 identified relate to agriculture (rice), fishing and tourism, and to the potential pollution of the Ebro
129 catchment area. The sampling was made along the mussel lines, with point SPS1 in more open
130 water. Note that the point SPS2 is situated within 500 m of a treated waste water outfall, serving a
131 16,046-population equivalent. The points SPS1 and SPS2 are 150 m and 500 m away, respectively.

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

138 A fish farm of **NW** Greece, on the Adriatic Sea, was selected. The area has a very small population
139 (nearest town of 600 inhabitants 10 km away), with no industrial or town sewage discharge, but a
140 dozen fish farms on a 10 km stretch of coast. The point GRF1 is the closest to the coast, whereas
141 GRF3 is about 200 m offshore.

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

146 Solvent-cleaned aluminium or combusted glass containers were used to collect and store the
147 samples. They were sent frozen to the analytical laboratories by courier delivery and stored at –
148 24 °C. Sediments and mussels were freeze-dried in the analytical laboratory. Several whole mussels
149 were collected from each point and the edible content was combined and homogenised after freeze-
150 drying.

151

152 **2.2 Chemicals and reagents**

153 The selected analytes were 19 PCPs (tonalide, galaxolide, galaxolidone, cashmeran, lillial, celestolide,
154 phantolide, musk xylene, musk ketone, traseolide, oxybenzone, octocrylene, homosalate,
155 ethylhexylmethoxycinnamate [EHMC], 4-methyl benzylidene camphor [4-MBC], triclosan, methyl
156 paraben, propyl paraben, and N, N-diethyl-meta-toluamide [DEET]), 2 sterols (coprostanol and
157 cholesterol), 16 PAHs (naphthalene, acenaphthylene, acenaphtene, fluorene, phenanthrene,

158 anthracene, fluoranthene, pyrene, benz[*a*]anthracene, chrysene, benzo[*k* + *f*]fluoranthene,
159 benzo[*a*]pyrene, indeno[1,2,3-*c,d*]pyrene, benzo[*ghi*]perylene, and dibenz[*ah*]anthracene) and 24
160 PFASs (PFPA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUDA, PFDoA, PFTrA, PFTeA, PFBS, PFHxS, PFOS,
161 PFDS, PFDoS, PFOSA, 6:2 F53B, 4:2 F53B, FOSAA, me-FOSAA, et-FOSAA, 4:2 FTS, 6:2 FTS, and 8:2
162 FTS). 12 labelled molecules were used as internal standards (Table S3)

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

168

169 **2.3 Extraction and analysis**

170 **2.3.1 PCPs and PAHs**

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

179 Sediment samples were freeze dried for approximately 3 days and stored in the dark at room
180 temperature. 2 g of sediment was accurately weighed, transferred to a 40-mL glass vial and spiked
181 with the internal standard mixture. **The analytes were extracted in a sonication bath with 10 mL of**
182 **DCM/acetonitrile (1:1, v:v) for 10 min, repeated 3 times.** The extracts were centrifuged for 5 min at
183 2,500 rpm to collect the supernatants and combined. Elemental sulphur was removed by adding
184 approximately 1 g of activated copper powder to the extracts. After nitrogen evaporation down to
185 200 µL, 30 mL of water was added, and the extracts were purified by SPE on HLB cartridges following
186 the water extraction protocol.

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

192

193 **2.3.2 PFASs**

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

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

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

208

209 **2.4 QA/QC**

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

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

221 **Accuracies calculated on fortified seawater samples (33.4 PSU, n=5) were 82-124 % and 44-124 % for**
222 **PCPs/PAHs and PFAS, respectively; and on sediment samples (0.7 % organic content, n=5) 80-131 %**
223 **and 79-103 % for PCPs/PAHs and PFAS, respectively (Tables S2 and S3).** In addition, NIST-1941b
224 reference sediment was analysed for PAHs in sediment and indicated good agreement and precision
225 (Figure S2).

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

228

229 **2.5 Risk assessment**

230 The concentration of contaminants measured during this survey in water and sediment (MEC) were
231 compared with threshold values to assess potential risks to the environment, following previously
232 published methodologies (Langford et al., 2015; Pintado-Herrera et al., 2017b). Predicted no effect
233 concentrations (PNEC) were used for the set of contaminants of emerging concern when available
234 and environmental quality standards (EQS) were used for the PAHs and selected PFAS (Table S5).
235 Hazard quotients (HQ) were calculated as the ratio of the MEC to the PNEC or EQS. **Because**
236 **potential tidal, daily or seasonal variations in water concentrations were not studied, the HQs were**
237 **determined from grab sample-derived MECs and may exhibit some variability.**

238

239 **3. Results and discussions**

240 **3.1 Occurrence in water**

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

242 3.1.1 Musks and fragrances

243 The polycyclic musk galaxolide was the most concentrated fragrance with concentrations of 5.7-6.1
244 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
245 lagoon and 92 ng/L in one spot of the Ebro delta site. Galaxolide's main transformation product, the
246 lactone derivative galaxolidone, was found at generally higher levels (ratio 2:1), with matching
247 geographical trends, and up to 196 ng/L in the Ebro delta. Galaxolide sources are associated with
248 treated or partially treated waste waters and galaxolidone can be formed during waste water
249 treatment and after discharge into the environment (Lange et al., 2015). Our results suggest a
250 sewage origin, as the contaminated spot of the Ebro delta is within 500 m of a treated waste water
251 outfall and the British Exe estuary site is situated 8 km downstream of the Exeter city main waste
252 water treatment plant. The site in the Italian Goro lagoon does not appear to be in a very populated
253 area but receives the waters of the densely populated Po basin, of known historical pollution from
254 municipal wastewater discharges (Casatta et al., 2015; European Commission, 2016). Conversely, the
255 Norwegian and Greek sites, in areas of low population density, indicated limited to no
256 galaxolide/galaxolidone contamination. In the Albanian lagoon, the higher values can relate to the
257 absence of wastewater treatment in the local town (Kumar, 2015). The concentrations of galaxolide
258 reported in our study are similar to those found in British coastal waters in 2007 (Sumner et al.,
259 2010) but higher than those found in the German bight (< 5 ng/L) in the early 1990's, reported in one
260 of the first observation of musks in marine waters (Bester et al., 1998). As the nitro-musks were
261 partially phased out for persistence and toxicity, increase in the use of galaxolide as a replacement
262 compound over the past 30 years most likely accounts for this increase.

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

274

275 3.1.2 Preservatives and insect repellents

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

278 The antiseptic compound triclosan was quantified in 10 samples, at concentrations below 2 ng/L.
279 The highest values were found in the waters from the urbanised Exe estuary in the UK (0.4 - 1.3
280 ng/L) and close to the sewage treatment plant outfall in the Ebro delta (1.9 ng/L). In previous

281 studies, low ng/L were also measured in the Hudson river estuary (Wilson et al., 2009) whilst 1-2
282 order of magnitude higher concentrations (27-314 ng/L) were found in estuarine waters from the
283 south of Spain (Pintado-Herrera et al., 2014). With concerns over its endocrine disrupting potential
284 and its broad-spectrum antibacterial activity that has led to restrictions on its use in cosmetics in EU
285 from the beginning of 2017, under ten tonnes of triclosan per year are currently
286 imported/manufactured in the European Union (REACH). Its occurrence in sewage-impacted coastal
287 zones needs to be documented in the coming years to evaluate the environmental impact of such
288 policies.

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

296

297 3.1.3 UV filters

298 Four of the 5 monitored UV filters were found in water samples. Octocrylene had the highest
299 concentrations (median 19 ng/L), followed by homosalate (median 13 ng/L), EHMC (median 9 ng/L)
300 and 4-MBC (median 2 ng/L). Octocrylene was ubiquitous from 1.2 ng/L to 509 ng/L. The Spanish Ebro
301 delta site indicated a similar contamination profile compared to other sewage related markers, with
302 the SPS2 spot (303 ng/L) exhibiting concentrations 8 times higher than the other spots of this site.
303 The levels in the Aveiro lagoon in Portugal, ranging from 27 to 46 ng/L, **were in agreement with**
304 **findings of another study of this site (Gadelha et al., 2019)** and comparable to those encountered in
305 the north Italian fish-farming site (19 to 77 ng/L) and in the north Greek fish farming site (24-87
306 ng/L). The concentrations measured in the Butrint lagoon (Albania) spanned a wider range, from 19
307 to 509 ng/L, with no clear geographical distribution but in agreement with galaxolide findings. In the
308 Exe estuary (UK), the Norwegian fjord and the Goro lagoon (Italy), octocrylene concentrations were
309 notably lower: 4.3, 9.8 and 4.2 ng/L, respectively. EHMC and homosalate showed generally similar
310 geographical distributions to octocrylene. The camphor-based compound 4-MBC had lower levels
311 and was quantified only in the Aveiro lagoon site (Portugal) and in the sewage-impacted Ebro delta
312 spot, at concentrations in the low ng/L. Interestingly, the UV filters contamination hot spots do not
313 necessarily match those of other sewage markers, in particular in the Exe estuary (UK) and Goro
314 lagoon (Italy). Previous studies have successfully correlated UV filter concentrations and touristic
315 recreational activities (Langford and Thomas, 2008; Mandaric et al., 2017; Picot-Groz et al., 2018).
316 The littoral of the Po delta is a preserved natural area where tourism is limited. The south coast of
317 the UK is a popular touristic destination in summer but the early sampling period (mid-June) was
318 likely in a period of lower sunscreen product use. Conversely, the higher touristic season at the same
319 period of time in milder southern European countries could account for the higher concentrations
320 observed in Spain, Portugal and Greece. **Use and occurrence of UV filters is seasonal (Gadelha et al.,**
321 **2019) and it is worth noting that a comprehensive understanding of their variability in the**
322 **environment would require long-term monitoring, in conjunction with alternative integrative**
323 **sampling techniques.**

324

325 3.1.4 Sewage biomarker

326 Coprostanol, a sterol produced in mammalian digestive systems, is a useful marker of faecal
327 contamination for tracing sewage inputs (Readman et al., 2005; Tolosa et al., 2014). Water
328 concentrations ranged from below the limit of detection (LD) to 250 ng/L in the British estuary.
329 Waters of the Norwegian fjord (bivalves and fish culture), the Albanian lagoon (mussels) and of the
330 Italian fish farming site exhibited negligible concentrations, attributed to the lower population of the
331 studied areas or the higher distance to the shore. In the Ebro delta (Spain), the concentration at the
332 site close to the sewage discharge (SPS2 - 46 ng/L) was more than 10 times higher than those 1 to 4
333 km further (SPS1 and SPS3, respectively), indicating its situation in the plume. In the Exe estuary, the
334 concentrations were found to decrease gradually from the site UKS3 to UKS1, i.e. from the middle
335 estuary to more open seas (250 to 134 ng/L). In the Aveiro lagoon (Portugal), the concentrations
336 ranged from 12 to 33 ng/L, suggesting incomplete collection of the sewage in the offshore
337 discharging collector. Coprostanol was found in the Greek site at values between 35 and 59 ng/L,
338 indicating possible contamination by faecal material in the surrounding waters.

339

340 3.1.5 PAHs

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

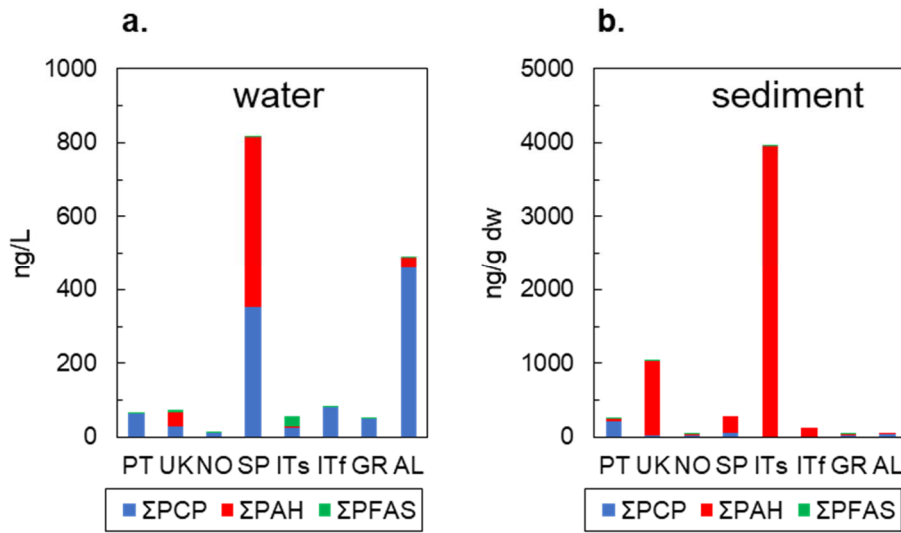
348

349 3.1.6 PFASs

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

359 The molecular profile observed in the water was generally in good agreement with previous reports,
360 with a predominance of short to medium perfluoroalkyl chain-length compounds such as PFHxA,
361 PFOA, PFBS and PFOS (Pignotti et al., 2017). Unusually high level of PFBS in the water such as those
362 measured consistently in the Po delta (16-21 times higher than PFOS in all 3 samples) have been
363 previously attributed to local industrial point sources, such as in the Rhine River (Kwadijk et al.,
364 2010) or in Shanghai surface waters (Sun et al., 2018). The higher turbidity measured in the British
365 Exe estuary and the high affinity of PFOS to suspended particles (Munoz et al., 2017b) accounted for
366 the relative prevalence of PFOS in this hydrosystem.

367



368

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

371

372

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	0.1	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.

358 **3.2 Occurrence in sediment**

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

360

361 3.2.1 Musks and fragrance

362 Galaxolide was detected in 18 of the 24 sediments, with quantifiable levels in the Aveiro lagoon
363 (4-8.5 ng/g dw) and in one Norwegian fjord sediment sample (4.6 ng/g dw). With lower LD/LQ,
364 its degradation product galaxolidone was detected in 23 out of 24 samples at levels between 0.9
365 and 16.3 ng/g dw. The Aveiro lagoon also showed the highest galaxolidone, whilst the Goro
366 lagoon, the Exe estuary, the Ebro delta and the Norwegian fjord had low ng/g dw levels. Among
367 other musks, tonalide had detectable but not quantifiable levels in 15 sampling spots and
368 phantolide was found at 0.6-0.8 ng/g dw in the Ebro delta (Spain) and Exe estuary (UK). This
369 geographical distribution is in agreement with the higher sewage pressure in the Po delta and
370 Exe estuary, as observed in water samples. Among other fragrances, only musk ketone was
371 detected below LOQ in Aveiro lagoon (Portugal) and in one of the Goro lagoon (Po delta, Italy)
372 sites.

373

374 3.2.2 Preservatives and insect repellents

375 The parabens were not found above quantification levels in any sample. Triclosan was detected
376 in 9 samples from sites with other sewage related markers (Ebro delta, Exe estuary, Goro
377 lagoon, Aveiro lagoon), and was quantified at 2 ng/g dw in one sample of the Exe estuary and
378 one of the Goro lagoon. In a previous study of Goro lagoon, similar concentrations of triclosan
379 (1.1 – 2.0 ng/g dw) were found in the fine fraction (< 63 µm) of sediments sampled in 2010
380 (Casatta et al., 2015). The insect repellent DEET was quantified in the Aveiro lagoon at
381 concentration between 0.9 and 2 ng/g dw and in the sewage impacted spot of the Ebro delta at
382 4.4 ng/g dw, where the DEET water concentration was also the highest.

383

384 3.2.3 UV filters

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

396 Barceló, 2009; Jamey et al., 2012). In recent years, octocrylene has emerged as a new persistent
397 and bioaccumulative pollutant, with measurements in coastal areas in water, sediment and
398 biota (Amine et al., 2012; Gago-Ferrero et al., 2013; Langford et al., 2015; Picot Groz et al.,
399 2014), whilst its toxicity is still largely unknown.

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

407 The Aveiro lagoon appears to be a hot spot of UV filter contamination in sediments essentially,
408 most likely with regards to its touristic activity. The collection and discharge of Aveiro's sewage
409 3.3 km offshore was realised in the past years. This would reduce the water contamination
410 rapidly, but sediment contamination, if not irreversible, can be much slower (Belles et al., 2017;
411 Mizukawa et al., 2017), so the levels measured here probably reflect contamination from past
412 inputs.

413

414 3.2.4 Sewage biomarker

415 Coprostanol was detected in 20 out of 24 sediments, at concentrations from 32 ng/g dw (LQ) to
416 4,300 ng/g dw. The fish farm in Greece had the highest values, consistently with our findings in
417 the water. In the Ebro delta, the concentrations were between 61 and 280 ng/g dw, with the
418 spot situated nearby the sewage outfall having the lowest value. This is likely related to the
419 nature of the sediment, i.e. visibly sandier and with a lower organic carbon content (Table S2).
420 After normalisation of the sediment concentration by its organic carbon percentage, the
421 concentration distribution of this site followed the one observed for water, with a notably
422 higher impact of faecal matter near the sewage discharge point. In the Exe estuary (UK), the
423 sediment coprostanol concentrations spanned 2 orders of magnitude, with up to 1,300 ng/g dw
424 in the higher estuary and below LD in the site near the estuary mouth. This latter sample was
425 very sandy, with a low organic carbon percentage of 0.02 %. There were similar discrepancies in
426 the sediment organic carbon of the Goro lagoon (Italy), where the most open-water spot
427 showed no quantifiable amounts of coprostanol. In the Aveiro lagoon, coprostanol
428 concentrations were relatively low, between 140 and 167 ng/g dw and in agreement with the
429 values found in a previous study on faecal sterols in the area (Rada et al., 2016).

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

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

436 2005). In our study, all values are <0.15, apart from 2 sediments from the Greek fish farm, with
437 values of 0.26 and 0.28. According to these criteria, the 9 European aquaculture areas studied
438 have low to moderate faecal matter contamination.

439

440 3.2.5 PAHs

441 The PAHs levels indicated very contrasting contamination between sites. The Ebro delta and the
442 Goro lagoon had moderate contamination, with total PAHs of 173-281 and 114-188 ng/g dw,
443 respectively (note that in each site a sample of much lower organic carbon content had non-
444 detectable PAHs levels). **This result in the Goro lagoon falls within the range of total PAHs (104-
445 572 ng/g dw) found in the Northern Adriatic Sea sediments under influence of the Po river
446 discharge in a previous study (Combi et al., 2016).** The Exe estuary (UK) and the Italian fish farm
447 site of the North Tyrrhenian Sea exhibited higher concentrations of the summed PAHs, up to an
448 order of magnitude higher, of 457-1,463 and 1,272-5,539 ng/g dw, respectively, while the other
449 sites had marginal contamination levels, i.e. below 50 ng/g dw. These discrepancies do not
450 apparently relate to the nature of the sediment as they remained after normalisation to the
451 organic carbon percentage. In both the Exe estuary and the Italian fish farm sites, 4-ring PAHs
452 were predominant, but the lower-to-higher molecular weight PAHs ratio (sum of the 2-3 ring
453 PAHs divided by the sum of the 4-6 ring PAHs) indicated a higher proportion of lower molecular
454 weight PAHs in the Italian sediment **of the Tyrrhenian Sea**. The PAHs isomer molecular ratios
455 were not dissimilar between samples and suggested mainly combustion-derived PAHs at both
456 sites. PAHs are historical hydrophobic pollutants, widely dispersed in the environment, resulting
457 from the combustion of coal, wood, oil, etc. Mainly formed in urban and industrial
458 environments, they bind to suspended particles and are washed off to the coast through rivers.
459 Their occurrence in the Exe estuary is attributed mainly to the discharges and runoff from the
460 upstream city of Exeter, together with the high suspended particle concentrations of these
461 estuarine waters. **PAHs were found at the same orders of magnitude in an earlier study of the
462 Exe estuary (Herrmann and Hübner, 1982), indicating limited decontamination of this site over
463 the past 35 years.** The origin of the high PAHs load in the Italian fish farm sample remains
464 unknown.

465

466 3.2.6 PFASs

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

476

477 **3.3 PFASs in mussels**

478 In the mussel tissues, only 2 of the 24 monitored PFAS were found at least once (Table S7). The
479 legacy PFAS compound PFOS was measured at 0.14 – 0.18 ng/g dw in the mussels of the 3 sites
480 of the Po delta. Trace levels of PFOSA (0.1 – 0.3 ng/g dw) were also measured in the mussels of
481 the Po delta, of the British Exe estuary and of the Norwegian coast. Despite the evidence of a
482 higher contamination of the Po delta waters, no PFBS or PFCA were found in the mussel tissues.
483 Similarly, although predominant in the waters of the British Exe estuary, PFOS was not found
484 above detection limits. The low bioaccumulation potential of mussels for PFAS has been
485 identified in previous work (Gómez et al., 2011). Only PFOS was found above detection limits in
486 a recent monitoring study of the French coast bivalves (Munsch et al., 2013) and the levels of
487 the sites selected in our study are in agreement with the low range of their reported
488 concentrations. PFOSA, a precursor of PFOS, was also measured in bivalves of a temperate
489 estuary at concentrations slightly higher, 0.45–0.85 ng/g dw (Munoz et al., 2017a). The authors
490 suggested that the lower metabolic capacity of filter-feeding bivalves for PFOSA could explain its
491 incomplete conversion to PFOS and its bioaccumulation in the tissues.

492

493 **3.4 Environmental risk assessment**

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

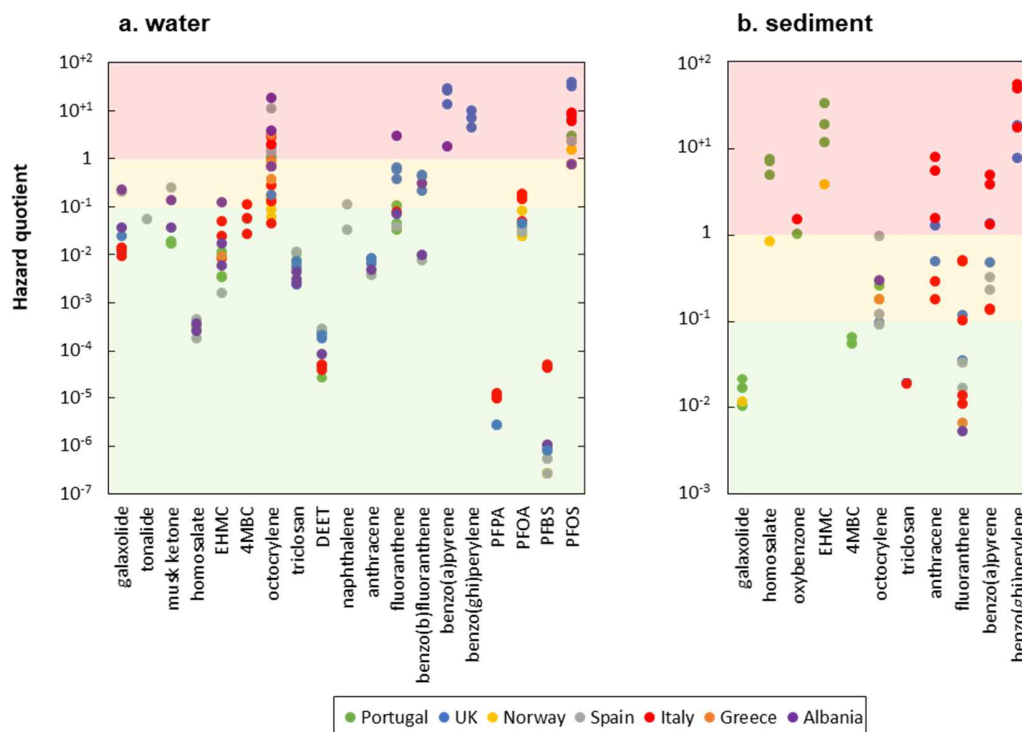
504 In sediment, benzo[*ghi*]perylene, benzo[*a*]pyrene, anthracene, EHMC, homosalate and
505 oxybenzone had a HQ >1 in respectively 6, 4, 4, 3, 3 and 2 sediments of the 24 studied sites. The
506 low PNEC for the UV filters EHMC and homosalate are derived from a toxicity study on snails
507 (Kaiser et al., 2012) and QSAR studies (Pintado-Herrera et al., 2017b). In the case of oxybenzone,
508 PNEC for both water and sediment are strict due to an assessment factor (uncertainty factor) of
509 10,000, associated with an EC50-72h of the test substance to a species of microalgae of 0.67
510 mg/L. There are no EQS or PNEC available for PFOS in sediment, quantified in 6 sediment
511 samples. Another 2 musks (galaxolide and musk ketone), 2 UV filters (4-MBC and EHMC), 2 PAHs
512 (naphthalene and benzo[*b*]pyrene) and the PFAS PFOA were found to have a HQ between 0.1
513 and 1 in at least one water sample.

514 Assuming an additive model, the HQ in water of all compounds were summed in each site to
515 allow for their comparison (Figure S3). When considering their contribution to the total HQ,

516 PAHs, PFOS and the UV filter octocrylene appear to be responsible for virtually all environmental
 517 risks. The UK estuarine site showed the highest risk (HQ between 48 and 75), with PAHs and
 518 PFAS accounting for 56 and 44 % of the total HQ, respectively, followed by a site in Albania (HQ
 519 of 19) and the site situated downstream of a domestic effluent discharge in the Ebro delta (HQ
 520 of 14), where the UV filter octocrylene contributed for 99.5 % and 79 % of the total HQ,
 521 respectively. In the Po delta, PFOS accounted for 99 % of the total HQ, between 6 and 9. The
 522 lack of information available on the environmental effects of other PCPs can explain their lower
 523 contribution to the risk, as further evidence for biomagnification for example would have a
 524 strong influence on the EQS (PFOS case). This simple approach also does not account for
 525 potential synergistic interactions between chemicals, known to occur for as little as 3
 526 constituents (Molins-Delgado et al., 2016; Moore et al., 2018).

527 The potential risk for the local aquatic environment from **contaminants of both legacy (PAHs)**
 528 **and emerging concern** (PFOS, UV filters) raises concerns over the sustainable use of coastal
 529 areas for aquaculture. Our results indicate that exposure to harmful chemicals is higher on sites
 530 set on anthropised coastlines. In addition to threatening the ecosystems, compounds such as
 531 PFOS, musks or UV filters can accumulate in the farmed species (Cunha et al., 2015; Munsch et
 532 al., 2013) and threaten food safety (Justino et al., 2016). Interestingly, the occurrence of
 533 contaminants originating from domestic use confirms that coastal pollution is not restricted to
 534 industrial activities, the usual public perception of marine environmental contamination (Jacobs
 535 et al., 2015).

536



537

538 Figure 2. HQ of the detected compounds for which PNEC or EQS were available.

539

540

541 **4 Conclusions**

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

553 The risk assessment for water and sediment indicated a potential risk for the local aquatic
554 environment from **contaminants of both legacy (PAHs) and emerging (PFOS, UV filter**
555 **octocrylene) concern**. The implications for the ecosystem and the aquaculture activities would
556 require further investigation. This risk assessment was based on EQS and PNEC values, available
557 in the literature for less than a third of the investigated compounds. These ecotoxicological
558 thresholds can be determined by *in-silico* approaches using large uncertainty factors (typically
559 10,000) and undergo regular revisions accounting for new scientific evidences, which can
560 drastically change the HQ determined here (e.g. case of PFOS potential for biomagnification).
561 Future research should focus on the refinement of these thresholds, especially in the context of
562 complex mixtures.

563

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568

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