



## Environmental risks associated with contaminants of legacy and emerging concern at European aquaculture areas<sup>☆</sup>

Yann Aminot<sup>a, b, \*</sup>, Stephen J. Sayfritz<sup>c</sup>, Kevin V. Thomas<sup>c, d</sup>, Lia Godinho<sup>e</sup>, Elena Botteon<sup>f, g</sup>, Federico Ferrari<sup>f</sup>, Vasiliki Boti<sup>h</sup>, Triantafyllos Albanis<sup>h</sup>, Marianne Köck-Schulmeyer<sup>i</sup>, M. Silvia Diaz-Cruz<sup>i</sup>, Marinella Farré<sup>i</sup>, Damià Barceló<sup>i</sup>, António Marques<sup>e, j</sup>, James W. Readman<sup>a, k</sup>

<sup>a</sup> Biogeochemistry Research Centre, University of Plymouth, Plymouth, United Kingdom

<sup>b</sup> IFREMER LBCO, Rue de l'Île d'Yeu, BP 21105, 44311, Nantes, Cedex 3, France

<sup>c</sup> Norwegian Institute for Water Research (NIVA), Gaustadalléen 21, 0349, Oslo, Norway

<sup>d</sup> QAEHS, Queensland Alliance for Environmental Health Science, The University of Queensland, Brisbane, Australia

<sup>e</sup> Division of Aquaculture and Upgrading (DivAV), Portuguese Institute for the Sea and Atmosphere (IPMA, I.P.), Avenida de Brasília, 1449-006, Lisbon, Portugal

<sup>f</sup> Aeiforia Srl, Località Faggiola 12-16, 29027, Gariga, Podenzano, PC, Italy

<sup>g</sup> Di.S.T.A.S., Università Cattolica del Sacro Cuore, Piacenza, Italy

<sup>h</sup> Department of Chemistry, University of Ioannina, Panepistimioupolis, 45110, Ioannina, Greece

<sup>i</sup> Institute of Environmental Assessment and Water Research, Department of Environmental Chemistry (IDAEA-CSIC), Jordi Girona, 18, 08034, Barcelona, Spain

<sup>j</sup> Interdisciplinary Centre of Marine and Environmental Research (CIIMAR), University of Porto, Porto, Portugal

<sup>k</sup> Plymouth Marine Laboratory, Prospect Place, the Hoe, Plymouth, PL1 3DH, United Kingdom

### ARTICLE INFO

#### Article history:

Received 11 March 2019

Received in revised form

17 May 2019

Accepted 26 May 2019

Available online 29 May 2019

#### Keywords:

Aquaculture

Contaminants of legacy and emerging concern

Personal care products

Per- and polyfluoroalkyl substances

### ABSTRACT

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

© 2019 Elsevier Ltd. All rights reserved.

### 1. Introduction

The conservation and sustainable use of the oceans, seas and marine resources is a worldwide concern identified as one of the 17 goals of the UN 2030 agenda for sustainable development. In 2016, the products of aquaculture and fisheries accounted for about 17% of the global population's intake of animal protein and offered

<sup>☆</sup> This paper has been recommended for acceptance by Christian Sonne

\* Corresponding author. Biogeochemistry Research Centre, University of Plymouth, Plymouth, United Kingdom.

E-mail address: [yann.aminot@ifremer.fr](mailto:yann.aminot@ifremer.fr) (Y. Aminot).

means of sustainable livelihoods to 10–12% of the world population (FAO, 2016). However, the coastal and estuarine environments supporting aquaculture are threatened by the presence of human-produced chemicals originating from industrial, domestic and agricultural applications. There are about 100,000 chemicals traded in Europe, of which about 30,000 have a production volume higher than 1 t/y and have been on the market for more than 20 years. Monitoring strategies for marine environments have essentially focused on the so-called legacy contaminants such as organochlorine pesticides or polychlorinated biphenyls of industrial and agro-industrial origins, and polycyclic aromatic hydrocarbons (PAHs) of petrogenic and pyrolytic origins. Water pollution is identified as one of the main environmental concerns of European citizens (Eurobarometer, European Union, 2017), and chemicals from industrial waste are generally perceived as the main cause of marine environmental contamination (Jacobs et al., 2015). However, daily use chemicals such as additives of personal care products (PCPs), are released to the marine environment. Among fragrance compounds, galaxolide, tonalide and lialil are produced or imported up to 10,000 tons per year in the EU (Table S1) and are found in coastal waters (Andresen et al., 2007; Sumner et al., 2010). UV filters are highly produced or imported chemicals (Table S1) and have been found in coastal waters, sediment and biota (Baron et al., 2013; Cunha et al., 2015; Picot Groz et al., 2014). Other PCPs such as triclosan, parabens and insect repellents have raised concerns over their environmental ubiquity and potential ecotoxicity as endocrine disruptors (Díaz-Cruz and Barceló, 2009; Merel and Snyder, 2016; Pintado-Herrera et al., 2017a). Contamination of triclosan and paraben in coastal areas and in particular aquaculture shellfish was found in South-East China, most likely originating from pharmaceuticals, foodstuffs, and PCPs via wastewater discharges (Lu et al., 2019). Per- and polyfluoroalkyl substances (PFASs) are also considered as contaminants of emerging concern, despite being first synthesised in the late 1940's. Their surfactant and thermal properties generated multiple industrial and domestic applications, such as fire-fighting foams, lubricants, surfactants, pesticides, and coating additives. The unintentional releases and day-to-day usages of PFAS have caused a ubiquitous contamination of ecosystems (Munoz et al., 2017a). Perfluorooctane sulfonate (PFOS) and long-chain perfluorocarboxylic acids (PFCAs) were found in coastal marine shellfish (Munschy et al., 2019), which is of high concern since diet and particularly seafood are major sources of PFAS in humans (Haug et al., 2010).

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

## 2. Materials and methods

### 2.1. Sites and sampling

The sites of study were selected in 7 European countries in order to be representative of the aquaculture activities throughout their region. Four sites are on the Atlantic Ocean and 5 in the Mediterranean Sea, and 3 spots were sampled in each site. Full details on the sampling locations and parameters are given in Table S2, Fig. S1 and further information is available in a joint study on flame retardants (Aznar-Alemany et al., 2018). Water ( $n = 27$ ), sediment ( $n = 24$ ) and mussel ( $n = 17$ ) were sampled between May and June

2016, and physico-chemical parameters were measured in-situ. Water grab samples were preferred to integrative sampling for which no consensus method is yet available for most of the contaminants of emerging concern targeted. Glass and PET bottles were used for water samples, and aluminium trays for sediment and biota samples. The samples were transported frozen and further stored in a freezer at  $-24^{\circ}\text{C}$  until analysis.

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

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

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

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

In Italy, the fish farm site was selected in the northern Tyrrhenian Sea, being 1.5 km offshore and away from two small towns (about 40,000 inhabitants combined). The other Italian site, the Goro lagoon, is situated in the northern Adriatic Sea and produces essentially clams and mussels. The local town of Goro has a 3582 population-equivalent sewage treatment plant and the lagoon receives the waters of the Po River basin, draining the North of Italy. The point ITS1 is situated in more open waters, with ITS2 and ITS3 about 2 km inside the lagoon.

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

In Albania, the site was in the Butrint lagoon, a semi enclosed water body in a rural area of low population. The lagoon is one of the 2 major mussel farming areas of the country. In 2015, the nearest town of Ksamil (about 3000 inhabitants) was reported to have septic tanks only for waste water treatment (Kumar, 2015).

Solvent-cleaned aluminium or combusted glass containers were used to collect and store the samples. They were sent frozen to the analytical laboratories by courier delivery and stored at  $-24^{\circ}\text{C}$ . Sediments and mussels were freeze-dried in the analytical laboratory. Several whole mussels were collected from each point and the edible content was combined and homogenised after freeze-drying.

### 2.2. Chemicals and reagents

The selected analytes were 19 PCPs (tonalide, galaxolide,

galaxolidone, cashmeran, lialial, celestolide, phantolide, musk xylene, musk ketone, traseolide, oxybenzone, octocrylene, homosalate, ethylhexylmethoxycinnamate [EHMC], 4-methyl benzylidene camphor [4-MBC], triclosan, methyl paraben, propyl paraben, and N, N-diethyl-meta-toluamide [DEET]), 2 sterols (coprostanol and cholesterol), 16 PAHs (naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benz[a]anthracene, chrysene, benzo[k + f]fluoranthene, benzo[a]pyrene, indeno[1,2,3-c,d]pyrene, benzo[ghi]perylene, and dibenz[ah]anthracene) and 24 PFASs (PFPA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUdA, PFDaA, PFTra, PFTeA, PFBS, PFHxS, PFOS, PFDS, PFDoS, PFOSA, 6:2 F53B, 4:2 F53B, FOSAA, me-FOSAA, et-FOSAA, 4:2 FTS, 6:2 FTS, and 8:2 FTS). 12 labelled molecules were used as internal standards (Table S3).

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

### 2.3. Extraction and analysis

#### 2.3.1. PCPs and PAHs

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

Sediment samples were freeze dried for approximately 3 days and stored in the dark at room temperature. 2 g of sediment was accurately weighed, transferred to a 40-mL glass vial and spiked with the internal standard mixture. The analytes were extracted in a sonication bath with 10 mL of DCM/acetonitrile (1:1, v:v) for 10 min, repeated 3 times. The extracts were centrifuged for 5 min at 2500 rpm to collect the supernatants and combined. Elemental sulphur was removed by adding approximately 1 g of activated copper powder to the extracts. After nitrogen evaporation down to 200 µL, 30 mL of water was added, and the extracts were purified by SPE on HLB cartridges following the water extraction protocol.

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

#### 2.3.2. PFASs

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

Sediment and biota samples were homogenized and 2 g aliquots

taken. Internal standards were added and the samples were shaken and sonicated for 1 h with acetonitrile (4 mL) and then centrifuged for 5 min at 3500 rpm. The solvent was decanted off and the procedure was repeated, and the two extracts were combined. One mL of the extract was diluted with 0.5 mL 5.2 mM ammonium acetate (aq) and 75 µL acetic acid (cons) before active coal was added. After mixing, the sample was finally centrifuged with a 0.2 µm nylon Spin-X filter (Costar).

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

### 2.4. QA/QC

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

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

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

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

### 2.5. Risk assessment

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

## 3. Results and discussions

### 3.1. Occurrence in water

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

### 3.1.1. Musks and fragrances

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

Within the exception of tonalide, found in one sample at 12 ng/L and matching a galaxolide contaminated spot (SPS2), the other polycyclic musks celestolide, phantolide and traseolide were not detected, in agreement with their lower reported use and previous reports in coastal waters (Aminot et al., 2017; Sumner et al., 2010). Among nitro-musks, only musk ketone was measured at low levels (<6 ng/L) in the samples also showing higher galaxolide concentrations. Nitro musks were banned or substituted with polycyclic musks in the 1980's and their lower concentrations match previous studies in coastal waters. Lilial, a less widely reported aromatic aldehyde fragrance, was not found in any of the studied sites despite its widespread use in cosmetics (1000–10,000 tonnes per

year in REACH; (Celeiro et al., 2015). Rapid degradation through wastewater treatment and after discharge can explain our results, as it is documented as readily biodegradable according to OECD criteria in the REACH chemicals database.

### 3.1.2. Preservatives and insect repellents

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

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

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

### 3.1.3. UV filters

Four of the 5 monitored UV filters were found in water samples. Octocrylene had the highest concentrations (median 19 ng/L), followed by homosalate (median 13 ng/L), EHMC (median 9 ng/L) and 4-MBC (median 2 ng/L). Octocrylene was ubiquitous from 1.2 ng/L to 509 ng/L. The Spanish Ebro delta site indicated a similar contamination profile compared to other sewage related markers, with the SPS2 spot (303 ng/L) exhibiting concentrations 8 times

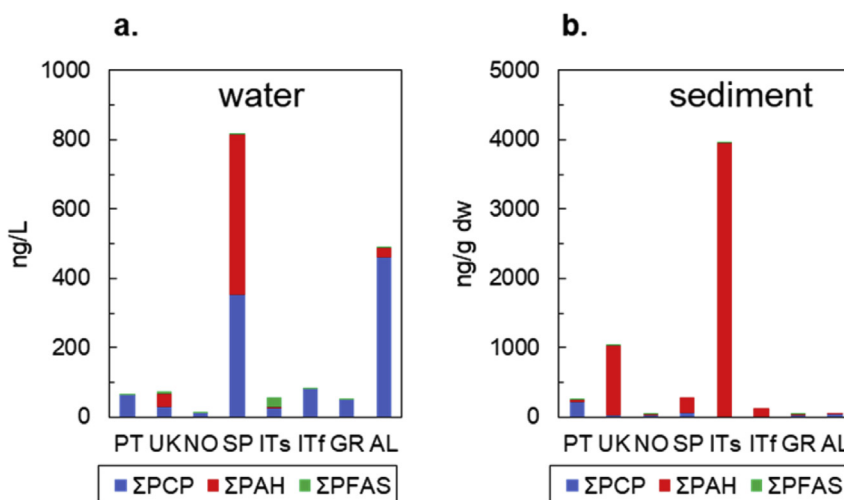


Fig. 1. Water and sediment concentrations of PCPs, PAHs and PFAS (average of the site 3 sampling spots).



higher than the other spots of this site. The levels in the Aveiro lagoon in Portugal, ranging from 27 to 46 ng/L, were in agreement with findings of another study of this site (Gadelha et al., 2019) and comparable to those encountered in the north Italian fish-farming site (19–77 ng/L) and in the north Greek fish farming site (24–87 ng/L). The concentrations measured in the Butrint lagoon (Albania) spanned a wider range, from 19 to 509 ng/L, with no clear geographical distribution but in agreement with galaxolide findings. In the Exe estuary (UK), the Norwegian fjord and the Goro lagoon (Italy), octocrylene concentrations were notably lower: 4.3, 9.8 and 4.2 ng/L, respectively. EHMC and homosalate showed generally similar geographical distributions to octocrylene. The camphor-based compound 4-MBC had lower levels and was quantified only in the Aveiro lagoon site (Portugal) and in the sewage-impacted Ebro delta spot, at concentrations in the low ng/L. Interestingly, the UV filters contamination hot spots do not necessarily match those of other sewage markers, in particular in the Exe estuary (UK) and Goro lagoon (Italy). Previous studies have successfully correlated UV filter concentrations and touristic recreational activities (Langford and Thomas, 2008; Mandaric et al., 2017; Picot-Groz et al., 2018). The littoral of the Po delta is a preserved natural area where tourism is limited. The south coast of the UK is a popular touristic destination in summer but the early sampling period (mid-June) was likely in a period of lower sunscreen product use. Conversely, the higher touristic season at the same period of time in milder southern European countries could account for the higher concentrations observed in Spain, Portugal and Greece. Use and occurrence of UV filters is seasonal (Gadelha et al., 2019) and it is worth noting that a comprehensive understanding of their variability in the environment would require long-term monitoring, in conjunction with alternative integrative sampling techniques.

### 3.1.4. Sewage biomarker

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

### 3.1.5. PAHs

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

acenaphthylene, attributed to a local oil spill.

### 3.1.6. PFASs

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

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

## 3.2. Occurrence in sediment

The sum of the PCPs, PAHs and PFAS is given per site in Fig. 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 LQ 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 4300 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 1300 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. PAHs

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). This result in the Goro lagoon falls within the range of total PAHs (104–572 ng/g dw) found in the Northern Adriatic Sea sediments under influence of the Po river discharge in a previous study (Combi et al., 2016). 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 457–1463 and 1272–5539 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 of the Tyrrhenian Sea. 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. PAHs were found at the same orders of magnitude in an earlier study of the Exe estuary (Herrmann and Hübner, 1982), indicating limited decontamination of this site over the past 35 years. The origin of the high PAHs load in the Italian fish farm sample remains unknown.

### 3.2.6. PFASs

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. PFASs 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 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 PFCA 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

HQ are given in Fig. 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 EQS (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 EC50-72 h 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 (Fig. 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 contaminants of both legacy (PAHs) and emerging concern (PFOS, UV

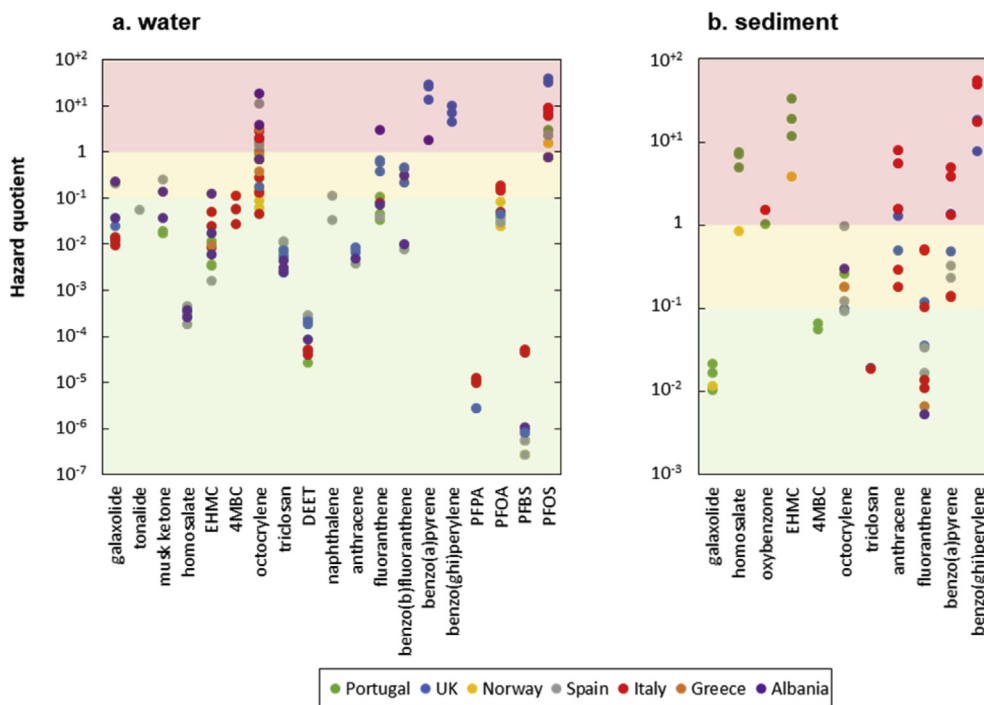


Fig. 2. HQ of the detected compounds for which PNEC or EQS were available.



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; Munsch 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).

#### 4. Conclusions

Compounds from PCPs, PAHs and PFASs, 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 PFASs. 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 contaminants of both legacy (PAHs) and emerging (PFOS, UV filter octocrylene) concern. 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 HQ 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.

#### Acknowledgments

This study was financially supported by the SEA-on-a-CHIP project, funded from European Union Seventh Framework Programme (FP7-OCEAN-2013) under grant agreement No. 614168. Antonio Marques is supported through the FCT Investigator program (IF).

#### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.envpol.2019.05.133>.

#### References

- Amine, H., Gomez, E., Halwani, J., Casellas, C., Fenet, H., 2012. UV filters, ethylhexyl methoxycinnamate, octocrylene and ethylhexyl dimethyl PABA from untreated wastewater in sediment from eastern Mediterranean river transition and coastal zones. *Mar. Pollut. Bull.* 64, 2435–2442. <https://doi.org/10.1016/j.marpollbul.2012.07.051>.
- Aminot, Y., Belles, A., Alary, C., Readman, J.W., 2017. Near-surface distribution of pollutants in coastal waters as assessed by novel polyethylene passive samplers. *Mar. Pollut. Bull.* 119, 92–101. <https://doi.org/10.1016/j.marpollbul.2017.03.022>.
- Andresen, J.A., Muir, D., Ueno, D., Darling, C., Theobald, N., Bester, K., 2007. Emerging pollutants in the north sea in comparison to lake Ontario, Canada, data. *Environ. Toxicol. Chem.* 26, 1081–1089. <https://doi.org/10.1897/06-416R.1>.
- Aznar-Alemany, Ö., Aminot, Y., Vilà-Cano, J., Köck-Schulmeyer, M., Readman, J.W., Marques, A., Godinho, L., Botteon, E., Ferrari, F., Boti, V., Albanis, T., Eljarrat, E., Barceló, D., 2018. Halogenated and organophosphorus flame retardants in European aquaculture samples. *Sci. Total Environ.* 612, 492–500. <https://doi.org/10.1016/j.scitotenv.2017.08.199>.
- Baron, E., Gago-Ferrero, P., Gorga, M., Rudolph, I., Mendoza, G., Zapata, A.M., Diaz-Cruz, S., Barra, R., Ocampo-Duque, W., Paez, M., Darbra, R.M., Eljarrat, E., Barceló, D., 2013. Occurrence of hydrophobic organic pollutants (BFRs and UV-filters) in sediments from South America. *Chemosphere* 92, 309–316. <https://doi.org/10.1016/j.chemosphere.2013.03.032>.
- Belles, A., Alary, C., Criquet, J., Ivanovsky, A., Billon, G., 2017. Assessing the transport of PAH in the surficial sediment layer by passive sampler approach. *Sci. Total Environ.* 579, 72–81. <https://doi.org/10.1016/j.scitotenv.2016.10.198>.
- Bester, K., Hühnerfuss, H., Lange, W., Rimkus, G.G., Theobald, N., 1998. Results of non target screening of lipophilic organic pollutants in the German Bight II: polycyclic musk fragrances. *Water Res.* 32, 1857–1863. [https://doi.org/10.1016/S0043-1354\(97\)00424-7](https://doi.org/10.1016/S0043-1354(97)00424-7).
- Casatta, N., Mascolo, G., Roscioli, C., Viganò, L., 2015. Tracing endocrine disrupting chemicals in a coastal lagoon (Sacca di Goro, Italy): sediment contamination and bioaccumulation in Manila clams. *Sci. Total Environ.* 511, 214–222. <https://doi.org/10.1016/j.scitotenv.2014.12.051>.
- Celeiro, M., Lamas, J.P., Garcia-Jares, C., Llompert, M., 2015. Pressurized liquid extraction-gas chromatography-mass spectrometry analysis of fragrance allergens, musks, phthalates and preservatives in baby wipes. *J. Chromatogr. A* 1384, 9–21. <https://doi.org/10.1016/j.chroma.2015.01.049>.
- Combi, T., Pintado-Herrera, M.G., Lara-Martin, P.A., Miserocchi, S., Langone, L., Guerra, R., 2016. Distribution and fate of legacy and emerging contaminants along the Adriatic Sea: a comparative study. *Environ. Pollut.* 218, 1055–1064. <https://doi.org/10.1016/j.envpol.2016.08.057>.
- Cunha, S.C., Fernandes, J.O., Vallecillos, L., Cano-Sancho, G., Domingo, J.L., Pocurull, E., Borrull, F., Maulvault, A.L., Ferrari, F., Fernandez-Tejedor, M., Van den Heuvel, F., Kotterman, M., 2015. Co-occurrence of musk fragrances and UV-filters in seafood and macroalgae collected in European hotspots. *Environ. Res.* 143, 65–71. Non-regulated environmental contaminants in seafood: contributions of the ECsafeSEAFOOD EU project. <https://doi.org/10.1016/j.envres.2015.05.003>.
- Díaz-Cruz, M.S., Barceló, D., 2009. Chemical analysis and ecotoxicological effects of organic UV-absorbing compounds in aquatic ecosystems. *TRAC Trends Anal. Chem. (Reference Ed.)* 28, 708–717. <https://doi.org/10.1016/j.trac.2009.03.010>.
- Eurobarometer, European Union, 2017. Attitudes of European Citizens towards the Environment.
- European Commission, 2016. High Levels of Endocrine-Disrupting Chemicals Found in Sediments and Fish from the Italian River Po and its Lambro Tributary, vol. 443.
- FAO, 2016. The State of World Fisheries and Aquaculture 2016, Contributing to Food Security and Nutrition for All. Rome, 200 pp.
- Gadelha, J.R., Rocha, A.C., Camacho, C., Eljarrat, E., Peris, A., Aminot, Y., Readman, J.W., Boti, V., Nannou, C., Kapsi, M., Albanis, T., Rocha, F., Machado, A., Bordalo, A., Valente, L.M.P., Nunes, M.L., Marques, A., Almeida, C.M.R., 2019. Persistent and emerging pollutants assessment on aquaculture oysters (*Crassostrea gigas*) from NW Portuguese coast (Ria De Aveiro). *Sci. Total Environ.* 666, 731–742. <https://doi.org/10.1016/j.scitotenv.2019.02.280>.
- Gago-Ferrero, P., Alonso, M.B., Bertozzi, C.P., Marigo, J., Barbosa, L., Cremer, M., Secchi, E.R., Azevedo, A., Lailson-Brito Jr., J., Torres, J.P.M., Malm, O., Eljarrat, E., Díaz-Cruz, M.S., Barceló, D., 2013. First determination of UV filters in marine mammals. octocrylene levels in Franciscana dolphins. *Environ. Sci. Technol.* 47, 5619–5625. <https://doi.org/10.1021/es400675y>.
- Gómez, C., Vicente, J., Echavarri-Erasun, B., Porte, C., Lacorte, S., 2011. Occurrence of perfluorinated compounds in water, sediment and mussels from the Cantabrian Sea (North Spain). *Mar. Pollut. Bull.* 62, 948–955. <https://doi.org/10.1016/j.marpollbul.2011.02.049>.
- Haug, L.S., Thomsen, C., Brantsæter, A.L., Kvale, H.E., Haugen, M., Becher, G., Alexander, J., Meltzer, H.M., Knutsen, H.K., 2010. Diet and particularly seafood are major sources of perfluorinated compounds in humans. *Environ. Int.* 36, 772–778. <https://doi.org/10.1016/j.envint.2010.05.016>.
- Herrmann, R., Hübner, D., 1982. Behaviour of polycyclic aromatic hydrocarbons in the ex estuary, devon. *Neth. J. Sea Res.* 15, 362–390. [https://doi.org/10.1016/0077-7579\(82\)90065-5](https://doi.org/10.1016/0077-7579(82)90065-5).
- Jacobs, S., Sioen, I., De Henauw, S., Rosseel, Y., Calis, T., Tediosi, A., Nadal, M., Marques, A., Verbeke, W., 2015. Marine environmental contamination: public awareness, concern and perceived effectiveness in five European countries. *Environ. Res.* 143, 4–10. <https://doi.org/10.1016/j.envres.2015.08.009>.
- Jamey, C., Tracqui, A., Ludes, B., 2012. Sexual abuse and anti-wrinkle cream: evidence from octocrylene. *Forensic sci. Int.*, the 48th annual meeting of the international association of forensic toxicologists (TIAFT). In: Joint Meeting with the Society of Toxicological and Forensic Chemistry (GTFC), 215, pp. 97–100. <https://doi.org/10.1016/j.forsciint.2011.02.012>.
- Justino, C.I.L., Duarte, K.R., Freitas, A.C., Panteleitchouk, T.S.L., Duarte, A.C., Rocha-Santos, T.A.P., 2016. Contaminants in aquaculture: Overview of analytical techniques for their determination. *TRAC Trends Anal. Chem. (Reference Ed.)* 80, 293–310. <https://doi.org/10.1016/j.trac.2015.07.014>.

- Kaiser, D., Sieratowicz, A., Zielke, H., Oetken, M., Hollert, H., Oehlmann, J., 2012. Ecotoxicological effect characterisation of widely used organic UV filters. *Environ. Pollut.* 163, 84–90. <https://doi.org/10.1016/j.envpol.2011.12.014>.
- Kumar, R., 2015. Conditions for Re-opening Exports of Albanian Mussels to the EU. Center for International Development, Harvard University.
- Kwadijk, C.J.A.F., Korytár, P., Koelmans, A.A., 2010. Distribution of perfluorinated compounds in aquatic systems in The Netherlands. *Environ. Sci. Technol.* 44, 3746–3751. <https://doi.org/10.1021/es100485e>.
- Lange, C., Kuch, B., Metzger, J.W., 2015. Occurrence and fate of synthetic musk fragrances in a small German river. *J. Hazard. Mater. Adv. Anal.* 282, 34–40. Treatment Technologies, and Environmental Fate of Emerging Contaminants. <https://doi.org/10.1016/j.jhazmat.2014.06.027>.
- Langford, K.H., Reid, M.J., Fjeld, E., Øxnevad, S., Thomas, K.V., 2015. Environmental occurrence and risk of organic UV filters and stabilizers in multiple matrices in Norway. *Environ. Int.* 80, 1–7. <https://doi.org/10.1016/j.envint.2015.03.012>.
- Langford, K.H., Thomas, K.V., 2008. Inputs of chemicals from recreational activities into the Norwegian coastal zone. *J. Environ. Monit.* 10, 894–898. <https://doi.org/10.1039/B806198J>.
- Lu, S., Wang, N., Ma, S., Hu, X., Kang, L., Yu, Y., 2019. Parabens and triclosan in shellfish from Shenzhen coastal waters: bioindication of pollution and human health risks. *Environ. Pollut.* 246, 257–263. <https://doi.org/10.1016/j.envpol.2018.12.002>.
- Mandarić, L., Diamantini, E., Stella, E., Cano-Paoli, K., Valle-Sistac, J., Molins-Delgado, D., Bellin, A., Chiogna, G., Majone, B., Diaz-Cruz, M.S., Sabater, S., Barceló, D., Petrovic, M., 2017. Contamination sources and distribution patterns of pharmaceuticals and personal care products in Alpine rivers strongly affected by tourism. *Sci. Total Environ.* 590–591, 484–494. <https://doi.org/10.1016/j.scitotenv.2017.02.185>.
- Merel, S., Snyder, S.A., 2016. Critical assessment of the ubiquitous occurrence and fate of the insect repellent N,N-diethyl-m-toluamide in water. *Environ. Int.* 96, 98–117. <https://doi.org/10.1016/j.envint.2016.09.004>.
- Mizukawa, A., Molins-Delgado, D., de Azevedo, J.C.R., Fernandes, C.V.S., Díaz-Cruz, S., Barceló, D., 2017. Sediments as a sink for UV filters and benzotriazoles: the case study of Upper Iguaçu watershed, Curitiba (Brazil). *Environ. Sci. Pollut. Res.* 24, 18284–18294. <https://doi.org/10.1007/s11356-017-9472-9>.
- Molins-Delgado, D., Gago-Ferrero, P., Díaz-Cruz, M.S., Barceló, D., 2016. Single and joint ecotoxicity data estimation of organic UV filters and nanomaterials toward selected aquatic organisms. Urban groundwater risk assessment. *Environ. Res.* 145, 126–134. <https://doi.org/10.1016/j.envres.2015.11.026>.
- Moore, M.N., Wedderburn, R.J., Clarke, K.R., McFadzen, I.R.B., Lowe, D.M., Readman, J.W., 2018. Emergent synergistic lysosomal toxicity of chemical mixtures in molluscan blood cells (hemocytes). *Environ. Pollut.* 235, 1006–1014. <https://doi.org/10.1016/j.envpol.2018.01.019>.
- Munoz, G., Budzinski, H., Babut, M., Drouineau, H., Lauzent, M., Menach, K.L., Lobry, J., Selleslagh, J., Simonnet-Laprade, C., Labadie, P., 2017a. Evidence for the trophic transfer of perfluoroalkylated substances in a temperate macrotidal estuary. *Environ. Sci. Technol.* 51, 8450–8459. <https://doi.org/10.1021/acs.est.7b02399>.
- Munoz, G., Budzinski, H., Labadie, P., 2017b. Influence of environmental factors on the fate of legacy and emerging per- and polyfluoroalkyl substances along the salinity/turbidity gradient of a macrotidal estuary. *Environ. Sci. Technol.* 51, 12347–12357. <https://doi.org/10.1021/acs.est.7b03626>.
- Munschy, C., Bely, N., Pollono, C., Aminot, Y., 2019. Perfluoroalkyl substances (PFASs) in the marine environment: spatial distribution and temporal profile shifts in shellfish from French coasts. *Chemosphere* 228, 640–648. <https://doi.org/10.1016/j.chemosphere.2019.04.205>.
- Munschy, C., Marchand, P., Venisseau, A., Veyrand, B., Zendong, Z., 2013. Levels and trends of the emerging contaminants HBCDs (hexabromocyclododecanes) and PFCs (perfluorinated compounds) in marine shellfish along French coasts. *Chemosphere* 91, 233–240. <https://doi.org/10.1016/j.chemosphere.2012.12.063>.
- Picot Groz, M., Martinez Bueno, M.J., Rosain, D., Fenet, H., Casellas, C., Pereira, C., Maria, V., Bebianno, M.J., Gomez, E., 2014. Detection of emerging contaminants (UV filters, UV stabilizers and musks) in marine mussels from Portuguese coast by QuEChERS extraction and GC–MS/MS. *Sci. Total Environ.* 493, 162–169. <https://doi.org/10.1016/j.scitotenv.2014.05.062>.
- Picot-Groz, M., Fenet, H., Bueno, M.J.M., Rosain, D., Gomez, E., 2018. Diurnal variations in personal care products in seawater and mussels at three Mediterranean coastal sites. *Environ. Sci. Pollut. Res.* 1–9. <https://doi.org/10.1007/s11356-017-1100-1>.
- Pignotti, E., Casas, G., Llorca, M., Tellbüscher, A., Almeida, D., Dinelli, E., Farré, M., Barceló, D., 2017. Seasonal variations in the occurrence of perfluoroalkyl substances in water, sediment and fish samples from Ebro Delta (Catalonia, Spain). *Sci. Total Environ.* 607–608, 933–943. <https://doi.org/10.1016/j.scitotenv.2017.07.025>.
- Pintado-Herrera, M.G., Combi, T., Corada-Fernández, C., González-Mazo, E., Lara-Martín, P.A., 2017a. Occurrence and spatial distribution of legacy and emerging organic pollutants in marine sediments from the Atlantic coast (Andalusia, SW Spain). *Sci. Total Environ.* 605 (606), 980–994. <https://doi.org/10.1016/j.scitotenv.2017.06.055>.
- Pintado-Herrera, M.G., González-Mazo, E., Lara-Martín, P.A., 2014. Determining the distribution of triclosan and methyl triclosan in estuarine settings. *Chemosphere* 95, 478–485. <https://doi.org/10.1016/j.chemosphere.2013.09.101>.
- Pintado-Herrera, M.G., Wang, C., Lu, J., Chang, Y.-P., Chen, W., Li, X., Lara-Martín, P.A., 2017b. Distribution, mass inventories, and ecological risk assessment of legacy and emerging contaminants in sediments from the Pearl River Estuary in China. *J. Hazard. Mater.* 323, 128–138. Special Issue on Emerging Contaminants in engineered and natural environment. <https://doi.org/10.1016/j.jhazmat.2016.02.046>.
- Rada, J.P.A., Duarte, A.C., Pato, P., Cachada, A., Carreira, R.S., 2016. Sewage contamination of sediments from two Portuguese Atlantic coastal systems, revealed by fecal sterols. *Mar. Pollut. Bull.* 103, 319–324. <https://doi.org/10.1016/j.marpolbul.2016.01.010>.
- Readman, J.W., Fillmann, G., Tolosa, I., Bartocci, J., Mee, L.D., 2005. The use of steroid markers to assess sewage contamination of the Black Sea. *Mar. Pollut. Bull.* 50, 310–318. <https://doi.org/10.1016/j.marpolbul.2004.11.002>.
- Sumner, N.R., Guitart, C., Fuentes, G., Readman, J.W., 2010. Inputs and distributions of synthetic musk fragrances in an estuarine and coastal environment; a case study. *Environ. Pollut.* 158, 215–222. <https://doi.org/10.1016/j.envpol.2009.07.018>.
- Sun, R., Wu, M., Tang, L., Li, J., Qian, Z., Han, T., Xu, G., 2018. Perfluorinated compounds in surface waters of Shanghai, China: source analysis and risk assessment. *Ecotoxicol. Environ. Saf.* 149, 88–95. <https://doi.org/10.1016/j.ecoenv.2017.11.012>.
- Tolosa, I., Mesa, M., Alonso-Hernandez, C.M., 2014. Steroid markers to assess sewage and other sources of organic contaminants in surface sediments of Cienfuegos Bay, Cuba. *Mar. Pollut. Bull.* 86, 84–90. <https://doi.org/10.1016/j.marpolbul.2014.07.039>.
- Wilson, B., Chen, R.F., Cantwell, M., Gontz, A., Zhu, J., Olsen, C.R., 2009. The partitioning of Triclosan between aqueous and particulate bound phases in the Hudson River Estuary. *Mar. Pollut. Bull.* 59, 207–212. Environmental Records of Anthropogenic Impacts on Coastal Ecosystems. <https://doi.org/10.1016/j.marpolbul.2009.03.026>.