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Targeted and untargeted discovery of UV filters and emerging contaminants with environmental risk assessment on the Northwestern Mediterranean coast

Aude Gandar^{a,b}, Maeva Giraud^b, Théo Perion^{a,b}, Emeline Houël^b, Thierry Noguer^{a,b}, Alice M.S. Rodrigues^b, Carole Calas-Blanchard^{a,b,*}, Didier Stien^{b,*}

^a Université de Perpignan Via Domitia, BAE, 52 Avenue Paul Alduy, F-66860 Perpignan Cedex, France

^b Sorbonne Université, CNRS, Laboratoire de Biodiversité et Biotechnologie Microbienne, UAR 3579, Observatoire Océanologique, Banyuls-sur-Mer, France

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ABSTRACT

Marine ecosystems, particularly coastal areas, are becoming increasingly vulnerable to pollution from human activities. Persistent organic pollutants and contaminants of emerging concern (CECs) are recognized as significant threats to both human and environmental health. Our study aimed to identify the molecules present in the seawater of two bathing areas in the Western Mediterranean Sea. Polar Organic Chemical Integrative Samplers were employed for passive sampling of UV filters and other contaminants in the seawater. The concentrations of UV filters bemotrizinol (BEMT), benzophenone-3 (BP3), diethylamino hydroxybenzoyl hexyl benzoate (DHHB), octyl triazone (ET), and octocrylene (OC) were measured at these bathing sites during the summer of 2022. In addition, non-targeted chemical analysis was used to complement the list of pollutants in the sampling areas, leading to the identification of 53 contaminants and three natural products. Dodecyltrimethylammonium (DTA) and tetradecyltrimethylammonium (TTA) ions, 1,3-diphenylguanidine (DPG), *N,N*-diethyl-*m*-toluamide (DEET), and crystal violet (CV) were successfully quantified. Risk assessments showed that DEET, DPG, and BP3 present low environmental risks at the detected concentrations, while CV, DTA, and TTA pose medium to high risks, warranting further investigation. OC was found to pose a significant risk to marine biodiversity, as its environmental concentrations exceeded predicted no-effect concentration values. Overall, this study highlights the complexity of environmental pollution in coastal bathing areas and underscores the urgent need for comprehensive risk assessments to safeguard marine life and public health.

1. Introduction

The Mediterranean Sea is a highly vulnerable biodiversity hotspot (Coll et al., 2010). This vulnerability is further exacerbated by both the current context of climate change and the growing burden of anthropogenic pollution. Coastal areas in the Mediterranean face unique challenges that exacerbate pollution levels, including limited water circulation, diverse human activities, tourism, aquaculture, and fishing, all of which contribute to the release of organic and inorganic pollutants at the land-sea interface (García-Pimentel et al., 2023). Additionally, the legacy of contamination and habitat degradation further complicates the situation, posing potential risks to human health (Aminot et al., 2019; Dietrich et al., 2025). In this context, there is an increasing need to better understand the coastal Mediterranean marine eco-exposome, to shed

light on this often invisible pollution and to enable a forward-looking assessment of its potential adverse effects on the marine ecosystem. Marine contaminants especially include persistent organic pollutants (POPs) and contaminants of emerging concern (CECs). The latter are defined as substances that, although not necessarily new, are not currently regulated, and for which the abundance, persistence in the environment, potential for degradation and bioaccumulation, and potential effects on ecosystems remain mostly unknown. The description of the diversity of CECs, their environmental fate and their long-term risks therefore require urgent investigation in a One-Health perspective for their inclusion in environmental monitoring programs.

Among the CECs, we can expect UV filters to be present in bathing areas in summer and possibly have an impact on local marine life. Some of these compounds, such as oxybenzone (benzophenone-3, BP3),

* Corresponding authors.

E-mail addresses: blanchard@univ-perp.fr (C. Calas-Blanchard), didier.stien@cnrs.fr (D. Stien).

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octinoxate (ethylhexyl methoxycinnamate, EM), octocrylene (OC) or avobenzone (butyl methoxydibenzoylmethane, BM), are now banned in several locations, including Palau for the first three substances (Republic of Palau, 2018), and Hawaii (State of Hawaii, 2021), so as to protect sensitive ecosystems (Downs et al., 2022). Avobenzone, OC or oxybenzone are toxic to coral at environmental concentrations (Clergeaud et al., 2023; Downs et al., 2016; Miller et al., 2022; Stien et al., 2019; Thorel et al., 2022). Other marine organisms were also shown to be impacted by UV filters. The brine shrimp *Artemia salina* or the marine microalga *Tetraselmis* sp. are affected upon exposition to homosalate and OC (Thorel et al., 2020). *Danio rerio* fish is impacted by BP3 (Balázs et al., 2016; Li et al., 2018). Furthermore, OC has been shown to bioaccumulate in the form of derivatives in marine organisms (Clergeaud et al., 2022; Stien et al., 2019), but also to be metabolized by the human body in a similar way (Bury et al., 2018, 2019). It also spontaneously degrades into the carcinogenic compound benzophenone (Downs et al., 2021a), posing a threat to human health.

Quantification of UV filters in aquatic environments is usually performed after extraction and concentration of a previously collected grab sample (Negreira et al., 2010; Vila et al., 2016). However, spot sampling provides only a snapshot of the chemical composition. An alternative is to use in situ passive samplers to accumulate the analytes over a period of time directly in the field. Various devices such as Diffusive Gradient in Thin films (Guibal et al., 2019), Chemcatchers® (Farrow et al., 2022), silicone rubber passive samplers (Pintado-Herrera et al., 2020) or Polar Organic Chemical Integrative Sampler (POCIS) (Morin et al., 2013) exist. By collecting and concentrating contaminants, passive samplers enable the detection of low levels of compounds. They also provide time-integrated concentrations via sampling rates (R_s). Interestingly, POCIS comply with regulatory requirements (The European Parliament and the Council of the European Union, 2013), and polyethylene membrane samplers were used to assess the near-surface distribution of UV filters in Sutton Harbour marina, Plymouth, UK (Aminot et al., 2017).

Our study focused on the Northwestern Mediterranean region of the Vermeille Coast. This area, located between Argelès-sur-Mer (France) and Port-Bou (Spain), is a popular tourist destination in summer, when recreational bathing activities may significantly contribute to the pollution of marine ecosystems (Fagervold et al., 2019; Gandar et al., 2022; Labille et al., 2020; Picot-Groz et al., 2018; Thallinger et al., 2023). Our objective was to determine the sampling rate of nine UV filters that are frequently used in sunscreens, and then quantify these compounds in two Mediterranean bathing areas. The aim was to assess the risk posed by these UV filters to local marine species. In a second phase, since UPLC-HRMS/MS analyses of the POCIS extracts had been generated for this purpose, it turned out that these data could be used to provide a more comprehensive understanding of the overall marine chemical eco-exposome by untargeted examination of the POCIS profiles.

2. Materials and methods

2.1. Chemicals and solvents

Benzophenone-3 (CAS 131-57-7, BP3), butyl methoxydibenzoylmethane (CAS 70356-09-1, BM), and octocrylene (CAS 6197-30-4, OC) were purchased from Merck (Darmstadt, Germany). Ethylhexyl methoxycinnamate (CAS 5466-77-3, EM) was obtained from Acros Organics (ThermoFisher Scientific, Waltham, Ma, USA). bis-Ethylhexyloxyphenol methoxyphenyl triazine (CAS 187393-00-6, BEMT), diethylamino hydroxybenzoyl hexyl benzoate (CAS 302776-68-7, DHHB), ethylhexyl salicylate (CAS 118-60-5, ES), ethylhexyl triazine (CAS 88122-99-0, ET), homosalate (CAS 118-56-9, HS), *N,N*-diethyl-3-methylbenzamide (CAS 134-62-3, DEET), crystal violet (CAS 548-62-9, CV), 2-cyano-3,3-diphenylacrylic acid (CAS 10380-41-3, CDAA), 1,3-diphenylguanidine (CAS 102-06-7, DPG), dodecyltrimethyl ammonium bromide (CAS 1119-94-4, DDAB), and

trimethyltetradecyl ammonium bromide (CAS 10182-92-0, TTAB) were purchased from Sigma-Aldrich (St Louis, MO, USA), and so were the LC-MS grade solvents [acetone, acetonitrile, dimethyl sulfoxide (DMSO), dichloromethane (DCM), ethanol, isopropanol and methanol (MeOH)]. Nonoxynol-9 (CAS 26571-11-9, N9) was obtained from Abcam (Cambridge, UK). Artificial Seawater was made with Instant Ocean salt (Aquarium Systems, Sarrebourg, France).

2.2. Sampling procedure

Sampling campaigns were conducted in Banyuls-sur-Mer (GPS: 42°28.986' N, 3°07.801' E) and Collioure (GPS: 42°31.491' N 3°5.149' E), France, during summer 2022 (Fig. S1). POCIS (Attract HLB, Affinisep, Le Houlme, France) were exposed to ambient seawater for 18 days during the following sampling periods: July 7 to July 25, July 25 to August 12, and August 12 to August 30. A stainless-steel cage containing three POCIS units was deployed at each sampling site. The cage protecting the POCIS was attached to a chain and buoy so that it remained 50 cm below the surface. Buoys were placed in the swimming area a few meters from the shore; maps of the sampling sites are shown in Fig. S1. After collection, POCIS were rinsed with distilled water, returned to their original packaging, and stored in a dark refrigerated ice chest before returning to the laboratory where they were frozen ($-20\text{ }^{\circ}\text{C}$) until extraction. One blank sample (POCIS exposed to ambient air when the cages were placed) was collected on the first day of the sampling campaign for both sites.

2.3. Extraction

POCIS were thawed overnight at $4\text{ }^{\circ}\text{C}$ before extraction. Empty cartridges (Affinisep, Le Houlme, France) were labelled and weighed. The HLB phase from POCIS was carefully transferred to the empty cartridges by gently rinsing the membrane with distilled water. The solid phase was then washed with 10 mL of 5 % MeOH in H_2O , followed by 5 mL of 40 % MeOH in H_2O . Elution was performed with 5 mL of 1:1 MeOH:DCM and the extracts were stored at $-80\text{ }^{\circ}\text{C}$ prior to UPLC-HRMS analysis. After elution, the cartridges containing the POCIS Attract HLB phase were dried at $50\text{ }^{\circ}\text{C}$ overnight and weighed to measure the amount of solid phase.

Water samples were extracted immediately after collection. They were filtered using GFA, homogenized, supplemented with 5 % MeOH, split into three fractions, and concentrated using Oasis HLB cartridges (200 mg, 6 mL, Waters, Milford, Ma, USA). The samples were percolated on preconditioned cartridges (3 mL MeOH followed by 10 mL H_2O) and frozen at $-20\text{ }^{\circ}\text{C}$. The same washing and elution protocol than the one used for POCIS was used for the Oasis HLB cartridges.

2.4. UHPLC-HRMS (quantification) and UHPLC-HRMS/MS (untargeted detection and annotations) analyses

UHPLC-HRMS and UHPLC-HRMS/MS analyses were performed using an Ultimate 3000 UHPLC system coupled to a MS/MS FT Q-Exactive Focus Orbitrap mass spectrometer (Thermo Fisher Scientific, Waltham, Ma, USA) as described by Rodrigues et al. (2021). Briefly, the mobile phase consisted of a mixture of water (solvent A) and methanol (solvent B), both supplemented with 0.1 % formic acid. The column was a Phenomenex Kinetex Biphenyl 2.6 μm , $150 \times 4.6\text{ mm}$, the column temperature was set at $50\text{ }^{\circ}\text{C}$, and the flow rate was 1 mL/min. A wash mixture made of 40 % acetonitrile, 40 % isopropanol and 20 % acetone (solvent C) was also used. Prior to injection, the mobile phase was kept at 40 % B for 5 min, then a non-linear gradient increased B to 100 % from 1 to 8 min (curve 2), followed by 100 % B for 4 min. From 12 to 14 min, a linear gradient increased the proportion of C to 100 %, which was maintained for 6 min. Finally, from 20 to 22 min, a linear gradient increased the amount of B to 100 %, maintained for 2 min. Chromatograms were recorded from 0 to 17 min. Injection volume was 2 μL .

Analyses of samples and standards for measurement of the concentration of UV filters (Table 1) were performed in the MS¹ electrospray positive ionization (ESI⁺) mode in the range of 80 to 1200 Da in centroid mode. The resolution was set to 70,000 and the AGC target was 3×10^6 . For untargeted annotation of the pollutants, samples and standards were analyzed again in the electrospray positive FullMS data dependent MS² mode (MS-dd²) mode as follows: in MS¹, the m/z range was 133.4 to 2000 Da, in centroid mode, the resolution was set to 70,000, the AGC target was 3×10^6 , and internal calibration was used (lock mass option set for ion at m/z 149.01213 between 1.5 and 14 min, corresponding to Ca(HCO₂)(MeOH)₂⁺ ion). In MS², the resolution was 17,500, AGC target 10^5 and isolation window 0.4 Da. Stepped normalized collision energy 15/30/45 was used, with 6 s dynamic exclusion.

The tune parameters were the following: spray voltage: 3.5 kV; sheath flow rate: 75; auxiliary gas pressure: 20; capillary temperature: 350 °C; heater temperature: 430 °C; S-lens RF level: 55.

2.5. Untargeted analysis and annotation of pollutants

Since profiles were very similar, the annotation of pollutants other than UV filters was conducted on 3 samples from Banyuls-sur-Mer and 3 from Collioure as follows: UHPLC-HRMS/MS profiles of the 6 POCIS extracts were processed using Compound Discoverer (CD) 2.1 (Thermo Fisher Scientific). The CD workflow allowed correction and alignment of the retention times, detection of unknown compounds, and grouping of compounds across all samples. Gap filling was also performed, and the background compounds were marked using blank samples (POCIS blanks and UHPLC/HRMS analytical blanks) to remove irrelevant ion peaks (an ion peak is only considered if the signal is at least 5 times more intense than in the blank). Finally, elemental compositions were predicted for all compounds using mzCloud (from MS²) and ChemSpider (formula or exact mass). The retention time window was set to 1.6–17 min. The maximum time shift for compound alignment was 0.1 min, the maximum mass tolerance for compound grouping and elemental composition calculation was 3 ppm, and the minimum peak intensity was 3×10^6 . This workflow generated an observation/variable matrix used to provide elemental compositions and preliminary annotations the often prove unreliable. The raw data were also subjected to GNPS (Global Natural Products Social Molecular Network, <https://gnps.ucsd.edu>) analysis (Wang et al., 2016). To deepen these preliminary annotations, a manual workflow was also applied to the major peaks of the UHPLC-HRMS profiles. Freestyle software (Thermo Fisher Scientific) was used to obtain the molecular formula, which was then submitted to databases search [SciFinder[®] (American Chemical Society), Reaxys (Elsevier), or LOTUS (Rutz et al., 2022)] for structure proposals. In parallel, MS/MS data were analyzed using Sirius (Lehrstuhl

Bioinformatik, Jena) software (Dührkop et al., 2019). All proposals were evaluated for their relevance using i) manual analysis of MS/MS fragments, ii) comparison of MS/MS data with reference spectra (e.g., MoNA – MassBank of North America, <https://mona.fiehnlab.ucdavis.edu>), and iii) comparison with commercial standards whenever possible.

2.6. POCIS calibration set-up for sampling rate measurement

An in-laboratory calibration step was performed to determine the sampling rates R_s of the nine UV filters studied (BP3, BM, DHHB, EM, ES, HS, OC, BEMT, ET) and of seven of the contaminants annotated subsequently to the metabolomic analysis (DEET, CV, CDAA, DPG, DDAB, TTAB, N9). This rate represents the volume of water purified by the POCIS per day, expressed in L/day. R_s (in L/d) is essential to correlate the average seawater concentration (C_w , in ng/L) to the final concentration in the POCIS phase (C_s , in ng/g) using Eq. (1) (Morin et al., 2013) where m_s is the mass of sorbent in the POCIS (in g), and t the exposure time (in days):

$$C_s = [C_w \cdot R_s \cdot t] / m_s \quad (1)$$

The calibration system consisted of two aquaria used alternatively. The objective was to reproduce as closely as possible the environmental conditions observed at the sampling site in summer 2022, i.e., a temperature of 25 °C, and a salinity of 39 g/L. To achieve this, 900 L of artificial seawater were prepared by mixing tap water with salt to reach the desired salinity. The aquarium was placed in a room thermostatically controlled at 24 °C to maintain a stable water temperature of 25 °C, and a day/night cycle of 10 h light and 14 h dark was implemented. Water agitation was ensured using a circulating thermostat (Lauda A100), with an outflow aligned parallel to the length of the aquarium (Fig. S2). The 45-l exposure aquarium was spiked at a known concentration of pollutants. For the spiking, stock solutions were prepared. In the first calibration experiment, the stock solutions were as follows: one solution containing six UV filters: BP3, BM, EM, ES, HS and OC, each of them at 45 mg/L in MeOH, and the second one containing BEMT and ET at 200 mg/L in DMSO. For the second calibration experiment, the stock solution contained the five compounds 1, 2, 47, 48, and 51 at a concentration of 45 mg/L in MeOH. Final concentration of each compound in the aquaria was 1 µg/L. To maintain this concentration as constant as possible in the water despite adsorption onto the POCIS phases throughout the 20-day period, the water was renewed daily for the first 10 days and every two days for the rest of the experiment of UV filters exposure, and daily for the second experiment with the other pollutants. To quickly renew the water without drying the POCIS, suspended POCIS were transferred to a second aquarium, prepared the same way as described above. Once the transfer was made, the first water tank was

Table 1
Analytical data for the UV filters used in this study.

UV filter	Cosing name	Alternative name	Molecular formula	CAS No.	Monitored ion in MS ¹ (m/z)	Ion type	t_R (min)	LOQ (vial, µg/L)
BEMT	bis-Ethylhexyloxyphenol methoxyphenyl triazine	Bemotrizinol	C ₃₈ H ₄₉ N ₃ O ₅	187393-00-6	628.3748	[M + H] ⁺	14.01	14.3
BM	Butyl methoxydibenzoylmethane	Avobenzone	C ₂₀ H ₂₂ O ₃	70356-09-1	311.644	[M + H] ⁺	7.58	22.6
BP3	Benzophenone-3	Oxybenzone	C ₁₄ H ₁₂ O ₃	131-57-7	229.0860	[M + H] ⁺	6.33	6.0
DHHB	Diethylamino hydroxybenzoyl hexyl benzoate		C ₂₄ H ₃₁ NO ₄	302776-68-7	398.2326	[M + H] ⁺	8.25	5.1
EM	Ethylhexyl methoxycinnamate	Octinoxate	C ₁₈ H ₂₆ O ₃	5466-77-3	291.1955	[M + H] ⁺	7.37	6.0
ES	Ethylhexyl salicylate	Octisalate	C ₁₅ H ₂₂ O ₃	118-60-5	139.0390	Frag.	7.02	61.9
ET	Ethylhexyl triazone	Octyl triazone	C ₄₈ H ₆₆ N ₆ O ₆	88,122-99-0	823.5117	[M + H] ⁺	11.09	12.9
HS	Homosalate		C ₁₆ H ₂₂ O ₃	118-56-9	139.0390	Frag.	7.29	47.9
OC	Octocrylene		C ₂₄ H ₂₇ NO ₂	6197-30-4	384.1933	[M + Na] ⁺	7.73	15.3

emptied and washed with ethanol and acetone and left empty until the next transfer.

Twenty POCIS were used for the calibration and were tied to a grid using a metallic wire. The POCIS were suspended vertically in the tanks. The system is shown in Fig. S2. For the UV filters experiment, one POCIS was collected daily from days 1 to 10 and at day 12, and then two POCIS were collected together every two days (Table S1). For the second experiment with other pollutants, one POCIS was collected each day from day 1 to day 20. POCIS were collected randomly. The order can be found in Table S1. After collection, POCIS were rinsed with distilled water, put back in their original packaging and frozen at -20°C until extraction.

2.7. Environmental risk assessment

The measured environmental concentrations (MECs) of five UV filters (BP3, OC, BEMT, DHHB, ET) and four annotated pollutants (DEET, GV, DPG, QAs) in the coastal waters of Banyuls-sur-Mer and Collioure were used to calculate the Risk Quotient (RQ) as $\text{RQ} = \text{MEC}/\text{PNEC}$. The Predicted No-Effect Concentration (PNEC) was derived either through species sensitivity distributions (SSDs) or by applying assessment factors (AF), depending on data availability.

For cases with sufficient data to construct SSDs, we followed European Commission guidelines, which require at least 10 species from 8 taxonomic groups and covering 3 trophic levels (European Commission, 2003). The PNEC was derived from the hazardous concentration for 5 % of the species (HC5), based on SSDs built using $L(E)C_{50}$ values for acute toxicity and $L(E)C_{10}$ values for chronic toxicity. An assessment factor (AF) of 5 was applied to the HC5, as recommended by European guidelines, to account for uncertainties (European Commission, 2003). In this context, $L(E)C_{50}$ refers to the concentration at which 50 % mortality or inhibition of a function (e.g., growth) occurs, while $L(E)C_{10}$ denotes the concentration causing a 10 % effect. These values are expressed as lethal concentration (LCx) or effect concentration (ECx), depending on the endpoint observed. REACH guidance recommends using EC10 over No Observed Effect Concentrations (NOEC) to improve accuracy in PNEC derivation (European Chemicals Agency, 2008). SSDs were constructed in R using the 'ssd4mosaic' and 'fitdistrplus' packages (Delignette-Muller and Dutang, 2015; King et al., 2013), allowing for distribution fitting and calculation of HC5 values to support environmental risk assessment.

When data were insufficient to construct SSDs, the PNEC was estimated by applying higher AFs to the most sensitive available toxicity endpoint (European Commission, 2003). Specifically: (i) an AF of 10,000 was applied if only $L(E)C_{50}$ data for algae, crustaceans, and fish across three trophic levels were available; (ii) an AF of 1000 was used when additional data from marine taxa (e.g., echinoderms, molluscs) were included; and (iii) an AF of 500 was applied when EC10 data were available from two trophic levels, particularly where short-term $L(E)C_{50}$ data were limited to freshwater or saltwater species. Due to limited data on marine organisms, REACH guidance suggests pooling freshwater and saltwater toxicity data for a more comprehensive risk assessment, stating that "The use of freshwater acute effects data in lieu of or in addition to saltwater effects data for risk assessment purposes is not contraindicated [...] Use of pooled data is therefore recommended" (European Chemicals Agency, 2008). As such, both freshwater and saltwater toxicity data were pooled to derive the PNEC based on the most sensitive endpoint, regardless of medium.

Chronic ($L(E)_{10}$) and acute ($L(E)C_{50}$) toxicity data were primarily obtained from the United States EPA ECOTOX knowledgebase (<https://cfpub.epa.gov/ecotox/>), the ECHA CHEM database (<https://chem.echa.europa.eu/>), and supplemented by peer-reviewed literature. In cases where experimental data were unavailable, acute toxicity values were predicted using the US EPA Ecological Structure Activity Relationships (ECOSARTM 2.2) class program with simplified molecular-input line-entry system (SMILES) strings as chemical input

(<https://www.epa.gov/tsca-screening-tools/ecological-structure-activity-relationships-ecosar-predictive-model>). Calculated RQ values were ranked to indicate potential adverse effects and ecological risks: $\text{RQ} < 0.01$: "Unlikely to pose risk"; $0.01 < \text{RQ} < 0.1$: "Low risk"; $0.1 < \text{RQ} < 1$: "Medium risk" and $\text{RQ} > 1$: "High risk" (European Commission, 2003; He et al., 2019; Tsui et al., 2019).

3. Results and discussion

3.1. Sampling rate measurement

During the calibration, EM, ES, HS were not detected following POCIS extraction. For EM, sampling rate was previously determined by Morrison and Belden (2016) in tap water. In their experiments, Morrison and Belden used POCIS with a nylon membrane combined with Oasis HLB phase, while in our study, we used POCIS with the same phase packed in between microporous polyethersulphone membranes. Reasons leading to the absence of EM in the extracts were not further investigated. ES and HS were not detected either in the extracts. Those molecules have the highest limit of quantification (LOQ) of the selected UV filters using the LC-MS method (Rodrigues et al., 2021). We hypothesize that the sampling rate was too low to reach quantification limits and/or that these molecules were not sampled by the POCIS.

The five remaining UV filters were properly detected in the extracts and calibration could be performed. BEMT, DHHB, ET and OC showed a linear accumulation profile during the 20 days experiment (Fig. S3). BM and BP3, both showed a lag phase. BM lag phase lasted 7.3 days and BP3 one lasted 6.3 days. Following the lag phase, the accumulation showed a linear profile as well. Sampling rates R_s (Table 2) were calculated as the slope of the calibration curves (Alvarez et al., 2004). R_s were calculated over the linear phase (20 days for BEMT, DHHB, ET and OC, from day 7 to day 20 for BM and BP3). UV filters' limits of quantification (LOQ) in sea water for a LC-MS quantification following passive sampling are also provided in Table 2.

3.2. UV filters occurrence and quantification

The concentrations of UV filters in the bathing areas for the three sampling periods are compiled in Table 3. EM, ES, and HS were not detected in the environmental samples. This aligns with the observation that no sampling rate could be calculated for these compounds in aquaria experiments. Consequently, it can be inferred that the collection method was not suitable for these compounds which may be retained by the polyethersulphone membrane (Scapuzzi et al., 2023; Vermeirssen et al., 2012), although they may have been present at the collection location. The presence of EM, ES and HS was indeed observed in other bathing zones in the Mediterranean coastal areas, including touristic bathing sites in the Gulf of Lion (García-Pimentel et al., 2023; Picot-Groz et al., 2018; Thallinger et al., 2023). The absence of environmental detection for BM was unexpected, given that a sampling rate could be determined in aquaria experiments and BM is widely used in sunscreen formulations. It is hypothesized that BM may have undergone significant degradation in the environment due to intense sunlight exposure (Maier

Table 2

Sampling rate (R_s), accumulation profile and limits of quantification (LOQ) of the studied UV filters in POCIS.

UV filter	R_s (L/d)	Accumulation profile	LOQ (ng/L)
BEMT	0.0101	Linear	390
BM	0.0123	Lag (6.3 d)	860
BP3	0.0816	Lag (7.3 d)	30
DHHB	0.0058	Linear	250
ET	0.0098	Linear	360
OC	0.0210	Linear	200

The sampling rates of compounds 1, 2, 47, 48 and 50 were measured with the same protocol (Fig. S4). Results are reported in chapter 3.4.

Table 3

UV filter quantifications according to the passive sampling in Côte Vermeille's bathing areas in Summer 2022.

Sampling site	UV filter	Average water concentration (ng/L) measured by POCIS sampling ^a		
		Period 1 7/07 to 25/07	Period 2 25/07 to 12/08	Period 3 12/08 to 30/08
Banyuls-sur-Mer	BEMT	10,760 ± 2	2100 ± 120	3070 ± 760
	BM	<LOQ	<LOQ	<LOQ
	BP3	70 ± 10	<LOQ	<LOQ
	DHHB	920 ± 6	<LOQ	<LOQ
	ET	8240 ± 110	1960 ± 40	4420 ± 1360
	OC	960 ± 80	320 ± 40	610 ± 90
Collioure	BEMT	14,020 ± 1130	12,400 ± 150	2700 ± 160
	BM	<LOQ	<LOQ	<LOQ
	BP3	50 ± 25	50 ± 10	<LOQ
	DHHB	710 ± 40	490 ± 20	<LOQ
	ET	11,430 ± 410	9830 ± 210	2030 ± 70
	OC	3510 ± 50	2920 ± 150	1060 ± 20

^a LOQs are reported in Table 2.

et al., 2005). However, the method used is not ideal for detecting BM, as it can only measure concentrations above 860 ng/L in seawater (Table 2).

The average concentration of BEMT ranged from approximately 3 µg/L at the end of the summer to 14 µg/L in July. The concentration of ET was also notably high, ranging between 2 and 11.4 µg/L. Both BEMT and ET are widely used in sunscreens across Europe, so elevated concentrations were anticipated. It appears that POCIS is particularly effective at capturing these two molecules, which might otherwise settle quickly into sediment.

Although OC was widely used in the past, its relatively low concentration in this study likely reflects its ongoing removal from cosmetic formulations following evidence that OC degrades into benzophenone, a compound known to be allergenic and carcinogenic (Downs et al., 2021a, 2021b). However, OC concentrations at the sampling sites remained concerning, ranging from 0.3 to 3.5 µg/L. This is alarming because OC is toxic to marine life (as discussed below), and the POCIS method averages concentrations over an 18-day period, meaning peak concentrations were likely higher than those reported in Table 3. Indeed, grab sampling has previously recorded OC concentrations as high as 170 µg/L in seawater, suggesting similar levels may occasionally be reached in Banyuls-sur-Mer and Collioure (Cadena-Aizaga et al., 2022; Vila et al., 2016).

BP3 was detected at relatively low concentrations (≤ 70 ng/L). While previous studies have reported significantly higher concentrations of this compound in marine coastal areas outside Europe (Downs et al., 2016), the low levels found in this study were expected, as BP3 is rarely used in cosmetic formulations in France and Europe.

Overall, the same concentration pattern was found in both sampling sites. Higher concentrations of UV filters were found during the first exposure period (July 7th to 25th). It was expected that higher concentrations would be found at the peak of the tourist season from July 14th to August 15th. Phenomena accounting for higher concentrations at the beginning of the summer were not investigated in this work.

3.3. Untargeted analysis of POCIS profiles: annotation and titration of other pollutants

Analyses performed on the representative POCIS extracts selected based on the analysis of the whole UHPLC-HRMS data allowed for the annotation of 53 compounds of anthropogenic origin, alongside with 3 natural compounds. The compounds are listed in Table 4. The detailed analytical data that allowed for annotation of compounds 1–56 are provided in the supporting information (Figs. S5-S145, Schemes S1-S8).

Dodecyltrimethylammonium (DTA, 1) and tetradecyltrimethylammonium (TTA, 2) ions were initially annotated on the basis of their MS² spectrum showing that the parent ion fragmented into almost a single product at m/z 60.0808 corresponding to the trimethylammonium ion. Eventually, annotations were confirmed by comparison with commercial standards. DTA bromide (DTAB) is manufactured in and/or imported to the European Economic Area, at 1–10 t per annum (European Chemicals Agency). It is used in many industrial applications, as detergent or in formulations of paints and coating, for example. DTA chloride is manufactured in and/or imported to the European Economic Area, at 10–100 t per annum. It is also used as detergent or for formulation of elaborated industrial products, and it is used for the manufacture of plasters and cement. TTA bromide (TTAB) is manufactured in and/or imported to the European Economic Area, at 10–100 t per annum. Both DTAB and TTAB are the active ingredients in cetrimide, an antiseptic dermatological drug, as well several topical specialties because it possesses various antibacterial and antifungal properties, preventing or reducing the risk of infection. TTAB is also widespread in cosmetics and personal care products, perfumes and fragrances, and pharmaceuticals as preservative. It is also likely to occur from detergents, paintings and so on.

Polyethylene glycol (PEG) derivatives typically manifest as a series of compounds with a 44.0262 Da difference in their protonated molecular ions or any adducts. This variation arises from the statistical distribution of PEG chain lengths. A series of PEG derivatives with retention times between 5.99 and 6.51 min was detected, and their formulas revealed that each contained three silicon atoms (compounds 3–8). Eventually, they were annotated as PEG trisiloxanes based on their [M + NH₄]⁺ adduct collision-induced fragmentation spectra. Shared diagnostic ions are at m/z 147.0472 (C₅H₁₁O₃Si⁺), 145.0679 (C₆H₁₃O₂Si⁺), 95.0159 (CH₇O₃Si⁺) and 77.0053 (CH₅O₂Si⁺) (see proposed fragmentation Scheme S1). PEG trisiloxanes are nonionic surfactants. They are used in many applications such as automotive, construction, consumer goods or personal care products. They are also used in agricultural pesticides for the formulation of many active principles including glyphosate. Their occurrence in the bathing waters of Banyuls and Collioure may originate from cosmetics, but also from leaching from the surrounding vineyards where glyphosate is still widely used.

Another group of PEG derivatives was annotated as a series of *ortho* and *para*-nonoxynols (compounds 9–27). Key ions for identification are at m/z 121.0648 (C₈H₉O⁺), 89.0597 (C₄H₉O₂⁺) and 71.0855 (C₅H₁₁⁺) (see proposed fragmentation Scheme S2). The two positional isomers of each nonoxynol have identical MS² spectra, making it impossible to differentiate them. However, the predominant isomer of monoalkylated phenols is the *para* form, which typically makes up 90 % of industrial preparations, compared with 10 % for the *ortho* form. The first, smaller chromatographic peak was therefore assigned to the *ortho* isomer and the second to the *para* isomer. The identification of these compounds was confirmed by comparison of retention times and MS² spectra with a commercially available standard containing all the nonoxynols trapped by the POCIS, thus confirming the annotation of compounds 9–27. Nonoxynol-9 is a surfactant widely referenced in the literature for its use in human public health. It was initially used as a spermicide in creams, gels, lubricants and condoms. However, studies have revealed that it is dangerous to humans, leading to less frequent use as a spermicide (Zhu et al., 2020). Nevertheless, this molecule is still used in industrial applications, for example as an active ingredient in Tergitol N9 or ROKafenol N9 (surfactants used in detergents and industrial cleaning products), for paper and textile processing, in agricultural products and in paints and coatings (De la Parra-Guerra and Olivero-Verbel, 2020). The occurrence of compounds 9–28 in the bathing waters of Banyuls-sur-Mer and Collioure is probably due to local agricultural activities.

A variety of C16- (29–37) and C18-alcohol ethoxylates (AEOs) (38–47), with different PEG chain lengths ranging from 5 or 6 to 14 PEG moieties, were also found to be present in the bathing areas. Annotation was performed upon examination of the collision-induced

Table 4

List of compounds other than UV filters detected in POCIS extracts.

Cmpd. No.	t _R (min)	Exp. m/z	Adduct	Molecular formula	Th. m/z	Annotation ^{b,c}	Compound class ^d
1 ^a	4.81	228.2686	[M] ⁺	C ₁₅ H ₃₄ N ⁺	228.2686	Dodecyltrimethylammonium (DTA)	CS
2 ^a	5.14	256.2997	[M] ⁺	C ₁₇ H ₃₈ N ⁺	256.2999	Tetradecyltrimethylammonium (TTA)	CS
3	5.99	430.2470	[M + NH ₄] ⁺	C ₁₆ H ₄₀ O ₆ Si ₃	430.2471	PEG-3 trisiloxane	NS
4	6.10	474.2734	[M + NH ₄] ⁺	C ₁₈ H ₄₄ O ₇ Si ₃	474.2733	PEG-4 trisiloxane	NS
5	6.21	518.2994	[M + NH ₄] ⁺	C ₂₀ H ₄₈ O ₈ Si ₃	518.2995	PEG-5 trisiloxane	NS
6	6.31	562.3260	[M + NH ₄] ⁺	C ₂₂ H ₅₂ O ₉ Si ₃	562.3257	PEG-6 trisiloxane	NS
7	6.41	606.3522	[M + NH ₄] ⁺	C ₂₄ H ₅₆ O ₁₀ Si ₃	606.3520	PEG-7 trisiloxane	NS
8	6.51	650.3784	[M + NH ₄] ⁺	C ₂₆ H ₆₀ O ₁₁ Si ₃	650.3785	PEG-8 trisiloxane	NS
9 ^a	6.66	370.2951	[M + NH ₄] ⁺	C ₂₁ H ₃₆ O ₄	370.2952	<i>o</i> -Nonoxynol-3	NS
10 ^a	6.71	370.2953	[M + NH ₄] ⁺	C ₂₁ H ₃₆ O ₄	370.2952	<i>p</i> -Nonoxynol-3	NS
11 ^a	6.82	414.3216	[M + NH ₄] ⁺	C ₂₃ H ₄₀ O ₅	414.3214	<i>o</i> -Nonoxynol-4	NS
12 ^a	6.87	414.3217	[M + NH ₄] ⁺	C ₂₃ H ₄₀ O ₅	414.3214	<i>p</i> -Nonoxynol-4	NS
13 ^a	6.96	458.3477	[M + NH ₄] ⁺	C ₂₅ H ₄₄ O ₆	458.3476	<i>o</i> -Nonoxynol-5	NS
14 ^a	7.02	458.3478	[M + NH ₄] ⁺	C ₂₅ H ₄₄ O ₆	458.3476	<i>p</i> -Nonoxynol-5	NS
15 ^a	7.09	502.3740	[M + NH ₄] ⁺	C ₂₇ H ₄₈ O ₇	502.3738	<i>o</i> -Nonoxynol-6	NS
16 ^a	7.15	502.3742	[M + NH ₄] ⁺	C ₂₇ H ₄₈ O ₇	502.3738	<i>p</i> -Nonoxynol-6	NS
17 ^a	7.22	546.4001	[M + NH ₄] ⁺	C ₂₉ H ₅₂ O ₈	546.4004	<i>o</i> -Nonoxynol-7	NS
18 ^a	7.28	546.4002	[M + NH ₄] ⁺	C ₂₉ H ₅₂ O ₈	546.4004	<i>p</i> -Nonoxynol-7	NS
19 ^a	7.34	590.4262	[M + NH ₄] ⁺	C ₃₁ H ₅₆ O ₉	590.4263	<i>o</i> -Nonoxynol-8	NS
20 ^a	7.42	590.4263	[M + NH ₄] ⁺	C ₃₁ H ₅₆ O ₉	590.4263	<i>p</i> -Nonoxynol-8	NS
21 ^a	7.48	634.4523	[M + NH ₄] ⁺	C ₃₃ H ₆₀ O ₁₀	634.4525	<i>o</i> -Nonoxynol-9	NS
22 ^a	7.55	634.4526	[M + NH ₄] ⁺	C ₃₃ H ₆₀ O ₁₀	634.4525	<i>p</i> -Nonoxynol-9	NS
23 ^a	7.61	678.4785	[M + NH ₄] ⁺	C ₃₅ H ₆₄ O ₁₁	678.4787	<i>o</i> -Nonoxynol-10	NS
24 ^a	7.68	678.4787	[M + NH ₄] ⁺	C ₃₅ H ₆₄ O ₁₁	678.4787	<i>p</i> -Nonoxynol-10	NS
25 ^a	7.74	722.5046	[M + NH ₄] ⁺	C ₃₇ H ₆₈ O ₁₂	722.5049	<i>o</i> -Nonoxynol-11	NS
26 ^a	7.82	722.5048	[M + NH ₄] ⁺	C ₃₇ H ₆₈ O ₁₂	722.5049	<i>p</i> -Nonoxynol-11	NS
27 ^a	7.82	766.5313	[M + NH ₄] ⁺	C ₃₉ H ₇₂ O ₁₃	766.5311	<i>o</i> -Nonoxynol-12	NS
28 ^a	7.88	766.5311	[M + NH ₄] ⁺	C ₃₉ H ₇₂ O ₁₃	766.5311	<i>p</i> -Nonoxynol-12	NS
29	7.67	524.4520	[M + NH ₄] ⁺	C ₂₈ H ₅₈ O ₇	524.4521	C16-AEO ₆	NS
30	7.80	568.4781	[M + NH ₄] ⁺	C ₃₀ H ₆₂ O ₈	568.4782	C16-AEO ₇	NS
31	7.93	612.5041	[M + NH ₄] ⁺	C ₃₂ H ₆₆ O ₉	612.5043	C16-AEO ₈	NS
32	8.05	656.5307	[M + NH ₄] ⁺	C ₃₄ H ₇₀ O ₁₀	656.5306	C16-AEO ₉	NS
33	8.17	700.5565	[M + NH ₄] ⁺	C ₃₆ H ₇₄ O ₁₁	700.5566	C16-AEO ₁₀	NS
34	8.30	744.5830	[M + NH ₄] ⁺	C ₃₈ H ₇₈ O ₁₂	744.5831	C16-AEO ₁₁	NS
35	8.43	788.6093	[M + NH ₄] ⁺	C ₄₀ H ₈₂ O ₁₃	788.6092	C16-AEO ₁₂	NS
36	8.55	832.6351	[M + NH ₄] ⁺	C ₄₂ H ₈₆ O ₁₄	832.6351	C16-AEO ₁₃	NS
37	8.69	876.6616	[M + NH ₄] ⁺	C ₄₄ H ₉₀ O ₁₅	876.6614	C16-AEO ₁₄	NS
38	7.95	508.4569	[M + NH ₄] ⁺	C ₂₈ H ₅₈ O ₆	508.4571	C18-AEO ₅	NS
39	8.08	552.4831	[M + NH ₄] ⁺	C ₃₀ H ₆₂ O ₇	552.4832	C18-AEO ₆	NS
40	8.21	596.5094	[M + NH ₄] ⁺	C ₃₂ H ₆₆ O ₈	596.5093	C18-AEO ₇	NS
41	8.33	640.5358	[M + NH ₄] ⁺	C ₃₄ H ₇₀ O ₉	640.5356	C18-AEO ₈	NS
42	8.46	684.5619	[M + NH ₄] ⁺	C ₃₆ H ₇₄ O ₁₀	684.5619	C18-AEO ₉	NS
43	8.58	728.5886	[M + NH ₄] ⁺	C ₃₈ H ₇₈ O ₁₁	728.5882	C18-AEO ₁₀	NS
44	8.71	772.6146	[M + NH ₄] ⁺	C ₄₀ H ₈₂ O ₁₂	772.6144	C18-AEO ₁₁	NS
45	8.84	816.6408	[M + NH ₄] ⁺	C ₄₂ H ₈₆ O ₁₃	816.6407	C18-AEO ₁₂	NS
46	8.97	860.6666	[M + NH ₄] ⁺	C ₄₄ H ₉₀ O ₁₄	860.6665	C18-AEO ₁₃	NS
47	9.10	904.6929	[M + NH ₄] ⁺	C ₄₆ H ₉₄ O ₁₅	904.6930	C18-AEO ₁₄	NS
48 ^a	2.91	212.1182	[M + H] ⁺	C ₁₃ H ₁₃ N ₃	212.1182	1,3-Diphenylguanidine (DPG)	Rubber additive
49 ^a	5.27	192.1383	[M + H] ⁺	C ₁₂ H ₁₇ NO	192.1383	<i>N,N</i> -diethyl- <i>m</i> -toluamide (DEET)	Insect repellent
50 ^a	7.64	250.0863	[M + H] ⁺	C ₁₆ H ₁₁ NO ₂	250.0863	2-Cyano-3,3-diphenylacrylic acid (CPAA)	UV filter derivative
51 ^a	7.71	372.2433	[M] ⁺	C ₂₅ H ₃₀ N ₃ ⁺	372.2434	Methyl violet 10B (Crystal violet, CV)	Colorant
52	6.93	358.2274	[M] ⁺	C ₂₄ H ₂₈ N ₃ ⁺	358.2278	Methyl violet 6B	Colorant
53	6.21	344.2119	[M] ⁺	C ₂₃ H ₂₆ N ₃ ⁺	344.2121	Methyl violet 2B	Colorant
54 ^a	6.19	496.3394	[M + H] ⁺	C ₂₄ H ₅₀ NO ₇ P	496.3398	1- <i>O</i> -hexadecanoyl- <i>sn</i> -glycero-3-phosphocholine	Natural lipid
55	7.82	703.5750	[M + H] ⁺	C ₃₉ H ₇₉ N ₂ O ₆ P	703.5749	Palmitoyl sphingomyelin	Natural lipid
56	7.54	659.4301	[M + H] ⁺	C ₄₂ H ₅₈ O ₆	659.4306	Fucoxanthin	Carotenoid

^a The structure was confirmed by comparison with a commercial standard, achieving an identification confidence of Level 1 (Schymanski et al., 2014). For other compounds, the identification confidence is classified as Level 2.

^b *o*: ortho; *p*: para.

^c AEO: Alcohol ethoxylate.

^d CS: Cationic Surfactant; NS: Nonionic surfactant.

fragmentation spectra of these compounds. One key daughter ion is at m/z 313.3101 for C16-AEOs (C₂₀H₄₁O₂⁺) and at m/z 341.3414 (C₂₂H₄₅O₂⁺) for C18-AEOs (see proposed fragmentation Scheme S3). This ion corresponds to the protonated 2-(alkanyloxy)ethanol, resulting from the loss of the PEG chain minus one unit. Other common key ions are at m/z 177.1121 (C₈H₁₇O₄⁺), 133.0859 (C₆H₁₃O₃⁺), 89.0597 (C₄H₉O₂⁺) and 71.0855 (C₅H₁₁⁺). AEOs are surfactants used in many industrial applications including detergents, cosmetics, pharmaceuticals and agricultural products.

Compound 48 had a protonated molecular ion at m/z 212.1181

corresponding to the formula C₁₃H₁₃N₃⁺ (Calcd. 212.1182). This compound exhibited a fragmentation pattern in which the protonated molecular ion lost ammonia to produce an ion at m/z 195.0917, lost aniline to produce protonated *N*-phenylcyanamide at m/z 119.0604, or lost *N*-phenylcyanamide to yield protonated aniline at m/z 94.0651 (see proposed fragmentation Scheme S4). The annotation as 1,3-diphenylguanidine (DPG) was confirmed by comparison with a commercial standard. DPG is primarily used in the rubber industry. It serves as an accelerator in the vulcanization process of rubber. This compound is commonly utilized in the production of tires, belts, hoses, and other rubber goods.

DPG has been detected in various environmental matrices, but its presence in sea water has not been extensively studied. Research has shown that DPG largely contaminates urban watersheds and can be present in aquatic environments, including surface waters like rivers and lakes (Ichihara et al., 2023; Johannessen et al., 2022). Banyuls-sur-Mer and Collioure are small towns that experience relatively heavy road traffic during the summer season. Bathing areas are contaminated by DPG despite the lack of precipitation during this period. It would be interesting to evaluate fluctuations in the concentration of this compound at the end of summer and in the fall when the rains return.

Compound **49** had a protonated molecular ion at m/z 192.1383 corresponding to the formula $C_{12}H_{18}NO^+$ (Calcd. 192.1383). This formula suggested that compound **49** might be *N,N*-diethyl-*m*-toluamide (DEET). Collision-induced dissociation of the protonated molecular ion produced a major product at m/z 109.0490 ($C_8H_7O^+$), resulting from the loss of diethylamine, and another cation, $C_5H_{10}NO^+$, at m/z 100.0757 (see proposed fragmentation Scheme S5). The latter then lost ethylene, yielding protonated ethyl isocyanate at m/z 72.0444. These findings supported putative annotation as DEET. The final confirmation was achieved by comparing compound **49** with a commercial standard of DEET. DEET is the active ingredient in many commercial insect repellents. It can enter marine environments either directly, as is likely the case in the bathing areas of Banyuls and Collioure, or indirectly through discharges from wastewater treatment plants (Costanzo et al., 2007; Weeks et al., 2012). Interestingly, the combined use of DEET-based repellent and sunscreen may significantly reduce the effectiveness of sunscreens (Murphy et al., 2000).

Compound **50** exhibited a protonated molecular ion at m/z 250.0863, corresponding to the formula $C_{16}H_{11}NO_2^+$ (Calcd. 250.0863), indicating a compound with 12 double bond equivalents. Upon collision-induced fragmentation, the protonated molecular ion sequentially lost water (resulting in $C_{16}H_{10}NO^+$ at m/z 232.0757), carbon monoxide (yielding $C_{15}H_{10}N^+$ at m/z 204.0808), and hydrogen cyanide (producing $C_{14}H_9^+$ at m/z 177.0699). These fragmentations suggested that compound **50** contained nitrile and carboxylic acid functional groups. Additionally, a lower molecular weight product at m/z 105.0335 ($C_7H_5O^+$) could be assigned to a putative benzylidyneoxonium ion. This latter product posed a challenge in determining the structure of compound **50** until it was considered that it resulted from the transposition of the acylium group of the product at m/z 232.0757 onto a phenyl substituent and the extrusion of 3-phenylpropionitrile (Fig. 1). **50** was then assigned to the 2-cyano-3,3-diphenylacrylic acid (CPAA). Confirmation was obtained by comparison with a commercial standard. This compound results from the hydrolysis of OC. It was never detected in environmental samples, nor was it seen in coral or marine worms exposed to OC (Clergeaud et al., 2022; Stien et al., 2019; Thorel et al., 2022). CPAA may be produced here by direct hydrolysis of OC in sea water. However, OC also passes through the skin, into the bloodstream, and is eventually metabolized and excreted in urine in the form of metabolites, the major one of which is CPAA (Bury et al., 2018). On average, the total mass of CPAA excreted over a 24-h period after sunscreen application corresponds to approximately 0.03 % of the mass of octocrylene applied to the skin (Hiller et al., 2019). The American Academy of Dermatology recommends applying 1 oz of cream (~ 28 g) every 2 h (American Academy of Dermatology). A sunscreen formulated with 10 % octocrylene (the maximum concentration allowed in Europe) therefore delivers 2.8 g of octocrylene per application. For two applications per day, a single person uses 5.6 g of octocrylene, resulting in an average of 1.68 mg of CPAA excreted in urine. The beaches of Banyuls-sur-Mer and Collioure are heavily frequented during the summer, making urinary excretion of CPAA a potentially significant source of environmental contamination. Unfortunately, the concentration of CPAA could not be quantified in this study, as it inexplicably failed to accumulate in POCIS during the calibration experiment. Nevertheless, its presence in the water column of bathing areas underscores the need for further investigation into the potential impact of this compound on

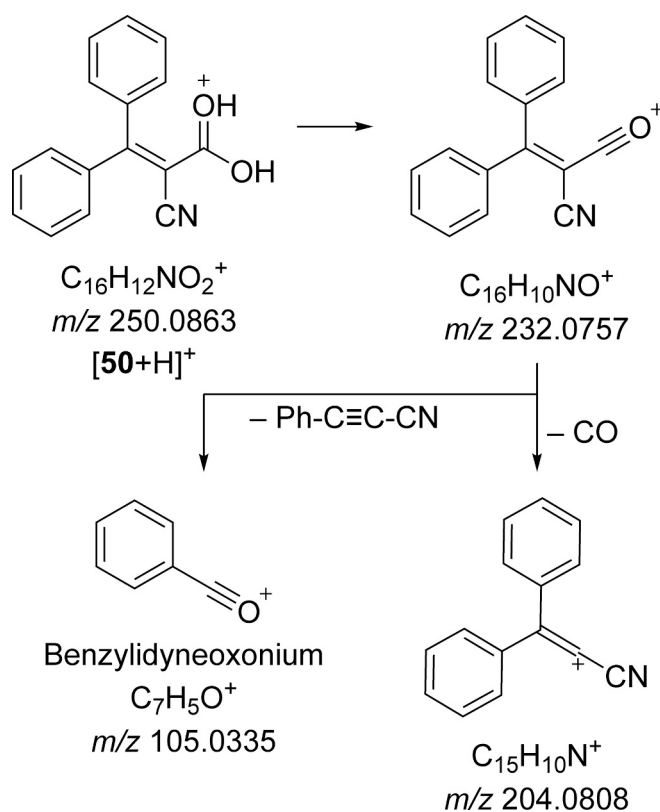


Fig. 1. Fragmentation scheme for $[50 + H]^+$.

marine organisms.

Compound **51** had a molecular ion at m/z 372.2433, corresponding to the formula $C_{25}H_{30}N_3^+$ (calcd. 372.2434). The collision-induced dissociation spectrum provided limited information, as the only fragment observed was at m/z 356.2121, corresponding to the loss of methane (see proposed fragmentation Scheme S6). The formula suggested that compound **51** might be methyl violet 10B, also known as crystal violet (CV). Comparison with a commercial standard confirmed its identification as CV. CV is a triphenylmethane dye often sold as a mixture of methyl violets 2B, 6B, and 10B. After identifying CV, we searched for its two analogues, which were also present in the collected samples (compounds **52** and **53**). CV (**51**) or gentiane violet (GV, the mixture of compounds **51–53**) are widely used in various applications, including the textile and paper industries, paints and printing ink, biological staining, and veterinary medicine (Tkaczyk et al., 2020). Despite being banned for use in food-producing animals in the European Union, CV remains among the most commonly detected synthetic dyes in aquaculture products in Europe (European Food Safety Authority (EFSA) et al., 2017). The source of GV in the Banyuls-sur-Mer and Collioure bathing areas is unclear. It may be used locally for a variety of poorly documented purposes, such as disinfection or colouring.

Finally, three natural products captured by the POCIS were annotated. The 1-*O*-hexadecanoyl-*sn*-glycero-3-phosphocholine (lysophosphatidylcholine 16:0, **54**) had been formally identified as in previous work by comparison with a standard (see proposed fragmentation Scheme S7) (Stien et al., 2020). Palmitoyl sphingomyelin (**55**) was annotated with Sirius with a high confidence level (Dührkop et al., 2019). In the MS² spectrum of the $[M + H]^+$ ion, the first product at m/z 184.0733 ($C_5H_{15}NO_4P^+$), resulting from the loss of the entire ceramide group, corresponds to the phosphocholine moiety. This moiety then fragments into characteristic ions at m/z 124.9998 ($C_2H_6O_4P^+$), 86.0964 ($C_5H_{12}N^+$), and 60.0808 ($C_3H_{10}N^+$) (see proposed fragmentation Scheme S8). Annotation as palmitoyl sphingomyelin was confirmed by comparison of our experimental spectrum with one from the GNPS

database (Wang et al., 2016). Fucoxanthin (56) was annotated by comparison with previous work on marine phytoplankton (Marcellin-Gros et al., 2020). Compounds 54 and 55 are prevalent in living organisms and are commonly found in the cell membranes of both animals and plants, including marine organisms (García-Montoya et al., 2023; Lauritano et al., 2020). Fucoxanthin (56) is a pigmentary carotenoid found in brown algae (Marcellin-Gros et al., 2020). Its capture in POCIS traps may be associated with increased marine phytoplankton mortality and lysis during the summer, a period when the coastal marine microbial community is dominated by bacteria (Lambert et al., 2019).

3.4. Environmental concentrations of annotated pollutants

As for UV filters, the environmental concentration of the pollutants that were annotated or identified by untargeted analysis were measured by calibration of the POCIS in tanks. It was possible to obtain a sampling rate (Rs) for compounds 1, 2, 48, 49 and 51, although for compounds 1 and 2, the accumulation stopped after 10 days. It was complicated to manage the PEG derivatives which are always sold as mixtures with varying chain length distributions and not individual components. The Rs and environmental concentrations are reported in Table 5.

It can be observed that there is no peak in the concentration of any of these compounds at any given time during the sampling period. However, this information needs to be considered in light of the fact that POCIS measures an average concentration over 18 days, and that climate and visitor numbers are relatively stable during the summer. Additionally, the two sites are relatively similar in terms of pollution, both qualitatively and quantitatively.

Limited data are available on the occurrence of many of these compounds in the marine environment. For DTAB and TTAB, our range of values aligns with environmental concentrations previously measured for quaternary ammonium compounds (QAs) in coastal marine areas in England (120–270 ng/L) (Bassarab et al., 2011). Although the method used did not allow us to determine the exact concentration of compounds 1 and 2, concentrations of 134 ng/L for the former and 501 ng/L for the latter can be used to assess the risk these compounds pose to marine life in the study area. Since the two compounds are close structural analogues, their environmental toxicity will be studied collectively (as quaternary ammoniums, QAs), using the sum of their concentrations as a QAs environmental concentration.

Table 5

Other pollutants quantification in Banyuls-sur-Mer and Collioure bathing areas in Summer 2022.

Sampling site	Cmpd.	Rs (L d ⁻¹) ^a	Concentration, in ng.L ⁻¹		
			Period 1 7/07 to 25/07	Period 2 25/07 to 12/08	Period 3 12/08 to 30/08
Banyuls-sur-Mer	1 (DTA)	0.1802 ^b	≥ 86	≥ 33	≥ 134
	2 (TTA)	0.0821 ^b	≥ 385	≥ 136	≥ 501
	48 (DPG)	0.1125	8.5	7.9	15.1
	49 (DEET)	0.3117	12.8	35.4	26.9
	51 (CV)	0.1320	8.4	8.5	10.0
Collioure	1 (DTA)	0.1802 ^b	≥ 86.1	≥ 69.6	≥ 55.1
	2 (TTA)	0.0821 ^b	≥ 373.8	≥ 321.0	≥ 254.8
	48 (DPG)	0.1125	6.7	6.2	9.4
	49 (DEET)	0.3117	32.2	23.2	18.9
	51 (CV)	0.1320	4.6	3.4	7.5

^a All accumulation curves were linear with no lag, except for CV accumulation which was linear with a 3.5 d lag.

^b The POCIS saturated after 10 days for compounds 1 and 2. Therefore, the reported value is higher than or equal to the actual environmental concentration.

The presence of DPG in aquatic ecosystems has been reported, with concentrations ranging from ng/L to µg/L (Johannessen et al., 2022; Rauert et al., 2022; Schulze et al., 2019). However, these earlier studies focused on urban environments and surface waters. Our findings highlight the need for further research to better assess the occurrence and fate of DPG in seawater, particularly in coastal regions.

DEET contamination in seawater has been previously observed, with reported environmental concentrations in the ng/L range, including in the Western Mediterranean Sea (0.506–1.21 ng/L) (Brumovský et al., 2017), the Northern Adriatic Sea (5.0 ng/L) (Loos et al., 2013), or the North Sea (1.1 ng/L) (Weigel et al., 2002). These concentrations are slightly lower than those found in our study. It's reasonably clear that the presence of DEET comes from the use of mosquito repellents by bathers.

Studies investigating the environmental concentrations of CV (51) are scarce. However, in previous research, it has been detected at low concentrations, typically below 1 µg/L, highlighting its potential persistence in the environment even at trace levels (Lian and Wang, 2013).

3.5. Risk assessment

The risk assessment was conducted for the five UV filters BP3, OC, BEMT, DHHB and ET, and the four annotated pollutants DEET, CV, DPG and QAs detected in the coastal waters of Banyuls-sur-Mer and Collioure, for which maximum average water concentrations were obtained as shown in Tables 3 and 5 (Table 6). An exhaustive summary of the toxicity data used for risk assessment is presented in Table S2.

The risk assessment of BEMT, ET, and DHHB was conducted using ECOSAR acute toxicity predictions due to the lack of published data for these UV filters. However, the high logKow values of these compounds limited the accuracy of the ECOSAR predictions, leading to no effects at saturation and preventing the calculation of RQs. According to two published studies, these filters showed no significant impact on corals (*Pocillopora damicornis*), algae (*Tetraselmis* sp.), and marine crustaceans (*Artemia salina*) at the highest doses tested (1000–2000 µg/L), with the exception of DHHB, which appears to affect esterase activity linked to metabolic activity in *A. salina* (Stien et al., 2020; Thorel et al., 2020). Given the solubility characteristics of these UV filters and the limitations of current predictive models, further empirical studies are necessary to accurately assess their environmental risks and to provide a more comprehensive understanding of their impact on marine ecosystems. This need is highlighted by the high concentrations measured for BEMT and ET in Banyuls-sur-Mer and Collioure, which exceeded 10 µg/L (Table 3).

Risk assessment indicated a high environmental risk for OC at the concentrations measured in the present study in the Banyuls-sur-Mer and Collioure areas (Table 5). The PNEC determined in this study was 0.03 µg/L, which aligns closely with other published PNEC values of 0.026 and 0.027 µg/L (Aminot et al., 2019; ANSES, 2023). These values are 100 times lower than the measured concentrations in Collioure (3.51 µg/L), resulting in a high RQ in that area. Levels of OC in Banyuls-sur-Mer (0.96 µg/L) were lower than in Collioure but still 30 times higher than the PNEC. OC has been identified as one of the most toxic organic UV filters in marine and freshwater organisms in various published studies (Boyd et al., 2021; Carve et al., 2021; Marcin and Aleksander, 2023; Stien et al., 2019; Thorel et al., 2020) and was identified as one of the three UV filters toxic for corals in a recent review of the impacts of chemicals on coral reefs by the French Agency for Food, Environmental and Occupational Health & Safety (ANSES, 2023). The present and published evidence indicates that OC poses a substantial risk to the marine biodiversity of the Côte Vermeille during the summer months.

Oxybenzone is one of the most extensively studied organic UV filters, with comprehensive acute and chronic toxicity data available for a wide range of aquatic organisms, including corals (Table S2). Sufficient ecotoxicity data were available to construct acute (26 taxa) and chronic (10

Table 6

Predicted No Effect Concentrations (PNEC) and Environmental risk quotients (RQ) calculated from the toxicity data in Table S2 for the nine chemical contaminants detected in the present study. Calculation methods are detailed in Section 2.7.

Name	Exposure	Toxicity endpoint ($\mu\text{g/L}$) ^a	AF ^b	PNEC ($\mu\text{g/L}$) ^c	Location	MEC ($\mu\text{g/L}$) ^d	RQ ^e	Risk
BEMT	acute	0.06 (LC50 Mysid - ECOSAR)*	10,000	6.15×10^{-2}	Banyuls	10.76	1.7×10^6	NA
					Collioure	14.02	2.3×10^6	NA
ET	acute	1.87×10^9 (EC50 algae - ECOSAR)*	10,000	1.87×10^{-13}	Banyuls	8.24	4.4×10^{13}	NA
					Collioure	11.42	6.1×10^{13}	NA
DHHB	acute	30.91 (EC50 algae - ECOSAR)*	10,000	0.0031	Banyuls	0.92	298	NA
					Collioure	0.71	230	NA
OC	acute	30 (EC50 daphnid)	1000	0.030	Banyuls	0.96	32	High
					Collioure	3.51	117	High
BP3	chronic	9.72 [1.55–99.62] (HC5)	5	1.944	Banyuls	0.07	0.0360	Low
					Collioure	0.05	0.0257	Low
	acute	171.73 [81.16–418.96] (HC5)	5	3.435	Banyuls	0.07	0.0020	Unlikely
					Collioure	0.05	0.0015	Unlikely
ΣQAs (1 + 2)	acute	36 (EC50 algae)	10,000	3.6×10^{-3}	Banyuls	0.635	176	High
					Collioure	0.459	127	High
DPG (48)	chronic	1820 (EC10 fish)	500	3.64	Banyuls	0.0151	4.2×10^{-3}	Unlikely
					Collioure	0.0094	2.6×10^{-3}	Unlikely
DEET (49)	acute	16,686 [8677–34,400] (HC5)	5	3337	Banyuls	0.0354	1.1×10^{-5}	Unlikely
					Collioure	0.0322	9.6×10^{-6}	Unlikely
CV (51)	acute	82 (LC50 fish)	10,000	8.2×10^{-3}	Banyuls	0.0100	1.22	High
					Collioure	0.0075	0.91	Medium

^a Toxicity endpoints used to derive PNECs are presented as HC5 values (with confidence intervals in brackets) for species sensitivity distribution (SSD) analyses, or as the lowest observed toxicity endpoint (specified in parentheses) when using the assessment factor (AF) method.

^b AF: Assessment Factor applied to account for uncertainties in toxicity data.

^c PNEC: Predicted No Effect Concentration.

^d MEC: Measured Environmental Concentration in the sampling location.

^e RQ: Risk Quotient, calculated as MEC/PNEC.

* For chemicals with a log Kow > 5.0 (for fish and daphnids) or > 6.4 (for green algae), ECOSAR estimates may be unreliable for acute effects. RQ values for these chemicals are provided for informational purposes but cannot be used for conclusive risk predictions (Risk = NA).

taxa) SSDs for BP3 (Fig. S146). The chronic HC5 derived from SSD models for BP3 was 9.72 $\mu\text{g/L}$ (95 % CI 1.55 - 99.62), suggesting low long-term environmental risks at the concentrations measured in Banyuls-sur-Mer and Collioure. In comparison, two studies reported higher chronic HC5 values for BP3 of 48.5 $\mu\text{g/L}$ (95 % CI 5.3–145.2) and 73.3 $\mu\text{g/L}$ (95 % CI 39.8–132.1), indicating an even lower risk (Jung et al., 2021; National Academies of Sciences, Engineering, and Medicine, 2022). Only one other study found a lower HC5 for BP3 (0.07 $\mu\text{g/L}$ for marine organisms), but this value was based on acute cell line data extrapolated to chronic endpoints, which may not be as reliable (Carve et al., 2021). The acute HC5 value from the present study indicated that 95 % of the potentially affected species are unlikely to be impacted by short-term exposure to concentrations up to 171.73 $\mu\text{g/L}$ of BP3 (95 % CI 81.2–419). These findings align with a previous review that reported acute HC5 values of 353 $\mu\text{g/L}$ (95 % CI 121–679) for BP3 (National Academies of Sciences, Engineering, and Medicine, 2022). The chronic and acute PNEC obtained from SSD-derived HC5 values were 1.9 and 3.4 $\mu\text{g/L}$, respectively, which is 30 to 40 times higher than the concentrations measured in Banyuls and Collioure. Altogether, results suggest low to unlikely acute and long-term risks of BP3 in the Collioure and Banyuls-sur-Mer bathing areas at the measured concentrations.

Risk assessment for QAs indicated high environmental risks for these compounds at the concentrations measured in the present study at both sites (Table 6). Despite the high AFs required due to the scarcity of toxicity data and contributing to the low PNEC for QAs, available data showed that half of the studies reported acute toxicity (LC and EC50) within the range of the average maximum concentration measured in Banyuls-sur-Mer and Collioure (0.086–0.501 $\mu\text{g/L}$). The only marine data available on microalgae suggested that these species seemed less sensitive to QAs (Quiroga et al., 2021) but further toxicity evaluations are needed for marine organisms, including fish, to better assess the risk of these compounds on the marine environment, especially given the high concentrations measured in the present study.

1,3-Diphenylguanidine (DPG) has been shown to cause neurotoxicity, reproductive toxicity, endocrine disruption, teratogenicity, and developmental toxicity in fish, mammals, and in vitro assays (Chibwe

et al., 2022; Ema et al., 2006; Shin et al., 2020). However, toxicity data for DPG in aquatic organisms are limited and non-existent for marine organisms (Table S2). Based on the available data, the PNEC for DPG was 3.64 $\mu\text{g/L}$, suggesting that environmental risks are unlikely at the maximum average concentrations measured in Banyuls-sur-Mer and Collioure of 0.015 and 0.009 $\mu\text{g/L}$, respectively (Table 6).

Studies have demonstrated the toxic effects of DEET on non-target aquatic organisms, including decreased androgen receptor activity in female fathead minnows *Pimephales promelas* (Zenobio et al., 2014), declines in photosynthetic biomass in microbial communities (Lawrence et al., 2019), and altered detoxification mechanisms in the aquatic midge *Chironomus riparius* (Campos et al., 2016). Acute toxicity data from 20 taxa (Table S2) allowed to calculate a HC5 of 16.6 mg/L (95 % CI 8.7–34.4 mg/L) for DEET from the SSD (Fig. S147), leading to a PNEC of 3.3 mg/L (Table 6). These values are consistent with previous SSD-derived acute PNECs for DEET, which ranged from 2.6 to 8.5 mg/L (Gao et al., 2020; Sun et al., 2016). The maximum average concentrations measured in Banyuls-sur-Mer and Collioure were 100 times lower than the PNEC, indicating an unlikely environmental risk for this compound. However, further data are needed on marine organisms and the chronic toxicity of DEET to assess the potential long-term environmental risk of this substance. This need is particularly important in the light of recent findings showing that the combination of the UV filter BP3 and DEET resulted in stronger-than-predicted effects in aquatic midges *C. riparius* (Campos et al., 2023).

Crystal violet is considered genotoxic (European Food Safety Authority (EFSA) et al., 2017), but aquatic toxicity data are limited to a few aquatic species (Table S2). The lowest acute toxicity was reported for *Orizias latipes* (EC50 = 82 $\mu\text{g/L}$) and resulted in a PNEC of 0.0082 $\mu\text{g/L}$, indicating a medium to high risk for CV at the concentrations measured in Collioure and Banyuls-sur-Mer (Table 6). The source of CV contamination remains unidentified, necessitating further investigation into its potential impact on marine ecosystems, for which data are currently lacking.

4. Conclusion

This study investigated the concentration levels of various pollutants and their potential impact on marine ecosystems, particularly during the peak tourist season, in two popular bathing areas of the Côte Vermeille, Banyuls-sur-Mer and Collioure. The findings revealed significant concentrations of UV filters such as BEMT and ET, with levels reaching up to 14 µg/L and 11.4 µg/L, respectively. The presence of these compounds, widely used in European sunscreen products, was expected due to high tourist activity. Untargeted analysis further identified another 52 anthropogenic compounds including industrial surfactants like PEG derivatives, detergents such as QAs, and pollutants from domestic and industrial sources like DEET and DPG.

The risk assessment indicated that while the environmental risks of DEET, DPG, and BP3 at their detected concentrations are low to unlikely, there is a high environmental risk associated with OC. OC concentrations as high as 3.5 µg/L are particularly critical for marine species that settle and reproduce in these areas. Additionally, the potentially high impact of the identified QA derivatives and crystal violet represent a point of vigilance and calls for further investigation due to their widespread use and reported toxicity.

This study emphasized the need for improved monitoring of UV filters and other pollutants in coastal areas, especially during peak tourist seasons. The results highlighted the importance of developing untargeted screening to identify the major contaminants in the sampling area and the necessity of increasing our understanding of the environmental toxicity of numerous anthropogenic compounds for which too little data is currently available. Further research is necessary to better understand the long-term effects of these contaminants on marine ecosystems and to develop effective strategies for mitigating their impact.

CRedit authorship contribution statement

Aude Gandar: Writing – original draft, Methodology, Investigation, Formal analysis, Data curation. **Maeva Giraud:** Writing – review & editing, Writing – original draft, Methodology, Investigation, Formal analysis, Data curation. **Théo Perion:** Methodology, Investigation, Formal analysis. **Emeline Houël:** Writing – review & editing, Writing – original draft, Investigation, Formal analysis, Data curation. **Thierry Noguier:** Supervision, Project administration, Data curation, Conceptualization. **Alice M.S. Rodrigues:** Methodology, Data curation. **Carole Calas-Blanchard:** Supervision, Project administration, Investigation, Funding acquisition, Data curation, Conceptualization. **Didier Stien:** Writing – review & editing, Writing – original draft, Validation, Supervision, Investigation, Formal analysis, Data curation, Conceptualization.

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Declaration of competing interest

The authors declare that they have no competing financial interests or personal relationships that could have appeared to influence the work reported in this article.

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Appendix A. Supplementary data

Supplementary material includes detailed map showing sampling locations, further information on POCIS calibration system, accumulation curves, LC-MS extracted ion chromatograms, MS spectra and collision-induced MS² spectra for compounds 1–56, an exhaustive table of the toxicity data used for risk assessment accompanied with a list of references, and species sensitivity distribution graphs for BP3 and DEET. Supplementary data to this article can be found online at <https://doi.org/10.1016/j.marpolbul.2025.117567>.

Data availability

Data will be made available on request.

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