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The invisible impact of tourism: organic UV filters in the coastal ecosystem of a remote Atlantic island

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ABSTRACT

Coastal tourism and recreational activities contribute to the release of Personal Care Products, including sunscreens, which contain organic ultraviolet filters (oUVFs), increasingly recognised as contaminants of emerging concern in marine ecosystems. Oceanic islands offer natural laboratories for studying these compounds due to their isolated ecosystems and varying levels of human pressure. This study investigates the occurrence and distribution of oUVFs in seawater, sediments, and biota from three locations in the Madeira Archipelago with varying human influence, sampled during both high and low tourist seasons. Solid-phase extraction (SPE) and microwave-assisted extraction (MAE) were used as extraction methods, followed by UHPLC-MS/MS for identification and quantification. Eight of 11 target compounds were detected in at least one matrix. Total maximum concentrations reached 70.61 ng/L in seawater, 299.8 ng/g d.w. in algae, 472.2 ng/g d.w. in fish, and 651.33 ng/g d.w. in zooplankton. Detection frequencies and levels were highest at the site with the most significant anthropogenic pressure during the high tourist season. Zooplankton showed the highest accumulation levels, followed by herbivorous fish and red algae, while no oUVFs were detected in mesopredators and some invertebrates. Contamination was associated with proximity to shore and direct inputs linked with anthropogenic pressure. However, the oceanographic (*e.g.*, currents, tides) and geological characteristics (rocky reefs) of oceanic islands must also be considered, as they can affect the environmental fate and distribution of oUVFs across different matrices. These findings highlight the need to monitor oUVFs in marine environments and identify susceptible species to improve ecological risk assessment and regulatory actions.

1. Introduction

Anthropogenic pressure on coastal areas has raised concerns about its impact on marine ecosystems. One of these pressures is the increased use of Personal Care Products (PCPs) such as sunscreens (Rizzi et al., 2023). These products are primarily designed to protect the skin from prolonged exposure to ultraviolet (UV) radiation, specifically UVA (320–400 nm) and UVB (290–320 nm) wavelengths, by preventing health issues such as skin cancer, premature skin ageing, depigmentation, and sunburn (Shetty et al., 2023). To enhance the effectiveness of PCPs in protecting against UV radiation, formulations include a combination of organic and inorganic ultraviolet filters (oUVFs and iUVFs, respectively), which determine the resulting sun protection factor (SPF). In Europe, only two iUVFs, titanium dioxide (TiO_2) and zinc oxide (ZnO), are permitted in nano- and micro-formulations, along with 29 oUVFs classified into 12 distinct families according to their chemical structure. These compounds can constitute between 5 and 25 % of the total cosmetic formulation, as regulated by Annex VI of EU Regulation 2022/2197 (Caloni et al., 2021).

The oUVFs are introduced into the environment through both indirect and direct pathways. Indirect sources include industrial discharges, effluents from wastewater treatment plants (WWTPs), and runoff from

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river mouths and streams. Beyond tourism-related inputs, continuous sources include leaching and abrasion from plastic materials (*e.g.*, consumer plastics, fishing gear, packaging) and releases from paints and coating formulations (*e.g.,* ship paints, antifouling, decorative coatings), supplying oUVFs to seawater, sediments, and biota year-round (Huang et al., 2021; Chen et al., 2024; Grant et al., 2025). The quantity of sunscreens introduced into marine environments in areas with high touristic pressure can be substantial, as seen in the French Atlantic Coast (Arcachon), where an estimated 8.13 kg/day of sunscreen products are released into coastal waters (Milinkovitch et al., 2024). On some of Hawaii's most visited beaches, *ca.* 36 kg/day of sunscreen enters the marine environment daily (Downs et al., 2022), while, in the Mexican Caribbean, home to the world's second-largest reef system, an estimated 229.76 tons per year of sunscreen are released annually into coastal and freshwater ecosystems (Casas-Beltrán et al., 2021). Given the large quantities of PCPs introduced into coastal ecosystems, the stability and resistance of oUVFs to degradation have become a growing concern. Their physicochemical properties, such as low solubility and high lipophilicity, often measured by the octanol-water partition coefficient (K_{ow}), contribute to their long-life expectancy and environmental persistence (O'Malley et al., 2021). As a result, these compounds are now classified as contaminants of emerging concern (CECs) (Castro et al., 2018).

Although direct-release pathways significantly impact coastal ecosystems, indirect sources also play an essential role (Downs et al., 2022). The widespread presence and physicochemical characteristics of oUVFs make their removal from water, sediments, and sludge challenging. WWTPs can achieve removal rates between 70 and 99 %, using advanced processes such as reverse osmosis, membrane separation, and advanced oxidation. However, these technologies are only available in secondary or tertiary treatments, which are costly and implemented in only a limited number of WWTPs (Tran et al., 2022). As CECs, oUVFs pose additional challenges due to gaps in understanding their degradation kinetics, transformation pathways, and potential derivative products, some of which may be more toxic than the parent compounds. These byproducts can interact with the environment and organisms, for example, leading to the production of reactive oxygen species (ROS), further complicating efforts to assess their ecological impact (Díaz-Cruz et al., 2008; Pintado-Herrera and Lara-Martín, 2020). Other significant indirect inputs of oUVFs arise from industrial products in which they are incorporated to enhance durability. These compounds can enter marine ecosystems through pathways such as ship and boat paints or coastal construction activities (Chen et al., 2024). In addition, microplastics (MPs) present in marine environments may further contribute to the transport and transfer of oUVFs, given their strong capacity to adsorb hydrophobic chemical compounds as oUVFs (Pacheco-Juárez et al., 2025).

Many laboratory experiments have been carried out describing oUVFs as endocrine disruptors affecting reproduction and sexual maturity, early development stages, and growth rate in marine biota (Corinaldesi et al., 2017; Carvalhais et al., 2025) as well as highlighting warning concentrations and possible effects in humans (Bury et al., 2023). Beyond laboratory findings, *in situ* environmental effects have been observed, such as coral bleaching linked to oUVFs exposure. As a result, several regions, including Hawaii, Key West, the U.S. Virgin Islands, Aruba, Bonaire, and Palau, have implemented bans on certain PCPs to mitigate their environmental impact (Danovaro et al., 2008; Mitchelmore et al., 2021). The oUVFs have been described worldwide in a wide range of concentrations (ng/g and ng/mL), which depend on the season, the anthropogenic pressure and the geological characteristics of the location, reaching remote areas such as the Antarctic, where scientific settlements and expeditions by boat are an input source of oUVFs (Duarte et al., 2021). Regarding biota; monitoring and assessment of oUVF in different organisms such as algae (Cadena-Aizaga et al., 2022a), seagrass (Pacheco-Juárez et al., 2019), phytoplankton (Duarte et al., 2021), invertebrates (Parra-Luna et al., 2020; Cuccaro et al., 2022), fishes (Gimeno-Monforte et al., 2020; Pintado-Herrera et al., 2024) and marine mammals (Íñiguez et al., 2025) have been described.

In recent years, efforts to study and disseminate information about the presence of oUVFs in the environment have increased (van Genuchten, 2024). However, significant knowledge gaps remain regarding the distribution and behaviour of these compounds in marine ecosystems (Mitchelmore et al., 2021; Lebaron, 2022). Monitoring studies are crucial for determining the actual presence of oUVFs and evaluating their potential risks to marine organisms and their implications for human exposure and consumption.

Oceanic islands are valuable natural laboratories for ecological studies because their isolation facilitates the evaluation of human-environment interactions with fewer external influences and a relatively pristine baseline (Vitousek, 2002). Despite increasing evidence on the occurrence and effects of oUVFs, significant knowledge gaps persist, partly due to the lack of standardised and sensitive analytical methods capable of simultaneously detecting multiple compounds in different taxonomic groups and determining their toxic or lethal concentrations in the environment. Several oUVFs, such as 4-MBC, are classified as hazardous to aquatic ecosystems by the European Chemicals Agency (ECHA) (Sobek et al., 2013). Advanced chromatographic and mass spectrometric approaches, such as UHPLC-MS/MS, have shown promise for achieving accurate identification and quantification across different environmental compartments (Cadena-Aizaga et al., 2020; Henderson et al., 2025). Mainly due to the physicochemical properties of the target compounds, low volatility and thermal stability, which makes the derivatisation needed for gas chromatography (GC) a harder task due to the high boiling points (Oubahmane et al., 2023).

Establishing such methodologies in island ecosystems provides a robust framework for assessing contamination dynamics in relatively isolated yet anthropogenically pressured regions. Tourism-related activities represent a major direct source of oUVFs in oceanic islands, yet their influence on environmental fate and trophic transfer remains largely unexplored.

This study investigates the presence and distribution of 11 commonly used oUVFs within the coastal marine environment around Madeira Island, Portugal. Anthropogenic pressure in terms of demography and tourist seasons (high and low) has been selected as a variable. Water was selected to assess the short-term presence of UVF, serving as a transport vector, while sediments were selected as a temporal integrator of persistent oUVFs, and organisms belonging to different trophic levels were used to assess oUVF accumulation in marine coastal communities. A similar study has monitored a wide range of organic contaminants in seawater, sediments, and coral species in La Herradura Bay (Mediterranean Sea, Spain), accounting for seasonal variation and spatial differences in contamination sources, presenting a similar procedure to the one proposed for this study (Tovar-Salvador et al., 2025). Involving the same ecoregion (Macaronesia), Montesdeoca-Esponda et al. (2021) researched the presence of benzotriazole UV Filters around Gran Canaria (Spain) beaches and organisms and evidenced the widespread distribution of these analytes in different compartments. However, to our knowledge, this is the first study carrying out the occurrence and distribution of oUVFs across multiple environmental matrices in different trophic levels, starting from plankton up to mesopredators, on an isolated oceanic island linked to different human pressures, providing novel insights into how insular ecological and geological settings influence their environmental fate and bioaccumulation.

2. Material and methods

2.1. Study area

This study was conducted in the waters of the Madeira Archipelago, Portugal. It lies in the Eastern North Atlantic, within the Macaronesia ecoregion, together with the Azores, the Canary Islands, and Cabo Verde. This archipelago comprises the inhabited islands of Madeira

(256,622 residents) and Porto Santo (5158 residents), and the uninhabited Desertas and Selvagens Islands, which are classified as partial and integral nature reserves (both terrestrial and, marine). The highest population density occurs along the south coast of Madeira Island, particularly in the main city of Funchal, with 107,562 inhabitants (Direção Regional de Estatística da Madeira, 2023). The mild climate, with annual mean sea surface temperatures ranging from 18 °C in winter to 23 °C in summer, is influenced by the Azores anticyclone and the prevailing northeast trade winds, making Madeira Island an attractive tourist destination. Hence, Madeira Island receives *ca.* 2.1 million tourists annually (Direção Regional de Estatística da Madeira, 2023), with tourism serving as the dominant economic sector (de Almeida and Machado, 2019).

Samples were collected for one year (2023) across different trophic levels and environmental matrices (Table 1), divided into two seasons: high tourist season (April–October) and low tourist season (November–March). The classification of seasons was based on official data from the Direção Regional de Estatística da Madeira (2023).

Sampling locations were defined based on anthropogenic pressure according to demography: Funchal (FX) (32° 38′ 27.920″ N; 016° 55′ 17.180″ W) as a highly impacted site, Lombada dos Marinheiros (LM) (32° 47′ 18.208″ N; 017° 14′ 52.372″ W) as a low anthropogenic pressure site due to limited accessibility; and Deserta Grande (DS) (32° 30′ 53.410″ N; 016° 30′ 45.418″ W) as a pristine/control site because of controlled human access (Marine Protected Area) (Fig. 1).

Sampling was organised to collect all samples in one day, during the morning at each location and season, resulting in a total of six sampling days. For zooplankton, an additional six nighttime fieldwork sessions were conducted, following the same design of one day per location and season. For each sampling day, three samples were collected for water, sediment, zooplankton, and algae. Additionally, five specimens of each invertebrate and five of each fish species were collected (except blacktail comber, which only five specimens were bought in the local market) (Table 1).

2.2. Reagents and consumables

Eleven oUVF were investigated in the present study. Their characteristics are summarized in Table S1. All oUVF and the internal standard (IS), deuterated benzophenone (Bp-d_{10}) (purity ≥99 %), were obtained from Sigma-Aldrich (Madrid, Spain). LC-MS grade solvents, including water, formic acid, methanol (MeOH), acetone (ACE), acetonitrile (ACN), dichloromethane (DCM) and hexane (HEX), were obtained from Panreac Química (Barcelona, Spain). Membrane filters (0.22 μm) were purchased from Millipore (Cork, Ireland). Sep-Pak C18 cartridges (500 mg) were obtained from Waters (Madrid, Spain), and CHROMAFIL polyethylene terephthalate disposable syringe filters (0.2 μm pore size) were obtained from Macherey-Nagel (Düren, Germany). Stock solutions of the target oUVFs (250 mg/L) were prepared in ACE and stored in amber glass vials at −20 °C. Working solutions were freshly prepared in MeOH daily.

2.3. Sampling collection and pre-treatment

Seawater and coastal sediment samples (Fig. 2a) were collected to assess the availability of oUVF in the short and long term, respectively, and to observe possible accumulation and distribution. Biota samples were selected based on lifestyle and trophic position (Table 1) (Dodds and Whiles, 2010). Accordingly, the red algae (*Asparagopsis taxiformis*) (Fig. 2b) were collected as a primary producer, while zooplankton samples represented primary consumers. The selected macroinvertebrates included the black sea urchin (*Arbacia lixula*) (Fig. 2c), which is a grazer, and the sea cucumber (*Holothuria sanctori*) (Fig. 2d), a detritivore. Additionally, three fish species were selected: the salema (*Sarpa salpa*), an herbivorous consumer; the parrot fish (*Sparisoma cretense*), an omnivorous secondary consumer; and the blacktail comber (*Serranus atricauda*), representing a mesopredator. Species selection was based on their ecological relevance, abundance, and year-round availability, aiming to minimize potential impacts on local populations.

Water samples were collected in pre-cleaned amber glass bottles (2.5 L capacity) with Teflon caps, always during the morning, right after the biota samples collection. Before filling, the bottles were rinsed with

Table 1
Description of the target species (trophic level and trophic guild) and sample size by location (FX, LM and DS) and season (High, Low).

Sample category	Species	Trophic Level	Trophic Guild	Samples per Location		Samples per Season		Total
Red algae[a]	Limu kohu (*Asparagopsis taxiformis*)	Primary producer	Photosynthetic	FX	7	High	10	19
				LM	6	Low	9	
				DS	6			
Zooplankton	–	Primary consumer	Mixed-feeder (omnivore)	FX	6	High	9	18
				LM	6	Low	9	
				DS	6			
Invertebrates	Black sea urchin (*Arbacia lixula*)	Primary consumer	Grazer	FX	10	High	15	30
				LM	10	Low	15	
				DS	10			
	Sea cucumber (*Holothuria sanctori*)	Primary consumer	Detritivore	FX	10	High	15	28
				LM	8	Low	13	
				DS	10			
Fish	Cow bream (*Sarpa salpa*)	Primary consumer	Herbivore	FX	9	High	13	27
				LM	8	Low	14	
				DS	10			
	Parrot fish (*Sparisoma cretense*)	Secondary consumer	Omnivore	FX	10	High	15	28
				LM	8	Low	13	
				DS	10			
	Blacktail comber (*Serranus atricauda*)	High-level consumer: Mesopredator	Macro-carnivore	Local market				5
Seawater	–	Environmental level	–	FX	6	High	9	18
				LM	6	Low	9	
				DS	6			
Sediments	–	Environmental level	–	FX	6	High	9	18
				LM	6	Low	9	
				DS	6			

[a] *A. taxiformis* (red algae) samples consist of multiple specimens of the same species, and zooplankton samples consist of a pool of organisms, rather than a single individual. FX: Funchal; LM: Lombada dos Marinheiros; DS: Deserta Grande).

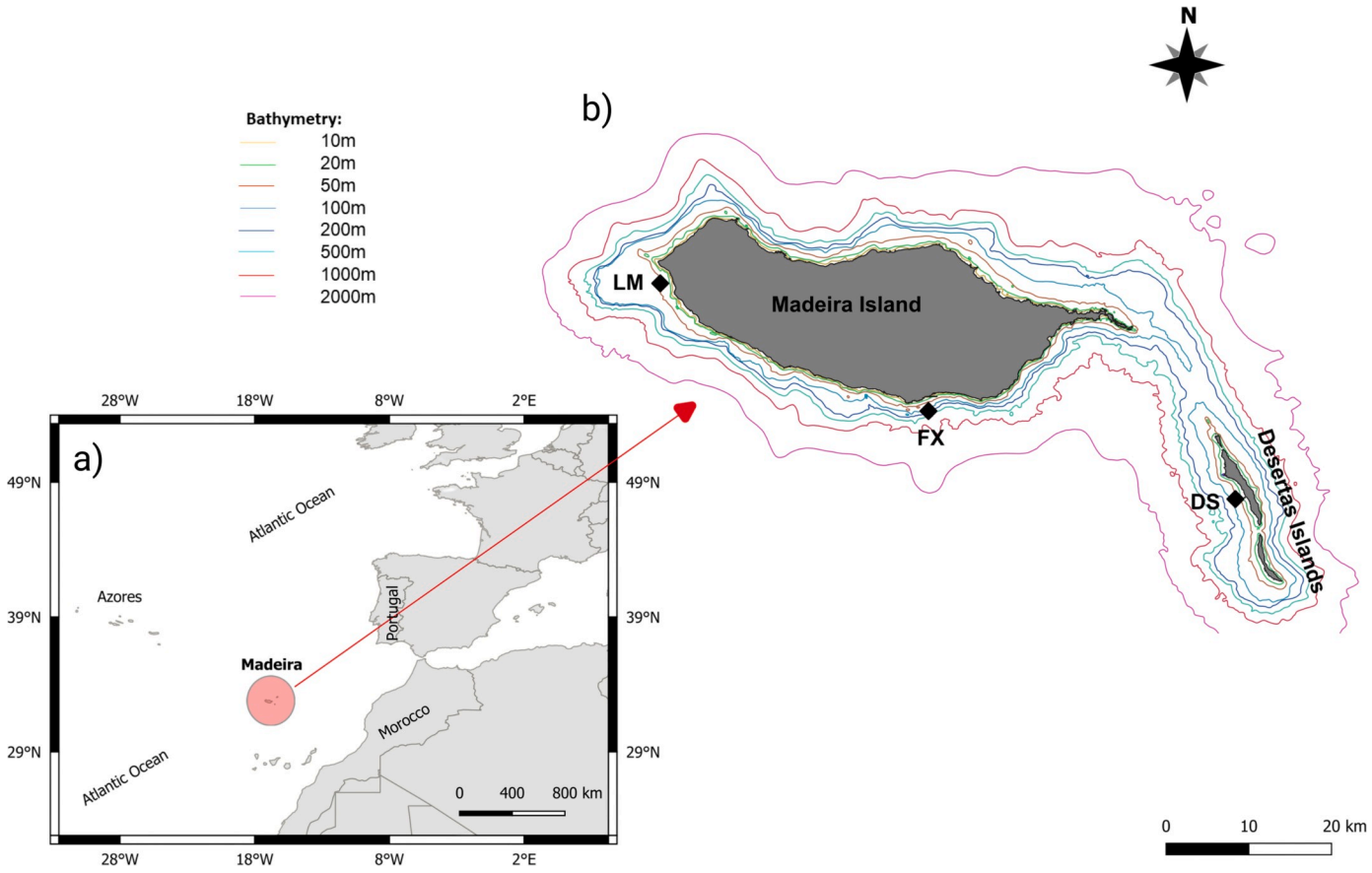

Fig. 1. (a) Location of the Madeira Archipelago in the Eastern North Atlantic; **(b)** Sampling sites and bathymetries around Madeira and Desertas Islands. LM: Lombada dos Marinheiros, FX: Funchal and DS: Deserta Grande.

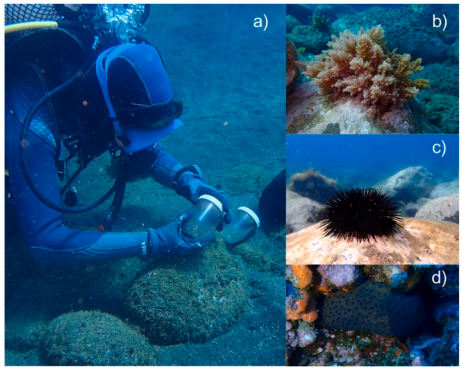

Fig. 2. Coastal sampling in August 2023, Funchal (FX): **(a)** sediment collection using pre-cleaned plastic jars; **(b)** Red algae: *A. taxiformis*, **(c)** Sea urchin: *A. lixula* and **(d)** Sea cucumber: *H. sanctori.*

seawater and then filled at *ca.* 50 cm below the surface. The samples were kept under cold and dark conditions until arrival at the laboratory. Upon arrival at the laboratory, the samples were acidified with formic acid (98 % purity) to pH 3 to halt biological activity. Subsequently, they were filtered through 0.22 μm membrane filters to remove particulate organic material and stored at 5 °C. Filters were not extracted, and particulate-bound oUVFs were not determined.

A team of two scientific SCUBA divers collected sediments, algae, and invertebrates, while accredited spear fishers sampled the pre-selected fish specimens. Biota and sediment (sand and gravel) samples were collected in the vicinity of rigid substrates (mainly volcanic boulders and blocks present at all three sampling locations) at 5–15 m depths. Immediately after collection, invertebrates and fish samples were wrapped in aluminium foil, placed in sterile insulated coolers with ice, and transported to the laboratory. Upon arrival at the lab, biometric measurements were recorded. Sediments were collected from the upper 0–10 cm of the sediment layer, placed in pre-cleaned polypropylene jars, and subsequently transferred to amber glass containers.

Algae samples were hand-collected in pre-cleaned plastic zip-lock bags. Once, on the boat, the algae samples were transferred to amber glass jars and stored in a cooler box. Upon arrival at the laboratory, they were rinsed with distilled water to remove epifauna and salt residues and transferred to amber glass jars. Invertebrate samples were collected within specific depth ranges: black sea urchins between 3 and 8 m and sand sea cucumbers between 8 and 15 m. Fish sampling was conducted at depths of up to 20 m in free diving. Additionally, five blacktail comber individuals were obtained from a local fish market to complement field sampling.

Zooplankton samples were collected at night, at least 1 h after sunset, using a Manta trawl with a 70 × 40 cm opening and a 200 μm mesh size. A flowmeter was attached to the centre of the net opening to determine the volume of filtered water. Each tow was conducted at the surface, parallel to the coast, for 30 min in waters with bathymetry between 30 and 50 m. Three transects per location and season were performed to obtain sufficient biomass for chemical contaminant analysis (150 mg per sample). After each tow, zooplankton were concentrated by rinsing the net with seawater over a 200 μm sieve, then washed with distilled water to remove residual salts and transferred to amber glass jars.

Invertebrates and fish were dissected in totality, homogenised, and stored at −20 °C in amber glass jars. Sediments, zooplankton, and algae were directly stored at −20 °C in amber glass jars. Once all sediment and biota (algae, zooplankton, and fish) samples were frozen and freeze-

dried using a lyophilizer (Savant RT 400, Thermo Scientific) for 72h at −50 °C. Then they were ground and sieved to a particle size of *ca.* 180 μm. The resulting powders were stored in amber glass vials under dry and dark conditions in the fridge (4 °C).

All samples were obtained under authorizations granted by the Instituto das Florestas e Conservação da Natureza, IP-RAM, Autonomous Region of Madeira, Portugal (Permits No. February 2023 D; January 2023 PNMPP).

2.4. Chemical compounds extraction: Solid-Phase Extraction (SPE) and Microwave-Assisted Extraction (MAE)

The extraction of oUVF in the seawater matrix was performed by SPE using C18 cartridges, which were conditioned with 5 mL MeOH (HPLC grade) followed by 5 mL Milli-Q water. Subsequently, 700 mL of seawater was passed through each cartridge, followed by a washing step with 5 mL Milli-Q water. The cartridges were dried under vacuum for 1 min and stored at −20 °C in the dark in aluminium foil until elution. All this process was carried out in Madeira. Elution and instrumental analysis were then performed later in Las Palmas de Gran Canaria. This workflow reduces transport contamination risk and is standard when collection and analytical labs are in different locations. Elution was carried out with 5 mL MeOH:ACN (1:1, v/v) (Cadena-Aizaga et al., 2022b).

Microwave-assisted extraction (MAE) was used for sediments and biota. Two systems were employed: a PerkinElmer unit equipped with 16 Teflon-modified vessels (Madrid, Spain) and an Anton Paar multiwave oven with 6 EVAP rotors and 6 MF100 vessels (Graz, Austria). For sediments: 1 g of sediment was mixed with 2 mL ACN and subjected to MAE at 300 W for 3 min (Montesdeoca-Esponda et al., 2013). Algae: One hundred mg algae powder was extracted twice with 2 mL ACE at 50 °C for 5 min, evaporated under N_2, and reconstituted in 2 mL MeOH (Cadena-Aizaga et al., 2022a), Invertebrates: One hundred mg tissue powder was mixed with 5 mL ACE and, extracted at 50 °C for 3 min (Cadena-Aizaga et al., 2022c). Fish: One hundred mg fish powder was mixed with 7 mL DCM, extracted at 60 °C for 10 min, evaporated under N_2, and reconstituted in 1 mL ACN in an LC vial (Gimeno-Monforte et al., 2020). Zooplankton: fifty mg zooplankton powder was mixed with 7 mL HEX and extracted at 68 °C for 2 min. As HEX is incompatible with UHPLC-MS/MS, the extract was evaporated under N_2 and reconstituted in 1 mL MeOH in an LC vial. As the last step, all extracts were filtered through 0.45 μm syringe filters prior to transfer into LC vials (Íñiguez et al., 2025). SPE clean-up was not applied to biota and sediment samples to minimize handling/blank risks and potential analyte losses.

Extraction and analytical analyses were carried out in November–December 2023 and April–May 2024 in Universidad de Las Palmas de Gran Canaria, Analytical Chemistry department.

2.5. Analytical determination

The eleven oUVFs were quantified using an ACQUITY UHPLC Xevo TQ-S system (Waters Chromatography, Barcelona, Spain) equipped with a Binary Solvent Manager, thermostated autosampler, column manager, and a triple quadrupole mass spectrometer with an electrospray ionization (ESI) source. Chromatographic data were acquired and processed with MassLynx software (Waters Chromatography, Barcelona, Spain). The mobile phases consisted of (A) methanol (MeOH, LC-MS grade, 0.1 % formic acid, v/v) and (B) ultrapure water (LC-MS grade, 0.1 % formic acid, v/v). The gradient programme, at a flow rate of 0.3 mL/min, started with 75 % A/25 % B for 3 min, increased to 100 % A by 5 min, and then returned to 75 % A/25 % B for 2 min for column re-equilibration. The injection volume was 10 μL. The ESI-MS/MS conditions were as follows: capillary voltage 3 kV, cone voltage 15 V, source temperature 120 °C, desolvation temperature 450 °C, nitrogen as desolvation gas at 500 L/h, and argon as the collision gas (all gases ≥99 % purity). Detailed compound-specific MS/MS detection parameters are provided in Table S2.

2.6. Quality assurance and quality control

Calibration curves were constructed using eight concentration levels ranging from 1 to 500 ng/mL. Each compound showed linearity with a coefficient of determination ($R^2 > 0.99$). Instrumental limits of detection (ILODs) and instrumental limits of quantification (ILOQs) were calculated from signal-to-noise (S/N) ratios of the analyte peaks, assuming minimum detectable S/N values of 3 (ILOD) and 10 (ILOQ), respectively. Methodological limits of detection (MLODs) and quantification (MLOQs), expressed as analyte per mass/volume of sample, were estimated by propagating ILOD/ILOQ with sample mass/volume and (pre-)concentration factors. Instrumental and methodological limits (ILOD/ILOQ; MLOD/MLOQ) are provided in Table S3.

Recoveries were assessed by spiking BP-d10 (200 ng/mL) as an IS into every sample. Each sample was analyzed in triplicate, and only those with a relative standard deviation (RSD) ≤ 30 % were retained for interpretation. To minimize external contamination or analyte degradation, all containers were amber glassware, thoroughly pre-cleaned and rinsed with distilled water and HPLC-grade ethanol before use. Laboratory personnel wore nitrile gloves throughout the procedure. All target compounds in procedural blanks were below the MLOD.

2.7. Statistical analyses

Kruskal-Wallis tests were used to evaluate differences in oUVF concentration across locations and seasons. When significant, post hoc pairwise comparisons were performed using the Wilcoxon test with the Bonferroni correction, considering a significance threshold of $p < 0.05$. Data for each species/Matrix were analyzed separately. All statistical analyses and visualisations were performed in R (R Core Team, 2021; version 2023). When the value was under the MLOQ, they were assigned half of the MLOD value (Cunha et al., 2015). Only the quantified values were considered for calculating means, standard deviation, ranges, and frequency of occurrence (FO) as well as for graphical representation. FO was computed as the proportion of samples with concentrations ≥ MLOD for each analyte.

3. Results

Eight out of the eleven investigated oUVFs: BP-3, HMS, DTS, OC, BM-DBM, OD-PABA, OMC, and EHS, were detected at least once across the analyzed matrices. Out of 191 total samples collected, 54 showed at least one of these compounds (Table S4). Considering the total oUVF concentrations of all samples with quantified target analytes, comparisons were carried out according to location and season. Wilcoxon tests showed significant differences between FX and DS ($p = 0.0004$) and LM and DS ($p = 0.018$), while no significant differences were observed between FX and LM (Fig. 3).

The same analyses were performed considering the season variable. When comparing high and low seasons across all locations, no significant differences were found. To explore this further, samples were classified by both location and season. Significant differences (Wilcoxon test, $p < 0.05$) were observed between high-season samples of FX (FX_HIGH) and DS (DS_HIGH), as well as LM (LM_HIGH) and DS (DS_HIGH) (Fig. 3).

3.1. Seawater and sediment levels of detected oUVF

No oUVF were detected above the MLOD in sediment samples. Seawater exhibited the lowest quantified concentrations of total oUVF across all matrices, ranging from 4.405 to 70.61 ng/L. Seawater samples from FX showed higher quantified concentrations (5.044–47.37 ng/L) and higher detection frequency (83 %) than DS (6.027–14.82 ng/L, 50 %) and LM (4.405–5.370 ng/L, 33 %) (Fig. 4). No significant differences

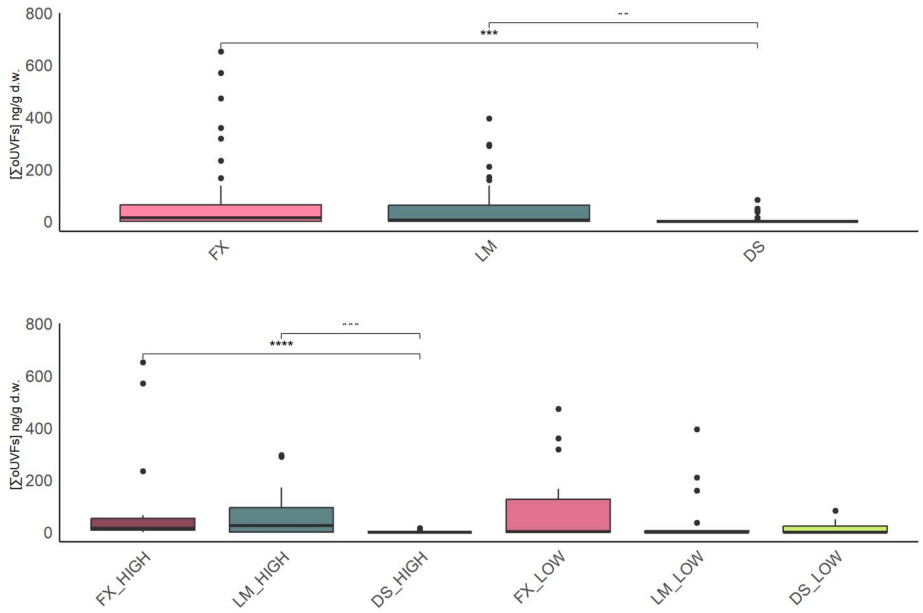

Fig. 3. Boxplots representing total oUVF concentrations (ΣoUVFs; ng/g d.w.) grouped by location (FX, LM, DS) and season within each location (HIGH = high season; LOW = low season). Boxes show median and interquartile range (IQR); points indicate outliers. Group differences were assessed with Kruskal-Wallis followed by pairwise Wilcoxon rank-sum tests with Bonferroni correction; *, **, ***, **** denote $p < 0.05$, 0.01, 0.001, 0.0001, respectively. Values below MLOQ were substituted by MLOD/2.

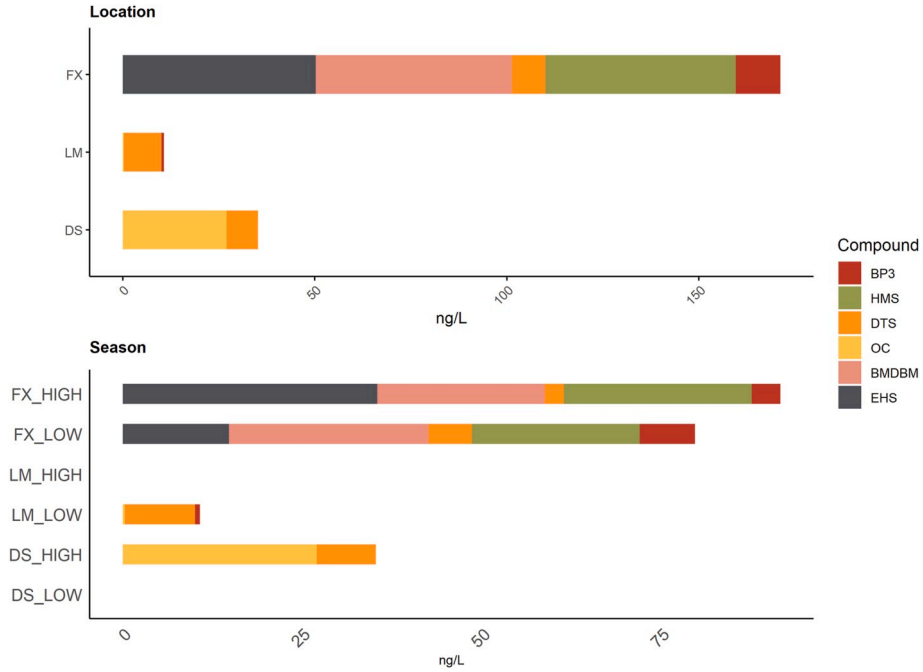

Fig. 4. Cumulative concentrations of organic UV filters (ΣoUVFs; ng/L) in seawater, grouped by location - Funchal (FX), Lombada dos Marinheiros (LM), and Desertas (DS)- and by season (HIGH and LOW) within each location. Values below MLOQ were settled as MLOD/2.

were detected in seawater samples among locations (Wilcoxon test, $p > 0.05$).

Consistent with these findings, the oUVF profile at FX was more diverse, with five compounds detected. Specifically, DTS (2.940 ± 0.155 ng/L) and EHS (16.752 ± 3.370 ng/L) were quantified, and FX was the only location where BP-3 (5.843 ± 1.843 ng/L), HMS (19.855 ± 3.290 ng/L), and BM-DBM (25.740 ± 2.240 ng/L) were detected above the MLOQ. In contrast, at LM, all compounds were below the LOD except DTS (4.890 ± 0.483 ng/L) and a single detection of BP-3 below the LOQ. At DS, only OC (9.010 ± 4.120 ng/L) and DTS (2.740 ± 0.110 ng/L) were detected and quantified (Fig. 3).

Regarding seasonal variation in seawater samples, assessed using pooled data from the three locations, mean concentrations did not differ substantially among sampling periods (Table S5) and no significant differences were observed, either overall or when divided by location (Wilcoxon test, $p > 0.05$).

The FX_HIGH and the low season in FX (FX_LOW) exhibited similar total oUVF concentrations, with mean values of 18.87 ± 22.08 ng/L and 22.23 ± 18.53 ng/L, respectively. In contrast, LM and DS showed distinct seasonal patterns. In LM_HIGH, no oUVFs were detected,

whereas during LM_LOW, DTS and BP-3 were detected at 3.26 ± 2.86 ng/L and 0.21 ± 0.97 ng/L, respectively. Conversely, in DS, no oUVFs were detected during the DS_LOW, while OC and DTS were measured at 9.010 ± 5.041 ng/L and 2.740 ± 2.804 ng/L, respectively, during the DS_HIGH (Table S6).

3.2. Presence and distribution of oUVF across different biota categories

Organisms were classified into predefined categories (Table 1). Within the invertebrate category, comprising sea cucumber and black sea urchin, no oUVFs were detected above the MLOD. Similarly, blacktail comber was excluded from the fish category analyses due to undetectable oUVFs concentrations. Considering all datasets, the FO of oUVFs ranged from 38.2 % in fish to 66.7 % in zooplankton. Zooplankton exhibited the broadest quantified concentration range, spanning from 37.84 to 651.3 ng/g dry weight (d.w.). Red algae represent the second most affected category, with nearly half (47.4 %) of the samples containing oUVFs above the MLOD. However, the maximum concentration quantified in algae was 299.8 ng/g d.w., with a mean concentration of 96.75 ± 99.55 ng/g d.w., lower than those observed in zooplankton and fish (129.2 ± 186.7 and 108.3 ± 145.0 ng/g d.w., respectively) (Table S7).

In the fish category, two species were included: parrot fish and salema. The salema exhibited an FO of 51.9 %, with the second-highest mean concentration (157.5 ± 158.7 ng/g d.w.) among the biota categories, following zooplankton. The quantified concentration range for salema spanned from 7.670 to 472.2 ng/g d.w. considering the quantified data (Table S7).

When examining the total oUVFs concentrations by location, all categories exhibited higher FO in FX, ranging from 30 % in parrot fish to 88.9 % in salema. Furthermore, all matrices, except algae (which showed higher and more variable concentrations in LM), presented greater and wider concentration ranges in FX, followed by LM and DS (Fig. 5; Table S8). Only fish category showed significant variation in total oUVF concentrations across locations, as indicated by the Wilcoxon test ($p = 0.001$ between FX and DS; $p = 0.002$ between LM and DS). When analyzed by individual fish species, significant differences were only detected in the salema matrix, between FX and DS (Wilcoxon test, $p = 0.001$) and LM and DS (Wilcoxon test, $p = 0.018$).

Considering seasonal variation, all categories except salema (and thus the fish category as a whole) exhibited their highest quantified concentrations during the high season, ranging from 15.49 to 185.1 ng/g d.w., compared to 4.51–331.5 ng/g d.w. in the low season. An exception was observed in zooplankton, where the FO was 22.2 % higher in the low season than in the high season. In contrast, the remaining categories showed higher FO values in the high season, ranging from 53.9 % in salema to 70 % in red algae (Table S5). Among all comparisons by to species and season, only parrot fish showed significant seasonal differences (Wilcoxon test, $p = 0.021$).

When considering seasonality within locations for deeper analysis, zooplankton showed no significant differences across seasons within locations (Kruskal-Wallis, $p = 0.18$). Nevertheless, the FX_HIGH showed nearly fourfold higher mean and FO of total oUVF concentrations (427.8 ± 319.4 ng/g d.w. and 100 %), followed by the LM_HIGH (127.6 ±

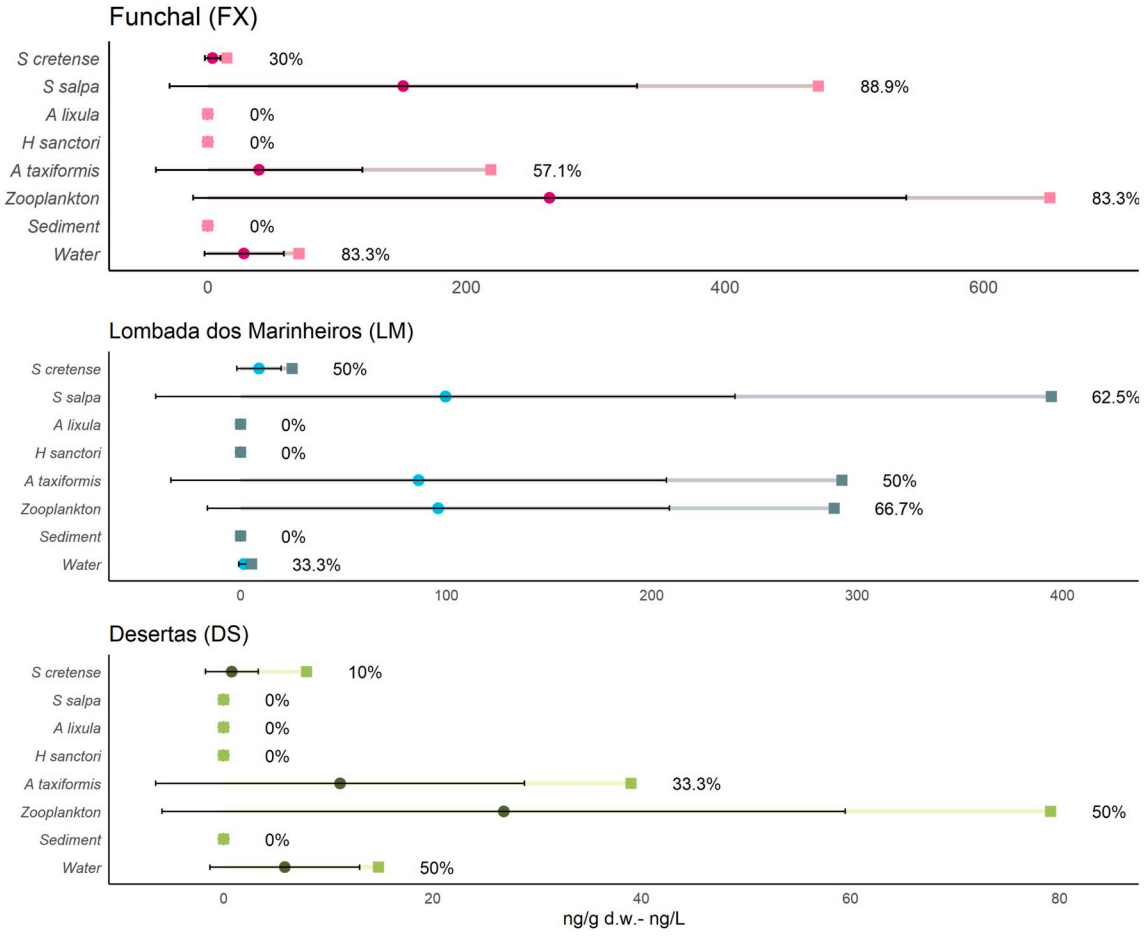

Fig. 5. Lollipop plots showing the total concentrations of oUVFs (∑oUVFs) per species across sampling locations (FX, LM, DS). Squares represent the maximum concentrations, while dots indicate the mean values with standard deviations (black lines). Numerical labels next to the bars represent the FO for each species at each location. Note: The X-axes have different scales in each graph to facilitate visualization. Values below the MLOD were considered *n.d.* and assigned a value of 0. Values below MLOQ were substituted by MLOD/2.

147.3 ng/g d.w. and 66.7 %), the FX_LOW (100.7 ± 88.5 ng/g d.w. and 66.7 %), the low season of LM (LM_LOW) (64.7 ± 147.3 ng/g d.w. 66.7 %), and the low season of DS (DS_LOW), this one with an exception of the FO because the 100 % of the samples showed to have detectable concentration of oUVFs (55.7 ± 23.4 ng/g d.w.). Other seasons among the locations with detectable levels showed similar FO values (around 67 %).

Red algae exhibited the highest mean concentrations of total oUVFs in the LM_HIGH (178.6 ± 112.2 ng/g d.w.), followed by FX_HIGH (72.80 ± 106.9 ng/g d.w.) and DS_LOW (27.00 ± 23.43 ng/g d.w.). Meanwhile, the other samples collected in the remaining season, according to the location, did not show detectable concentrations of oUVFs. Regarding FO, in both high season from FX and LM, 100 % of the samples present detectable concentrations of oUVFs, whereas in DS_LOW, only 66.7 %. Differences among seasons according to locations were significant according to the Kruskal–Wallis test ($p = 0.012$), although pairwise Wilcoxon tests did not identify significant contrasts between individual factors.

Within the fish category, salema from DS showed no detectable oUVFs. In contrast, the highest mean concentrations were observed during the FX_LOW (311.0 ± 158.0 ng/g d.w.) and LM_LOW (120.9 ± 178.0 ng/g d.w.), followed by the LM_HIGH (66.7 ± 60.8 ng/g d.w.) and FX_HIGH (23.2 ± 25.4 ng/g d.w.). However, the FO was 100 % in LM_HIGH as well as FX_LOW; meanwhile, FX_HIGH presented 80 % of the samples contaminated, followed by LM_LOW with 40 %. No oUVF were detected in DS for this species. Parrot fish generally showed lower levels, with quantifiable concentrations detected only in the LM_HIGH (14.4 ± 10.3 ng/g d.w.), the FX_HIGH (7.34 ± 7.02 ng/g d.w.), and in a single sample from the DS_LOW (1.59 ng/g d.w.). Both species showed significant differences among the factors (Kruskal-Wallis = 0.0004 and 0.012, respectively).

None of the species showed a detectable concentration during DS_HIGH.

Statistical analyses were conducted with caution due to the small sample sizes of the different species, which limited the possibility of more detailed statistical assessments. Taking this into account, the Wilcoxon test revealed significant differences in the fish matrix (considering both species) between FX_HIGH and DS_HIGH ($p = 0.0332$), LM_HIGH and DS_HIGH ($p = 0.007$), and LM_HIGH and DS_LOW ($p = 0.019$). But non-significant differences were detected per specie.

3.3. oUVF presence in biota

The oUVFs detected in biota matrices were HMS, OC, OMC, EHS and OD-PABA (Table 2; Fig. 6). HMS and OC were the most frequently detected oUVFs and exhibited the highest concentrations across all locations. In contrast, EHS, although present at all locations, was only detected in the red algae and salema matrices (Table 2). Regarding FO, samples collected in LM showed the highest percentage for these oUVFs, with FOs of 21.74 % for HMS, 23.91 % for OC, and 13.04 % for EHS. This was followed by FX, with FOs of 17.31 % for HMS, 23.08 % for OC, and 7.69 % for EHS, and by DS, with FOs of 9.62 %, 11.54 %, and 5.77 % for HMS, OC, and EHS, respectively. Nevertheless, the mean concentrations of the identified oUVFs were highest in FX, with mean values of 108.0 ± 29.21 ng/g d.w. for HMS, 130.1 ± 211.9 ng/g d.w. for OC, and 218.8 ± 121.4 ng/g d.w. for EHS. These were followed by LM, with concentrations of 65.19 ± 56.60 ng/g d.w. for HMS, 51.87 ± 47.94 ng/g d.w. for OC, and 150.15 ± 90.70 ng/g d.w. for EHS. The least affected location was DS, with mean concentrations of 8.910 ± 5.538 ng/g d.w. for HMS, 29.04 ± 24.35 ng/g d.w. for OC, and 33.50 ± 5.500 ng/g d.w. for EHS (Fig. 6).

Regarding the seasonal variation, the presence of HMS appears to be similar in both seasons, with an FO of 14.29 % and a mean concentration of 82.80 ± 50.56 ng/g d.w. in the high season, compared to 20.55 % and 70.84 ± 54.70 ng/g d.w. in the low season when the samples are pooled without considering the location. However, HMS seems to have more presence in FX_LOW (46.52 ± 61.51 ng/g d.w.) and DS_LOW (2.479 ± 5.320 ng/g d.w.), meanwhile, it is in higher mean concentration in LM_HIGH (25.13 ± 50.55 ng/g d.w.) with respect to LM_LOW (9.467 ± 26.54 ng/g d.w.). On the other hand, OC seems to have a greater impact during the high season with an FO of 28.57 % and a mean concentration of 95.21 ± 165.4 ng/g d.w. In the low season, it was present in only 8.22 % of the samples, collected during LM_LOW (3.286 ± 12.29 ng/g d.w.) and DS_LOW (9.142 ± 19.74 ng/g d.w.). The least frequent oUVFs were OMC, detectable in only three salema samples from FX_HIGH (29.63 ± 10.82 ng/g d.w.). OD-PABA was detected solely in the zooplankton matrix, collected in LM with similar concentration in both seasons (LM_HIGH = 8.429 ± 31.54 and LM_LOW = 8.714 ± 28.82 ng/g d.w.), while it was not detected in FX. A deeper analysis of the matrices revealed that zooplankton, red algae, and the herbivorous fish, the salema, exhibited the highest diversity of oUVFs. In contrast, the parrot fish showed detectable concentrations of only OC (Table S6).

Every individual concentration, as well as the characteristics of the different collected samples, are summarized in Table S4.

4. Discussion

4.1. Occurrence of oUVF according to human pressure

In the present study, only 30 % of the samples exhibited oUVF concentrations above the MLOD. Madeira Island, as an oceanic island, is subject to various oceanographic phenomena, including erosion, water mass movement driven by waves and tides, upwellings, ocean currents

Table 2
Mean ± standard deviation for samples with detectable concentrations (≥MLOD) of individual oUVFs, in ng/g (d.w.) for biota and ng/L for seawater, and frequency of occurrence (FO, %).

Samples	BP3	HMS	DTS	OC	BM-DBM	OD-PABA	OMC	EHS
A. taxiformis	<MLOD	137.0 ± 33.00 10.53 %	<MLOD	51.47 ± 70.49 26.32 %	<MLOD	<MLOD	<MLOD	56.61 ± 32.81 31.58 %
Zooplankton	<MLOQ 11.11 %	52.52 ± 55.01 55.56 %	<MLOD	188.4 ± 221.9 44.44 %	<MLOD	80.00 ± 46.85 16.67 %	<MLOD	<MLOD
A. lixula	<MLOD	<MLOD	<MLOD	<MLOD	<MLOD	<MLOD	<MLOD	<MLOD
H. sanctori	<MLOD	<MLOD	<MLOD	<MLOD	<MLOD	<MLOD	<MLOD	<MLOD
S. salpa	<MLOD	99.03 ± 6.590 25.93 %	<MLOD	44.04 ± 43.83 18.52 %	<MLOD	<MLOD	29.63 ± 12.48 11.11 %	270.7 ± 54.07 18.52 %
S. cretense	<MLOD	<MLOD	<MLOD	13.73 ± 6.130 32.14 %	<MLOD	<MLOD	<MLOD	<MLOD
S. atricauda	<MLOD	<MLOD	<MLOD	<MLOD	<MLOD	<MLOD	<MLOD	<MLOD
Seawater	5.843 ± 1.843 16.67 %	19.86 ± 3.285 27.78 %	3.350 ± 0.931 44.44 %	9.010 ± 4.116 22.22 %	25.50 ± 2.237 11.11 %	<MLOD	<MLOD	16.75 ± 3.370 16.67 %
Sediments	<MLOD	<MLOD	<MLOD	<MLOD	<MLOD	<MLOD	<MLOD	<MLOD

MLOD: Methodological Limit of Detection; MLOQ: Methodological Limit of Quantification.

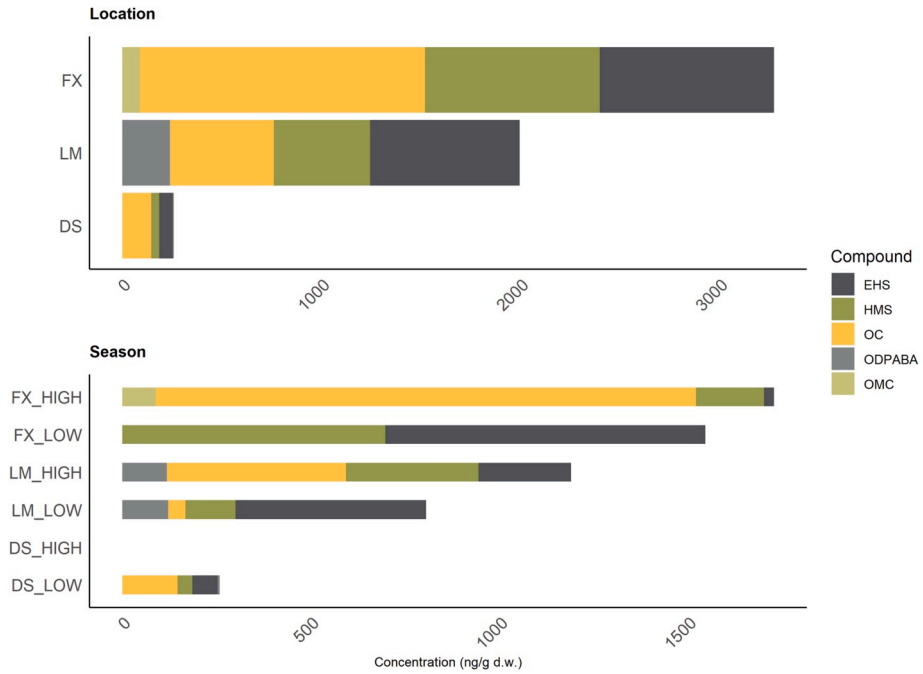

Fig. 6. Cumulative concentrations (ng/g d.w.) of the different oUVF detected in biota matrices (algae, zooplankton, and fishes) by location- Funchal (FX), Lombada dos Marinheiros (LM), and Desertas (DS) - and by season (HIGH and LOW). Values below MLOQ were substituted by MLOD/2.

and eddies (Caldeira et al., 2002)Caldeira and Sangrà, 2012. These events modify the coastline and contribute to the dilution of contaminants in the marine environment (Tsui et al., 2014). Furthermore, the sampling sites in this study were in open nearshore areas rather than closed or semi-enclosed beaches, which supports the hypothesis of dilution effects for the detected oUVFs (Sánchez Rodríguez et al., 2015; Mozas-Blanco et al., 2023).

Due to the island's steep and abrupt continental slope, the proximity of Madeira Island's coastline to deep-sea environments may also influence the environmental fate of oUVFs. It is plausible that they undergo vertical transport through the water column, ultimately reaching bathypelagic zones or accumulating in deep-sea sediments. The mentioned deep-sea environments are already considered sink regions for Persistent Organic Pollutants (POPs) (Pinheiro et al., 2023). This potential redistribution and long-term storage of oUVFs in the deeper marine environments could contribute to the relatively low FO observed in coastal samples collected from the Madeira archipelago and the low concentration detected in seawater samples.

Spatial and seasonal variation in oUVF presence across environmental and biological matrices appears to follow a pattern related to anthropogenic pressure. Among the sampling sites, FX is Madeira Island's capital and receives *ca.* 1.3 million of tourists annually, being also the city with the most significant tourist infrastructure. In contrast, LM (located in Calheta municipality) receives significantly fewer tourists, around 174 thousand per year (2024), and is therefore under considerably lower tourist pressure compared to FX. DS, on the other hand, is an uninhabited and protected area with minimal anthropogenic activity, only with the presence of a team of local rangers and occasional boat visits in a reduced area far away, where the samples were collected, thus reducing the likelihood of direct human contamination compared to the other locations (Instituto das Florestas e da Conservação da Natureza, IFCN, 2024). This gradient in human activity correlates with the observed concentrations and frequencies of oUVFs, supporting the notion that human activities are a significant contributor to the presence of these contaminants (Casas-Beltrán et al., 2021; Combi et al., 2022).

An exception was observed in DS, where 50 % of seawater samples contained at least one oUVF, exceeding the FO in LM. The main explanation for this unexpected pattern in seawater could be linked to the way oUVFs are released into the environment (Combi et al., 2022). The Madeira archipelago offers a diverse range of activities, many of which involve aquatic environments, such as scuba diving, hiking along water channels, surfing, and other water-based activities. These activities promote the use of PCPs, which are subsequently released directly into the marine environment (Lopes and Bicudo, 2017). Moreover, the rapid growth of tourism in recent years has led to increased waste generation, thereby raising the likelihood of various chemicals being released into the environment (Martins and Cró, 2021). Madeira Island's WWTP system comprises 24 stations (excluding Porto Santo Island), distributed across 10 municipalities. However, only seven stations could apply tertiary treatments, six secondary treatments, and 11 pre-primary treatments, including the one serving Madeira Island's capital, Funchal. The effluents are discharged through submarine outfalls, and in many areas, due to the lack of proper sewage systems, wastewater ends up in septic tanks or illegal outfalls (Direção Regional do Ambiente e Alterações Climáticas (DRAAC), 2025). Hence, LM does not have easy access to the sea and may cause more exposure to indirect pathways through the discharges of WWTPs (which correspond to WWTPs located in Calheta municipality with preliminary treatment and Paúl do Mar with possible tertiary treatment) and the travel of direct inputs from the closest artificial sandy beaches in Calheta, which could undergo degradation or transformation into by-products not detectable with the methodology used in this study (Ruíz-Gutierrez et al., 2022). In contrast, DS is likely influenced by direct inputs from skin washing during swimming activities permitted in the marine protected area (MPA), making the detection of the target compounds more frequent. The higher impact due to direct inputs of PCPs in the environment, in contrast with indirect inputs, has already been described in other cases and locations, for example, in Hawai'i as an example of another oceanic island (Downs et al., 2022), and around the entire Iberian Peninsula (Mozas-Blanco et al., 2023).

The same pattern is found according to both high and low tourist seasons; in this study, the seasonal differences are minimal for FX. However, the general higher presence of oUVFs during the high season (except in LM) reinforces the influence of tourism pressure (Sánchez Rodríguez et al., 2015; Casas-Beltrán et al., 2021; Milinkovitch et al., 2024).

4.2. Environmental occurrence of oUVF

The distribution pattern of POPs is strongly associated with their physicochemical properties, as well as the input sources (Tsui et al., 2014; Carve et al., 2021; Lebaron, 2022). Due to their high K_{ow} and low solubility, oUVFs are expected to associate primarily with solid matrices, such as sediments and fatty tissues (Volpe et al., 2017). This is consistent with the lower concentrations detected in seawater matrices in this study, as the sampling sites are in open coastal areas with limited shoreline extent (Tsui et al., 2014; Sánchez Rodriguez et al., 2015). In contrast, neighbouring regions such as the Canary Islands, which have sandy, semi-enclosed beaches as primary ocean access points, show significantly higher concentrations of oUVFs in seawater. For example, concentrations as high as 172 μg/L have been reported (Cadena-Aizaga et al., 2022b, 2022c). Specifically, in Gran Canaria, mean concentrations of BP-3, OC, HMS, and BM-DBM were 46.6, 109.7, 13.3, and 59.4 ng/L, respectively, higher than those observed in Madeira Island (Sánchez Rodriguez et al., 2015). Similar trends have been observed in other regions with higher anthropogenic coastal impacts. In China, oUVF concentrations ranged from 9 to 31 ng/L, with BP-3 detected between 13 and 32 ng/L, and OC between 9 and 14 ng/L (Tsui et al., 2017). In South Carolina (USA), concentrations ranged from 10 to 2013 ng/L, with BP-3, BM-DBM, OC, OMC, and OD-PABA detected. Here, BP-3 was the most abundant compound, followed by OC (Bratkovics and Sapozhnikova, 2011). Tsui et al. (2014) monitored eight different locations with different population density where the median value of oUVF was <250 ng/L in surface seawaters. However, Hong Kong, the city with the highest population density, showed the highest concentrations reaching up to 1000 ng/L, mainly due to incomplete removals from WWTP and recreational activities being the primary sources. Meanwhile, locations as the North Arctic present lower concentrations, influenced mainly by long-range transport through ocean currents and atmospheric pathways (Tsui et al., 2014).

Additionally, daily patterns of oUVF concentrations in surface waters have been described in several studies, generally showing higher levels during recreational activity peaks—up to 10 times greater than those measured during night sampling (Thallinger et al., 2023; Grant et al., 2025). This highlights the importance of the sampling plan. In this study, surface water samples were collected over six different days at three locations during two seasons (i.e., one day per season and location, with three samples collected each day). All samples were taken in the morning; however, the exact sampling time, the number of people in the water, and the intensity of recreational activities at the sites were not recorded. This lack of contextual information may have obscured potential inputs, or the absence thereof, of oUVFs in seawater. Furthermore, analyses were conducted only on the dissolved fraction, without considering the possible presence of oUVFs in the particulate material removed during pre-treatment filtration. Hence, this approach may have underestimated oUVF concentrations, as potential adsorption onto particulates or the filter itself was not accounted for, which should be considered when interpreting the results.

Regarding the oUVF identified in this matrix, a greater diversity of compounds was observed in FX, likely the most developed area among the sampling locations, receiving both direct and indirect inputs (Tsui et al., 2014). Notably, certain oUVFs, such as OC, are commonly formulated in combination with other compounds, like BM-DBM, to enhance photostability, water resistance, and SPF. This is due to BM-DBM's high susceptibility to degradation, often resulting in its co-occurrence with OC (Sánchez Rodríguez et al., 2015; da Silva et al., 2022). By this, BM-DBM was detected only in seawater samples, which is consistent with its degradation potential. Its presence as an intact compound is typically limited to shortly after its release, as it rapidly transforms into degradation products and metabolites (da Silva et al., 2022). HMS is less stable and less effective than OC. As a result, higher concentrations of HMS are typically required in product formulations, which may explain its frequent detection in environmental samples (de Oliveira e Sá et al., 2014). The detection of DTS remains puzzling due to the limited data available on its occurrence in seawater matrices (Cadena-Aizaga et al., 2020). Given its high K_{ow}, the presence of DTS in the dissolved phase is unexpected, as it would be more likely to associate with sediments or biota.

Contrary to the initial hypothesis, oUVFs were not detected in sediment samples. This result may be explained by the geological characteristics of the Madeira Island seafloor in the sampling area, which is predominantly composed of rocky reefs with a rigid substrate. Only a thin layer of coarser sediment, primarily derived from erosion, overlays the rocky bottom. This limited sediment accumulation may hinder the retention of oUVFs, in contrast to marine environments where finer sandy substrates predominate and facilitate contaminant deposition. For example, mean concentrations of oUVFs in sediments have been reported as 21 and 17 ng/g d.w. in Hong Kong and Tokyo bays, respectively (Tsui et al., 2014), and between 0.12 and 11.2 ng/g d.w. in the Baltic Sea (Apel et al., 2018). The absence of detectable UVFs in sediments may also explain the non-detection of these compounds in benthic organisms such as sea cucumbers. As detritivores, their exposure to UVFs is closely linked to sediment contamination, and previous studies have identified them as effective bioindicators of oUVF presence (Parra-Luna et al., 2020).

4.3. Distribution of oUVF among biota matrices

Concerning biota matrices, zooplankton appears to be more affected by the presence of oUVFs, both in terms of mean and range of concentration values. Zooplankton is composed of a diverse assemblage of organisms, including early developmental stages of various taxa such as echinoderms, fish larvae, polychaetes, and crustaceans (Ershova et al., 2021). Alongside phytoplankton, zooplankton form the base of the marine trophic food web and play a critical role in ecosystem sustainability. Due to their sensitivity to environmental changes and ecological importance, zooplankton are effective bioindicators, acting as sentinels of anthropogenic pressure and environmental disturbances (Lomartire et al., 2021). Additionally, zooplankton exhibit vertical migratory behaviour driven primarily by predation risk. During daylight hours, they remain in deeper waters to avoid predators, ascending to near-surface layers at night for feeding. This diel vertical migration plays a vital role in the vertical transport of carbon in the ocean (McGinty et al., 2011). Due to this migratory pattern, zooplankton spend a significant portion of the night within the uppermost surface layer, where the samples were collected, which includes the surface microlayer (SML). The SML represents the top boundary of the ocean and serves as a dynamic interface between the atmosphere and the sea, mediating key physical, chemical, and biological processes (Engel et al., 2017). This layer is particularly relevant for the exchange and accumulation of chemical compounds. Organic material present in the SML can act as a reservoir for POPs, especially during the initial phases following their release into the marine environment, being sporadically in higher concentrations than the bulk water column (Grant et al., 2025). Due to their high lipophilicity, oUVFs tend to accumulate in the SML, potentially increasing exposure for organisms residing in or feeding near this layer (Caloni et al., 2021; Grant et al., 2025). This includes phytoplankton, the primary food source of zooplankton, where POPs have already been described (Duarte et al., 2021). However, no monitoring studies have yet reported the presence of oUVFs in phytoplankton in marine environments. The association of zooplankton with the SML, combined with their continuous vertical migration through the water column, may therefore heighten their susceptibility to oUVF uptake. In addition to this pathway, dietary exposure through the ingestion of microplastics (MPs) and phytoplankton also represents a significant route of intake (Rani et al., 2017).

Madeira, situated within the Atlantic subtropical gyre, is affected by current systems that promote both the transformation and accumulation of plastic particles (Sambolino et al., 2022). Studies on MPs from the

Macaronesian bioregion have revealed the presence of oUVF, with OC being the most frequent, representing 69.12 % of oUVFs detected in MPs collected around Madeira Island, which aligns with the results obtained in the present study (Pacheco-Juárez et al., 2025).

Consistent with these findings, the MP-to-zooplankton ratio on Madeira has been shown to favour MPs, with concentrations varying seasonally and compositionally. This ratio correlates positively with WWTP discharges and rainfalls, and it tends to be higher during the warm season (Herrera et al., 2020; Sambolino et al., 2022). Taken together, these results suggest that spatial and seasonal variability in zooplankton contamination may be partly driven by the high presence of MPs in Madeira's coastal waters. Furthermore, oUVFs associated with MPs, which may be collected simultaneously with zooplankton trawls, could artificially inflate the apparent burdens of oUVFs detected and quantified in zooplankton, potentially leading to an over-interpretation of the reported values and of the possible trophic transfer.

An exception observed within the zooplankton matrix was the detection of OD-PABA. This compound is known to have a higher photodegradation potential compared to other oUVFs (Díaz-Cruz et al., 2008). Its presence may be limited to organisms that reside for extended periods in the SML, the uppermost ocean layer, directly exposed to atmospheric and land-based inputs and characterized by a higher concentration of organic material (Tsui et al., 2014; Caloni et al., 2021).

The fish matrix presented the second-highest mean and range of oUVF concentrations. Previous studies have consistently reported the widespread presence of these compounds in various fish species (Cunha et al., 2015). The primary pathways through which fish are exposed to oUVFs are via ingestion (diet) and respiration, due to the filtration of large volumes of water through the gills (Molins-Delgado et al., 2017). In the present study, the entire fish bodies were analyzed. However, previous research has demonstrated that oUVF concentrations can vary significantly across different tissues and organs. The gills, being the most directly exposed surface, the liver, as the main metabolic organ, and muscle tissue, which can act as a reservoir, all show differing contamination levels. For instance, in Lebranche mullet (*Mugil lisa*) from Brazil, concentrations of OMC ranged from 7.27 ng/g d.w. in gills to 33.30 ng/g d.w. in muscle, while OC concentrations varied from 10.2 to 24.7 ng/g d.w., respectively (Molins-Delgado et al., 2017). These values are consistent with the concentration ranges observed in the present study in the salema matrix. Still, it is essential to consider the mix of different organs and tissues that can give variations in the quantified concentrations according to the methodology. Three different fish species were analyzed, each representing a different trophic level. Interestingly, the herbivorous species exhibited the broadest range and highest concentrations of oUVFs. The salema is a coastal rocky reef species that primarily feeds on macroalgae and turf (Jadot et al., 2006). Due to its proximity to the shore, it is more likely to be exposed to human activities, leading to higher concentrations of these compounds compared to pelagic species such as mackerel. For instance, in Portuguese waters, mackerel has been found to contain OC in concentrations ranging from *n.d.* to 18.5 ng/g d.w., OMC from *n.d.* to 2.5 ng/g d.w., EHS from *n.d.* to 48.1 ng/g d.w., and HMS from *n.d.* to 5.1 ng/g d.w., all lower than the concentrations observed in salema (Cunha et al., 2015). Macrophytes with long life spans can be effective bioindicators of oUVF presence in the marine environment due to their sessile nature, which exposes them to various environmental factors such as currents and temperature fluctuations. This makes it easier to assess realistic concentrations across different locations and levels of anthropogenic pressure in the marine ecosystem (Cadena-Aizaga et al., 2020; Lyu et al., 2022). The presence of oUVFs in macrophytes has been documented in several regions. For example, in Gran Canaria (Canary Islands), concentrations as high as 19.37 ng/g d.w. were detected in macroalgae (Cadena-Aizaga et al., 2022a). Similarly, in coral reefs in China, 99 % of the macroalgae showed detectable levels of oUVFs, ranging from 8 to 29 ng/g d.w. (Lyu et al., 2022). In contrast, in the Tagus Estuary and the Ebro Delta, macroalgae did not exhibit detectable concentrations of oUVFs (Cunha et al., 2015).

In this study, red algae represented the third matrix in which oUVFs were detected. Although it is a non-indigenous species, its year-round presence allows it to serve as a proxy for native primary producers that form the food web base. Given that the salema's diet includes such algae, this suggests a greater likelihood of trophic transfer of oUVFs, which can accumulate in different tissues, particularly in metabolically active organs like the liver and storage tissues like muscle (Chebaane et al., 2024; Pintado-Herrera et al., 2024). This may explain the higher concentrations observed in salema compared to parrot fish, an omnivorous species that feeds on turf algae and small invertebrates (Lozano-Bilbao et al., 2023). Additionally, parrot fish typically inhabit deeper waters than salema, and the availability of organic contaminants may be closely linked to each species' spatial distribution and foraging zones. Areas farther from the shore are generally less impacted by direct anthropogenic inputs (Munschy et al., 2020). It is also possible that the turf algae in those areas are either not located close enough to UVF inputs or do not occupy a sufficient area to accumulate significant concentrations. Moreover, due to the structural complexity of turf algae, they may have the capacity to metabolise or transform parent compounds, potentially reducing detectable levels of oUVFs (Pintado-Herrera and Lara-Martín, 2020; Cadena-Aizaga et al., 2020). Further targeted analyses are required to confirm this hypothesis. This reasoning also aligns with the absence of quantifiable levels of oUVFs in sea urchins from the Madeira archipelago, whose diet consists predominantly of coralline algae found within turf assemblages (Privitera et al., 2011). Another factor that may influence the accumulation of oUVFs in biotic tissues is the total lipid content. In this study, total lipid content was higher in salema than parrot fish, which may partly explain the higher concentrations of oUVFs observed in the former, given the lipophilic nature of these compounds (Lyu et al., 2022). OC was the most consistently present across matrices among all the compounds detected. OC is bioavailable through the gastrointestinal tract and readily absorbed by organisms (Berardesca et al., 2019). Additionally, it has been reported to be associated with fatty acids in some marine organisms, such as sponges, which may facilitate its bioaccumulation in tissues without requiring prior transformation. This characteristic increases its detectability in biota compared to other oUVFs (Clergeaud et al., 2022). Overall, these findings demonstrate that the environmental fate of oUVFs in oceanic islands deviates markedly from patterns typically reported in coastal and estuarine systems. The unexpected absence in sediments and echinoderms, the sentinel role of zooplankton linked to the surface microlayer, as well as the MPs intake and diet sources, and the trophic differences observed between salema and pelagic species collectively underline that insular ecological and geological settings play a decisive role in shaping exposure and bioaccumulation pathways. This perspective provides a novel framework for assessing emerging contaminants in insular ecosystems, where human pressure interacts with unique oceanographic processes, with peak concentrations and detection frequencies coinciding with high-tourism periods and nearshore recreational hotspots, underscoring tourism as a dominant, direct driver of local oUVF contamination.

Future directions of this research should address several current gaps. First, the determination of oUVFs in phytoplankton is needed, as these primary producers represent a critical entry point for contaminants into the marine food web. A broader sampling strategy, including a wider range of seawater and sediment samples collected at different times of the day and across multiple seasons, would provide a clearer understanding of temporal and seasonal variations in both oUVF concentration and composition, beyond punctual snapshots. Expanding the range of organisms studied, such as filter feeders like limpets, which are also an important local seafood, would allow a more accurate evaluation of potential human health risks. Additionally, the presence of microplastics in zooplankton should be assessed to clarify whether oUVF intake occurs through direct exposure or via MP-mediated pathways. Finally, increasing the sample size for each species will strengthen the

robustness of the analyses and the reliability of the conclusions.

5. Conclusion

As Madeira is an oceanic island, various oceanographic processes may contribute to a dilution effect of contaminants released along the coast. However, tourism intensity, coastal infrastructure, and proximity to human activities were positively correlated with oUVF occurrence in seawater, sediment, and biota. Sessile organisms, such as algae and other biota with distributions closely linked to the shoreline or water surface, were the most affected, whereas offshore or pelagic species showed no detectable contamination**.** Larger sample sizes and broader species representation are necessary to determine better the trends of accumulation of these compounds in the marine environment. Additionally, the presence of metabolites and transformation products may lead to an underestimate of the real ecological impact of oUVFs. Improving analytical methodologies by lowering the LOD and LOQ, and establishing harmonized monitoring protocols, will enhance comparability across regions. Overall, such efforts are essential to support ecological risk assessment and the development of evidence-based regulatory measures for coastal ecosystems under growing tourism pressure. The results highlight the dominant role of anthropogenic impact in shaping oUVF occurrence in island ecosystems and provide the first evidence that insular settings display distinct patterns of oUVF distribution and trophic transfer compared to continental coasts. These findings call for island-specific monitoring and management strategies, particularly in regions where tourism and coastal pressures are intensifying.

CRediT authorship contribution statement

Eva Iñiguez: Writing – review & editing, Writing – original draft, Visualization, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Rodrigo Pires da Silva:** Writing – review & editing, Visualization, Methodology, Conceptualization. **Sarah Montesdeoca-Esponda:** Writing – review & editing, Visualization, Validation, Resources, Methodology, Conceptualization. **Elli Dimou:** Writing – review & editing, Methodology. **Filipe Alves:** Writing – review & editing, Visualization, Resources, Funding acquisition. **Manfred Kaufmann:** Writing – review & editing, Visualization, Supervision, Resources, Funding acquisition. **Ana Dinis:** Writing – review & editing, Visualization, Supervision, Resources, Funding acquisition, Conceptualization. **Nereida Cordeiro:** Writing – review & editing, Visualization, Supervision, Resources, Funding acquisition, Conceptualization.

Ethics approval

All sample collections and access to study sites were conducted under the appropriate institutional authorizations following the regulations of the Autonomous Region of Madeira, Regional Government (*Região Autónoma da Madeira, Governo Regional*), through the Regional Secretariat for Environmental and Sea and, the Institute of Forests and Nature Conservation (Instituto das Florestas e Conservação da Natureza, IP-RAM). Specifically, access to Desertas Islands was authorized under permit n° 392283/2023.

Consent for publication

The authors consent to publication.

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Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Filipe Alves and Ana Dinis reports financial support was provided by Interreg Europe. Ana Dinis, Filipe Alves, Nereida Cordeiro reports financial support was provided by Foundation for Science and Technology. Rodrigo Pires da Silva reports financial support was provided by Horizon Europe. Eva Iniguez reports financial support was provided by Foundation for Science and Technology. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Glossary

4-MBC	4-methylbenzylidene camphor
ACE	Acetone
BM-DBM	Butyl methoxydibenzoylmethane
BP-3	Benzophenone-3
Bp-d_{10}	Deuterated benzophenone
ACN	Acetonitrile
CECs	Contaminants of Emergent Concern
DCM	Dichloromethane
DS	Desertas Islands
DTS	Drometrizole trisiloxane
EHS	2-ethylhexyl salicylate
ESI	Electrospray Ionization
FO	Frequency of Occurrence
FX	Funchal
FX_HIGH	High tourist season in Funchal
LM_HIGH	High tourist season in Lombada dos Marinheiros
DS_HIGH	High tourist season in Desertas
HMS	Homosalate
ILOD	Instrumental Limit of Detection
ILOQ	Instrumental Limit of Quantification
IMC	Isoamyl p-methoxycinnamate
IS	Internal Standard
iUVFs	Inorganic Ultraviolet Filters
K_{ow}	Octanol-water partition coefficient
LC-MS	Liquid Chromatography-Tandem Mass Spectrometry
LM	Lombada dos Marinheiros
LOD	Limit of Detection

LOQ Limit of Quantification
FX_LOW Low tourist season in Funchal
LM_LOW Low tourist season in Lombada dos Marinheiros
DS_LOW Low tourist season in Desertas
MAE Microwave-Assisted Extraction
MeOH Methanol
MLOD Methodological Limit of Detection
MLOQ Methodological Limit of Quantification

MPs *Microplastics*
OC Octocrylene
OD-PABA Ethylhexyl dimethyl PABA
OMC Ethylhexyl methoxycinnamate
oUVFs Organic Ultraviolet Filters
PCPs Personal Care Products
POPs Persistent Organic Pollutants
ROS Reactive Oxygen Species
SML Surface Microlayer
SPE Solid-Phase Extraction
UHPLC-MS/MS Ultra-High Performance Liquid Chromatography-Tandem Mass Spectrometry
UV Ultraviolet
UV-360 Methylene bis-benzotriazolyl
UVF Ultraviolet Filter
WWTPs Wastewater Treatment Plants

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envres.2025.123153.

Data availability

Data will be made available on request.

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