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UV-filters from insular ocean-cities
Impact on the marine sustainability

DOCTORAL THESIS

Eva Íñiguez Santamaría
DOCTORATE IN BIOLOGICAL SCIENCES

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Thesis presented to obtain the PhD degree in
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“The sea is everything. It is like the immensity of the desert; but one must remember that man never feels alone in it, for he senses the pulsation of life around him. The sea is, in my view, something like the vehicle of a supernatural and prodigious existence. It is movement and love.”

— Jules Verne, *Twenty Thousand Leagues Under the Sea*

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Abstract

Organic ultraviolet filters (oUVFs) are synthetic chemical compounds widely used in industrial applications and personal care products to protect human skin and materials from solar radiation. Over recent decades, increasing demand for these products has resulted in a substantial rise in production and consumption, leading to their release into the environment. Despite widespread use, information on environmental concentrations, chemical behaviour, spatial distribution, persistence, and potential adverse effects on marine organisms remains limited. Consequently, oUVFs are classified as Contaminants of Emerging Concern. Coastal ecosystems are particularly vulnerable to oUVF contamination due to intensified tourism and recreational activities, which constitute the main direct input pathways through activities such as swimming and bathing. Indirect pathways, including wastewater treatment plant effluents, industrial discharges, and terrestrial runoff, also contribute to inputs to marine environments and may influence their persistence and distribution. This doctoral thesis investigates the distribution, accumulation, and persistence of oUVFs, as well as their potential trophic transfer, using an oceanic island as a representative study scenario. This approach enables the assessment of oUVF contamination across a spatial gradient from coastal zones to deep-sea environments and across multiple trophic levels through the analysis of diverse marine organisms. Results indicate that areas influenced by direct coastal activities exhibit higher oUVF concentrations than locations affected by indirect sources. Sessile organisms, such as macroalgae, were particularly vulnerable, displaying elevated concentrations in areas subjected to higher anthropogenic pressure. Herbivorous species exhibited the highest diversity and concentrations of oUVFs, consistent with greater exposure and bioaccumulation potential at lower trophic levels. Similar patterns were observed at higher trophic levels, including pelagic species such as skipjack tuna (*Katsuwonus pelamis*), bathypelagic species such as black scabbardfish (*Aphanopus carbo*), and deep-diving cetaceans. While sperm whales (*Physeter*

macrocephalus) showed higher concentrations, resident short-finned pilot whales (*Globicephala macrorhynchus*) exhibited a higher frequency of occurrence. Furthermore, oUVFs were more prevalent in water column compartments characterized by elevated organic matter, including the surface microlayer associated with zooplankton communities, and the deep-sea bottom, associated with black scabbardfish habitat. In contrast, highly mobile species with broad vertical and horizontal distributions showed low or undetectable concentrations. Among the analyzed compounds, OC, EHS, HMS, BDBDM, and DTS were the most frequently detected, underscoring their persistence. Overall, this thesis demonstrates the widespread distribution of oUVFs beyond coastal environments, their impact on commercial species, and their accumulation in top predators. It also presents the first validated methodology for detecting oUVFs in marine zooplankton and provides concentration data across multiple species and habitats, thereby addressing critical knowledge gaps.

Keywords: Chemical pollution, solar protection, marine environment, monitoring, contaminants of emerging concern.

Resumo

Os filtros ultravioleta orgânicos (oUVFs) são compostos sintéticos amplamente utilizados em produtos de cuidado pessoal e em aplicações industriais para proteger a pele humana e os materiais da radiação solar. O aumento do seu consumo nas últimas décadas conduziu à sua libertação para o ambiente, sobretudo nos ecossistemas costeiros. Apesar da sua utilização generalizada, o conhecimento sobre as suas concentrações ambientais, comportamento químico, distribuição, persistência e efeitos adversos em organismos marinhos permanece limitado, levando à sua classificação como contaminantes de preocupação emergente. Os ecossistemas costeiros são particularmente vulneráveis à contaminação por oUVFs devido à intensificação do turismo e das atividades recreativas, que constituem vias diretas de entrada destes compostos no meio marinho, nomeadamente através da natação e do banho. Para além destas fontes diretas, vias indiretas, incluindo efluentes de estações de tratamento de águas residuais (ETAR), descargas industriais e escoamento terrestre, contribuem igualmente para a introdução de oUVFs no ambiente marinho e podem influenciar a sua persistência e distribuição. Esta tese de doutoramento investiga a distribuição, acumulação, persistência dos oUVFs, bem como o seu potencial de transferência trófica, utilizando uma ilha oceânica como cenário de estudo. Esta abordagem permitiu avaliar a contaminação ao longo de um gradiente espacial, desde zonas costeiras até ambientes de mar profundo, bem como ao longo de múltiplos níveis tróficos, através da análise de diferentes organismos marinhos. Os resultados demonstraram que as áreas diretamente influenciadas por atividades costeiras apresentam concentrações mais elevadas de oUVFs do que os locais predominantemente afetados por fontes indiretas. Os organismos sésseis, como as macroalgas, revelaram-se particularmente vulneráveis, apresentando concentrações elevadas em áreas com maior pressão antropogénica. As espécies herbívoras exibiram maior diversidade e concentrações de oUVFs, sendo estes resultados consistentes com maior exposição e potencial de bioacumulação nos níveis tróficos

inferiores, observando-se padrões semelhantes em níveis tróficos superiores, incluindo espécies pelágicas, batipelágicas e cetáceos mergulhadores profundos. Os cachalotes (*Physeter macrocephalus*) apresentaram as concentrações mais elevadas, enquanto as baleias-piloto-de-barbatana-curta residentes (*Globicephala macrorhynchus*) revelaram maior frequência de ocorrência. Adicionalmente, os oUVFs foram mais prevalentes em compartimentos da coluna de água ricos em matéria orgânica, como a microlâmina superficial, associada a comunidades de zooplâncton, e o fundo marinho profundo, habitat do peixe-espada-preto (*Aphanopus carbo*), enquanto espécies altamente móveis apresentaram concentrações baixas ou não detetáveis. Entre os compostos analisados, OC, EHS, HMS, BMDBM e DTS destacaram-se pela sua elevada persistência ambiental. De um modo geral, esta tese demonstra a ampla distribuição dos oUVFs para além dos ambientes costeiros, a sua acumulação ao longo da cadeia trófica, o seu impacto em espécies de interesse comercial e a sua acumulação em predadores de topo. Apresenta ainda a primeira metodologia validada para a deteção de oUVFs no zooplâncton marinho e fornece dados de concentração em diversas espécies e habitats, contribuindo para colmatar lacunas de conhecimento existentes.

Palavras-chave: Poluição química, proteção solar, ambiente marinho, monitorização, contaminantes de preocupação emergente

Content

List of Abbreviations / Acronyms

4-MBC	4-methylbenzylidene camphor
ACE	Acetone
ACN	Acetonitrile
BMDBM	Butyl methoxydibenzoylmethane
BMF	Biomagnification factor
BP-1	Benzophenone-1
BP-3	Benzophenone-3
BP-8	Benzophenone-8
BP-d_{10}	Deuterated benzophenone
CAS	Chemical Abstracts Service
CECs	Contaminants of emerging concern
DCM	Dichloromethane
DDT	Dichlorodiphenyltrichloroethane
DOM	Dissolved organic matter
DS	Desertas Islands
DTS	Drometrizole trisiloxane
OMC	Ethylhexyl methoxycinnamate
EHS	2-ethylhexyl salicylate
ESI	Electrospray ionization
EtOH	Ethanol
FO	Frecuency of occurrence
FQ	Frequency of quantification
FX	Funchal
HEX	Hexane
DS_HIGH	High tourist season in Desertas

FX_HIGH	High tourist season in Funchal
LM_HIGH	High tourist season in Lombada dos Marinheiros
HMS	Homosalate
HPLC	High-performance liquid chromatography
ILOD	Instrumental limit of detection
ILOQ	Instrumental limit of quantification
IMC	Isoamyl p-methoxycinnamate
INCI	International Nomenclature of Cosmetic Ingredients
IS	Internal standard
iUVF(s)	inorganic ultraviolet filter(s)
Kow	Octanol-water partition coefficient
LC-MS	Liquid chromatography-mass spectrometry
LM	Lombada dos Marinheiros
LOD	Limit of detection
K_d	Organic-carbon-based sorption coefficient
LOQ	Limit of Quantification
DS_LOW	Low tourist season in Desertas
FX_LOW	Low tourist season in Funchal
LM_LOW	Low tourist season in Lombada dos Marinheiros
MAE	Microwave-Assisted Extraction
MeOH	Methanol
MLOD	Methodological Limit of Detection
MLOQ	Methodological Limit of Quantification
MPs	Microplastics
MRM	Multiple reaction monitoring
MS	Mass spectrometry

MS/MS	Tandem mass spectrometry
NOAEL(s)	No observed adverse effect level(s)
OC	Octocrylene
OD-PABA	Ethylhexyl dimethyl PABA
oUVF(s)	Organic ultraviolet filter(s)
PCBs	Polychlorinated biphenyls
PCPs	Personal care products
pK_a	Dissociation constant
POPs	Persistent organic pollutants
REACH	Registration, evaluation, authorisation and restriction of chemicals
ROS	Reactive oxygen species
RSD	Relative standard deviation
RT	Retention time
S/N	Signal-to-noise ratio
SML	Surface microlayer
SPE	Solid-phase extraction
SPF	Sun protection factor
TL	Total lipid content
TPs	Transformation products
UHPLC-MS/MS	Ultra-high performance liquid chromatography-tandem mass spectrometry
UNCLOS	United Nations Convention on the Law of the Sea
UNESCO	United Nations Educational, Scientific and Cultural Organization
UV	Ultraviolet
UV-360	Methylene bis-benzotriazolyl tetramethylbutylphenol
UVA	Ultraviolet A

UVB	Ultraviolet B
UVF	Ultraviolet filter
WWTPs	Wastewater treatment plants
λ_{max}	Wavelength of maximum absorption
ΣoUVFs	Sum of organic oUV filters

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CHAPTER I

General Introduction

CHAPTER I: General Introduction

1. Marine pollution

Marine ecosystems are essential to human life. Many of the world's earliest cities were established along coastal areas, where human populations depend on natural marine resources provided by these ecosystems, including fisheries, nutritional inputs, cultural services, coastal protection, and economic opportunities (Selig et al., 2019; Day et al., 2021). Today, human populations continue to maintain a strong connection with coastal zones and benefit from them. The increasing intensity of human activities over recent decades has increased the pressure on marine environments, threatening their sustainability, biodiversity, and, consequently, both ecosystem integrity and human health. Overfishing, the introduction of invasive aquatic species, climate change, and pollution represent the main threats associated with the poor management and governance of these marine natural resources (Buonocore et al., 2021; Zhou et al., 2022).

The United Nations Convention on the Law of the Sea (UNCLOS) defines "pollution of the marine environment" as "*the introduction by man, directly or indirectly, of substances or energy into the marine environment, which results or is likely to result in such deleterious effects as harm to living resources and marine life, hazards to human health, hindrance to marine activities, including fishing and other legitimate uses of the sea, impairment of seawater quality, and reduction of amenities*" (Vikas and Dwarakish, 2015). Pollution has long been associated with human activities, and the Industrial Revolution marked a turning point in the scale of pollutant emissions. While this period brought significant improvements in human quality of life, driven by the expansion of services and social progress, it also initiated profound environmental changes (Saxena, 2025). One of the major advancements of that era was the application of chemistry to meet emerging societal needs. This included enhancing agriculture

with new pesticides and fertilizers that increased crop yields, as well as developing pharmaceuticals that extended and improved human life expectancy. The invention and mass production of plastics also revolutionized manufacturing by speeding up and making production chains more cost-effective (Brander and Betjemann, 2023).

Many of these compounds, including heavy metals, micro- and nanoplastics, antibiotics, and pesticides, pose long-term environmental challenges due to their persistence in ecosystems. In some cases, ineffective regulations allow the continued release of these substances into the environment (Zhou et al., 2022; Zhang et al., 2024). In this context, chemical pollution, particularly that arising from organic compounds, has become an increasingly significant environmental concern (Li et al., 2023).

2. Persistent Organic Pollutants (POPs) and Contaminants of Emerging Concern (CECs)

POPs are organic substances characterized by their environmental persistence, tendency to bioaccumulate through marine trophic webs, and potential to cause adverse effects in ecosystems and human health (Li et al., 2023). These substances can be transported through the atmosphere, via precipitation, oceanographic events, or by migratory species across international borders, reaching regions where they were never produced or used. This transboundary movement requires global management, as no single region can effectively address the risks posed by these substances on its own (ECHA, 2025).

Several international agreements, including the Aarhus Protocol (1998) and the Stockholm Convention (2001), established global frameworks that aim to prohibit and/or restrict the production, sale, and use of POPs to minimize their release into the environment. However, even though many POPs have been banned (*e.g.*, Polychlorinated biphenyls (PCBs))

or have faced strict restrictions on their production and use (like dichlorodiphenyltrichloroethane, more commonly known as DDT), a cumulative total of 31.31×10^6 t of 25 POPs were synthesized and commercialized worldwide by 2020. The United States and the European Union have been identified as major hotspots, with China also representing a significant source at the single-country level (Li et al., 2023). Recent studies have detected these substances at quantifiable concentrations in waters, sediments, and organisms, emphasizing their persistence in the environment (López-Berenguer et al., 2023).

The continuous growth of human needs has led to the synthesis and incorporation of new chemicals for a wide range of industrial and consumer applications. Some of these emerging substances exhibit physicochemical properties and environmental behaviours similar to those of POPs. Nevertheless, due to limited knowledge regarding their environmental fate, quantification, and toxicity thresholds, they are classified under a different category: CECs (Mortimer and Batley, 2023). Although there is no universally accepted definition for this concept, the United Nations Educational, Scientific and Cultural Organization (UNESCO) defines CECs as: "*Emerging pollutants are synthetic or naturally occurring chemicals or any microorganism that is not commonly monitored or regulated in the environment, with potentially known or suspected adverse ecological and human health effects. These contaminants include mainly chemicals found in pharmaceuticals, personal care products (PCPs), pesticides, industrial and household products, metals, surfactants, industrial additives, and solvents. Many of them are used and released continuously into the environment even in very low quantities, and some may cause chronic toxicity, endocrine disruption in humans and aquatic wildlife, and the development of bacterial pathogen resistance.*" (Zandaryaa et al., 2025).

There is still considerable uncertainty regarding the categorization and assessment of CECs. Most classifications are conducted compound-by-compound. However, these

substances are released into the environment as complex mixtures. This approach overlooks the potential interactions among different compounds and their dynamic interactions with environmental components. Moreover, there are currently no standardized protocols for determining lethal concentrations, assessing long-term exposure effects, or identifying patterns of bioaccumulation and biomagnification (Nilsen et al., 2019).

More than 100 million chemical substances have been registered globally, with approximately 4,000 new compounds being added each day. Among these, pharmaceuticals and PCPs are currently one of the most prevalent categories considered as CECs (Mortimer and Batley, 2023; Roman et al., 2023). Their commercialization has increased significantly in recent decades, driven by a rise in medical prescriptions, as well as improved economic accessibility. As a result, many of these products are now an integral part of daily life, including items such as shampoos, detergents, and sunscreens (Khalid and Abdollahi, 2021).

2.1 Personal Care Products (PCPs)

PCPs are natural or synthetic chemicals used for personal hygiene, cleaning, grooming, and beautification. In general, the physicochemical properties of these substances, guided by factors such as dissociation constant (pK_a), octanol-water partition coefficient ($logK_{ow}$), organic-carbon-based sorption coefficient ($logK_{oc}$), and solid-water distribution coefficient ($logK_d$), contribute to their persistence in the environment. Their high lipophilicity and low water solubility make them readily absorbed through the skin or lipid matrices, making their removal difficult. Consequently, many PCPs are considered pseudo-persistent contaminants (Hawash et al., 2023). Their presence in the ecosystem raises concern due to their persistence, ubiquitous occurrence, and ability to act as endocrine disruptors, causing toxicity through long-term chronic exposure (Adeleye et al., 2022).

PCPs can enter the marine ecosystem through two primary pathways. The first pathway is direct and occurs during human recreational activities. PCPs applied to the skin can wash off during activities such as swimming, surfing, snorkelling, or even showering at the beach (Pintado-Herrera and Lara-Martin, 2020; Downs et al., 2022). The second pathway is indirect and involves transporting PCPs to the sea for subsequent processing. These include runoff from streams, discharges from urban areas and industries, infiltration through aquifers, both legal and illegal dumping, the release of plastics and industrial products (such as paints and varnishes), and effluents from wastewater treatment plants (WWTPs) (Fig. I. 1) (Hawash et al., 2023). WWTPs are not designed to neutralize or remove such contaminants and are not included in regular quality controls; therefore, they are not routinely monitored (Anand et al., 2022; Hawash et al., 2023). Consequently, some PCPs can be released through effluents in their original forms, while others may undergo chemical or metabolic transformations. It is also important to consider the release of transformation products, which are formed during the degradation of the parent compounds and may exhibit higher toxicity levels than the original substances (Adeleye et al., 2022).

PCPs include formulations intended for product preservation, packaging, and direct application to human skin. One example of widely used PCPs is sunscreens, whose main goal is to protect the skin against harmful UV radiation (Wijesooriya et al., 2025).

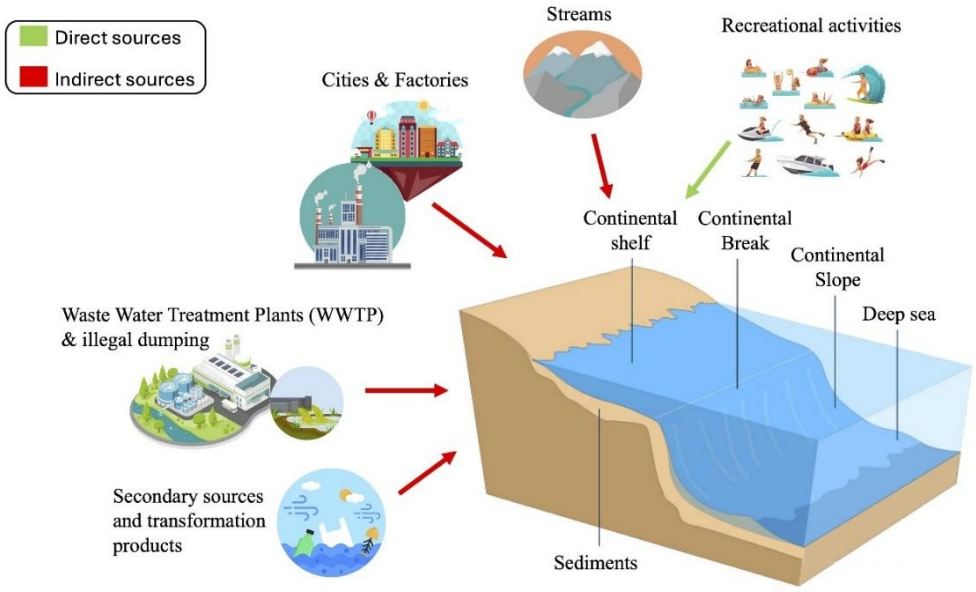


Fig. I. 1. Graphical summary of the main release pathways of personal care products (PCP_S) into the marine environment, classified as direct and indirect sources. Source: Author's own elaboration using Canva.

2.1.1 Solar Radiation and Ultraviolet Filters (UVFs)

Solar radiation consists of electromagnetic waves that include visible, infrared, and ultraviolet (UV) regions, each characterized by different wavelength ranges. The visible spectrum extends from 400 to 700 nm, accounting for approximately 36% of total solar radiation, while the infrared spectrum ranges from 800 to 5000 nm and represents the largest portion. In contrast, UV radiation spans wavelengths between 280 and 400 nm and is subdivided into three regions according to wavelength: UVA (315-400 nm), UVB (280-315 nm), and UVC (100-280 nm) (Nieradko-Iwanicka and Wysokinska, 2022).

The ozone layer completely absorbs UVC radiation, and although it is the most energetic and therefore the most harmful, it does not reach the Earth's surface. UVA and UVB radiation, on the other hand, are only partially absorbed by the atmosphere (Nieradko-Iwanicka and Wysokinska, 2022).

Although these forms of radiation can provide some health benefits, such as stimulating the production of vitamin D and melanin, they also have harmful effects (Robinson et al., 2023). UVA and UVB exposure can induce oxidative reactions in the skin, leading to mutagenesis, carcinogenesis, and cellular mortality, as well as lipid and protein oxidation and immunosuppressive effects (Hazel et al., 2022; Nieradko-Iwanicka and Wysokinska, 2022). Skin protection is essential to minimize the adverse effects. Ultraviolet filters (UVFs) are organic or inorganic chemical compounds incorporated into PCPs, mainly sunscreens, as well as into industrial materials such as paints, varnishes, and food packaging, to protect against harmful solar radiation (Pintado-Herrera and Lara-Martín, 2020).

The UVFs are broadly divided into two main categories: inorganic (mineral) and organic (chemical) filters. The fundamental difference between them lies in their mechanism of protection against UV radiation. Inorganic UVFs (iUVFs) attenuate UV radiation primarily through absorption, with additional scattering and reflection that depend on particle size, crystal form, surface coating/aggregation, and the formulation matrix. Upon absorption, electrons are promoted to an excited state, and the excess energy is then dissipated as heat (and to a lesser extent as re-emitted radiation) as the molecule returns to the ground state. This absorption–dissipation process is also characteristic of organic UVFs (oUVFs) (Fig. I. 2) (Milutinov et al., 2024).

The European Union currently authorizes oUVFs for use at concentrations typically up to 15% (w/w), whereas iUVFs (titanium dioxide and zinc oxide, including authorised nano forms under specific conditions) are permitted at levels up to 25% (w/w) (Table I. 1).

Considering the greater diversity and complexity of oUVFs compared with iUVFs, this thesis will focus primarily on the former. This focus provides a more suitable framework for examining their chemical properties, environmental behaviour, and potential risks, which are central to the scope of this research.

2.1.2 Organic UV filters

The oUVFs are typically composed of aromatic structures conjugated with a carbonyl group and a carbon–carbon double bond. Upon exposure to UV radiation, the molecule is excited to a higher energy state and subsequently returns to its original state, releasing the absorbed energy as fluorescence or heat. This process dissipates energy and converts harmful UV radiation to a non-damaging wavelength, thereby protecting the skin (Caloni et al., 2021; Nitulesco et al., 2023).

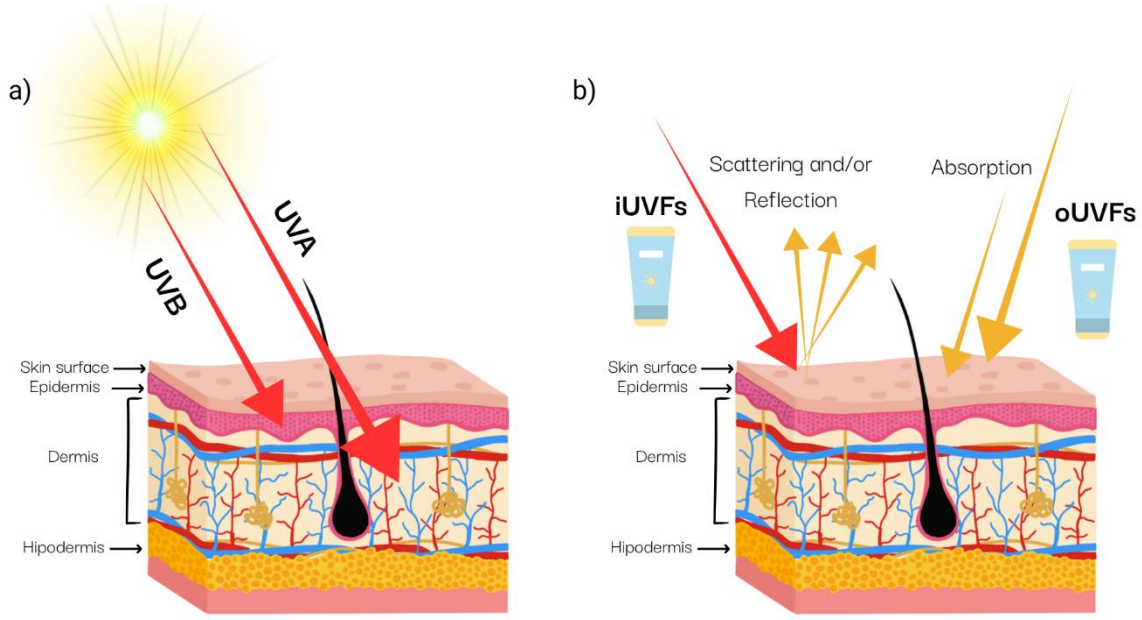
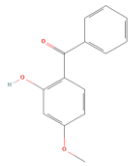
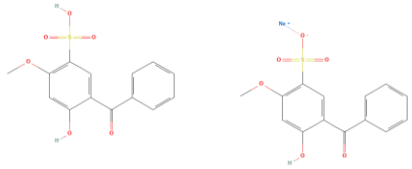
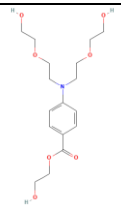


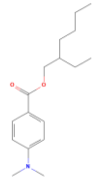
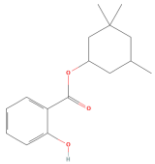
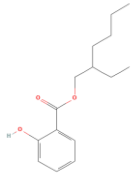
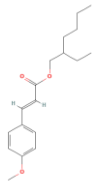
Fig. I. 2. (*a*) Representation of UV rays penetrating the skin. (*b*) Representation of how inorganic (iUVFs) and organic (oUVFs) ultraviolet filters act to protect against radiation. Figure modified from Milutinov et al. (2024). Author's own elaboration using Canva.

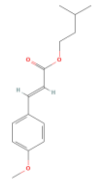
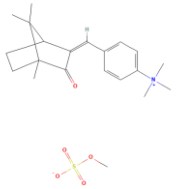
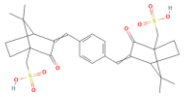
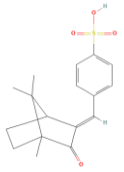
The degree of protection and the specific wavelength range covered by an oUVF depend on the chemical structure of each compound (Table I. 1). The oUVFs are characterized by the wavelength at which they absorb the maximum amount of energy, known as the absorption peak (λ_{max}). This λ_{max} determines which portion of the UV spectrum the compound can effectively absorb: UVA, UVB, or broad spectrum (covering both). Furthermore, additional

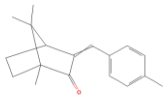
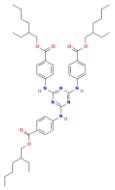
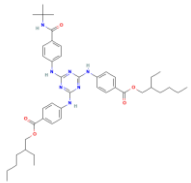
structural features of the molecule, such as the number and position of conjugated double bonds, the presence of aromatic rings, and specific functional groups (for example, alkyl and cycloalkyl fragments), can influence its absorption capacity. These features can also influence the molecule's photostability, lipophilicity, and persistence in the environment (Nitulesco et al., 2023). Based on structural and functional criteria, oUVFs are classified into eleven families (Table I. 1).

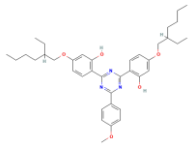
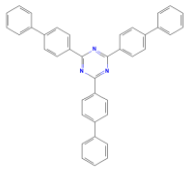
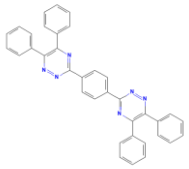
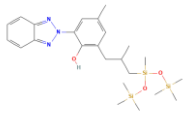
Table I. 1. Summary of the organic and inorganic UV filters permitted in the European Union (EU), grouped by chemical family. EU Ref. No.: reference number assigned to each UV filter in Annex VI of Regulation (EC) No 1223/2009. INCI: International Nomenclature of Cosmetic Ingredients. CAS No.: Chemical Abstracts Service number. LogK_{ow}: n-octanol/water partition coefficient. Solubility: water solubility. pKa: acid dissociation constant. Max. (% w/w): maximum permitted concentration in cosmetic products in the EU, expressed as % (w/w). UV range: UV spectral region covered (UVA, UVB or UVA/B).

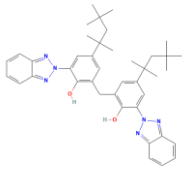
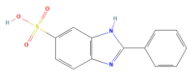
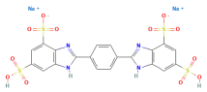
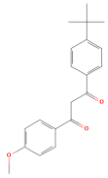
Chemical family	Chemical structure	EU Ref. No.	INCI name	Abbreviation	CAS No.	Log K_{ow}	Solubility (g/L)	pKa	Max. conc. (%)	UV range
Benzophenones		4	Benzophenone-3	BP-3	131-57-7	3.79	0.21	7.56	6	UVA/B
		22	Benzophenone-4, Benzophenone-5	BP-4, BP-5	4065-45- 6, 6628- 37-1					UVA/B
p-Aminobenzoic acid and derivatives		13	Ethoxylated ethyl-4-aminobenzoate	PEG-25 PABA	116242-27-4	-0.66			10	UVB

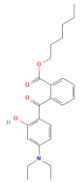
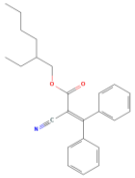
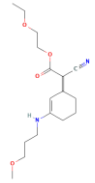
Chemical family	Chemical structure	EU Ref. No.	INCI name	Abbreviation	CAS No.	Log K_{ow}	Solubility (g/L)	pKa	Max. conc. (%)	UV range
		21	Ethylhexyl dimethyl PABA	OD-PABA	21245-02-3	6.15	$2.1x10^{-3}$	2.39	8	UVB
Salicylates		3	Homosalate	HMS	118-56-9	6.16	0.02	8.09	10	UVB
		20	2-Ethylhexyl salicylate	EHS	118-60-5	5.97	0.028	8.13	5	UVB
Cinnamates		12	2-Ethylhexyl 4-methoxycinnamate	OMC	83834-59-7 / 5466-77-3	5.8	0.15		10	UVB

Chemical family	Chemical structure	EU Ref. No.	INCI name	Abbreviation	CAS No.	Log K_{ow}	Solubility (g/L)	pKa	Max. conc. (%)	UV range
		14	Isopentyl-4-methoxycinnamate	IMC	71617-10-2	4.33	0.06		10	UVB
Camphor derivatives		2	N,N,N-Trimethyl-4-(2-oxoborn-3-ylidenemethyl) anilinium methyl sulfate	CBM	52793-97-2	0.28	0.007		6	UVB
		7	Ecamsule	PDSA	92761-26-7 / 90457-82-2	3.83	0.014	-1.05	10	UVA
		9	alpha-(2-Oxoborn-3-ylidene)-toluene-4-sulphonic acid	BCSA	56039-58-8	2.22	0.038	-0.7	6	UVB

Chemical family	Chemical structure	EU Ref. No.	INCI name	Abbreviation	CAS No.	Log K_{ow}	Solubility (g/L)	pKa	Max. conc. (%)	UV range
		11	Polyacrylamidomethyl benzylidene camphor	PBC	113783-61-2				6	UVB
		18	4-Methylbenzylidene camphor	4-MBC	36861-47-9/ 38102-62-4	4.95	$5.1x10^{-3}$		4	UVB
Triazines		15	Ethylhexyl triazone	OT	88122-99-0	17.05		3.17	5	UVB
		17	Diethylhexyl butamido triazole	DBT	154702-15-5	14.03	$4.6x10^{-3}$	3.04	10	UVB

Chemical family	Chemical structure	EU Ref. No.	INCI name	Abbreviation	CAS No.	Log K_{ow}	Solubility (g/L)	pKa	Max. conc. (%)	UV range
		25	Bis-ethylhexyloxyphenol methoxyphenyl triazine	EMT	187393-00-6	8.03	$4.9x10^{-8}$	6.37	10	UVA/B
		29		TBPT	31274-51-8	10.38	$5.5x10^{-10}$	1.2	10	UVA
		31		TiAsorB	55514-22-2	10.5	$2x10^{-8}$		5	UVA/B
Benzotriazoles		16	Drometrizole trisiloxane	DTS	155633-54-8	10.82	$1.3x10^{-5}$	9.72	15	UVA/B

Chemical family	Chemical structure	EU Ref. No.	INCI name	Abbreviation	CAS No.	Log K_{ow}	Solubility (g/L)	pKa	Max. conc. (%)	UV range
		23	Methylene bis-benzotriazolyl tetramethylbutylphenol	UV-360	103597-45-1	12.46	$3x10^{-8}$	7.56	10	UVA/B
Benzimidazole derivatives		6	Phenylbenzimidazole sulfonic acid	PMDSA	27503-81-7	-0.16	0.26	-0.87	8	UVA
		24	Disodium phenyl dibenzimidazole tetrasulfonate	DPDT	180898-37-7	-6.79	0.5	-0.27	10	UVA
Dybenzoylmethane derivatives		8	Butyl methoxydibenzoylmethane	BMDBM	70356-09-1	4.51	0.037	9.74	5	UVA

Chemical family	Chemical structure	EU Ref. No.	INCI name	Abbreviation	CAS No.	Log K_{ow}	Solubility (g/L)	pKa	Max. conc. (%)	UV range
		28	Diethylamino hydroxybenzoyl hexyl benzoate	DHHB	302776-68-7	6.54	$9.5x10^{-4}$	7.29	10	UVA
Crilenes		10	Octocrylene	OC	6197-30-4	6.88	$2x10^{-4}$		10	UVB
Benzyl malonate derivatives		26	Polysilicone-15	BMP	207574-74-1	5.66	0.001		10	UVB
Others		32	Ethoxyethyl cyanoacetate of methoxypropylamino cyclohexenylidene	MCE	1419401-88-9	1.7	0.45	13.3	3	UVA
Inorganic or mineral			Titanium dioxide	TiO_2	13463-67-7					
			Zinc oxide	ZnO	1314-13-2					

3. Organic UV filters in the marine ecosystem

The highest inputs of oUVF release in marine ecosystems are associated with the application of sunscreens during recreational and touristic activities in coastal areas. Several studies have estimated the quantities of sunscreen introduced into marine environments through such activities, reporting values ranging from approximately 8 kg per day along the Atlantic coast of France to as much as 630 kg per day in the Mexican Caribbean (Casas-Beltrán et al., 2021; Milincovitch et al., 2024). The second major source of oUVF input into aquatic ecosystems is the discharge of effluents from WWTPs (Těšínská et al., 2024).

Conventional WWTP methods, such as microbiological processes, filtration, flocculation, and adsorption, tend to remove or degrade only a limited proportion of oUVFs, typically achieving removal efficiencies of around 30%. Advanced treatment technologies, including membrane separation, membrane bioreactors, adsorption, oxidation, photodegradation, and biodegradation, exhibit substantially higher removal efficiencies, reaching up to 99%. However, these advanced techniques require significant financial investment and complex infrastructure, thereby considerably increasing the overall cost of water treatment (Ramos et al., 2015; Tran et al., 2022).

Moreover, some processes, such as photodegradation, can promote the formation of TPs, which often possess physicochemical properties distinct from the parent compounds and, in many cases, exhibit higher potential toxicity (Díaz-Cruz et al., 2008; Ramos et al., 2015; Sun et al., 2024). These processes primarily occur when oUVFs are released into marine ecosystems and become exposed to sunlight. Upon irradiation, oUVFs can undergo direct photolysis, which includes photoionization events where excited molecules interact with surrounding species, leading to bond cleavage. Additionally, indirect photochemical processes may occur, involving interactions between the parent compounds and dissolved organic matter (DOM), reactive oxygen species (ROS), and nitrates and nitrites (Těšínská et al., 2024).

Another relevant transformation pathway involves biotransformation, whereby microorganisms degrade or modify oUVFs through enzymatic processes (Volpe et al., 2021). This mechanism is particularly significant in sediment environments, where these compounds tend to adsorb, and microbial activity is more pronounced. Biotransformation can lead to partial mineralization or the formation of transformation products with different environmental behaviours and toxicological properties (Volpe et al., 2017; Fagervold & Lebaron, 2022). Direct and indirect photoreactions and biotransformation processes are significantly influenced by environmental conditions (temperature, salinity, organic matter concentration, and pH) and affect the half-life of these compounds in marine systems (Medici et al., 2022; Těšínská et al., 2024). For instance, Medici et al. (2022) reported that the half-life of BP-3 under lab conditions remains relatively short, between 2 and 3 minutes, under pH 6-8 at 20 °C with added NaCl. In contrast, OD-PABA exhibited a longer degradation time of approximately 27 minutes in pure water. Similarly, Chou et al. (2024) determined that in seawater (lab conditions: pH = 8.11, salinity = 47.7), the half-lives of HMS and BMDBM exceed 6.9×10^4 hours, while OMC displayed a half-life ranging from 1.3×10^4 to 2.6×10^4 hours. Under different light conditions in freshwater, O'Malley et al. (2021) observed that the half-lives of several oUVFs varied considerably, with IMC (6.6 h), BP-1 (20 h), OMC (23 h), 3-BC (30 h), 4-MBC (34 h), and BP-8 (140 h). Among these, OC, BMDBM, and 4-MBC were identified as the most persistent and prevalent compounds.

3.1 Ecotoxicological effects of oUVFs in the marine environment

The oUVFs have been studied in various environmental matrices, including water, sediment, and biota, using diverse extraction and detection methods (Cadena-Aizaga et al., 2020). Laboratory assays have shown that oUVFs, at concentrations ranging from ng/L to mg/L, may act as endocrine disruptors, affecting reproductive, endocrine, and immune systems,

as well as causing cellular and DNA damage, and alterations in gene expression (Caloni et al., 2021; Hodge et al., 2025). For example, exposure to increasing concentrations of sunscreen components (10, 20, and 50 µL/L) induced developmental abnormalities in *Paracentrotus lividus* larvae (Corinaldesi et al., 2018). Similarly, larvae of the Pacific oyster (*Magallana gigas*) exposed to 1, 10, and 100 ng/L of OC and BP-3 exhibited impaired development and reduced survival rates (Carvalhais et al., 2025). OC, HMS, and BMDBM were toxic to *Artemia salina* nauplii and disrupted zebrafish (*Danio rerio*) larval development at 2 mg/L during 48-hour exposure. Additionally, HMS, BP-3, and EHS significantly reduced the growth rate of the microalgae *Tetraselmis* sp., altering cell morphology, metabolic activity, and autofluorescence (Thorel et al., 2020).

In-vitro toxicological studies face several limitations in replicating real environmental conditions (Wheater, 2022). Typically, the concentrations of compounds tested are higher than those found in natural settings, and exposure times at constant concentrations do not reflect the dynamic behaviour of these compounds in the water column (Lebaron, 2022).

The occurrence and biological effects of oUVFs have been documented in various *in-situ* organisms. Maternal transfer of oUVFs to foetuses has been observed in cetacean species (Alonso et al., 2015), potential bioaccumulation has been reported, for example, in both benthic organisms (Peng et al., 2017; Wang et al., 2022) and cetaceans (Gago-Ferrero et al., 2013), environmental concentrations of these compounds have been linked to coral bleaching and increased susceptibility to coral's viral infections, prompting several coral-reef destinations to restrict or ban the use of sunscreens to protect these fragile ecosystems (Mitchelmore et al., 2021; Caloni et al., 2021).

The limited knowledge of the environmental fate and transformation of individual oUVFs hinders accurate evaluation of their potential for bioaccumulation and trophic transfer (Lozano et al., 2020; Lebaron, 2022; Damikouka et al., 2024). Moreover, their detection in

seafood raises concerns about human exposure, as their physicochemical properties suggest a high potential for accumulation along the food web, potentially increasing exposure in both humans and top marine predators. Despite that, only a limited number of organism groups and geological locations have been studied, and there is a lack of standardized protocols and experimental procedures for toxic assessments (Hodge et al., 2025; Grant et al., 2025). Only a few studies have provided data on No Observed Adverse Effect Levels (NOAELs), which can serve as a reference when evaluating the detected and quantified concentrations in marine matrices (Barbosa et al., 2018; Cunha et al., 2018).

4. Monitoring of the presence of oUVFs in coastal and pelagic waters

The monitoring of oUVFs in biota has steadily increased in recent years. These compounds have been detected from primary producers such as seaweeds (Cunha et al., 2015; Cadena-Aizaga et al., 2022a) and seagrasses (Agawin et al., 2022) to primary consumers, including molluscs, crustaceans, and echinoderms (Cadena-Aizaga et al., 2022b), as well as in higher trophic levels and top predators, such as tunas and marine mammals (Nakata et al., 2010; Pintado-Herrera et al., 2024; Íñiguez et al., 2025).

Offshore and deep-sea environments remain poorly studied with respect to oUVFs (Avellan et al., 2022; Pinheiro et al., 2023). This issue gains relevance as the exploration and exploitation of new environmental resources (deep-sea mining (Amon et al. 2022)) increasingly target the deep sea, which has already been described as a major sink for organic contaminants (Koenig et al., 2013; Dasgupta et al., 2021; Ge et al., 2021). To date, only a limited number of studies have directed their efforts toward offshore and deep-sea environments (Avellan et al., 2022). With respect to biota, monitoring activities have predominantly focused on commercially valuable species such as tuna and redfish (Moualek et

al., 2024; Pintado-Herrera et al., 2024). Regarding sediments, Combi et al. (2016) investigated the Adriatic Sea, assessing the concentrations of various oUVFs in deep-sea sediments exposed to differing degrees of anthropogenic influence in the vicinity of sampling sites. Similarly, Goksøyr et al. (2009) examined oUVF concentrations along a coastal-to-offshore transect in the Pacific Ocean, demonstrating a clear dilution gradient with increasing distance from emission sources.

Most monitoring efforts to date have been conducted in coastal environments, particularly in areas influenced by industrial activities, WWTP effluents, and tourism. Europe is the continent with the highest level of monitoring, followed by Southeast Asia and specific coastal zones of the United States. However, significant geographical gaps remain, particularly in regions such as Africa and South America (Cadena-Aizaga et al., 2020; Lozano et al., 2020; Caloni et al., 2021; Těšínská et al., 2024). The global scarcity of monitoring studies represents a major concern, as understanding the distribution of these compounds is essential for the development of effective management policies and for the identification of vulnerable sites and contamination hotspots. This issue becomes even more critical considering that these compounds have already been detected in remote regions, including Antarctica and the Arctic (Duarte et al., 2021; D'Amico et al., 2022; Costa et al., 2024), highlighting their high potential for long-range transport and environmental dispersion.

5. Site of the study: Madeira Islands

Considering all the information presented in this introduction, oceanic islands remain natural laboratories due to their isolation and the relative ease with which human–environment relationships can be studied (Vitousek, 2002). The Madeira Archipelago, together with the Canary Islands, the Azores, and Cabo Verde, forms part of the Macaronesia biogeographic

region located in the Northeast Atlantic (Fig. I. 3) (Fernández-Palacios et al., 2024). The Madeira Archipelago comprises a group of volcanic islands, which includes Madeira, Porto Santo, the Desertas, and the Selvagens Islands; the last two are uninhabited islands classified as partial and integral natural reserves, respectively. All of them are in subtropical latitudes, approximately 1,000 km from the European continent and about 550 km off the west coast of Africa. It is characterized by oligotrophic waters and a steep island shelf that provide significant depths close to shore, as well as numerous submarine canyons that constitute important habitats for several taxa, including deep-diving cetaceans (Spalding et al., 2007; Kim et al., 2008). In addition to these geographical features and nutrient-poor waters, physical processes such as upwelling, currents, and eddies create localized peaks of productivity that help sustain the region's high biodiversity (Carracedo & Troll, 2021; Cartagena-Matos et al., 2021; Fernandez et al., 2021).

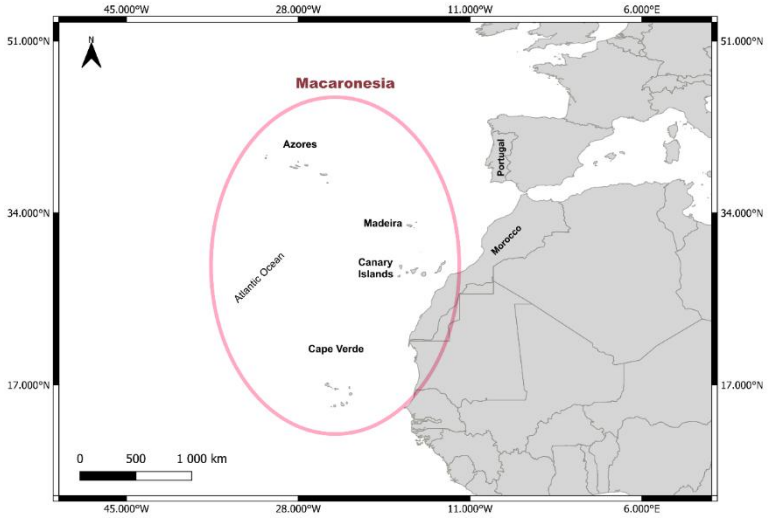


Fig. I. 3. Geographical location of the Macaronesia bioregion.

Characterized by temperate conditions throughout the year and generally calm sea states, mainly due to the high mountains (≈1,800 m) that influence the prevailing northeasterly

trade winds (Tomczak and Godfrey, 1994), the islands have become a major tourist hotspot. From January to October 2025, Madeira hosted approximately 1,645,000 tourists staying in hotels and local accommodations, in contrast with the 260,000-resident population of Madeira and Porto Santo. In addition, about 390,000 cruise passengers visited the islands as short-term visitors, most of whom docked at Funchal Harbour, the capital city (Direção Regional de Estatística da Madeira, 2025). This transforms tourism into the main economic source in the area.

Considering the concentrated anthropogenic pressures within a relatively small area of Madeira, the island represents an optimal location to assess and monitor how human presence influences the occurrence of oUVFs in the marine environment. Its proximity to offshore areas, facilitated by the island's geological characteristics, allows relatively easy access to pelagic and deep-sea waters, thereby enabling a more comprehensive understanding of oUVFs in these habitats. Collectively, this setting provides a unique opportunity to gain novel insights into the distribution and occurrence of oUVFs throughout the water column.

6. Research questions

1. Are marine protected and remote areas detectably less affected by oUVF contamination originating from adjacent urban and touristic zones?
2. Do organic UV filters (oUVFs) released in highly anthropised coastal areas persist and disperse into the pelagic and deep-sea environments of oceanic island systems?
3. To what extent are oUVFs transferred and accumulated along coastal and pelagic trophic trophic webs?
4. How does trophic position, habitat use, and organism mobility influence the accumulation of oUVFs in marine organisms, including top predators?

7. Thesis objectives and outline

This thesis aims to investigate the occurrence and distribution of oUVFs in the marine environment, ranging from coastal and offshore waters to the deep sea. To achieve this, several marine species representing different trophic levels within both coastal and pelagic trophic webs were included, as well as organisms inhabiting distinct depths throughout the water column. The study focuses on an oceanic island system, Madeira and the Desertas Islands, which provides an optimal natural setting for addressing the following objectives:

1. To reduce the existing knowledge gap regarding the occurrence and concentration of oUVFs in marine matrices.
2. To evaluate the vulnerability of coastal ecosystems to human-derived inputs, assessing their exposure to oUVF contamination and spatial/seasonal variability in occurrence and concentrations.
3. To assess the occurrence and distribution of oUVFs in pelagic and deep-sea ecosystems, determining whether these compounds are transported beyond coastal zones.
4. To determine the extent to which top predators are exposed to oUVFs, characterising their occurrence and concentration profiles in relation to trophic position and habitat use, as a basis to discuss potential bioaccumulation and trophic transfer.

To achieve these objectives, the following efforts were undertaken:

i) Zooplankton samples were collected to develop and optimize, for the first time, a methodology based on Microwave-Assisted Extraction coupled with UHPLC-MS/MS. This method enabled the identification and quantification of oUVFs in zooplankton, a key matrix in the marine environment due to its essential role at the base of the food web (Chapter II).

ii) Coastal matrices (water and sediments), along with coastal marine species representing different trophic levels, were sampled at locations subjected to varying degrees of human pressure and during different seasons associated with tourism peaks. This approach enabled monitoring of oUVF occurrence, assessment of their behaviour in coastal environments, and identification of the matrices most affected by these compounds (Chapter III).

iii) Seawater, sediments, and pelagic species from multiple trophic levels, including one bathypelagic species, were analysed to determine oUVF occurrence and potential offshore transport, thereby tracking their presence across the water column, including deep habitats (Chapter IV).

iv) Biopsies from two deep-diving cetacean species were collected and analysed for oUVFs to evaluate how organic pollutants released in coastal areas may reach and affect top predators whose habitats extend from surface waters to the deep sea (Chapter V).

8. Thesis publications

Chapter II:

Eva Íñiguez, Margaux Gouazé, Ana Dinis, Zoraida Sosa-Ferrera, Nereida Cordeiro, Manfred Kaufmann, and Sarah Montesdeoca-Esponda. (2026). Development and preliminary validation of an analytical methodology for the determination of organic UV filters in zooplankton samples. *Marine Pollution Bulletin. Marine Pollution Bulletin*, 225, 119204. https://doi.org/10.1016/j.marpolbul.2025.119204

Author's contribution:

Eva Íñiguez: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Writing – original draft.

Margaux Gouazé: Methodology, Validation, Formal analysis, Investigation, Writing – original draft, Visualization.

Ana Dinis: Conceptualization, Funding acquisition, Reviewing – original draft, Supervision

Zoraida Sosa-Ferrera: Supervision, reviewing and editing

Nereida Cordeiro: Project administration, Funding acquisition, Reviewing- original draft, Supervision, Writing - review & editing.

Manfred Kaufmann: Conceptualization, Reviewing – original draft, Supervision

Sarah Montesdeoca-Esponda: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Writing – original draft, Supervision.

Chapter III:

Eva Íñiguez, Rodrigo Pires da Silva, Sarah Montesdeoca-Esponda, Elli Dimou, Filipe Alves, Manfred Kaufmann, Ana Dinis, and Nereida Cordeiro. (2025). 'The invisible impact of tourism: Organic UV filters in the coastal ecosystem of a remote Atlantic island'. *Environmental Research*, 287, 123153. https://doi.org/10.1016/j.envres.2025.123153

Author's contribution

Eva Íñiguez: Conceptualization; Data curation; Formal analysis; Investigation; Methodology; Visualization; Writing – original draft; Writing – review and editing

Rodrigo Pires da Silva: Conceptualization; Methodology; Visualization; Writing – review and editing

Sarah Montesdoca-Esponda: Conceptualization; Methodology; Resources; Validation; Visualization; Writing – review and editing.

Elli Dimou: Methodology; Writing – review and editing

Filipe Alves: Funding acquisition; Resources; Visualisation; Writing – review and editing

Manfred Kaufmann: Funding acquisition; Resources; Visualisation; Writing – review and editing; Supervision

Ana Dinis: Conceptualization; Funding acquisition; Resources; Visualisation; Writing – review and editing; Supervision

Nereida Cordeiro: Conceptualization; Funding acquisition; Resources; Visualisation; Writing – review and editing; Supervision

Chapter IV:

Eva Íñiguez, Sarah Montesdeoca-Esponda, Raquel Alves, Pedro Ideia, Nereida Cordeiro, Ana Dinis, Zoraida Ferrera-Sosa and Manfred Kaufmann. (2026). Organic ultraviolet filters across the surface, pelagic, and bathypelagic compartments of an oceanic island system. *Environmental Science and Pollution Research*, submitted.

Author's contribution

Eva Íñiguez: Conceptualization; Data curation; Formal analysis; Investigation; Methodology; Visualization; Writing – original draft; Writing – review and editing

Sarah Montesdoca-Esponda: Conceptualization; Methodology; Resources; Validation; Visualization; Writing – review and editing.

Raquel Alves: Methodology; Writing – review and editing

Pedro Ideia: Methodology; Resources; Writing – Review and editing.

Nereida Cordeiro: Conceptualization; Funding acquisition; Resources; Visualisation; Writing – review and editing; Supervision

Ana Dinis: Conceptualization; Funding acquisition; Resources; Visualisation; Writing – review and editing; Supervision

Zoraida Sosa Ferrera: Resources; Visualisation; Writing – review and editing

Manfred Kaufmann: Funding acquisition; Resources; Visualisation; Writing – review and editing; Supervision

Chapter V:

Eva Íñiguez, Sarah Montesdeoca-Esponda, Filipe Alves, Zoraida Sosa-Ferrera, Manfred Kaufmann, Nereida Cordeiro and Ana Dinis. (2025). 'Organic ultraviolet filters in the blubber of two free-ranging deep-diving cetacean species'. *Environmental Pollution*, 383, 126830. https://doi.org/10.1016/j.envpol.2025.126830

Author's contribution

Eva Íñiguez: Writing – original draft, Visualization, Investigation, Formal analysis, Data curation, Conceptualization.

Sarah Montesdeoca-Esponda: Writing – review & editing, Visualization, Validation, Supervision, Resources, Methodology, Investigation, Formal analysis, Conceptualization.

Filipe Alves: Writing – review & editing, Visualization, Validation, Resources, Funding acquisition.

Zoraida Sosa-Ferrera: Writing – review & editing, Validation, Resources.

Manfred Kaufmann: Writing – review & editing, Validation, Supervision, Resources.

Nereida Cordeiro: Writing – review & editing, Validation, Supervision, Resources, Funding acquisition.

Ana Dinis: Writing – review & editing, Validation, Supervision, Resources, Project administration, Funding acquisition, Conceptualization.

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CHAPTER II

Development and Preliminary Validation of an Analytical Methodology for the Determination of Organic UV Filters in Zooplankton Samples

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CHAPTER II: Development and preliminary validation of an analytical methodology for the determination of organic UV filters in zooplankton samples

Abstract

The release of chemicals into marine environments from coastal human activities has raised growing concern about pollution. Among these chemicals, organic ultraviolet filters (oUVFs), widely used in personal care products and industrial applications, have recently been identified as pollutants of emerging concern. Their extensive use and persistence highlight the need to assess their occurrence and potential impacts on aquatic ecosystems. This study aimed to optimize and apply an analytical methodology for the determination of eleven oUVFs in zooplankton matrices. Microwave-assisted extraction (MAE) was employed for sample preparation, while ultra-high-performance liquid chromatography coupled with tandem mass spectrometry (UHPLC-MS/MS) enabled the identification and quantification of the target compounds. Extraction parameters, including solvent, temperature, and time, were systematically optimized to enhance recovery and ensure accuracy and precision in complex biological samples. The method achieved method limits of detection (MLOD) between 1.47 and 5.98 ng/g dry weight (d.w.) and method limits of quantification (MLOQ) between 6.06 and 19.92 ng/g d.w. Recovery efficiencies were low, ranging from 28 to 63%, reflecting the diverse physicochemical properties of oUVFs and the strong matrix effects associated with zooplankton heterogeneity. Application of the validated method to zooplankton collected around Madeira Island (Portugal) revealed the presence of six oUVFs. Homosalate was the most frequently detected compound (53% of samples), while octocrylene exhibited the highest concentrations, ranging from 24.01 to 1029 ng/g d.w. These findings demonstrate the relevance of zooplankton as bioindicators of oUVF contamination and support the need for regulatory monitoring and ecological risk assessments in coastal ecosystems.

Keywords: Emerging contaminants, zooplankton, microwave-assisted extraction, ultrahigh-performance liquid chromatography, mass spectrometry.

1. Introduction

Since the 1950s, beach resorts have become increasingly subject to mass tourism. Today, coastal areas remain significant destinations for visitors, promoting human activities within the aquatic ecosystem (Tovar-Sánchez et al., 2013). These activities, along with recent healthy recommendations for skin protection to prevent diseases such as cancer caused by prolonged sun exposure, promote the use and release of personal care products (PCPs), such as sunscreen (Gao and Zhang, 2021).

Both organic (oUVFs) and inorganic (iUVFs) ultraviolet filters are used extensively in PCPs to prevent skin damage, as well as in food packaging and industrial products like paints to protect against degradation caused by UV radiation (Huang et al., 2021). These UVFs act in the wavelength ranges of 320-400 nm (UVA) and 280-320 nm (UVB) (Tovar-Sánchez et al., 2018; Caloni et al., 2021). Currently, 33 UVFs are accepted by the European Union (European Commission, 2024). Among these, only two iUVFs, zinc oxide (ZnO) and titanium dioxide (TiO2), are added in both micrometric and nanometric forms (Fastelli & Renzi, 2019; Caloni et al., 2021). The oUVFs are classified into eleven distinct families characterised by simple or multiple aromatic ring structures linked to hydrophobic groups (Caloni et al., 2021). The use of these oUVFs in PCPs is governed by regulatory frameworks such as REACH (Registration, Evaluation, Authorisation and Restriction of Chemicals) in Europe (Council Regulation (EC) No 1354/2007), which limits their concentration in PCP formulations to between 2 and 25% of the total product (European Parliament and Council, 2009). According to their physicochemical properties, oUVFs typically exhibit high lipophilicity, as measured by the n-

octanol-water partition coefficient (K_{ow}), and low water solubility (Vila et al., 2016). They are characterised by exhibiting good environmental stability due to their poor degradability and photostability, which tend to accumulate in solid matrices and organisms (Barón et al., 2013). Marine organisms can absorb oUVFs through two primary mechanisms: directly by ingestion or indirectly by absorption via exposed surfaces (Rani et al., 2017). Once absorbed, marine organisms can degrade, metabolize, or accumulate oUVFs in their tissues or organs (Jentzsch et al., 2023).

Due to their widespread use and continuous release, significant amounts of oUVFs reach seawater directly through skin washing and indirectly through treated wastewater, industrial discharges, and runoff (Daughton, 2013). A study on the French Mediterranean coast has shown that an average of 15.7 kg of sunscreen is released daily on a highly touristic beach during the peak season (Labille et al., 2020). Their worldwide presence, even in polar regions (*e.g.* the Arctic and Antarctic), underscores their global distribution (Román et al., 2011; Magi et al., 2012; Tsui et al., 2014; Langford et al., 2015).

Research on the risks associated with these compounds has increased significantly over the past few decades (Daughton, 2013; González et al., 2022; Pawlowski et al., 2023). Numerous harmful physiological effects on marine organisms, such as impaired reproduction, physical deformities, and increased mortality rates, have been previously observed under laboratory conditions (Danovaro et al., 2008; Schmitt et al., 2008; Araujo et al., 2018). These studies often rely on exposure concentrations exceeding those typically detected in the natural environment (Thorel et al., 2020). However, some effects have already been described *in situ*, including coral bleaching on tourist beaches (Mitchelmore et al., 2021), which has led to a ban on sunscreen use in some coastal areas (Downs et al., 2016). Hence, in Europe, three sunscreen agents (avobenzone, octocrylene, and benzophenone-3) were already included in the European "Watch List" tool in July 2022 (European Commission, 2022). The updated list of 2025 has

also included a fourth UVF, the octisalate (2-ethylhexyl salicylate) (European Commission, 2025).

Zooplankton encompasses a wide range of taxa, including copepods (Crustacea), molluscs, and Cnidaria and Ctenophora, which are among the most abundant groups in the NE Atlantic region (Gueroum et al., 2021; Dos Santos et al., 2023; Torres-Martinez and Herrera, 2025). As the foundation of the marine food web, zooplankton play a critical role in transferring energy and organic matter to higher trophic levels (Richardson, 2008).

Zooplankton remain sensitive to environmental changes, serving as valuable bioindicators of ecosystem health (Taylor et al., 2002; Fullgrabe et al., 2020). The introduction of non-indigenous species and the release of pollutants, as chemical contaminants, can contribute to changes in zooplankton community composition, which can lead to triggering cascading effects throughout the marine ecosystem (Bettinetti and Manca, 2013; Gueroum et al., 2021).

To date, only limited research in freshwater ecosystems has addressed the detection of oUVFs in zooplankton matrices (Yang et al., 2020). However, numerous studies have addressed marine and aquatic contamination in zooplankton, mainly focusing on persistent organic pollutants (POPs), such as pesticides, industrial chemicals, and their by-products (Hallanger et al., 2011; Boldrocchi et al., 2018; Pascariello et al., 2019; Sørensen et al., 2023). oUVFs could negatively impact zooplankton communities by affecting their population dynamics, reducing growth rates, and altering reproductive success, potentially disrupting the balance of marine trophic webs (Morin-Crini et al., 2021; Henderson et al., 2025).

In this context, the present study aims to focus on the development of a methodology an analytical methodology for quantifying eleven oUVFs in zooplankton samples, using microwave-assisted extraction (MAE) coupled with ultra-high-performance liquid chromatography-tandem mass spectrometry (UHPLC-MS/MS). MAE, though less commonly

applied, is particularly suited for solid or semi-solid samples. It offers several advantages, including enhanced extraction efficiency, reduced extraction time, lower solvent consumption, and improved analyte recovery compared to conventional solid-sample preparation methods (Cadena-Aizaga et al., 2020; Oubahmane et al., 2023; Nieddu et al., 2024). These benefits result from the direct heating of the sample by microwaves, which accelerates extraction and enables effective analyte release using smaller volumes of solvent (Narloch and Wejnerowska, 2021). To achieve optimal performance, parameters such as extraction temperature, solvent type, and extraction time must be carefully optimized in accordance with the specific matrix involved (Ferrara et al., 2023). Given these attributes, MAE represents a promising approach within the framework of green analytical chemistry compared to conventional solid-sample preparation methods such as extraction by ultrasound or Soxhlet (Destandau and Michel, 2022). To assess the environmental sustainability of the sample preparation process, the AGREEprep metric was applied to evaluate its overall greenness (Pena-Pereira et al., 2022).

To the best of our knowledge, this is one of the first studies to apply this approach to marine zooplankton matrices in marine ecosystems. The validated method was used to analyze samples collected in Madeira Island (Portugal), providing new insights into the environmental occurrence of oUVFs and their potential link with anthropogenic pressure.

2. Materials and methods

2.1 Study area, sampling collection, and pre-treatment

Thirty-six zooplankton samples were collected in six different stations during two distinct seasons in 2023 around Madeira and Desertas Islands (Portugal) (Table II. SM1; Fig. II. 1). These islands, located in the northeast Atlantic Ocean, are characterized by oligotrophic waters

and subtropical temperatures ranging from 17 to 24 ºC (Santos et al., 2004; Spalding et al., 2007).

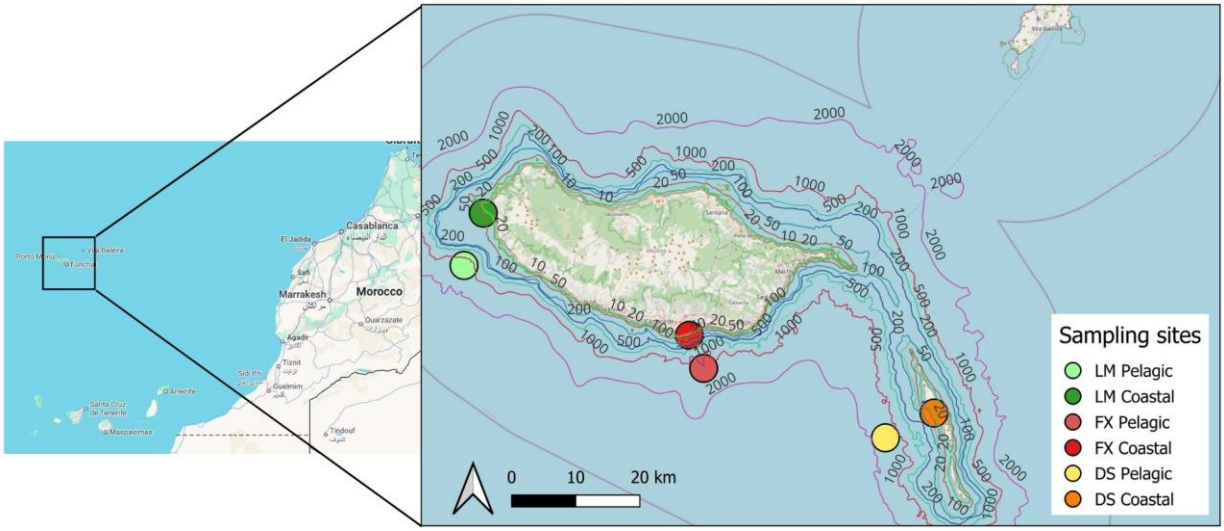

Fig. II. 1. Location of Madeira and the Desertas Islands. The dots represent the sampling sites: Lombada dos Marinheiros (LM): LM_pelagic (32º 73.296 N, 17º 30.542 W), LM_coastal (32º 78.771 N, 17º 25.797 W); Funchal (FX): FX_pelagic (32º 35.545 N, 16º 53.605 W), FX_coastal (32º 38.210 N, 16º 52.010 W); and Desertas (DS): DS_pelagic (32º 49.234 N, 16º 63.051 W), DS_coastal (32º 52.241 N, 16º 52.516 W).

Zooplankton samples were collected at night, at least one hour after sunset, to take advantage of the migration of the mesopelagic layer toward the surface (Andersen et al., 1998). Sampling was conducted using a Manta trawl (Hydro-Bios) with a surface area of 70 x 40 cm and a mesh size of 200 µm. Transects were performed parallel to the coastline for 30 min.

After completing each transect and retrieving the Manta trawl onboard, samples were rinsed with seawater over a 200 µm sieve, followed by a wash with distilled water to remove residual salt. Then, each sample was transferred to an amber glass jar and frozen (-20 °C) for 24 h, and then freeze-dried. Then, the whole sample was ground and sieved to obtain a homogeneous powder (<180 µm particle size) to get an adequate quantity for the target analyses (150 mg per

sample collected, considering triplicates) and stored in dry and dark conditions until further analysis.

2.2 Reagents and consumables

The 11-target oUVFs (Table II. SM2) and the internal standard (IS) BP-d_{10} were purchased from Sigma-Aldrich (Madrid, Spain). Ethanol (EtOH), methanol (MeOH), acetonitrile (ACN), acetone (ACE), hexane (HEX), LC-MS grade (purity > 99%), water, and formic acid LC-MS grade were supplied by Panreac Química (Barcelona, Spain). The 0.45 µm polyethylene terephthalate syringe filters were purchased from Macherey-Nagel (Dueren, Germany).

The stock solution of the target compounds was prepared in ACE at 250 µg/mL and stored in capped glass vials at -20 ºC in the dark. Daily intermediate standards were freshly prepared in MeOH from the stock solution.

2.3 Instrumental analysis

The target oUVFs were extracted using a Titan MPS MAE system with 16 Teflon containers (PerkinElmer, Madrid, Spain). The oUVFs were determined and quantified using an ACQUITY UHPLC (Waters Chromatography, Barcelona, Spain) equipped with a binary solvent manager for eluting the analytes, a thermostatically controlled 2777 autosampler, and a column for temperature control. This system was coupled to a triple quadrupole tandem mass spectrometer (MS/MS) detector with electrospray ionization (ESI). Instrument control and data acquisition were performed using MassLynx mass spectrometry software (Waters Chromatography, Barcelona, Spain).

2.4 Chromatography and detection conditions

Separation used a Waters ACQUITY BEH C18 column (50 × 2.1 mm, 1.7 μm) at 35 °C with a flow rate of 0.30 mL/min. The mobile phase consisted of MeOH (LC-MS grade) (A) and water (LC-MS grade) (B), each with 0.1% (v/v) formic acid. The gradient was initiated with a MeOH: water ratio of 3:1, reaching 100% MeOH after 3 min. This concentration was maintained for up to 5 min. By the end of the 6th min, the composition returned to the initial conditions, and the system was allowed to balance until reaching the 7th min before the next injection. These conditions were chosen to optimize chromatographic efficiency and reduce analysis time, considering the hydrophobic nature of the target compounds (Cadena-Aizaga et al., 2022). This approach provided sufficient separation, minimizing co-elution and matrix effects. MS/MS detection was performed using ESI in positive mode, as appropriate for each analyte. Source settings were capillary voltage 3.0 kV, cone 15 V, extractor 2.5 V, RF lens 1.0 V, source temperature 150 °C, desolvation temperature 450 °C, desolvation gas 500 L/h, cone gas 50 L/h; nitrogen was used as the desolvation gas and argon as the collision gas. Compound-specific precursor/product ion transitions and collision energies are provided in Table II. SM3, with a summary in the Methods. Additionally, the chromatograms of the eleven target compounds have been included in the Supplemental material as Fig. II. SM1.

2.5 Quality control

The linearity, method limit of detection (MLOD), and method limit of quantification (MLOQ), as well as instrumental limit of detection (ILOD) and instrumental limit of quantification (ILOQ), were evaluated for each compound under optimal extraction conditions from the matrix. Calibration curves using the IS approach were prepared using eight concentration points ranging from 1 to 500 ng/mL for each compound (with estimated concentrations between 20 and 10000 ng/g d.w. in the zooplankton samples). ILOD and ILOQ were determined based on the signal-to-noise ratio (S/N) of individual compound responses at

the lowest point of the calibration curve, assuming minimum detectable S/N levels of 3 and 10, respectively.

To evaluate the extraction efficiencies, recoveries at theoretical concentrations of 25 and 250 ng/mL in the final extract were determined by comparing spiked samples before and after extraction (n=6 for each level). Repeatability expressed as inter-day precision of six replicates was also calculated for both concentration levels (25 and 250 ng/mL in the final extract). This assessment was performed by adding known amounts of a standard mixture to 50 mg of the sample to achieve these concentrations in the final theoretical extract. The IS-BP-d_{10} was added at a final concentration of 200 ng/mL in all samples and the calibration curve before injection. It was chosen to account for instrumental variability and matrix effects, as it shares chemical and chromatographic behaviour with the target compounds. Using a single IS simplifies analysis, reduces costs, and ensures reproducibility across matrices, as demonstrated by Van Den Houwe et al. (2014). The matrix effect is calculated as the ratio between the analyte signal in the solvent after extraction of a blank matrix, and the signal of the analyte prepared in a pure solvent, multiplied by 100 to express it as a percentage. A value of 100% indicates the absence of a matrix effect, whereas values below or above this threshold indicate signal suppression or enhancement, respectively.

Each sample was processed in triplicate when the available material exceeded 150 mg, and only those triplicates with a relative standard deviation (RSD) of ≤ 30% were considered for analysis. To minimize the risk of external contamination and compound degradation, all procedures were carried out using amber glass containers that had been thoroughly cleaned and rinsed with distilled water, followed by HPLC-grade ethanol. Laboratory personnel wore gloves throughout the handling process. All procedural blanks showed concentrations of the target compounds below the respective MLODs.

2.6 Software

A Wilcox paired test was done to test possible statistical differences between the areas of the different compounds according to the extraction with two different solvents carried out in the first experimental design. That and bar plot were performed in R (R Core Team, 2021; version 2024.12.1).

The AGREEprep greenness tool (https://agreeprep.anvil.app/) was used to assess the sustainability and environmental impact of the developed methodology.

All the analyses of the Pareto Chart and contour plots were performed using Minitab version 22.1 software (Minitab, LLC, State College, PA, USA).

3. Results and discussion

3.1 MAE optimization

Three factors, temperature, extraction time, and extraction solvent, were considered to optimise the extraction of the eleven oUVFs. With this purpose, three experimental designs were developed and tested based on these factors (Table II. SM4), allowing for consideration of how variables interact with each other and saving time, reagents, and effort. All experimental designs were carried out using 50 mg d.w. of sample and 7 mL of solvent, the minimum volume compatible with the available MAE system. Following MAE, the samples were filtered using 0.45 µm PET syringe filters and analyzed via UHPLC-MS/MS.

The first experimental design consisted of 2^3 runs based on a 2-level factorial design (Table II. SM4). The variables tested were extraction temperatures of 50 °C and 55 °C, extraction times of 5 and 10 min., and two solvents: MeOH and ACN. This first experimental design was conducted to determine which variables had the most significant impact on the recovery area

of the target analytes, and to assess whether temperature and time exhibited positive or negative correlations with extraction efficiency. For that, Pareto chart analysis (Fig. II. 2 and Fig. II. SM2) was conducted to prioritise and determine the most influential variables impacting the extraction results. It was observed that the peak areas obtained for the main target compounds (4-MBC, BP-3, DTS, BMDBM, UV-360, and OMC) were significantly influenced by both temperature and solvent type, either independently, as in the case of DTS and UV-360, or through the interaction of both factors, as observed for OMC, OD-PABA, and BP-3. In contrast, extraction time did not show a significant effect on the recovery areas, except for BMDBM, where a combined effect with temperature was observed (Fig. II. 2 and Fig. II. SM2).

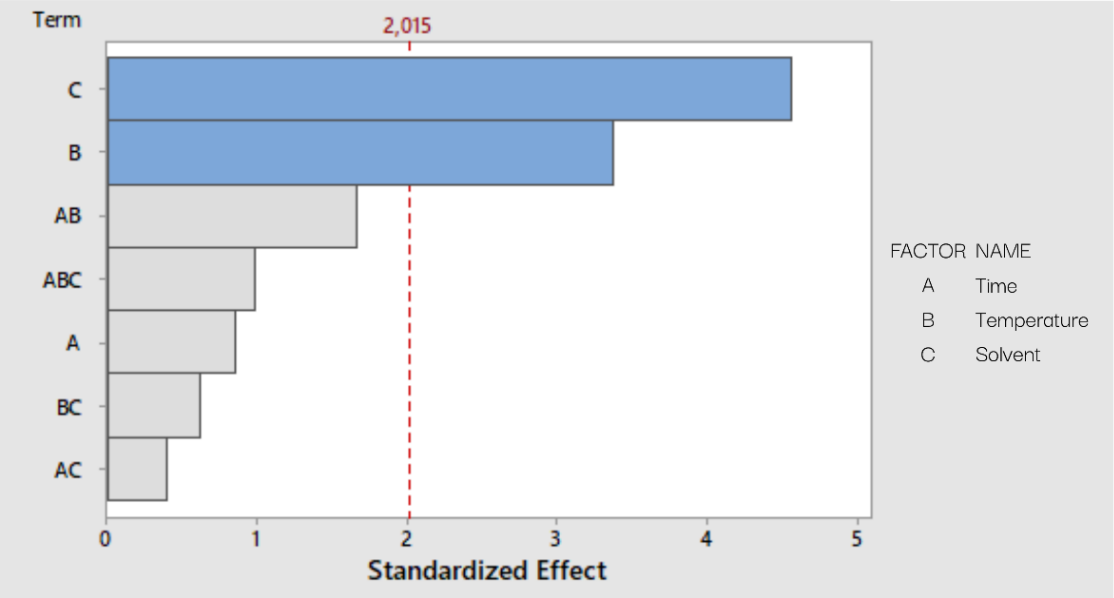

Fig. II. 2. Pareto chart of the standardized effects of the three variables, solvent, temperature, and time for UV-360, as an example. The Pareto chart for all the target compounds is available in Fig. II. SM1. The red dashed line corresponds to the value at which the factor has a significant effect. The blue bars correspond to factors that exceed the significance level, and the grey bars to those that do not.

Additionally, Pearson correlation coefficients were calculated to evaluate the experimental results and to identify potential linear relationships between the tested variables and the extraction efficiency. These correlations enable us to observe the trend of the variables' effects

and establish them for subsequent experimental designs. When the result of the test is 0, it indicates no variable influence. -1 represents the maximum adverse effect of the variable, and 1 represents the maximum positive effect of the variable. Correlation analysis revealed that most compounds exhibited higher recovery at higher temperatures (except EHS) (Table II. 1). Time was excluded from this design due to the absence of an impact, as indicated by the Pareto chart test. Furthermore, ACN consistently yielded higher peak areas than MeOH (Fig. II. 3).

Table II. 1. Values of Pearson correlation according to the temperature variable, considering ACN as the extraction solvent.

Compound	Temperature (ºC)
4-MBC	0.712
BP-3	0.828
HMS	0.027
DTS	0.152
OC	0.339
BMDBM	0.716
IMC	0.599
UV-360	0.807
OD-PABA	0.908
OMC	0.784
EHS	-0.020

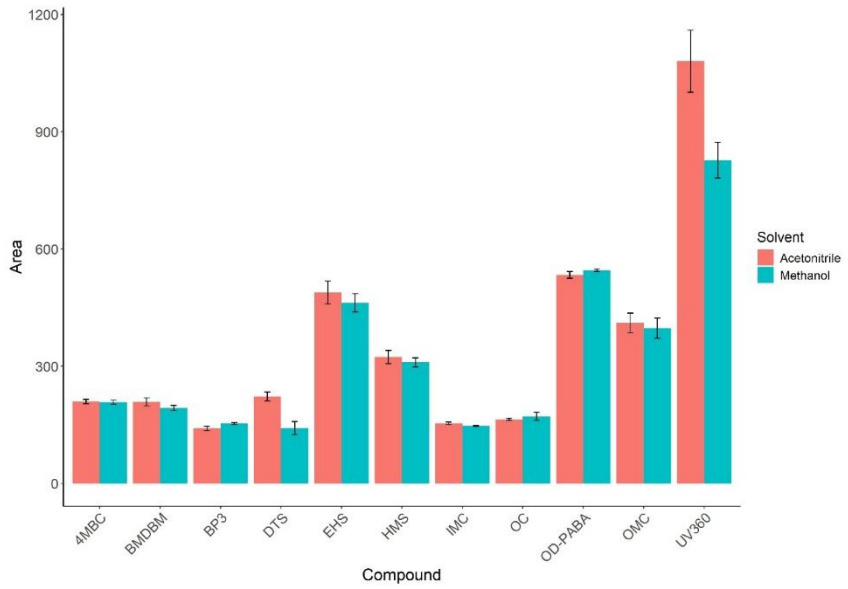

Fig. II. 3. Comparison of the chromatographic peak areas and standard deviation (black bars) of target compounds obtained with two organic solvents during the first experimental design, highlighting the influence of solvent selection on compound response. Wilcox paired text $p > 0.05$. Area values are included in Table II. SM5.

Based on the findings of the first experimental design, which used ACN as the extraction solvent, the second experimental design focused on two variables, temperature and extraction time, at three levels, employing a 3^2-factorial model. The tested temperatures were 56, 58, and 60 °C, higher than those in the previous experimental design, due to the positive correlation observed for this variable. Extraction times of 2, 4, and 6 minutes were selected, reduced from the 8 minutes used in the previous experiment, since longer extraction did not contribute to improved recovery. This adjustment also aimed to optimize the procedure by reducing analysis time and facilitating easier application of the methodology.

Contour plots (Fig. II. 4a and Fig. II. SM3) showed that all compounds, except OMC, achieved good extraction recovery at the minimum extraction time of 2 min. However, temperature proved to be a more complex variable. Half of the compounds (OC, OMC, UV-360, 4-MBC, BMDBM, and DTS) exhibited higher peak areas around 58 °C, while the others (HMS, IMC, BP-3, EHS, and OD-PABA) performed better at 60 °C.

To improve the method, an attempt was made to explore other factors after assessing the time variable. A third experimental design was implemented, utilizing a 3^2 factorial model and incorporating HEX as the extraction solvent. HEX was selected for its lower polarity compared to ACN. To test higher extraction temperatures than those used in the previous experimental design, temperatures of 60, 64, and 68 °C were employed, along with extraction times of 2, 4, and 6 min. As observed in the initial experimental design, some analytes exhibited improved extraction efficiency depending on the combination of temperature and solvent. Therefore, exploring other suitable solvents appeared to be a reasonable approach. Due to HEX's incompatibility with the UHPLC-MS/MS system, the former was evaporated under a nitrogen stream after extraction, and the residues were reconstituted in 1 mL of MeOH. The solution was then sonicated before being filtered.

The analysis revealed that all compounds, except UV-360 and EHS, followed the same trend (Fig. II. 4b and Fig. II. SM4) with a temperature of 68 °C and a reaction time of 2 min. being the most efficient extraction conditions. Although ACN provided the best overall performance, HEX showed greater efficiency for less polar compounds, as indicated by a higher $LogK_{ow}$ value (Table II. SM2).

Therefore, the extraction of 50 mg of sample with 7 mL of HEX at 68 °C for 2 min. was established as the optimum condition.

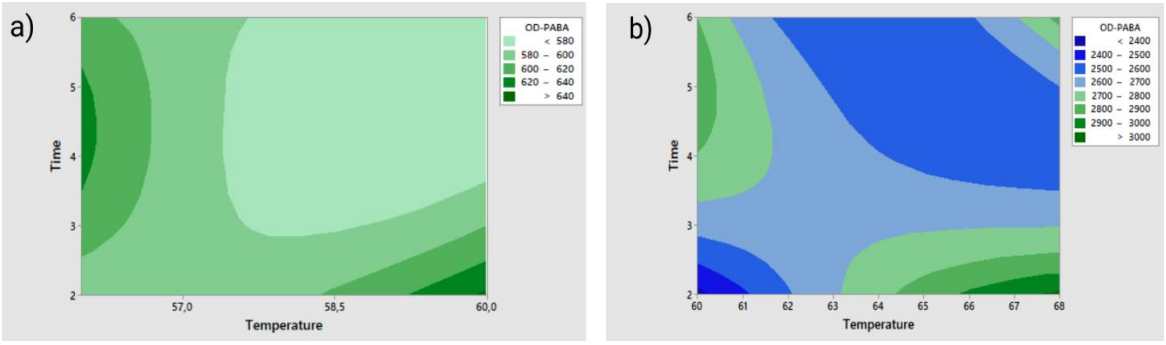

Fig. II. 4. Contour plots as examples of the response areas showing the effect of temperature and extraction time on the extraction efficiency for two different experimental designs: (a) the second experimental design extraction for OD-PABA and (b) the third experimental design extraction for OD-PABA, both as examples. All the contour plots are included in Fig. II. SM3 and Fig. II. SM4. In both plots, the colour gradient represents concentration levels, with dark green indicating higher concentrations and light green indicating lower concentrations. Contour lines indicate regions of equal concentration.

3.2 Method performance

Analytical parameters of the optimised MAE procedure followed by UHPLC-MS/MS are shown in Table II. 2. The linearity coefficients were greater than 0.99 for all target compounds. The ILODs ranged from 0.073 to 0.299 ng/mL while ILOQs ranged from 0.245 to 0.996 ng/mL. The MLODs were between 1.470 and 5.976 ng/g d.w. MLOQs ranged from 4.900 to 19.92 ng/g d.w. These values are generally in line with those reported in previously developed UHPLC-MS/MS-based methods. For instance, Bachelot et al. (2012) reported MLODs of ng/g d.w. and MLOQs of 5 ng/g d.w. for OMC, OC, and OD-PABA in mussel tissue. Similarly, Tsui et al. (2017) described MLODs ranging from 0.11 to 7.05 ng/g d.w. in coral tissues, while Peng et al. (2015) reported LOQs from 0.004 to 10 ng/g across various fish tissues. Higher MLOQ values were observed for BMDBM, BP-3, and EHS when compared with those reported in previous studies. This may be due to the physicochemical properties and behaviour of these analytes in zooplankton samples, which can lead to greater matrix interferences or lower extraction efficiency, thus requiring more extensive clean-up procedures.

Table II. 2. Analytical parameters: recoveries (mean of the three replicates), intra-day precision (mean of the three replicates) at two levels of concentrations, and detection limits for each oUVF using the developed MAE-UHPLC-MS/MS method.

Compounds	Recovery (%)		Intra-day precision (%)		Matrix effect	ILOD	ILOQ	MLOD	MLOQ
	25 ng/mL *	250 ng/mL *	25 ng/mL *	250 ng/mL *	After extraction**	(ng/mL)	(ng/mL)	(ng/mL)	(ng/mL)
4-MBC	46.01	40.10	20.61	11.61	96.46	0.138	0.46	2.757	9.191
BP-3	27.64	26.61	10.95	15.69	95.83	0.269	0.895	5.372	17.91
HMS	47.37	41.30	14.91	7.910	93.03	0.101	0.337	2.024	6.745
DTS	45.54	38.71	17.75	5.250	84.92	0.091	0.303	1.818	6.059
OC	63.32	51.61	9.380	6.680	93.29	0.149	0.498	2.988	9.96
BMDBM	43.48	35.41	9.540	6.460	89.37	0.270	0.901	5.405	18.02
IMC	48.27	42.80	15.77	10.05	94.13	0.158	0.527	3.16	10.53
UV-360	51.25	26.76	10.75	3.190	119.8	0.094	0.314	1.886	6.288
OD-PABA	41.06	41.40	13.61	8.350	103.1	0.073	0.245	1.470	4.900
OMC	49.98	49.62	18.80	13.98	93.65	0.125	0.416	2.495	8.316
EHS	50.67	31.21	9.220	10.43	105.5	0.299	0.996	5.976	19.92

*Theoretical concentration in the final extract; The respective spiking-level concentrations in mass–mass units are 500 ng/g and 5,000 ng/g. **Samples spiked after the extraction (100 ng/mL); ILOD: Instrumental Limit of Detection; ILOQ: Instrumental Limit of Quantification; MLOD: Method Limit of Detection; MLOQ: Method Limit of Quantification.

A linear range of 3.3 orders of magnitude, from the lowest calibration point (1 ng/mL) up to 500 ng/mL, was obtained ($R^2 > 0.99$ for all analytes). This broad range is supported by experimental data and by the sensitivity and resolution of the UHPLC-MS/MS method

Recovery efficiencies at both concentration level were around ≈50% except for BP-3 (Table II. 2). The compounds exhibiting the most significant differences in recovery between the two concentrations were UV-360 (24.5%), EHS (19.5%), and OC (11.7%). All other compounds showed differences of less than 10%, with OD-PABA, OMC, and BP-3 being the only ones that exhibited almost identical recoveries at both concentration levels, with differences of less than 5%. The method's repeatability (intra-day precision) was evaluated using six replicates, resulting in RSD ranging from 3.19 to 20.61%.

The recovery efficiencies obtained for the target compounds in the zooplankton matrix were lower than those reported in previous studies using the same extraction methods on other sample matrices. For instance, Bachelot et al. (2012) and Gomez et al. (2012) reported recovery efficiencies above 85% in mussels. However, these values were achieved using larger sample quantities (3 g) and longer extraction processes at higher temperatures. Hence, the analytes were detected and quantified by GC-MS/MS, but only for three compounds: OMC, OC, and OD-PABA. Similarly, Cadena-Aizaga et al. (2022) reported recovery values ranging from 31 to 94% for oUVFs in primary producers. The wide variability observed in the present study, as well as in previous research (Cadena-Aizaga et al., 2022), may be attributed to the diverse chemical structures and physicochemical properties of the target compounds. Differences in polarity, functional groups, and molecular weight lead to distinct extraction behaviours, making the optimization process complex (Nitulescu et al., 2023). Taken together, these findings support the interpretation that the relatively low recovery efficiencies observed could be linked to the matrix effect due to the complexity of the zooplankton matrix (Sørensen et al., 2023). This variability can be observed in the matrix effects results, where 4-MBC and OD-PABA

shows the lowest matrix effects (96.46 and 103.1, respectively). HMS, DTS, OC, BMDBM, IMC and OMC showed noticeable ion suppression (in the range 89.37-94.13) while UV-360 and EHS showed ion enhancement (119.8-105.5) (Table II. 2). Zooplankton is typically composed of multiple species from various taxa, including gelatinous specimens, such as jellyfish, crustaceans, molluscs, and fish larvae, among others, with a constantly shifting community composition (Kléparski et al., 2021; Bucklin et al., 2021, 2022). Each group exhibits distinct accumulation capacities influenced by lipid content, feeding behaviour, and habitat (Sørensen et al., 2023). This biodiversity could contribute to variability in analyte extraction and quantification, potentially influencing residual signals and, consequently, the MLOD and MLOQ, due to the different nature and composition of the various species. For example, the high lipophilicity of certain compounds may lead to preferential accumulation in lipid-rich species within the zooplankton assemblage, such as copepods (Connelly et al., 2012). Moreover, zooplankton have been collected in subtropical areas, mainly consisting of omnivorous species that present smaller lipid reserves (Lee et al., 2006). Considering the lipophilic behaviour of the target compounds, low quantities of lipid content in the matrix could affect the observed recovery rates (Nieddu et al., 2024).

Furthermore, the methodology used for zooplankton collection is similar to that applied for microplastics (MPs). Previous studies have already reported a higher abundance of MPs compared to plankton in trawls from the same region (Sambolino et al., 2022). Given the well-documented ability of MPs to absorb and transport hydrophobic chemical compounds, including those targeted in this study, it is highly probable that the presence of MPs in zooplankton samples contributed to matrix interferences (Pacheco-Juárez et al., 2025). This, in turn, may have amplified the matrix effect and influenced the recovery efficiencies obtained.

3.3 Greenness of the developed methodology

To evaluate the preparation greenness of the proposed MAE-UHPLC-MS/MS method, AGREEprep was implemented. It is a metric tool based on ten categories of impact that are recalculated to a 0-1 scale sub-score, assigning them different weights according to the criteria's importance (Wojnowski et al., 2022). The choice and use of solvents, materials, and reagents, as well as factors such as waste generation, energy consumption, sample size, and throughput, are evaluated. The criteria with better results were the "size economy" of the sample (smaller sample sizes should be favoured, provided sample representativeness is assured) and sample throughput (the overall duration of the sample preparation stage). The lowest scoring criteria (0.00) were related to the sample preparation site, which could not be online or *in situ*, and the number of distinct hazards of chemical (threats indicated in *pg* labelling used chemicals) and physical nature. Despite these unfavourable criteria, the final mark obtained for the sustainability of the proposed method was 0.31 (Fig. II. 5). To the authors' knowledge, no studies to date have evaluated the greenness of methodologies that combine MAE extraction and UHPLC-MS/MS analysis in biota matrices. However, previous methods developed for the determination of oUVFs in cosmetic products have reported similar, or even lower, greenness scores (the highest reported being 0.41). These lower scores are mainly associated with the complexity of the matrices, as well as the use of organic solvents and high energy consumption. Improvements have been demonstrated when micro-extraction techniques are employed, as reported by Wejnerowska and Narloch (2023). Detailed scores obtained for each criterion are shown in the Supplementary Material (Fig. II. SM5).

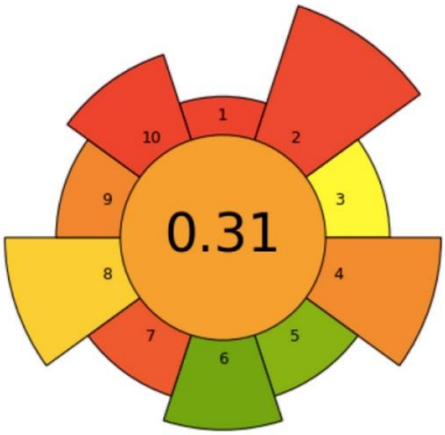

Fig. II. 5. Overall AGREEprep assessment of the proposed method (center) and the ten involved criteria: (1) sample preparation placement; (2) hazardous materials; (3) sustainability, renewability and reusability of materials; (4) waste; (5) size economy of the sample; (6) sample throughput; (7) integration and automation; (8) energy use; (9) postsample preparation configuration for the analysis; (10) operator's safety. The length of each criterion represents weight (on the final score), and color depicts performance: Green: High greenness, Red: Low greenness, and Yellow/ Orange: Moderate greenness, more details in Fig. II. SM5.

3.4 Monitoring the presence of organic UVFs in the zooplankton matrix

The validated method was applied for the first time to 36 marine zooplankton samples, enabling the detection of six target compounds. The measured concentrations of each compound, along with sample characteristics, are provided in the Supplementary Material (Table II. SM1). It is important to note that, due to the relatively low recovery efficiencies obtained for the analytes, certain concentrations may fall below the MLOQ and therefore remain undetected.

The measured analytes were BP-3, DTS, EHS, HMS, OC, and OD-PABA (Table II. 3). HMS had the highest frequency of quantification (FQ) (52.8%), followed by OC, OD-PABA, and BP-3. OC presented the highest concentration, followed by BP-3, HMS, and OD-PABA (Table II. 3). The compounds DTS and EHS were found to be the least FO, in 8.33% and 5.56% of the samples, respectively, and presented the lowest quantified concentrations. BP-3, EHS, HMS, OC, and OD-PABA, at concentrations ranging from 4.2 to 8.9, 15.5 to 20.5, 3.3 to 25.5,

5.6 to 10.9, and 4.6 to 19.5 ng/g w.w. (wet weight), respectively, together with six additional oUVFs (some optimized in the present study), have previously been reported in aquatic zooplankton from urban river systems in China (Yang et al., 2020). Although concentrations observed in Madeira appear higher, the values reported by Yang et al. (2020) were expressed on a wet weight basis, which likely underestimates values compared to d.w. based on measurements. This difference may be particularly relevant considering that the Chinese samples were collected in areas with greater human influence (urban rivers). In addition, the Madeira concentrations were corrected for recovery efficiencies, which may slightly overestimate the values (Table II. 2; 3). Regardless of concentration, similar oUVF profiles were observed in both ecosystems, indicating a high release rate of these compounds and suggesting their widespread occurrence in aquatic environments. These results also imply that zooplankton at lower trophic levels are particularly susceptible to exposure and accumulation of organic contaminants, including oUVFs, and highlight the global presence and ecological impact of these compounds in aquatic and marine biota. Considering that zooplankton, together with phytoplankton, constitute the base of the aquatic trophic chain, the presence of CECs in these organisms must be considered. Previous studies have already demonstrated the trophic transfer potential of BP-3, OC, HMS, and OMC from plankton to higher trophic levels (Yang et al., 2020).

Table II. 3. Concentration range of the values detected, mean, median, and frequency of quantification (FQ) of the target compounds in zooplankton samples. All the values have been normalized according to the method of recovery.

Compounds	Range (ng/g d.w)	Mean (ng/g d.w)	Median (ng/g d.w)	FQ (%)
BP-3	101.3 - 658.5	336.5	289.4	19.44
DTS	93.76 - 193.2	134.5	116.4	8.33
EHS	38.16 - 51.31	44.73	44.7	5.56
HMS	9.503 - 350.4	117.7	51.8	52.78
OC	24.01 - 1029	249.7	72.6	41.67
OD-PABA	39.10 - 287.4	191.2	221.6	16.67

Relative to the presence of the different target compounds in the zooplankton samples, OC and HMS are characterised by high lipophilicity and low water solubility (Table II. SM1). Their widespread use and global regulatory approval could contribute to their ubiquitous environmental presence (Al-Jamal et al., 2014; Holt et al., 2020; Fivenson et al., 2021). OC has been reported in a wide range of marine organisms and geographic locations, including molluscs and mussels, with concentrations reaching up to 256 ng/g d.w., along the French, Portuguese, and Hong Kong coasts (Bachelot et al., 2012; Cunha et al., 2015; Sang et al., 2016). OC, OD-PABA, and BP-3 have also been detected in crustaceans collected in Norway, with concentrations up to 68.9 ng/g d.w. (Langford et al., 2015). In polar regions, clams have been found to contain BP-3 concentrations as high as 112 ng/g d.w., while sea urchins have contained up to 8.6 ng/g d.w. (Emnet et al., 2015). Furthermore, fish, cephalopods, and crustaceans collected in China exhibited total oUVFs concentrations ranging from 35.566 to 596.31 ng/g d.w. (Peng et al., 2015).

Their detection across diverse taxonomic groups indicates a broad environmental occurrence. Due to their physicochemical properties, some oUVFs have been described as potentially bioaccumulated, for example, OC (Gago-Ferrero et al., 2013; Peng et al., 2017).

Among the oUVFs detected in the zooplankton matrix, OD-PABA and BP-3 were found at comparatively lower concentrations (Table II. 3). Although OD-PABA is highly lipophilic, its reduced presence may be attributed to the progressive exclusion of PABA derivatives from sunscreen formulations due to their potential for causing photoallergic reactions (Waters et al., 2009; Sánchez Rodríguez et al., 2015). In contrast, BP-3 was detected at relatively high concentrations, despite its low $\log K_{ow}$, which indicates low lipophilicity and high-water solubility, properties that typically limit bioaccumulation (Cadena-Aizaga et al., 2022).

BP-3 is one of the most frequently detected UVFs in marine waters globally, with concentrations ranging from a few ng/L to mg/L in regions such as Spain, China, and the United States (Downs et al., 2016; Tsui et al., 2014; Vila et al., 2016). Specifically, in the Macaronesia region (*e.g.*, Canary Islands), BP-3 has been reported in various marine species, including cetaceans (5.920 ng/g w.w) (González-Bareiro et al., 2023) and fish, with concentrations ranging from 0.07 to 0.29 µg/g d.w. (Gimeno-Monforte et al., 2020). It has also been detected in seawater, with peak values reaching 46.6 ng/L (Rodríguez et al., 2015), suggesting its widespread distribution across different environmental compartments in this region. The detection of BP-3 in zooplankton may be due to its collection at the sea surface microlayer (SML), a zone known to accumulate high concentrations of organic contaminants. As the SML is in direct contact with the atmosphere and contains elevated levels of organic matter, it can enhance the sorption and retention of organic compounds, even those with lower lipophilicity such as BP-3 (Pintado-Herrera and Lara Martín, 2020). Moreover, the presence of BP-3 might be associated with co-formulated oUVFs such as HMS and EHS, which are commonly used

together in PCPs to improve formulation stability and enhance UV protection (Nieddu et al., 2024).

DTS was also detected at low concentrations, potentially due to its distinct physicochemical properties and limited use in commercial sunscreens. Despite its high lipophilicity ($logK_{ow}$ > 5), DTS appears to be less frequently included in sunscreen products (Jesus et al., 2022).

These findings appear consistent with those of Sang et al. (2016), who identified BP-3, OC, and OD-PABA as dominant oUVFs in marine organisms along the coasts of Norway, Portugal, and France.

The variations in the presence or absence of oUVFs can be linked to their environmental availability and persistence, which is based on their environmental half-lives. Although only a limited number of studies have investigated this aspect in detail, some values are available for the target compounds. Reported half-lives range from as short as 1.13 h for OMC to up to 30 h for 3-benzylidene camphor. Their susceptibility to degradation is strongly related to the structural class of each compound, as well as the concentration of organic matter present in the water column, which helps in the absorption of the organic chemicals (O'Malley et al., 2021).

4. Conclusions

This study presents the first methodology specifically designed for the detection and quantification of oUVFs in environmental zooplankton samples. Considering the zooplankton as the base of trophic webs is important for monitoring the concentrations and presence of oUVF in lower trophic levels to assess possible bioaccumulation and biomagnification, information that is still limited for these contaminants (Lozano et al., 2020).

An optimized method combining MAE with UHPLC-MS/MS was developed to detect and quantify eleven oUVFs in zooplankton matrices. Despite the challenges presented by these

complex biological matrices, such as low lipid content and high taxonomic diversity, the method was validated and demonstrated reliability, but low efficiency due to the complexity of the matrix.

Application of this method led to the identification of six target UVFs in zooplankton samples collected around Madeira Island (Portugal). Among these, OC and HMS were the most prevalent, based on concentration and FQ, respectively. In contrast, BP-3 was detected at relatively high levels despite its higher hydrophilicity, possibly due to the close association of zooplankton with surface seawater.

This finding highlights the need for standardized and improved methodology protocols for detecting and quantifying oUVF in environmental samples. It explores the gaps in the environmental behaviour of these compounds in marine ecosystems, including their potential for bioaccumulation and biomagnification. Overall, the results raise important questions about the presence of oUVF in marine ecosystems. Further studies are required to better understand the absorption and metabolic pathways of these contaminants, as well as to assess their potential risks within the marine food web.

Supplementary data

Supplementary data can be found online at the following URL: https://doi.org/10.1016/j.marpolbul.2025.119204 (APPENDIX. A)

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CHAPTER III


Photo by: Rodrigo Pires da Silva

The Invisible Impact of Tourism: Organic UV Filters in the Coastal Ecosystem of a Remote Atlantic Island

Íñiguez, E., Pires da Silva, R., Montesdeoca-Esponda, S., Dimou, E., Alves, F., Kaufmann, M., Dinis, A., and Cordeiro, N. (2025). The invisible impact of tourism: Organic UV filters in the coastal ecosystem of a remote Atlantic island. *Environmental Research,* 287, 123153. https://doi.org/10.1016/j.envres.2025.123153.

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

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, 292.67 ng/g d.w. in algae, 394.64 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.

Keywords: Anthropogenic pressure; emerging contaminants; organic ultraviolet filters; marine monitoring; Madeira.

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 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; Cheng et al., 2024; Grant et al., 2025). The quantity of

sunscreens introduced into marine environments in areas with high tourist 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 et al., 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. Materials 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 (5,158 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

– census 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 et al., 2019).

Samples were collected for one year (2023) across different trophic levels and environmental matrices (Table III. 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).

Table III. 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*	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			

Sample category	Species	Trophic level	Trophic guild	Samples per location		Samples per season		Total
Fish	Sea cucumber (*Holothuria sanctori*)	Primary consumer	Detritivore	FX	10	High	15	28
				LM	8	Low	13	
				DS	10			
	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			

Sample category	Species	Trophic level	Trophic guild	Samples per location		Samples per season		Total
	Blacktail comber (*Serranus atricauda*)	High-level consumer: Mesopredator	Macro-carnivore	Local market				5
Seawater	-	Environmental level	-	FX	6	High	9	18
				LM	6			
				DS	6	Low	9	
Sediments	-	Environmental level	-	FX	6	High	9	18
				LM	6			
				DS	6	Low	9	

* *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).

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. III. 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 5 specimens were bought in the local market) (Table III. 1).

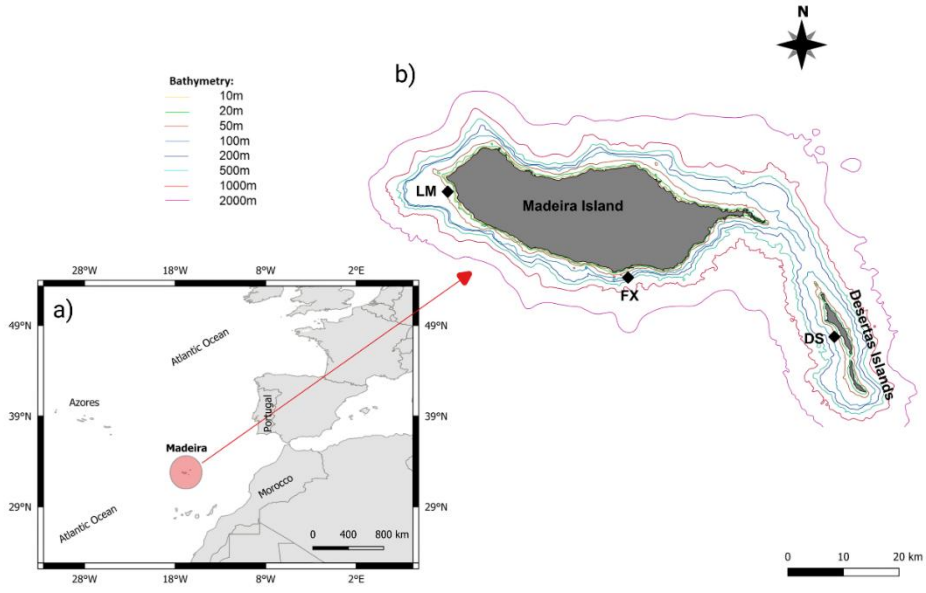

Fig. III. 1. (a) Location of the Madeira Archipelago in the Eastern North Atlantic; (b) Sampling sites and bathymetries around Madeira and Desertas Islands. LM: Lombada dos Marinheiros, FX: Funchal and DS: Deserta Grande.

2.2 Reagents and consumables

Eleven oUVF were investigated in the present study. Their characteristics are summarised in Table III. SM1. 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. III. 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 III. 1) (Dodds & Whiles, 2010). Accordingly, the red algae (*Asparagopsis taxiformis*) (Fig. III. 2b) were collected as a primary producer, while zooplankton samples represented primary consumers. The selected macroinvertebrates included the black sea urchin (*Arbacia lixula*) (Fig. III. 2c), which is a grazer, and the sea cucumber (*Holothuria sanctori*) (Fig. III. 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 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 3-8 m and sand sea cucumbers between 8-15 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.

Fig. III. 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.*

Zooplankton samples were collected at night, at least one hour 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 freezer-dried using a lyophilizer (Savant RT 400, Thermo Scientific) for 72h at -50 ºC. 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 ºC).

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. 2/2023 D; 1/2023 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 Perkin Elmer unit equipped with 16 Teflon-modified vessels (Madrid, Spain) and an Anton Paar multi-wave oven with 6 EVAP rotors and 6 MF100 vessels (Graz, Austria). For sediments: one gram 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., under review). SPE clean-up wasn't 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 the 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 ionisation (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 III. SM2.

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 III. SM3.

Recoveries were assessed by spiking BP-d_{10} (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 analysed 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, BMDBM, OD-PABA, OMC, and EHS, were detected at least once across the analysed matrices. Out of 191 total samples collected, 54 showed at least one of these compounds (Table III. SM4). 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. III. 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. III. 3).

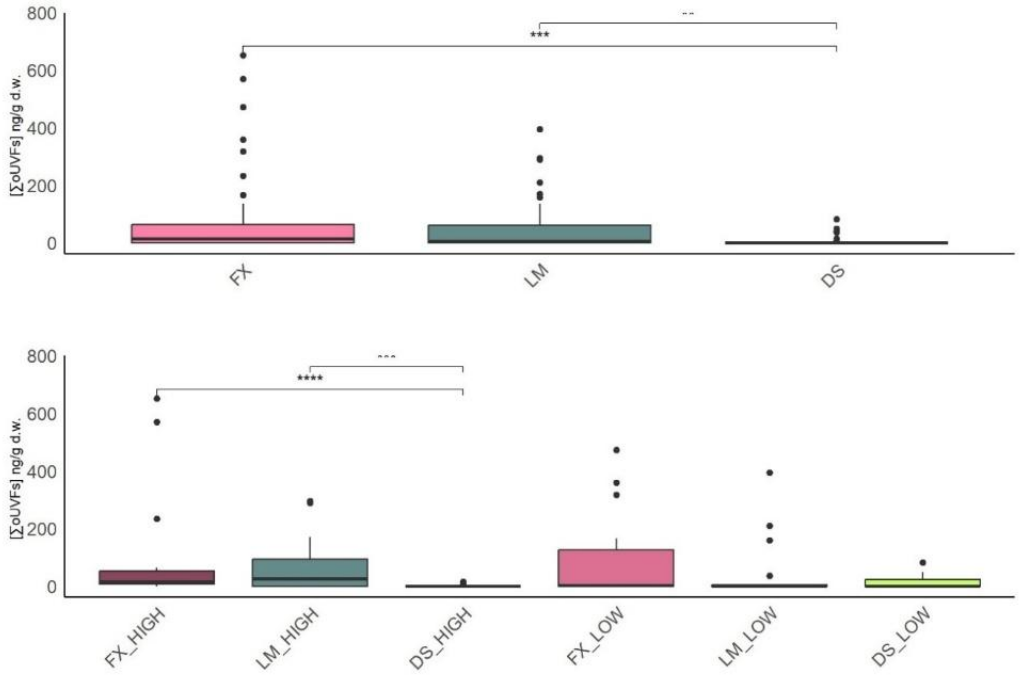

Fig. III. 3. Boxplots representing total oUVF concentrations (ΣoUVFs; ng/g d.w.) grouped by location (FX, LM, DS) and season within each location (HIGH = high season; LOW = low season). Boxes show median and interquartile range (IQR); points indicate outliers. Group differences were assessed with Kruskal-Wallis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

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. III. 4). No significant differences 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 BMDBM (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. III. 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 III. SM5) 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 III. SM6).

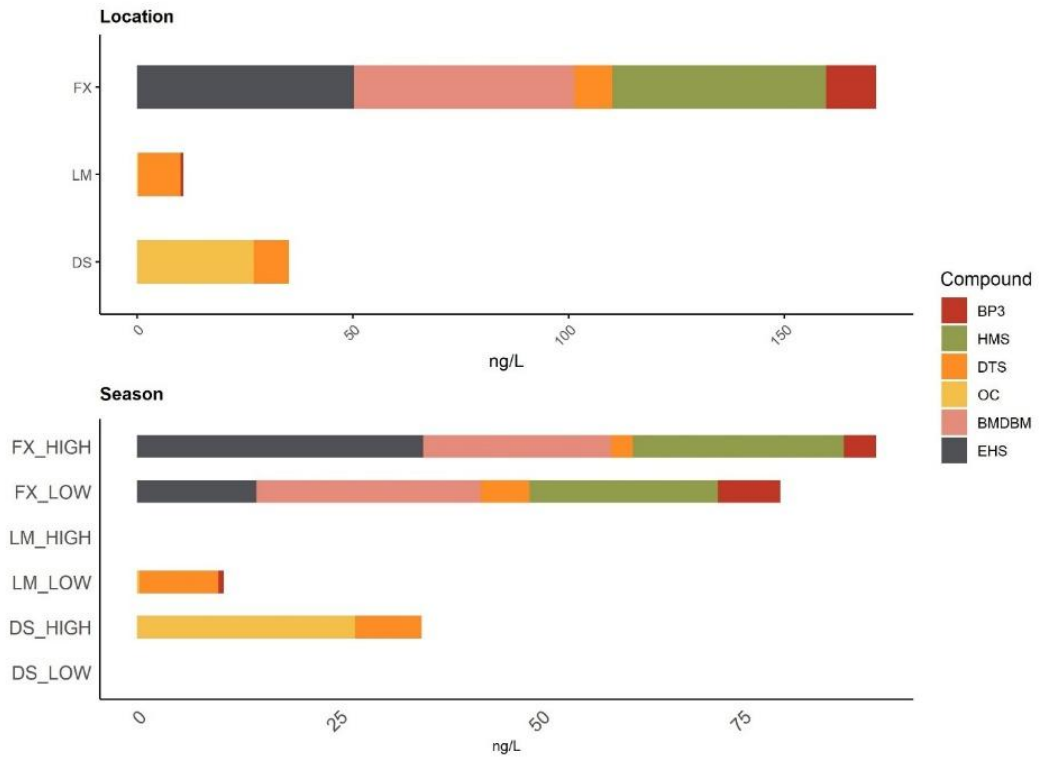

Fig. III. 4. Cumulative concentrations of organic UV filters (ΣoUVFs; ng/L) in seawater, grouped by location and season within each location. Values < MLOQ were settled as MLOD/2.

3.2. Presence and distribution of oUVF across different biota categories

Organisms were classified into predefined categories (Table III. 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 III. SM7).

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 III. SM7).

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. III. 5; Table III. SM8). 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 to 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 III. SM5). 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 ± 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.

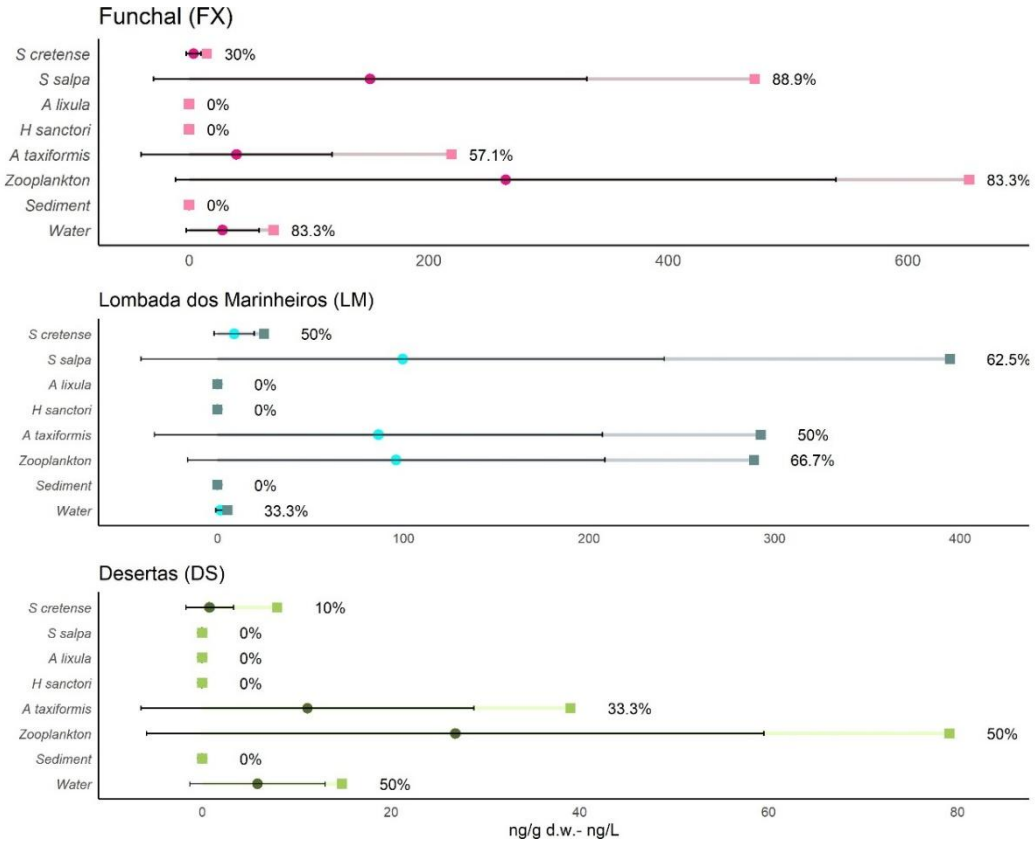

Fig. III. 5. Lollipop plots showing the total concentrations of oUVFs (∑oUVFs) per species across sampling locations (FX, LM, DS). Squares represent the maximum concentrations, while dots indicate the mean values with standard deviations (black lines). Numerical labels next to the bars represent the 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 under MLOQ as MLOD/2.

3.3 oUVF presence in biota

The oUVFs detected in biota matrices were HMS, OC, OMC, EHS and OD-PABA (Table III. 2; Fig. III. 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 III. 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. III. 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 III. SM6). Every individual concentration, as well as the characteristics of the different collected samples, are summarized in Table III. SM4. Every individual concentration, as well as the characteristics of the different collected samples, are summarized in Table III. SM4. Every individual concentration, as well as the characteristics of the different collected samples, are summarized in Table III. SM4.

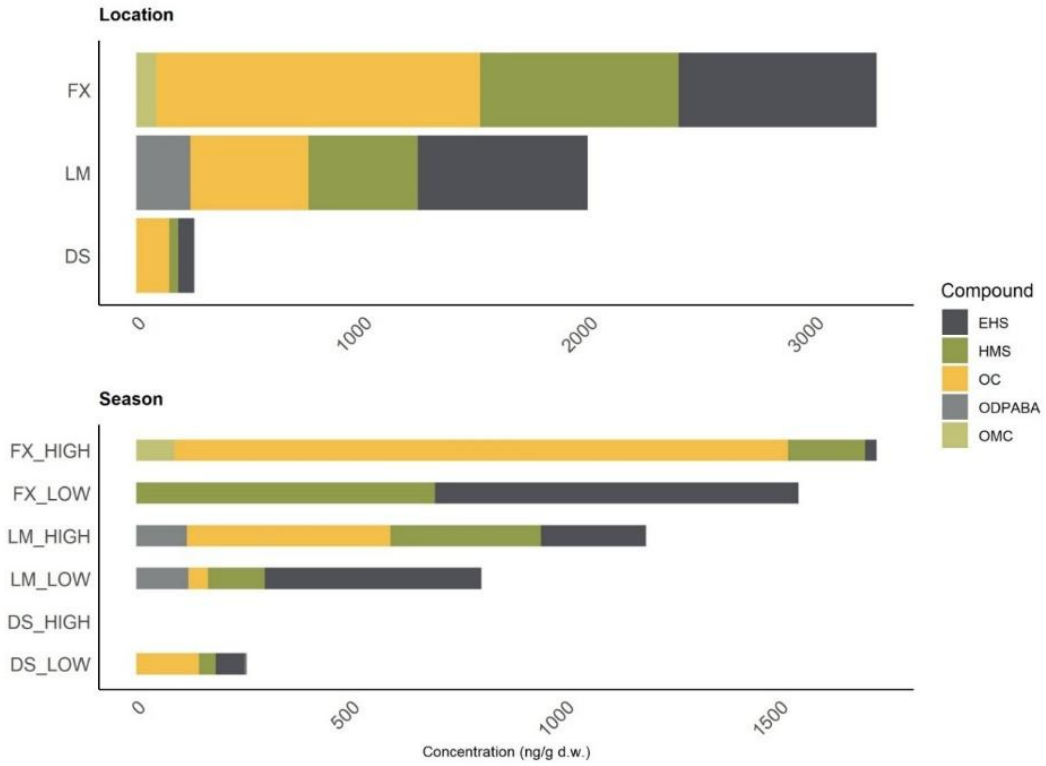

Fig. III. 6. Cumulative concentrations (ng/g d.w.) of the different oUVF detected in biota matrices (algae, zooplankton, and fishes) by location- Funchal (FX), Lombada dos Marinheiros (LM), and Desertas (DS) - and by season (HIGH and LOW). Considering the values under MLOQ as MLOD/2.

Table III. 1. 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	BP-3	HMS	DTS	OC	BMDBM	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.

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 and eddies (Caldeira et al., 2002; 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 Rodrigues 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 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 de Estatística da Madeira; 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 23 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 Mar, Planos de Inspeção, 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 Rodriguez 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; Cadena-Aizaga et al., 2022c). Specifically, in Gran Canaria, mean concentrations of BP-3, OC, HMS, and BMDBM 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, BMDBM, 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). In addition, certain oUVFs, such as OC, are commonly formulated in combination with other compounds, like BMDBM, to enhance photostability, water resistance, and SPF. This is due to BMDBM's high susceptibility to degradation, often resulting in its co-occurrence with OC (Sánchez Rodriguez et al., 2015; da Silva et al., 2022). By this, BMDBM 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 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 to 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 (Cruz-Díaz 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 et al., 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.

Supplementary data

Supplementary data can be found online at the following URL: https://doi.org/10.1016/j.envres.2025.123153 (APPENDIX B.)

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CHAPTER IV

Organic ultraviolet filters across the surface, pelagic, and bathypelagic compartments of an oceanic island system

Íñiguez, E., Montesdeoca-Esponda, S., Alves, R., Ideia, P., Cordeiro, K., Dinis, A., Ferrera-Sosa, Z., & Kaufmann, M. (2026). Organic ultraviolet filters across the surface, pelagic, and bathypelagic compartments of an oceanic island system. *Environmental Science and Pollution Research*, submitted.

NOTE

Following the rejection of the manuscript in the *Environmental Science and Technology* journal and the reviewers' comments received shortly after the submission of this thesis, the corresponding chapter has been revised. The modifications include changes to the title from "*Organic Ultraviolet Filters from Surface Seawater to Bathypelagic species in an Oceanic Island System*" to "*Organic ultraviolet filters across the surface, pelagic, and bathypelagic compartments of an oceanic island system*" and minor adjustments to the overall focus and discussion to address the reviewers' suggestions and improve the manuscript's suitability for publication.

These revisions do not affect the underlying data, statistical analyses, or the scientific rationale and hypotheses presented in the chapter. Consequently, the objectives, results, and conclusions of the thesis remain unchanged with respect to the previous version of the manuscript.

CHAPTER IV: Organic ultraviolet filters across the surface, pelagic, and bathypelagic compartments of an oceanic island system

Abstract

Organic ultraviolet filters (oUVFs), mainly used in personal care products, including sunscreens, are released into the marine environment through human activities. As a result, research efforts have been focused largely on coastal areas, while their occurrence in offshore and deep-sea environments remains poorly understood. This study investigated the presence and distribution of 11 oUVFs in offshore and deep-sea ecosystems by analyzing water, sediment, and organisms across different habitats and trophic levels across the water column. Surface waters showed concentrations within the range reported for nearby coastal settings, whereas sediments contained only residual oUVF concentrations. Regarding biota, pelagic species inhabiting the water column, such as *Trachurus picturatus* and *Scomber colias*, showed no detectable target oUVFs, and *Katsuwonus pelamis* exhibited low mean ΣoUVF concentrations (22.99 ± 26.28 ng/g d.w.). However, 90% of the samples showed detectable oUVFs concentrations. The highest mean ΣoUVF concentrations were observed in the bathypelagic species *Aphanopus carbo* and in surface-collected zooplankton (141.5 ± 105.6 and 114.4 ± 186.1 ng/g d.w., respectively). Overall, oUVFs appear to follow a distribution pattern driven by organic matter accumulation, with higher concentrations in surface waters and in bathypelagic compartments. Octocrylene (OC), butyl methoxydibenzoylmethane (BMDBM), and homosalate (HMS) were among the most frequently detected compounds, which may be consistent with broader environmental occurrence, higher persistence, and/or matrix-specific retention. The detection of the regulated compound 4-methylbenzylidene camphor (4-MBC) in *A. carbo*. These findings support the need to move beyond dissolved-

water monitoring and to include particulate fractions, transformation products, microplastics, and tissue-specific analyses in future assessments of oUVFs in offshore marine systems.

Keywords: Organic contaminants, commercial fish species, monitoring, water-column compartments, zooplankton.

1. Introduction

The Industrial Revolution is often cited as a turning point for large-scale pollution, harming human and environmental health. For example, the intensification of agricultural production has led to the widespread use of pesticides and fertilizers, some of which have subsequently been banned due to their detrimental impacts (Saxena et al., 2025). Furthermore, the significant rise in plastic consumption has led to widespread contamination of terrestrial and marine ecosystems, leaving no area on Earth untouched by plastics and their additives (Jaikumar et al., 2025). Although growing concern over these issues has led to the establishment of legislation addressing many contaminants, some of which are classified as Persistent Organic Pollutants (POPs), continuous monitoring and further research remain needed (Saxena et al., 2025). At the same time, new chemicals continue to be developed and incorporated into industrial products. However, their long-term impacts, environmental release, and ecological consequences remain largely unknown. Many of these compounds are considered Contaminants of Emerging Concern (CECs), including pharmaceuticals, hormones, and personal care products (PCPs) (Nilsen et al., 2019; Tang et al., 2019).

Some PCPs, as well as other widely used products such as varnishes, paints, plastics, and food packaging, contain organic ultraviolet filters (oUVFs) and inorganic ultraviolet filters (iUVFs) in their formulations, some of them already categorized as CECs (Couteau et al., 2024). These chemical agents protect against ultraviolet radiation by absorbing or reflecting

harmful rays, thereby preventing degradation, sunburn, and skin disorders (Shetty et al., 2023). In the European Union, UVFs authorised for cosmetic use are listed in Annex VI to Regulation (EC) No 1223/2009, as amended, including by Commission Regulation (EU) 2022/1176, which updated the permitted uses and restrictions for some substances (Caloni et al., 2021).

oUVFs are generally characterised by high lipophilicity, commonly expressed as the octanol-water partition coefficient (logKow), and low water solubility, although these properties vary among analytes (Castro et al., 2018; Law et al., 2021). Such characteristics can contribute to relatively long environmental half-lives. Different oUVF families contain distinct aromatic rings and hydrophobic groups, which influence their solubility, lipophilicity, and environmental behaviour. In commercial formulations, combinations of oUVFs are often used to improve stability, durability, and sun protection factor (SPF) (Woźnica and Starosta, 2022).

The release of oUVFs into marine environments is primarily linked to recreational activities in coastal areas. Additional inputs may arise from surface runoff and the incomplete removal of these compounds in wastewater treatment plants (WWTPs). Once in the marine environment, their distribution may be influenced by physical transport processes such as currents, eddies, winds, and tides, which can redistribute contaminated particles and floating plastic debris, including microplastics (MPs). Because MPs can adsorb and transport organic chemicals, they may also contribute to the environmental redistribution of oUVFs (Grant et al., 2025; Pacheco-Juárez et al., 2025).

Research conducted over the last decades has confirmed the ubiquitous presence of oUVFs in coastal ecosystems, as evidenced by their concentrations in seawater and sediment worldwide (Tsui et al., 2014; Cadena-Aizaga et al., 2020) and marine taxa, including invertebrates, fish, marine mammals (Gago-Ferrero et al., 2013; Cadena-Aizaga et al., 2020: Iñiguez et al., 2025a), and even humans (Giokas et al., 2007; Huang et al., 2021). Laboratory studies have described adverse effects on marine organisms, highlighting the potential role of

oUVFs as endocrine disruptors that affect reproduction, development, and immune function (Carve et al., 2021; Carvalhais et al., 2025; Grant et al., 2025). In situ observations have further reported effects such as coral bleaching (Tsui et al., 2017; Mitchelmore et al., 2021).

Additionally, chemical compounds are often transformed either through degradation during environmental exposure or via metabolism after ingestion or absorption by organisms (Lozano et al., 2020). Consequently, parent compounds are converted into transformation products, which are frequently reported to be more soluble, more toxic, and more persistent than the original compound itself (Lu et al., 2023).

Most studies on oUVFs have focused on coastal areas, where recreational activities, wastewater discharges, runoff, and tourism-related pressure are expected to generate higher inputs of sunscreen-derived compounds (Caloni et al., 2021; Casas-Beltrán et al., 2021; Milinkovitch et al., 2024). In contrast, only a few studies have investigated the occurrence and behavior of oUVFs in open waters or deep-sea habitats, which are often described as sinks for POPs (Lyu et al., 2022; Pinheiro et al., 2023). In the offshore and deep-water context, Combi et al. (2016) reported ethylhexyl methoxycinnamate (OMC), octocrylene (OC), and benzophenone-3 (BP-3) in surface sediments from the Adriatic Sea, with distribution patterns reflecting inputs from surrounding coastal areas. More recently, Moualek et al. (2024) identified BP-3 in a commercially important deep-water species, the redfish (*Sebastes mentella*), which inhabits depths of approximately 500 m. In pelagic habitats, Pintado-Herrera et al. (2024) quantified six different oUVFs in liver and muscle tissues of Atlantic bluefin tuna (*Thunnus thynnus*), Atlantic bonito (*Sarda sarda*), and skipjack tuna (*Katsuwonus pelamis*), collected from the Gulf of Cádiz, reporting a maximum concentration of 2931 ng/g d.w. of total oUVFs. Other studies have also reported oUVFs or related UV-absorbing compounds in commercial fish species, including *Scomber colias (*Atlantic chub mackerel), *Scomber*

scombrus (Atlantic mackerel), and *Sarda sarda* (Atlantic bonito) (Gimeno-Monforte et al., 2020; Barbosa et al., 2018).

Despite these studies, information remains fragmented, which raises several research questions: 1) What happens beyond the coast? 2) Do these analytes persist in the marine environment? 3) How are they distributed across offshore matrices and habitats, including bathypelagic biota?

Addressing this gap is crucial, as they highlight the need for monitoring studies to better assess the risks and potential impacts of organic compounds, including oUVFs. Previous studies suggest that oUVFs and other hydrophobic contaminants may occur in offshore or deeper compartments, although the specific mechanisms controlling their redistribution, transformation, and biological occurrence remain poorly resolved (Combi et al., 2016; Pintado-Herrera et al., 2020; Avellan et al., 2022).

Based on this context, the present study aimed to assess the occurrence and compartment-specific distribution of 11 oUVFs in an offshore oceanic island system. Seawater, sediment, surface-collected zooplankton, and fish species occupying different water-column habitats and trophic levels were analysed, including small pelagic and benthopelagic species, a pelagic predator, and the bathypelagic species *Aphanopus carbo* (black scabbardfish). By combining matrix-level occurrence data, compound-specific profiles, and ecological information on the analysed species, this study provides an integrated interpretation of oUVF distribution patterns across the surface-associated, pelagic, and bathypelagic compartments. The study does not aim to demonstrate specific transport mechanisms, but rather to identify occurrence patterns and plausible exposure pathways that should be tested in future targeted studies.

2. Materials and methods

2.1 Study area

The Madeira Archipelago (Portugal) represents an exceptional natural laboratory for the study of pelagic and deep-sea ecosystems, owing to the steep bathymetric gradients near the coast and the presence of submarine canyons (Spalding et al., 2007; Kim et al., 2008). In addition, geological structures and physical oceanographic processes, such as upwelling and mesoscale eddies, enhance local productivity and support the occurrence of deep-diving predators, highlighting the ecological importance and dynamic nature of these offshore environments (Fernandez et al., 2021). Moreover, the Madeira Archipelago lies within an Exclusive Economic Zone (EEZ) where fisheries are primarily focused on pelagic and bathypelagic species, representing one of the world's longest-standing examples of meso- and bathypelagic fisheries exploitation. The main fishing effort targets skipjack tuna, bigeye tuna (*Thunnus obesus*), and two species of black scabbardfish *A. carbo* (Biscoito et al., 2011) and *Aphanopus intermedius*, which are not easily distinguished; this leads to about 20% of captures of black scabbardfish in Madeira being *A. intermedius* (Delgado et al., 2018). In addition, smaller-scale fisheries exploit small pelagic species, such as blue jack mackerel (*Trachurus picturatus*) and Atlantic chub mackerel (*Scomber colias*). These resources are not only pivotal to the regional economy but also hold strong cultural importance, constituting an integral part of the island's gastronomy (Hermida and Costa, 2020).

2.2 Chemicals

Eleven oUVFs (Table IV. 1), 4-methylbenzylidene camphor (4-MBC), benzophenone-3 (BP-3), octocrylene (OC), butyl methoxydibenzoylmethane (BMDBM), isoamyl p-methoxycinnamate (IMC), homosalate (HMS), ethylhexyl dimethyl PABA (OD-PABA),

ethylhexyl salicylate (EHS), ethylhexyl methoxycinnamate (OMC), drometrizole trisiloxane (DTS), methylene bis-benzotriazolyl tetramethylbutylphenol (UV-360), and the internal standard (IS) deuterated benzophenone (BP-d_{10}, purity ≥99%) were obtained from Sigma-Aldrich (Madrid, Spain). Stock solutions (250 mg/L) were prepared in acetone (ACE) and stored in amber glass at –20 °C. Working solutions were prepared daily in methanol (MeOH). LC-grade solvents, including water, formic acid, MeOH, 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 syringe filters (0.2 µm) were obtained from Macherey-Nagel (Düren, Germany).

Table IV. 1. Physicochemical properties of the selected oUVFs (Íñiguez et al., 2025a).

Chemical family	**INCI name**	**Abbreviation**	**CAS N°**	**LogK$_{ow}$**	**Solubility (g/L)**
Benzophenones	Benzophenone-3	BP-3	131-57-7	3.79	0.21
Salicylates	Ethylhexyl dimethyl PABA	OD-PABA	21245-02-3	6.15	$2.1x10^{-3}$
	Homosalate	HMS	118-56-9	6.16	0.02
	Ethylhexyl salicylate	EHS	118-60-5	5.97	0.028
Cinnamates	Ethylhexyl methoxycinnamate	OMC	5466-77-3	5.8	0.15
	Isoamyl p-methoxycinnamate	IMC	71617-10-2	4.33	0.06
Camphor derivatives	4-methylbenzylidene camphor	4-MBC	36861-47-9	3.83	0.014
Benzotriazoles	Drometrizole trisiloxane	DTS	155633-54-8	10.82	$1.3x10^{-5}$
	Methylene bis-benzotriazolyl tetramethylbutylphenol	UV-360	103597-45-1	12.46	$3x10^{-8}$
Dibenzoylmethane derivatives	Butyl methoxydibenzoylmethane	BMDBM	70356-09-1	4.51	0.037
Crylenes	Octocrylene	OC	6197-30-4	6.88	$2x10^{-4}$

2.3 Sample collection and sample preparation

Sediments, seawater, and zooplankton matrices (n=18 each) were collected around two sites on the south coast of Madeira Island (Lombada dos Marinheiros and Funchal) and one on the west coast of Deserta Grande, a marine protected area (MPA), over the course of one year (2023), with a total of six sampling days. Three samples of each matrix were collected per sampling day. Seawater and zooplankton samples were collected at the surface between the 1000 and 2000 m bathymetric lines (Fig. IV. 1). The 1000-2000 m bathymetric interval refers to the offshore position of the sampling transects and not to the depth of seawater collection; all seawater samples were collected from the surface layer.

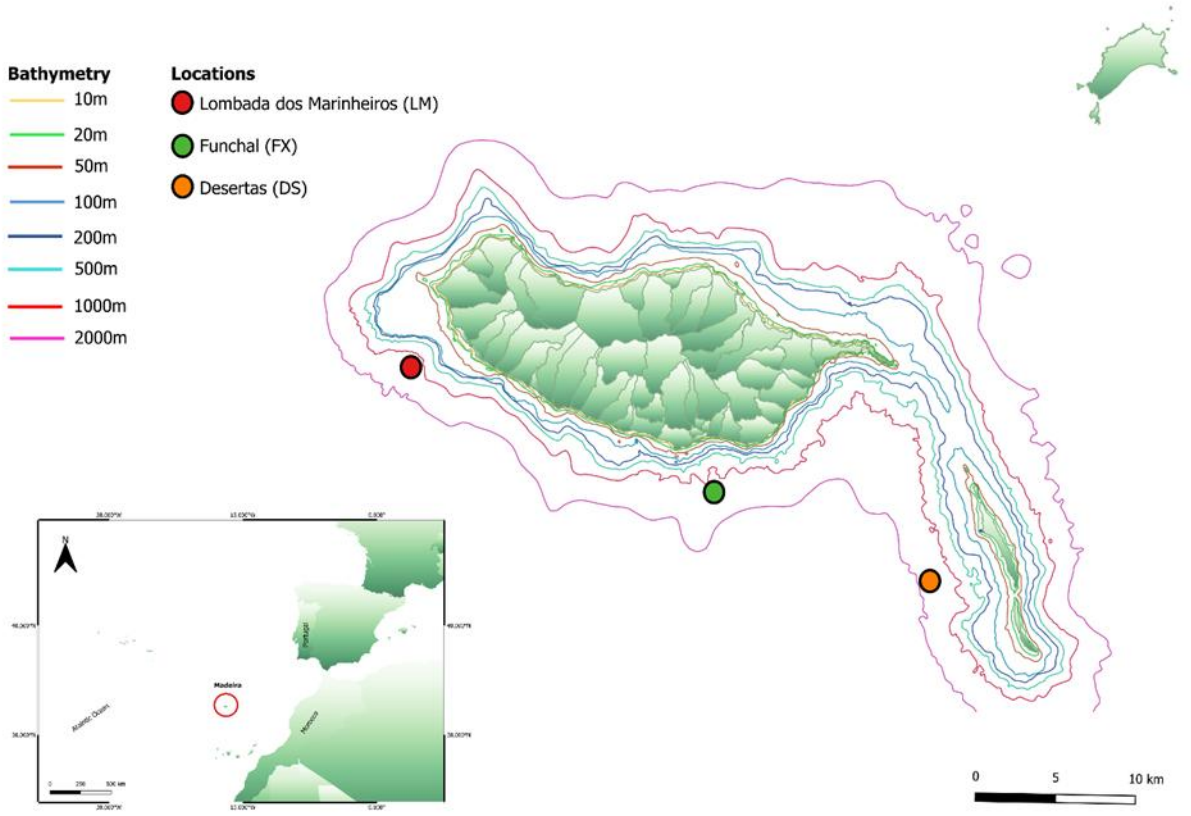

Fig. IV. 1. Location of the Madeira Archipelago in the eastern North Atlantic and the Madeira Archipelago, composed of Madeira, the main island, the Desertas Islands, and Porto Santo. The dots indicate the locations of zooplankton and water sampling.

Seawater samples were collected in three 2.5 L amber glass bottles (Teflon-lined caps) during the morning each sampling day, pre-rinsed three times with seawater. Samples were collected from a depth of *ca.* 10 cm below the surface. In the laboratory, each seawater sample was acidified to pH 3 and filtered through 0.22 µm membrane filters to remove particulate organic material.

Sediment samples were collected using a Van Veen SG-400 grab (5 L capacity; 400 cm^2 sampling area). Due to the difficulty of manually retrieving the grab, sediment samples were collected at 80 m depth, closer to the coast of the three sampling locations. On each sampling day, the grab was deployed once, yielding three subsamples that were stored in small amber glass jars. Samples were frozen at –20 °C and later freeze-dried, ground, and sieved to obtain a powder of 180 µm.

Zooplankton samples were collected at the surface using a Manta trawl with a 70 × 40 cm opening and 200 µm mesh size. All sampling was conducted at night, at least 1 h after sunset, to guarantee a higher concentration of biomass, taking advantage of the migration of the mesopelagic layer toward the surface (Andersen et al., 1998). Hence, enough material for further analyses. Each transect lasted 20 min at a speed of 1.5 - 2 knots. After each transect, the net was rinsed with seawater over a 200 µm sieve, followed by distilled water to remove residual salts, and the samples were transferred to amber glass jars. Samples were kept in a cold box during transport to the laboratory, where they were stored at –20 °C. Subsequently, samples were freeze-dried, ground, and sieved to 180 µm. Zooplankton samples were analysed as bulk community samples rather than being separated into taxonomic groups because the main objective was to characterise the integrated oUVF signal of the surface-collected zooplankton compartment and to obtain enough biomass for multi-residue chemical analysis.

Fish species were selected based on their trophic level and position in the water column. Pelagic-neritic species (Atlantic chub mackerel) and benthopelagic species (blue jack

mackerel) were purchased from the local fish market, while pelagic skipjack tuna and bathypelagic black scabbardfish were provided by the Fisheries Regional Directorate (DRP). Biometric measurements were taken before freezing. For Atlantic chub mackerel and blue jack mackerel, entire individuals were cut into small pieces and frozen. Once completely frozen, samples were freeze-dried, ground, and homogenized to obtain a fine powder (≤ 180 µm). Due to the big size of the specimens, skipjack tuna and black scabbardfish were dissected, and only muscle tissue was used, following the same freeze-drying, grinding, and homogenization procedure as described for the other species.

All the characteristics of the different samples collected are summarised in Table. IV. SM1. The position in the water columns as well as the trophic level have been described according to FishBase (Froese and Pauly, 2025).

2.4 Extraction procedures

The target compounds in seawater samples were extracted using Solid-Phase Extraction (SPE). The C18 cartridges were conditioned with 5 mL of methanol, followed by 5 mL of Milli-Q water. Subsequently, 700 mL of each seawater sample (in triplicate) was passed through each cartridge, which was then washed with 5 mL of Milli-Q water. The cartridges were dried under vacuum for 1 min and stored at –20 °C until elution, as described by Cadena-Aizaga et al. (2022). Elution was carried out with 5 mL of MeOH: ACN (1:1, v/v), and 1 mL of the extract was transferred to a chromatographic vial.

All the solid matrices, sediments, zooplankton, and the different fish species were exposed to Microwave-assisted extraction (MAE). Two different microwaves were used: a Perkin Elmer unit equipped with 16 Teflon-modified vessels (Madrid, Spain) and an Anton Paar multi-wave

oven with 6 EVAP rotors and 6 MF100 vessels (Graz, Austria). The different methodologies are summarized in Table IV. 2.

Table IV. 2. Parameters of the MAE-based extraction procedures used for the different matrices.

Matrix	Quantity of sample (mg d.w.)	Solvent	Solvent volume (mL)	Temperature (ºC)/ power (W)	Extraction time (min)	Bibliography
Sediments	1000	ACN	2	300	3	Montesdeoca-Esponda et al. 2013
Zooplankton	50	HEX	7	68	2	Íñiguez et al. 2026
Fishes	100	DCM	7 (evaporated and reconstituted in ACN 1mL)	60	2 cycles of 10 min	Gimeno-Monforte et al. 2020

2.5 UHPLC-MS/MS

To determine the eleven oUVF, 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 was used. Methanol (MeOH), LC–MS grade, containing 0.1% (v/v) formic acid (A), and ultrapure water, LC–MS grade, containing 0.1% (v/v) formic acid (B), were used as mobile phases.

The chromatographic separation was performed using a gradient elution at a flow rate of 0.3 mL/min. The mobile phase composition was initially maintained at 75% A and, 25% B for 3 min, subsequently increased linearly to 100% A at 5 min, and then returned to the initial conditions (75% A and 25% B) for 2 min to allow column re-equilibration. The injection volume was 10 µL.

Positive electrospray ionization tandem mass spectrometry (ESI-MS/MS) was conducted under the following conditions: capillary voltage, 3 kV; cone voltage, 15 V; source temperature, 120 °C; desolvation temperature, 450 °C. Nitrogen (≥ 99% purity) was employed as the desolvation gas at a flow rate of 500 L/h, while argon (≥ 99% purity) served as the collision gas. Compound-specific MS/MS parameters are provided in Table IV. SM2.

Calibration curves were established using eight concentration levels spanning 1–500 ng/mL. All target analytes exhibited good linearity ($R^2 > 0.99$). Instrumental limits of detection (ILODs) and quantification (ILOQs) were determined from signal-to-noise (S/N) ratios of analyte peaks, using thresholds of S/N = 3 for ILOD and S/N = 10 for ILOQ. The methodological limits of detection (MLODs) and quantification (MLOQs), reported as analyte per unit mass or volume of sample, were calculated by combining the ILOD/ILOQ with the

sample mass or volume and the corresponding (pre-)concentration factors. Instrumental and methodological LOD and LOQ values are summarised in the Table IV. SM3.

BP-d_{10} (200 ng/mL) was added to all extracts and calibration solutions immediately before instrumental analysis. In the present study, BP-d_{10} was used as an instrumental internal standard to monitor signal stability, retention time consistency, and injection-to-injection variability throughout the analytical sequence, following its previous application as a single internal standard in multiresidue LC-MS/MS workflows for chemically diverse aromatic UV-related additives (Van Den Houwe et al., 2014). Because a single internal standard cannot fully compensate for analyte-specific extraction behaviour across heterogeneous matrices, BP-d_{10} was not considered a surrogate for matrix-specific recovery correction. Therefore, the quantitative results reported here should be interpreted primarily as robust evidence of occurrence and broad concentration patterns rather than as fully recovery-corrected absolute concentrations across all matrices. Each sample was analysed in triplicate and only results with relative standard deviations (RSD) ≤ 30% among replicate injections were considered valid for interpretation. To minimise external contamination and analyte degradation, all containers were amber glassware, thoroughly pre-cleaned and rinsed with distilled water, followed by HPLC-grade ethanol before use. Laboratory personnel wore nitrile gloves throughout the analytical procedure. Procedural blanks analyzed during the determination and quantification process showed analyte levels below the LOD.

2.6 Total lipid content extraction

Total lipids (TL) were extracted from freeze-dried fish matrix powder (~150 mg) following a modification of the method of Folch et al. (1957). Briefly, 150 mg of dried sample was homogenized with 10 mL of chloroform/methanol (2:1, v/v) using a magnetic stir bar. The

homogenate was filtered to remove suspended organic debris, and 2.5 mL of KCl solution (0.88% w/v) was subsequently added. Samples were centrifuged at 7,000 rpm for 5 min, resulting in two distinct phases. The lower organic phase was carefully transferred into a pre-weighed tube and evaporated under vacuum. After complete drying, the tube was weighed again. The difference in weight corresponded to the total lipid content (mg). Lipid content was expressed as a percentage of the initial sample weight using the following equation:

$$\% \text{ TL} = \left(\frac{\text{Lipid weight (mg)}}{\text{Sample weight (mg)}} \right) \text{ x } 100$$

Eq. IV. 1

2.7 Statistical analyses

Descriptive statistics, including mean, standard deviation, and frequency of occurrence (FO), were calculated for all matrices. Individual sample-level results are provided in Table IV. SM4. FO was defined as the percentage of samples in which each target oUVF was quantified and detected at concentrations ≥MLOD, including values between MLOD and MLOQ, which were reported as <MLOQ. ΣoUVFs were calculated for each sample using only quantified values (>MLOQ), and matrix/species-level means were calculated considering all samples within each group, with samples without quantified oUVFs contributing zero to the group burden.

For statistical testing, and to minimize potential biases from extreme variability, values below the MLOD or MLOQ were replaced with a random number between 0 and the respective MLOD or MLOQ for each matrix following the approach of Remili et al. (2025) to handle censored observations. Data were $\log_{10}$-transformed before testing. Normality and homogeneity of variance were assessed using the Kolmogorov–Smirnov and Levene's tests,

respectively. Differences in ΣoUVF concentrations among biota matrices were evaluated using the Kruskal–Wallis test, followed by pairwise Wilcoxon tests with Bonferroni correction. Statistical significance was set at $p < 0.05$. Boxplots were used to visualise the distribution of ΣoUVF concentrations among biota matrices.

Spearman's rank correlation was applied to explore associations between ΣoUVF concentrations and fish biometric variables (length, weight, and total lipid content) within species for which quantifiable oUVF concentrations were available. Results were expressed as Spearman's rho and corresponding p-values. Spearman correlation results are provided in Table IV. SM5, including the matrix/species, variables tested, Spearman's rho, *p*-value, and sample size (n). Additional descriptive plots, including cumulative bar plots, were generated from raw data to summarise compound occurrence and composition across matrices. All statistical analyses and visualisations were performed in R (R Core Team, 2024).

3. Results and Discussion

3.1 Occurrence and distinction between detection and quantification

Out of the 11 target oUVFs, 9 compounds, 4-MBC, BP-3, HMS, DTS, OC, BMDBM, OD-PABA, OMC, and EHS, were quantified in at least one of the analyzed matrices. Considering all 99 samples, 45 samples (45.5%) contained at least one detected oUVF at concentrations ≥MLOD (Fig. IV. 2). Values between MLOD and MLOQ were considered detections but were not included in ΣoUVF calculations.

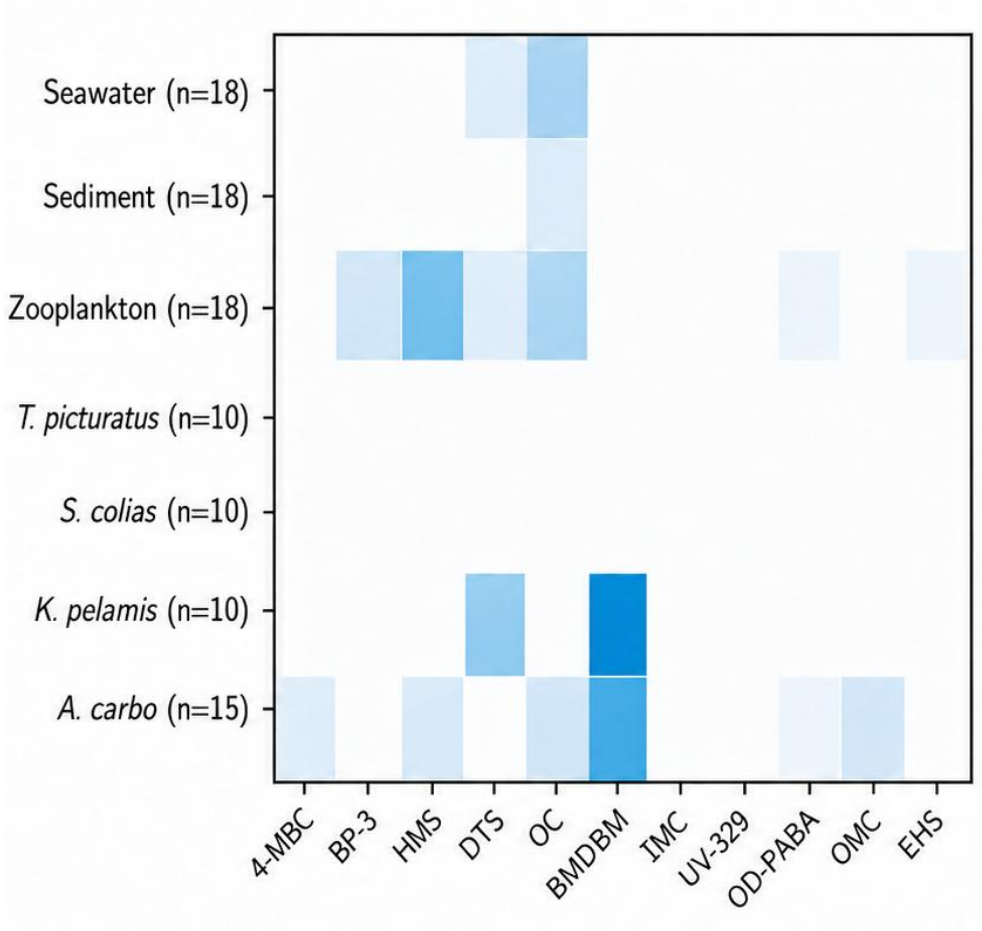

Fig. IV. 2. Occurrence profile of the target oUVFs across the analysed matrices. Values reported as <MLOQ were included in FO.

Several compounds were recurrently detected without being frequently quantified, showing the importance of distinguishing occurrence from quantified burden. This was particularly relevant for sediment and some biota samples, where detections close to the methodological limits contributed to FO but not to ΣoUVF values. In contrast, zooplankton and A. carbo showed broader compound diversity and higher occurrence frequencies for selected oUVFs, supporting their potential relevance as biological compartments for offshore oUVF monitoring.

3.2 oUVFs in environmental matrices

Seawater and sediment samples were analyzed to establish baseline concentrations of the target compounds in pelagic environments distant from coastal influence. Seawater was expected to favour the detection and quantification of the less lipophilic and more recently released oUVFs, whereas sediments were examined as potential compartments for more hydrophobic compounds associated with particles or longer-term deposition (Avellan et al., 2022). However, the results showed a low FO, 28% for seawater and 33% for sediment, together with limited compound diversity. Seawater showed the second-lowest mean ΣoUVF concentration among all analysed matrices, with only OC and DTS quantified and a maximum quantified ΣoUVF concentration of 38.36 ng/L. In sediment, only OC was quantified, at 3.00 ng/g d.w. in a single sample (Tables IV. 3 and 4). These results indicate that dissolved-water and shallow sediment signals were low in the offshore areas sampled.

Table IV. 3. Summary of the matrices included in the study, sample size (n), mean value (± standard deviation, SD) of ΣoUVFs calculated considering all samples within each matrix/species, quantified ΣoUVF concentration range, and frequency of occurrence (FO). FO was calculated as the percentage of samples in which at least one target oUVF was detected at concentrations ≥MLOD. Individual sample-level data are provided in Table SM4.

Scientist name	Common name	Sample Size	∑oUVFs		FO (%)
			Mean value ± SD (ng/g d.w. or ng/L)	Range (ng/g d.w. or ng/L)	
	Seawater	18	5.494 ± 12.01	7.925 - 38.36	28
	Sediment	18	0.167 ± 0.707	3.000*	33
	Zooplankton	18	114.4 ± 186.1	8.050 - 753.0	61
Trachurus picturatus	Blue jack mackerel	10	0.000 ± 0.000	-	0
Scomber colias	Atlantic chub mackerel	10	0.000 ± 0.000	-	0
Katsuwonus pelamis	Skipjack tuna	10	22.99 ± 26.28	0.999 - 73.13	90
Aphanopus carbo	Black scabbardfish	15	141.5 ± 105.6	57.25 - 398.5	93

* Only one quantified ΣoUVFs value was available for this matrix; therefore, a single concentration is reported instead of a range.

Table IV. 4. Mean concentration (± standard deviation, SD) and frequency of occurrence (FO) of the target compounds detected or quantified in at least one matrix. Concentrations are reported as ng/L for seawater and ng/g d.w. for sediment and biota. Mean ± SD values were calculated only for samples in which the compound was quantified (>MLOQ). FO refers to the percentage of samples in which the compound was detected at concentrations ≥MLOD. Results detected between MLOD and MLOQ were considered in FO but were not included in mean concentration calculations. Individual sample-level results are shown in Table SM4.

Samples	**4-MBC**	**BP-3**	**HMS**	**DTS**	**OC**	**BMDBM**	**OD-PABA**	**OMC**	**EHS**
	Mean ± SD FO (%)	Mean ± SD FO (%)	Mean ± SD FO (%)	Mean ± SD FO (%)	Mean ± SD FO (%)	Mean ± SD FO (%)	Mean ± SD FO (%)	Mean ± SD FO (%)	Mean ± SD FO (%)
Seawater	<MLOD 0	<MLOD 0	<MLOD 0	27.51 ± 9.257 17	5.882 ± 3.271 28	<MLOD 0	<MLOD 0	<MLOD 0	<MLOD 0
Sediments	<MLOD 0	<MLOD 0	<MLOD 0	<MLOD 0	3.000 ± 0.000 33	<MLOD 0	<MLOD	<MLOD 0	<MLOD 0
Zooplankton	<MLOD 0	93.00 ± 51.41 28	53.50 ± 45.90 44	61.23 ± 19.39 17	123.4 ± 210.3 39	<MLOD 0	74.00 ± 0.000 5	<MLOD 0	22.67 ± 3.333 11
Trachurus picturatus	<MLOD 0	<MLOD 0	<MLOD 0	<MLOD 0	<MLOD 0	<MLOD 0	<MLOD 0	<MLOD 0	<MLOD 0
Scomber colias	<MLOD 0	<MLOD 0	<MLOD 0	<MLOD 0	<MLOD 0	<MLOD 0	<MLOD 0	<MLOD 0	<MLOD 0
Katsuwonus pelamis	<MLOD 0	<MLOD 0	<MLOD 0	1.413 ± 0.414 50	<MLOD 0	37.74 ± 24.55 60	<MLOD 0	<MLOD 0	<MLOD 0
Aphanopus carbo	189.6 ± 117.4 27	<MLOD 0	143.9 ± 17.57 40	<MLOD 0	15.01 ± 9.979 40	79.11 ± 26.43 53	5.998 ± 0.000 13	43.72 ± 58.01 33	<MLOD 0

In seawater, the low FO and concentrations of oUVFs could be related to the offshore sampling location. Previous studies have demonstrated that oUVF concentrations in coastal waters are strongly influenced by anthropogenic pressure and coastal characteristics (Sánchez-Rodríguez et al., 2015; Tovar-Sánchez et al., 2013). In contrast, pelagic waters, such as those sampled in this study, are not directly affected by human inputs. This interpretation is supported by comparison with coastal data from the same region, where coastal seawater samples showed mean ∑oUVF concentrations of 20.65 ng/L, about three times higher than those measured in pelagic seawater (Íñiguez et al., 2025b). Supporting this view, a study along the Pacific coast reported that concentrations of several POPs, including some oUVFs, decreased with distance from shore, suggesting that anthropogenic impacts become diluted offshore (Goksøyr et al., 2009).

Another factor that could influence oUVF levels is the amount of organic matter and nutrients in the water column. For example, Mediterranean islands such as Mallorca (Balearic Archipelago) are surrounded by nutrient-rich waters where higher concentrations of lipophilic pollutants have been reported (Tovar-Sánchez et al., 2013). In contrast, the waters around the Madeira Archipelago are subtropical and oligotrophic, with low concentrations of organic material and nutrients, primarily influenced by episodic upwelling events (Spalding et al., 2007; Fernandez et al., 2021). Given the physicochemical characteristics of oUVFs summarised above, these compounds tend to associate with organic matter or precipitate rapidly under conditions of low organic matter availability (Pintado-Herrera & Lara Martín, 2020). However, it is necessary to consider that the particulate organic matter in the seawater samples was filtered and not analyzed in this work. This may have led to an underestimation of total oUVF levels in seawater samples.

Sediment results showed very limited quantification of target oUVFs, with only OC quantified in one sample and most detections remaining below the MLOQ. Although these

samples were collected at depths of up to 80 m, where some influence from coastal inputs could still be expected, previous studies have shown that sediments from impacted coastal areas or those influenced by riverine discharges and/or industrial activities typically exhibit higher concentrations and greater diversity of oUVFs, whereas sediments from more pristine regions and/or areas more distant from industrial activities tend to be less affected (Combi et al., 2016; Avellan et al., 2022).

The steep insular shelf and fully open coastline of the Madeira Archipelago likely enhance oceanic dynamics that promote the dilution and dispersal of these compounds. Moreover, sediments around the archipelago are highly heterogeneous, ranging from muddy deposits to calcareous biogenic fragments and even rhodolite-rich samples (Ribeiro and Neves, 2020; Braga-Henriques et al., 2022). This variability reflects the complex sedimentary environment of the region, and total organic carbon, grain size, and clay content can significantly influence both the accumulation and detectability of POPs as oUVFs (Li et al., 2016; Ge et al., 2021). These characteristics may favour the transport of oUVFs to deeper sediments, while coastal sediments remain below detectable concentrations (Iñiguez et al., 2025b). Additionally, sediment composition can shape local microbial communities, thereby influencing the biodegradation potential and environmental half-lives of different compounds, which may partly account for the limited number of detected oUVFs and the generally low concentrations observed, most of them below the MLOQ (Volpe et al., 2017). In both matrices analyzed in this study, sediment and seawater, OC was the predominant compound detected. This oUVF has been reported in a wide range of environmental matrices and is among the most studied oUVF, largely because it is one of the most widely used ingredients in PCPs (Sánchez-Rodríguez et al., 2015; da Silva et al., 2022). Furthermore, OC is frequently identified as the dominant oUVF in sediment samples in previous studies (Combi et al., 2016; Apel et al., 2018; Iñiguez et al., 2025a, b), reflecting its widespread environmental occurrence and persistence.

Given the offshore conditions of this study, it is plausible that the target compounds were not detectable in their original form and/or had already been metabolized, accumulated, or redistributed into other compartments such as the sea-surface microlayer (SML), deeper sediments, or marine organisms (Combi et al., 2016; Fagervold et al., 2019). Transformation products (TPs) were not considered in this work; therefore, the actual environmental presence and impact of oUVFs may be underestimated, as several TPs are known to be more toxic, persistent, and mobile than their parent compounds, while also exhibiting distinct and still poorly understood environmental behavior (Law et al., 2021).

The low dissolved-water concentration observed here should not be interpreted as evidence of the absence of oUVFs from the offshore system. Filtered seawater represents only the dissolved fraction at the time of sampling and does not account for compounds associated with suspended particles, sea-surface microlayer material, microplastics, or biological matrices. This limitation is particularly relevant for hydrophobic oUVFs, which may partition into organic matter or biota even when dissolved concentrations remain low. Therefore, the environmental matrices analysed here provide a conservative view of oUVF occurrence in offshore waters.

3.3 oUVF in biota samples

Zooplankton and four fish species were analysed to assess oUVF occurrence across biological compartments occupying different positions in the water column (Table IV. SM1). None of the targeted oUVFs were detected above the MLOD in *T. picturatus* or *S. colias*. In contrast, *K. pelamis* showed a high frequency of detections but low quantified concentrations, while surface-collected zooplankton and the bathypelagic species *A. carbo* showed the highest mean ΣoUVF concentrations among the analysed biota (Table IV. 3; Fig. IV. 3).

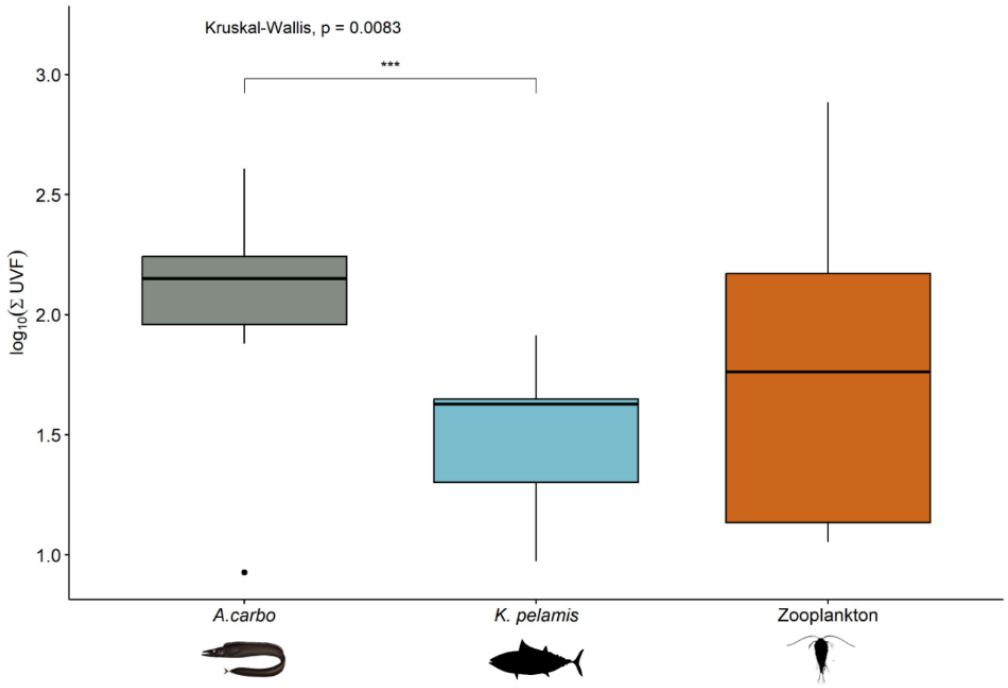

Fig. IV. 3. Boxplots of log_{10}-transformed ∑oUVF concentrations in biota matrices where target compounds were quantified. Significant differences among matrices are shown. Differences among matrices were assessed using the Kruskal–Wallis test (p = 0.0083), followed by pairwise Wilcoxon comparisons with Bonferroni correction, as described in Methods. Asterisks indicate significant pairwise differences.

Regarding FO, oUVFs were highly prevalent in samples of black scabbardfish (93%) and skipjack tuna (90%), while only 61% of zooplankton samples contained at least one compound (ca. 30% lower than in fish species). In the case of skipjack tuna, this high FO reflects the detection of at least one oUVF in 9 out of 10 individuals, even though only BMDBM and DTS were quantified, and their absolute concentrations remained comparatively low (Table IV. 4; Table IV. SM4). The high occurrence frequency in *K. pelamis*, therefore, reflected repeated detection of at least one oUVF, not high quantified ΣoUVF concentrations.

The Kruskal–Wallis test revealed significant differences in ∑oUVF concentrations among matrices ($p < 0.05$). Pairwise Wilcoxon comparisons with Bonferroni correction indicated significant differences between black scabbardfish and skipjack tuna, whereas zooplankton did not differ significantly from either fish species, likely due to the wide ∑oUVF concentration

range observed (Fig. IV. 3). This broad variability may be related to the complex heterogeneous nature of the zooplankton community, which encompasses a wide range of taxa, including crustaceans, molluscs, and cnidarians, as well as invertebrate larvae such as echinoderms and vertebrate larvae such as fish (Ershova et al., 2021). Such biodiversity forms an intricate trophic network, in which different species feed on one another within a planktonic food web, promoting possible bioaccumulation and biomagnification of oUVFs and other organic contaminants (Merquiol et al., 2023). Additionally, zooplankton assemblages may differ in biochemical composition, such as varying total lipid contents among taxa and different trophic roles (herbivorous, carnivorous, or omnivorous), which altogether could contribute to the wide range of concentrations quantified in the present study (Lee et al., 2006; Connelly et al., 2012; Nieddu et al., 2024).

Moreover, zooplankton were collected in surface waters, including the SML, a zone previously reported to contain high concentrations of organic chemicals (Grant et al., 2025). The SML, which represents the interface between the ocean and the atmosphere, is typically enriched in organic matter, facilitating the adsorption and accumulation of hydrophobic compounds such as oUVFs (Pintado-Herrera & Lara Martín, 2020). Consequently, the exposure of zooplankton to this layer, combined with their diel vertical migration behavior, and the complexity of the matrix may explain the elevated and variable concentrations observed, as well as the detection of a broad range of compounds (McGinty et al., 2011). However, the specific contribution of the SML to the concentrations observed here could not be assessed directly in the present study.

It is also important to note that the zooplankton sampling methodology is similar to that commonly used for MP collection, increasing the likelihood of co-collection of surface-floating MPs, which were not separated from the analyzed samples (Sambolino et al., 2022). Since MPs are known to adsorb and transport organic contaminants, including oUVFs, their presence in

the samples could contribute the broad concentration ranges observed, potentially obscuring the true oUVF levels in the biological matrix itself (Pacheco-Juarez et al., 2025). Additionally, several studies have demonstrated the ingestion of MPs by zooplankton and their subsequent transfer through the trophic web, suggesting that MPs may have been collected and present in the zooplankton samples used for this study (Beiras et al., 2019; Gunaalan et al., 2023). This is particularly relevant in the Madeira Archipelago, where oceanic currents associated with the subtropical gyre transport and accumulate plastic particles, increasing the rate between MPs and zooplankton (Sambolino et al., 2022; Iñiguez et al., 2025b).

Additionally, the small pelagic fish species targeted in this study typically inhabit depths ranging from the surface to 300–500 m. Although their trophic niches are not fully understood, they may feed on prey suspended in the water column, which may be less likely to accumulate organic contaminants (Romero et al., 2021). These water-column compartments may also contain lower concentrations of oUVFs and microplastics than surface-associated or sediment-linked compartments (Pinheiro et al., 2023; Wang et al., 2022). Furthermore, previous studies from nearby regions, such as the Canary Islands, also reported Atlantic chub mackerel with oUVF concentrations below the MLOQ (Gimeno-Monforte et al., 2020). Taken together, these observations suggest that both ecological exposure patterns and the use of whole-body homogenates may have contributed to the absence of detectable oUVFs in *T. picturatus* and *S. colias*. Therefore, the absence of detectable parent oUVFs should not be interpreted as absence of exposure, but rather as absence of detectable target compounds under the analytical and sampling conditions applied in this study. Future studies should include tissue-specific analyses whenever possible.

Previous information also supports the low concentrations and limited diversity of oUVF detected and quantified in *K. pelamis* in this study. This species is a pelagic top predator that feeds on smaller pelagic species, as those targeted in this study (Romero et al., 2021). Factors

such as metabolic rate, total lipid content, body size, age, and reproductive stage can influence the accumulation of oUVFs (Pintado-Herrera et al., 2024). In skipjack tuna, no significant correlations were observed between ΣoUVF concentrations and total lipid content, length, or weight, as shown in Table IV. SM5. Although these results should be taken carefully due to the small sample size per species collected for the present study, which encompassed individuals in a similar stage. *K. pelamis* exhibits seasonal patterns throughout its life cycle, with temperature being a key driver of their distribution. In the Madeira Archipelago, most individuals remain in juvenile stages, likely due to their stricter thermal requirements compared to adults and the relatively stable water temperatures in the region (Gouveia and Mejuto, 2003). Furthermore, similar concentrations were quantified for other species of fish in the Canary Islands, including Atlantic bonito, which did not show detectable concentrations of oUVFs (only for a UV stabilizer, UV-329, in a low concentration of 0.36 ± 0.02 µg/g d.w. (Gimeno-Monforte et al., 2020), which further supports this interpretation.

Different tissues and organs can display distinct capacities for metabolizing or accumulating organic contaminants. Pintado-Herrera et al. (2024) demonstrated this by analyzing oUVFs and other organic pollutants in the liver and muscle of three tuna species, including *K. pelamis.* Their results showed that some organic contaminants tend to accumulate preferentially in the liver, making it a suitable tissue for short-term exposure assessments, whereas oUVFs generally presented higher concentrations in muscle (except for 4-MBC), which reflects medium-term accumulation. Moreover, in their study conducted in Cádiz, where skipjack tuna arrives at adult stages and are more exposed to coastal influences, higher oUVF concentrations were reported, with maximum levels of 1273 ng/g d.w. for 4-MBC. These findings support the hypothesis that both diet and exposure duration, closely linked to age and life stage, play a crucial role in the accumulation of oUVFs. This high FO combined with low quantified burdens suggests frequent low-level exposure rather than high contaminant

accumulation. Because only muscle tissue was analysed in *K. pelamis*, the possibility that more lipophilic compounds were retained differently in other tissues cannot be excluded. One possible explanation is intermittent exposure to surface-associated compartments, although this cannot be demonstrated directly from the present dataset (Nieddu et al., 2024; Pintado-Herrera et al., 2024).

Descending from surface waters to the bathypelagic zone, *A. carbo* showed the highest overall concentration and FO among all species analyzed in this study. This result is relevant because *A. carbo* is a commercially important deep-water species in the Madeira Archipelago, where it is exploited for human consumption (Delgado et al., 2018). Its distribution range extends from the United Kingdom to the Madeira Islands. Around the Madeira Archipelago, individuals can inhabit depths of down to 1700 m, whereas closer to the mainland, they are typically found and fished at depths of approximately 200 m. Madeira Island has also been described as a reproductive area for the species, where individuals at all maturity stages can be found (Pajuelo et al., 2008). To our knowledge, this is the first study to report the presence of oUVFs in this bathypelagic species, although previous studies have already described the presence of other contaminants, such as heavy metals for *A.carbo* from Portuguese waters (Costa et al., 2009).

However, the occurrence of oUVFs in *A. carbo* should not be interpreted as direct evidence of vertical transport from coastal sources. Instead, it indicates that parent oUVFs can be detected in bathypelagic biota and supports the need to investigate the exposure pathways involved. Possible mechanisms include particle-associated redistribution, ingestion of contaminated prey, contact with sinking organic material, and matrix-specific retention of hydrophobic compounds, but these pathways were not directly tested in the present study.

The deep-sea environment has long been recognized as a sink for POPs and plastic-associated contaminants (Jamieson et al., 2017; Avellan et al., 2022). This background is

consistent with the occurrence of oUVFs and could support the hypothetical distribution patterns described in this study. oUVFs tend to occur at detectable and often elevated concentrations in regions where the water column is rich in organic matter, or in organisms associated with those layers (Apel et al., 2018). Madeira Island, as an oceanic island with a steep insular shelf, reaches substantial depths close to shore, a geomorphological characteristic that increases the likelihood that anthropogenic pressures from coastal zones may extend to the deeper environments (Spalding et al., 2007; Kim et al., 2008; Vági et al., 2021).

Accordingly, concentrations detected in species inhabiting Madeira's coastal areas, with 157.45 ng/g d.w. in *Sarpa salpa*, were similar to those quantified in the deep-sea with the black scabbardfish (141.5 ng/g d.w). A similar pattern was observed for coastal and offshore zooplankton, both of which present similar concentrations of 129.2 and 114.4 ng/g d.w. respectively (Íñiguez et al., 2025b). This highlights both the high transport potential of oUVFs and the broader environmental impact of organic contaminants released in coastal zones, which could ultimately reach and affect deep-sea ecosystems.

Furthermore, aggregation of oUVFs with MPs and nanoplastics has been proposed as one possible mechanism contributing to vertical redistribution in the marine environment (Vagi et al., 2021). Vertical transport processes associated with ecological phenomena such as "whale falls", in which dead organisms sink to the seabed and become sources of nutrients and carbon for deep-sea fauna, may also facilitate oUVF transfer into the tissues and organs of deep organisms which could bioaccumulate, as these compounds have already been reported in several macrofauna species, including cetaceans (Estes et al., 1998; Becker et al., 2021; Íñiguez et al., 2025a). All these possible direct and indirect sources could increase the potential of consumption and absorption of oUVFs by bathypelagic top predators, such as the black

scabbard fish. Such pathways remain plausible but untested explanations for the occurrence of oUVFs in bathypelagic predators such as black scabbardfish.

3.4 Presence and distribution of oUVFs in organisms inhabiting different depths of the water column

Compound-specific profiles differed markedly among biological matrices. In zooplankton, the quantified profile included BP-3, HMS, DTS, OC, OD-PABA, and EHS, whereas K. pelamis showed a narrower profile dominated by BMDBM and DTS. In A. carbo, the quantified profile included 4-MBC, HMS, BMDBM, OMC, OC, and OD-PABA. This compositional contrast supports the interpretation that oUVF occurrence across organisms was matrix- and species-dependent, rather than a simple reflection of total environmental concentration (Table IV. 4, Fig. IV. 4).

The predominance of BP-3 and EHS in zooplankton is consistent with a stronger association with surface-related exposure, although this cannot be confirmed without parallel analysis of the sea-surface microlayer and particulate fractions. OC and HMS were also relevant in zooplankton, supporting the role of this matrix as an integrative surface-associated compartment. In contrast, 4-MBC, BMDBM, OMC, and OD-PABA were more relevant in *A. carbo*, suggesting that some parent oUVFs can occur in bathypelagic biota. BMDBM was detected in both *K. pelamis* and *A. carbo*, indicating a broader biological occurrence than compounds restricted to a single matrix.

Several compounds detected in this study are also under regulatory scrutiny in the European Union. Within the framework of Regulation (EC) No 1223/2009 on cosmetic products, BP-3, OC, HMS, and 4-MBC were prioritised by the European Commission for endocrine-disruptor assessment, while OMC was identified for further data gathering (European Commission,

2019, 2021). In addition, 4-MBC camphor is of particular regulatory relevance because it has recently been subject to restriction in cosmetic products in the European Union under Commission Regulation (EU) 2024/996.

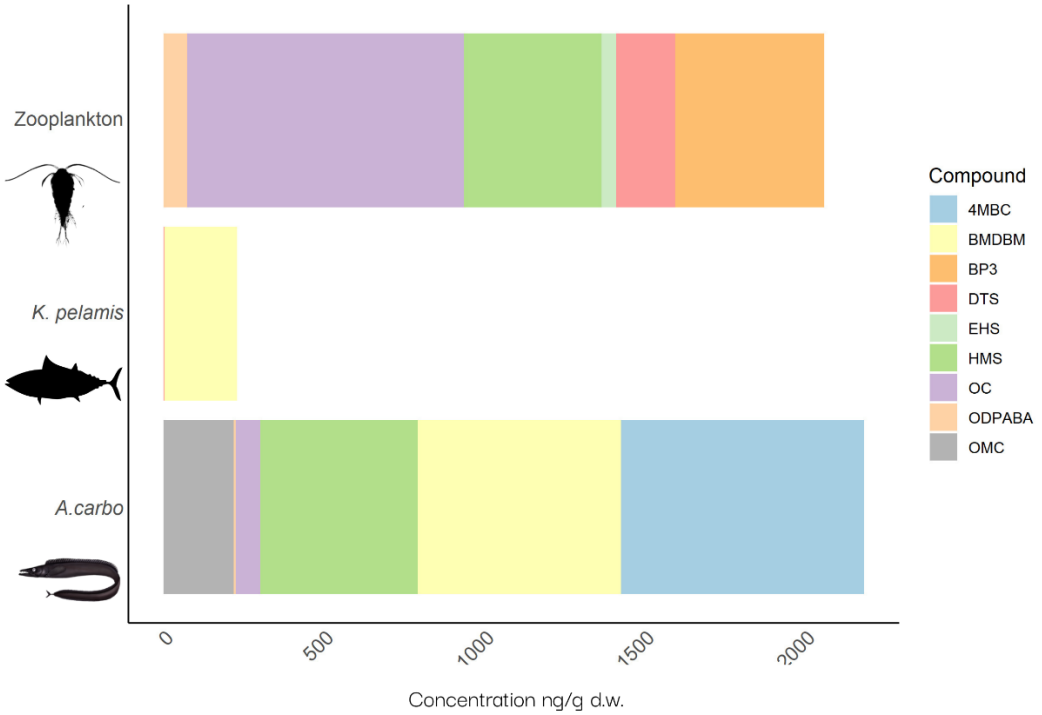

Fig. IV. 4. Stacked bar plots of mean concentrations of the different ∑oUVFs quantified in the biota matrices included in the study (ng/g d.w.; ΣoUVFs per matrix). Abbreviations are as in Table IV. 1. Black scabbardfish (*A. carbo*); skipjack tuna (*K. pelamis*).

BP-3 and EHS were quantified exclusively in the zooplankton matrix. BP-3 is among the least hydrophobic compounds included in this study and has been reported to show relatively limited environmental persistence, with degradation influenced by environmental conditions such as temperature, salinity, and irradiation (Damikouka et al., 2024). EHS, in turn, has been reported mainly in surface waters and is known to associate with MPs (Zhao et al., 2023; López-Vázquez et al., 2024). Therefore, the occurrence of these compounds in surface-collected zooplankton may be consistent with recent or surface-associated exposure, although this cannot

be confirmed without parallel analysis of the sea-surface microlayer, suspended particles, and microplastic-associated fractions.

In contrast, 4-MBC, OD-PABA, and OMC were more relevant in *A. carbo* than in the other biological matrices analysed. Both 4-MBC and OMC are relatively hydrophobic oUVFs and may show limited photodegradation under some environmental conditions (Capela et al., 2019; Cuccaro et al., 2022). Furthermore, 4-MBC has been reported in wastewater and may not be efficiently removed by conventional treatment processes (Araújo et al., 2018). Li et al. (2016) reported high absorption potential for 4-MBC, BMDBM, and OD-PABA under laboratory conditions, which may help explain their reduced dissolved-phase occurrence and their potential association with particles or biological matrices. In that study, biotransformation could be a primary degradation pathway, while these compounds showed resistance to the microbiota present in sediments (Volpe et al. 2017). In addition, the occurrence of these compounds has been associated with dissolved organic matter, which is relatively scarce in Madeira Archipelago waters (Santonocito et al., 2020). Taken together, the low organic content of subtropical water columns, combined with the persistence and high sorption capacity of these compounds, may contribute to their accumulation and precipitation in deep-sea ecosystems. However, the present study did not directly assess particulate transport, sedimentation, or trophic transfer. Therefore, the detection of these compounds in *A. carbo* should be interpreted as evidence of occurrence in bathypelagic biota, not as direct proof of vertical redistribution or accumulation in deep-sea ecosystems.

Conversely, BP-3 and OC were found in higher concentrations in organisms associated with surface waters, while BMDBM was detected throughout the entire water column. OC and BMDBM are often used together in sunscreen formulations to enhance SPF and improve photostability (Sánchez-Rodriguez et al., 2015; da Silva et al., 2022). This may explain their

co-occurrence in pelagic biota exposed to direct inputs of organic contaminants, in contrast to the more stable compounds that tend to accumulate in deep-sea environments.

The higher abundance of BMDBM compared to OC could be related to differences in their susceptibility to degradation and transformation into transformation products (TPs). While OC appears to be more sensitive to environmental factors, BMDBM shows greater resistance and a longer half-life, which depends on marine environmental conditions. Under certain conditions, BMDBM can persist as a parent compound for up to 101 days (Cantrell and McGarvey, 2001; Li et al., 2016; da Silva et al., 2022).

Nine of the 11 target oUVFs were quantified in at least one analysed matrix, with zooplankton and *A. carbo* together accounting for most of the compound diversity observed in biota. In contrast, a previous study in Madeira Island's coastal waters quantified 5 oUVFs in biota matrices and 6 in seawater (Iñiguez et al., 2025b). Taken together, these findings expand the evidence that oUVFs may occur across multiple compartments of the island marine system. However, the present dataset does not allow the vertical distribution, persistence, or retention of individual compounds to be resolved mechanistically.

4. Conclusion

This study provides an initial assessment of how coastal activities may influence both pelagic and deep-sea ecosystems. The oUVFs appeared to be associated with organic matter, which may facilitate their transport to deep environments previously considered pristine. However, further analyses are needed to demonstrate this relationship. The detection of eleven oUVFs in organisms known to inhabit different depth ranges revealed possible distribution patterns consistent with their physicochemical properties and the ecological traits of the analyzed species. Offshore waters around Madeira Island appear relatively unpolluted with

regard to UVFs, although surface layers remain affected by coastal inputs, while the deep sea appears to act as a sink for oUVFs, showing concentrations similar to those reported in coastal areas. Monitoring oUVFs in zooplankton and commercially important species is essential to evaluate their bioaccumulation potential within the trophic web, as well as the associated risks to human health. Expanding research to remote marine areas will improve our understanding of chemical transport pathways and support the development of more effective management and mitigation strategies for emerging pollutants in marine environments.

Supplementary data

Supplementary data can be found in the Annex - Supplementary data C.

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CHAPTER V

Organic Ultraviolet Filters in the Blubber of Two Free-Ranging Deep-Diving Cetacean Species

Íñiguez, E., Montesdeoca-Esponda, S., Alves, F., Sosa-Ferrera, Z., Kaufmann, M., Cordeiro, N., and Dinis, A. (2025). Organic ultraviolet filters in the blubber of two free-ranging deep-diving cetacean species. *Environmental Pollution*, 383, 126830. https://doi.org/10.1016/j.envpol.2025.126830

CHAPTER V: Organic ultraviolet filters in the blubber of two free-ranging deep-diving cetacean species

Abstract

The increasing use of personal care products has led to the widespread of organic UV filters (oUVFs) in marine ecosystems, yet their occurrence and potential impacts on pelagic and deep-sea environments remain unclear. This study assessed oUVFs contamination in the blubber of two deep-diving cetacean species, the short-finned pilot whale (*Globicephala macrorhynchus*) and the sperm whale (*Physeter macrocephalus*), off Madeira Island, Eastern North Atlantic. Using microwave-assisted extraction and UHPLC-MS/MS, four of eleven targeted oUVFs were detected in blubber: homosalate, 2-ethylhexyl salicylate, octocrylene, and methylene bis-benzotriazole (UV-360). Concentrations reached up to 352.3 ng/g wet weight (w.w.) in pilot whales and 1505 ng/g w.w. in sperm whales. Detection frequencies were higher in pilot whales (60–100%) than in sperm whales (30–50%). This study provides the first evidence of UV-360 concentration in cetaceans. These findings suggest that pilot whales' greater site fidelity in Madeiran waters may increase their exposure to oUVF, whereas sperm whales may accumulate oUVF through benthopelagic feeding at higher trophic levels. These results highlight the potential for oUVF to disperse into deep marine ecosystems and underscore the importance of monitoring emerging contaminants in oceanic apex predators.

Keywords: Emergent pollutants, *Globicephala macrorhynchus*, human pressure, *Physeter macrocephalus,* sunscreens

1. Introduction

Public health recommendations promoting protection against Ultraviolet (UV) radiation, mainly UVA (320-400 nm) and UVB (280-320 nm) to prevent skin problems, has led to increased global use of personal care products (PCPs) like sunscreens, which contain organic and inorganic chemicals known as UV Filters (UVF) (Moloney et al., 2002; Castro et al., 2018; Shetty et al., 2023). In the European Union, thirty-one organic UV filters (oUVFs), divided into eleven different families, and two inorganic UVFs (iUVF) - the zinc oxide (ZnO) and titanium dioxide (TiO_2) - in their micro and nano forms (Table V. S1), were approved for use in PCPs according to Annex VI (EU) Regulation 2022/2197 (Caloni et al., 2021; Nitulescu et al., 2023; Pantelic et al., 2023). These compounds exhibit high photostability and lipophilicity (determined by the high octanol-water partition coefficient (K_{ow})) (Castro et al., 2018). Marine contamination occurs through both direct inputs, such as recreational bathing, and indirect sources, including wastewater and industrial discharges (Sang and Laung, 2016; Cadena-Aizaga et al., 2020).

Due to the increased interest in these compounds, most studies in European waters have focused on the presence and effects of oUVFs based on multiple methodologies and provide results that do not follow standard protocols, thus making it difficult to have a global risk assessment (Manová et al., 2013; Ramos et al., 2016; Cadena-Aizaga et al., 2020). This lack of agreement and information about these contaminants and their description as hazardous to the environment has led to their classification as Contaminants of Emerging Concern (CEC) (Nilsen et al., 2019; Tang et al., 2019).

The increased assessment of these compounds worldwide offers an idea about the range of environmental levels. However, the concentration levels vary depending on the matrix (sediments, water, mud, sand, etc.), location and anthropogenic pressure (Ramos et al., 2016; Cadena-Aizaga et al., 2020). A similar trend is observed according to the half-life of oUVFs in

marine environments. The oUVFs are described as stable and persistent in the environment, with half-lives ranging from 0.5 to 357 hours in surface seawater. This high variation depends on the compound, whether they are released into a mix or as a single chemical, in which matrix is evaluated and needs to be considered degradation and dilution processes as well as the transformation products originated (Volpe et al., 2017; O'Malley et al., 2021; Marcin and Aleksander, 2023). Due to physicochemical properties as well as the possible persistence into the water column, they are prone to accumulation in solid matrices in animal tissues and biomagnified through the trophic chain, reaching top consumers like cetaceans or humans (Paredes et al., 2014; Peng et al., 2017; Yang et al., 2020; Wang et al., 2022). Adverse effects of oUVFs on biota, including negative impacts on endocrine, reproductive, and immune systems, have been described in many species (Tang et al., 2019; Parra-Luna et al., 2020; Shetty et al., 2023; Akinboye et al., 2024). Hence, some critical effects on the ecosystem have been reported, including coral bleaching (Downs et al., 2016; Tsui et al., 2017; Mitchelmore et al., 2021; Moeller et al., 2021), which has prompted the banning of sunscreen and cosmetic use on coral reef beaches (Raffa et al., 2019; Suh et al., 2020; Levine, 2021).

However, data on oUVF contamination in offshore and deep-sea ecosystems, as well as in higher trophic levels in the marine environment, remains scarce (Lozano et al., 2020; Pinheiro et al., 2023). There are only a limited number of studies on coastal cetacean species, and most rely on stranded animals, which may not accurately represent the real situation of individuals in good health (Nakata et al., 2010; Gago-Ferrero et al., 2013; Alonso et al., 2015; Lu et al., 2019; Carve et al., 2021; Blouin et al., 2022; Combi et al., 2022; González-Bareiro et al., 2023). To address this gap, this study assessed the presence of eleven oUVFs in the blubber of two free-ranging cetacean species - the short-finned pilot whale (*Globicephala macrorhynchus*) and the sperm whale (*Physeter macrocephalus*). This is the first study assessing oUVFs in deep-

diving mammals, thus showing the possible wide distribution of the target compounds from surface seawater to the deep-sea using both species as bioindicators.

2. Materials and methods

2.1 Reagents and consumables

Eleven oUVFs were analyzed in the present study. Their characteristics are summarized in Table V. 1. The 4-MBC, BP-3, OC, BMDBM, IMC, HMS, OD-PABA, EHS, OMC, DTS, UV-360, and the Internal Standard (IS) deuterated benzophenone (BP-d_{10}) (purity ≥99%) were obtained from Sigma-Aldrich (Madrid, Spain). Water LC-grade, formic acid, methanol (MeOH), acetone, and hexane (HEX), of LC-MS grade, were obtained from Panreac Química (Barcelona, Spain). The CHROMAFIL polyethylene terephthalate (PET) disposable syringe filters (0.2 μm, pore size) were obtained from Macherey-Nagel (Duren, Germany). The stock solution of the target compounds (250 mg/L) was prepared in acetone and stored in amber glass at -20 ºC. Working solutions were prepared daily in MeOH.

Table V. 1. Characteristics of the eleven organic UV filters (oUVFs) analysed in this study, including their names according to the International Nomenclature ff Cosmetic Ingredients (INCI), Chemical Abstracts Service number (CAS No.), physicochemical properties (lipophilicity and solubility), and intensity of production in the European Economic Area (EEA).

INCI name	Abbreviation	CAS No.	$LogK_{ow}$	Solubility (g/L)	EEA production
Benzophenone-3	BP-3	131-57-7	3.79	0.21	LPV
Ethylhexyl dimethyl PABA	OD-PABA	21245-02-3	6.15	$2.1 \cdot 10^{-3}$	LPV
Homosalate	HMS	118-56-9	6.16	0.02	HPV
2-ethylhexyl salicytate	EHS	118-60-5	5.97	0.028	HPV
Ethylhexyl methoxycinnamate	OMC	5466-77-3	5.8	0.15	-
Isoamyl p-methoxycinnamate	IMC	71617-10-2	4.33	0.06	LPV
4-methylbenzylidene camphor	4-MBC	36861-47-9	3.83	0.014	LPV
Drometrizole trisiloxane	DTS	155633-54-8	10.82	$1.3 \cdot 10^{-5}$	-
Methylene bis-benzotriazole	UV-360	103597-45-1	12.46	$3 \cdot 10^{-8}$	LPV
Butyl methoxydibenzoylmethane	BMDBM	70356-09-1	4.51	0.037	HPV
Octocrylene	OC	6197-30-4	6.88	$2 \cdot 10^{-4}$	HPV

LPV: Low Production Volume between 10 and 100 tonnes/year; HPV: High Production Volume between 1000 and 10000 tonnes/year, produced or imported in the European Economic Area. Data on $LogK_{ow}$ solubility and EEA Production were extracted from Cadena-Aizaga et al., 2022.

2.2 Study area

Madeira Island (Portugal) is an oceanic island with 741 km^2 in the Eastern North Atlantic, with approximately 260 thousand inhabitants (Fig. V. 1). Its subtropical weather attracts up to

two million tourists annually (Direção Regional de Estatística da Madeira, 2022), causing a high anthropogenic pressure mainly on the island's south coast (Majdak and De Almeida, 2022; Sambolino et al., 2022). This volcanic island is characterized by submarine canyons and deep water close to a small insular shelf (Geldmacher and Hoernle, 2000), making its waters an optimal habitat for pelagic life, including marine mammals (Caldeira et al., 2002; Alves et al., 2018; Fernandez et al., 2021).

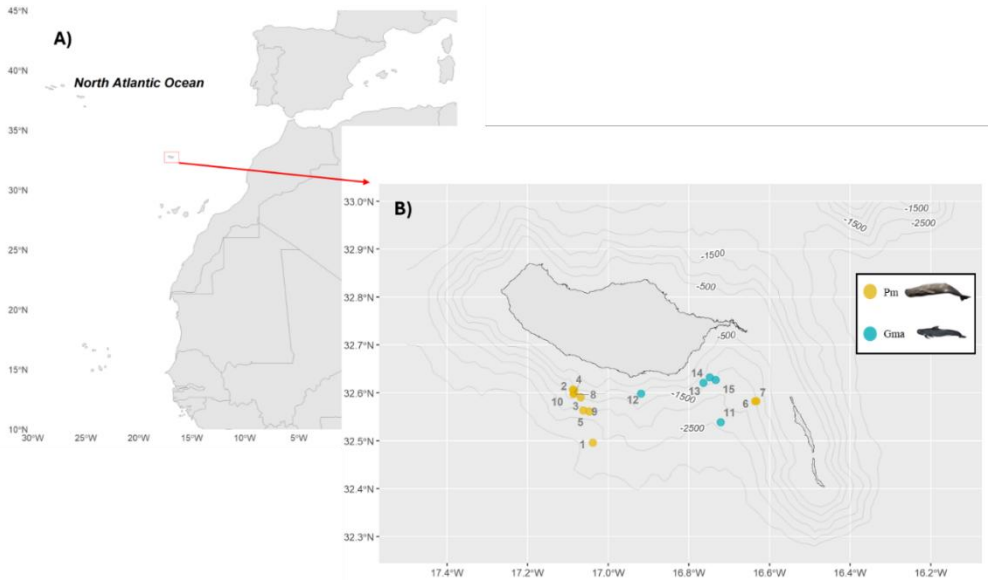

Fig. V. 1. A) Geographic location of Madeira in the Eastern North Atlantic. B) Map of Madeira (bigger island) and Desertas Islands (smaller ones) with bathymetric contours (in meters). The yellow and blue dots indicate the locations where biopsies were collected for sperm whales (*Physeter macrocephalus*, Pm) and short-finned pilot whales (*Globicephala macrorhynchus*, Gma), respectively.

The short-finned pilot whale has a tropical and warm temperate global distribution, including several island-associated populations such as in Madeira (Kasuya and Marsh, 1984; Mahaffy et al., 2015; Alves et al., 2013, 2019; Hill et al., 2019; Servidio et al., 2019). In contrast, the sperm whale has a wide global distribution, with females and calves living in warmer waters, including Madeira (Ferreira et al., 2022), and males spending extended periods at higher latitudes for feeding and migrating to warmer regions for reproduction (Engelhaupt et al., 2009; Cantor et al., 2019; Lefort et al., 2022).

2.3 Sample collection and pre-treatment

Biopsy samples (skin and blubber) of short-finned pilot whales (five samples) and sperm whales (ten samples) were collected off the south coast of Madeira Island between 2017-2022 (Fig. V. 1; Table V. SM4) through a remote system that uses modified tip darts (150-lb crossbow, with arrows and darts specially designed for small and larger cetaceans by Finn Larsen, Ceta-Dart40). Biopsies were collected at 5-15 m from the animal, aiming at the medial-lateral flank, under the dorsal fin, by experienced researchers (see Ethics approval). Only adult or sub-adult and apparently healthy animals not associated with calves were sampled. On board, samples were stored in liquid nitrogen until they reached the laboratory, where the skin was separated from the blubber with a scalpel and stored at −80 °C.

The oUVFs extraction was carried out by adapting the method previously developed by González-Bareiro et al. (2023, based on Titan Microwave-Assisted Extraction with Ultra High-Performance Liquid Chromatography and Mass Spectrometry (MAE-UHPLC-MS/MS).

The MAE equipped with 16 Tetrafluoroethylene Modified vessels (Perkin Elmer, Madrid, Spain) was used for the extraction. One hundred mg of blubber per individual was weighed, and 50 mg of diatomaceous earth was added to the MAE vessels to remove the humidity from the samples. For the extraction, 7 mL of HEX was added and heated to 50 ºC for 10 min. Then the content was recovered and evaporated under a stream of N_2 gas. Once dried, 1 mL of MeOH was added and sonicated for 5 min for posterior centrifugation at 3000 rpm (605 g-force) for 10 min (LanTechnics model DM0412; 100-240 V, 850/60 Hz, 70 W). Finally, samples were filtered through CHROMAFIL syringe filters with 0.2 µm pore size in a vial to detect oUVFs.

2.4 Analytical determination

Eleven oUVFs were determined by an Xevo ACQUITY-UHPLC (Waters Chromatography, Barcelona, Spain) equipped with a Binary Solvent Manager, a thermostated autosampler, a column manager, and a triple quadrupole mass spectrometry detector with an electrospray interface (ESI). All the components were monitored by the MassLynx Mass Spectrometry software (Waters Chromatography, Barcelona, Spain). The mobile phase consisted of an organic phase (A) composed of MeOH and an aqueous phase (B) of water, both LC-MS grade with 0.1% (v/v) formic acid and a flow rate of 0.3 mL/min. The gradient employed with a flow rate of 0.3 mL/min started with 75% A and 25% B for 3 min, then phase A increased to 100% until min 5. As a last step, phase A returned to the start condition 75% and stabilised for 2 min. The injected volume was 10 µL. The ESI parameters for mass spectrometry were capillary voltage at 3 kV, cone voltage at 15 V, source and desolvation at 120 and 450 ºC, respectively, and N_2 as desolvation gas at 50 L/h. Argon was employed as a collision gas (all the gases >99% purity). The detection parameters of the MS/MS for each compound under study are provided in the APPENDIX D (Table V. SM2).

2.5 Quality assurance and quality control

Calibration curves were prepared with eight points plotted within the 1-500 µg/L concentration range. Linear range coefficients ($R^2 > 0.99$) were obtained for each compound. Two blank solvent injections were performed per sample to check for possible external contamination.

The instrumental limits of detection (ILODs) and instrumental limits of quantification (ILOQs) were calculated from the signal-to-noise (S/N) for the analyte peaks, assuming minimum detectable S/N levels of 3 and 10, respectively. The methodological limits of

detection (MLODs) and methodological limits of quantification (MLOQs), expressed as analyte/mass of the sample, were estimated considering that 100 mg of sample was analysed. The values of instrumental and methodological LODs and LOQs are reported in Table V. SM3. BP-d_{10} was spiked as an IS into every sample, calibration points and blanks at a concentration of 200 µg/L.

Each biopsy was analysed in triplicate whenever the quantity available was ≥ 300 mg, and only the triplicates with a reproducibility below 30% or less of relative standard deviation (RSD) were used. To prevent external contamination or degradation of the compounds, all containers used were amber glass, thoroughly cleaned, and rinsed with distilled water and ethanol (HPLC grade) before use. Additionally, gloves were worn throughout the process. All the analysed compounds were below the MLODs in procedural blanks.

2.6 Statistical Analyses

Non-parametric Mann–Whitney U tests (Wilcoxon test) and Kruskal-Wallis tests were used to compare the median concentrations and the variance, respectively, of each detected oUVFs between the two species, with a significance level of 95%. The mean, standard error (SE), median, range, and frequency of occurrence (FO) were calculated for each species and compound. All statistical analyses and visualisations were conducted using the R Core Team (2021).

To ensure comparability between previous findings and the results obtained in this study all contaminant concentrations were standardized to wet weight (w.w.). Conversion from lipid weight (l.w.) to wet weight was performed using the equation:

$$C_{w.w.} = C_{l.w.} \times \frac{\text{Lipid (\%)}}{100} \quad \textbf{Eq. V. 1}$$

where the mean lipid content per species was considered.

Transformation from dry weight (d.w.) to wet weight followed the method previously applied by Yang and Miyazaki (2003):

$$C_{d.w.} = C_{w.w.} \times 4$$

Eq. V. 2

3. Results and discussion

Of the eleven oUVFs analysed, four were detected in the blubber of both species: HMS, OC, EHS, and UV-360 (Table V. 2, Fig. V. 2).

Table V. 2. The mean, range, and frequency of occurrence (FO) of the four organic UV filters (oUVFs) detected in both species under study.

Sperm whale (*P. macrocephalus*)				
	Mean ± SE (ng/g w.w)	Median (ng/g w.w)	Range (ng/g w.w)	FO (%)
HMS	151.5 ± 13.23	178.0	n.d-184.2	30
OC	50.48 ± 7.947	44.78	n.d-96.69	50
UV-360	171.1 ± 21.21	147.4	n.d-276.9	40
EHS	800.9 ± 140.4	668.8	n.d-1505	50
Short-finned pilot whale (*G. macrorhynchus*)				
	Mean ± SE (ng/g w.w)	Median (ng/g w.w)	Range (ng/g w.w)	FO (%)
HMS	109.0 ± 11.72	99.73	90.45-160.9	100
OC	89.84 ± 13.14	91.69	51.26-137.7	100
UV-360	92.66 ± 1.748	95.37	n.d-95.49	60
EHS	232.2 ± 31.10	196.5	n.d-352.3	80

w.w: wet weight; n.d: non-detected

This study reports for the first time the presence of UV-360 in cetaceans (Table V. 3). UV-360 is an oUVF and UV stabilizer belonging to the benzotriazole chemical family (BUVSs). This compound exhibits poor biodegradability and bioavailability, primarily due to its exceptionally high lipophilicity (Table V. 1) (Akinboye et al., 2024).

In this study, oUVFs were detected in the outer blubber layer of both species, which is consistent with their physicochemical properties (Table V. 1), allowing them to strongly bind to fatty tissues. (Bagge et al., 2012; Ellisor et al., 2013). Blubber stratification varies by species (Budget et al., 2008). Sperm whales, which migrate through cold and warm waters, have more stratified blubber with waxes predominant in the outer layers, providing better insulation (Koopman, 2007; Bagge et al., 2012; Lefort et al., 2022). In contrast, short-finned pilot whales are subtropical, experience stable temperatures, and show less blubber stratification dominated by triglycerides (Westell et al., 2022; Thorne et al., 2017; Bagge et al., 2012; Lonati et al., 2019). Some oUVFs, like OC, can form conjugates with fatty acids, as observed in ragworms and corals (Thorne et al., 2017; Clergeaud et al., 2022), suggesting UV-360 may bind more strongly to fatty acids in sperm whales' blubber than in pilot whales (Fig. V. 2).

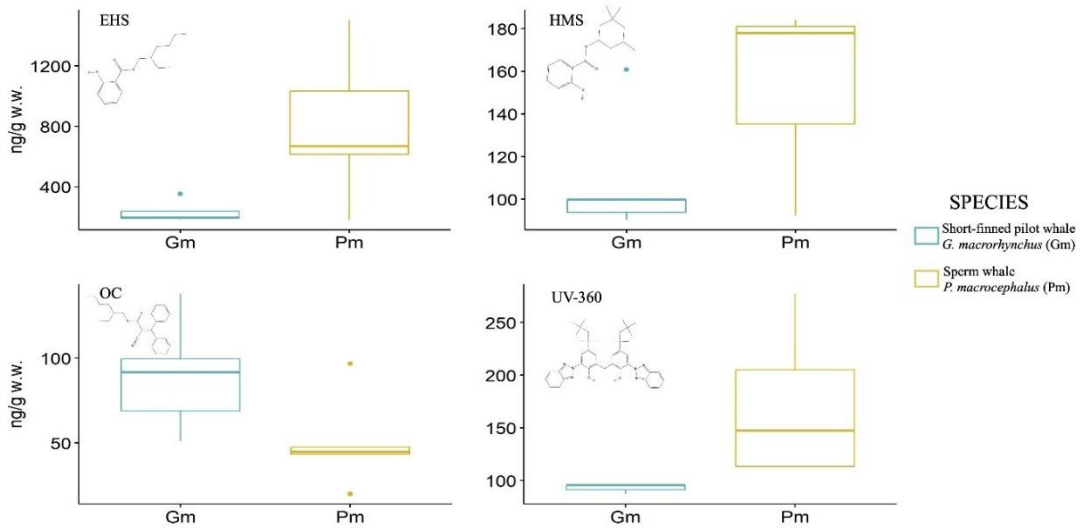

Fig. V. 2. Boxplots representing the distribution of four organic UV filters (oUVFs), EHS, HMS, OC, and UV-360, detected in both species. The line within each box represents the median value, while the bars indicate the range. Single dots represent individual data points.

Contaminants in these species may be acquired directly through diet and marine litter ingestion, or indirectly via atmospheric transport, maternal transfer, and dermal absorption (Rani et al., 2017; Bachman et al., 2014; Alonso et al., 2015; Blouin et al., 2022). Skin absorption is particularly relevant given the time both species spend at the surface, where the surface microlayer, a pollutant-rich boundary layer with high organic content, can serve as a major source of organic compounds (Hill et al., 2019; Guerra et al., 2023; Tsui et al., 2014; Caloni et al., 2021).

Among the compounds detected in this study, three - the HMS, EHS, and the OC are oUVFs with comparable lipophilicity (Table V. 1). These compounds are widely used in European cosmetic production (Cadena-Aizaga et al., 2020; European Union Annex XVI 2022/2197; Medici et al., 2022). Comparative data from other studies show that EHS has rarely been detected in cetaceans and was previously reported only in belugas, while HMS has only been reported in belugas and spinner dolphins (*Stenella longirostris*) (Blouin et al., 2022; Combi et

al., 2022). OC is the most frequently reported oUVF in cetaceans, having been detected in multiple studies (Gago-Ferrero et al., 2013; Alonso et al., 2015; Blouin et al., 2022; Combi et al., 2022; González-Bareiro et al., 2023). Belugas from the St. Lawrence Estuary exhibited lower HMS and EHS concentrations in blubber than the species examined in the present study (Blouin et al., 2022). In contrast, free-ranging spinner dolphins from Fernando de Noronha Island, Brazil, showed higher HMS concentrations than both deep-diving species and belugas (Combi et al., 2022). A similar trend was observed for OC, with spinner dolphins displaying the widest concentration range (n.d.–172.7 ng/g w.w.) (Combi et al., 2022). Other coastal species, such as the Guiana (*Sotalia guianensis*) and Franciscana dolphins (*Pontoporia blainvillei*) highly linked to populated coastal waters in Brazil, exhibited slightly lower OC levels in blubber (n.d.–94.58 ng/g w.w. and n.d.–70.40 ng/g w.w., respectively) compared to the results of this study (Table V. 3) (Alonso et al., 2015).

Moreover, it must be taken into consideration that free-ranging animals are generally considered healthy, while stranded animals are often in poor condition, experience tissue degradation, transformation, or excretion of compounds, which can affect the detectable concentrations of compounds (Bossart, 2010; Williams et al., 2023).

Variations in oUVFs concentration across species and locations may reflect differences in anthropogenic coastal pressures and species-specific distribution patterns (Combi et al., 2016; Prakash & Anbumani, 2021; Medici et al., 2022). For example, Gago-Ferrero et al. (2013) found higher OC concentrations in Franciscana dolphin livers collected along the Brazilian coast, where direct inputs are more prevalent, compared to samples near São Paulo, where indirect sources dominate. Tourist destinations such as Fernando de Noronha and Madeira Islands are heavily influenced by recreational marine activities, likely making direct UVF emissions the primary input source (Combi et al., 2022; Rizzi et al., 2023). In contrast, in colder regions like the St. Lawrence Estuary that have fewer human recreational activities, oUVFs

mainly enter through indirect pathways (Downs et al., 2022). This study does not account for oUVFs transformation products, which may also contribute to contamination (Díaz-Cruz et al., 2008; Pestotnik et al., 2014), as direct inputs tend to occur in larger quantities and undergo less degradation than indirect sources. Declines in oUVFs concentrations during the COVID-19 pandemic, when tourism was greatly reduced (Downs et al., 2024), support this hypothesis. These findings highlight the need for further research that explicitly considers tourism pressure as a contributing variable (Combi et al., 2022; Kwon & Choi, 2021).

Additionally, this study shows variation in the total concentration of oUVFs per individual in both species. Sperm whales showed a wider range (n.d. – 1782 ng/g w.w.) than those observed in short-finned pilot whales (246.6-746.2 ng/g w.w.). However, the latter exhibited a higher FO of oUVFs with HMS and OC in 100% of the samples, compared to the former species (Table V. 2; Fig. V. 2). These differences may be attributed to variations in their distribution range, feeding ecology, site fidelity, and behaviour, all of which influence exposure to oUVFs in the environment (Tsui et al., 2017; Rizzi et al., 2023; Aguilar de Soto and Alves, 2023; Shetty et al., 2023).

The fact that short-finned pilot whales in Madeiran waters present a high island-association distribution (Alves et al., 2013, 2019) may increase their chronic exposure to coastal oUVFs inputs due to the constant link to the same area (Alonso et al., 2015). This may be the reason why the FO is higher in this specie. Moreover, some oUVFs, like OC, resist degradation and can even reach pelagic and deep-sea habitats (Medici et al., 2022; Grant et al., 2025). In contrast, sperm whales, with their broader distribution and long-range migrations, may be more indirectly exposed to coastal pollutants (Ferreira et al., 2022; Guerra et al., 2023). The BUVS and oUVFs have been found in deep-sea environments and are linked to benthic systems, considered final sink destinations for organic pollutants (Wang et al., 2022; Apel et al., 2018; Parra-Luna et al., 2020; Akinboye et al., 2024; Pinheiro et al., 2023; Combi et al., 2016;

Moualek et al., 2024). Sperm whales primarily forage in benthic and bathypelagic zones (Guerra et al., 2022; Westell et al., 2022), while pilot whales in Madeira target pelagic prey (Escánez et al., 2024; Íñiguez et al., 2025). This difference may explain the higher average of most contaminant levels in sperm whales (Fig. V. 2).

Table V. 3. Summary of the organic UV filters (oUVFs) and benzotriazole ultraviolet stabilizers (BUVSs) detected in cetaceans worldwide, along with their reported concentration ranges. The (*) indicates the compounds that were included in this study.

Scientific name	Location	Animal status	oUVFs/BUVSs	Tissue	Concentration range (ng/g w.w.)	References
Neophocoena phocaenoides	Ariahe Sea (Western Japan)	Stranded and accidentally caught by a fishing net	UV327	Blubber	4.1-31	Nakata et al., 2010
			UV328		11-64	
			UV320		< 0.05	
Pontoporia blainvillei	Espirito Santo (Brazil)	Stranded (calves, juveniles, and adults)	OC*	Liver	n.d-39.16	Gago-Ferrero et al., 2013
	São Paulo (Brazil)				n.d-28.82	
	Paraná (Brazil)				n.d-7.10	
	Sta Catarina (Brazil)				n.d-22.10	
	Rio Grance do Sul (Brazil)				n.d-43.01	
Sotalia guianensis	Southeast and Northeastern Brazil coast	Stranded (pregnant females)	OMC*	Blubber	15.36-65.6	Alonso et al., 2015
				Muscle	3.97-30.90	
			4-MBC*	Blubber	n.d-15.36	
				Muscle	13.04-32.32	
			OD-PABA*	Blubber	n.d-10.88	
				Muscle	n.d.-59.54	

Scientific name	Location	Animal status	oUVFs/BUVSs	Tissue	Concentration range (ng/g w.w.)	References
Pontoporia blainvillei			OC*	Blubber	n.d-70.4	
				Muscle	55-471.18	
			OMC*	Blubber	n.d.-489.65	
				Muscle	2.26-3.54	
			4-MBC*	Blubber	n.d.-39.76	
				Muscle	n.d.-44.89	
			OD-PABA*	Blubber	n.d.-2.64	
				Muscle	n.d.	
			OC*	Blubber	n.d.-94.58	
				Muscle	n.d.	
Tursiops truncatus	North America	Free-ranging	UV234	Blood	n.d-0.16	Lu et al., 2019
			UV328		n.d-0.54	
			UV329		n.d-0.86	
Stenella longirostris	Ilha de Fernando de Norona (Brazil)	Free-ranging	OC*	Blubber	n.d.-172.65	Combi et al., 2022
			HMS*		n.d.-125.48	
			OMC*		n.d.-147.1	

Scientific name	Location	Animal status	oUVFs/BUVSs	Tissue	Concentration range (ng/g w.w.)	References
Delphinapterus leucas	St. Lawrence Estuary	Stranded (adults, clasified as males and females)	BP	Blubber	n.d. - 10.8	Blouin et al., 2022
				Liver	n.d. - 13.8	
			BP-3*	Blubber	n.d.- 1170	
				Liver	n.d. - 13.20	
			4-MBC*	Blubber	n.d. - 41	
				Liver	n.d. - 1120	
			HMS*	Blubber	n.d. - 50.6	
				Liver	n.d. - 1120	
			EHS*	Blubber	n.d.- 23.1	
				Liver	n.d.	
			OC*	Blubber	n.d.	
				Liver	n.d.	
			OMC*	Blubber	n.d. - 315	
				Liver	n.d.	
			UVP	Blubber	n.d. - 24.1	
				Liver	n.d.	
			UV9	Blubber	n.d. - 217	

Scientific name	Location	Animal status	oUVFs/BUVSs	Tissue	Concentration range (ng/g w.w.)	References
				Liver	n.d.	
			UV090	Blubber	n.d. - 283	
				Liver	n.d. - 11.6	
			UV234	Blubber	n.d.	
				Liver	n.d.	
			UV320	Blubber	n.d. - 25.3	
				Liver	n.d.	
			UV326	Blubber	n.d.-10.5	
				Liver	n.d. - 35	
			UV327	Blubber	n.d. - 1560	
				Liver	n.d.	
			UV328	Blubber	n.d.- 75.5	
				Liver	n.d.	
			UV329	Blubber	n.d. - 370	
				Liver	n.d.	
			UV350	Blubber	n.d. - 2.50	
				Liver	n.d.	

Scientific name	Location	Animal status	oUVFs/BUVSs	Tissue	Concentration range (ng/g w.w.)	References
Tursiops truncatus	Canary Islands	Stranded	OC*	Blubber	13.15-27	González-Bareiro et al., 2023
			BP-3*		n.d.-1.48	
			IMC*		n.d-2.14	
Globlicephala macrorhynchus	Madeira Island, Portugal	Free-ranging	HMS*	Blubber	95.5-160.9	Present study
			OC*		51.3-137.7	
			UV-360*		n.d.-95.50	
			EHS*		n.d.-352.3	
Physeter macrocephalus			HMS*		n.d.-184.2	
			OC*		n.d.- 96.70	
			UV-360*		n.d.-276.9	
			EHS*		n.d.-1505	

4. Conclusion

This study provides the first evidence of oUVFs contamination in free-ranging individuals of two deep-diving cetacean species around Madeira Island. The presence of these compounds appears to be influenced by their direct and indirect release pathways, species site fidelity, and significant coastal anthropogenic impact, highlighting their widespread distribution and potential for long-range transport. However, the limited sample size restricts a detailed analysis, and definitive conclusions about population-level exposure and risk. Including variables like total lipid content and temporal sampling variability that would offer deeper insight into the true impact of oUVFs. Thus, these findings should be interpreted cautiously and seen as a preliminary hypothesis on how oUVFs reach top marine predators, including deep-sea pelagic species.

Supplementary material

Supplementary data can be found online at the following URL: https://doi.org/10.1016/j.envpol.2025.126830 (APPENDIX D).

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CHAPTER VI

General Discussion, Final Conclusions, and Future Perspectives

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1. General Discussion

Monitoring activities constitute a fundamental first step in conducting a risk assessment of CECs, including oUVFs. Such efforts are crucial for establishing baseline environmental concentrations, identifying vulnerable taxa, and characterizing the chemical behaviour and distribution of these compounds. Additionally, monitoring enables the identification of major sources and the human activities responsible for their release (Azaroff et al., 2020). The interaction of multiple stressors, including contamination, in marine ecosystems leads to degradation and a loss of functionality, thereby increasing the likelihood of a significant decline in marine resources needed for human well-being.

Throughout this work, several key knowledge gaps have been identified related to the presence and distribution of oUVFs in the marine environment. This thesis aims to address these gaps, contributing to research aligned with the United Nations Sustainable Development Goals, specifically goal 14: "Conserve and sustainably use the ocean, seas and marine resources for sustainable development".

This thesis was guided by a set of research questions addressing the spatial distribution, trophic transfer, and ecological relevance of organic UV filters in oceanic island systems. The following discussion integrates the results presented in Chapters II-V to address these questions in a system-level context.

1) The limited availability of studies across a wide range of taxa.

The complexity of environmental samples further highlights the need for improved analytical protocols to ensure reliable extraction, detection, and quantification of target

compounds across different matrices. However, research remains concentrated on a few taxa, mainly mussels and anthozoans (Hodge et al., 2025). Despite the well-known interconnectedness of marine ecosystems, research on primary producers and base trophic levels remains limited, even though groups such as zooplankton also play a critical role in the distribution and accumulation of oUVFs and may serve as indicators of water quality (Lomartire et al., 2021). Only one study reports data for freshwater zooplankton (Yang et al., 2020). The remaining research efforts have been focused toxicological effects in different organisms, including phytoplankton and zooplankton species such as the microalgae *Tetraselmis* sp. and the copepod Artemia salina, widely used as a source of food in aquaculture (Thorel et al., 2020), although the main toxicological tests have been done with Daphnia, which is the usual model species (Park et al., 2017; Marcin and Aleksander, 2023; Boyd et al., 2024).

Chapter II addressed this gap by providing the first optimized methodology for detecting and quantifying eleven oUVFs in marine zooplankton. Although additional refinements could further improve recovery efficiencies, this represents a significant step towards expanding oUVF monitoring to a key group of organisms that support marine trophic webs. Zooplankton communities include multiple early life stages (e.g., larvae) of diverse taxa, which can be particularly sensitive to chemical stressors. Exposure to oUVFs and co-occurring contaminants may therefore affect development, survival, and recruitment, with potential downstream consequences for biomass and community structure. For this reason, extending monitoring to zooplankton is important for evaluating ecosystem health and for contextualising contaminant transfer at the base of marine trophic webs (Corinaldesi et al., 2017; Lomartire et al., 2021; Thorpe, 2024).

2) Assess the relative contribution of different oUVF input sources and characterise oUVF behaviour in coastal and offshore areas.

As discussed throughout this thesis, oceanic islands such as Madeira offer a strategic natural laboratory for studying oUVFs along continental margins and within submarine canyon systems. These islands, considered biodiversity hotspots (McIvor et al., 2022), provide relatively easy access to both coastal shelves and offshore environments, enabling the assessment of pollutant transport across broad depth gradients. In addition, human pressure is easier to quantify, particularly in regions where tourism, one of the main sources of oUVF emissions, is the dominant economic activity (Vitousek, 2002; de Almeida et al., 2019). The release of oUVFs is closely tied to the expansion of tourism; international travel and human mobility have been projected to increase substantially by 2035. Estimates indicate that global sunscreen production reached around 10,000 tons, with UV filters representing around 30% of the formulation. The combination of intense tourism in coastal areas and public health recommendations encouraging sunscreen use has generated substantial pressure on marine ecosystems, contributing to the disruption of their fragile ecological balance (Caloni et al., 2021; Damikouka et al., 2024).

Chapters III and IV further advance this understanding by characterizing the presence and concentrations of eleven oUVFs across coastal, offshore, and deep-sea ecosystems of Madeira. The coastal zones showed the strongest influence of human activities, with oUVF inputs largely associated with the use and wash-off of PCPs containing oUVFs, together with contributions from insufficient wastewater treatment (Downs et al., 2024). A positive relationship was observed between oUVF presence and the degree of human pressure along the coast, with higher occurrence at sites subject to greater direct use, even in marine-protected areas where the anthropogenic activities are restricted (Azcune et al., 2022). In particular, OC showed higher occurrence and/or concentrations at coastal sites with greater recreational use, a spatial pattern consistent with direct inputs via sunscreen wash-off. However, without source-specific tracers or temporal/source profiling, this pattern should be interpreted as an association rather

than definitive source attribution. In contrast, EHS was more frequently detected at sites potentially influenced by wastewater pathways (*e.g.,* areas receiving treated effluents), suggesting that WWTP-related discharges may contribute to its presence. Nonetheless, this remains an indicative interpretation in the absence of complementary evidence (*e.g.*, sewage markers, outfall proximity gradients, or diagnostic compound ratios). These findings clarify how different release sources contribute to the presence and distribution of specific oUVFs in the environment.

Several species representing different habitats were analysed to identify the affinities and accumulation patterns of various oUVFs. Higher quantifiable concentrations were detected in zooplankton and algae, as well as in herbivorous fish species that directly depend on them for food. Previous research has shown that benthic organisms tend to be more vulnerable to oUVF accumulation (Wang et al., 2022). This study supports those findings and further indicates that sessile organisms, such as algae, appear to act as more effective reservoirs than mobile benthic invertebrates, such as sea urchins or sea cucumbers. This output is important because algae are essential for the ecosystem's sustainability, mainly due to the role of refuge, food, and nursery areas (Alves et al., 2019). In Madeira, the algae populations are threatened by several impacts. One of the most important ones was an unregulated proliferation of sea urchins that has resulted in the formation of "barren grounds," characterized by extensive loss of algal cover (Bernal-Ibáñez et al., 2021). Moreover, the arrival and colonization of the invasive species *Rugulopteryx okamurae* has led to a significant reduction in native algal species, hence the refuge and food sources of several biota species (Bernal-Ibáñez et al., 2022). Many of these species face not only habitat alteration but also contamination, which may compromise their health and reproductive capacity, as is the case for the *Sarpa salpa*, which was the fish species most affected in coastal areas. These ecological disturbances highlight the need for an integrated evaluation of anthropogenic impacts on coastal areas. Without such assessment and

management, these pressures may contribute to the loss of multiple species, including commercially valuable ones (Miranda et al., 2021).

The surface microlayer can preferentially concentrate lipophilic chemicals such as oUVFs and is also exposed to atmospheric inputs and intense coastal disturbance, making it an initial accumulation layer for pollutants, including oUVFs and microplastics. This layer presents a close relation with zooplankton because zooplankton undergoes diel vertical migrations, ascending to surface waters at night (Bandara et al., 2021). These nocturnal interactions increase the interaction of zooplankton with the anthropogenic pollutants associated with this layer. Even in oligotrophic offshore waters, where suspended organic matter is minimal and physical processes associated with Madeira's steep slope could act as dilution mechanisms, zooplankton showed persistent oUVFs presence in similar concentrations to those samples collected closer to the coast. This extended impact in offshore waters caused by anthropogenic pressure on the coast has also been observed in offshore coral reefs (Pei et al., 2023). However, pelagic organisms distributed along the water column seem to be less affected. This appears to follow a pattern in which oUVFs accumulate in zones where organic matter is abundant; therefore, organisms associated with habitats that follow this pattern are more affected, showing higher oUVF concentrations.

3) Explore the presence of oUVFs in deep-sea habitats.

The impact of oUVFs is not restricted to coastal or surface environments. According to the previously explained pattern, comparable concentrations were detected in bathypelagic organisms, such as the black scabbardfish.

In higher trophic levels, particularly in deep-sea predators, accumulation likely results from their reliance on prey inhabiting what is often described as the deep-sea floor "reservoir" of

organic chemicals (Pinheiro et al., 2023). As discussed in Chapter IV, deep-sea sediments reflect clear human pressure, acting as sinks for organic contaminants such as oUVFs (Combi et al., 2016). Considering that the black scabbardfish is a top predator closely associated with the seafloor, this species becomes an important indicator of oUVF presence in the deep sea.

Furthermore, the black scabbardfish, together with offshore zooplankton samples, were the matrices that exhibited the widest range of oUVFs detected at quantifiable concentrations. This is consistent with previous statements indicating that zones within the water column characterized by higher accumulations of organic matter tend to present elevated concentrations of organic chemicals, including oUVFs. However, as discussed in Chapter IV, the occurrence of oUVFs in deep-sea habitats remains largely unexplored. Assessing their presence and quantification in these environments is essential to anticipate potential increases in their release through resuspension driven by human activities occurring at such depths, including bottom trawling and deep-sea mining. Fortunately, such activities are not practised in the Madeira Archipelago.

Top predators, including several cetacean species, are indicator species that can be used to assess environmental risks and infer potential impacts on human health, as they occupy comparable positions in the trophic web. Deep-diving cetaceans occupy ecological niches that span the entire water column, effectively linking surface waters with the deep sea (Kiszka et al., 2015, 2022). Hence, they represent a significant source of organic matter and potential vectors of contaminants to the deep sea via natural carbon flux pathways, including whale-fall events described in the literature. Although this mechanism is conceptually consistent with deep-sea contaminant transfer, it was not directly evaluated in this thesis. Their ecological roles, as well as the relevance of investigating oUVFs in these species, are further detailed in Chapter V.

Studying deep divers and deep species provides valuable insights into the behaviour of some oUVFs, such as EHS, HMS, and OC, which were detected in nearly all matrices. Their presence highlights the persistence and/or transfer of these compounds through the food web, consistent with trophic transfer and warrants targeted biomagnification assessment. Additionally, deep-diving cetaceans exhibit diverse residency patterns, migrations, and foraging behaviours, which influence their continuous exposure to oUVF inputs and increase the likelihood of storing these compounds in lipid-rich tissues, as discussed in Chapter V.

Marine mammals represent an excellent choice for monitoring organic contaminants in the marine environment for several reasons. First, small tissue samples, without requiring the collection of entire animals, can provide robust information, which can be complemented by samples obtained from stranded individuals. Second, their contaminant concentrations reflect ongoing accumulation processes, making them reliable sentinels of short and long-term exposure to organic chemicals. Finally, their position at the top of the trophic web is comparable to the human position, being a good indicator for human health in terms of intake and exposure. Altogether, these characteristics reinforce the value of marine mammals, especially deep-diving species, as bioindicators for assessing the environmental distribution, trophic transfer, and potential ecological risks associated with oUVFs (Bossart, 2011).

This thesis provides a comprehensive assessment of the presence, distribution, and ecological implications of oUVFs across an oceanic island system, spanning from coastal habitats to deep-sea ecosystems. By combining methodological expansion with multi-trophic and multi-matrix analyses, this work establishes a foundational understanding of how these emerging contaminants enter, move through, and persist within the marine environment.

The methodological optimisation developed in Chapter II represents a major contribution to the field, enabling the extraction and quantification of oUVFs from zooplankton, a taxonomic group that had never been analysed for these compounds despite its ecological

relevance. This advancement enabled the exploration of the earliest stages of contaminant incorporation into the marine food web.

Chapters III and IV demonstrate that oUVFs are widely distributed across coastal and offshore ecosystems, with concentrations closely linked to human activity and to the presence of organic-rich environments. Their detection in water, sediments, zooplankton, algae, and, fish highlights both their ubiquity and their capacity to be transferred through the trophic chain. The consistent detection of specific compounds (*e.g.*, EHS, HMS and OC) along the entire water column further suggests persistence and mobility that had not been previously documented in remote oceanic systems.

The findings presented in Chapter IV and V reveal that deep-sea predators and deep-diving cetaceans also accumulate oUVFs, indicating that these contaminants reach the most remote and least accessible components of the marine ecosystem. The trophic position, feeding strategies, and wide vertical distribution of these species make them particularly informative bioindicators for long-term exposure and for evaluating potential biomagnification processes.

In general, this work provides a broad perspective on the potential distribution of oUVFs, from their release into coastal ecosystems to their eventual storage in deep-sea environments. Several taxa have been identified as potential bioindicators for future toxicological testing and for assessing overall ecosystem health. Although biomagnification patterns were not explored in depth, three compounds were consistently detected and quantified throughout the entire water column. This finding offers important guidance for future management measures, including considerations for their regulation in PCP formulations. Moreover, the detection of oUVFs in species of commercial interest provides valuable information for evaluating potential dietary exposure, supporting the development of consumption advisories aimed at reducing the risk of accumulated concentrations that could impact human health.

Overall, the results of this thesis demonstrate that oUVFs are global contaminants capable of reaching even the most remote oceanic environments. Their presence, from the coastal zone to deep-sea predators, underscores the need for further research, improved regulatory frameworks, and continuous environmental monitoring to better understand and mitigate their ecological and human health risks.

2. Final Conclusions

1) The limited availability of research across a broad range of taxa hampers the accurate assessment of the presence of oUVFs in marine ecosystems and the evaluation of their potential toxicological effects at environmentally relevant concentrations. Multi-species matrices, such as those comprising zooplankton, can act as key ecological compartments, providing valuable insights into the occurrence and distribution of oUVFs in the marine environment. To achieve this, it is essential to develop and optimize analytical methodologies that allow for the reliable detection and quantification of these target compounds.
2) Human pressure in coastal areas contributes significantly to increase oUVF inputs and concentrations. Direct inputs resulting from coastal activities, often intensified by tourism, promote the introduction of a wide range of oUVFs and lead to elevated concentrations in coastal ecosystems. although source attribution could not be confirmed without complementary tracers. OC showed higher occurrence and/or concentrations at more intensively used coastal locations, supporting an association with recreation-related inputs.
3) Indirect sources and/or locations with lower direct human pressure appear to be less affected by the presence of oUVFs. However, due to the intermediate processes that these compounds undergo before reaching the marine environment, such as wastewater

treatment, industrial discharges, runoff, or dumping, the original chemical structures may be altered, leading to the formation of transformation products. These transformation processes can complicate the interpretation of oUVF contamination patterns and may influence their potential environmental impacts.

4) Surface seawater samples contain a wider variety of oUVFs, although generally at low concentrations. This is largely because surface waters are the first matrix to come into direct contact with release sources; however, the physicochemical properties of oUVFs, particularly their high lipophilicity, favour their association with solid or lipid-rich matrices rather than remaining dissolved in the water column. Oceanographic dynamics (tides, currents, upwelling, island-mass effects), sediment characteristics (rocky reefs, grain size, and sediment composition), and transformation processes further contribute to the frequent near-absence of detectable oUVFs in coastal sediments, consistent with the absence of detectable concentration in detritivores species such as sea cucumbers in Madeira. Overall, the prevailing pattern suggests that these compounds tend to accumulate in deep-sea sediments.

5) Benthic sessile species, such as macrophytes, appear to be particularly susceptible to the accumulation of oUVFs. This is likely due to their continuous exposure because of their proximity to coastal release sources, making them valuable bioindicators of oUVF presence. Furthermore, fish species that directly feed on macrophytes, such as salema, show higher concentrations of these compounds in their tissues, suggesting potential bioaccumulation. These findings identify benthic ecosystems as important reservoirs of oUVFs.

6) In coastal areas, seawater showed the presence of BP-3, DTS, and BMDBM, which were detected in seawater but not in the other coastal matrices analysed, this pattern may indicate rapid transformation and/or preferential partitioning away from the dissolved

phase. Their detection in black scabbardfish is compatible with vertical transport and/or persistence associated with sinking vectors (e.g., organic matter or plastics), which could facilitate transfer towards deeper compartments. In contrast, HMS and EHS were detected in all coastal samples analysed, suggesting greater persistence and/or resistance to transformation under the conditions assessed. Additionally, OC exhibited a strong affinity for biota matrices, showing higher occurrence and/or concentrations in lipid-rich tissues.

7) In offshore areas, the water-column layers with higher concentrations or accumulations of suspended organic matter shape the pattern of oUVF occurrence at quantifiable levels. This is supported by the higher concentrations observed in zooplankton collected from surface waters (both coastal and pelagic) and in the bathypelagic black scabbardfish. In contrast, pelagic organisms whose habitat is restricted to mid-water layers showed considerably lower concentrations, as observed in skipjack tuna, Atlantic chub mackerel, and blue jack mackerel. This pattern may also be influenced by the role of oUVF vectors, potentially including microplastics, which have been reported to accumulate these compounds at the surface and, through vertical transport processes, described in the literature *e.g.,* via organism movement and particle sinking), may contribute to their transfer to deeper habitats. This mechanism was not directly assessed in the present thesis and warrants targeted investigation.

8) Black scabbardfish exhibited quantifiable concentrations of 4-MBC, an oUVF that is restricted and/or banned in several jurisdictions for use in PCPs. This specie also showed the greatest diversity of oUVFs (together with zooplankton), supporting the idea that these compounds may follow patterns like other well-studied POPs, for which the deep-sea floor acts as a major sink. Given the high commercial relevance of black scabbardfish, its contamination profile positions it as a potential indicator of human exposure through

consumption and highlights the need to evaluate ingestion-related toxicity associated with oUVFs.

9) Deep-diving cetaceans showed the highest concentrations of total oUVFs, with the main representation of EHS, HMS, and OC being the three most frequently detected and quantified compounds across all matrices. This finding highlights the potential for bioaccumulation and trophic transfer of these substances within deep-sea trophic webs, although biomagnification cannot be concluded without dedicated food-web modelling and trophic metrics.

10) The first detection and quantification of UV-360 in deep-diving cetaceans, likely facilitated by its extremely lipophilic properties, illustrates how different compounds can exhibit distinct behaviours and affinities within marine ecosystems. This underscores the need to investigate oUVFs across a broader range of taxa to fully understand their distribution and ecological implications.

11) Distribution patterns, trophic niche differences, and migration behaviours influence exposure levels and, consequently, the concentrations of oUVFs accumulated in the tissues of different cetacean species. Short-finned pilot whales, which are closely associated with oceanic island systems and frequently exploit deep-sea environments for feeding, are therefore more continuously exposed to human-derived inputs of oUVFs and exhibited higher proportions of contaminated individuals. In contrast, sperm whales, although migratory in the region, feed in deeper, bottom-associated habitats and consequently showed higher oUVF concentrations, likely reflecting their foraging behaviour and the pollutant load of deep-sea ecosystems.

12) Deep-diving cetaceans are valuable sentinel species for monitoring oUVFs due to their lifestyle, which links the deep sea with surface waters. Moreover, their role as top

predators positions them as effective umbrella species in conservation and management strategies, helping to safeguard broader marine ecosystems.

3. Future Perspectives

Despite the extensive monitoring conducted in this thesis, significant knowledge gaps remain, highlighting the need for further research, management strategies, and regulatory actions.

1) Future studies should focus on standardized protocols for monitoring and laboratory analyses that are essential to enable global assessments of oUVF occurrence, persistence, and toxic potential in the short and long term. This would contribute to comparisons between studies; furthermore, improvements in analytical methodologies are needed to achieve better recoveries and avoid matrix effects.
2) Research should also expand beyond regions with high direct usage, addressing areas where PCPs are less prevalent but where oUVFs may accumulate due to long-range transport. Offshore and deep-sea environments, which may act as contaminant reservoirs, remain largely unexplored and merit focused investigation.
3) Given that microplastics can act as vectors for oUVFs and other contaminants, and that chemical interactions may appear among co-occurring pollutants, future studies should assess the combined presence, behaviour, and toxicity of these mixtures. Research should also move beyond individual compounds to consider whole product formulations, which are directly released into ecosystems and may exhibit different environmental behaviours.
4) Toxicological studies should include a wider range of taxa, while bioaccumulation and biomagnification patterns in top predators should be investigated to evaluate ecological risks and potential human health implications from seafood consumption. Addressing these points will provide a more comprehensive understanding of oUVFs in marine ecosystems and guide effective conservation and management strategies for future regulations.

5) Identifying appropriate biomarkers can yield important insights into the toxicological impact on wild biota.

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APPENDICES

Rodrigo Pires da Silva

APPENDIX A – Supplementary data for Chapter II

Appendix A consists of the supplementary data associated with the published article:

Íñiguez, E., Gouazé, M., Dinis, A., Sosa-Ferrera, Z., Cordeiro, N., Kaufmann, M., and Montesdeoca-Esponda, S. (2026). Development and preliminary validation of an analytical methodology for the determination of organic UV filters in zooplankton samples. *Marine Pollution Bulletin*, *225*, 119204.

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APPENDIX A – Supplementary Data to Chapter II

Table II. SM1. Concentration (ng/g d.w.) of each target compound detected per sample. Sample characteristics according to the locations and the zone where they were collected.

Sample code	BP-3	HMS	DTS	OC	OD-PABA	EHS	Location	Zone	Collected data
LM1P	658.5	232.2	116.4	n.d.	n.d.	n.d.	LM	Pelagic	16/04/2023
LM2P	390.7	228.0	193.2	n.d.	n.d.	n.d.	LM	Pelagic	16/04/2023
LM3P	n.d.	n.d.	93.76	n.d.	n.d.	n.d.	LM	Pelagic	16/04/2023
LM4P	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	LM	Pelagic	18/08/2023
LM5P	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	LM	Pelagic	18/08/2023
LM6P	n.d.	67.55	n.d.	48.96	n.d.	n.d.	LM	Pelagic	18/08/2023
LM1C	n.d.	45.78	n.d.	n.d.	34.10	n.d.	LM	Coastal	16/04/2023
LM2C	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	LM	Coastal	16/04/2023
LM3C	n.d.	9.503	n.d.	72.65	263.0	n.d.	LM	Coastal	16/04/2023
LM4C	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	LM	Coastal	18/08/2023
LM5C	n.d.	27.07	n.d.	249.5	287.4	n.d.	LM	Coastal	18/08/2023
LM6C	n.d.	92.89	n.d.	78.96	n.d.	n.d.	LM	Coastal	18/08/2023
FX1P	101.3	n.d.	n.d.	146.9	n.d.	38.16	FX	Pelagic	02/03/2023
FX2P	289.4	29.55	n.d.	26.85	n.d.	51.31	FX	Pelagic	02/03/2023
FX3P	242.4	51.84	n.d.	24.01	180.2	n.d.	FX	Pelagic	02/03/2023
FX4P	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	FX	Pelagic	14/08/2023
FX5P	n.d.	249.1	n.d.	1003	n.d.	n.d.	FX	Pelagic	14/08/2023
FX6P	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	FX	Pelagic	14/08/2023
FX1C	n.d.	287.1	n.d.	n.d.	n.d.	n.d.	FX	Coastal	02/03/2023
FX2C	n.d.	350.4	n.d.	n.d.	n.d.	n.d.	FX	Coastal	02/03/2023
FX3C	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	FX	Coastal	02/03/2023
FX4C	n.d.	130.9	n.d.	n.d.	n.d.	n.d.	FX	Coastal	14/08/2023
FX5C	n.d.	219.5	n.d.	735.9	n.d.	n.d.	FX	Coastal	14/08/2023
FX6C	n.d.	n.d.	n.d.	1029	n.d.	n.d.	FX	Coastal	14/08/2023
DS1P	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	DS	Pelagic	12/06/2023
DS2P	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	DS	Pelagic	12/06/2023

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Sample code	BP-3	HMS	DTS	OC	OD-PABA	EHS	Location	Zone	Collected data
DS3P	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	DS	Pelagic	12/06/2023
DS4P	n.d.	28.29	n.d.	52.07	n.d.	n.d.	DS	Pelagic	03/12/2023
DS5P	n.d.	n.d.	n.d.	62.30	<LOQ	n.d.	DS	Pelagic	03/12/2023
DS6P	n.d.	16.98	n.d.	n.d.	n.d.	n.d.	DS	Pelagic	03/12/2023
DS1C	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	DS	Coastal	12/06/2023
DS2C	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	DS	Coastal	12/06/2023
DS3C	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	DS	Coastal	12/06/2023
DS4C	n.d.	<LOQ	n.d.	56.47	n.d.	n.d.	DS	Coastal	03/12/2023
DS5C	<LOQ	18.99	n.d.	110.8	<LOQ	n.d.	DS	Coastal	03/12/2023
DS6C	<LOQ	33.04	n.d.	47.81	n.d.	n.d.	DS	Coastal	03/12/2023

n.d: not detected; < LOQ: Below Limit of Quantification; FX: Funchal; LM: Lombada dos Marinheiros; DS: Desertas

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Table II. SM2. Physicochemical properties of the selected oUVFs (Íñiguez et al., 2025).

Chemical family	INCI name	Abbreviation	CAS N°	$LogK_{ow}$	Solubility (g/L)
Benzophenones	Benzophenone-3	BP-3	131-57-7	3.79	0.21
Salicylates	Ethylhexyl dimethyl PABA	OD-PABA	21245-02-3	6.15	$2.1x10^{-3}$
	Homosalate	HMS	118-56-9	6.16	0.02
	Ethylhexyl salicylate	EHS	118-60-5	5.97	0.028
Cinnamates	Ethylhexyl methoxycinnamate	OMC	5466-77-3	5.8	0.15
	Isoamyl p-methoxycinnamate	IMC	71617-10-2	4.33	0.06
Camphor derivatives	4-methylbenzylidene camphor	4-MBC	36861-47-9	3.83	0.014
Benzotriazoles	Drometrizole trisiloxane	DTS	155633-54-8	10.82	$1.3x10^{-5}$
	Methylene bis-benzotriazolyl tetramethylbutylphenol	UV-360	103597-45-1	12.46	$3x10^{-8}$
Dibenzoylmethane derivatives	Butyl methoxydibenzoylmethane	BMDBM	70356-09-1	4.51	0.037
Crylenes	Octocrylene	OC	6197-30-4	6.88	$2x10^{-4}$

INCI: International Nomenclature of Cosmetic Ingredients; CAS No.: Chemical Abstracts Service registry number; LogKow: Octanol-water partition coefficient (indicative of hydrophobicity); Solubility: Solubility of the compound in water (g/L)

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Table II. SM3. Multiple-reaction monitoring (MRM) transitions for the target organic UV filters (oUVFs) and the internal standard. All transitions were acquired by ESI on a Waters instrument; full source settings are reported in the Methods section.

oUVFs	Parent ion (m/z)	Cone voltage (V)	Quantification ion (m/z)	Collision potential (V)	Confirmation ion (m/z)	Collision potential (V)
4-MBC	255.4	25	105.0	27	171.0	19
BP-3	229.0	32	151.0	20	105.0	25
HMS	263.1	12	139.0	10	121.0	30
DTS	502.0	12	412.2	15	396.2	25
OC	362.4	28	250.0	12	232.0	20
BMDBM	311.2	30	161.2	23	135.1	23
IMC	249.1	15	161.2	15	179.2	9
UV-360	659.8	40	336.3	25	224.2	35
OD-PABA	278.4	45	166.1	30	150.8	30
OMC	291.2	20	161.4	30	179.0	30
EHS	251.1	15	139.2	10	138.9	10
BP-d_{10}*	193.0	30	82.20	40	109.8	30

*BP-d_{10}: benzophenone-d10 (internal standard); 4-MBC: 4-methylbenzylidene camphor; BP-3: benzophenone-3; HMS: homosalate; DTS: drometrizole trisiloxane; OC: octocrylene; BMDBM: butyl methoxydibenzoylmethane; IMC: isoamyl p-methoxycinnamate; UV-360: methylene bis-benzotriazolyl tetramethylbutylphenol (UV-360; bisoctrizole); OD-PABA: ethylhexyl dimethyl PABA; OMC: ethylhexyl methoxycinnamate; EHS: ethylhexyl salicylate.

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Table II. SM4. Combination of three experimental designs varying temperature, extraction time, and solvent.

Experimental design		Temperature (ºC)	Extraction time (min)	Organic solvent
1	1	50	5	MeOH
	2	55	5	MeOH
	3	50	10	MeOH
	4	55	10	MeOH
	5	50	5	ACN
	6	55	5	ACN
	7	50	10	ACN
	8	55	10	ACN
2	1	56	2	ACN
	2	56	4	ACN
	3	56	6	ACN
	4	58	2	ACN
	5	58	4	ACN
	6	58	6	ACN
	7	60	2	ACN
	8	60	4	ACN
	9	60	6	ACN
3	1	60	2	HEX
	2	60	4	HEX
	3	60	6	HEX
	4	64	2	HEX
	5	64	4	HEX
	6	64	6	HEX
	7	68	2	HEX
	8	68	4	HEX
	9	68	6	HEX

MeOH: methanol; ACN: acetonitrile; HEX: hexane. Design 1: full factorial 2×2×2 (temperature×time×solvent); Designs 2–3: 3×3 factorial (temperature×time) at fixed solvent (ACN or HEX).

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Table II. SM5. Concentration in ng/g d.w. of each analyte according to the first experimental design, considering the two different solvents tested.

Exp.	Solvent	4-MBC	BP-3	HMS	DTS	OC	BMDBM	IMC	UV-360	OD-PABA	OMC	EHS
1	MeOH	217.1	160.3	287.1	112.3	175.8	181.4	150.0	744.6	548.6	437.2	469.4
2	MeOH	196.7	151.7	335.7	174.8	195.1	205.4	148.5	935.0	552.3	325.0	466.2
3	MeOH	215.4	153.8	294.6	114.4	145.6	204.2	144.6	756.8	544.5	431.4	400.2
4	MeOH	202.7	147.0	322.3	165.5	169.7	180.6	145.3	871.9	536.4	396.5	512.3
5	ACN	212.2	128.1	296.7	196.8	157.4	191.7	152.8	930.7	517.0	413.0	475.5
6	ACN	215.6	155.7	357.4	241.3	170.0	239.0	151.1	1298.8	555.8	455.7	558.9
7	ACN	193.1	137.3	348.6	242.0	167.5	200.0	147.5	1008.7	523.2	338.9	503.7
8	ACN	217.2	142.8	291.0	209.5	161.6	204.4	163.20	1083.4	539.1	434.3	416.1

MeOH: methanol; ACN: acetonitrile; HEX: hexane; 4-MBC: 4-methylbenzylidene camphor; BP-3: benzophenone-3; HMS: homosalate; DTS: drometrizole trisiloxane; OC: octocrylene; BMDBM: butyl methoxydibenzoylmethane; IMC: isoamyl p-methoxycinnamate; UV-360: methylene bis-benzotriazolyl tetramethylbutylphenol (UV-360; bisoctrizole); OD-PABA: ethylhexyl dimethyl PABA; OMC: ethylhexyl methoxycinnamate; EHS: ethylhexyl salicylate.

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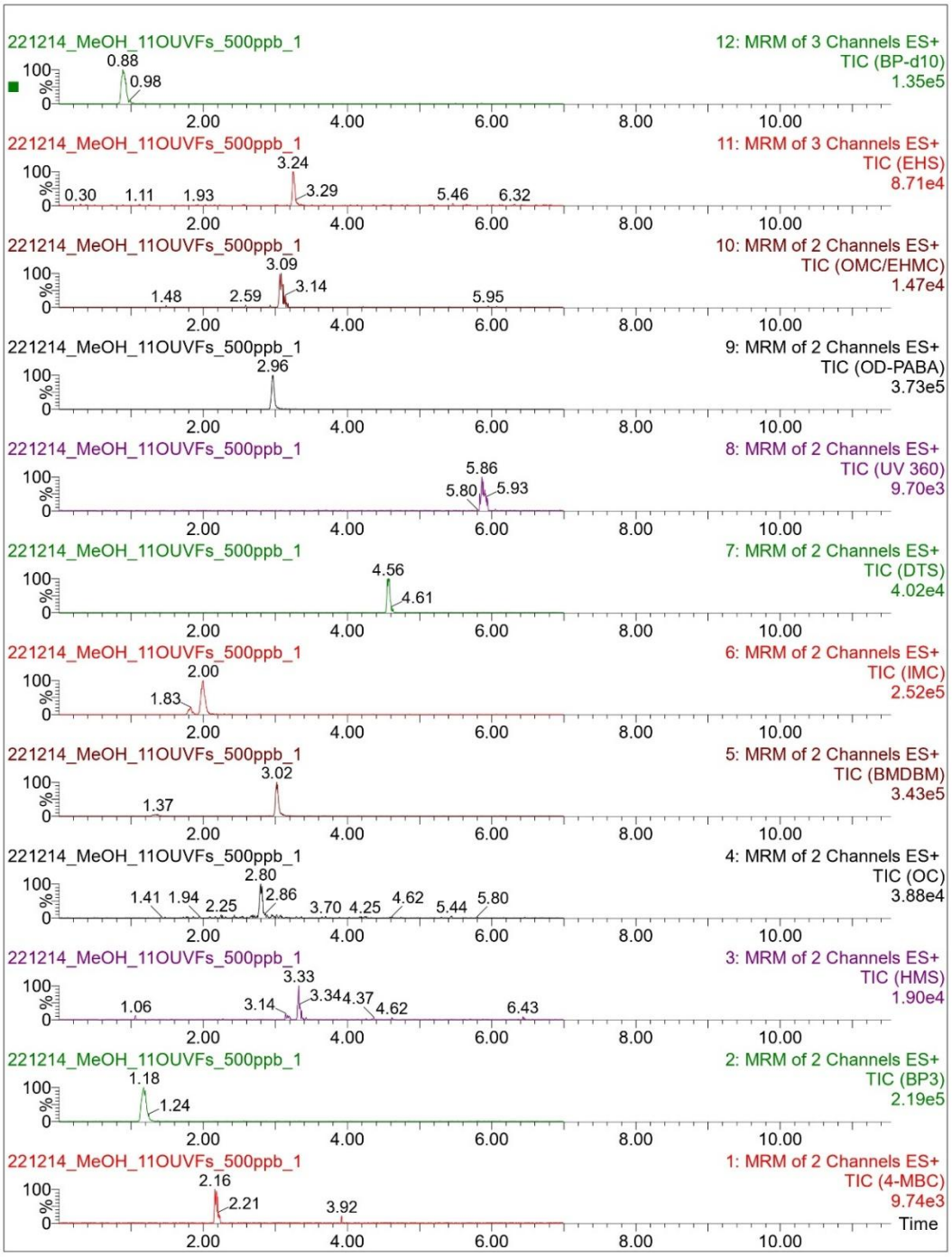

Fig. II. SM1. UHPLC-MS/MS chromatograms of the eleven target oUVFs and the internal standard (IS), BP-d_{10}, at a concentration of 500 µg/L in methanol. Each panel represents a separate compound monitored using multiple reaction monitoring (MRM) in positive electrospray ionization (ES+) mode. The retention time (RT) for each compound is indicated by the peak apex in its corresponding trace.

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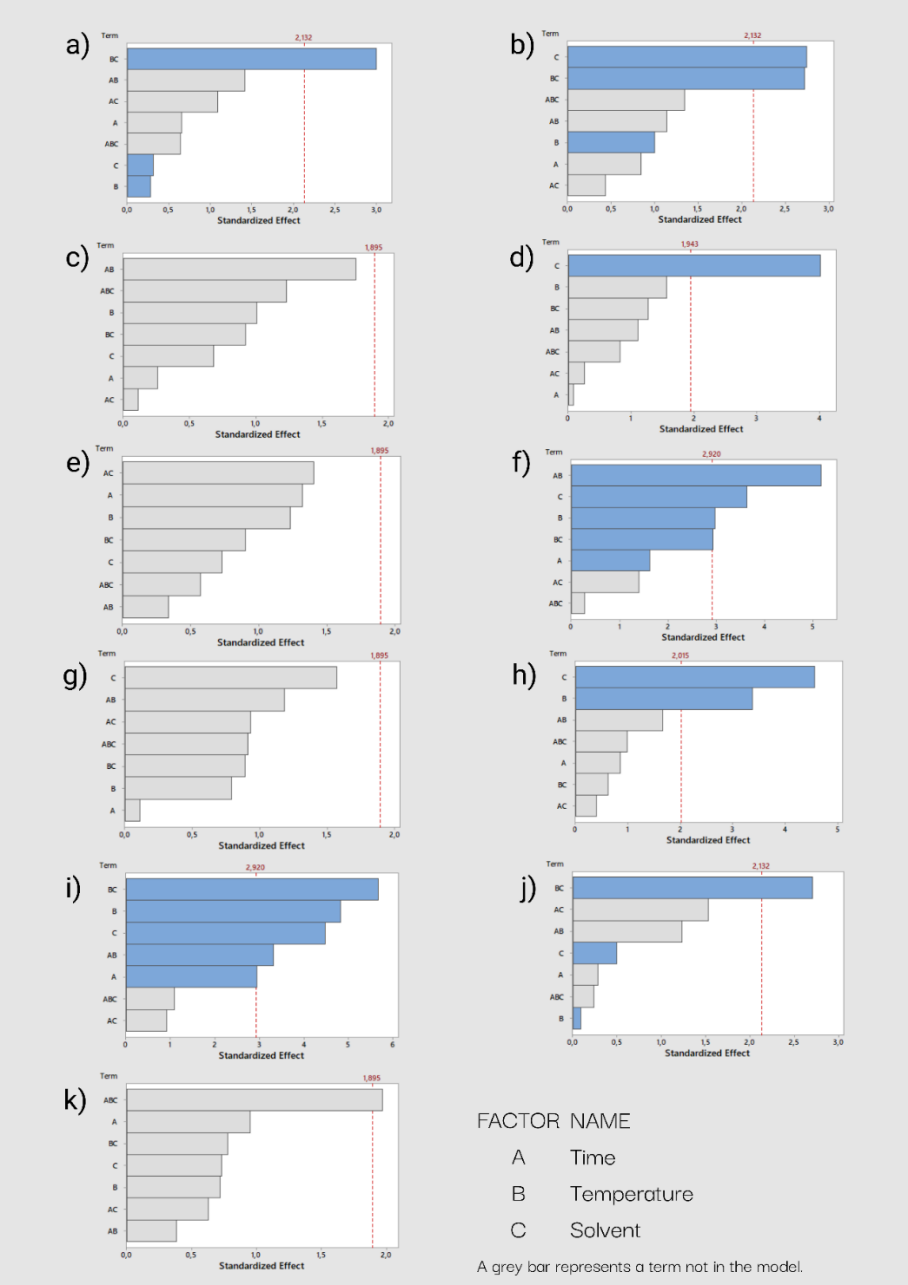

Fig. II. SM2. Pareto charts of standardized effects for the combined extraction designs (total 26 runs; see Table SM3) for each oUVF:a) 4-MBC (4-methylbenzylidene camphor), b) BP-3 (benzophenone-3), c) HMS (homosalate), d) DTS (drometrizole trisiloxane), e) OC (octocrylene), f) BMDBM (butyl methoxydibenzoylmethane), g) IMC isoamyl p-methoxycinnamate, h) UV-360 (methylene bis-benzotriazolyl tetramethylbutylphenol), i) OD-PABA (ethylhexyl dimethyl PABA), j) OMC (ethylhexyl methoxycinnamate), k) EHS (ethylhexyl salicylate). The red dashed line marks the critical value (p = 0.05); bars to the right are statistically significant. Blue bars denote terms retained in the model; grey bars denote terms not in the model. Factor coding: A = time, B = temperature, C = solvent; two- and three-way interactions are labelled AB, AC, BC and ABC. Abbreviations are as in Table II. SM2.

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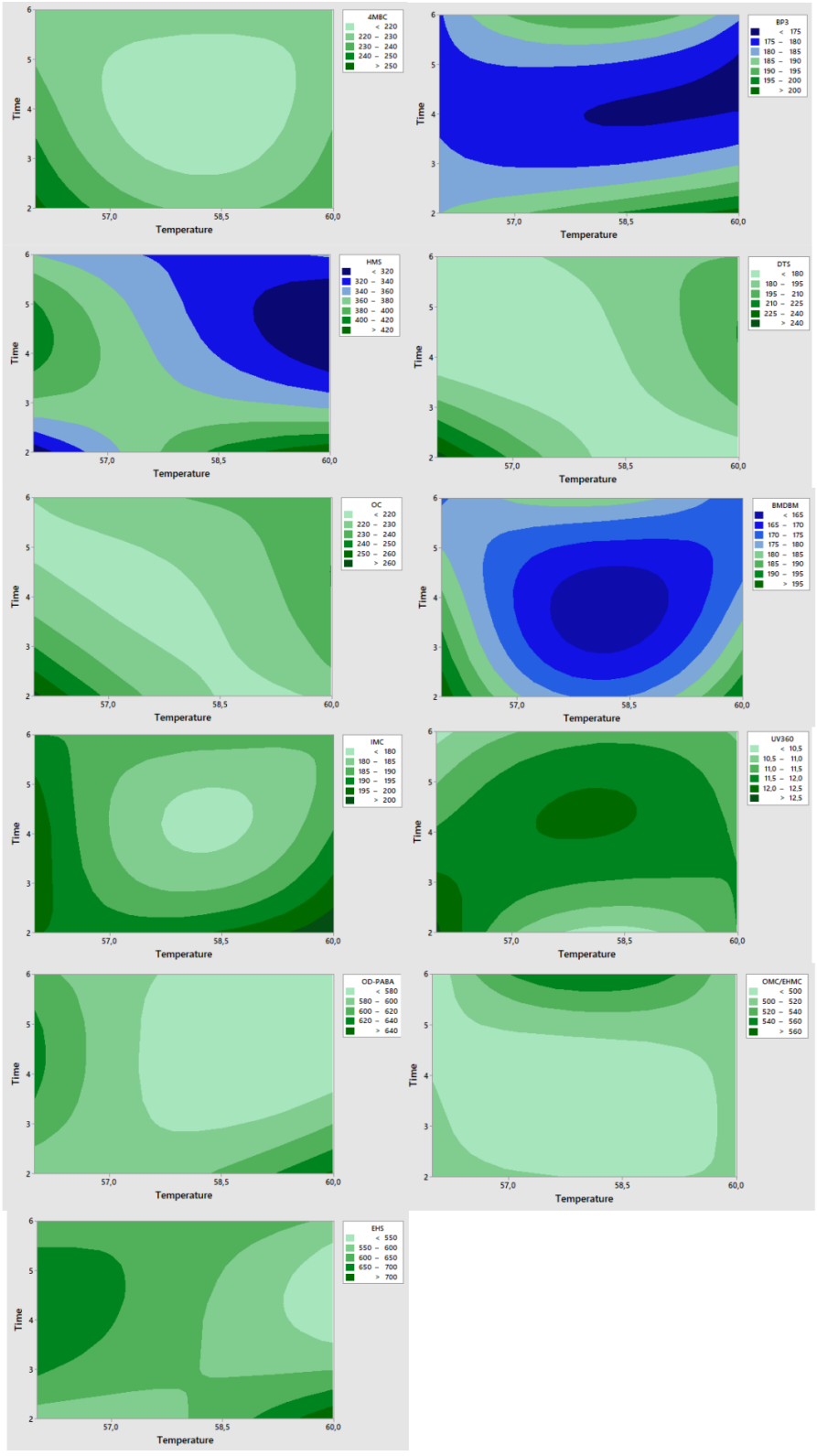

Fig. II. SM3. Contour plots of the predicted extraction response as a function of temperature (56, 58, 60 °C) and extraction time (2, 4, 6 min) for Design 2 (solvent = ACN). One panel per oUVF, ordered as in Fig. II. SM1. MAE conditions as in Methods; responses derived from the fitted response-surface models. The color scale represents the extracted concentration (ng/mL) for each compound.

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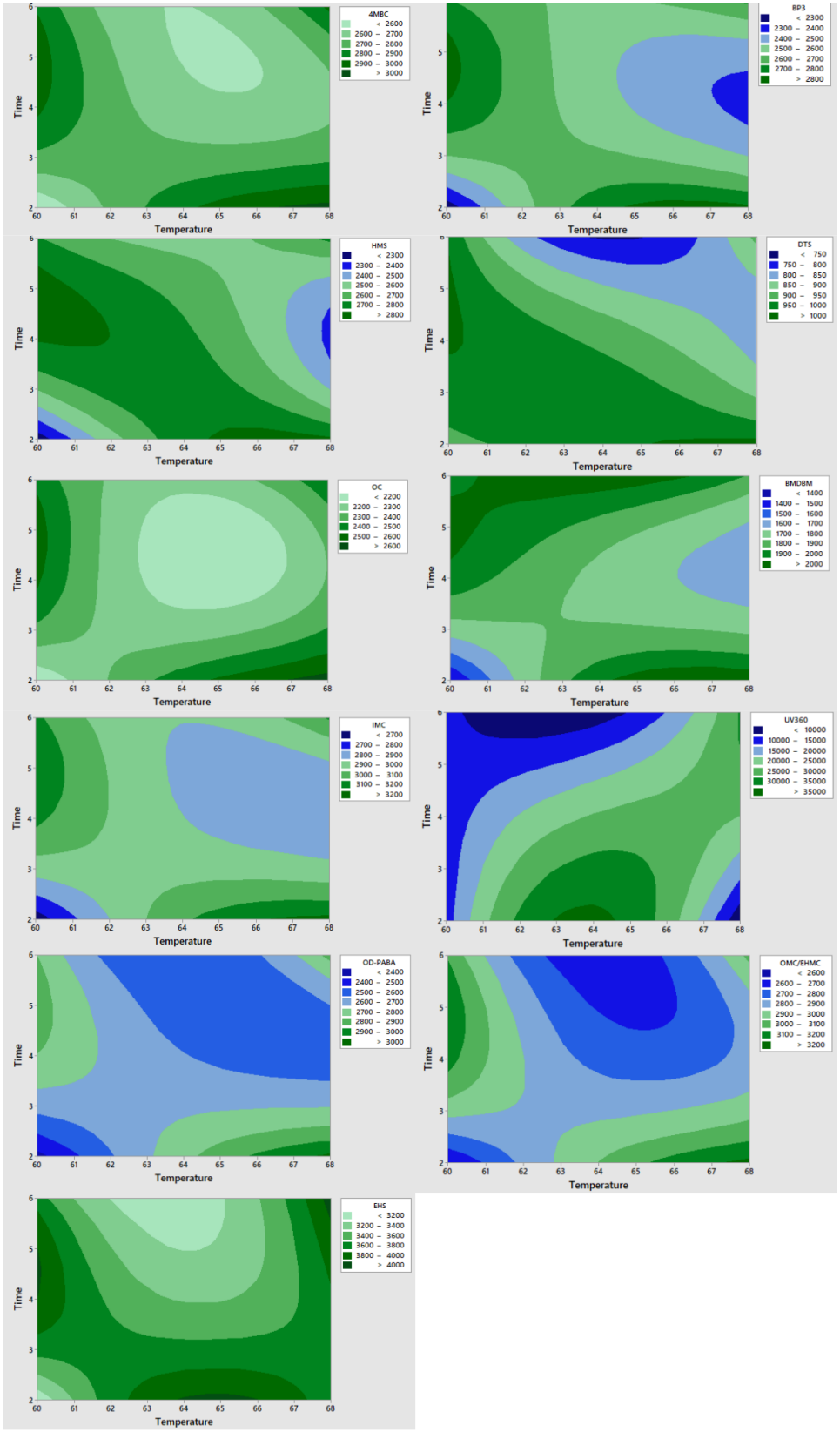

Fig. II. SM4. Contour plots of the predicted extraction response as a function of temperature and extraction time for Design 3 (solvent = HEX). One panel per oUVF, ordered as in Fig. II. SM1. MAE conditions as described in Methods.

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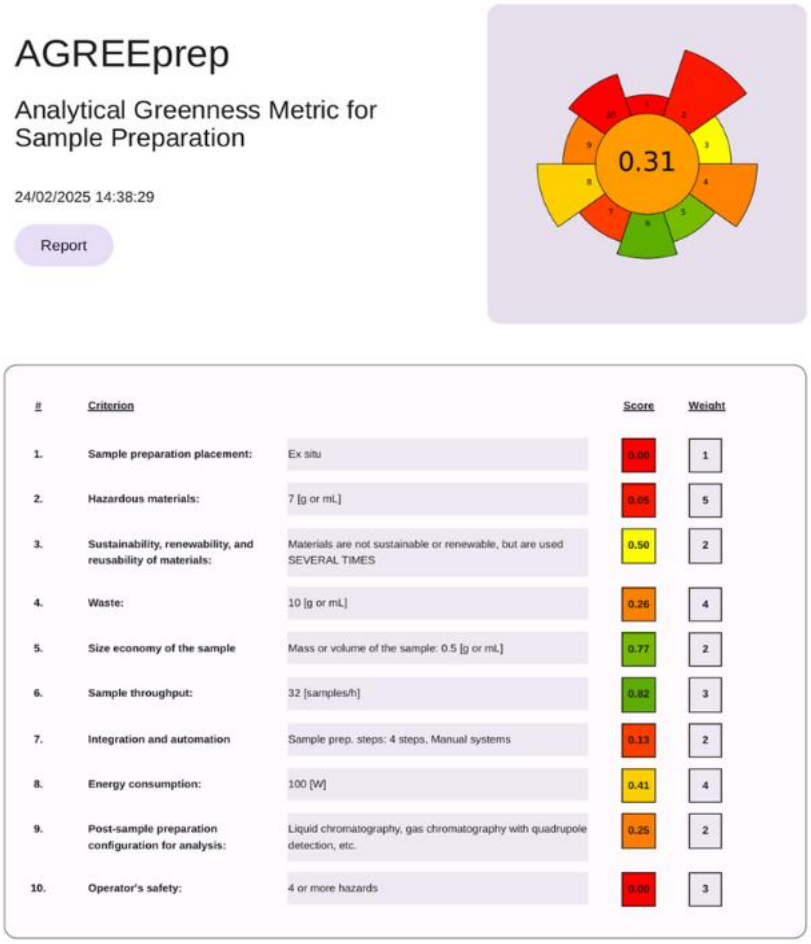

#	Criterion		Score	Weight
1.	Sample preparation placement:	Ex situ	0.00	1
2.	Hazardous materials:	7 [g or mL]	0.05	5
3.	Sustainability, renewability, and reusability of materials:	Materials are not sustainable or renewable, but are used SEVERAL TIMES	0.50	2
4.	Waste:	10 [g or mL]	0.26	4
5.	Size economy of the sample	Mass or volume of the sample: 0.5 [g or mL]	0.77	2
6.	Sample throughput:	32 [samples/h]	0.82	3
7.	Integration and automation	Sample prep. steps: 4 steps, Manual systems	0.13	2
8.	Energy consumption:	100 [W]	0.41	4
9.	Post-sample preparation configuration for analysis:	Liquid chromatography, gas chromatography with quadrupole detection, etc.	0.25	2
10.	Operator's safety:	4 or more hazards	0.00	3

Fig. II. SM5. AGREEprep dashboard for the proposed sample-preparation method. Overall score 0.31, indicating a low level of greenness. The radial plot summarizes the ten AGREEprep criteria (1-10) with their weights; the table reports individual criterion scores. Green = high greenness; yellow/orange = moderate; red = low.

APPENDIX B – Supplementary Data to Chapter III

Appendix B consists of the supplementary data associated with the published article:

Íñiguez, E., Pires da Silva, R., Montesdeoca-Esponda, S., Dimou, E., Alves, F., Kaufmann, M., Dinis, A., and Cordeiro, N. (2025). The invisible impact of tourism: Organic UV filters in the coastal ecosystem of a remote Atlantic island. *Environmental Research*, 287, 123153. https://doi.org/10.1016/j.envres.2025.123153

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Table III. SM1. Characteristics of the eleven organic UV filters (oUVF) analyzed in this study, including their names according to the International nomenclature cosmetic ingredient (INCI), Chemical Abstracts Service number (CAS No.), physicochemical properties (lipophilicity and solubility), and intensity of production in the European economic area (EEA).

INCI name	**Abbreviation**	**CAS No.**	**LogK_{ow}**	**Solubility (g/L)**	**EEA**
Benzophenone-3	BP-3	131-57-7	3.79	0.21	LPV
Ethylhexyl dimethyl PABA	OD-PABA	21245-02-3	6.15	$2.1x10^{-3}$	LPV
Homosalate	HMS	118-56-9	6.16	0.02	HPV
2-ethylhexyl salicytate	EHS	118-60-5	5.97	0.028	HPV
Ethylhexyl methoxycinnamate	OMC	5466-77-3	5.8	0.15	-
Isoamyl p-methoxycinnamate	IMC	71617-10-2	4.33	0.06	LPV
4-methylbenzylidene camphor	4-MBC	36861-47-9	3.83	0.014	LPV
Drometrizole trisiloxane	DTS	155633-54-8	10.82	$1.3x10^{-5}$	-
Methylene bis-benzotriazolyl tetramethylbutylphenol	UV-360	103597-45-1	12.46	$3x10^{-8}$	LPV
Butyl methoxydibenzoylmethane	BMDBM	70356-09-1	4.51	0.037	HPV
Octocrylene	OC	6197-30-4	6.88	$2x10^{-4}$	HPV

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Table III. SM2. Detection parameters for the eleven organic UV filters (oUVFs) under study using positive electrospray ionization (ESI+).

UVF NAME	Parent (m/z)	Daughter (m/z)	Cone (V)	Collision (V)
4-MBC	255.4	105	25	27
		171		19
BP-3	229	105	32	25
		151		20
HMS	263.1	121	12	30
		139		10
OC	362.4	232	28	20
		250		12
BMDBM	311.2	135.1	30	23
		161.2		23
IMC	249.1	161.15	15	15
		179.15		9
DTS	502	396.2	12	25
		412.15		15
UV-360	659.8	224.2	40	35
		336.3		25
OD-PABA	278.4	150.78	45	40
		166.1		30
OMC	291.19	161.43	20	30
		178.99		20
EHS	251.13	138.9	15	10
		139.18		10
BP-d_{10}	193.04	82.14	30	40
		109.78		30

APPENDIX B – Supplementary Data to Chapter III

Table III. SM3. Instrumental and methodological limits of detection (ILOD and MLOD) and quantification (ILOQ and MLOQ) for the eleven organic UV filters (oUVFs) under study in the different matrices analysed.

	Zooplankton				**Algae**				**Invertebrates**			
	ILOD (ug/L)	ILOQ (ug/L)	MLOD (ng/g)	MLOQ (ng/g)	ILOD (ug/L)	ILOQ (ug/L)	MLOD (ng/g)	MLOQ (ng/g)	ILOD (ug/L)	ILOQ (ug/L)	MLOD (ng/g)	MLOQ (ng/g)
4MBC	0.138	0.46	2.757	9.191	0.212	0.706	4.234	14.11	0.212	0.706	10.59	35.29
BP-3	0.269	0.895	5.372	17.91	1.103	3.676	22.06	73.53	1.103	3.676	55.15	183.82
HMS	0.101	0.337	2.024	6.745	1.4	4.666	28	93.33	1.4	4.666	70	233.32
DTS	0.091	0.303	1.818	6.059	0.026	0.086	0.518	1.725	0.026	0.086	1.294	4.313
OC	0.149	0.498	2.988	9.96	0.215	0.716	4.295	14.32	0.215	0.716	10.74	35.79
BMDBM	0.27	0.901	5.405	18.02	0.136	0.452	2.712	9.042	0.136	0.452	6.781	22.6
IMC	0.158	0.527	3.16	10.53	0.15	0.501	3.006	10.02	0.15	0.501	7.515	25.05
UV360	0.094	0.314	1.886	6.288	0.122	0.407	2.444	8.148	0.122	0.407	6.111	20.37
OD-PABA	0.073	0.245	1.47	4.9	0.152	0.505	3.03	10.1	0.152	0.505	7.576	25.25
OMC	0.125	0.416	2.495	8.316	0.204	0.681	4.084	13.61	0.204	0.681	10.21	34.04
EHS	0.299	0.996	5.976	19.92	0.224	0.746	4.478	14.93	0.224	0.746	11.19	37.31

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	Fishes				Sediments				Seawater			
	ILOD (ug/L)	ILOQ (ug/L)	MLOD (ng/g)	MLOQ (ng/g)	ILOD (ug/L)	ILOQ (ug/L)	MLOD (ng/g)	MLOQ (ng/g)	ILOD (ng/L)	ILOQ (ng/L)	MLOD (ng/L)	MLOQ (ng/L)
4-MBC	0.212	0.706	2.117	7.057	0.212	0.706	0.423	1.411	24.17	1000	0.887	2.955
BP-3	1.103	3.676	11.03	36.76	1.103	3.676	2.206	7.353	83.6	5000	1.282	4.272
HMS	1.400	4.666	14.00	46.66	1.400	4.666	2.800	9.333	71.43	1000	3.000	10.00
DTS	0.026	0.086	0.26	0.863	0.026	0.086	0.052	0.173	28.98	250	0.185	0.616
OC	0.215	0.716	2.147	7.158	0.215	0.716	0.429	1.432	33.97	1000	0.631	2.103
BMDBM	0.136	0.452	1.356	4.521	0.136	0.452	0.271	0.904	22.12	1000	0.969	3.229
IMC	0.15	0.501	1.503	5.01	0.15	0.501	0.301	1.002	19.96	1000	1.074	3.579
UV-360	0.122	0.407	1.222	4.074	0.122	0.407	0.244	0.815	18.41	750	0.873	2.91
OD-PABA	0.152	0.505	1.515	5.051	0.152	0.505	0.303	1.01	9.9	500	1.082	3.608
OMC	0.204	0.681	2.042	6.807	0.204	0.681	0.408	1.361	14.69	1000	1.459	4.862
EHS	0.224	0.746	2.239	7.463	0.224	0.746	0.448	1.493	13.4	1000	1.599	5.33

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Table. III. SM4. Concentrations of target analytes in each collected sample and their characteristics. Location – FX: Funchal; LM: Lombada dos Marinheiros; DS: Deserta Grande.

Sample code	CHEMICAL COMPOUNDS											∑UVF	Length (cm)	Weight (g)	Specie	Location	Season	Category
	4MBC	BP3	HMS	DTS	OC	BMDBM	IMC	UV360	OD-PABA	OMC	EHS							
ScFx2	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	27.3	371.59	*S cretense*	FX	Low	Fish
ScFx3	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	25.1	281	*S cretense*	FX	Low	Fish
ScFx4	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	26.0	301.13	*S cretense*	FX	Low	Fish
ScFx5	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	25.9	299.63	*S cretense*	FX	Low	Fish
ScFx6	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	25.2	282.8	*S cretense*	FX	Low	Fish
ScFx9	< LOD	< LOD	< LOD	< LOD	8.971	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	8.971	32.8	625.93	*S cretense*	FX	High	Fish
ScFx10	< LOD	< LOD	< LOD	< LOD	14.82	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	14.82	31.0	493.17	*S cretense*	FX	High	Fish
ScFx11	< LOD	< LOD	< LOD	< LOD	<LOQ	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	25.6	337.3	*S cretense*	FX	High	Fish
ScFx12	< LOD	< LOD	< LOD	< LOD	12.89	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	12.89	30.3	470	*S cretense*	FX	High	Fish
ScFx13	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	30.1	413.91	*S cretense*	FX	High	Fish
ScLM1	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	29.5	482.85	*S cretense*	LM	Low	Fish
ScLM2	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	29.0	435.55	*S cretense*	LM	Low	Fish
ScLM3	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	31.5	550.6	*S cretense*	LM	Low	Fish
ScLM7	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	33.5	627.69	*S cretense*	LM	High	Fish
ScLM8	< LOD	< LOD	< LOD	< LOD	19.25	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	19.25	31.3	544.91	*S cretense*	LM	High	Fish
ScLM9	< LOD	< LOD	< LOD	< LOD	25.07	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	25.07	33.5	645.4	*S cretense*	LM	High	Fish
ScLM10	< LOD	< LOD	< LOD	< LOD	19.94	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	19.94	33.4	581.1	*S cretense*	LM	High	Fish
ScLM11	< LOD	< LOD	< LOD	< LOD	7.491	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	7.491	30.5	505.28	*S cretense*	LM	High	Fish
ScDS1	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	32.6	575.4	*S cretense*	DS	High	Fish
ScDS2	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	29.6	405.12	*S cretense*	DS	High	Fish
ScDS3	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	29.5	445.78	*S cretense*	DS	High	Fish
ScDS4	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	29.7	407.86	*S cretense*	DS	High	Fish
ScDS5	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	34.0	658.12	*S cretense*	DS	High	Fish
ScDS7	< LOD	< LOD	< LOD	< LOD	7.948	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	7.948	31.1	489.49	*S cretense*	DS	Low	Fish

APPENDIX B – Supplementary Data to Chapter III

Sample code	CHEMICAL COMPOUNDS											∑UVF	Length (cm)	Weight (g)	Specie	Location	Season	Category
	4MBC	BP3	HMS	DTS	OC	BMDBM	IMC	UV360	OD-PABA	OMC	EHS							
ScDS8	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	31.4	477.68	*S cretense*	DS	Low	Fish
ScDS9	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	31.7	531.39	*S cretense*	DS	Low	Fish
ScDS10	< LOD	< LOD	< LOD	< LOD	1.07	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	34.0	622.3	*S cretense*	DS	Low	Fish
ScDS11	< LOD	< LOD	< LOD	< LOD	<LOQ	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	32.7	551.6	*S cretense*	DS	Low	Fish
SsFx1	< LOD	< LOD	110.82	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	361.40	472.2	27.0	200.64	*S salpa*	FX	Low	Fish
SsFx2	< LOD	< LOD	98.57	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	260.73	359.3	25.1	142.52	*S salpa*	FX	Low	Fish
SsFx3	< LOD	< LOD	90.99	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	226.22	317.2	28	246.93	*S salpa*	FX	Low	Fish
SsFx4	< LOD	< LOD	95.41	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	95.41	21.9	104.3	*S salpa*	FX	Low	Fish
SsFx7	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	13.85	< LOD	13.85	25.5	211.71	*S salpa*	FX	High	Fish
SsFx8	< LOD	< LOD	< LOD	< LOD	19.53	< LOD	< LOD	< LOD	< LOD	44.36	< LOD	63.89	19.7	115.14	*S salpa*	FX	High	Fish
SsFx9	< LOD	< LOD	< LOD	< LOD	7.666	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	7.67	26.5	222.49	*S salpa*	FX	High	Fish
SsFx10	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	23.8	203.55	*S salpa*	FX	High	Fish
SsFx11	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	30.69	< LOD	30.69	22.5	133.5	*S salpa*	FX	High	Fish
SsLM1	< LOD	< LOD	99.35	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	295.28	394.6	24	195.12	*S salpa*	LM	Low	Fish
SsLM2	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	209.79	209.8	19	96.53	*S salpa*	LM	Low	Fish
SsLM3	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	19.7	107.8	*S salpa*	LM	Low	Fish
SsLM4	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	19.4	111.59	*S salpa*	LM	Low	Fish
SsLM5	< LOD	< LOD	< LOQ	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	24.4	185.05	*S salpa*	LM	Low	Fish
SsLM7	< LOD	< LOD	< LOQ	< LOD	129.67	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	129.67	20.5	110.93	*S salpa*	LM	High	Fish
SsLM8	< LOD	< LOD	< LOD	< LOD	36.33	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	36.33	21.9	145.37	*S salpa*	LM	High	Fish
SsLM9	< LOD	< LOD	< LOD	< LOD	27.00	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	27.00	21.15	128.95	*S salpa*	LM	High	Fish
SsDS1	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	25.3	22.2	*S salpa*	DS	High	Fish
SsDS2	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	21.9	19.4	*S salpa*	DS	High	Fish
SsDS3	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	25.5	22.1	*S salpa*	DS	High	Fish
SsDS4	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	22.5	19.9	*S salpa*	DS	High	Fish
SsDS5	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	24.1	21.2	*S salpa*	DS	High	Fish

APPENDIX B – Supplementary Data to Chapter III

Sample code	CHEMICAL COMPOUNDS											∑UVF	Length (cm)	Weight (g)	Specie	Location	Season	Category
	4MBC	BP3	HMS	DTS	OC	BMDBM	IMC	UV360	OD-PABA	OMC	EHS							
SsDS7	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	24.24	21.22	*S salpa*	DS	Low	Fish
SsDS8	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	24.1	20.9	*S salpa*	DS	Low	Fish
SsDS9	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	24.5	21.2	*S salpa*	DS	Low	Fish
SsDS10	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	21.5	18.7	*S salpa*	DS	Low	Fish
SsDS11	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	21.6	18.8	*S salpa*	DS	Low	Fish
Garoupa1	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	22.9	137.38	*S atricauda*	X	NS	Fish
Garoupa2	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	21.2	122.51	*S atricauda*	X	NS	Fish
Garoupa3	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	24	171.75	*S atricauda*	X	NS	Fish
Garoupa4	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	21.4	120.89	*S atricauda*	X	NS	Fish
Garoupa5	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	25.1	190.35	*S atricauda*	X	NS	Fish
AlixFx1	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	57.98	72.28	*A lixula*	FX	Low	Invertebrate
AlixFx2	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	63.61	78.7	*A lixula*	FX	Low	Invertebrate
AlixFx3	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	61.8	55.7	*A lixula*	FX	Low	Invertebrate
AlixFx4	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	54.49	44.77	*A lixula*	FX	Low	Invertebrate
AlixFx5	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	62.75	74.99	*A lixula*	FX	Low	Invertebrate
AlixFx7	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	54.98	62.23	*A lixula*	FX	High	Invertebrate
AlixFx8	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	62.64	83.03	*A lixula*	FX	High	Invertebrate
AlixFx9	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	61.59	67.74	*A lixula*	FX	High	Invertebrate
AlixFx10	< LOD	< LOD	< LOQ	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	51.69	42.5	*A lixula*	FX	High	Invertebrate
AlixFx11	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	65.24	79.2	*A lixula*	FX	High	Invertebrate
AlixLM1	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	48.13	39.9	*A lixula*	LM	Low	Invertebrate
AlixLM2	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	49.03	49.3	*A lixula*	LM	Low	Invertebrate
AlixLM3	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	43.38	25.74	*A lixula*	LM	Low	Invertebrate
AlixLM4	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	43.29	31.28	*A lixula*	LM	Low	Invertebrate
AlixLM5	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	50.82	44.72	*A lixula*	LM	Low	Invertebrate
AlixLM7	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	43.84	34.89	*A lixula*	LM	High	Invertebrate

APPENDIX B – Supplementary Data to Chapter III

Sample code	CHEMICAL COMPOUNDS											∑UVF	Length (cm)	Weight (g)	Specie	Location	Season	Category
	4MBC	BP3	HMS	DTS	OC	BMDBM	IMC	UV360	OD-PABA	OMC	EHS							
AlixLM8	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	42.08	35.85	*A lixula*	LM	High	Invertebrate
AlixLM9	< LOD	< LOD	< LOQ	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	40.43	27.82	*A lixula*	LM	High	Invertebrate
AlixLM10	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	45.82	41.14	*A lixula*	LM	High	Invertebrate
AlixLM11	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	46.86	38.92	*A lixula*	LM	High	Invertebrate
AlixDS1	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	60.03	78.64	*A lixula*	DS	High	Invertebrate
AlixDS2	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	67.50	< LOD	n.d.	57.2	73.92	*A lixula*	DS	High	Invertebrate
AlixDS3	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	58.33	72.15	*A lixula*	DS	High	Invertebrate
AlixDS4	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	69.33	101.34	*A lixula*	DS	High	Invertebrate
AlixDS5	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	62.57	72.01	*A lixula*	DS	High	Invertebrate
AlixDS7	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	49.76	45.98	*A lixula*	DS	Low	Invertebrate
AlixDS8	< LOD	< LOD	< LOQ	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	45.82	35.7	*A lixula*	DS	Low	Invertebrate
AlixDS9	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	46.76	40.45	*A lixula*	DS	Low	Invertebrate
AlixDS10	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	102.50	n.d.	46.89	43.22	*A lixula*	DS	Low	Invertebrate
AlixDS11	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	41.91	27.83	*A lixula*	DS	Low	Invertebrate
HsanctoriFX1	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	-	99.86	*H sanctori*	FX	Low	Invertebrate
HsanctoriFX2	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	-	206.9	*H sanctori*	FX	Low	Invertebrate
HsanctoriFX3	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	-	151.08	*H sanctori*	FX	Low	Invertebrate
HsanctoriFX4	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	-	176.54	*H sanctori*	FX	Low	Invertebrate
HsanctoriFX5	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	-	154.41	*H sanctori*	FX	Low	Invertebrate
HsanctoriFX7	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	-	162	*H sanctori*	FX	High	Invertebrate
HsanctoriFX8	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	-	242.2	*H sanctori*	FX	High	Invertebrate
HsanctoriFX9	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	-	126.39	*H sanctori*	FX	High	Invertebrate
HsanctoriFX10	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	-	203.11	*H sanctori*	FX	High	Invertebrate
HsanctoriFX11	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	-	246.11	*H sanctori*	FX	High	Invertebrate
HsanctoriLM1	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	-	191.33	*H sanctori*	LM	Low	Invertebrate
HsanctoriLM2	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	-	211.8	*H sanctori*	LM	Low	Invertebrate

APPENDIX B – Supplementary Data to Chapter III

Sample code	CHEMICAL COMPOUNDS											∑UVF	Length (cm)	Weight (g)	Specie	Location	Season	Category
	4MBC	BP3	HMS	DTS	OC	BMDBM	IMC	UV360	OD-PABA	OMC	EHS							
HsanctoriLM3	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	-	113.17	*H sanctori*	LM	Low	Invertebrate
HsanctoriLM7	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	57.50	n.d.	-	134.21	*H sanctori*	LM	High	Invertebrate
HsanctoriLM8	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	-	162.45	*H sanctori*	LM	High	Invertebrate
HsanctoriLM9	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	-	157.57	*H sanctori*	LM	High	Invertebrate
HsanctoriLM10	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	-	221.58	*H sanctori*	LM	High	Invertebrate
HsanctoriLM11	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	-	230.4	*H sanctori*	LM	High	Invertebrate
HsanctoriDS1	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	-	275.35	*H sanctori*	DS	High	Invertebrate
HsanctoriDS2	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	-	346.69	*H sanctori*	DS	High	Invertebrate
HsanctoriDS3	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	-	276.28	*H sanctori*	DS	High	Invertebrate
HsanctoriDS4	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	-	308.87	*H sanctori*	DS	High	Invertebrate
HsanctoriDS5	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	-	293.15	*H sanctori*	DS	High	Invertebrate
HsanctoriDS7	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	-	291.92	*H sanctori*	DS	Low	Invertebrate
HsanctoriDS8	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	-	226.74	*H sanctori*	DS	Low	Invertebrate
HsanctoriDS9	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	-	186.23	*H sanctori*	DS	Low	Invertebrate
HsanctoriDS10	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	-	208.55	*H sanctori*	DS	Low	Invertebrate
HsanctoriDS11	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	-	235.08	*H sanctori*	DS	Low	Invertebrate
AtaxFx1	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	-	-	*A taxiformis*	FX	Low	Red algae
AtaxFx2	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	-	-	*A taxiformis*	FX	Low	Red algae
AtaxFx3	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	-	-	*A taxiformis*	FX	Low	Red algae
AtaxFx7	< LOD	< LOD	< LOD	< LOD	24.85	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	24.85	-	-	*A taxiformis*	FX	High	Red algae
AtaxFx8	< LOD	< LOD	< LOD	< LOD	17.42	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	17.42	-	-	*A taxiformis*	FX	High	Red algae
AtaxFx9	< LOD	< LOD	< LOD	< LOD	15.93	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	15.93	-	-	*A taxiformis*	FX	High	Red algae
AtaxFx10	< LOD	< LOD	<LOQ	< LOD	192.00	< LOD	< LOD	< LOD	< LOD	< LOD	27.00	219.0	-	-	*A taxiformis*	FX	High	Red algae
AtaxLM1	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	-	-	*A taxiformis*	LM	Low	Red algae
AtaxLM2	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	-	-	*A taxiformis*	LM	Low	Red algae
AtaxLM3	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	-	-	*A taxiformis*	LM	Low	Red algae

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Sample code	CHEMICAL COMPOUNDS											∑UVF	Length (cm)	Weight (g)	Specie	Location	Season	Category
	4MBC	BP3	HMS	DTS	OC	BMDBM	IMC	UV360	OD-PABA	OMC	EHS							
AtaxLM7	< LOD	< LOD	170.00	< LOD	< LOQ	< LOD	< LOD	< LOD	< LOD	< LOD	122.67	292.7	-	-	*A taxiformis*	LM	High	Red algae
AtaxLM8	< LOD	< LOD	104.00	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	66.00	170.0	-	-	*A taxiformis*	LM	High	Red algae
AtaxLM9	< LOD	< LOD	<LOQ	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	57.00	57.00	-	-	*A taxiformis*	LM	High	Red algae
AtaxDS1	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	-	-	*A taxiformis*	DS	High	Red algae
AtaxDS2	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	-	-	*A taxiformis*	DS	High	Red algae
AtaxDS3	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	-	-	*A taxiformis*	DS	High	Red algae
AtaxDS7	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	39.00	39.00	-	-	*A taxiformis*	DS	Low	Red algae
AtaxDS8	< LOD	< LOD	<LOQ	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	28.00	28.00	-	-	*A taxiformis*	DS	Low	Red algae
AtaxDS9	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	0.00	-	-	*A taxiformis*	DS	Low	Red algae
zoo_coast_FX_1	< LOD	< LOD	136.0	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	136.00	-	-	-	FX	Low	Zooplankton
zoo_coast_FX_2	< LOD	< LOD	166.0	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	166.00	-	-	-	FX	Low	Zooplankton
zoo_coast_FX_3	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	-	-	-	FX	Low	Zooplankton
zoo_coast_FX_4	< LOD	< LOD	62.00	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	62.00	-	-	-	FX	High	Zooplankton
zoo_coast_FX_5	< LOD	< LOD	104.0	< LOD	466.0	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	570.0	-	-	-	FX	High	Zooplankton
zoo_coast_FX_6	< LOD	< LOD	< LOD	< LOD	651.3	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	651.3	-	-	-	FX	High	Zooplankton
zoo_coast_LM_1	< LOD	< LOD	21.69	< LOD	< LOD	< LOD	< LOD	< LOD	14	< LOD	< LOD	35.69	-	-	-	LM	Low	Zooplankton
zoo_coast_LM_2	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	-	-	-	LM	Low	Zooplankton
zoo_coast_LM_3	< LOD	< LOD	4.502	< LOD	46	< LOD	< LOD	< LOD	108	< LOD	< LOD	158.5	-	-	-	LM	Low	Zooplankton
zoo_coast_LM_4	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	0.00	-	-	-	LM	High	Zooplankton
zoo_coast_LM_5	< LOD	< LOD	12.82	< LOD	158	< LOD	< LOD	< LOD	118	< LOD	< LOD	288.8	-	-	-	LM	High	Zooplankton
zoo_coast_LM_6	< LOD	< LOD	44.00	< LOD	50	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	94.00	-	-	-	LM	High	Zooplankton
zoo_coast_DS_1	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	-	-	-	DS	High	Zooplankton
zoo_coast_DS_2	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	-	-	-	DS	High	Zooplankton
zoo_coast_DS_3	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	-	-	-	DS	High	Zooplankton
zoo_coast_DS_4	< LOD	< LOD	<LOQ	< LOD	35.76	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	35.76	-	-	-	DS	Low	Zooplankton
zoo_coast_DS_5	< LOD	< LOQ	8.998	< LOD	70.16	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	79.15	-	-	-	DS	Low	Zooplankton

APPENDIX B – Supplementary Data to Chapter III

Sample code	CHEMICAL COMPOUNDS											∑UVF	Length (cm)	Weight (g)	Specie	Location	Season	Category
	4MBC	BP3	HMS	DTS	OC	BMDBM	IMC	UV360	OD-PABA	OMC	EHS							
zoo_coast_DS_6	< LOD	< LOQ	15.65	< LOD	30.27	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	45.92	-	-	-	DS	Low	Zooplankton
C_wat_FX1	< LOD	< LOD	16.57	3.030	< LOD	27.74	< LOD	< LOD	< LOD	< LOD	14.80	62.14	-	-	-	FX	Low	Seawater
C_wat_FX2	< LOD	7.685	6.784	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	14.47	-	-	-	FX	Low	Seawater
C_wat_FX3	< LOD	< LOD	<LOD	3.058	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	3.058	-	-	-	FX	Low	Seawater
C_wat_FX4	< LOD	< LOD	23.14	2.717	< LOD	23.26	< LOD	< LOD	< LOD	< LOD	21.49	70.61	-	-	-	FX	High	Seawater
C_wat_FX5	< LOD	4	<LOQ	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	13.96	17.96	-	-	-	FX	High	Seawater
C_wat_FX6	< LOD	< LOD	<LOQ	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	-	-	-	FX	High	Seawater
C_wat_LM1	< LOD	< LOD	< LOD	5.37	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	5.370	-	-	-	LM	Low	Seawater
C_wat_LM2	< LOD	< LOQ	< LOD	4.405	< LOQ	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	4.405	-	-	-	LM	Low	Seawater
C_wat_LM3	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	-	-	-	LM	Low	Seawater
C_wat_LM4	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	-	-	-	LM	High	Seawater
C_wat_LM5	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	-	-	-	LM	High	Seawater
C_wat_LM6	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	-	-	-	LM	High	Seawater
C_wat_DS1	< LOD	< LOD	< LOD	2.589	12.23	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	14.82	-	-	-	DS	High	Seawater
C_wat_DS2	< LOD	< LOD	< LOD	2.804	11.60	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	14.40	-	-	-	DS	High	Seawater
C_wat_DS3	< LOD	< LOD	< LOD	2.827	3.200	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	6.027	-	-	-	DS	High	Seawater
C_wat_DS4	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	-	-	-	DS	Low	Seawater
C_wat_DS5	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	-	-	-	DS	Low	Seawater
C_wat_DS6	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	-	-	-	DS	Low	Seawater
C_sed_FX1	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	-	-	-	FX	Low	Sediment
C_sed_FX2	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	-	-	-	FX	Low	Sediment
C_sed_FX3	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	-	-	-	FX	Low	Sediment
C_sed_FX4	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	-	-	-	FX	High	Sediment
C_sed_FX5	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	-	-	-	FX	High	Sediment
C_sed_FX6	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	-	-	-	FX	High	Sediment
C_sed_LM1	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	-	-	-	LM	Low	Sediment

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Sample code	CHEMICAL COMPOUNDS											∑UVF	Length (cm)	Weight (g)	Specie	Location	Season	Category
	4MBC	BP3	HMS	DTS	OC	BMDBM	IMC	UV360	OD-PABA	OMC	EHS							
C_sed_LM2	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	-	-	-	LM	Low	Sediment
C_sed_LM3	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	-	-	-	LM	Low	Sediment
C_sed_LM4	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	-	-	-	LM	High	Sediment
C_sed_LM5	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	-	-	-	LM	High	Sediment
C_sed_LM6	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	-	-	-	LM	High	Sediment
C_sed_DS1	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	-	-	-	DS	High	Sediment
C_sed_DS2	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	-	-	-	DS	High	Sediment
C_sed_DS3	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	-	-	-	DS	High	Sediment
C_sed_DS4	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	-	-	-	DS	Low	Sediment
C_sed_DS5	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	-	-	-	DS	Low	Sediment
C_sed_DS6	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	-	-	-	DS	Low	Sediment

APPENDIX B – Supplementary Data to Chapter III

Table. III. SM5. Sample size (n), mean ± standard deviation (SD), range (ng/g d.w. and ng/L), and frequency of detection (FO) of total oUVF concentrations in the different matrices, analyzed by season.

				High season	
Sample	**n**	**Mean**	**SD**	**Range**	**FO (%)**
Asparagopsis taxiformis	10	113.8	± 104.4	15.93 - 292.7	70
Zooplankton	9	185.1	± 244.2	62.00 - 651.33	55.6
Arbacia lixula	15		n.d	n.d	0
Holothuria sanctori	15		n.d	n.d	0
Sarpa salpa	13	44.16	± 38.71	13.85 -129.7	53.9
Sparisoma cretense	15	15.49	± 5.850	8.97-25.07	46.7
Seawater	9	20.81	± 14.15	6.030 – 47.37	55.6
Sediments	9	n.d		n.d	0
				Low season	
Asparagopsis taxiformis	9	33.5	± 5.500	28.00- 39.00	22.2
Zooplankton	9	73.23	± 61.45	35.69 - 166.0	77.8
Arbacia lixula	15		n.d	n.d	0
Holothuria sanctori	13		n.d	n.d	0
Sarpa salpa	14	331.5	± 123.9	95.41 - 472.2	42.9
Sparisoma cretense	17	4.509	± 3.440	1.07 - 7.950	11.8
Seawater	9	12.74	± 11.46	4.410- 34.43	55.6
Sediments	9		n.d	n.d	0
Serratus atricauda	5		n.d	n.d	0

**Asparagopsis taxiformis* and Zooplankton samples are composed of a pool of specimens.

Table. III. SM6. Mean ± standard deviation of all the samples according to season variable collected with detectable concentration of oUVF, in ng/g d.w. for solid matrices and ng/L for seawater matrix, and frequency of occurrence (as %).

HIGH SEASON

Samples	BP-3	HMS	DTS	OC	BMDBM	OD-PABA	OMC	EHS
	Mean ± SD FO (%)	Mean ± SD FO (%)	Mean ± SD FO (%)	Mean ± SD FO (%)	Mean ± SD FO (%)	Mean ± SD FO (%)	Mean ± SD FO (%)	Mean ± SD FO (%)
Asparagopsis taxiformis	<LOD	137 ± 33 20%	<LOD	62.55 ± 74.82 40%	<LOD	<LOD	<LOD	68.17 ± 34.62 40%
Zooplankton	<LOD	55.71 ± 32.97 44.44%	<LOD	331.33 ± 239.65 44.44%	<LOD	<LOQ 11.11%	<LOD	<LOD
Arbacia lixula	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Holothuria sanctori	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Sarpa salpa	<LOD	<LOD	<LOD	44.04 ± 43.83 38.46%	<LOD	<LOD	29.63 ± 12.48 23.10%	<LOD
Sparisoma cretense	<LOD	<LOD	<LOD	15.49 ± 5.847 46.67%	<LOD	<LOD		<LOD
Serratus atricauda	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Seawater	4.000 ± - 11.11%	10.81 ± 8.771 33.33%	2.734 ± 0.094 44.44%	9.010 ± 4.116 33.33%	23.26 ± - 11.11%	<LOD	<LOD	<LOD
Sediments	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD

LOW SEASON

Samples	**BP-3**	**HMS**	**DTS**	**OC**	**BMDBM**	**OD-PABA**	**OMC**	**EHS**
	Mean ± SD FO (%)	Mean ± SD FO (%)	Mean ± SD FO (%)	Mean ± SD FO (%)	Mean ± SD FO (%)	Mean ± SD FO (%)	Mean ± SD FO (%)	Mean ± SD FO (%)
Asparagopsis taxiformis	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	33.50 ± 5.500 22.22%
Zooplankton		50.70 ± 64.23 77.78%	<LOD	45.55 ± 15.29 44.44	<LOD	61.00 ± 47.00 22.22%	<LOD	<LOD
Arbacia lixula	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Holothuria sanctori	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Sarpa salpa	<LOD	99.03 ± 6.589 42.86%	<LOD	<LOD	<LOD	<LOD	<LOD	270.68 ± 54.07 35.70%
Sparisoma cretense	<LOD	<LOD	<LOD	4.509 ± 3.439 23.01%	<LOD	<LOD	<LOD	<LOD
Serratus atricauda	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Seawater	7.686 ± - 11.11%	8.450 ± 6.069 33.33%	3.966 ± 0.983 44.44%	<LOD	27.737 ± - 11.11%	<LOD	<LOD	14.80 ± - 11.11%
Sediments	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD

Table. III. SM7. Summary of sample size per matrix, together with total lipid content, frequency of occurrence (FO), mean total oUVF concentration, and range.

Category	Common name	Scientific name	N	Lipid content (%)	FO(%)	∑oUVF (ng/g d.w)	Range (ng/g d.w.)
Fish	Salema	*Salpa sarpa*	27	6.09	51.85	157.45 ± 158.71	7.67 ± 472.22
	Parrot fish	*Sparisoma cretense*	28	4.89	32.14	13.73 ± 6.13	7.49 ± 25.07
Total			55		38.18	108.29 ± 144.98	7.49 - 472.22
	Blacktail comber	*Serratus atricauda*	5	7.03	0	n.d.	n.d.
Invertebrates	Sea cucumber	*Holothuria sanctori*	28	3.1	0	n.d.	n.d.
	Black sea urchin	*Arbacia lixula*	30	2.18	0	n.d.	n.d.
Zooplankton			18	n.d.	66.67	129.18 ± 186.65	35.69 ± 651.33
Red sea algae	Limu kohu	*Asparagopsis taxiformis*	19	2.24	47.37	96.75 ± 99.55	15.93 ± 292.67
Seawater			18	-	55.55	20.65 ±23.42	3.060 ± 70.613
Sediments			18	-	0	n.d.	n.d.

APPENDIX B – Supplementary Data to Chapter III

Table. III. SM8. Sample size (n), mean ± standard deviation (SD), range (ng/g d.w. and ng/L), and frequency of detection (FO) of total oUVF concentrations in the different matrices, analyzed by location.

Specie	n	∑oUVF mean (ng/g)	Range (ng/g)	FO(%)
Funchal				
Asparagopsis taxiformis	7	69.30 ± 86.5	n.d - 219.00	57.14%
Zooplackton	6	264.2 ± 251.7	n.d - 558.7	83.33%
Arbacia lixula	10	n.d	n.d	0%
Holothuria sanctori	10	n.d	n.d	0%
Sarpa salpa	9	170.0 ± 171.8	n.d - 472.2	88.88%
Sparisoma cretense	10	12.23 ± 2.430	n.d - 14.82	30%
Seawater	6	0.032 ± 0.290	n.d. - 0.063	83%
Sediments	6	n.d	n.d	0%
Lombada dos marinheiros				
Asparagopsis taxiformis	6	175.6 ±99.21	n.d - 299.8	50%
Zooplankton	6	96.18 ± 102.6	n.d - 84.67	66.67%
Arbacia lixula	10	n.d	n.d	0%
Holothuria sanctori	8	n.d	n.d	0%
Sarpa salpa	8	140.7 ± 133.5	n.d - 394.6	75%
Sparisoma cretense	8	17.94 ± 6.44	n.d - 25.07	50%
Seawater	6	0.005 ± 0.001	n.d. - 0.005	33%
Sediments	6	n.d	n.d	0%
Desertas				
Asparagopsis taxiformis	6	33.50 ± 5.50	n.d – 77.00	33.33%
Zooplankton	6	138.2 ± 173.3	n.d - 191.3	50%
Arbacia lixula	10	85.00 ± 17.50	n-d - 102.5	20%
Holothuria sanctori	10	n.d	n.d	0%
Sarpa salpa	10	n.d	n.d	0%
Sparisoma cretense	10	7.560 ± 0	n.d - 7.56	10%
Seawater	6	0.012 ± 0.004	n.d - 0.015	50%
Sediments	6	n.d	n.d	0%
Serratus atricauda	5	n.d	n.d	0%

APPENDIX C – Supplementary Data to Chapter IV

Appendix C contains the supplementary data associated with the submitted manuscript:

> Íñiguez, E., Montesdeoca-Esponda, S., Alves, R., Ideia, P., Cordeiro, K., Dinis, A., Ferrera-Sosa, Z., and Kaufmann, M, (2026). Oganic Ultraviolet Filters from Surface Seawater to Bathypelagic species in an Oceanic Island System. *Environmental Science and Technology*, submitted.

Table IV. SM1. Characteristics of the samples included in this study. Trophic levels were obtained from Froese and Pauly (2025). DRM: Direção Regional do Mar. *Aphanopus carbo* (Acarbo), black scabbardfish; *Katsuwonus pelamis* (Kpelamis), skipjack tuna; *Scomber colias* (Sc), Atlantic chub mackerel; *Trachurus picturatus* (Tp), blue jack mackerel. Zoo: zooplankton samples (each sample represents a pooled collection of organisms). Sed: sediment samples. Total lipids (TL; %) refers to the lipid content of biota samples. FX/LM/DS: Funchal/Lombada dos Marinheiros/Deserta Grande, sampling locations. n.a.: not applicable or not available for the corresponding sample type or variable.

Code	Location	Data collection	Water column position	Trophic level	Lenght (cm)	Weight (g)	TL (%)
Acarbo030	DRM	29/03/2023	Bathypelagic	4.5	1147	1965	6.3
Acarbo031	DRM	29/03/2023	Bathypelagic	4.5	1137	1860	4.7
Acarbo032	DRM	29/03/2023	Bathypelagic	4.5	1158	1956	7.0
Acarbo033	DRM	29/03/2023	Bathypelagic	4.5	1210	2050	7.6
Acarbo034	DRM	29/03/2023	Bathypelagic	4.5	1155	2071	2.8
Acarbo035	DRM	29/03/2023	Bathypelagic	4.5	1136	1678	n.a
Acarbo069	DRM	08/05/2023	Bathypelagic	4.5	1165	1935	2.8
Acarbo071	DRM	08/05/2023	Bathypelagic	4.5	1281	2561	n.a
Acarbo074	DRM	08/05/2023	Bathypelagic	4.5	1242	2335	n.a
Acarbo150	DRM	08/05/2023	Bathypelagic	4.5	1230	2481	5.0
Acarbo151	DRM	08/05/2023	Bathypelagic	4.5	1160	2233	7.8
Acarbo152	DRM	08/05/2023	Bathypelagic	4.5	1170	1989	5.6
Acarbo153	DRM	08/08/2023	Bathypelagic	4.5	1190	2273	14.5
Acarbo154	DRM	08/08/2023	Bathypelagic	4.5	1160	1741	11.8
Acarbo155	DRM	08/08/2023	Bathypelagic	4.5	1190	2345	10.5
Kpelamis228	DRM	11/01/2024	Pelagic	4.4	45	1381	3.1
Kpelamis229	DRM	11/01/2024	Pelagic	4.4	52	2574	7.3
Kpelamis230	DRM	11/01/2024	Pelagic	4.4	44	1299	4.4
Kpelamis231	DRM	11/01/2024	Pelagic	4.4	44	1112	4.1

Code	Location	Data collection	Water column position	Trophic level	Lenght (cm)	Weight (g)	TL (%)
Kpelamis233	DRM	11/01/2024	Pelagic	4.4	44	1267	30.1
Kpelamis971	DRM	26/03/2024	Pelagic	4.4	56	2802	8.7
Kpelamis972	DRM	26/03/2024	Pelagic	4.4	51	2059	10.8
Kpelamis973	DRM	26/03/2024	Pelagic	4.4	52	2108	12.6
Kpelamis974	DRM	26/03/2024	Pelagic	4.4	51	2053	9.7
Kpelamis975	DRM	26/03/2024	Pelagic	4.4	50	1790	8.4
Sc_1	Fish market	10/03/2023	Pelagic-Neritic	3.9	26.6	161.63	6.2
Sc_2	Fish market	10/03/2023	Pelagic-Neritic	3.9	29.2	179.42	3.9
Sc_3	Fish market	10/03/2023	Pelagic-Neritic	3.9	25.6	150.02	5.5
Sc_4	Fish market	10/03/2023	Pelagic-Neritic	3.9	27.2	157.35	5.4
Sc_5	Fish market	10/03/2023	Pelagic-Neritic	3.9	25	144.07	5.5
Sc_7	Fish market	20/09/2023	Pelagic-Neritic	3.9	32.9	328.98	21.1
Sc_8	Fish market	20/09/2023	Pelagic-Neritic	3.9	34	345.77	21.3
Sc_9	Fish market	20/09/2023	Pelagic-Neritic	3.9	32.6	313.38	20.5
Sc_10	Fish market	20/09/2023	Pelagic-Neritic	3.9	31.4	286.47	20.3
Sc_11	Fish market	20/09/2023	Pelagic-Neritic	3.9	31.5	287.21	22.1
Tp_1	Fish market	23/03/2023	Bentopelagic	3.3	20	50.504	4.6
Tp_2	Fish market	23/03/2023	Bentopelagic	3.3	20	62.22	6.1
Tp_3	Fish market	23/03/2023	Bentopelagic	3.3	17.4	41.81	4.8
Tp_4	Fish market	23/03/2023	Bentopelagic	3.3	19	50.98	6.6
Tp_5	Fish market	23/03/2023	Bentopelagic	3.3	17.6	44.95	6.1
Tp_7	Fish market	20/09/2023	Bentopelagic	3.3	21.1	73.18	7.2
Tp_8	Fish market	20/09/2023	Bentopelagic	3.3	23.6	118.68	18.8

Code	Location	Data collection	Water column position	Trophic level	Lenght (cm)	Weight (g)	TL (%)
Tp_9	Fish market	20/09/2023	Bentopelagic	3.3	21.4	81.35	n.a
Tp_10	Fish market	20/09/2023	Bentopelagic	3.3	22.4	102.55	n.a
Tp_11	Fish market	20/09/2023	Bentopelagic	3.3	25.1	142.18	20.4
zoo_pelag_FX_1	FX	02/03/2023	Zooplankton	-	-	-	n.a
zoo_pelag_FX_2	FX	02/03/2023	Zooplankton	-	-	-	n.a
zoo_pelag_FX_3	FX	02/03/2023	Zooplankton	-	-	-	n.a
zoo_pelag_FX_4	FX	14/08/2023	Zooplankton	-	-	-	n.a
zoo_pelag_FX_5	FX	14/08/2023	Zooplankton	-	-	-	n.a
zoo_pelag_FX_6	FX	14/08/2023	Zooplankton	-	-	-	n.a
zoo_pelag_LM_1	LM	16/04/2023	Zooplankton	-	-	-	n.a
zoo_pelag_LM_2	LM	16/04/2023	Zooplankton	-	-	-	n.a
zoo_pelag_LM_3	LM	16/04/2023	Zooplankton	-	-	-	n.a
zoo_pelag_LM_4	LM	18/08/2023	Zooplankton	-	-	-	n.a
zoo_pelag_LM_5	LM	18/08/2023	Zooplankton	-	-	-	n.a
zoo_pelag_LM_6	LM	18/08/2023	Zooplankton	-	-	-	n.a
zoo_pelag_DS_1	DS	12/06/2023	Zooplankton	-	-	-	n.a
zoo_pelag_DS_2	DS	12/06/2023	Zooplankton	-	-	-	n.a
zoo_pelag_DS_3	DS	12/06/2023	Zooplankton	-	-	-	n.a
zoo_pelag_DS_4	DS	03/12/2023	Zooplankton	-	-	-	n.a
zoo_pelag_DS_5	DS	03/12/2023	Zooplankton	-	-	-	n.a
zoo_pelag_DS_6	DS	03/12/2023	Zooplankton	-	-	-	n.a
water_pelagic_FX_1	FX	28/03/2023	Seawater	Environmental	-	-	n.a
water_pelagic_FX_2	FX	28/03/2023	Seawater	Environmental	-	-	n.a

Code	Location	Data collection	Water column position	Trophic level	Lenght (cm)	Weight (g)	TL (%)
water_pelagic_FX_3	FX	28/03/2023	Seawater	Environmental	-	-	n.a
water_pelagic_FX_4	FX	16/08/2023	Seawater	Environmental	-	-	n.a
water_pelagic_FX_5	FX	16/08/2023	Seawater	Environmental	-	-	n.a
water_pelagic_FX_6	FX	16/08/2023	Seawater	Environmental	-	-	n.a
water_pelagic_LM_1	LM	20/05/2023	Seawater	Environmental	-	-	n.a
water_pelagic_LM_2	LM	20/05/2023	Seawater	Environmental	-	-	n.a
water_pelagic_LM_3	LM	20/05/2023	Seawater	Environmental	-	-	n.a
water_pelagic_LM_4	LM	10/09/2023	Seawater	Environmental	-	-	n.a
water_pelagic_LM_5	LM	10/09/2023	Seawater	Environmental	-	-	n.a
water_pelagic_LM_6	LM	10/09/2023	Seawater	Environmental	-	-	n.a
water_pelagic_DS_1	DS	12/06/2023	Seawater	Environmental	-	-	n.a
water_pelagic_DS_2	DS	12/06/2023	Seawater	Environmental	-	-	n.a
water_pelagic_DS_3	DS	12/06/2023	Seawater	Environmental	-	-	n.a
water_pelagic_DS_4	DS	03/12/2023	Seawater	Environmental	-	-	n.a
water_pelagic_DS_5	DS	03/12/2023	Seawater	Environmental	-	-	n.a
water_pelagic_DS_6	DS	03/12/2023	Seawater	Environmental	-	-	n.a
Sed_pelag_FX_1	FX	22/03/2023	Sediment	Environmental	-	-	n.a
Sed_pelag_FX_2	FX	22/03/2023	Sediment	Environmental	-	-	n.a
Sed_pelag_FX_3	FX	22/03/2023	Sediment	Environmental	-	-	n.a
Sed_pelag_FX_4	FX	26/08/2023	Sediment	Environmental	-	-	n.a
Sed_pelag_FX_5	FX	26/08/2023	Sediment	Environmental	-	-	n.a
Sed_pelag_FX_6	FX	26/08/2023	Sediment	Environmental	-	-	n.a
Sed_pelag_LM_1	LM	20/05/2023	Sediment	Environmental	-	-	n.a

Code	Location	Data collection	Water column position	Trophic level	Lenght (cm)	Weight (g)	TL (%)
Sed_pelag_LM_2	LM	20/05/2023	Sediment	Environmental	-	-	n.a
Sed_pelag_LM_3	LM	20/05/2023	Sediment	Environmental	-	-	n.a
Sed_pelag_LM_4	LM	10/09/2023	Sediment	Environmental	-	-	n.a
Sed_pelag_LM_5	LM	10/09/2023	Sediment	Environmental	-	-	n.a
Sed_pelag_LM_6	LM	10/09/2023	Sediment	Environmental	-	-	n.a
Sed_pelag_DS_1	DS	03/06/2023	Sediment	Environmental	-	-	n.a
Sed_pelag_DS_2	DS	03/06/2023	Sediment	Environmental	-	-	n.a
Sed_pelag_DS_3	DS	03/06/2023	Sediment	Environmental	-	-	n.a
Sed_pelag_DS_4	DS	11/11/2023	Sediment	Environmental	-	-	n.a
Sed_pelag_DS_5	DS	11/11/2023	Sediment	Environmental	-	-	n.a
Sed_pelag_DS_6	DS	11/11/2023	Sediment	Environmental	-	-	n.a

APPENDIX C – Supplementary Data to Chapter IV

Table IV. SM2. Detection parameters for the eleven organic UV filters (oUVFs) under study using positive electrospray ionization (ESI+).

oUVFs	Parent (m/z)	Daughter (m/z)	Cone voltage (V)	Collision energy (eV)
4-MBC	255	105	25	27
		171		19
BP-3	229	105	32	25
		151		20
HMS	263	121	12	30
		139		10
OC	362	232	28	20
		250		12
BMDBM	311	135	30	23
		161		23
IMC	249	161	15	15
		179		9
DTS	502	396	12	25
		412		15
UV-360	660	224	40	35
		336		25
OD-PABA	278	150	45	40
		166.		30
OMC	291	161	20	30
		179		20
EHS	251	139	15	10
		139		10
BP-d_{10}	193	82	30	40
		110		30

Table IV. SM3. Instrumental and methodological limits of detection (ILOD and MLOD) and quantification (ILOQ and MLOQ) for the eleven organic UV filters (oUVFs) under study in the different matrices analysed.

oUVFs	Zooplankton				Fishes			
	ILOD (ug/L)	ILOQ (ug/L)ç	MLOD (ng/g)	MLOQ (ng/g)	ILOD (µg/L)	ILOQ (µg/L)	MLOD (ng/g)	MLOQ (ng/g)
4-MBC	0.138	0.460	2.757	9.191	0.212	0.706	2.117	7.057
BP-3	0.269	0.895	5.372	17.91	1.103	3.676	11.03	36.76
HMS	0.101	0.337	2.024	6.745	1.400	4.666	14.00	46.66
DTS	0.091	0.303	1.818	6.059	0.026	0.086	0.26	0.863
OC	0.149	0.498	2.988	9.960	0.215	0.716	2.147	7.158
BMDBM	0.270	0.901	5.405	18.02	0.136	0.452	1.356	4.521
IMC	0.158	0.527	3.160	10.53	0.150	0.501	1.503	5.010
UV-360	0.094	0.314	1.886	6.288	0.122	0.407	1.222	4.074
OD-PABA	0.073	0.245	1.470	4.900	0.152	0.505	1.515	5.051
OMC	0.125	0.416	2.495	8.316	0.204	0.681	2.042	6.807
EHS	0.299	0.996	5.976	19.92	0.224	0.746	2.239	7.463

oUVFs	Sediments				Seawater			
	ILOD (µg/L)	ILOQ (µg/L)	MLOD (ng/g)	MLOQ (ng/g)	ILOD (ng/L)	ILOQ (ng/L)	MLOD (ng/L)	MLOQ (ng/L)
4-MBC	0.212	0.706	0.423	1.411	0.124	0.414	0.887	2.955
BP-3	1.103	3.676	2.206	7.353	0.179	0.598	1.282	4.272
HMS	1.400	4.666	2.800	9.333	0.420	1.400	3.000	10.00
DTS	0.026	0.086	0.052	0.173	0.026	0.086	0.185	0.616
OC	0.215	0.716	0.429	1.432	0.088	0.294	0.631	2.103
BMDBM	0.136	0.452	0.271	0.904	0.136	0.452	0.969	3.229
IMC	0.150	0.501	0.301	1.002	0.150	0.501	1.074	3.579
UV-360	0.122	0.407	0.244	0.815	0.122	0.407	0.873	2.910
OD-PABA	0.152	0.505	0.303	1.010	0.152	0.505	1.082	3.608
OMC	0.204	0.681	0.408	1.361	0.204	0.681	1.459	4.862
EHS	0.224	0.746	0.448	1.493	0.224	0.746	1.599	5.330

Table IV. SM4. Individual sample-level results for the eleven oUVFs analysed in each sample. Results are reported as n.d. when the compound was not detected (<MLOD), as <MLOQ when the compound was detected but not quantified (≥MLOD and <MLOQ), and as numerical values when the compound was quantified (>MLOQ). ΣoUVFs was calculated using only quantified values (>MLOQ). *Trachurus picturatus* (blue jack mackerel) and *Scomber colias* (Atlantic chub mackerel) are not included because none of the target oUVFs were detected.

Sample ID	Matrix/Specie	4-MBC	BP-3	HMS	DTS	OC	BMDBM	IMC	UV-360	OD-PABA	OMC	EHS	∑oUVFs (>MLOQ)
Acarbo030	*Aphanopus carbo*	71.09	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	<MLOQ	n.d.	n.d.	71.09
Acarbo031	*Aphanopus carbo*	349.8	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	5.998	n.d.	n.d.	355.8
Acarbo032	*Aphanopus carbo*	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Acarbo033	*Aphanopus carbo*	83.38	n.d.	122.1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	205.5
Acarbo034	*Aphanopus carbo*	n.d.	n.d.	165.2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	165.2
Acarbo035	*Aphanopus carbo*	n.d.	n.d.	n.d.	n.d.	n.d.	50.19	n.d.	n.d.	n.d.	11.69	n.d.	61.88
Acarbo069	*Aphanopus carbo*	254.0	n.d.	144.5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	398.5
Acarbo071	*Aphanopus carbo*	n.d.	n.d.	<MLOQ	n.d.	10.55	118.6	n.d.	n.d.	n.d.	9.753	n.d.	138.9
Acarbo074	*Aphanopus carbo*	n.d.	n.d.	n.d.	n.d.	<MLOQ	38.69	n.d.	n.d.	n.d.	18.56	n.d.	57.25
Acarbo150	*Aphanopus carbo*	n.d.	n.d.	<MLOQ	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	159.5	n.d.	159.5
Acarbo151	*Aphanopus carbo*	n.d.	n.d.	n.d.	n.d.	33.98	114.7	n.d.	n.d.	n.d.	n.d.	n.d.	148.7
Acarbo152	*Aphanopus carbo*	n.d.	n.d.	n.d.	n.d.	15.81	87.10	n.d.	n.d.	n.d.	n.d.	n.d.	102.9
Acarbo153	*Aphanopus carbo*	n.d.	n.d.	<MLOQ	n.d.	7.391	83.98	n.d.	n.d.	n.d.	19.07	n.d.	110.4
Acarbo154	*Aphanopus carbo*	n.d.	n.d.	n.d.	n.d.	n.d.	73.87	n.d.	n.d.	n.d.	n.d.	n.d.	73.87
Acarbo155	*Aphanopus carbo*	n.d.	n.d.	n.d.	n.d.	7.287	65.75	n.d.	n.d.	n.d.	n.d.	n.d.	73.04
Kpelamis228	*Katsuwonus pelamis*	n.d.	n.d.	n.d.	<MLOQ	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	<MLOQ
Kpelamis229	*Katsuwonus pelamis*	n.d.	n.d.	n.d.	<MLOQ	n.d.	19.04	n.d.	n.d.	n.d.	n.d.	n.d.	19.04
Kpelamis230	*Katsuwonus pelamis*	n.d.	n.d.	n.d.	n.d.	n.d.	27.27	n.d.	n.d.	n.d.	n.d.	n.d.	27.27
Kpelamis231	*Katsuwonus pelamis*	n.d.	n.d.	n.d.	0.999	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.999
Kpelamis233	*Katsuwonus pelamis*	n.d.	n.d.	n.d.	<MLOQ	n.d.	19.21	n.d.	n.d.	n.d.	n.d.	n.d.	19.21
Kpelamis971	*Katsuwonus pelamis*	n.d.	n.d.	n.d.	n.d.	n.d.	16.66	n.d.	n.d.	n.d.	n.d.	n.d.	16.66
Kpelamis972	*Katsuwonus pelamis*	n.d.	n.d.	n.d.	n.d.	n.d.	73.12	n.d.	n.d.	n.d.	n.d.	n.d.	73.12
Kpelamis973	*Katsuwonus pelamis*	n.d.	n.d.	n.d.	1.827	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	1.827
Kpelamis974	*Katsuwonus pelamis*	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Kpelamis975	*Katsuwonus pelamis*	n.d.	n.d.	n.d.	n.d.	n.d.	71.17	n.d.	n.d.	n.d.	n.d.	n.d.	71.17
zoo_pelag_FX_1	Zooplankton	n.d.	28.00	n.d.	n.d.	93.00	n.d.	n.d.	n.d.	n.d.	n.d.	19.33	140.3
zoo_pelag_FX_2	Zooplankton	n.d.	80.00	14.00	n.d.	17.00	n.d.	n.d.	n.d.	n.d.	n.d.	26.00	137.0

APPENDIX C – Supplementary Data to Chapter IV

Sample ID	Matrix/Specie	4-MBC	BP-3	HMS	DTS	OC	BMDBM	IMC	UV-360	OD-PABA	OMC	EHS	∑oUVFs (>MLOQ)
zoo_pelag_FX_3	Zooplankton	n.d.	67.00	24.56	n.d.	15.20	n.d.	n.d.	n.d.	74.00	n.d.	n.d.	180.8
zoo_pelag_FX_4	Zooplankton	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
zoo_pelag_FX_5	Zooplankton	n.d.	n.d.	118.00	n.d.	635.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	753.0
zoo_pelag_FX_6	Zooplankton	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
zoo_pelag_LM_1	Zooplankton	n.d.	182.0	110.0	53.00	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	345.0
zoo_pelag_LM_2	Zooplankton	n.d.	108.0	108.0	88.00	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	304.0
zoo_pelag_LM_3	Zooplankton	n.d.	n.d.	n.d.	42.70	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	42.70
zoo_pelag_LM_4	Zooplankton	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
zoo_pelag_LM_5	Zooplankton	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
zoo_pelag_LM_6	Zooplankton	n.d.	n.d.	32.00	n.d.	31.00	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	63.00
zoo_pelag_DS_1	Zooplankton	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
zoo_pelag_DS_2	Zooplankton	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
zoo_pelag_DS_3	Zooplankton	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
zoo_pelag_DS_4	Zooplankton	n.d.	n.d.	13.40	n.d.	32.97	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	46.37
zoo_pelag_DS_5	Zooplankton	n.d.	n.d.	n.d.	n.d.	39.45	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	39.45
zoo_pelag_DS_6	Zooplankton	n.d.	n.d.	8.045	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	8.045
water_pelagic_FX_1	Seawater	n.d.	n.d.	n.d.	n.d.	7.925	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	7.925
water_pelagic_FX_2	Seawater	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
water_pelagic_FX_3	Seawater	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
water_pelagic_FX_4	Seawater	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
water_pelagic_FX_5	Seawater	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
water_pelagic_FX_6	Seawater	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
water_pelagic_LM_1	Seawater	n.d.	n.d.	n.d.	n.d.	<MLOQ	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	<MLOQ
water_pelagic_LM_2	Seawater	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
water_pelagic_LM_3	Seawater	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
water_pelagic_LM_4	Seawater	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
water_pelagic_LM_5	Seawater	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
water_pelagic_LM_6	Seawater	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
water_pelagic_DS_1	Seawater	n.d.	n.d.	n.d.	28.42	8.455	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	36.88
water_pelagic_DS_2	Seawater	n.d.	n.d.	n.d.	15.74	<MLOQ	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	15.74
water_pelagic_DS_3	Seawater	n.d.	n.d.	n.d.	38.36	<MLOQ	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	38.36
water_pelagic_DS_4	Seawater	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
water_pelagic_DS_5	Seawater	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
water_pelagic_DS_6	Seawater	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

APPENDIX C – Supplementary Data to Chapter IV

Sample ID	Matrix/Specie	4-MBC	BP-3	HMS	DTS	OC	BMDBM	IMC	UV-360	OD-PABA	OMC	EHS	∑oUVFs (>MLOQ)
Sed_pelag_FX_1	Sediment	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Sed_pelag_FX_2	Sediment	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Sed_pelag_FX_3	Sediment	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Sed_pelag_FX_4	Sediment	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Sed_pelag_FX_5	Sediment	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Sed_pelag_FX_6	Sediment	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Sed_pelag_LM_1	Sediment	n.d.	n.d.	n.d.	n.d.	<MLOQ	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	<MLOQ
Sed_pelag_LM_2	Sediment	n.d.	n.d.	n.d.	n.d.	<MLOQ	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	<MLOQ
Sed_pelag_LM_3	Sediment	n.d.	n.d.	n.d.	n.d.	3.000	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	3.000
Sed_pelag_LM_4	Sediment	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Sed_pelag_LM_5	Sediment	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Sed_pelag_LM_6	Sediment	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Sed_pelag_DS_1	Sediment	n.d.	n.d.	n.d.	n.d.	<MLOQ	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	<MLOQ
Sed_pelag_DS_2	Sediment	n.d.	n.d.	n.d.	n.d.	<MLOQ	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	<MLOQ
Sed_pelag_DS_3	Sediment	n.d.	n.d.	n.d.	n.d.	<MLOQ	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	<MLOQ
Sed_pelag_DS_4	Sediment	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Sed_pelag_DS_5	Sediment	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Sed_pelag_DS_6	Sediment	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

APPENDIX C – Supplementary Data to Chapter IV

Table IV. SM5. Spearman correlation results for the associations tested between ΣoUVF concentrations and biometric variables in fish species with quantifiable oUVF concentrations. Results are expressed as Spearman's rho and corresponding *p*-values.

Species	**Variable 1**	**Variable 2**	**Spearman's rho**	***p*-value**
A. carbo	ΣoUVFs	Length	0.365	0.244
		Weight	0.189	0.558
		Total lipid content	0.319	0.313
K. pelamis	ΣoUVFs	Length	0.173	0.633
		Weight	0.273	0.448
		Total lipid content	0.018	0.973

APPENDIX D – Supplementary Data to Chapter V

Appendix D consists of the supplementary data associ

ated with the published manuscript:

Íñiguez, E., Montesdeoca-Esponda, S., Alves, F., Sosa-Ferrera, Z., Kaufmann, M., Cordeiro, N., & Dinis, A. (2025). Organic ultraviolet filters in the blubber of two free-ranging deep-diving cetacean species. Environmental Pollution, 383, 126830. https://doi.org/10.1016/j.envpol.2025.126830

APPENDIX D – Supplementary Data to Chapter V

Table V. SM1. UV filters: organic (oUVF) and inorganic (iUVF) allowed in the European Union according to Annex VI of the EU Cosmetic Regulation. The absence of data indicates that no information is currently available for those compounds.

Family	UE Number	INCI Nomenclature	Abbreviated name	CAS number	EC number	Log K_{ow}	Solubility (g/L)	pKa	Max. Concentration (%)
Benzophenones	4	Benzophenone-3	BP3	131-57-7	205-031-5	3.79	0.21	7.56	6
	22	Benzophenone-4, Benzophenone-5	BP4, BP5	4065-45- 6, 6628- 37-1	223-772-2, 613-918-7	0.37	0.65	-0.7	5
P-Aminobenzoic acid and derivates	21	Etylhexyl dimethyl PABA	OD-PABA	21245- 02-3	244-289-3	6.15	$2.1x10^{-3}$	2.39	8
	13	Ethoxylated Ethyl-4-Aminobenzoate	PEG-25 PABA	116242-27-4					
Salicytates	3	Homosalate	HMS	118-56-9	204-260-8	6.16	0.02	8.09	10
	20	2-Ethylhexyl salicylate	EHS	118-60-5	204-263-4	5.97	0.028	8.13	5
Cinnamates	12	2-Ethylhexyl 4-methoxycinnamate	OMC	83834- 59-7/ 5466-77- 3	226-775-7	5.8	0.15		10
	14	Isopentyl-4-methoxycinnamate	IMC	71617- 10-2	275-702-5	4.33	0.06		10

Family	UE Number	INCI Nomenclature	Abbreviated name	CAS number	EC number	Log K_{ow}	Solubility (g/L)	pKa	Max. Concentration (%)
Camphor derivates	2	N,N,N-Trimethyl-4-(2-oxoborn-3-ylidenemethyl) anilinium methyl sulfate	CBM	52793- 97-2	258-190-8	0.28	0.007		6
	7	Ecamsule	PDSA	92761- 26-7/ 90457- 82-2	410-960-6	3.83	0.014	-1.05	10
	9	alpha-(2-Oxoborn-3-ylidene)-toluene-4-sulphonic acid	BCSA	56039- 58-8	809-459-9	2.22	0.038	-0.7	6
	11	Poyacrylamidomethyl benzylidene camphor	PBC	113783- 61-2					6
	18	4-Methybenzylidene camphor	4MBC	36861- 47-9/ 38102- 62-4		4.95	$5.1x10^{-3}$		4
Triazines	15	Ethylhexyl triazone	OT	88122- 99-0	402-070-1	17.05		3.17	5
	17	Diethylhexyl butamido triazole	DBT	154702- 15-5	421-450-8	14.03	$4.6x10^{-7}$	3.04	10

Family	UE Number	INCI Nomenclature	Abbreviated name	CAS number	EC number	Log K_{ow}	Solubility (g/L)	pKa	Max. Concentration (%)
	25	Bis-ethylhexyloxyphenol methoxyphenyl triazine	EMT	187393- 00-6	425-950-7	8.03	$4.9x10^{-8}$	6.37	10
	29	Tris-biphenyl triazine	TBPT	31274-51-8	479-950-7	10.38	$5.5x10^{-10}$	1.2	10
	31	Phenylene bis-diphenyltriazine	TiAsorB	55514-22-2	700-823-1	10.5	$2x10^{-8}$		5
Benzotriazoles	16	Dometrizole trisiloxane	DTS	155633-54-8	423-660-5	10.82	$1.3x10^{-5}$	9.72	15
	23	Methylene bis-benzotriazolyl trtra-methylbutylphenol	MBP	103597-45-1	403-800-1	12.46	$3x10^{-8}$	7.56	10
Benzimidazole derivates	6	Phenylbenzimidazole sulfonic acid	PMDSA	27503-81-7	248-502-0	-0.16	0.26	-0.87	8
	24	Disodium phenyl dibenzimidazole tetrasulfonate	DPDT	180898-37-7	429-750-0	-6.79	0.5	-0.27	10
Dybenzoyl methane derivates	8	Butyl methoxidibenzoylmethane	BMDBM	70356-09-1	274-581-6	4.51	0.037	9.74	5
	28	Diethylamino hydroxybenzoyl hexyl benzoate	DHHB	302776-68-7	443-860-6	6.54	$9.5x10^{-4}$	7.29	10
Crilenes	10	Octocrylene	OC	6197-30-4	228-250-8	6.88	$2x10^{-4}$		10

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Family	UE Number	INCI Nomenclature	Abbreviated name	CAS number	EC number	Log K_{ow}	Solubility (g/L)	pKa	Max. Concentration (%)
Benzyl malonate derivatives	26	Polysilicone-15	BMP	207574-74-1	606-621-9	5.66	0.001		10
	33	Bis-Piperazine	HAA299	919803-06-8	485-100-6	6.8	$1.6x10^{-6}$		10
Others	32	Ethoxyethyl cyanoacetate of methoxypropylamino cyclohexenylidene	MCE	1419401-88-9	700-860-3	1.7	0.45	13.3	3
Inorganic or mineral	27	Titanium dioxide	TiO_2	13463-67-7	236-675-5				
	30	Zinc oxide	ZnO	1314-13-2	215-222-5				

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Table V. SM2. Detection parameters for the eleven organic UV filters (oUVF) under study using positive electrospray ionization (ESI+).

oUVF	Parent ion (m/z)	Cone voltage (V)	Quantification ion (m/z)	Collision potential (V)	Confirmation ion (m/z)	Collision potential (V)
4-MBC	255.4	25	105.0	27	171.0	19
BP-3	229.0	32	151.0	20	105.0	25
HMS	263.1	12	139.0	10	121.0	30
OC	362.4	28	250.0	12	232.0	20
BMDBM	311.2	30	161.2	23	135.1	23
IMC	249.1	15	161.2	15	179.2	9
DTS	502.0	12	412.2	15	396.2	25
UV-360	659.8	40	336.3	25	224.2	35
OD-PABA	278.4	45	166.1	30	150.8	30
OMC	291.2	20	161.4	30	179.0	30
EHS	251.1	15	139.2	10	138.9	10
BP-d10	193.0	30	82.20	40	109.8	30

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Table V. SM3. Instrumental and methodological limits of detection (ILOD and MLOD) and quantification (ILOQ and MLOQ) for the eleven organic UV filters (oUVF) under study.

Compound	ILOD (ug/L)	ILOQ (ug/L)	MLOD (ng/g)	MLOQ (ng/g)
4-MBC	0.212	0.706	2.117	7.057
BP-3	1.103	3.676	11.03	36.77
HMS	1.400	4.666	14.00	46.66
DTS	0.026	0.086	0.259	0.863
OC	0.215	0.716	2.147	7.158
BMDBM	0.136	0.452	1.356	4.521
IMC	0.150	0.501	1.503	5.010
UV-360	0.122	0.407	1.222	4.074
OD-PABA	0.152	0.505	1.515	5.051
OMC	0.204	0.681	2.042	6.807
EHS	0.224	0.746	2.239	7.463

Table V. SM4. Database of organic UV filters (oUVF) detected in blubber samples from two deep-diving cetaceans (ng/g, w.w.), along with the code, date, and sex of the biopsied animals.

Specie	Sample Code	Sex	Collection Day	HMS	OC	UV360	EHS	∑oUVF
Physeter macrocephalus	Pm071	F	14/10/2022	n.d	n.d	n.d	n.d	0.000
	Pm067	F	27/05/2022	178.0	47.56	n.d	n.d	225.5
	Pm070	F	04/10/2022	n.d	96.69	n.d	n.d	96.69
	Pm064	F	27/05/2022	n.d	19.96	n.d	n.d	19.96
	Pm081	F	15/11/2022	n.d	43.41	n.d	n.d	43.41
	Pm055	F	19/10/2021	n.d	n.d	276.9	1505	1782
	Pm052	F	12/10/2021	n.d	n.d	181.2	182.2	363.4
	Pm059	F	02/11/2021	184.2	44.78	n.d	668.8	897.8
	Pm080	F	15/11/2022	n.d	n.d	112.8	614.2	727.0
	Pm066	F	27/05/2022	92.46	n.d	113.6	1034	1240
Globicephala macrorhynchus	Gma026	F	18/04/2018	99.88	51.26	95.49	n.d	246.6
	Gma028	F	21/05/2018	160.9	137.7	95.37	352.3	746.2
	Gma05	F	03/11/2017	90.45	99.61	n.d	199.1	389.2
	Gma015	F	18/11/2017	99.73	68.94	n.d	193.9	362.5
	Gma065	M	22/11/2022	93.85	91.69	87.14	183.6	456.3

APPENDIX D – Supplementary Data to Chapter V

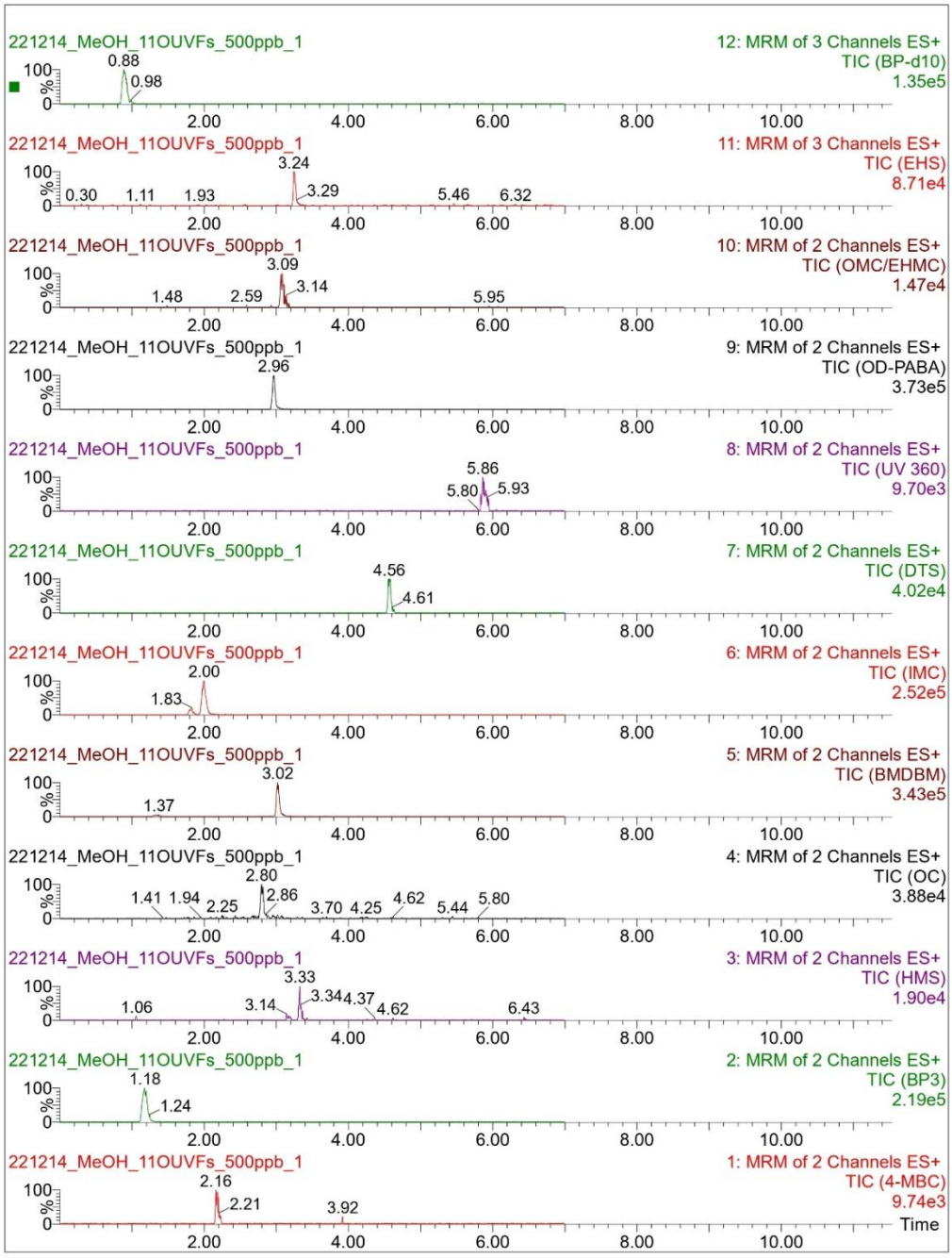

Fig. V. SM1. UHPLC-MS/MS chromatograms of the eleven target oUVFs and the internal standard (IS), BP-d_{10}, at a concentration of 500 ug/L in methanol. Each panel represents a separate compound monitored using multiple reaction monitoring (MRM) in positive electrospray ionization (ES+) mode. The retention time (RT) for each compound is indicated by the peak apex in its corresponding trace.