EVALUACIÓN E IMPACTO DE LA PRESENCIA DE FILTROS ULTRAVIOLETA ORGÁNICOS POR ACTIVIDADES ANTROPOGÉNICAS EN EL MEDIO MARINO COSTERO

Evaluation and impact of the presence of organic ultraviolet filters due to anthropogenic activities in the coastal marine environment

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RESUMEN

La calidad química y la ecológica del medio marino dependen tanto de procesos naturales como de procesos antropogénicos. Problemas relacionados con la absorción de contaminantes y su posterior bioacumulación en organismos vivos han sido descritos a nivel global. Por tanto, es necesario identificar las fuentes de contaminación y las nuevas familias de compuestos que están continuamente llegando al entorno marino.

Uno de estos nuevos grupos de contaminantes son los denominados Productos de Cuidado Personal (PCP). Este término hace referencia a un amplio grupo de compuestos químicos que son

incluidos en una gran diversidad de productos extensamente utilizados en el día a día.

Entre estos productos, los filtros ultravioleta (UV) orgánicos son un grupo de compuestos utilizados en varios PCP y cremas solares para proteger la piel de los efectos nocivos de la radiación solar. Debido a su continuo uso, estos compuestos son liberados constantemente al medio acuático, donde ya se han detectado en diferentes matrices medioambientales. Así, la presente Tesis Doctoral, expone los resultados del estudio de ocho filtros UV orgánicos ampliamente usados en muestras ambientales marinas. A lo largo de la Memoria, se presentan en gran detalle los resultados obtenidos del análisis de los compuestos seleccionados en aguas residuales y costeras, además de su efecto (bioconcentración y bioacumulación) en macrofitas marinas (macroalgas y fanerógamas) y en consumidores primarios marinos.

Para llevar a cabo el análisis de estas muestras, fue necesario el desarrollo de nuevos métodos de análisis altamente sensibles y selectivos. Estos métodos estuvieron basados en la aplicación de dos técnicas de extracción, usándose la extracción en fase sólida para muestras líquidas, y la extracción asistida por microondas para muestras sólidas. A continuación, se usó la cromatografía líquida de ultra resolución con espectrometría de masas en tándem como sistema de separación y detección, respectivamente.

Con el fin de evaluar las consecuencias de la entrada constante e intensa de filtros UV en zonas costeras por las actividades humanas, se han estudiado tres playas de la isla de Gran Canaria. La isla de Gran Canaria forma parte del Archipiélago Canario (España), el cual está localizado en el Océano Atlántico. En esta isla, uno de los pilares económicos fundamentales es el turismo, principalmente el de playa. Por lo tanto, es un escenario idóneo para estudiar el impacto ambiental relacionado con la entrada de filtros UV, ya que sus costas están bajo una gran presión turística.

Las tres playas seleccionadas son: la playa de Las Canteras, la playa de Arinaga y Playa del Inglés, las cuales tienen diferentes características geomorfológicas y frecuencias de uso. Se estudió en primer lugar la presencia y variación espaciotemporal de estos compuestos en aguas costeras, y luego se evaluó su riesgo ambiental.

Puesto que en el medio marino los organismos se hallan expuestos a esta contaminación, se estableció la presencia de los filtros UV orgánicos seleccionados en macrofitas provenientes de las mismas tres playas de Gran Canaria. Esto complementa el estudio del impacto de los analitos en estas localidades. Se analizaron diferentes tipos de algas (rojas, pardas y verdes) y una especie de fanerógama marina. La presencia de estos contaminantes

demostró la idoneidad de usar dichos organismos como centinelas o bioindicadores, ya que son sésiles y capaces de acumular los analitos objetivo. Por otro lado, también se estableció la presencia de los filtros UV orgánicos escogidos en diferentes tipos de consumidores primarios marinos para evaluar su impacto ambiental. Así mismo, se estudió las relaciones entre dos niveles de la cadena trófica, es decir, la bioconcentración en niveles bajos y la posible biomagnificación en niveles superiores.

Los resultados obtenidos en la presente Memoria de Tesis Doctoral se estructuran en cuatro capítulos. En el primer capítulo se incluye una discusión sobre el estado del arte del tema con un exhaustivo trabajo bibliográfico, profundizando en los riesgos que presentan los filtros UV en el contexto del medioambiente marino. También se introducen las metodologías analíticas desarrolladas a lo largo de los últimos años, poniendo de manifiesto el perfeccionamiento de éstas hacia una maximización de la especificidad, resolución y sensibilidad.

En el siguiente capítulo se exponen los objetivos de la Tesis. El tercer capítulo se centra en los trabajos experimentales realizados. Esta sección comprende una breve introducción sobre el tema en cuestión, sus objetivos, el desarrollo experimental, y una discusión de los resultados obtenidos de cada trabajo experimental.

Para finalizar, el último capítulo recoge las Conclusiones de esta Tesis, destacando la presencia y destino de los compuestos seleccionados en el medio marino, aportando información nueva sobre la posible amenaza que estos representan para los organismos marinos.

ABSTRACT

The ecology and chemical quality of the marine environment relies heavily on natural and anthropogenic processes. Several problems related to the uptake of pollutant and their subsequent bioaccumulation in organisms have been described worldwide. Therefore, it is essential determine the pollution sources and type of pollutants that are continuously releasing into the marine environment.

One of the new kind of pollutants refers to Personal Care Products (PCPs). A wide range of chemical compounds added to daily life products are included in this group.

Among these chemicals, the organic ultraviolet (UV) filters are a group of compounds used in sunscreens and different PCPs to protect the skin against the harmful effects of the solar radiation. Due to their intense release into the environment, they have been already detected in several environmental matrices. Hence, this Doctoral Thesis presents the results of the determination of eight widely used organic UV filters in environmental marine matrices. The results about the analysis of the target compounds in seawater, wastewater and marine biota are explained in great detail throughout this Thesis, moreover, the effects (bioconcentration and bioaccumulation) on macrophytes (seaweeds and seagrass) and primary marine consumers.

Highly sensitive and selective analytical methodologies were developed to accomplish this Thesis. These methodologies were based on the use of extraction techniques such as solid-phase extraction in the case of liquid samples, and microwave assisted extraction for solid samples, followed by ultra-high resolution liquid chromatography with tandem mass spectrometry detection.

In order to assess the effects of the constant and intense input of organic UV filters into coastal areas because of human activities, three beaches of Gran Canaria Island were selected. The Gran Canaria Island is part of Canary archipelago, which is located in the Atlantic Ocean. One of the mainstays of its economy is the tourism,

mainly beach tourism. Therefore, this is a perfect scenario to analyse the environmental impact associated to the input of UV filters, since its coasts are subjected to the intense tourism pressure.

The selected beaches are: Las Canteras beach, Arinaga beach and Playa del Inglés beach, they were selected because all of them have different geomorphological characteristics and tourisms pressure. Firstly, the presence and environmental hazard of the target analytes in coastal waters was assessed, and then their spatiotemporal variation.

Due to the continuous exposure of organisms to the pollutants in the marine environment, the presence of organic UV filters in macrophytes from the three selected beaches was established. Thus, carrying out an extensive study of their impact in the three beaches. Different seaweeds (red, green, and brown) and one seagrass were analysed. The presence of the target compounds demonstrates the suitability of use them as bioindicators, since the macrophytes are sessile and accumulate the target analytes. In addition, the presence of the selected organic UV filters in different primary marine consumers was established to assess their environmental impact. Moreover, the relationship between two trophic, *i.e.* bioaccumulation at lower levels and possible biomagnification at higher levels were evaluated.

The results of this Thesis is structured in four chapters. The first one includes an exhaustive bibliographic revision of the state of the art of the field, delving deeper into the risk posed by organic UV filters for the marine environment. The analytical methodologies developed over the last few years are also reviewed, highlighting their improvement towards a maximization of specificity, resolution, and sensitivity.

The following chapter exposes the objectives of this Thesis. The next one focus on the experimental work carried out. This chapter comprises in a short introduction on the theme, its objectives, the experimental development, and a discussion of the results of each experimental work.

Finally, the last chapter contains the Conclusions of this Thesis, highlighting the presence and fate of the selected compounds in the marine environment, thus diving new information about the possible hazard that organic UV filters represent for the marine organisms.

CAPÍTULO 1. INTRODUCCIÓN

El medio acuático como sistema en sí mismo es considerado como un recurso. Este medio es vital para los organismos vivos y los ecosistemas de los cuales depende, además de ser un recurso esencial para varios tipos de actividades económicas. La calidad del entorno acuático es, en consecuencia, de gran interés debido a nuestra interacción con sus recursos naturales en la vida cotidiana, personal e industrial. Por ello, el control de su calidad es esencial para conservarlo, pues es un recurso crítico del que dependen varias actividades sociales y económicas.

De hecho, una gran proporción de la población mundial está concentrada en la zona costera, de alrededor del 60 % en un radio de 100 km (Pintado-Herrera and Lara Martín, 2020). Existe una creciente preocupación acerca de las acciones humanas que son capaces de afectar el ecosistema acuático a través de la introducción de diferentes compuestos antropogénicos.

Como consecuencia del aumento de las actividades humanas y del desarrollo industrial, productos químicos de diferente naturaleza se vierten constantemente al entorno acuático, resultando un riesgo para el propio medio y la población que interactúa con él. De hecho, la problemática de productos químicos provenientes de aguas residuales urbanas, industriales y de la agricultura, ha ido incrementando con el tiempo (Pintado-Herrera and Lara Martín, 2020). Existe una constante generación de nuevos productos químicos, que pueden constituir contaminantes potenciales cuyos efectos a corto, medio y largo plazo para los organismos expuestos, son todavía desconocidos. Además, en la mayoría de los casos, la ausencia de esta información impide la actuación de las autoridades competentes para desarrollar regulaciones, estableciendo límites máximos permisibles, o prohibiciones de uso en bienes comerciales, así como su control en el medio amiente. Por tanto, la continua descarga al medio ambiente de estos compuestos químicos, su presencia y su persistencia son factores de una creciente preocupación.

Dependiendo de las características químicas de cada compuesto, éstos pueden sufrir diferentes transformaciones, así pues, tendrán una distribución u otra. Obedeciendo al ritmo de transformaciones o degradación de estos compuestos, dentro del compartimiento donde se encuentran retenidos (agua, sedimentos o biota) (Pintado-Herrera and Lara Martín, 2020) se podrán eliminar o no del medio acuático receptor. Además, estas sustancias pueden transportarse y ser encontradas a grandes distancias de la fuente de emisión. Dada la reducida capacidad natural de depuración del entorno y la constante entrada de estos compuestos al medio, éstos pueden quedar retenidos en diferentes matrices, convirtiéndose en sustancias pseudo-persistentes. Adicionalmente, debido a la lipoficidad de estos compuestos, puede producirse una acumulación en los tejidos de organismos. La bioacumulación puede calcularse como la ratio de la substancia absorbida por el organismo vivo y la cantidad de la misma que se encuentra en el ambiente en el cual vive. Para poder evaluar este proceso, es necesario conocer sus propiedades fisicoquímicas para predecir y entender su hidrofobicidad, y por ende su potencial de bioacumulación.

Un proceso estrechamente relacionado con la bioacumulación es el de biomagnificación. Éste es el proceso por el cual una substancia bioacumulada en un organismo es transferida a un organismo superior, aumentando por tanto la concentración del compuesto en este último.

De entre las toneladas de sustancias vertidas al medio acuático, se diferencian dos grandes grupos, los contaminantes orgánicos y los inorgánicos. Dentro del grupo de compuestos orgánicos se distinguen, a su vez, dos grupos, los contaminantes prioritarios y los contaminantes emergentes, los cuales fueron establecidos dentro de la Unión Europea por la Directiva Europea 2013/39/CE (Commission, 2013). Las principales diferencias entre estos grupos son que los contaminantes prioritarios están sujetos a la legislación y sus efectos adversos han sido establecidos. Por otro lado, los contaminantes emergentes se encuentran bajo estudio y no están sujetos a ninguna normativa. Aunque las concentraciones de los contaminantes emergentes, en general, son bajas, el posible impacto sobre el medioambiente, los seres humanos y animales tras una larga exposición es aún desconocido (Thomaidis et al., 2012). Entre estos contaminantes emergentes se encuentran medicamentos de diferentes usos terapéuticos, (antibióticos, analgésicos, esteroides, hormonas, etc.) así como los productos de cuidado personal (PCP), los aditivos industriales, drogas de abuso, productos de derivados de la vida cotidiana como la cafeína, nicotina, edulcorantes artificiales, aditivos alimentarios, etc. (Stuart et al., 2012; Teijon et al., 2010; Thomaidis et al., 2012).

Estos contaminantes emergentes de diversa naturaleza, así como sus derivados, son substancias mayoritariamente nuevas que han sido liberadas al medio ambiente durante las últimas décadas

debido a cambios socioeconómicos y que, hasta tiempos recientes, no han sido reconocidos como tales. Estos compuestos pueden suponer un riesgo potencial para el medio acuático, ya que grandes cantidades son vertidas al medio ambiente a diario y generalmente presentan una baja biodegradabilidad (Thomaidis et al., 2012). Algunos de estos contaminantes emergentes han mostrado tener efectos nocivos sobre organismos, uno de los cuales es el efecto de disrupción endocrina, el cual puede ser causado por retardantes de llama, productos de cuidado personal y algunos fármacos (Gmurek et al., 2017).

Pese al creciente interés en el estudio de estos contaminantes, hay poca información disponible, lo cual hace difícil la predicción sobre la posible toxicidad para los organismos marinos, e incluso su propio destino dentro del medioambiente (Poynton and Vulpe, 2009), aún más, cuando las cantidades que se pueden verter siguen sin estar bajo regulación. Por lo tanto, el estudio de estos contaminantes es necesario para ayudar a crear y mantener regulaciones que permitan el crecimiento responsable de la sociedad mediante la protección del medioambiente.

1.1. Filtros ultravioleta

La exposición moderada a la radiación solar tiene efectos positivos sobre la salud humana, como, por ejemplo, la síntesis de

la vitamina D. Sin embargo, la excesiva exposición al sol puede causar efectos adversos como quemaduras solares, el envejecimiento prematuro de la piel y, en casos más graves, cáncer de piel. Esto unido a la actual tendencia de pasar más tiempo bajo la influencia del sol, ha propiciado el desarrollo de protección solar contra la radiación ultravioleta (UV). Recientemente se ha observado un aumento de problemas cutáneos relacionados con la radiación UV, llegando a considerarla una amenaza para la salud pública (Ramos et al., 2015).

La incidencia de la radiación UV sobre la tierra llega en dos rangos de longitud de onda, los cuales corresponden a la radiación UVA y UVB. La radiación UVA comprende la longitud de onda de entre 320 y 400 nanómetros (nm). Esta radiación potencia los efectos adversos de la radiación UVB, es la responsable del bronceado, la fotosensibilidad y contribuye al envejecimiento de la piel. La radiación UVB comprende la longitud de onda entre 280 y 320 nm y es la responsable principal de las quemaduras solares, el envejecimiento de la piel y el desarrollo de cáncer.

Los filtros UV usados como protección solar han sido diseñados para absorber, reflejar y dispersar tanto la radiación UVA como la UVB, evitando sus efectos nocivos e impidiendo así el impacto no deseados sobre la piel (Crista et al., 2015). Existen dos tipos de filtros UV en función de su mecanismo de acción, los filtros

UV inorgánicos y los filtros UV orgánicos (Figura 1). Los filtros UV inorgánicos, o también conocidos como minerales o físicos, absorben, reflejan y dispersan la energía (Klimová et al., 2013). Estos filtros están basados en dióxido de titanio y el óxido de zinc (Santos et al., 2012) y son menos empleados (Nash et al., 2004; Shaath, 2010). Por el contrario, los filtros UV orgánicos, también considerados químicos, absorben la radiación UV eliminando el exceso de energía, disipándola mediante la emisión de calor o la relajación mediante procesos fotoquímicos que liberan isómeros.

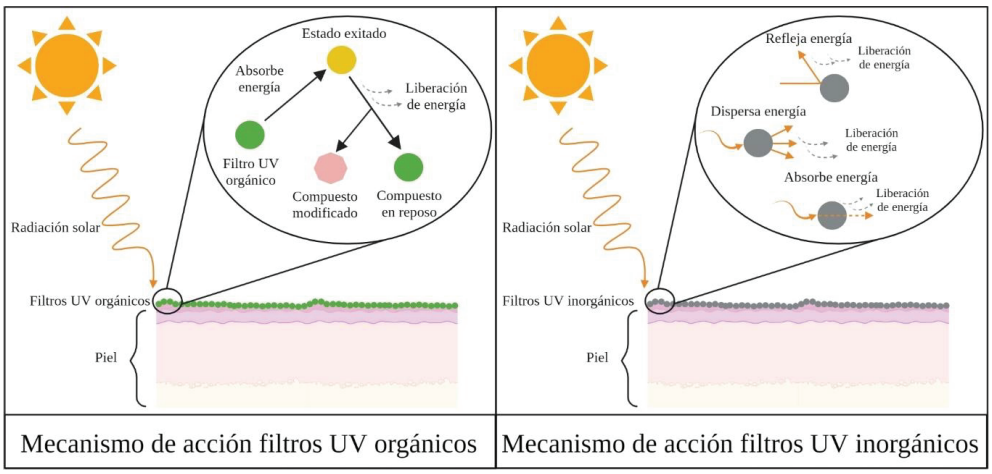


Figura 1: Mecanismo de acción de los filtros UV orgánicos e inorgánicos.

Estos filtros UV orgánicos son los más populares y ampliamente usados en productos de cuidado personal (PCP) y cremas solares. Aunque el mayor uso de estos compuestos está

relacionado con los PCP, son usados también en productos industriales como plásticos, pinturas, pegamentos, envasado de alimentos, textiles, etc., con el fin evitar la fotodegradación de polímeros y pigmentos (Ash, 2004). Se clasifican atendiendo a dos criterios, el primero se refiere a la categoría de radiación UV que absorben (UVA e UVB) y el segundo a su estructura química, siendo esta última la más usada.

La presente Tesis se centrará en los compuestos pertenecientes a los filtros UV orgánicos, ya que son los más ampliamente utilizados como aditivos en productos de cuidado personal, así como en la industria. Además, su presencia y persistencia en el medio ambiente supone un riesgo dado los indicios de efectos adversos para el ecosistema, lo cual es motivo de una creciente preocupación. En consecuencia, se han llevado a cabo acciones legislativas para regular su uso o establecer límites legales máximos autorizados en formulaciones comerciales (Shaath, 2016).

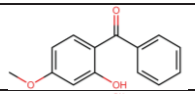
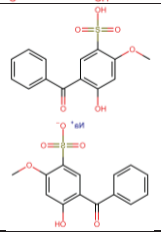
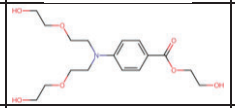
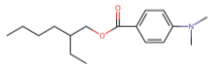
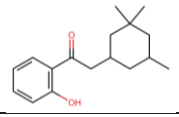
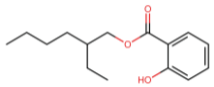
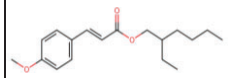
1.2. Caracterización de los filtros ultravioleta orgánicos

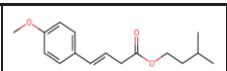
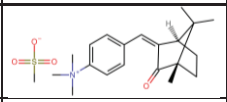
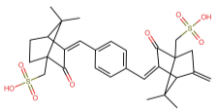
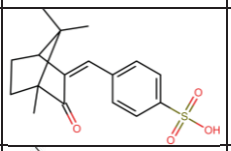
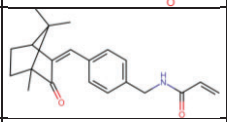
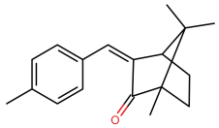
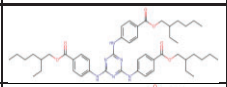
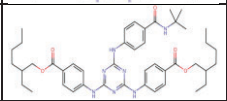
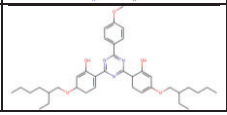
Debido a la problemática por los efectos nocivos de la radiación solar y a las recomendaciones de las autoridades sanitarias, la utilización de filtros UV orgánicos se ha extendido (Fent et al., 2010; Gago-Ferrero et al., 2012b). Sin embargo, un

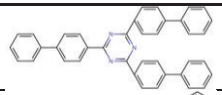
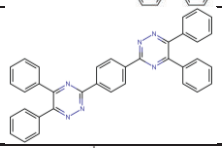
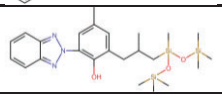
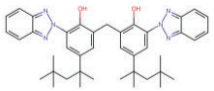
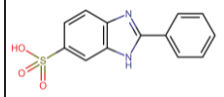
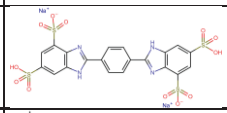
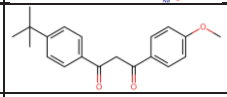
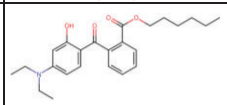
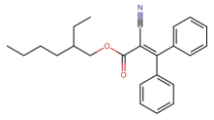
filtro UV orgánico por sí solo tiene una banda limitada de absorción, haciendo necesario el uso de combinaciones de varios de ellos para obtener la protección deseada contra ambas bandas de radiación (UVA e UVB) (Giokas et al., 2005). Existen en torno a 55 filtros UV orgánicos permitidos en los PCP, los cuales están sujetos a legislación. Por ejemplo, en la Unión Europea (UE) están controlados por la Regulación número 12223/2009 (EC., 2009), en Estados Unidos de América por la Administración de Alimentos y Medicamentos (FDA, 2007) y en Japón por la Norma Japonesa de Ingredientes Cosméticos (Nippo, 1994).

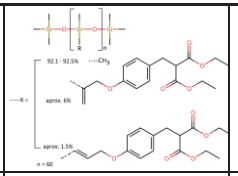
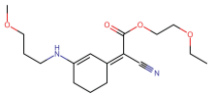
En la UE se permite el uso de 27 filtros UV orgánicos con una concentración individual entre el 3 y el 15 %, mientras que los dos filtros UV inorgánicos (dióxido de titanio y óxido de zinc) están autorizados en una concentración máxima de 25 % (EC., 2009). Una de las características comunes de los filtros UV orgánicos es la presencia de una fracción aromática unida a una cadena lateral, mostrando diferentes grados de saturación (Díaz-Cruz et al., 2008) para incrementar sus propiedades. Atendiendo a su estructura química, estos 27 filtros UV orgánicos se pueden clasificar en once familias (Bester, 2007; Crista et al., 2015; Díaz-Cruz et al., 2008). En la Tabla 1 se incluyen sus principales características. Debido a las múltiples abreviaciones usadas para estos compuestos, el número CAS y el número de referencia de la UE para ingredientes para cosméticos han sido incluidos.

Tabla 1. Principales características de los filtros UV orgánicos permitidos en productos cosméticos en la Unión Europea.

Familia	Número de ref. UE	Nomenclatura INCI[a]	Nombre abreviado	Número CAS	Estructura química	Log K_{ow}[b]	Solubilidad (g/L)[g]	pKa[h]	Región del UV	Conc. máx (%)[k]
Benzofenonas	4	Benzofenona-3	BP3	131-57-7		3.79[c]	0.21	7.56[f]	UVA/B	6
	22	Benzofenona-4, Benzofenona-5	BP4, BP5	4065-45-6, 6628-37-1		0.37[d]	0.65	-0.70[f]	UVA/B	5
Ácido p-aminobenzoico y derivados	13	4-aminobenzoato de etilo etoxilado	PEG-25 PABA	116242-27-4		-0.66[e]	-	-	UVB	10
	21	Etilhexil dimetil PABA	OD-PABA	21245-02-3		6.15[f]	$2.1x10^{-3}$	2.39[f]	UVB	8
Salicilatos	3	Homosalato	HMS	118-56-9		6.16[d]	0.02	8.09[f]	UVB	10
	20	Salicilato de 2-etilhexilo	EHS	118-60-5		5.97[f]	0.028	8.13[f]	UVB	5
Cinamatos	12	Metoxicinamato de etilhexilo	OMC	83834-59-7/ 5466-77-3		5.8[d]	0.15	-	UVB	10

	14	p-metoxicinamato de isoamilo	IMC	71617-10-2		4.33[d]	0.06	-	UVB	10
Derivados del alcanfor	2	Metosulfato de benzalconio de alcanfor	CBM	52793-97-2		0.28[e]	0.007	-	UVB	6
	7	Ácido tereftaliliden dicanforsulfónico	PDSA	92761-26-7/ 90457-82-2		3.83[e]	0.014	-1.05[h]	UVA	10
	9	Ácidos sulfónicos de bencilideno alcanfor	BCSA	56039-58-8		2.22[e]	0.038	-0.7[h]	UVB	6
	11	Alcanfor de poliacrilamido metilbencilideno	PBC	113783-61-2		-	-	-	UVB	6
	18	Alcanfor 4-metilbencilideno	4MBC	36861-47-9/ 38102-62-4		4.95[d]	$5.1x10^{-3}$	-	UVB	4
Triazinas	15	Etilhexil triazona	OT	88122-99-0		17.05[e]	-	3.17[f]	UVB	5
	17	Dietilhexil butamido triazona	DBT	154702-15-5		14.03[e]	$4.6x10^{-7}$	3.04[f]	UVB	10
	25	Bis-etilhexiloxiloxifenol metoxifenil triazina	EMT	187393-00-6		8.03[e]	$4.9x10^{-8}$	6.37[h]	UVA/B	10

	29	Tris-bifenil triazina	TBPT	31274-51-8		10.38[e]	$5.5x10^{-10}$	1.2[h]	UVA	10
	31	Fenileno bis-difeniltriazina	TriAsorB	55514-22-2		10.5[i]	$2x10^{-8}$[j]	-	UVA/B	5
Salicizoles	16	Drometrizol trisiloxano	DTS	155633-54-8		10.82[e]	$1.3x10^{-5}$	9.72[h]	UVA/B	15
	23	Metileno bis-benzotriazolil tetrametilbutilfenol	MBP	103597-45-1		12.46[e]	$3x10^{-8}$	7.56[h]	UVA/B	10
Derivados de bencimidazol	6	Ácido fenilbencimidazol sulfónico	PMDSA	27503-81-7		-0.16[e]	0.26	-0.87[f]	UVB	8
	24	Tetrasulfonato de fenil dibencimidazol disódico	DPDT	180898-37-7		-6.79[e]	0.5	-0.27[f]	UVA	10
Derivados de dibenzoil metano	8	Butil metoxidibenzoilmetano	BMDBM	70356-09-1		4.51[d]	0.037	9.74[f]	UVA	5
	28	Benzoato de dietilamino hidroxibenzoil hexilo	DHHB	302776-68-7		6.54[e]	$9.5x10^{-4}$	7.29[h]	UVA	10
Crilenos	10	Octocrileno	OC	6197-30-4		6.88[d]	$2x10^{-4}$	-	UVB	10

Derivados de bencilmalonato	26	Polisilicona-15	BMP	207574-74-1		5.66[j]	0.001[j]	-	UVB	10
Otras	32	Metoxipropilamino ciclohexenilideno cianoacetato de etoxietilo	MCE	1419401-88-9		1.7[j]	0.45[j]	13.3[j]	UVA	3

[a] Nomenclatura Internacional de Ingredientes Cosméticos (INCI, por su nombre en inglés), [b] Coeficiente de partición octanol-agua (K_{ow}), [c] Valores experimentales y [d] estimados tomados de la base de datos de la Corporación de Investigación de Syracuse, [e] Valores calculados usando la Interfaz del Programa de Estimación (EPI) v4.11, [f] Valor calculado por el software de SciFinder Scholar Database 2006: http://www.cas.org/products/sfacad/, [g] Valores tomados de Díaz-Cruz et al. (Díaz-Cruz et al., 2008) indicados en agua a 25 ºC, [h] Valores obtenidos de la web Chemicalize, [i] Valores tomados de Bacqueville et al. (Bacqueville et al., 2021), [j] Valores tomados de la Agencia Europea de Químicos (ECHA, por su nombre en inglés), [k] Concentración máxima permitida en la UE.

En la Figura 2 se incluyen las características estructurales de las 11 familias de filtros UV orgánicos.

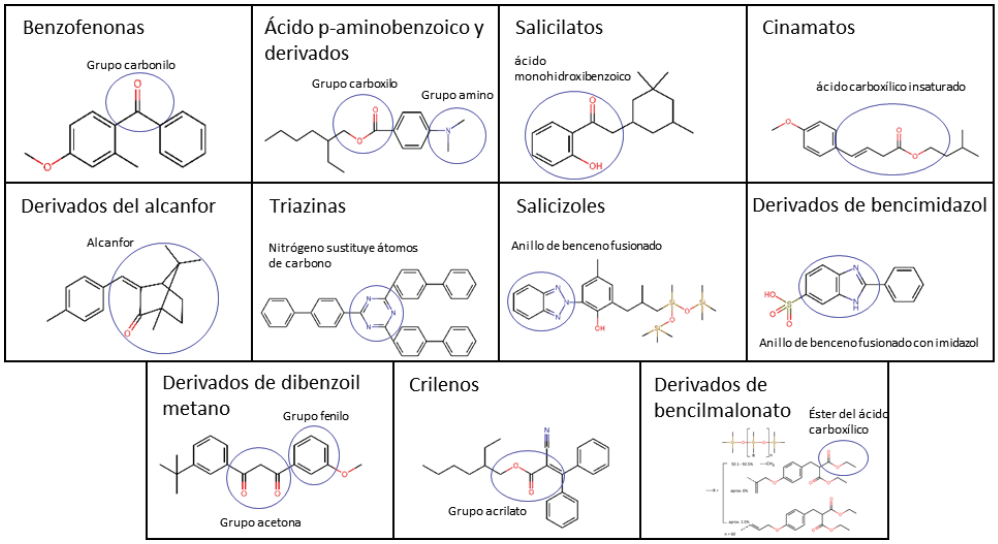


Figura 2: Principales características estructurales de las 11 familias de filtros UV orgánicos.

La familia de las benzofenonas está conformada por tres compuestos, cuya característica común es la presencia de dos anillos bencénicos unidos por un grupo carbonilo. El grupo de los ácidos p-aminobenzoicos y derivados consiste en dos compuestos, cuyo factor común es un anillo bencénico unido a un grupo amino y un grupo carboxilo. En cuanto a los salicilatos, éstos son dos compuestos, donde el rasgo distintivo es la presencia de un grupo de ácido monohidroxibenzoico. La familia de cinamatos está

integrada por dos compuestos, los cuales se caracterizan por tener ácidos carboxílicos insaturados (Ramos et al., 2016).

Los derivados del alcanfor son 5 compuestos, y son clasificados como terpenoides, para los que la característica principal es la presencia de una cetona monoterpénica cíclica, también conocida como alcanfor. Las triazinas abarcan 5 compuestos, en los que, en uno de sus anillos bencénicos, tres átomos de carbono son sustituidos por nitrógeno. La familia de los salicizoles o también llamada familia de los benzotriazoles, está integrada por dos compuestos, éstos tienen un anillo bencénico fusionado con un anillo insaturado de 5 átomos de carbono, en el cual tres carbonos son sustituidos por 3 nitrógenos.

Los derivados de bencimidazol son dos compuestos, cuyo rasgo distintivo es la presencia de un anillo bencénico fusionado a un anillo imidazol. Los derivados de dibenzoil metano son dos compuestos provenientes de la acetilacetona, donde ambos grupos metilo han sido sustituidos por dos grupos fenilo. La familia de crilenos son acrilatos aromáticos, representada por un solo compuesto. Los derivados de bencilmalonato son ésteres de ácidos dicarboxílicos con un anillo bencénico, siendo un único compuesto. El último compuesto, (Metoxipropilamino ciclohexenilideno cianoacetato de etoxietilo) no está agrupado en ninguna familia ya

que ha sido recientemente admitido como filtro UV orgánico en la UE, y aún no ha sido clasificado

Algunos de estos filtros UV orgánicos presentan compuestos quirales, es decir, tienen isómeros. Estos isómeros no presentan propiedades fisicoquímicas diferentes, sin embargo, pueden diferir en su comportamiento biológico y sus efectos. En general los isómeros E (*cis*) y Z (*trans*) son los más comunes en estos filtros UV orgánicos (Díaz-Cruz et al., 2008).

1.2.1. Propiedades fisicoquímicas de los filtros ultravioleta orgánicos

Las características fisicoquímicas influyen en el comportamiento de los filtros UV orgánicos en el medioambiente. Estos parámetros determinan su distribución y destino entre los distintos compartimentos ambientales (sólidos o líquidos) y son, además, fundamentales a la hora de elegir un método analítico adecuado para su extracción y determinación. Estas características están expuestas en la Tabla 1.

El coeficiente de partición octanol-agua (Log K_{ow}) es un indicador de la afinidad de los compuestos por fases sólidas (que hace referencia a lípidos y grasas de la biota) o líquidas. Valores de Log K_{ow} <1 indican una preferencia por fases líquidas (compuestos

hidrófilos), es decir, una gran solubilidad en agua. En cambio, valores de Log K_{ow} >4 indican una preferencia por la fase sólida (compuestos hidrófobos). Por otro lado, compuestos con valores de Log K_{ow} por encima de 8 se consideran poco biodisponibles, y aquellos con valores de Log K_{ow} por encima 10 se consideran como no biodisponibles en absoluto (Ramos et al., 2015).

La familia de los derivados de bencimidazol y los compuestos CBM, PEG-25 PABA y BP4 tienen valores de Log K_{ow} menores de 1, por lo que son considerados como hidrófilos. Las familias de los salicilatos, cinamatos, crilenos, derivados de bencilmalonato, los derivados de dibenzoil metano y los compuestos OD-PABA y 4MBC presentan valores de Log K_{ow} entre 4 y 8, los cuales son calificados como hidrofóbicos, estando en esta categoría la mayoría de los filtros UV orgánicos. Con valores de Log K_{ow} entre 8 y 10 se encuentra el compuesto EMT, el cual es considerado como no fácilmente biodisponible. Compuestos como OT, DBT, TBPT, TrisAsorB y la familia de los salicizoles tienen un Log K_{ow} mayor de 10, por lo que se trata de compuestos no biodisponibles. El compuesto con el valor más alto de todos los filtros UV orgánicos permitidos en la UE es OT (Log K_{ow} = 17.05).

La solubilidad informa sobre la probable distribución de los compuestos entre distintos compartimientos, sobre todo entre suelo/sedimento y agua. Compuestos con valores de solubilidad

mayor de 10 $g \cdot L^{-1}$ son altamente solubles, valores de entre 10 $g \cdot L^{-1}$ y 1 $g \cdot L^{-1}$ se consideran como solubles, valores entre 1 $g \cdot L^{-1}$ y 0.1 $g \cdot L^{-1}$ se consideran como moderadamente solubles, valores de entre 0.1 $g \cdot L^{-1}$ y $1 \cdot 10^{-4}$ $g \cdot L^{-1}$ son poco solubles y, por último, valores por debajo de $1 \cdot 10^{-4}$ $g \cdot L^{-1}$ se consideran como nada solubles.

Atendiendo a la solubilidad de los filtros UV orgánicos, estos van desde moderadamente solubles a nada solubles. La familia de las benzofenonas, los derivados de bencimidazol y el compuesto OMC están considerados como moderadamente solubles. La mayoría de los filtros UV orgánicos están considerados como poco solubles, ya que en esta categoría se encuentran cuatro familias (salicilatos, derivados del alcanfor, crilenos y derivados de bencilmalonato) y los compuestos OD-PABA, IMC, DHHB y BMDBM. Por el contrario, los compuestos pertenecientes a las familias triazinas y salicizoles están considerados como nada solubles, lo que hace poco probable encontrarlos en matrices líquidas.

La constante de disociación (pKa) da idea de la forma molecular de una molécula en diferentes condiciones de pH. No obstante, para la mayoría de los filtros UV orgánicos los valores experimentales son escasos, por tanto, son calculados mediante software (Tabla 1). Siguiendo este criterio, los compuestos BP3, EMT, DTS y MBP, las familias de los salicilatos y los derivados de

benzoil metano son poco probable que se disocien significativamente al pH habitual de muestras ambientales (6-7). En cambio, los compuestos como BP4, PDSA, BCSA y la familia de los derivados de bencimidazol tienen valores negativos de pKa, lo que indica que estos compuestos son afectados negativamente a pH ambientales, es decir, se encuentran disociados en este tipo de muestras (Pestotnik et al., 2014).

Además de las propiedades mencionadas anteriormente, la capacidad de degradación es otra característica que considerar. Dependiendo de las condiciones a las que sean sometidos, pueden presentar productos de degradación/transformación, subproductos, metabolitos, productos de fotodegradación y subproductos de procesos de desinfección (Santos et al., 2012). Es más, debido a la característica lipofílica (Log K_{ow} 4-8) y la relativa estabilidad frente a la degradación biológica de la mayoría estos filtros UV orgánicos, muchos de ellos no terminan de degradarse durante el tratamiento de aguas residuales, llegando a acumularse en sedimentos y biota cuando estas aguas son liberadas (Barón et al., 2013; Langford et al., 2015; Nakata et al., 2009b), afectando así a la cadena trófica. De hecho, varios filtros han sido detectados en múltiples especies de peces (Peng et al., 2015; Sang and Leung, 2016; Tsai et al., 2014), mamíferos marinos como delfines (Alonso et al., 2015; Gago-Ferrero et al., 2013a) e incluso en humanos (Giokas et al., 2007). Considerando que estos compuestos se usan en muchos PCP

y se aplican en grandes cantidades, es primordial estudiar los compuestos originales y sus derivados (Ramos et al., 2015).

1.2.2. Procesos de degradación en medios acuáticos

En general, los filtros UV orgánicos son fabricados para ser fotoestables bajo la influencia de la radiación UV, sin embargo, varios estudios han demostrado degradación de algunos de ellos bajo la influencia de radiación solar natural (Crista et al., 2015; De Laurentiis et al., 2013; Santos et al., 2012; Vione et al., 2013) o artificial (Santos et al., 2012). Una de las principales razones por las cuales se produce esta degradación es por la incapacidad de ciertos compuestos de convertir la energía que absorben con suficiente rapidez, por lo que las moléculas quedan en estado excitado (Figura 1) y reaccionan químicamente (Díaz-Cruz et al., 2008). Debido a estas reacciones, se producen subproductos indeseados, los cuales tienen características fisicoquímicas diferentes a sus compuestos precursores, pudiendo acumularse en diferentes matrices ambientales (Y. Li et al., 2016) e incluso en la piel humana (Santos et al., 2012).

Los filtros UV orgánicos pueden sufrir diferentes procesos de degradación: fotodegradación, fotoisomerización, por procesos de desinfección (cloración) o metabolización (Díaz-Cruz et al., 2008).

Cuando la acción de la luz solar induce reacciones químicas sobre estos compuestos se conoce como proceso de fotodegradación (Díaz-Cruz et al., 2008; Ramos et al., 2015). La fotodegradación puede producirse por fotólisis directa o indirecta. Por un lado, la fotólisis directa hace referencia a la autodescomposición del compuesto, por escisión de los enlaces, ciclación o reagrupamiento (Pintado-Herrera and Lara Martín, 2020). Por otro lado, la fotólisis indirecta implica otros agentes (fotosensibilizadores) para que la reacción tenga lugar. Durante este último proceso, la materia orgánica disuelta (MOD), las especies reactivas del oxígeno y otras especies inorgánicas como nitratos, bicarbonatos y cloruro de sodio pueden actuar como agentes fotosensibilizadores (Giokas and Vlessidis, 2007). Además, este proceso puede resultar ser más complejo, ya que el comportamiento de un solo compuesto es afectado por la presencia de otros filtros UV orgánicos. Por consiguiente, debido al alto número de especies químicas que pueden actuar como agentes fotosensibilizadores, pueden existir varias rutas de fotólisis indirecta (Díaz-Cruz et al., 2008). Estos dos procesos han sido estudiados para varios filtros UV orgánicos (Celeiro et al., 2019; Jentzsch et al., 2016; Rodil et al., 2009), donde se ha identificado la formación de diferentes subproductos (Gackowska et al., 2016b; Li et al., 2022; Vione et al., 2015).

Estos dos procesos de fotodegradación pueden ser los mecanismos más importantes de degradación en aguas naturales (Pintado-Herrera and Lara Martín, 2020). Por ejemplo, la BP3 (Gago-Ferrero et al., 2012a; Liu et al., 2011) y OC (Celeiro et al., 2019; Jentzsch et al., 2019) han demostrado ser altamente estables frente a la fotólisis directa. Contrariamente, compuestos como HMS, EHS, IMC, 4MBC y BMDBM resultaron ser altamente degradados por este proceso (Celeiro et al., 2019; Huong et al., 2007). Ahora bien, la BP3 y la BP4 presentaron una alta fotodegradación por fotolisis indirecta (Cao et al., 2021; Y. Li et al., 2016; Semones et al., 2017), mientras que los compuestos BMDBM y OC resultaron ser bastante estables (Celeiro et al., 2019). Las diferencias reportadas en los diferentes estudios sobre fotodegradación demuestran la importancia de considerar las propiedades del sistema acuático receptor de estos contaminantes a la hora de evaluar su posible destino (Kotnik et al., 2016; Sakkas et al., 2003).

El proceso de la fotoisomerización ocurre cuando la molécula es fotoexcitada por la acción de la luz solar, produciéndose un cambio en su configuración creando isómeros, del tipo *cis-trans*, keto-enol y fragmentación (Carve et al., 2021). Este proceso se ha observado como una forma de desactivación de las moléculas para reducir la energía UV absorbida (Rodil et al., 2009). En el caso de los filtros UV orgánicos, la formulación

comercial está compuesta por un 100% de compuestos en su forma *trans*. En algunos casos se ha observado que al formarse isómeros del tipo *cis* pierden su capacidad de filtrar la luz (Díaz-Cruz et al., 2008; Serpone et al., 2002). Sin embargo, cuando llegan a un medio acuoso la fotoisomerización es rápida y reversible para algunos compuestos, quedando en este entorno una mezcla de isómeros (Plagellat et al., 2006; Poiger et al., 2004). Los isómeros o la proporción de ellos encontrados en el medioambiente está influenciada por procesos bióticos durante el tratamiento de aguas, ríos, lagos, la acción de la biota (Buser et al., 2005) y la posible estereoselectividad (acumulación preferencial de un isómero sobre el otro) (Gago-Ferrero et al., 2012b).

Diversos estudios informaron isomerización del tipo *cis-trans* de los compuesto OMC (Gackowska et al., 2016a; MacManus-Spencer et al., 2011), 4MBC (Rodil et al., 2009; Serpone et al., 2002) e IMC (Rodil et al., 2009), mientras que del tipo keto-enol para BMDBM (Huong et al., 2008). Varios estudios han demostrado que estos compuestos son preferentemente fotoisomerizados que fotodegradados (Celeiro et al., 2019; Li et al., 2022; Rodil et al., 2009). Por el contrario, se ha identificado que el compuesto OC no presenta fotoisomerización (Díaz-Cruz et al., 2008).

La cloración es el proceso más usado para desinfectar/purificar varios tipos de agua (agua potable, aguas residuales, aguas de piscinas) (Ramos et al., 2015). La cloración consiste en la reacción del átomo de cloro siguiendo tres rutas; oxidación, adición a enlaces insaturados y por sustitución electrofílica (Tsui et al., 2014a). El átomo de cloro puede sustituir un átomo de carbono del anillo aromático o de los grupos hidroxilos (OH) presentes (Negreira et al., 2008). En los filtros UV orgánicos la ruta más probable de cloración es la sustitución (Tsui et al., 2014a), como ya ha sido informado por varios autores para diferentes compuestos (Chugunova et al., 2017; Crista et al., 2015; Nakajima et al., 2009). Consecuencia de esta reacción con el cloro libre en las aguas tratadas se pueden crear/formar subproductos (Liu et al., 2015), los cuales se conocen como subproductos de desinfección (DBP, por sus siglas en inglés), y que éstos pueden ser más tóxicos que los compuestos originales (Díaz-Cruz et al., 2008; Ramos et al., 2015; Santos et al., 2012).

Otro aspecto importante de este tipo de degradación es la posible reacción de los compuestos originales y subproductos de otros procesos (Sakkas et al., 2003), puesto que, por ejemplo, puede darse la acción conjunta de la radiación solar y la cloración (Díaz-Cruz et al., 2008), pudiendo resultar en una degradación aún mayor (Jia et al., 2019; Lu et al., 2018). Sin embargo, puede darse una inhibición de la cloración de algunos compuestos en presencia de

MOD (Crista et al., 2015; Jia et al., 2019; Lee et al., 2020). Cabe destacar, por ejemplo que el compuesto OC mostró una alta estabilidad frente a la cloración, y a la acción conjunta de cloración e irradiación (Manasfi et al., 2017). Esto puede deberse a su diferencia estructural con los otros compuestos (Tabla 1).

Por último, otro de los procesos de degradación que pueden sufrir los filtros UV orgánicos es por procesos metabólicos. Ciertamente, la información sobre biodegradación de los filtros UV orgánicos en biota es escasa (Pintado-Herrera and Lara Martín, 2020). El contaminante puede descomponerse o transformarse parcialmente pero no ser usado como fuente de energía, o por el contrario, descomponerse y ser usado como fuente de carbono y energía (Ternes et al., 2004). Los compuestos degradados por este proceso se conocen como metabolitos, los cuales en algunos casos han demostrado ser más tóxicos que sus compuestos originales (Suzuki et al., 2005; Wang and Kannan, 2013).

Por ejemplo en los seres humanos estos compuestos son absorbidos a través de la piel (Chisvert et al., 2012; Giokas et al., 2007), inhalados o ingeridos (Kim and Choi, 2014), posteriormente metabolizados (Chisvert et al., 2012; Díaz-Cruz et al., 2008; Y. Li et al., 2016) y luego excretados como compuestos originales y/o como metabolitos (Giokas et al., 2007), terminando en aguas residuales (Y. Li et al., 2016), ríos, lagos y el medio marino (Díaz-

Cruz et al., 2008). Una vez entran en las EDAR también pueden ser metabolizados por los microorganismos durante el tratamiento con lodos activos (Ramos et al., 2016). No obstante, se ha demostrado que no hay una eliminación completa durante el tratamiento de las aguas residuales (Kasprzyk-Hordern et al., 2009; Y. Li et al., 2016; Ramos et al., 2016), por lo que compuestos originales, metabolitos, productos degradados/transformados son irremediablemente liberados al medio acuático, representando un riesgo para los organismos allí presentes (Kim and Choi, 2014).

En el caso del medio marino, la posible biodegradación de los filtros UV orgánicos se ve limitada, ya que en este medio la cantidad de microorganismos es menor comparada con las aguas residuales, por lo que se asume que la biodegradación no es la ruta principal de degradación (Pestotnik et al., 2014). No obstante, en corales se ha demostrado que OC es metabolizado como ácidos grasos conjugados (Clergeaud et al., 2022; Stien et al., 2019).

Como se acaba de exponer, los filtros UV orgánicos pueden ser degradados por varios procesos. Estos pueden influir en las cantidades y donde pueden ser encontrados. Tras estas transformaciones, los subproductos formados se pueden considerar como compuestos nuevos con diferentes características a los originales, pudiendo representar un riesgo aún mayor. Por tanto, para una evaluación real del posible riesgo ambiental para los

organismos expuestos a estos contaminantes, se requiere del conocimiento acerca de sus procesos de transformación (Li et al., 2016).

1.2.3. Toxicidad de los filtros UV orgánicos

Los filtros UV orgánicos pueden terminar en ríos, aguas residuales y en última instancia en el ambiente marino. Sin embargo, en este entorno la información sobre la toxicidad en los organismos es limitada. Asimismo, la posible bioacumulación y biomagnificación de los compuestos a través de la cadena trófica, puede estar asociada a efectos perjudiciales (Fent et al., 2008).

La naturaleza generalmente lipofílica de estos compuestos hace que sean especialmente proclives a acumularse en sedimentos, material particulado en suspensión y en el tejido lipídico de los organismos vivos. Por lo que los organismos acuáticos son especialmente sensibles a la presencia de contaminantes, al estar en la primera línea de exposición. La mayor preocupación reside en su potencial como disruptores endocrinos y su citotoxicidad.

El efecto estrogénico (disruptor endocrino) hace referencia a perturbar la síntesis, secreción, unión y mecanismos de transporte de las hormonas naturales (Kudłak and Namieśnik, 2008), lo cual se traduce en una alteración de la homeostasis (función de

autorregulación), función regenerativa y comportamiento normal del organismo.

La citotoxicidad se refiere al efecto nocivo a nivel celular por agentes citotóxicos. Estos agentes son todos los elementos que son dañinos para las células, entre los cuales se encuentran los cambios en el crecimiento, la inhibición de la síntesis celular, los cambios en la producción de energía celular, la atenuación de la integridad de la membrana celular, e incluso la muerte celular (Istifli et al., 2019). Por tanto, cuanto más alta es la tasa de supervivencia celular, menor es el efecto citotóxico (Jia et al., 2019). Además, la presencia de agentes citotóxicos es usado como indicador de la calidad del agua, ya que indica la potencial exposición a estos contaminantes en por ejemplo, agua potable (Buschini et al., 2004).

El efecto tóxico hace referencia a varios efectos perjudiciales en los organismos generados por la exposición a un compuesto químico, y puede medirse usando diferentes criterios para establecer el grado de toxicidad. Entre estos criterios se encuentran los cambios en el crecimiento, mortalidad, presencia de enzimas antioxidantes, blanqueamiento (en el caso de corales), comportamiento anómalo, alteración del metabolismo, anomalías morfológicas y daños en el ADN (Lozano et al., 2020); el uso del criterio dependerá del organismo sujeto a estudio. Se pueden diferenciar dos tipos: toxicidad aguda y toxicidad crónica. La

primera alude a los efectos de una exposición puntual en un organismo, mientras que la segunda hace referencia a los efectos causados por la exposición al mismo compuesto durante un periodo de tiempo prolongado. Debido a los diferentes tiempos de exposición, las concentraciones necesarias para producir efectos nocivos suelen ser menores cuanto más larga es la exposición (Brausch and Rand, 2011).

Para realizar estudios de toxicidad de las sustancias, es necesario poder realizar las estimaciones del riesgo ambiental (ERA). Las concentraciones sin efecto observado (NOEC) y las concentraciones sin efecto previstas (PNEC) son utilizadas para poder calcular los coeficientes de riesgo ambiental (HQ). El cálculo de los HQ ofrece una estimación cuantitativa sobre el riesgo que estos compuestos químicos pueden producir a los organismos acuáticos de referencia. No obstante, cuando los NOEC o los PNEC no están disponibles, la determinación de las concentraciones efectivas medias (EC50) y las concentraciones letales medias (LC50) son usadas para realizar la estimación, dividiéndolas por un factor de incertidumbre variable adecuado (Commission, 2003).

Uno de los primeros estudios que se reportaron sobre los efectos nocivos en organismos marinos fue el trabajo de Danovaro y Corinaldesi (Danovaro and Corinaldesi, 2003), encontrándose que, como consecuencia de la exposición a cremas solares que

contenían filtros UV orgánicos, existía un aumento en los virus, lo que provocó un disminución en el bacterioplancton marino. Posteriormente se informó de que este fenómeno podría provocar blanqueamiento en corales (Danovaro et al., 2008).

La mayoría de los estudios sobre la toxicidad de estos compuestos han sido desarrollados en corales. Múltiples especies de corales como *Acropora pulchra*, *Pocillopora damicornis*, *Seriatopora caliendrum*, *Stylophora pistillata*, *Acropora sp.* han sido expuestos a varios filtros UV orgánicos (4MBC, BP1, BP3, BP4, BMDBM, DTS, OMC, EHS, OC, PDSA y OT) mostrándose efectos tóxicos (Danovaro et al., 2008; Downs et al., 2016; Fel et al., 2019; He et al., 2019a, 2019b). El efecto nocivo que se le atribuye a la exposición de estos organismos es principalmente el blanqueamiento, seguido de la mortalidad. Aunque también se han reportado cambios en la eficiencia fotosintética, el metabolismo y daños en el ADN en el caso de la exposición con la BP3.

Otros organismos como por ejemplo mejillones han sido expuestos a varios compuestos (OC, ODPABA, OMC, 4MBC y BP3) resultando en deformidades (Downs et al., 2016; Giraldo et al., 2017). Por otro lado, efectos en el crecimiento larval y deformidades morfológicas han sido mostradas por la exposición de erizos marinos (*Paracentrotus lividus*) a 4MBC (Torres et al., 2016), BP3 (Paredes et al., 2014), ODPABA (Giraldo et al., 2017),

OMC (He et al., 2019a) y OC (Stien et al., 2019). Además, efectos citotóxicos han sido reportados para algunas baterías que habita en simbiosis con organismos marinos debido a la exposición de la BP4 (Jia et al., 2019) y la BP3 (Li et al., 2016).

Sin embargo, existe poca información acerca de los posibles efectos crónicos y sub-crónicos que los filtros UV orgánicos pueden causar en peces marinos. En el lenguado *Senegalese sole* (Araújo et al., 2018) se manifestaron cambios en la actividad enzimática, el nado, la mortalidad y el crecimiento, además de un efecto en la tasa de éxito de la eclosión de huevos, por la exposición al 4MBC. En el pez comúnmente conocido como dorada (*Sparus aurata*), se observaron alteraciones en el metabolismo, la morfología y mortalidad debido a la exposición a la BP3 (Ziarrusta et al., 2018). Finalmente, en el pez payaso (*Amphiprion ocellaris*) se detectaron cambios en la mortalidad, en los hábitos alimenticios y el comportamiento de nado (Barone et al., 2019) de la exposición a cremas solares que contenían benzofenonas.

Los estudios de toxicidad se han realizado mayoritariamente en organismos de agua dulce (Carve et al., 2021; Kwon and Choi, 2021), aunque el medio marino es el último receptor de estos contaminantes y la exposición es constante. Por lo tanto, los efectos de la exposición a largo plazo en este entorno pueden ser más acusados. Además, los estudios donde se expone a larvas o huevos

de los organismos tienen especial relevancia ambiental, ya que tiene implicaciones en la supervivencia de la especie en el medio natural.

1.2.4. Fuentes de emisión

Los filtros UV orgánicos están principalmente asociadas a la industria cosmética (Sánchez-Quiles et al., 2020), pero también son empleados en productos industriales. Pueden ser encontrados en cremas solares (Molins-Delgado et al., 2014), cremas corporales, lacas para el pelo, champús, perfumes, barras de labios, líquidos autobronceadores, etc. (Díaz-Cruz et al., 2008; Eriksson et al., 2008). Por otra parte, también son usados en una amplia variedad de productos industriales para proteger los materiales y pinturas de la luz solar, evitando así la fotodegradación de polímeros y pigmentos (Lowe, 1996). Entre los productos que contienen estas sustancias están los plásticos, detergentes, productos de desinfección, pinturas, tintas, productos para el mantenimiento de coches y botes (pulimentos y ceras), productos para limpiar zapatos, pesticidas, etc. (Eriksson et al., 2008; Kwon and Choi, 2021).

Por el amplio uso de estos compuestos, varias toneladas son emitidas al medio marino (Danovaro et al., 2008; Eriksson et al., 2008; Kwon and Choi, 2021) y ríos (Kasprzyk-Hordern et al., 2009), en consecuencia, son considerados como un nuevo tipo de

contaminante emergente (Sánchez-Quiles et al., 2020; Tovar-Sánchez et al., 2013).

Estos compuestos siguen dos rutas principales hacia el medioambiente; la via directa y la via indirecta, las cuales se encuentran esquematizadas en la Figura 3.

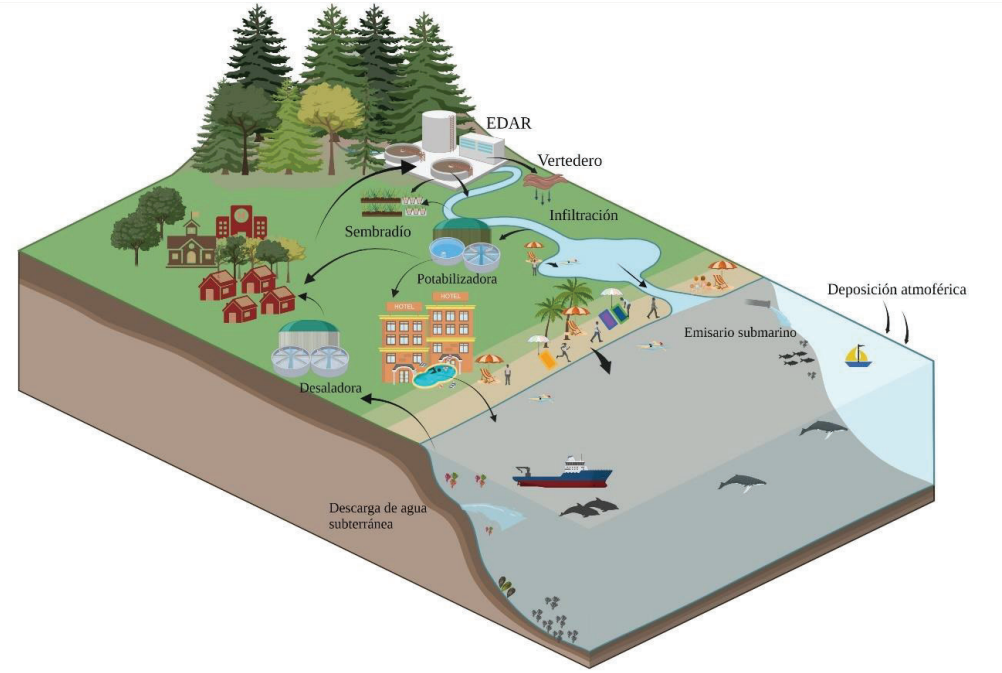


Figura 3: Vías de entrada al medio ambiente que siguen los filtros UV orgánicos.

La via directa hace referencia a la entrada directa de estos contaminantes al medio acuático (mar, ríos y lagos) mediante el lavado de la piel y la ropa durante las actividades que allí se

realizan. Por otro lado, la via indirecta indica la entrada de estos contaminantes por otros medios, tales como las descargas industriales, efluentes de agua residuales, escorrentías y usos domésticos (Fent et al., 2008; Gago-Ferrero et al., 2015; Molins-Delgado et al., 2014).

Otros procesos de la via indirecta pueden ser, por ejemplo, resultado de la absorción y posterior excreción, actividades de baño y lavado de ropa (Ramos et al., 2016), terminando en las EDAR (Badia-Fabregat et al., 2012; Negreira et al., 2012; Rodil et al., 2008), donde son parcialmente eliminados ya sea por procesos de cloración o adsorbidos en la materia orgánica (Ramos et al., 2016). En el efluente de agua residual, los compuestos que son más polares, los que no han sido eliminados durante el tratamiento o los subproductos que han aumentado su polaridad (Jentzsch et al., 2019) son descargados en ríos o directamente en el medio marino (Ramos et al., 2016), donde pueden acumularse (Buser et al., 2006; Fent et al., 2010) y ser fuente de riesgo para los organismos del medio receptor (Tsui et al., 2014a). Además, las posibles descargas ilegales de aguas sin tratar también constituyen otra fuente de entrada de estos contaminantes (Tsui et al., 2019). Asimismo, estas aguas de efluentes que contienen filtros UV orgánicos también pueden ser usadas para regadío en agricultura (Li et al., 2007; Liu et al., 2012) o incluso como fuente indirecta de agua potable (Levine and Asano, 2004), donde los efectos (de los compuestos

originales y subproductos) sobre las plantas que son regadas con estas aguas y la potencial amenaza en la seguridad en agua potable (Zhang et al., 2016) aún son poco estudiados.

Por otro lado, otra de las entradas indirectas de estos contaminantes al medio marino es a través de la liberación de aguas de piscina (tanto de agua dulce como de agua salada), donde no solo los compuestos originales (Li et al., 2020; Manasfi et al., 2015; Ramos et al., 2015) sino también sus metabolitos (Giokas et al., 2007) y DBP (Manasfi et al., 2015; Negreira et al., 2012) pueden ser descargados.

Otra de las entradas indirectas es por el agua potable, cuya fuente de filtros UV orgánicos puede ser por la contaminación de aguas subterráneas (Gago-Ferrero et al., 2013b; Ho and Ding, 2012; Jurado et al., 2014), de ríos o lagos (Balmer et al., 2005; Gago-Ferrero et al., 2013b; Ramos et al., 2015) cuyas aguas son usadas para potabilizar. De hecho, ya se han detectado varios filtros UV orgánicos en agua de grifo (Li et al., 2019; Ramos et al., 2015), que puede terminar igualmente en las EDAR y continuar con el proceso antes mencionado. Además, estos compuestos también pueden estar presentes en el agua potable debido a que algunas zonas se usa procesos de desalación para la obtención de agua dulce.

Durante el tratamiento de agua, una parte de estos contaminantes termina también en los lodos de las EDAR, donde

quedan retenidos debido a sus características lipofílicas y baja disponibilidad a ser biodegradados (Gago-Ferrero et al., 2011; Plagellat et al., 2006). Después, estos lodos pueden terminar en vertederos y contaminar el agua subterránea por infiltración (Díaz-Cruz and Barceló, 2015) o siendo usados en agricultura.

Además, estos también han sido detectados en polvo atmosférico (Pegoraro et al., 2020), lo que podría constituir otra entrada indirecta al medio marino al depositarse el polvo, o por efecto de la lluvia, aunque esta deposición (por lluvia o por deposición de polvo) nunca ha sido evaluada. Igualmente, se han detectado estos compuestos en áreas remotas del Ártico, lo que podría indicar un transporte por las corrientes oceánicas o por el transporte atmosférico (Tsui et al., 2014b).

Como se acaba de exponer, la contaminación producida por estos filtros debido a sus múltiples entradas al medio marino supone un problema importante. Además, según lo que indican las vías de entrada (y salida), estos compuestos podrían constituir un ciclo de contaminación, ya que se ha demostrado que algunos de los subproductos pueden volver a formar sus compuestos originales bajo ciertas condiciones (Jia et al., 2019).

1.3. Presencia de los filtros ultravioleta orgánicos en el medio marino

Una vez los filtros UV orgánicos (y sus subproductos y metabolitos) alcanzan el medio marino, pueden comportarse de diferente manera en este entorno dependiendo de sus características químicas. La característica más usada para predecir el destino de estos compuestos es el Log K_{ow}. Como se indicó en apartados anteriores, la mayoría de los filtros UV orgánicos tienen un Log K_{ow} entre 4-8, lo que implica un comportamiento altamente lipofílico y por lo tanto es más probable que sean encontrados en sedimentos y biota (Gago-Ferrero et al., 2012b). Por otro lado, los compuestos con valores de Log K_{ow} <4 tienen un comportamiento hidrofílico, lo que hace más probable que estén presentes en matrices líquidas, como el agua de mar.

1.3.1. Fase líquida

Los filtros UV orgánicos han sido detectados globalmente en agua de mar (Cadena-Aizaga et al., 2020; Diaz-Cruz, 2020; Pintado-Herrera and Lara Martín, 2020), lo que indica que este entorno está altamente afectado (Kwon and Choi, 2021; Sánchez-Quiles et al., 2020).

En el continente europeo se han detectado 14 de los 27 filtros UV orgánicos permitidos en la UE, siendo España el país que más ha reportado la presencia de estos compuestos, mientras que en el continente americano y en las regiones polares (Ártico y Antártida) se han detectado 10 y en Asia 9 de esos compuestos (Cadena-Aizaga et al., 2020). Recientes estudios han reportado estos compuestos en Australia (Allinson et al., 2018) y Túnez (Fenni et al., 2022). Por lo que ya han sido detectados en todos los continentes.

Las concentraciones medidas más altas corresponden a la BP3 (1.395 $mg \cdot L^{-1}$) en Hawaii (Downs et al., 2016), seguido del OC (171 000 $ng \cdot L^{-1}$) en España (Vila et al., 2016b). Ambas concentraciones fueron encontradas en zonas de una intensa actividad recreativa, lo que pone de manifiesto la importancia de la entrada directa de estos compuestos al medio marino.

Además, la concentración de estos contaminantes presenta variación estacional y diurna, midiéndose concentraciones más altas en verano que en invierno (Cadena-Aizaga et al., 2021; Cunha et al., 2022; Li et al., 2017) y más altas durante el día que durante la noche (Sankoda et al., 2015). Lógicamente, esto puede estar relacionado con la mayor afluencia a las playas en verano (Chisvert et al., 2017) y el uso de crema solar durante el día (Sankoda et al., 2015).

En esta matriz, el compuesto más frecuentemente detectado globalmente fue la BP3 (Allinson et al., 2018; Cadena-Aizaga et al., 2020; Fenni et al., 2022). Esto puede deberse a varias razones, entre las cuales está su bajo Log K_{ow} (<4), su alta estabilidad frente a la fotodegradación, la baja concentración de organismos que biodegraden este compuesto en aguas superficiales y que es uno de los más usado en formulaciones de PCP (Tarazona et al., 2010). Los tres compuestos que predominan en este tipo de muestras son BP3, OC y OMC, ya sea por mayor frecuencia de detección (BP3 y OMC) o por alta concentración (BP3 y OC) lo que puede ser atribuido a que son los más ampliamente usados en las formulaciones comerciales (Jiménez-Díaz et al., 2014; Vila et al., 2016a).

Por otro lado, los subproductos de los filtros UV orgánicos son mucho menos investigados. No obstante, el estudio de Chririac et al. (Chiriac et al., 2021) reportó diferentes subproductos de la BP3 en agua costeras del Mar Negro y el estudio de Mansafi et al. (Manasfi et al., 2017) informó de DBP de la BP3 en piscinas de agua de mar en Francia.

1.3.2. Fase sólida

De las fases sólidas, los sedimentos representan un sumidero para los compuestos lipofílicos, los cuales, como se mencionó en

apartados anteriores, son la mayoría de los filtros UV orgánicos. Además, debido a la nula acción de la luz, los compuestos fotosensibles pueden permanecer intactos en esta matriz (Amine et al., 2012).

Al igual que en agua de mar, estos compuestos han sido detectados en el continente europeo, asiático, americano y regiones polares (Cadena-Aizaga et al., 2020), siendo OC el compuesto más frecuentemente detectado. Además, este compuesto presentó la concentración más alta 670 $ng \cdot g^{-1}$ (en peso seco, dw) en Gran Canaria (España) (Vila et al., 2018b). Esta concentración fue reportada en una playa que es usada todo el año para actividades recreativas (Vila et al., 2018b). Otro compuesto altamente detectado fue OMC, (Cadena-Aizaga et al., 2020; Fenni et al., 2022; Kwon and Choi, 2021), donde la concentración más alta detectada fue en China 456 $ng \cdot g^{-1}$ (dw) (Huang et al., 2016).

Por otro lado, la BP3, el compuesto más detectado en agua de mar, también fue detectado en sedimentos de varios países (Barón et al., 2013; Benedé et al., 2018; Sánchez-Brunete et al., 2011) pero en menor concentración. Esto puede deberse a que este compuesto fue determinado como su compuesto original, pudiendo encontrarse en este compartimento como subproductos, como sucede con otros compuestos (Li et al., 2017). De hecho, el estudio de Chiriac et al. (Chiriac et al., 2021) reportó varios subproductos

de la BP3 en sedimentos del Mar Negro, donde en algunos casos se informó de una frecuencia de detección de un 91 %.

También se ha identificado variación estacional en sedimentos de varios compuestos; así en el estudio de Tsui et al. (Tsui et al., 2017) en China se encontraron mayores concentraciones en la estación húmeda que en la estación seca y en el estudio de Cunha et al. (Cunha et al., 2022) se encontraron mayores concentraciones en inverno que en verano en Portugal.

En comparación con la información disponible de agua y de sedimentos, la información sobre la presencia de filtros UV orgánicos en biota es muy limitada.

La mayoría de estudios llevados a cabo en biota marina están hechos en filetes de pescado, ya que forman parte de la dieta humana (Gago-Ferrero et al., 2012b). Análogamente a las otras matrices (agua de mar y sedimentos), en los tres continentes (Europa, Asia y América) y regiones polares estos compuestos han sido reportados en diferentes tipos de organismos marinos (Cadena-Aizaga et al., 2020).

Como era esperable, los compuestos más detectados en biota marina fueron OC, OMC y BP3 (Cadena-Aizaga et al., 2020), ya que éstos han sido identificados en las matrices con las que los organismos están en contacto, pudiendo haber una transferencia por ingestión o por absorción desde el medio circundante (Cadena-

Aizaga et al., 2022b; Huang et al., 2021). Así, la concentración más altas encontrada en filete de pescado y mejillones fueron determinadas para la BP3 y el OC, respectivamente, mientras que OC ha sido, además, el más frecuentemente detectado en toda la biota analizada (Cadena-Aizaga et al., 2020).

En el algunos casos, se ha observado una acumulación selectiva de estos compuestos en las diferentes partes del animal (Emnet et al., 2015; Molins-Delgado et al., 2018). Además, el propio comportamiento del organismo puede ser selectivo a la hora de acumular un compuesto u otro, o por la naturaleza propia del compuesto, como se ha indicado en apartados anteriores.

Respecto a la determinación de estos compuestos en algas, tres estudios han reportado filtros UV orgánicos en macroalgas de España (Cadena-Aizaga et al., 2022a; Pacheco-Juárez et al., 2019) y del Mar Negro (Chiriac et al., 2021). Asi mismo, el estudio de Chiriac et al. (Chiriac et al., 2021) encontró subproductos de la BP3 en macroalgas. Finalmente, sólo dos estudios han informaron de la presencia de estos contaminantes en fanerógamas marinas (Agawin et al., 2022; Cadena-Aizaga et al., 2022a).

1.4. Metodologías para la extracción y determinación de filtros UV orgánicos en muestras ambientales marinas

Los métodos que se empleen en el análisis de filtros UV deben ir dirigidos a una determinación eficiente y selectiva de los analitos de interés a concentraciones ambientales, que como se ha visto en apartados anteriores es baja. La aplicabilidad de las técnicas de extracción depende en gran medida de las características fisicoquímicas de los analitos y del tipo de matriz de la que se van a extraer. Por otra parte, los métodos de separación, detección y cuantificación también están sujetos a las características de los analitos y al efecto matriz.

1.4.1. Extracción desde muestras líquidas

Las muestras ambientales en general necesitan la aplicación de uno o varios pasos previos para poder llevar a cabo la extracción. En el caso de las muestras líquidas, este pretratamiento suele incluir la acidificación (para evitar la degradación de la muestra) (Emnet et al., 2015) y filtración (eliminar la parte particulada de la muestra) (Rodil et al., 2008), aunque también se puede trabajar con muestras sin filtrar (Bratkovics and Sapozhnikova, 2011).

Las técnicas de extracción de filtros UV orgánicos desde agua de mar pueden dividirse en extracción con líquidos, con

materiales sólidos (polímero o barra) y miniaturización de otros métodos.

Basándose en su forma de extracción, una de las técnicas tradicionales y más simples es la extracción líquido-líquido (LLE, por sus siglas en ingles), la cual se basa en el principio de inmiscibilidad de dos líquidos (Aranas et al., 2011). Basándose en la LLE, se han desarrollado nuevas técnicas de microextracción en la que se utiliza un pequeño volumen de disolvente orgánico como extractante (Tarazona et al., 2010), se sustituye el disolvente orgánico por líquido iónico (Vidal et al., 2010) o usando diferentes procedimientos para llevar a cabo la extracción (Clavijo et al., 2016; Horstkotte et al., 2014; Vila et al., 2016b).

La extracción con material sólido (fase sólida) se produce por la afinidad de los analitos de interés a este material, donde quedan retenidos (adsorción) y se produce la extracción, posteriormente se produce la desorción de los analitos retenidos desde la fase sólida por el disolvente apropiado, desorción líquida (LD, por sus siglas en inglés), o desorción térmica por acción de la temperatura (TD, por sus siglas en inglés). En la Figura 4 se encuentra esquematizado este proceso.

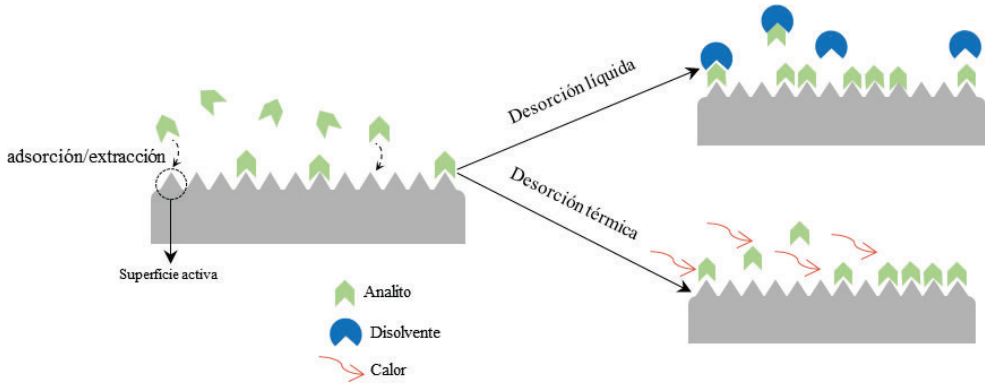


Figura 4: extracción de los analitos sobre un material sólido

Basándose en este mecanismo, tenemos las distintas técnicas de extracción basadas en la retención por una fase sólida. La extracción en fase sólida, o SPE por sus siglas en inglés, es la técnica más usada (Cadena-Aizaga et al., 2020; Diaz-Cruz, 2020). Para ello, se usan diferentes tipos de polímeros dependiendo de la naturaleza del analito (Goksøyr et al., 2009). Esta técnica es ampliamente usada porque extrae y preconcentra los analitos de interés, es fácil de emplear y consta de pocos pasos:

a) Acondicionamiento del material: en este paso se activa el polímero para la retención de los analitos.
b) Paso de muestra: se produce la retención de los analitos por el polímero previamente activado.
c) Limpieza: para eliminar las posibles impurezas de la muestra que hayan quedado retenidas en el material. En el caso del agua de mar, este paso permite la eliminación de sales.

d) Desorción: en este paso se recuperan los analitos de interés retenidos con un disolvente orgánico que es más afín a ellos que el polímero.

La Figura 5 esquematiza este proceso. La elección del polímero, del paso o pasos de limpieza y del disolvente orgánico dependen ampliamente de las características de los analitos de interés. Por ejemplo, para la extracción de los filtros UV orgánicos más apolares, el sorbente de sílice C_{18} es ampliamente usado (Tsui et al., 2014b). Por el contrario, cuando la mezcla de filtros UV orgánicos tiene varias polaridades, se usan polímeros de fase reversa (Goksøyr et al., 2009). Por otro lado, la elección del extractante (generalmente un disolvente orgánico) también depende de la polaridad de los analitos, siendo el metanol (MeOH) el más ampliamente usado ya que tiene una polaridad media y es capaz de extraer una amplia variedad de filtros UV orgánicos (Bratkovics and Sapozhnikova, 2011; Goksøyr et al., 2009; Rodil et al., 2008). La versión automatizada y miniaturizada de este proceso, conocida como SPE online, también es usada para la extracción de estos analitos desde agua de mar, en la que todo el proceso es realizado automáticamente, minimizando la cantidad de muestra y disolvente (Montesdeoca-Esponda et al., 2012).

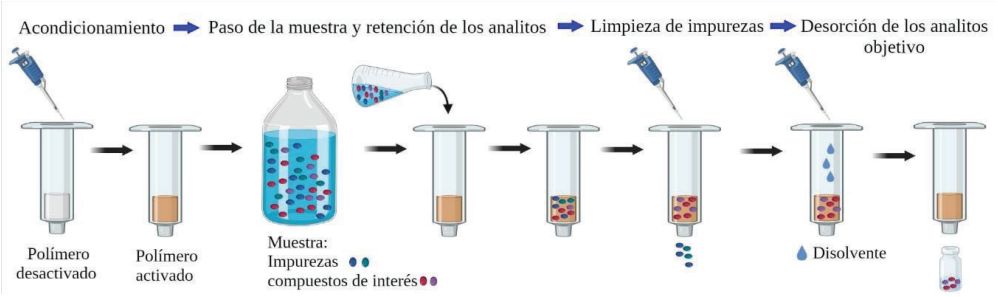


Figura 5: Etapas de la extracción en fase sólida

Basado en la técnica de SPE, se han desarrollado nuevos procedimientos en la línea de reducir la cantidad de disolvente (Vila et al., 2016a), muestra (Montesdeoca-Esponda et al., 2013) y tiempo (Román et al., 2011).

Otra de las técnicas basadas en una fase estacionaria sólida es la extracción por adsorción en barra agitadora (SBSE, por sus siglas en inglés), la cual se basa en el uso de una barra cubierta con el extractante, que es sumergida en la muestra (Pintado-Herrera et al., 2014). Sin embargo, en esta técnica sigue siendo necesario el uso de un extractante (LD) (Nguyen et al., 2011). Con esta técnica como base, se han desarrollado otras miniaturizaciones, con diferentes formas unión del extractante a la barra (Benedé et al., 2014; Chisvert et al., 2017; Neng et al., 2010).

Además de las técnicas antes mencionadas, también se ha usado una técnica de extracción indirecta, la extracción por dispositivos de membranas semipermeables (SPMDs, por sus siglas

en inglés). Los analitos son retenidos en continuo al estar expuestas las membranas directamente al medio de análisis (Goksøyr et al., 2009).

Los diferentes procedimientos de extracción presentan un rango de recuperaciones adecuados para la extracción de filtros UV orgánicos desde agua de mar (en general >65 %). Algunas de ellas han sido desarrolladas con el fin de minimizar o evitar el uso de solventes orgánicos, lo que va en la línea de la química verde. Sin embargo, muchas de estas técnicas han sido usadas solo puntualmente. Además, algunas de ellas usan solventes o líquidos iónicos que no están disponibles comercialmente, lo que implica tener que sintetizarlos.

1.4.2. Extracción desde muestras sólidas

Para las muestras sólidas, por lo general es necesario varios pretratamientos previos a la extracción, dependiendo del tipo de matriz que se va a analizar. En el caso de sedimentos o arena, estos suelen ser la homogeneización (Peng et al., 2017) y el secado, ya sea a temperatura ambiente, a altas temperaturas o por liofilización (Amine et al., 2012; Peng et al., 2017; Vila et al., 2018a). Otro de los posibles pretratamientos son la trituración y tamizado (Huang et al., 2016; Sánchez-Brunete et al., 2011).

En el caso de las muestras de biota marina, los pretratamientos incluyen la eliminación de concha, piel y/o huesos, disección, etc. (Peng et al., 2015; Sang and Leung, 2016), aunque algunos organismos son usados enteros, debido a su pequeño tamaño (Cadena-Aizaga et al., 2022b; Peng et al., 2015). El paso siguiente suele ser la homogeneización, tanto en el organismo húmedo (Sang and Leung, 2016) como seco (Alonso et al., 2015). En general, las muestras suelen ser trituradas hasta obtener polvo (Bachelot et al., 2012), para favorecer una muestra homogénea y una mejor acción del extractante.

Una de las técnicas tradicionales para la extracción de muestras sólidas, Soxhlet, ha sido utilizada en la extracción de filtros UV orgánicos desde sedimentos (Nakata et al., 2009a). Sin embargo, esta técnica no es de las más usadas por el uso de grandes cantidades de disolvente orgánico y los grandes tiempos necesarios para la extracción.

Las técnicas que usan dispositivos que favorecen la acción del extractante, reduciendo los tiempos de extracción y volumen de disolvente, son más usadas. Estas son la extracción asistida por microondas (MAE, por sus singlas en inglés) (Amine et al., 2012), extracción por ultrasonido (USE, por sus singlas en inglés) (Sánchez-Brunete et al., 2011), la extracción por vórtex (VE, por sus singlas en inglés) (Tsui et al., 2017) y la extracción por líquidos

presurizados (PLE, por sus singlas en inglés) acoplado con un sistema extractor de solvente acelerado (ASE, por sus singlas en inglés) (Sang and Leung, 2016; Tsui et al., 2015). Estas técnicas han sido usadas para la extracción desde sedimentos y desde biota marina (Cadena-Aizaga et al., 2020). Por la acción de los dispositivos se mejora la acción del líquido extractante, reduciendo así el tiempo de extracción y aumentan la eficiencia de extracción.

Otras técnicas también usadas para muestras de biota marina son la extracción Rápida, Fácil, Económica, Eficaz, Robusta y Segura o QuEChERS por sus singlas en inglés (Picot Groz et al., 2014) y la extracción por dispersión de matriz en fase sólida, o MSPD por sus siglas en inglés (Barker, 2000). La QuEChERS consiste en el uso un tubo de polipropileno con una cantidad pequeña de disolvente orgánico. Por otro lado, en la MSPD la muestra y la fase de dispersión son mezcladas en un mortero, después, la mezcla resultante es colocada en un cartucho con disolvente orgánico para la extracción.

En general, después de la extracción suele ser necesario un paso de limpieza para la eliminación de interferencias o lípidos, así como para preconcentrar los analitos. Estas técnicas usualmente emplean líquidos extractantes (Cunha et al., 2018, 2015) o columnas de cromatografía por permeación en gel (GPC, por sus siglas en inglés) o de sílice (Gago-Ferrero et al., 2012b).

Las ventajas que presenta la técnica MAE respecto a las otras técnicas es la posibilidad de analizar varias muestras a la vez y que el procedimiento es sencillo. Respecto a la muestra, en esta técnica se pueden usar pequeñas cantidades, lo que puede ser un factor determinante en algunos casos. Además, respecto a la técnica PLE-ASE, los costes son menores ya que se usan cantidades menores de disolvente orgánico. La figura 6 esquematiza el procedimiento de extracción por MAE.

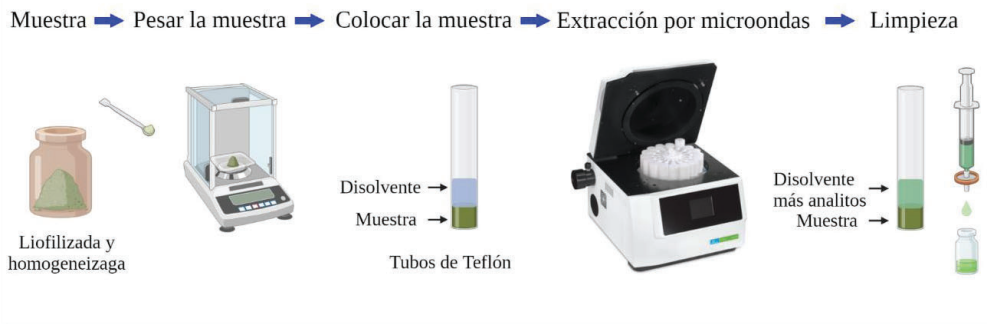


Figura 6: Etapas de la extracción mediada por ondas microondas

1.4.3. Sistemas de separación y determinación

Una vez se han extraído (y limpiado) los analitos de interés de la matriz, el extracto resultante es sometido a diferentes técnicas de separación y detección instrumentales.

En general, la cromatografía líquida (CL) es la más empleada en el análisis de filtros UV orgánicos para muestras ambientales (Cadena-Aizaga et al., 2020; Diaz-Cruz, 2020; Ramos et al., 2015). A su vez, dentro de la CL, la cromatografía liquida de alta resolución (HPLC, por sus siglas en inglés) suele ser la elegida debido a que ofrece un análisis rápido, selectivo, proporciona picos cromatográficos más estrechos y reduce la cantidad de disolvente y del efecto matriz (Ramos et al., 2015). Esta técnica es empleada cuando la mezcla de filtros UV orgánicos a ser determinada tiene un amplio rango de características químicas (Benedé et al., 2014; Tsui et al., 2014b), como por ejemplo para la determinación en agua de mar (Cadena-Aizaga et al., 2020; Diaz-Cruz, 2020). La CL aplicada a la determinación de filtros UV orgánicos emplea dos tipos ionización, la ionización por electrospray (ESI, por sus siglas en inglés) y la ionización química a presión atmosférica (APCI, por sus siglas en inglés) (Nguyen et al., 2011), donde la APCI muestra mejor ionización para compuestos polares y ESI para compuestos de polaridad media-alta (Nguyen et al., 2011; Peng et al., 2015).

Por otra parte, la cromatografía de gases (CG) se suele utilizar para la separación de compuestos que son volátiles (Jurado et al., 2014). Sin embargo, debido la alta estabilidad térmica de algunos filtros UV orgánicos, es necesario un paso previo de derivatización (Sánchez-Brunete et al., 2011), para aumentar su volatibilidad (Vila et al., 2017). La derivatización puede realizarse

usando varios agentes derivatizantes (Tarazona et al., 2010), dependiendo de la naturaleza de los analitos objetivo. Este paso es necesario por ejemplo para la determinación de compuestos como la BP3 (Emnet et al., 2015). Esta técnica instrumental presenta la ventaja de ser menos sensible al efecto matriz, por lo tanto es la elegida en el análisis de matrices complejas, como por ejemplo muestras de biota (Cadena-Aizaga et al., 2020).

1.4.3.1. Espectrometría de masas

Acoplada a la cromatografía líquida o de gases, la detección por espectrometría de masas (MS, por sus siglas en inglés) es habitualmente usada, ya que tiene una alta sensibilidad y proporciona límites de detección bajos (Downs et al., 2016). La MS suele ser usada en tándem (MS/MS), ya que proporciona límites de detección aún más bajos (Barón et al., 2013; Kung et al., 2018) y una inequívoca selectividad. Por esta razón este método de detección suele ser el más usado (Cadena-Aizaga et al., 2020).

Acoplado a la CL y CG el detector de MS de alta resolución (HRMS, por sus siglas en inglés) también ha sido empleado en la determinación de filtros UV orgánicos en muestras marinas (Langford et al., 2015).

Con el objetivo de determinar subproductos, la MS también se usa acoplada a un cuadrupolo de tiempo de vuelo (QToF, por sus siglas en inglés) (Langford et al., 2015; Paredes et al., 2014). Esta técnica permite la identificación y confirmación de los compuestos originales y sus metabolitos.

1.4.3.2. Otras técnicas instrumentales

Otros tipos de detección también son acoplados a la CL para la determinación de filtros UV orgánicos en muestras ambientales. Estos son; el detector de UV (Benedé et al., 2015; Sánchez Rodríguez et al., 2015; Suárez et al., 2016; Volpe et al., 2017) y el detector de diodo Array (DAD, por sus siglas en inglés) (Almeida et al., 2013; Vidal et al., 2010).

Aunque proporcionan límites de detección y cuantificación aceptables para algunos análisis, estos detectores (UV y DAD) son bastante menos usados en muestras medioambientales marinas respecto a la MS (Cadena-Aizaga et al., 2020).

1.4.3.3. Efecto matriz

En el análisis de filtros UV orgánicos en muestras ambientales, el efecto matriz es uno de los principales inconvenientes (Zenker et al., 2008). Este problema hace referencia

a la coelución de componentes propios de la matriz que impiden la correcta ionización durante la detección por MS (Reemtsma, 2001). Este efecto es particularmente preocupante en la CL con ESI, ya que este tipo de ionización se realiza en la fase líquida, donde todos los componentes están presentes (Nguyen et al., 2011).

Aunque el efecto matriz sea inherente en algunos análisis, existen estrategias que ayudan a reducirlo. Estas ayudan a la cuantificación de los analitos de interés, haciendo uso de estándares internos deuterados de los analitos objetivo, el uso de calibración de matriz enriquecida (matrix-matched calibration) o el uso del método de adiciones estándar (Diaz-Cruz, 2020). Sin embargo, cuando el efecto matriz no se pueda evitar, la señal debe ser corregida (Matuszewski et al., 2003).

1.5. Filtros ultravioleta orgánicos en el medio marino: una actualización de las metodologías, presencia y distribución

Como se ha expuesto con anterioridad, los filtros UV orgánicos son motivo de preocupación por su constante y extensiva liberación al medio marino. En consecuencia, es necesario determinar su presencia y distribución en los diferentes compartimentos de este medio, ya que esto ayuda a crear una visión

global de problemática real de la contaminación por estos compuestos.

Dado que las concentraciones en las que se encuentran estos contaminantes en este medio son relativamente bajas, es necesario disponer de metodologías lo suficientemente sensibles y selectivas para determinarlos en muestras ambientales.

Considerando lo antes mencionado, se ha llevado a cabo una revisión bibliográfica de los métodos de extracción, y determinación empleados para filtros UV orgánicos en los últimos 10 años, así como de la presencia de aquellos permitidos en la UE, tanto en muestras líquidas (agua de mar) como en muestras sólidas (sedimentos, arena y biota). De este trabajo se destacan los siguientes puntos:

i. La amplia bibliografía disponible debido al auge y preocupación del tema.
ii. La extracción en fase sólida (SPE) es la técnica más ampliamente utilizada para muestras líquidas, aunque se observa una tendencia al desarrollo de técnicas miniaturizadas para muestras líquidas que implican el menor uso de muestra y disolventes orgánicos.
iii. Las técnicas de extracción desde matrices sólidas se han desarrollado en favor de una menor manipulación de la muestra.

iv. La cromatografía liquida acoplada a la espectrometría de masas es la técnica más usada para determinar estos compuestos en muestras ambientales marinas.
v. La distribución de estos compuestos es global, encontrándose incluso en regiones polares.

Este trabajo ha sido publicado en la revista *Trends in Environmental Analytical Chemistry* en 2020, la cual está dedicada a publicar revisiones bibliográficas en el campo de la química analítica y medioambiental. Esta revista se encontraba en el primer cuartil (posición 5 de 87) con un índice de impacto de 9.600 en el año de la publicación, según el *Jounal Citation Reports*.

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Organic UV filters in marine environments: An update of analytical methodologies, occurrence and distribution

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ABSTRACT

Ultraviolet filters (UV Filters) are compounds that are widely employed in personal care products such as sunscreens to protect the skin from sun damage, but they are also added to other products, such as food packaging, plastics, paints, textiles, detergents, etc. The continuous use of these products causes the release of a substantial amount of these products into the marine environment through direct input or wastewater discharge, and thus they are becoming an important class of contaminants of emerging concern. A correlation between their occurrence and different negative effects on marine biota has been reported.

Taking into account all the possible impacts on the environment, knowledge of their presence and distribution in the different compartments of the ecosystems, ranging from waters and sediments to aquatic organisms, which potentially suffer from bioaccumulation and biomagnification processes, is essential. High concentrations of ultraviolet filters have been found in samples collected from across the entire planet, even in polar regions, revealing their global distribution.

Therefore, interest in the sensitive determination of ultraviolet filters in several marine matrices has increased. In this article, an overall review of the more recently reported analytical chemistry methods for identifying and quantifying these compounds in marine environmental samples is presented. We compare and discuss the potential advantages and disadvantages of every step involved in the analytical procedure, including the pre-treatment, treatment and extraction processes that are required to avoid matrix effects. Moreover, we describe the worldwide occurrence and distribution of those most important UV filters.

Abbreviations: 4-MBC, 4-methylbenzylidene camphor; Ac, acetone; CAN, acetonitrile; APCI, atmospheric pressure chemical ionisation; APGC, atmospheric pressure gas chromatography; ASE, accelerated solvent extractor; BAME, bar adsorptive microextraction; BP-3, benzophenone-3; BP-4, benzophenone-4; BSTFA, N,O-bis(trimethylsilyl) trifluoroacetamide; CHL, chloroform; d.w., dry weight; DCM, dichloromethane; DLLME, dispersive liquid-liquid microextraction; DTS, drometrizole trisiloxane; EA, ethyl acetate; EHS, 2-ethylhexyl salicylate; ESI, electrospray ionisation; FPSE, fabric phase sorptive extraction; GC, gas chromatography; Hex, hexane; HCl, hydrochloric acid; HMS, homosalate; HRMS, high resolution mass spectrometry; HS, headspace; IL-MSA-DLLME, on-line *in-syringe* magnetic stirring assisted ionic liquid dispersive liquid-liquid microextraction; IL-SDME, ionic liquid-based single-drop microextraction; IL, ionic liquid; IMC, isoamyl p-methoxycinnamate; iSAME, in-situ suspended aggregate microextraction; l.w., lipid weight; LC, liquid chromatography; LD, liquid desorption; LLE, liquid-liquid extraction; LOD, limit of detection; LOQ, limit of quantification; MAE, microwave-assisted extraction; MBP, methylene bis- benzotriazolyl tetramethylbutylphenol; MeOH, methanol; MNPs-based dSPE, magnetic nanoparticles dispersive solid-phase extraction; MS, mass spectrometry; MSA-DLLME, magnetic stirring assisted dispersive liquid-liquid microextraction; USAEME, ultrasound assisted emulsification microextraction; MSPD, matrix solid-phase dispersion; OC, octocrylene; OD-PABA, ethylhexyl dimethyl para-aminobenzoic acid; OMC, ethylhexyl methoxycinnamate; IPA, isopropanol; PCPs, personal care products; PDSA, terephthalylidene dicamphor sulfonic acid; PHWE, pressurised hot water extraction; PLE, pressurised liquid extraction; QTOF, quadrupole time-flight; QuEChERS, Quick, Easy, Cheap, Effective, Rugged and Safe technique; SBDLME, stir-bar dispersive liquid microextraction; SBSDME, stir-bar sorptive-dispersive microextraction; SBSE, stir-bar sorptive extraction; SPE, solid-phase extraction; SPLE, selective pressurised liquid extraction; SPME, solid-phase microextraction; TD, thermal desorption; TPs, transformation products; UHPLC, ultra-high performance liquid chromatography; USE, ultrasonic extraction; USSPME, ultrasonic extraction followed by SPME; VE, vortex extraction; w.w., wet weight.

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1. Introduction

Short-term exposure to ultraviolet (UV) radiation exerts positive effects on human health, *i.e.*, it facilitates D vitamin synthesis. However, excess exposure to solar radiation can cause numerous harmful effects, such as sunburns and skin cancers [1]. Additionally, the human tendency to spend more time in the sun is attributed to growth of the solar protection industry [2]. Since the late nineteenth century, several formulas containing organic and inorganic UV filters have been developed to protect the skin from UV damage [3].

Currently, the European legislation set the maximum allowed concentration for each UV filter in cosmetic products (Regulation no. 1223/2009 of the European Commission) [4]. The European Union (EU) allows the use of 27 UV filters in concentrations ranging from 2 % to 15 % [5], of which only two are inorganic (titanium dioxide and zinc oxide). Organic UV filters are the most popular and widely used filters in sunscreens and personal care products (PCPs) [6,7]. They frequently contain single or multiple aromatic structures attached to hydrophobic groups to improve their properties, with a limited absorption band spectrum. Therefore, different combinations are generated to obtain the desired protection against both regions of solar radiation: UVA (320−400 nm) and UVB (280−320 nm) [8]. Although the main use of these compounds is associated with PCPs, these compounds are also present in other industrial goods, such as food packaging, plastics, paints, textiles, products for vehicle maintenance to prevent polymer and pigment photodegradation [9], detergents and disinfection products [10]. The increasing production and use of organic UV filters has generated a new kind of environmental pollutants [11]. For example, ethylhexyl methoxycinnamate (OMC), a common UV filter, was included in 2015 in the Watch List under the Environmental Quality Standards Directive [12], although it was removed in 2018 due to the few data reported in sediments [13].

Organic UV filters are classified based on their structure according to the chemical family and main physicochemical properties, as shown as in Table 1. Most exhibit some of the typical characteristics of priority organic pollutants [14]. The common feature is the presence of an aromatic moiety with a side chain displaying different grades of saturation [15], high lipophilicity and stability against biotic degradation [16]. These physicochemical properties determine the fate of organic UV filters in the environment, and it is a relevant issue when choosing an appropriate analytical method for determining the levels of these filters in the different matrices. K_{ow} provides information about their distribution. Compounds with K_{ow} values <1 are considered hydrophilic, while compounds with values >4 are hydrophobic. Analytes with K_{ow} >8 are not considered readily bioavailable and compounds with values >10 are considered not bioavailable at all [17]. Solubility (S) also provides information about the likely distribution of compounds between the different environmental compartments, particularly the soil/sediment and water. The majority of organic UV filters are slightly soluble, as shown in Table 1.

Organic UV filters follow two major pathways to enter the environment: direct input from human activities through wash off

Table 1
Main characteristic of organic ultraviolet filters authorized by the EU (regulation number 12223/2009).

Families	Name (INCI nomenclature)[a]	Abbreviation	CAS Nº	Log K_{ow}[b]	Solubility ($g \cdot L^{-1}$)[g]	pKa[h]
Benzophenones	Benzophenone-3	BP-3	131-57-7	3.79[c]	0.21	7.56[f]
	Benzophenone-4	BP-4	4065-45-6	0.37[d]	0.65	−0.70[f]
p-aminobenzoic acid and derivatives	Ethoxylated ethyl 4-aminobenzoate	PEG-25 PABA	116242-27-4	−0.66[e]	–	
	Ethylhexyl dimethyl PABA	OD-PABA	21245-02-3	6.15[f]	2.1×10^{-3}	2.39[f]
Salicylates	Homosalate	HMS	118-56-9	6.16[d]	0.02	8.09[f]
	2-ethylhexyl salicylate	EHS	118-60-5	5.97[f]	0.028	8.13[f]
Cinnamates	Ethylhexyl methoxycinnamate	OMC	5466-77-3	5.8[d]	0.15	–
	Isoamyl p-methoxycinnamate	IMC	71617-10-2	4.33[d]	0.06	–
Camphor derivatives	Camphor benzalkonium methosulfate	CBM	52793-97-2	0.28[e]	0.007	–
	Terephthalylidene dicamphor sulfonic acid	PDSA	92761-26-7 / 90457-82-2	3.83[e]	0.014	−1.05[h]
	Benzylidene camphor sulfonic acid	BCSA	56039-58-8	2.22[e]	0.038	−0.7[h]
	Polyacrylamidomethyl benzylidene camphor	PBC	113783-61-2	–	–	–
	4-methylbenzylidene camphor	4-MBC	36861-47-9 / 38102-62-4	4.95[d]	5.1×10^{-3}	–
Triazines	Ethylhexyl triazone	OT	88122-99-0	17.05[e]	–	3.17[f]
	Diethylhexyl butamido triazone	DBT	154702-15-5	14.03[e]	4.6×10^{-7}	3.04[f]
	Bis-ehylhexyloxyloxyphenol methoxyphenyl triazine	EMT	187393-00-6	8.03[e]	4.9×10^{-8}	6.37[h]
	Tris-biphenyl triazine	–	31274-51-8	10.38[e]	5.5×10^{-10}	1.2[h]
Benzotriazoles	Drometrizole trisiloxane	DTS	155633-54-8	10.82[e]	1.3×10^{-5}	9.72[h]
	Methylene bis- benzotriazolyl tetramethylbutylphenol	MBP	103597-45-1	12.46[e]	3×10^{-8}	7.56[h]
Benzimidazole derivatives	Phenylbenzimidazole sulfonic acid	PMDSA	27503-81-7	−0.16[e]	0.26	−0.87[f]
	Disodium phenyl dibenzimidazole tetrasulfonate	DPDT	180898-37-7	−6.79[e]	0.5	−0.27[f]
Dybenzoyl methane derivatives	Butyl methoxydibenzoylmethane	BM-DBM	70356-09-1	4.51[d]	0.037	9.74[f]
	Diethylamino hydroxybenzoyl hexyl benzoate	DHHB	302776-68-7	6.54[e]	9.5×10^{-4}	7.29[h]
Crylenes	Octocrylene	OC	6197-30-4	6.88[d]	2×10^{-4}	–
Benzylmalonate derivatives	Polysilicone-15	BMP	207574-74-1	–	–	–

[a] INCI International Nomenclature for Cosmetic Ingredients.
[b] Octanol-water partition coefficient (K_{ow}).
[c] Experimental values from Syracuse Research Corporation database.
[d] Estimated values from Syracuse Research Corporation database.
[e] Calculated by use of Estimation Program Interface (EPI) suite v4.11 (2012).
[f] Software calculated value, from SciFinder Scholar Database 2006: http://www.cas.org/products/sfacad/.
[g] From Díaz-Cruz et al., [15]. Indicates in water at 25 °C.
[h] Values obtained from Chemicalize website.

Table 2
Analytical methodologies for UV filters determination in seawater. Grouped by extraction techniques.

Extraction technique	Kind of sorbent	Compounds	Instrumental method	Eluent	Recoveries (%)	LOD ($ng \cdot L^{-1}$)	LOQ ($ng \cdot L^{-1}$)	Reference
SPE	STRATA-X	BP-3	GC-TOF-MS	EA and DCM mixture	60	1-5	–	[74]
		4-MBC						
		OC						
		OMC						
	OASIS HLB	BP-3	HPLC-ESI-MS/MS	MeOH	79	7	–	[42]
		BP-4			91	10		
		IMC			66	46		
		4-MBC			69	20		
		OC			66	18		
		OD-PABA			71	12		
		BM-DBM			69	25		
		PMDSA			88	8		
		DPDT			81	25		
	OASIS HLB	BP-3	GC-MS	MeOH	–	1-5	–	[50]
		E-OMC						
		Z-OMC						
		4-MBC						
	OASIS HLB	BP-3	HPLC-ESI-MS/MS	MeOH	128	4	13	[76]
		BP-4			105	0.9	3	
		IMC			77	5	16	
		4-MBC			84	2.7	9	
		OC			88	30	99	
		OMC			103	3	10	
		OD-PABA			76	1.6	5	
		PMDSA			85	0.8	3	
	OASIS HLB	BP-3	HPLC-ESI-MS/MS	MeOH and Ac mixture	71-111	0.5	–	[44]
		BP-4				1		
		OC				25		
		OMC				25		
		OD-PABA				1		
		BM-DBM				12.5		
	Discovery DSC-18LT and Discovery DSC-PH	BP-3	GC–MS	DCM	80-113	0.1-3.0	–	[45]
		4-MBC						
		OC						
		OMC						
		OD-PABA						
		EHS						
		HMS						
	OASIS HLB	BP-3	HPLC-ESI-QTOF-MS	MeOH	–	–	10	[27]
		BP-4					–	
		4-MBC					9	
		OMC					10	
	Bond Elut C18	BP-3	HPLC–ESI-MS/MS	MeOH and EA mixture	93	0.04	–	[29]
		BP-4			104	0.03		
		IMC			77	1.04		
		4- MBC			83	0.28		
		OC			76	1.38		
		OMC			83	0.41		
		OD-PABA			73	0.03		
		EHS			63	0.10		
		HMS			65	0.11		
		BMDBM			74	0.13		
	STRATA X	BP-3	UPLC-DAD	EA and DCM mixture	94-104	1.4	4.8	[40]
		4-MBC			91-98	0.9	3.1	
		OC			80-100	2.8	9.3	
		OMC			79-92	1.6	5.2	
		OD-PABA			84-93	1.2	3.9	
		HMS			78-110	2.4	8.0	
		BM-DBM			86-90	2.0	6.7	
		DHHB			88-91	1.3	4.2	
SPE	OASIS HLB	BP-3	GC-MS	EA	95	0.5	2.0	[54]
	OASIS HLB	BP-3	HPLC-ESI-MS	MeOH and Ac mixture	100	0.5	–	[47]
		BP-4				12.5		
		OC				25		
		OMC				25		
		OD-PABA				12.5		
		BM-DBM				1		
	OASIS HLB	BP-3	GC-MS	DCM and MeOH mixture	124.4	–	2.6	[10]
		4-MBC			118.7		3.2	
		OMC			94.5		1.9	
	C18E	BP-3	GC-MS	Ac and DCM	>95	100	5000	[31]
	C18E		HPLC-MS	MeOH	>85	100	5000	
	Bond Elut C18	BP-3	UPLC-ESI-MS/MS	MeOH and EA mixture	93	0.04	–	[32]
		4-MBC			83	0.28		
		OC			76	1.38		

Table 2 (*Continued*)

Extraction technique	Kind of sorbent	Compounds	Instrumental method	Eluent	Recoveries (%)	LOD ($ng \cdot L^{-1}$)	LOQ ($ng \cdot L^{-1}$)	Reference
		OMC			83	0.41		
		OD-PABA			73	0.03		
	SPE-DEX 4790	BP-3	GC-MS	Methylene	50-130	1.0	–	[41]
		4-MBC		chloride, EA		0.5		
		OMC		and mixture of		1.0		
		OD-PABA		methylene		1.0		
		EHS		chloride and EA		2.0		
	LC-18 SPE	BP-3	UPLC-ESI-MS/MS	MeOH and	94.3-105.2	2.12	6.41	[24]
		4-MBC		Mili-Q water	85.3-110.3	2.59	7.84	
		OC			87.7-104.6	3.03	9.19	
		OMC			91.6-114.4	3.25	9.85	
		OD-PABA			101.3-111.2	4.91	14.88	
	ENVI-Chrom-P 500	BP-3	HPLC-ESI-MS/MS	MeOH	80	6.3	10	[33]
		4-MBC			73	5.1	10	
		OC			63	3.2	20	
On-line SPE	OASIS HLB	MBP	UPLC-MS/MS	MeOH	61-66	1.1	3.8	[39]
MNPs-based dSPE	$CoFe_2O_4$-oleic acid	BP-3	GC-MS	Hex	125	0.2	0.8	[48]
		IMC			80	6	20.0	
		4-MBC			80	5.8	19.3	
		OC			88	1.8	5.9	
		OMC			73	2.5	8.3	
		OD-PABA			101	3.1	10.2	
		EHS			86	0.2	0.5	
		HMS			81	0.4	1.5	
SPME	Polyacrylate fibre	BP-3	GC-MS/MS	–	73-115	1.5	–	[70]
		IMC			94-108	0.068		
		4-MBC			73-108	1.5		
		OC			104-128	0.16		
		OMC			75-117	0.22		
		OD-PABA			82-106	0.25		
		EHS			84-112	0.69		
		HMS			89-117	0.34		
		BM-DBM			–	12		
		DHHB			89-99	6.0		
		DTS			94-121	3.0		
In-vial SPME	Divinylbenzene-carboxen-polydimethylsiloxane fibre	BP-3	GC-MS/MS	–	86.9-89.7	0.30	1.0	[16]
		BP-4			86.9-89.7	0.30	1.0	
		IMC			94.9-96.5	0.069	0.23	
		4-MBC			90.6-95.3	0.84	2.8	
		OC			98.5-102	0.18	0.60	
		OMC			86.8-98.0	0.06	0.20	
		OD-PABA			95.9-101	0.096	20	
		EHS			93.1-95.9	0.066	0.22	
		HMS			85.6-90.8	0.15	0.49	
SBSE	Polydimethylsiloxane coated stir bar (Twister)	BP-3	HPLC-APCI-MS/MS	MeOH	71-100	80	25	[49]
		OC				200	101	
		OMC				70	25	
		OD-PABA				10	25	
		EHS				2650	3900	
		HMS				1700	3900	
	Polydimethylsiloxane coated stir bar (Twister)	BP-3	HPLC-APCI-MS/MS	MeOH	64	0.9	3.0	[43]
		OC			76	3.3	11.1	
		OMC			84	2.8	9.2	
		OD-PABA			82	0.6	2.4	
		EHS			83	114	382	
		HMS			85	94	313	
	Polydimethylsiloxane coated stir bar	MBP	UHPLC-MS/MS	ACN	18.4-19.9	22.9	76.3	[37]
	Polydimethylsiloxane coated stir bar	PB-3	GC-MS	EA	27.6	2	–	[38]
		OC			59.6	0.6		
	Polydimethylsiloxane coated stir bar	BP-3	GC-APGC–TOF-MS	EA	–	0.17	–	[77]
		4-MBC				0.01		
		OC				0.02		
		OMC				0.46		
		OD-PABA				0.6		
		EHS				0.28		
		HMS				0.44		
		BM-DBM				12.4		
SBDLME	$[P^{+}_{6,6,6,14}][Ni(hfacac)_3^{-}]$	BP-3	GC-MS	–	91-95	10.4	34.3	[78]
		IMC			109-113	13.1	43.1	
		4-MBC			97-102	15.2	50.2	
		OC			95-103	21.2	69.9	
		OMC			95-91	15.3	50.5	
		OD-PABA			110-112	26.7	88.8	
		EHS			114-117	9.9	32.5	
		HMS			102-104	11.3	37.3	

SBSDME	$CoFe_2O_4$-oleic acid	BP-3	HPLC-UV	Ethanol	84-116	30600	100000	[71]
		IMC			79-116	2400	8000	
		4-MBC			96-120	3200	10700	
		OC			98-103	2700	9100	
		OMC			97-107	2400	8000	
		OD-PABA			100-107	3000	9900	
		EHS			83-95	3000	9700	
		HMS			87-97	3200	10000	
	$CoFe_2O_4$-oleic acid	BP-3	GC-MS	–	103	148	493	[79]
		IMC			104	28	95	
		4-MBC			112	23	78	
		OC			89	27	91	
		OMC			88	28	95	
		OD-PABA			111	30	99	
		EHS			109	23	77	
		HMS			112	13	43	
	$CoFe_2O_4$-SiO_2-nylon	BP-4	HPLC-UV	HCl	95-103	1600	5400	[80]
		DPDT			91-97	1900	6300	
		PMDSA			104-115	2800	9200	
		PDSA			97-105	2900	9600	
BAME	Modified pyrrolidone	BP-3	HPLC-DAD	MeOH and ACN mixture	76.6-98.4	300-400	1000- 1300	[82]
LLE	–	4-MBC	GC-MS	Hex	89	0.15	0.5	[84]
		OMC			90	0.082	0.27	
		OD-PABA			86	0.096	0.32	
		EHS			120	0.099	0.33	
	–	BP-3	HPLC-MS/MS	n-octanol	86.2-109.3	10.3	34.4	[87]
		4-MBC			95.0-109.7	10.9	36.4	
DLLME	–	BP-3	GC-MS	Ac dispersive solvent CHL extractant	82-126	33	110	[86]
	–	BP3	GC–MS	Ac dispersive solvent CHL extractant	–	–	–	[11]
		4-MBC						
	–	BP-3	GC-MS	Ac dispersive solvent CHL extractant	111-114	30	99	[46]
		IMC			97-107	23	78	
		4-MBC			82-88	10	33	
		OC			91-104	27	91	
		OMC			87-99	14	47	
		OD-PABA			90-95	29	98	
		EHS			112-117	26	85	
		HMS			88-97	14	46	
IL-SDME	–	BP-3	HPLC-DAD	$[C_6MIM][PF_6]$	99	110	370	[89]
		IMC			92	160	530	
		4-MBC			96	60	200	
		OC			92	3000	10000	
		OMC			107	190	640	
		OD-PABA			92	70	230	
On-line *In-syringe* IL-MSA-DLLME	–	BP-3	HPLC-UV	ACN dispersive solvent	92	180	620	[72]
		4-MBC		$[C_6MIM][PF_6]$ extractant	52	80	250	
		OC			48	2500	8340	
		OD-PABA			49	890	2980	
		EHS			46	11820	39390	
		HMS			51	1024	34150	
In-syringe MSA-DLLME	–	BP-3	GC-MS	Ac dispersive solvent	95.6-104.4	79	23	[34]
		4-MBC		Trichloroethylene extractant	88.4-111	380	160	
		OC			95.1-110.7	291	130	
		OMC			82.5-108.3	191	86	
		EHS			98.4-104.3	31	19	
		HMS			95.4-110.8	95	28	
USAEME	–	IMC	GC-MS//GC-MS/MS	CHL	98.4-105	5.8//1	19//3.3	[69]
		4-MBC			92.4-96.7	0.22//0.29	0.73//9.7	
		OC			97.7-102	25//0.5	83//1.7	
		OMC			90.8-102	2.1//0.66	7//2.2	
		OD-PABA			75.5-84.2	5.4//0.08c	18//0.27	
		EHS			98.0-108	3//0.29	10//0.97	
		HMS			91.5-94.2	15//1.3	50//4.3	
FPSE	Sol-gel poly	MBP	UHPLC-ESI-MS/MS	MeOH	32.4-51.4	2.72	9.08	[73]
iSAME	Cetyltrimethylammonium bromide and sulfosalicylic acid	BP-3	HPLC-UV	2-propanol	102	1500	4800	[85]
		IMC			88	300	1000	
		4-MBC			93	300	900	
		OC			93	800	2600	
		OMC			89	300	1100	
		OD-PABA			95	300	1100	
		EHS			80	1700	5700	

Table 2 (*Continued*)

Extraction technique	Kind of sorbent	Compounds	Instrumental method	Eluent	Recoveries (%)	LOD ($ng{\cdot}L^{-1}$)	LOQ ($ng{\cdot}L^{-1}$)	Reference
SPMDs	Semipermeable-membrane	HMS BP-3 E-OMC Z-OMC 4-MBC	GC-MS	Cyclohexane	84 –	1700 (pg/SPMD) 150-510	5800 –	[50]

from skin and clothing during recreational activities, and indirect entry through industrial discharges, wastewater effluents, runoffs and domestic uses [9,18,19]. When the compounds are released into sewage and reach the wastewater treatment plants, some might be transported to the sludge due to their high lipophilicity and poor biodegradability [20]. This sludge may be destined for landfills or used in agriculture, which potentially pollutes underground water [9]. A fraction of treated wastewater containing organic UV filters will be discharged into natural water supplies [21] are potentially retained in sediments [22] or bioaccumulated in biota [3,9,23].

Moreover, some organic UV filters undergo photodegradation upon exposure to UV radiation or biodegradation in environmental matrices; accordingly, they are often not detected because they are degraded into transformation products (TPs) [15,24]. Nevertheless, scarce information is available on UV degradation in marine environments [25].

Different negative effects of organic UV filters on marine ecosystem have been described. For example, these filters significantly increase the viral abundance in marine bacterioplankton through prophage induction, and they also modify the carbon, nitrogen and phosphorous biogeochemical cycle in seawater [26]. Furthermore, hard corals exposed to organic UV filters suffer rapid and complete coral bleaching, even at extremely low concentrations. Additionally, the toxic effects of benzophenone-3 (BP-3), OMC and 4-methylbenzylidene camphor (4-MBC) on marine organisms at three different trophic levels were reported and, show similar toxicity to copper, mercury, cadmium lead and zinc [27].

The presence of organic UV filters must be analysed to determine their impact on the environment and their possible deleterious on human health [28]. Due to their low concentrations in environmental samples and the appearance of matrix effects, different methods have been developed to analyse several families of organic UV filters in a variety of matrices, including marine samples such as seawater [29], sediments [30] and biota [10].

The aims of this review are describe and compare, the available information about the analytical procedures for the extraction and determination of the concentrations of organic UV filters in different marine matrices (seawater, sediments and biota) in the last ten years (2008–2018). Although this review encompasses global studies, only the compounds allowed in the European Union for which determination methods are described in the literature have been included. Similarly, the present work provides a broad overview of the occurrence and distribution of these compounds in different marine compartments, which highlights their extensive use.

2. Analytical procedures for detecting organic UV filters in the marine environment

The concentration of organic UV filters measured in the marine environment are very low and these filters are encapsulated in complex matrices. Thus, suitable preparation techniques must be applied to the samples to isolate and preconcentrate the analytes prior to their determination. Tables 2–4 summarize the procedures for the extraction and determination of organic UV filters in marine samples.

2.1. Sample extraction

The employed extraction methods depend on the properties of the matrix and the analytes. The extraction techniques used for different marine environmental compartments are summarised in the next sections.

2.1.1. Sampling and pre-treatment

The determination of this kind of contaminants presents several issues. Sample contamination is a common risk due to the occurrence of organic UV filters in different products. For this reason several authors suggest that the analyst avoid the use of PCPs that contain organic UV filters, before [31–33] and during the sampling [10,33] and in the laboratory [34–36]. Due to the lipophilic behaviour of these compounds, they are easily transferred to the glass (adsorption problems), for that, organic modifiers are added to the bottle that contain the sample [37,38].

Analysis of environmental samples frequently requires a pretreatment, depending on the subsequent extraction technique and the type of matrix.

For liquid samples, the collected samples are stored in an amber glass bottles [10,39–41], previously washed with an organic solvent [10,42,43] or in a certified clean amber bottle [31]. Acidification [10,40,41,44] and filtration [10,27,39,40,42,45] are also common pre-treatments. When the water is filtered, the fraction resulting should also be analysed because a fraction of the target analytes is likely adsorbed into the particles and their concentration might be underestimated [46]. Furthermore, unfiltered seawater has also been used in some studies [44,47]. If the samples are not analysed immediately, they must be kept refrigerated [29,40,42,45] in the dark [29,43] and in amber glass bottles [42,48,49] to prevent photodegradation [29]. For seawater, a continuous sampling process has also been reported. This procedure consists on a semipermeable membrane devices (SPMDs), where the sample passed through a membrane and the analytes are retained [50]. This device is attached to the boat in order to sample during a cruise route and it not requires pretreatment.

In the case of sediments, the samples are often taken with a stainless steel grab [51,52]. The possible pre-treatments include homogenization [35,51,53], air dried [51,53] or dried at high temperature [36,54,55] and sieved using different size fractions [51,53,54]. Other pre-treatments are frozen [35,51,52], freeze-dried [35,52,56] and ground into powder [52]. This kind of samples are stored in aluminium boxes [51] or amber glass containers [36,54] in the dark [51,55] and dry environment [51], at the freezer [36,53,54], or in a dessicator in the dark at the freezer [57].

For biota samples, it is important maintain it fresh during the transportation [58,59], and then measure their length and weight [59,60]. Different pre-treatments are carried out depending on the species, such as skin removed, bone removed, peeled, dissection,

Table 3
Analytical methodologies for UV filters determination in sediments. Grouped by extraction technique.

Extraction technique	Compounds	Instrumental method	Eluent	Recoveries (%)	LOD ($ng \cdot g^{-1}$ d.w.)	LOQ ($ng \cdot g^{-1}$ d.w.)	Reference
Soxhelt	4-MBC	GC-MS	DCM and Hex mixture	93	–	–	[56]
	4-MBC	GC-MS	DCM	70-90	0.01-0.17	–	[52]
	OC						
	OMC						
MAE	OC	GC-MS/MS	Ac and heptane mixture	97-115	2.0	6.0	[51]
	OMC			99-113	1.5	5.0	
	OD-PABA			98-104	1.5	5.0	
	MBP	UHPLC-ESI-MS/MS	ACN	50.1-55.7	0.0533	0.176	[114]
	BP-3	GC-MS	MeOH and Ac mixture	80	0.1	0.2	[54]
USE	BP-3	GC-MS/MS	EA and MeOH mixture	98.9-101.3	0.28	0.90	[53]
	EHS			99.4-102	0.11	0.36	
	HMS			97.4-101.3	0.12	0.40	
	BP-3	HPLC-ESI-MS/MS	MeOH	55.1	–	0.3	[35]
	4-MBC			68.9		0.1	
	OC			117.6		0.03	
	OMC			101.4		0.5	
	OD-PABA			86.9		0.03	
	BP-3	GC-MS/MS	EA	98.3-115	–	2.5	[36]
	IMC			100-107		0.40	
	4-MBC			96.3-107		4.6	
	OC			98.3-117		0.43	
	OMC			107-110		1.8	
	OD-PABA			88.2-104		0.10	
	EHS			100-101		0.32	
	HMS			84.2-103		2.0	
VE	BP-3	GC-MS	Ac	106	0.041	0.140	[55]
	IMC			86	0.041	0.140	
	4-MBC			92	0.029	0.096	
	OC			95	0.035	0.117	
	OMC			82	0.018	0.061	
	OD-PABA			84	0.046	0.150	
	EHS			80	0.038	0.130	
	HMS			9	0.053	0.180	
	BP-3	UPLC-ESI-MS/MS	Ac and n-hexane mixture	81	0.43	–	[32]
	4-MBC			58	0.09		
	OC			76	0.09		
	OMC			76	7.55		
	OD-PABA			63	0.16		
	BP-3	GC-MS/MS	EA	86-121	–	3.2	[36]
	IMC			96.4-106		0.42	
	4-MBC			99.7-99.2		4.9	
	OC			103-112		0.33	
	OMC			100-112		1.6	
	OD-PABA			89.7-106		0.30	
	EHS			92.2-103		0.16	
	HMS			91-95.3		2.3	
PLE-ASE	BP-3	UPLC-ESI-MS/MS	MeOH and EA mixture	83	0.71	–	[57]
	IMC			82	2.10		
	4-MBC			91	7.33		
	OC			89	0.58		
	OMC			100	0.51		
	OD-PABA			94	0.61		
	EHS			84	4.26		
	HMS			75	7.55		
	BM-DBM			78	3.94		
	BP-3	GC-MS	DCM	70-100	0.003- 0.54	–	[93]
	OC						
	OMC						
	BP-3	GC-MS/MS	DCM	61-91	0.009	0.029	[94]
	4-MBC			53-91	0.221	0.737	
	OC			92-120	0.024	0.080	
	OMC			86-134	0.039	0.129	
	OD-PABA			85-138	0.408	1.361	
	EHS			68-94	0.065	0.216	
	HMS			70-130	0.022	0.073	
	BP-3	GC-MS/MS	DCM	61-91	0.009	0.029	[95]
	4-MBC			53-91	0.221	0.737	
	OC			92-120	0.024	0.080	
	OMC			86-134	0.039	0.129	
	EHS			68-94	0.065	0.216	
	HMS			70-130	0.022	0.073	
	4-MBC	UPLC-UV	EA and Hex mixture	74.4-102.4	–	0.00036	[96]
	OD-PABA			66.4-77.0		0.00040	
	BP-3	UHPLC-ESI-MS/MS	DCM	92-106	0.03	0.1	[30]
	IMC			98-108	0.02	0.07	
	4-MBC			97-100	0.12	0.38	

Table 3 (*Continued*)

Extraction technique	Compounds	Instrumental method	Eluent	Recoveries (%)	LOD ($ng \cdot g^{-1}$ d.w.)	LOQ ($ng \cdot g^{-1}$ d.w.)	Reference
	OC			103-108	0.084	0.28	
	OMC			100-101	0.016	0.06	
	OD-PABA			90-99	0.001	0.004	
	EHS			88-105	0.02	0.07	
	HMS			83-94	0.007	0.024	
	OT			<5	–	–	
	DBT			<5	–	–	
SPLE-ASE	BP-3	UPLC-MS/MS	MeOH	125	0.4	1.3	[22]
	4-MBC			89	1.1	3.6	
	OC			85	9.9	33	
	OMC			90	4.1	14	
	OD-PABA			120	0.7	2.5	
	BP-3	UPLC-HRMS and GC-HRMS	Hex and DCM mixture	72	5	10	[61]
	OC			102	7	5	
	OMC			98	–	5	
	OD-PABA			81	4	4	
PHWE	BP-3	GC-MS	Water 10 % MeOH	13.5	0.07	–	[38]
	OC			22.4	0.3		
SPME	BP-3	GC-MS/MS	–	77.6-107	0.052	0.17	[99]
	IMC			83.8-104	0.010	0.033	
	4-MBC			89.6-106	0.014	0.046	
	OC			89.0-119	0.059	0.18	
	OMC			70.8-111	0.087	0.15	
	OD-PABA			70.1-124	0.001	0.003	
	EHS			93.3-111	0.031	0.053	
	HMS			93.8-120	0.023	0.039	
SBSDME	BP-3	GC-MS	Ethanol	99-111	0.55	1.79	[100]
	IMC			100-110	0.02	0.07	
	4-MBC			105-107	0.15	0.49	
	OC			94-98	0.01	0.04	
	OMC			103-107	0.02	0.05	
	OD-PABA			98-108	0.04	0.12	
	EHS			95-103	0.03	0.09	
	HMS			91-103	0.04	0.14	
USSPME	BP-3	GC-MS/MS	MeOH	81.3-98.1	–	0.30	[36]
	IMC			85.5-86.8		0.080	
	4-MBC			91.5-96.3		0.50	
	OC			96.7-116		0.50	
	OMC			80.6-89.8		0.30	
	OD-PABA			88.4-91.8		0.010	
	EHS			87.9-94.4		0.10	
	HMS			88.3-95.6		0.10	

deshelled, etc. [58,60–64]. The homogenization could be done in wet and then freeze-dried [58,59] or homogenized after the lyophilisation [60,62,64–68]. Normally the samples are grounded into powder [58,64,67,68] and stored in aluminium foils [60,65] or amber container [65] at the freezer [61,62]. Other pre-treatments are homogenization in wet and dry at high temperatures [10], or homogenized and extracted in wet [61].

Regarding the quality assurance, different criteria related with repeatability, sensitivity and extraction efficiency must be taken into account. Inter-day or intra-day repeatability, expressed as relative standard derivation (RSD) performed for 3 or more replicates has been reported with acceptable ranges from 0.2 % [69] to below 20 % [43,46,51,59,70–73]. Other quality criteria are also employed, such as blanks below the limits of detection (LODs) [32] or less than 1 % [52]. In relation with the sensitivity, the LODs are determined as three times the standard deviation of blank peaks areas [32,58,70]. The extraction efficiency, reported as recoveries are carried out with spiked samples with a known concentration [51] or with surrogate standards [51,53,55,59].

2.1.2. Seawater

Several extraction techniques have been employed for measuring organic UV filters in seawater, although solid-phase extraction (SPE) is the most frequently used, as summarized in Table 2. SPE is simple and easy to perform; nevertheless, its main disadvantage is related to the occasional consumption of a high sample volume, sometimes up to 1 L [74]. C_{18} SPE cartridges are commonly employed because they retain a large amount of organic analytes. Recoveries ranging from 80 % to 113 % were obtained during the extraction of a mixture of BP-3, 4-MBC, octocrylene (OC), OMC, ethylhexyl dimethyl para-aminobenzoic acid (OD-PABA), 2-ethylhexyl salicylate (EHS) and homosalate (HMS) [45].

However, SPE is not adequate for the extraction of polar analytes [50,75]. New polymeric reverse phase sorbents that extract diverse analytes with distinct properties are used for this process [50]. Due to the relatively polar characteristics of the majority of organic UV filters, methanol (MeOH) is the solvent that is most frequently used as the eluent [44]. Other more polar solvents have also been used; for example, a mixture of dichloromethane (DCM) and ethyl acetate (EA) has been used and achieved recoveries ranging from 79 % to 110 % [40].

On-line SPE is an automated version of the conventional SPE procedure that presents advantages such as better reproducibility and reduced sample preparation, minimizing sample contamination. The study by Montesdeoca-Esponda et al. [39] is the only one to apply this technique in the extraction of methylene bis-benzotriazolyl tetramethylbutylphenol (MBP), obtaining similar recoveries (61–66 %) to traditional SPE (60–61 %). However, the LODs achieved using on-line SPE were lower ($1.1\ ng \cdot L^{-1}$) than conventional SPE ($6.2\ ng \cdot L^{-1}$) due to a higher preconcentration factor.

Table 4
Analytical methodologies for UV filters determination in marine biota. Grouped by extraction technique.

Extraction technique	Compounds	Type sample	Instrumental method	Eluent	Recoveries (%)	LOD ($ng \cdot g^{-1}$ d.w.)	LOQ ($ng \cdot g^{-1}$ d.w.)	Reference
PLE-ASE	OC	Dolphin liver expressed in $ng \cdot g^{-1}$ l.w.	UPLC-ESI-MS/MS	DCM and Hex mixture	–	23	75	[65]
	BP-3	Clams tissues	GC-MS	Water and IPA mixture	53.0	–	6.6	[10]
	4-MBC				–		8.0	
	OMC				–		4.8	
	BP-3				67.4	–	6.6	
	4-MBC				–		8.0	
	OMC				–		4.8	
	BP-3	Fish fillet	ULPC-ESI-MS/MS	EA and DCM mixture	94.8-113.0			[58]
	4-MBC				88.6-96.4			
	OC				94.6-113.1			
	OMC				94.9-99.8			
	OD-PABA				89.2-110.0			
	BP-3	Mussels tissues			95.5-102.9	0.9	2.9	
	4-MBC				90.9-95.0	1.8	6.0	
	OC				83.7-98.0	1.4	4.5	
	OMC				80.4-93.7	1.2	4.0	
	OD-PABA				88.8-109.8	1.9	6.2	
	BP-3	Fish tissues			92.2-114.8			
	4-MBC				94.8-113.8			
	OC				95.7-106.8			
	OMC				92.7-112.3			
	OD-PABA				94.4-111.4			
	BP-3	Fish fillet	HPLC-ESI-MS/MS	EA and DCM mixture	107	0.93	3.20	[59]
	4-MBC				95	0.39	1.30	
	OC				75	0.39	1.30	
	OMC				66	0.33	1.10	
	OD-PABA				42	1.77	5.90	
SPLE-ASE	BP-3	Fish tissues expressed in ng/g w.w.	UPLC-HRMS and GC-HRMS	Hex and DCM mixture	75	–	20	[61]
	OC				75		20	
	OMC				85		30	
	OD-PABA				51		20	
USE	BP-3	Fish fillet	UHPLC-APCI-MS/MS	MeOH	88.3-102.0	–	0.08	[62]
	4-MBC				86.0-102.4		0.2	
	OC				97.8-115.6		0.1	
	OMC				98.3-109.5		10	
	OD-PABA				85.5-102.3		0.005	
	BM-DBM				41.1-82.8		1	
	BP-3	Fish belly			93.6			
	4-MBC				80.8			
	OC				87.9			
	OMC				81.1			
	OD-PABA				64.2			
	BM-DBM				58.4			
	4-MBC	Dolphin liver expressed in ng/g l.w.	HPLC-ESI-MS/MS	Hex and DCM mixture	60-115	1.50-25	1.90-75	[60]
	OC							
	OMC							
	OD-PABA							
	BP-3	Fish fillet	UHPLC-MS/MS	DCM and EA	70-120	–	0.003-1.0	[66]
	4-MBC							
	OC							
	OMC							
	OD-PABA							
	BM-DBM							
VE	BP-3	Coral tissues and skeleton	UPLC-ESI-MS/MS	Ac and n-hexane mixture	86	0.50	–	[32]
	4-MBC				83	0.11		
	OC				65	0.12		
	OMC				64	7.06		
	OD-PABA				61	0.22		
MAE	OC	Mussels tissues	GC-MS/MS	Ac and heptane mixture	89-101	2	5	[64]
	OMC				89-99	2	5	
	OD-PABA				103-116	2	5	
	OC	Mussels tissues	GC- MS	Ac and heptane mixture	89-101	2	5	[68]
	OMC				89-99	2	5	
QuEChERs	OC	Mussels tissues	GC-MS/MS	ACN	99-126	5	5	[67]
	OMC				93-106	1	5	
	OD-PABA				90-93	2.5	10	
	BP-3	Fish fillet	GC-MS	Deionized water and ACN	72-83	3	20	[104]
	IMC				89-95	6	20	
	4-MBC				79-86	2	5	
	OC				75-76	23	100	
	OMC				93-115	3	20	
	OD-PABA				69-79	2	5	
	EHS				83-91	2	5	
	HMS				76-82	6	20	

Table 4 (*Continued*)

Extraction technique	Compounds	Type sample	Instrumental method	Eluent	Recoveries (%)	LOD ($ng \cdot g^{-1}$ d.w.)	LOQ ($ng \cdot g^{-1}$ d.w.)	Reference
	DHHB				59-62	–	–	
	BP-3	Fish fillet	GC-MS/MS	Deionized water and ACN	72-77	0.5	2	[103]
	IMC				68-77	1	5	
	4-MBC				57-88	2	5	
	OC				77-79	3	10	
	OMC				90-107	0.5	1	
	OD-PABA				61	2	5	
	EHS				70-82	2	5	
	HMS				92-108	2	5	
	DHHB				82	7	20	
MSPD	BP-3	Fish fillet	GC-MS	ACN	97-99	9	28	[63]
	IMC				97-104	3	10	
	4-MBC				97-101	4	12	
	OC				99-106	1	4	
	OMC				94-98	2	6	
	OD-PABA				86-96	4	12	
	EHS				70-76	6	18	
	HMS				84-93	9	28	
	BP-3	Mussels tissues			89-96			
	IMC				94-107			
	4-MBC				90-101			
	OC				96-112			
	OMC				97-111			
	OD-PABA				70-101			
	EHS				80-97			
	HMS				80-85			
	BP-3	Striped bass fillet	GC-MS/MS	ACN	90	0.03	0.1	[102]
	EHS				84	0.02	0.05	
	HMS				98	0.02	0.05	
	BP-3	Cod fillet			75			
	EHS				88			
	HMS				76			
	BP-3	Salmon fillet			96			
	EHS				77			
	HMS				78			
	BP-3	Mussels tissues	HPLC-ESI-MS/MS	ACN	90-110	–	0.2-3	[115]
	BP-4							
	4-MBC							
	OC							
	OD-PABA							

Another variant of SPE, the magnetic nanoparticles dispersive solid-phase extraction (MNPs-based dSPE), has also been employed to extract some UV compounds [48]. This technique consists of a SPE mediated by nanoparticles that are released into the sample. The advantages are its application in a wide pH range, it is a matrix independent method, it requires less time for the extraction (5 min) and it reduces the solvent volumes required, 3 mL [48], compared to traditional SPE, 30 mL [76]. The MNPs-based dSPE technique using hexane was successfully applied to quantify BP-3, isoamyl p-methoxycinnamate (IMC), 4-MBC, OC, OMC, OD-PABA, EHS and HMS, obtaining good recoveries (70–128 %) [48].

Microextraction techniques have also been used to extract organic UV filters. Specifically, solid-phase microextraction (SPME) by headspace (HS) was used. The main advantages of this technique are the reduction of the matrix effect and the reuse of the fibres. It does not require the use of organic solvents for thermal desorption (TD), integrating the extraction and preconcentration in one step. It is also faster than conventional SPE [70]. Good recoveries (85–102 %) were obtained for the extraction of a group of nine organic UV filters using the *in-vial* SPME technique [16]. This technique consists of the addition of acetic anhydride (acetylation) to the sample prior to extraction for the derivatization of the polar compounds. The main advantage of this methodology is the low cost of the derivatization process. Acetylation and extraction are performed in the same vial, reducing the analyte loss and sample contamination, and less time is required than conventional derivatization, reducing the overall analysis time. The obtained LODs using *in-vial* SPME [16] are lower (0.060-0.84 $ng \cdot L^{-1}$) than conventional SPME (0.068−12 $ng \cdot L^{-1}$) [70] (Table 2).

Stir-bar sorptive extraction (SBSE) combined with liquid desorption (LD) [49], which is compatible with liquid chromatography (LC), was employed to extract BP-3, OC, OMC, OD-PABA, EHS and HMS, with recoveries ranging from 64 to 85 % [43]. Compared to conventional SPME, this technique has a better sensitivity for BP-3, OC and EHS because of its higher surface contact area [77]. Nevertheless, it requires a long analysis time, as 5 h are required in some cases [43,77], which is the main disadvantage compared to SPME and *in-vial* SPME that require 10 min [16,70].

Different devices have been employed to solve the disadvantages of SBSE. Stir-bar dispersive liquid microextraction (SBDLME) uses a stir bar coated with a magnetic ionic liquid. It requires less time (10 min) and presents better recoveries (91–117 %) [78] than SBSE (time, 3−5 hours [49,77]; recoveries, 18.4–100 % [37,43,49]). Stir-bar sorptive-dispersive microextraction (SBSDME) uses a stir bar that is coated with a hydrophobic magnetic nanosorbent; compared to SBSE, the extraction time is shorter (25−30 min) [71,79] and it presents better recoveries (83–120 %) [71,79,80]. Nonetheless, the extraction time is longer than SBDLME [78]. Bar adsorptive microextraction (BAME) uses a bar coated with an appropriate powdered sorbent subjected to an ultrasonic

treatment [81]. Compared to traditional SBSE, it provides the possibility of selecting the most suitable sorbent for the target analytes. Better recoveries were obtained for the extraction of BP-3 (76.6–98.4 %) [82] than SBSE (27.6 %) [38].

Liquid-liquid extraction (LLE) is a traditional technique used to extract different contaminants from environmental samples [83]. The disadvantage of this technique is the use of large amounts of toxic solvents and the requirement of a post-extraction treatment, such as extract filtration [84] or solvent evaporation [85]. However, the sample volume used (200−500 mL) is comparable other techniques, such as SPE [42,76]. This process was used to extract four UV filter (4-MBC, OMC, OD-PABA and EHS) obtaining recoveries between 89 to 120%

Dispersive liquid-liquid microextraction (DLLME) relies on the relative solubility of analytes in two different immiscible liquids. In this method, a small volume of extractant solvent is dispersed by the action of a second solvent. DLLME uses a small volume of organic solvent compared to SPE (60 μL [86] and 6 mL [74], respectively); it has a low cost of implementation, is normally fast and decreases the matrix effect. The recoveries obtained for BP-3, IMC, 4-MBC, OC, OMC, OD-PABA, EHS and HMS mixture are equivalent to the recoveries obtained with other extraction processes, such as SPE [29,45], MNPs-based dSPE [48], LLE [87] and SPME [70].

In ionic liquid-based single-drop microextraction (IL-SDME), the extractant is an ionic liquid (IL) with organic salts as the acceptor phase [88]. In this technique, the use of organic solvents is minimized or eliminated, and therefore it is inexpensive, simple, fast, precise and sensitive compared with conventional LLE and SPE. Good recoveries (92–99 %) have been obtained using a small sample volume (20 mL) of 1-hexyl-3-methylimidazolium hexafluorophosphate ([C_6MIM][PF_6]) as the IL for the extraction of six organic UV filters with an extraction time of 37 min [89]. The recoveries reported are comparable to SPE (Table 2).

On-line *in-syringe* ionic liquid magnetic stirring-assisted dispersive liquid-liquid microextraction (on-line *in-syringe* IL-MSA-DLLME) is a novel technique that is conducted inside an automated syringe containing a magnetic stir bar for the homogeneous mixing of the sample and dispersion of the extractant (*i.e.*, IL). The extract is aspirated and pushed into the detector [90]. This technique is environmentally friendly because it avoids the use of chlorinated solvents, minimizes waste generation, uses less sample volume (3.5 mL) and improves the analysis throughput [72]. Nevertheless, the recoveries obtained for BP-3, 4-MBC, OC and OD-PABA are lower (48–92 %) [72] than the values reported using the IL-SDME technique (92–107 %) [89].

During *in-syringe* magnetic stirring-assisted dispersive liquid-liquid microextraction (*in-syringe* MSA-DLLME), a derivatisation agent such as N,O-bis(trimethylsilyl) trifluoroacetamide (BSTFA) is added prior to the gas chromatography (GC) analysis. The advantage of this technique is that the extraction, derivatization and preconcentration performed at the same time, reducing the overall analysis time (6 min for each sample) [34]. It present better recoveries (88.4–111 %) [34] than on-line *in-syringe* IL-MSA-DLLME (46–92 %) [72].

Other microextraction techniques have been also employed to measure organic UV filters. Ultrasound-assisted emulsification microextraction (USAEME) relies on the emulsification of the organic extractant in the sample by ultrasound and centrifugation. Comparable recoveries were achieved (75.5–108 %) [69] compared to SPE (Table 2). In contrast to SPE, no significant matrix effect has been reported and hence the quantification is performed using conventional external calibration, presenting an advantage in the extraction of organic UV filters from complex matrices.

A new microextraction technique based on the use of a flexible and permeable substance coated with a sorbent chemically bonded to its surface, fabric-phase sorptive extraction (FPSE), was used for MBP, obtaining recoveries ranging from 32.4 to 51.4% [73]. The advantages of this technique are the low consumption of organic solvents, high surface area for the sorbent-analyte interaction, stability in a wide range of pH values and fast back extraction with a small solvent volume. When comparing the sample volume, FPSE usually uses less sample volume and organic solvent than SBSE. Furthermore, FPSE presents better recoveries than SBSE (18.4–19.9 %) [37]. Nevertheless, SPE and on-line SPE result in higher recoveries, 60–61 % and 61–66 %, respectively [39].

In-situ suspended aggregate microextraction (iSAME) relies on the formation of a supramolecular aggregate phase, which is formed in the sample with a cationic surfactant. Afterwards, it is filtered to collect the aggregate and the elution performed by adding an organic solvent to dissolve the aggregate. The principal advantage of this technique is simple the requirement for fewer for its development; it is also simple, fast and precise [85].

Water samples have also been measured with an indirect analysis, using SPMDs that are based on a thin, lay flat tube composed of semipermeable polyethylene membranes. The devices are mounted and then exposed to the medium subject to analysis. This method is used to integrate *in situ* concentrations of more lipophilic compounds. The extraction step is performed using dialysis, and the solvents are generally cyclopentane or hexane. This technique is passive sample uptake and has been applied to extract BP-3, E-OMC, Z-OMC and 4-MBC during a raft expedition crossing the Pacific, expressing the concentration in pg·$SPMD^{-1}$ [50].

Some of the new techniques have been applied only once to extract organic UV filters from seawater (Table 2), but resulted in satisfactory recoveries. The techniques that use IL or specific sorbents present the disadvantage that most reagents are not commercially available, thus they must be synthesize.

2.1.3. Sediments

Less information is available about techniques for extracting organic UV filters from sediments than from water (Table 3).

Traditional techniques, such as the Soxhlet technique have been used to extract organic UV filters from sediments [52,91]. Recoveries ranging from 70 to 90 % have been achieved in the case of 4-MBC, OC and OMC, but its main disadvantages are the use of large quantities of organic solvents and the time required for the extraction (hours).

Microwave-assisted extraction (MAE) [51,54] and ultrasonic extraction (USE) [35,53] have been also used for the extraction of organic UV filters. In MAE, the extraction is faster and consumes less solvent [92], due to the use of microwaves to heat the solvent. In the USE technique, the clean-up step is performed at the same time as the extraction, and the method is efficient and selective; nonetheless, some matrix effects have been observed. For example, the extraction time for BP-3 was shorter (5 min) and better recoveries (98.3–115 %) were obtained [36] than the process using MAE (time, 30 min; recovery, 80 %) [54].

A similar extraction technique that uses a small volume of organic solvent (1−5 mL) is vortex extraction (VE) [32,36,55]. In this case, a lower volume of an appropriate organic solvent is added to the sample, and the extraction is performed with vortex agitation followed by centrifugation. After extraction, an additional step is usually required (SPE [32] and DLLME [55]) for clean-up or preconcentration. Recoveries of 58–76 % were achieved for the extraction of BP-3, 4-MBC, OC, OMC and OD-PABA using 2 mL of Ac and n-hexane [32], a lower volume than employed in the USE technique for the same compounds (8 mL) [35].

Pressurised liquid extraction (PLE) is the most frequently used extraction technique for measuring organic UV filters (Table 3). The clean-up step is frequently performed at the same time as

extraction (in-cell clean-up) by adding sorbents such as alumina, copper or primary secondary amine in the extraction cell [61,93]. Additionally, these compounds facilitate the removal of matrix interferences. Depending on the mixture of the target analytes, different solvents are employed, and DCM is the typical solvent [93–95]. The PLE technique is also performed using an accelerated solvent extractor (ASE) system that automatically extracts the target analytes from the sediment samples [57,93–95]. The use of the PLE-ASE technique is increasing due to the reduced time (10−45 min) [30,57,93–96] compared to traditional techniques. It also increases the efficiency of extraction by operating at high temperature and pressure. In this way, only 15 min are needed to extract BP-3, obtaining recoveries raging from 70 to 100% [93], whereas MAE requires 30 min [54]. In addition, the LODs are very appropriate with the detection of trace contaminants (Table 3).

Selective pressurised liquid extraction (SPLE) is a variation of PLE that consists of incorporating matrix compound retainers into the extraction cell [97] using the ASE system. Compared to PLE-ASE, the addition of the hydromatrix increases the solvent flow through the ASE cell. Good recoveries were achieved (81–102 %) when this technique was applied to the extraction of BP-3, OC, OMC and OD-PABA using an intermediate polarity mixture of hexane and DCM [61].

Pintado-Herrera et al. [38] applied a PLE modification known as pressurised hot water extraction (PHWE) that uses water at high temperatures (100–374.1 °C), which modifies its properties to resemble another solvent, to extract compounds with low and medium polarity and semi-volatile organic compounds from solid samples. The main advantage is the minimal use of organic solvents [98]. Organic solvents such as DCM, EA and hexane are employed in In SPLE and PLE-ASE (Table 3), while a mixture of water and MeOH (10 %) are used in PHWE obtaining recoveries of 13.5 and 22.4 % for the extraction of BP-3 and OC, respectively [38].

A technique that is typically applied to liquid samples, SPME, was used for first the time to extract organic UV filters from beach sand. The process consists of placing the sample in a vial containing Milli-Q water and sealing the vial. Then, the vial is submerged in a water bath with magnetic stirring. After equilibration, the SPME technique is performed using HS and the desorption is conducted using TD. The main advantage of this technique is that it avoids the use of organic solvents (environmentally friendly), requires a shorter extraction time and provides high sample throughput. Recoveries ranging from 70 to 1.4 % were achieved during the extraction of BP-3, IMC, 4-MBC, OC, OMC, OD-PABA, EHS and HMS [99], consistent with other extraction techniques, such as Soxhlet [52] and MAE [51].

Another technique used for liquid samples, SBSDME, was also applied to beach sand. The application of this technique starts with the placement of the sample in a vial containing stir bar and water, which acts as the dispersion medium. The sample is stirred to extract the analytes and then the stir bar is subjected to LD. This technique reduces the sample manipulation and the use of organic solvent (150 μL) compared with the MAE (30 mL) [51] and USE (1 mL) [36] techniques. The LODs and recoveries (between 91–111 %) [100] were consistent with the values obtained using other techniques, such as Soxhlet [52] and SPME [99].

Vila et al. [36] employed a combination of two techniques for extraction: ultrasonic extraction followed by SPME (USSPME). First, the USE technique was applied to the sample, and the extract (diluted with water) was placed in a vial containing a stir bar. Then, the SPME technique was performed using HS and the desorption was performed using TD. Because this technique reduced the interference from the matrix, external calibration was possible. During SPME, the extraction and preconcentration occur in a single step. In addition, the same authors compared the effectiveness of three different methods (USE, VE and USSPME) in extracting BP-3, IMC, 4-MBC, OC, OMC, OD-PABA, EHS and HMS. Higher recoveries were found using the VE technique, obtaining at the same time the lowest limits of quantification, proving to be most sensitive technique in determining the levels of organic UV filters (Table 3).

2.1.4. Biota

The most common extraction technique for marine biological samples is PLE using an ASE system (Table 4). This technique has been applied to determine organic UV filters in different biota samples, such as dolphin liver [65], clam tissues [10], fish fillets [10,59] and prawn tissues [58].

However, other techniques that have also been used to extract these compounds from sediment samples have been employed for the extraction of biota samples, shown in Tables 3 and 4. SPLE-ASE was employed in the wet extraction of BP-3, OC, OMC, and OD-PABA from the soft tissues of fish, achieving recoveries ranging from 51 to 85% [61]. This study is the only report to present extraction from wet samples; moreover, the compounds were extracted from a combination of all soft tissues (muscle, stomach, intestines and liver).

The USE technique was used to analyse 4-MBC, OC, OMC and OD-PABA in dolphin liver, with recoveries ranging from 60 to 115 % [60]. Furthermore, the USE and PLE-ASE techniques both present similar recoveries (98.8–115.6 % for USE [62] and 94.6–113.1 % for PLE-ASE [58]) for OC and OMC extraction, from fish fillet.

A single study has reported the extraction and determination of organic UV filters in corals [32]. The VE technique was used to extract BP-3, 4-MBC, OC, OMC and OD-PABA from coral tissues, obtaining recoveries ranging from 61 to 86 %.

MAE technique was also applied to extract OC, OMC and OD-PABA from mussels (soft tissues). Better recoveries were obtained (89–116 %) [64] using a mixture of acetone (Ac) and heptane, and the values were comparable to the recoveries reported using the PLE-ASE technique (80–110 %) for the same biota matrix and compounds with an EA and DCM mixture [58].

The Quick, Easy, Cheap, Effective, Rugged and Safe technique (QuEChERS) was employed to extract OC, OMC and OD-PABA from mussel samples [67], obtaining good recoveries (90–126 %) using acetonitrile (ACN) and water as extractants. The main advantage of this technique is that it is flexible and selective. It is also simple, effective and uses a small amount of solvent compared to the PLE-ASE [10,58] and USE [60,62,66] techniques. However, it presents a low enrichment factor, which can be solved by the use of other extraction technique, such as DLLME.

Matrix solid-phase dispersion (MSPD) extraction was also used for the extraction of organic UV filters in biota matrices. In this technique, the sample is placed in a mortar with the bonded phase and blended. Then, the mixture is placed in an appropriate cartridge, depending on the analytes to be determined, and a solvent is added for extraction [101]. The extraction and clean-up steps are integrated in a single step; thus, it is fast, simple and uses a small volume of solvents (5−7 mL) [63,102] compared to the USE (60 mL) [62], PLE-ASE (25 mL) [58] and QuEChERS (10 mL) [103,104] techniques for fish fillet extraction. Moreover, the study by Tsai et al. [102] is the only report to present recoveries for each species studied (striped bass, cod and salmon), providing additional accuracy in the study.

After comparing the four techniques employed for the extraction of OC and OMC from mussels (QuEChERS, PLE-ASE, MSPD and MAE), QuEChERS presents better recoveries for both compounds (Table 4). MAE and MSPD obtained comparable results, whereas PLE-ASE presents lower recoveries.

2.2. Detection and determination

Chromatographic techniques are usually employed to determine the levels of organic UV filters because they are selective to

both parental compounds and TPs, as many organic UV filters undergo different transformations processes. For polar and less volatile compounds, LC is preferred, while GC is chosen for volatile compounds (and their TPs) [105].

LC and ultra-high performance liquid chromatography (UHPLC) coupled with different detectors are used to measure the concentration of organic UV filters in cosmetics [106] and environmental samples, such as seawater, sediments and biota (Tables 2,3 and 4). Diode-array detectors (DAD) or UV detectors are employed because they provide a fast analysis with good resolution [40,85,89,96]. However, mass spectrometry (MS) detection [31] or tandem MS/MS produce lower LODs [22,61,87]. The coupling with a quadrupole time-flight (QTOF) mass spectrometry detector provides accurate mass detection of the parent ions [MH]+, and identifies and confirms their metabolites [27,61]

Due to the different characteristics of these analytes, they are able to be ionized by electrospray ionisation (ESI) and atmospheric pressure chemical ionisation (APCI) in positive or negative mode. The ESI mode is reported to display better sensitivity for identifying and quantifying compounds with medium to high polarity, while APCI presents better ionisation for compounds with low polarity [49,62]. ESI mode is the most frequently used mode because it provides an efficient ionization in a wide range of *m/z*. Nevertheless, it presents matrix effects [107], while APCI approach is less affected [107] due to the ionisation in the gas phase [49]. Nguyen et al. [49] reported a comparison between ESI and APCI approach for UV filters determination in seawater, in which APCI provided better sensitivity and reproducibility for BP-3, OC, OD-PABA, OMC, HMS and EHS.

GC is the most frequently used technique to determine the levels of organic UV filters in marine biota and sediments (Tables 3 and 4). Although GC coupled with MS or MS/MS detectors yields low LODs for the analysis of trace contaminants in environmental matrices [54], this approach presents an issue due to the low volatility and thermal stability of some organic UV filters, containing phenolic hydroxyl groups. Therefore, an additional derivatization step is needed [53] such as salicylates and benzophenones [16,34]. This step increases the volatility, reduces the polarity, prevents co-elution in complex matrices, and improves the reproducibility and sensitivity of the detection of polar compounds [16,53,108,109]. Different strategies, such as silylation, alkylation and esterification acylation, are the most frequently used derivatisation methods [86]. Agents such as N-(tert-butyldimethylsilyl)-N-methyltrifluoroacetamide, BSTFA and N-methyl-N-(trimethylsilyl)trifluoroacetamide are employed to improve the signal intensity and peak shape of some polar compounds [10,86,93]. Another type of derivatization, acetylation, is also used because it requires a shorter reaction time than silylation [16]. Some extraction techniques incorporate the derivatization step in the extraction process, resulting in an overall shorter analysis time [16,34]. Nonetheless, derivatization of the different matrix components can affect its precision and accuracy [107].

When the mixture of organic UV filters subject to analysis has a great range of different properties, LC coupled with a MS/MS detector is the main option [29,71]. Moreover, this technique is the most appropriated method for the simultaneous determination of the parental compounds and their TPs, which generally have a higher polarity than their parental compounds [107].

On the other hand, the matrix effect represents a potential problem for the quantitative determination of organic UV filters in environmental samples [110] using both GC and LC [107] because the coextracted matrix components may affect the analyte ionisation during MS detection [111]. However, the matrix effect in GC is not so critical [107] and it presents less matrix effect of coeluted lipids for thermally stable organic UV filters [110]. Even through LC presents higher matrix effect; this technique is the

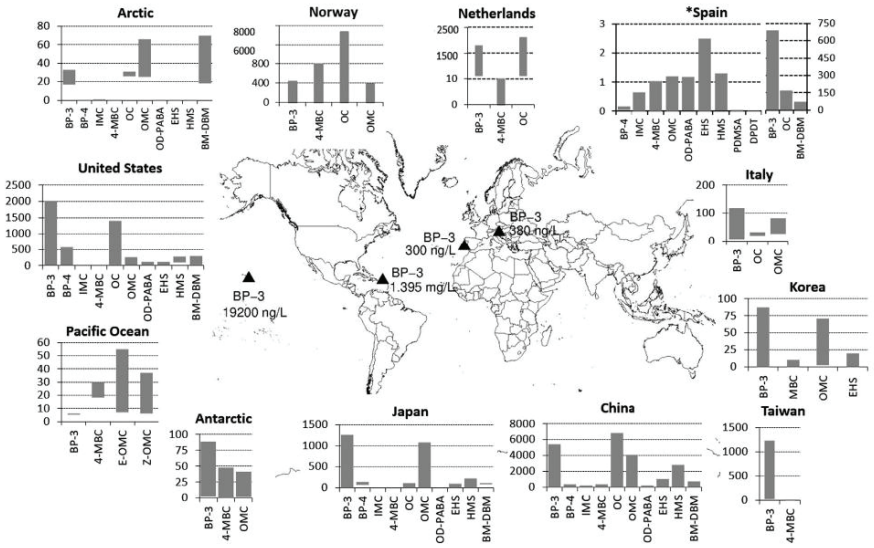

Fig. 1. Global occurrence of UV filters in seawater. Y-axis are in ng·L^{-1}. Triangles represent a single value reported, * Values presented in µg·L^{-1}. Concentration expressed in pg·SPMD^{-1} for the Pacific Ocean.

most frequently used in the organic UV filters determination in seawater (Table 2). Therefore, a highly sensitive and selective detection method to prevent a matrix effect is needed. However, in some cases, the matrix effect is unavoidable, and must be corrected [112] to prevent signal suppression or enhancement [113].

3. Occurrence in the marine environment

The global use of organic UV filters, 10,000 tons annually [105], requires their frequent and recurrent detection in the marine environment. The next section presents the occurrence for those organic UV filters allowed in the EU for which extraction methodologies in seawater, sediments and biota samples collected around the world has been described in the literature. Detailed data are presented in the Supplementary Material (SM).

3.1. Seawater

A wide variety of organic UV filters has been detected in seawater samples collected around the world. Fig. 1 illustrates the global occurrence and concentrations of the different organic UV filters. Detailed information is shown in the SM (Table S1).

Most of the samples are normally collected during the summer season, highlighting the importance of the direct input of these compounds, although high concentrations have also been detected in other seasons in areas near wastewater effluents [29,74]. Seasonal variations were observed in Hong Kong [24], Japan [84] and Korea [41], where lower concentrations were observed in winter (Table S1). In some cases, the UV filter concentration increased up to 4.4 times during the holiday season (June-August) compared to the pre-holiday period [41].

Fourteen of the twenty-five compounds allowed in the EU were detected in various countries; almost all the UV filter families (except triazines and benzylmalonate derivatives) have been detected. Based on the collected data, the most studies have been conducted in Spain, China and the USA. BP-3 is the most recurrent organic UV filter detected, probably because it is one of the most commonly used organic UV filters [86] and it is allowed in all countries [116]. It also has a slower photodegradation rate than other organic UV filters [25]. BP-3 appears in concentrations ranging from ng·L^{-1} to mg·L^{-1} (Table S1).

The highest BP-3 concentration (1.395 mg L^{-1}) was found in USA at the Trunk Bay of St. John Island (USA Virgin Islands). Samples were collected from coral reef areas at approximately noon, when more than 180 swimmers were present in the bay at the time of sampling (the bay receives up to 2000 visitors per day [31]). In the same study, in Hawaii a high value was detected (19,200 ng·L^{-1}), specifically in Maunalua Bay (Oahu, Hawaii, USA); sampling was performed in June in a public beach with over 500 swimmers per day in the peak of tourism season [31]. The second highest measured concentration was recorded in Spain (Galicia) (692,000 ng·L^{-1}) in water samples collected during the summer season in different bathing areas [70].

Lower but significant concentrations of BP-3 were also detected in China (5429 ng·L^{-1}) in samples collected from a popular beach in Hong Kong during the summer season, as well as from the Victoria Harbour channel near to a wastewater effluent, which received 70 % of discharges from the Hong Kong population. Those results represent the indirect and direct pathway of organic UV filters [29]. In Spain, a concentration of 3316.7 ng·L^{-1} was measured in a beach of Spain (Gran Canaria island), which is located close to various resorts and has an artificial barrier; therefore it is considered a semi-closed beach. Additionally, because of its good weather, the summer season lasts for most of the year in Gran Canaria island; thus, temporary fluctuations are less pronounced [40].

In South Carolina (USA), The Netherlands, Japan and Taiwan, BP-3 has also been frequently detected with average concentrations of 10–2013, 10–1540, 9–1258 and 18.8 – 1233 ng·L^{-1}, respectively. These values correspond to samples collected during the summer season at beaches where different recreational activities have been developed [33,44,45,87]. Other European countries, such as Norway, Slovenia and Portugal, present lower concentrations, 13–439.9, 96–380 and <300 ng·L^{-1}, respectively, although the samples were collected from beaches during the summer [54,74,82].

The second most frequently detected UV filter in seawater is OMC (Fig. 1). The highest concentrations were found in China (4043 ng·L^{-1}) [29], Spain (1200 ng·L^{-1}) [69] and Japan (1080 ng·L^{-1}) [84]. These high values also correspond to samples collected from beaches in the summer season (Table S1).

Another recurrent compound is OC, for which the maximum concentration (171,000 ng·L^{-1}) was reported in bathing areas in Spain during the summer [69]. In Norway, a high concentration (7301 ng·L^{-1}) was also reported in samples collected from a crowded beach during the summer season, where the majority of users were children [74]. This compound was also detected in other areas, such as The Netherlands [33], China [29], USA [29,44,47], Spain [40,100], the Arctic [29], Italy [43] and Japan [29,45].

The predominant presence of these compounds corresponds with those organic UV filters (BP-3, OC, EHS, OMC and IMC) that are commonly added to PCP formulations [70,117] and frequently used during the summer season [77], when beaches tend to be crowded [78].

Two different studies were conducted in the same beach in Spain (Valencia) in summer using different extraction techniques (SBDLME and SBSDME) and comparable concentrations were obtained; the compound with the highest concentration was EHS in both cases [78,79]. Similarly, two studies were performed at Alicante (Spain) in the summer of 2009. The study by Tarazona et al. [86] reported a higher concentration of BP-3 (3300 ng·L^{-1}) than the study by Román et al. [48] (879 ng·L^{-1}); this discrepancy is potentially attributed to the dependence of the UV filter concentrations on the users (children or adults), the water tides, water renovation and other factors [78]. In Gran Canaria island (Spain), MBP was detected at two beaches, where García-Guerra et al. [73] reported higher concentrations than those reported by Montesdeoca-Esponda et al. [39], probably due to visitor habits as tourists travel to these areas almost year-round [40].

The UV filter OD-PABA was measured in concentrations ranging from 0.03 to 1187 ng·L^{-1} in the Arctic [29], China [24,29,32], Japan [29,45], Spain [42,46,48,78,79,100] and USA [29,44,47]. However, this compound was not detected in Korea, probably because it is no longer used [41]. In addition, OD-PABA was the compound with the lowest concentration detected (5.8 ng·L^{-1}) in Gran Canaria island (Spain), likely; because this compound has been progressively excluded [40] for its potential photoallergic effect on humans [118]. However, it is a permitted organic UV filter in the EU [4].

Other less common organic UV filters have been also quantified in different places, such as the Arctic, China, Japan, Spain, USA, Korea, The Netherlands, Norway, Antarctic and Taiwan (Fig. 1). In the Antarctic Ocean waters, the reported concentrations are comparable to the levels detected in other parts of the world [10] (Table S1). The occurrence of organic UV filters in oceanic waters far away from coastal areas suggests their transport via ocean currents or the atmosphere [119].

3.2. Sediments

The sediment matrix constitutes a compartment that traps lipophilic compounds [51]. Thus, the sediments subject to wastewater discharges (submarine outfall) are a localised reservoir

for these compounds, where the highest values are present at sites located close to the wastewater release and their concentrations decrease at greater distances [57,61]. Due to the limited light penetration, the photosensitive compounds are stably retained [51].

Limited information is available regarding the occurrence of organic UV filters in marine sediments compared with freshwater sediments [57]. Fig. 2 presents the global occurrence and concentrations of organic UV filters in marine sediments; presenting more detailed information in the SM, Table S2.

Compounds with log K_{ow} between 4 and 7 show the potential to accumulate in sediments and the biota [120], similar to reports from different countries (Fig. 3A and 3B). Most of the organic UV filters present in this kind of matrix are considered hydrophobic (Table 1).

Much of the occurrence data has been reported in studies conducted in Spain and China (Table S2). The UV filter most frequently detected is OC, probably due to its highly lipophilic behaviour (log K_{ow} = 6.88) and its tendency to be absorbed in sediments or organic matter. The maximum concentration, expressed in dry weigh (d.w.), of this compound was reported in Spain (Gran Canaria island) (670 ng·g^{-1} d.w.), a crowded beach visited all year [86,99]. The second highest concentration of OC (551 ng·g^{-1} d.w.) was measured in two fishing harbours in China that are used for recreational activities and were built in semi-closed coastal regions that decrease water exchange [52].

Another recurrent compound is OMC (Fig. 2), for which the highest concentration was determined in China (456 ng·g^{-1} d.w.) in a fishing harbour [52]. With a log K_{ow} = 5.8, the adsorption of OMC by sediments is expected to contribute to its persistence against dilution effects [84].

BP-3 is also a recurrent compound that is present in sediments in different countries around the world [22,32,35,38,53–55,57,61,93–95,99,100]. Nevertheless, it is present at relatively low concentrations (0.05−47 ng·g^{-1} d.w.) due to its lower log K_{ow} (4.79), and thus it is less likely that other compounds to be found in sediments [93].

Although EHS is not one of the most frequently recurring compounds, it was detected at the second highest concentration in samples collected from beaches in Spain and Portugal during summer [55,99].

The highest concentration of OD-was detected in China (150 ng·g^{-1} d.w.) at Victoria Harbour that receives 70 % of the wastewater from the total population in Hong Kong and Sai Kung (popular recreational area) [57]. In Spain, OD-PABA has been measured in concentrations 10.2 ng·g^{-1} d.w. as a consequence of recreational activities [55,100]. In other countries, such as Japan [57], Lebanon [51], the Northwest Pacific Ocean [30] and Norway [61], 0.8-13.9 ng·g^{-1} d.w. levels have been reported and are related to wastewater discharges from different origins (domestic, industrial and agricultural).

Two studies were conducted in different seasons (winter and summer) to analyse beach sand from a beach in Spain (Valencia), and similar concentrations of eight studied organic UV filters were observed in both seasons [55,100]. However, in two studies performed at Cadiz Bay (Spain), in different seasons, different concentrations were reported for BP-3 and OC. The concentrations reported for sediments collected in summer [38] were higher than sediments influenced by urban wastewater discharges in winter [94].

Sediments from the Oslo Fjord in Norway were also investigated, and the compounds BP-3, OC, OMC and OD-PABA were detected at concentrations of <5, <7-82.1, 8.5–16.4 and <4 ng·g^{-1} d.w., respectively. If we compare these results with the compounds reported in seawater samples collected from the same place, OD-PABA was not present in this matrix [61,74], potentially due to the higher degradation rate following exposure to natural radiation [121] and its hydrophobic behaviour (log K_{ow} = 6.15) [17].

Two studies were performed along the Pearl River Estuary (China) and reported similar concentrations for 4-MBC, OC and

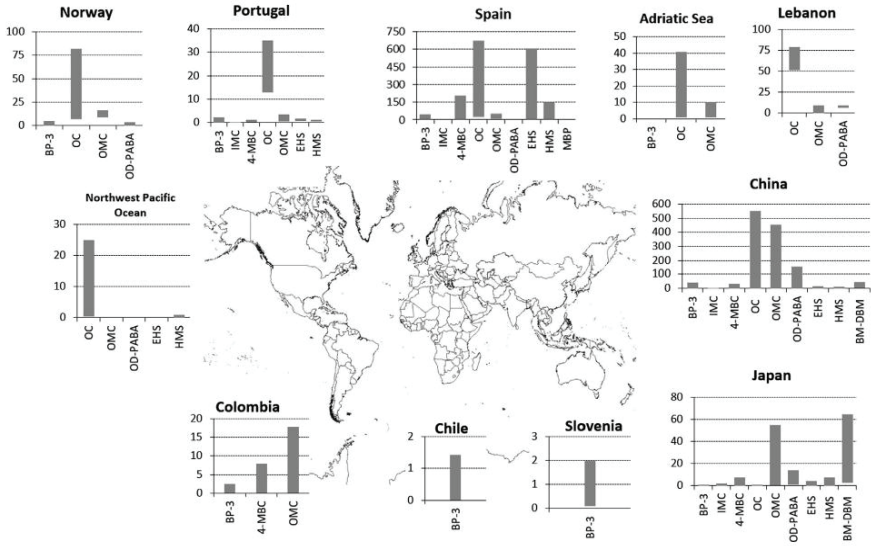

Fig. 2. Global occurrence of UV filters in sediments.

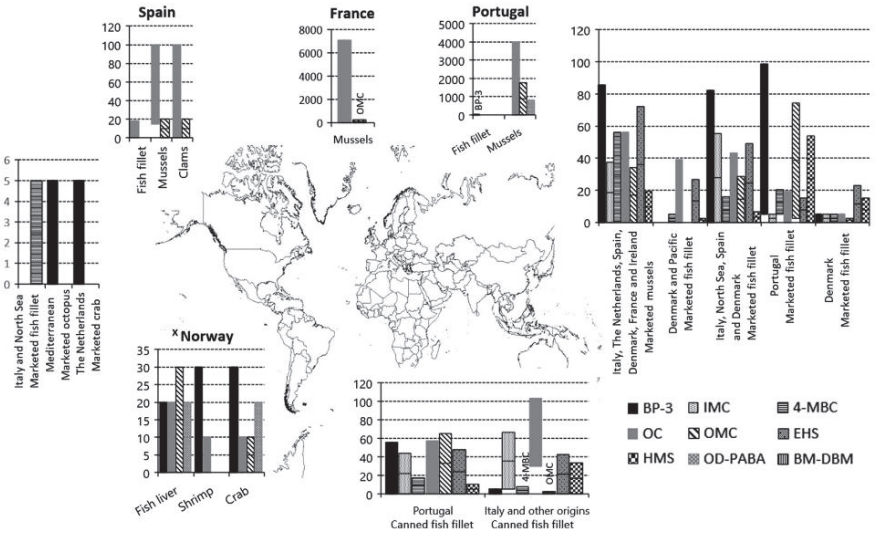

Fig. 3. (A) European occurrence of UV filters in different marine biota. Y-axis are in ng·g^{-1} d.w. ˣ Concentration in ng·g^{-1} w.w. ˜ Concentration in ng·g^{-1} l.w. related to dolphins. (B) Not European occurrence of UV filters in different marine biota. Y-axis are in ng·g^{-1} d.w. ˣ Concentration in ng·g^{-1} w.w. ˜ Concentration in ng·g^{-1} l.w. related to dolphins.

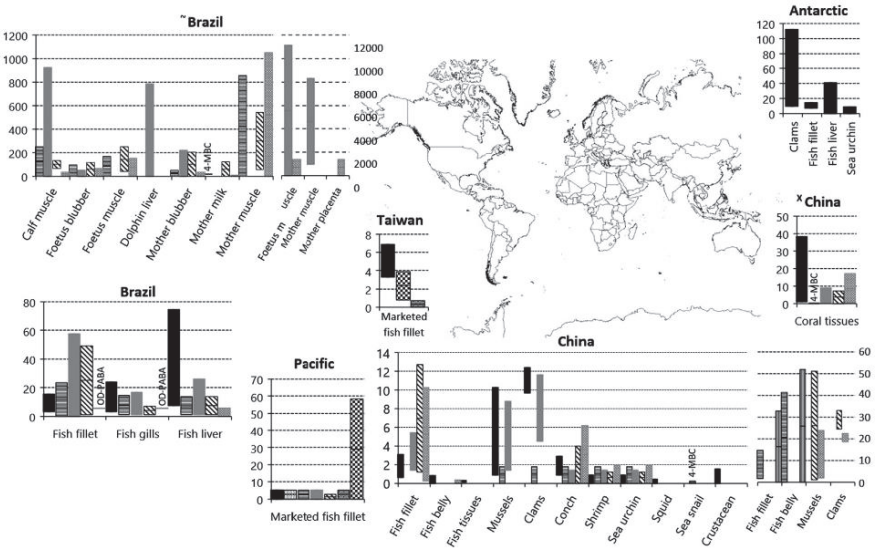

Fig. 3. (Continued)

OMC [35,95], because of the input from wastewaters. In addition, in the river outlet, another study reported lower concentrations [52]. Moreover, in Hong Kong (China), seasonal variations were reported between the wet and dry seasons [32]. During the wet season higher concentrations were detected for 4-MBC, OC, OMC, and OD-PABA due to the extensive increase of recreational activities during this season [32].

3.3. Biota

Little information is available about the occurrence of organic UV filters in marine biota compared with seawater and sediments. Due to the lipophilic characteristics of some compounds (with log K_{ow} between 4–8) and their relative stability against biotic degradation, they tend to accumulate in the food chain [15] and are transferred to humans through alimentation [59]. Different species have been collected from different part of the world and in different seasons with the aim of determining their occurrence (Table S3). Their concentrations have been reported in d.w., lipid weight (l.w.) and wet weight (w.w.).

The majority of studies examining the marine biota has been conducted in China, as shown in Fig. 3B. Most studies have been conducted on fish fillets from a wide variety of species [102,104] (Table 4), because they are part of the human diet [122]. Other fish tissues that are not components of the human diet have also been examined, such as fish belly and other inedible fish tissues [62].

The most frequently detected compounds (BP-3, 4-MBC, OC, OMC, and OD-PABA) are widely used not only in PCPs but also in food additives [67], and they have been detected at different concentrations (Table S3). BP-3 was detected at higher concentrations (82.2 ng·g^{-1} d.w.) in fish fillets [103], while OC is the most frequently detected compound. It presents a greater log K_{ow} (6.88), which contributes to its bioaccumulation.

The study by Molins-Delgado et al. [59] reported the distribution and concentration of organic UV filters (BP-3, 4-MBC, OC, OMC and OD-PABA) in different parts of the fish (*Mugil liza*), including the gills. In addition, the same authors and Emnet et al. [10] reported greater accumulation of BP-3 in fish liver (7.55–74.4 and 41.0 ng·g^{-1} d.w., respectively) than in muscle tissues (<3.20-15.4 and <6.6-14.1 ng·g^{-1} d.w., respectively).

Cunha et al. [104] and Picot Groz et al. [67] studied the presence of OC, OMC and OD-PABA in mussels from Portugal. However, the first authors [104] did not detect any compound. A potential explanation for these results is the collection of samples from September-December, while Picot Groz et al. [67] collected samples in summer. Thus, recreational activities exert an effect on these organisms. These results are consistent with the findings reported in other places showing the seasonal variation in seawater [24,41,84]. In addition, OMC was detected after the summer period, suggesting that other sources in addition to recreational activities also contribute to its accumulation [64].

Also, OC and OMC were detected in *Mytilus galloprovincialis* and *Mytilus edulis* mussels, with the highest concentration observed for OC (7112 ng·g^{-1} d.w.) [64]. The samples were collected from June to November at a closed beach in France with a population size of greater than 50,000 inhabitants, revealing the effects of both recreational activities and the geomorphological structure on the concentration of organic UV filters in this kind of organisms.

In addition, a bioaccumulation study in mussels (*Mytilus galloprovincialis*) was conducted under laboratory conditions by Vidal-Liñán et al. [115]. The mussels were exposed to artificial seawater that contained BP-3, benzophenone (BP-4), 4-MBC, OC and OD-PABA for 30 days. After exposure, rapid uptake of 4-MBC, BP-4 and OC was registered, while BP-3 and OD-PABA presented lower accumulation. Moreover, the mussels are able to biotransform OD-PABA after exposure until undetectable levels are observed. The concentrations observed after exposure are comparable to the results reported for wild mussels (*Mytilus galloprovincialis* and *Mytilus edulis*) [64], confirming the bioaccumulation of some organic UV filters in mussels.

In Brazil, two studies analysed organic UV filters in dolphins (Table S3). Gago-Ferrero et al. [65] were the first to report the levels of these compounds in dolphins (*Pontoporia blainvillei*) liver. The concentration of OC was up to 782 ng·g^{-1} l.w. The second study performed by Alonso et al. [60] was related to the transfer of organic UV filters between the dolphin mother to the foetus or calf in two different dolphin species, Franciscana (*Pontoporia blainvillei*) and Guiana (*Sotalia guianensis*). Of all the samples analysed, the most recurrent compound was OC, and the highest concentration of OC (11,130 ng·g^{-1} l.w.) was measured in muscle of foetal Franciscana dolphins (Table S3). This study also reported the presence of other organic UV filters (4-MBC, OMC, and OD-PABA) in dolphins. These filters likely accumulate due to feeding, as these animals are homeotherms and their rates of feeding are higher than fish [122]. Therefore, biomagnification is also suggested [60].

Marketed mussels, octopus, crab and fish fillets have also been analysed with the aim of evaluating the presence of organic UV filters in seafood in the EU [103]. BP-3, IMC, 4-MBC, OC, OMC, EHS and HMS were detected at different concentrations. BP-3 appears to be the compound present at the highest concentration in fish fillets (82.2 ng·g^{-1} d.w.). In addition, the same organic UV filters were also detected in canned fish fillets (seabream) [103]. Other biota species, such as shrimp [61], sea urchin [10], clams [10,58,104], conch, squids, *Squilla* and sea snails [62], were also analysed and different organic UV filters were also detected (Fig. 3A and 3B).

Finally, in other kind of organism like corals, the occurrence of organic UV filters (BP-3, 4-MBC, OC, OMC and OD-PABA) was reported for five different species of corals (*Platygyra acuta*, *Porites sp.*, *Pavona decussata*, *Acropora valida*, and *Favites abdita*) sampled along the Pearl River Estuary (Hong Kong, China) [32]. In samples collected during the wet and dry seasons, BP-3 was the only compound reported in both seasons. Additionally, higher concentrations were reported for BP-3 in the wet season revealing seasonal variations, this is potentially attributed to the seawater patterns also observed in the same place [32].

4. Conclusions

Organic UV filters are present in several marine matrices and are compounds of increasing concern because their toxicity and adverse effects on different marine organisms have been already reported. The most frequently used separation and detection technique for their measurement in environmental samples is gas chromatography coupled to mass spectrometry. Liquid chromatography is also selected for non-volatile compounds.

Organic UV filters exhibit a wide range of different characteristics that must be considered before their extraction from the matrix. A wide variety of extraction techniques have been performed to extract these compounds from seawater, sediment and biota, due to the wide range of polarities, solubilities, and other properties. Each technique offers distinct advantages and disadvantages in its analytical approach. In this way the new on-line techniques offer a high sample analysis frequency, allowing to analyse 2–5 samples per hour. Moreover, they present considerable improvements respect to traditional techniques such as LLE and SPE, like the reduction of solvent, sample volumes and sample handling. These characteristics are consistent with the principles of the green chemistry for determining the levels of trace contaminants.

Solid matrices (sediments and biota) represent a special challenge due to the low concentrations and matrix effects.

Usually, this kind of matrices requires pre-treatments, post clean-up process and preconcentration steps. In this sense, there is not a common pre-treatment stablished, resulting difficult to compare the values obtained in some cases. Moreover, in biota samples the concentration is not always presented in the same units of concentration (*i.e.* l.w., w.w., d.w.).

The developed techniques are usually focused in some compounds, setting aside other compounds. In seawater only for the 64 % of the compounds allowed in the EU, an appropriated methodology have been performed. For sediments and biota the percentages fall to 48 % and 40 %, respectively. Further methodology capable of extract a large number of compounds and their TPs are needed.

Most of the studies conducted to determine the occurrence of organic UV filters in the environment have been performed in seawater, where seasonal variations have been observed. Highest concentrations are reported in summer, principally due to recreational activity. The occurrence of organic UV filters in seawater also depends on the presence of marine outfalls of sewage. Studies in seawater have been reported the presence of only fourteen of the twenty-five compounds allowed in the EU since there is no methodology developed for the rest of organic UV filters. BP-3 was the most recurrent compound. From the reviewed studies in seawater, BP-3 was present in the 85 % of the cases, OC and OMC in the 58 %, 4-MBC in the 55 %, and HMS, EHS and OD-PABA from 29 % to 35 %.

In the case of sediments, OC and OMC was reported in the 80 % of the analysed samples, BP-3 in the 73 %, 4-MBC and OD-PABA in the 47 % and EHS and HMS in the 33 %. In biota samples, OC was found in the 92 %, of the samples, BP-3 and OC in the 64 %, OD-PABA in the 50 % and 4-MBC in the 42 %.

To analyse the frequency of the results obtained in biota, it is necessary to take into account the different kind of organisms. Different frequencies were found for organic UV filters in diverse tissues from dolphins. The same pattern was observed in fish tissues. Different canned organisms presented 4-MBC, HMS, BP-3, OMC, EHS and OC. 4-MBC and BP-3 have also been found in organisms that comes from aquaculture, while BP-3 and HMS were reported in analysed marketed organisms taken in different places. In addition, wild organisms presented OC as the most frequent compound. These results provide a broad perspective of the possible bioaccumulation process. In corals taken from different places from China, BP-3 was reported in the 100 % of the analysed samples.

Furthermore, the presence of organic UV filters in biota and seawater in polar regions (Arctic and Antarctic) confirms their global occurrence and relation to wastewater release, which highlights the risk that these contaminants poses to vulnerable ecosystems.

In general, the organic UV filters determination is focused in the compounds allowed in the country where the studied is carried out. Nevertheless, in some cases, several prohibited compounds have been found. This could be explained due to the use of PCPs brought by foreigner tourists, which demonstrates the widespread use of organic UV filters.

Declaration of Competing Interest

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

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.teac.2019.e00079.

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1.6. Compuestos seleccionados para su análisis

En esta Tesis Doctoral se han seleccionado 8 filtros UV orgánicos para su análisis, escogidos de entre los 27 permitidos en la UE, estos son: BP3, HMS, IMC, 4MBC, DTS, MBP, BMDBM y OC. Los cuales corresponden a 7 familias diferentes, teniendo una amplia variación de características fisicoquímicas.

Basado en su Log K_{ow} y solubilidad, los 8 compuestos seleccionados pueden agruparse en dos grupos. Los compuestos BP3, IMC, BMDBM, HMS y 4MBC presentan la solubilidad más alta de todos los compuestos objetivo, además de presentar un Log K_{ow} menor de 6.16, por lo cual, este grupo de compuestos es más probable encontrarlos en muestras líquidas. Por otro lado, los compuestos OC, DTS y MBP presentan una solubilidad menor ($5.1 \cdot 10^{-3}$ $g \cdot L^{-1}$), por lo que están considerados como poco solubles, asimismo presentan los Log K_{ow} más altos de todos los filtros UV orgánicos permitidos en la UE (Tabla 1). Por lo tanto, este grupo de compuestos es más probable encontrarlos en fases sólidas que en las líquidas.

Estos compuestos han sido elegidos ya que la BP3, HMS, 4MBC, BMDBM y OC han sido ampliamente detectados en varias matrices marinas (Cadena-Aizaga et al., 2020), por lo tanto se pretende establecer su presencia en el medio marino de la isla de Gran Canaria. Por otro lado, la información disponible acerca de

los otros compuestos seleccionados (DTS, IMC y MBP) es escasa, y con este trabajo se pretende arrojar nueva información sobre su presencia. Además, estos compuestos tienen una producción entre 10 y 10000 toneladas·año^{-1} dentro de la UE, según la Agencia Europea de Químicos (ECHA, por sus siglas en inglés). La concentración máxima permitida de estos compuestos está entre un 4 y 15% en formulaciones cosméticas (EC., 2009) y no han sido determinados conjuntamente en ningún estudio previo.

Por último, según la ECHA, todos estos compuestos están bajo estudio para ser incluidos como compuestos de interés por sus efectos nocivos para la fauna acuática. En este sentido, la BP3 se encuentra en la lista de evaluación de disruptores endocrinos de la ECHA. El 4MBC ha sido identificado como disruptor endocrino y ha sido incluido en la lista de sustancias candidatas extremadamente preocupantes para su autorización (SVHCs, por sus siglas en inglés) en enero del 2022. Los compuestos BMDBM y OC han sido aceptados en la lista de compuestos persistentes, bioacumulables y tóxicos (PBT, por sus siglas en inglés) para ser evaluados. Además, los compuestos BP3, BMDBM y OC están incluidos en la lista del plan de acción móvil comunitario, donde se evalúa su potencial de ser persistentes (o muy persistentes), bioacumulables (o muy bioacumulable) y tóxicos. Por lo que la presente Tesis Doctoral aporta información nueva y relevante en esta línea.

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CAPÍTULO 2. OBJETIVOS

Como se ha mostrado en el Capítulo 1, la presencia y distribución de los filtros UV orgánicos y la problemática ambiental que pueden causar, despiertan un gran interés. Debido a ello es necesario caracterizar su distribución en los diferentes compartimentos ambientales, puesto que conocer su distribución y procedencia puede ayudar a la creación de futuras estrategias de prevención de la contaminación y de remediación ambiental. Por consiguiente, se hace necesario contar con metodologías analíticas sensibles y selectivas que permitan su determinación en los diferentes compartimentos medioambientales.

De acuerdo con lo dicho anteriormente, el objetivo de esta Tesis es determinar la presencia de ocho filtros UV orgánicos usado ampliamente en productos de cuidado personal en el medio marino de la isla de Gran Canaria. Para ello, se estudiarán diferentes matrices marinas (agua de mar, algas y organismos) en diferentes playas de Gran Canaria, así como como las aguas residuales de diferentes EDAR. Obteniéndose con esto una primera aproximación de la entrada directa e indirecta de estos contaminantes a este entorno. Con el establecimiento de la presencia de estos contaminantes en las diferentes matrices marinas, se puede llevar a cabo una primera evaluación de los focos de contaminación más probables e identificar el impacto de las actividades antropogénicas en términos de contaminación por estos compuestos en las diferentes áreas estudiadas.

Por esta razón, para llevar a cabo este objetivo, se ha realizado una aproximación al estado actual del tema, con el fin de conocer los estudios previo sobre este tema. Como se pudo comprobar en este primer trabajo las concentraciones reportadas son a niveles traza. Por lo tanto, se hace necesario el desarrollo y validación de metodologías analíticas capaces de extraer y detectar la mezcla de compuestos seleccionados a bajos niveles de concentración, en complejas muestras marinas, arrojando nuevo conocimiento sobre este tema. Con el desarrollo de estas metodologías de extracción y determinación, se puede conocer y

establecer la presencia de estos contaminantes en los distintos compartimentos ambientales.

Posteriormente, para poder establecer las posibles relaciones entre las distintas matrices del medio marino, se establecerá la presencia de estos contaminantes en el agua de mar, así como en aguas residuales, para conocer la posible entrada directa e indirecta de estos compuestos hacia este entorno. Y posteriormente se establecerá su presencia en macroalgas y organismos. Con la información en macroalgas, se pretende conocer la posible acumulación de estos contaminantes desde su entorno (agua de mar). Por último, y con el objetivo de conocer la posible acumulación y biomagnificación de estos compuestos desde su entorno y desde su dieta, se analizarán los organismos consumidores primarios marinos presentes en esas mismas playas. Con esto se obtiene una visión más amplia de la magnitud de la problemática proveniente de la contaminación antropogénica por la presencia de estos compuestos y de las posibles relaciones entre las distintas matrices, en las que podrá esbozar una posible magnificación en la cadena trófica desde los niveles inferiores hacia niveles superiores.

Así pues, el objetivo general de la presente Tesis es: evaluar la presencia de ocho filtros UV orgánicos en las playas de la isla de

Gran Canaria. Los compuestos han sido escogidos por su alto uso en productos de cuidado personal, los cuales son:

Benzofenona-3 (BP3), homosalato (HMS), p-metoxicinamato de isoamilo (IMC), alcanfor 4-metilbencilideno (4MBC), drometrizol trisiloxano (DTS), metileno bis-benzotriazolil tetrametilbutilfenol (MBP), butil metoxidibenzoilmetano (BMDBM) y octocrileno (OC).

Teniendo en cuenta el objetivo principal, los objetivos específicos de la presente Tesis son:

I. Desarrollar y validar metodologías analíticas para la apropiada determinación de los filtros UV orgánicos en distintas matrices marina, las cuales son; agua de mar, algas y organismos
    a. Establecer las condiciones óptimas para la determinación de los analitos de interés mediante la cromatografía líquida de ultra resolución acoplada a espectrometría de masas en tándem (UHPL-MS/MS).
    b. Desarrollar y validar un método de extracción adecuado para la extracción de los analitos objetivo tanto desde agua de mar como desde aguas residuales, usando la técnica de extracción en fase sólida (SPE, por sus siglas en inglés)

c. Optimizar e implementar un método de extracción de los filtros UV orgánicos seleccionados desde muestras de macrofitas marinas usando la técnica de extracción asistida por microondas (MAE, por sus siglas en inglés)
d. Desarrollar y validar un proceso de extracción para los analitos objetivo desde muestras de organismos marinos consumidores primarios, usando la técnica MAE

II. Establecer la presencia de estos compuestos en las matrices marinas seleccionadas en tres playas de la isla de Gran Canaria: la playa de Las Canteras, la playa de Arinaga y Playa del Inglés. Además de establecer la presencia de estos contaminantes en aguas residuales de tres estaciones depuradoras de aguas residuales (EDAR) de Gran Canaria.

e. Llevar a cabo un muestreo en las tres playas y tres EDAR seleccionadas para determinar la presencia de filtros UV orgánicos, usando el método desarrollado
f. Evaluar el posible riesgo ambiental resultante de la entrada de estos contaminantes en el medio marino
g. Identificar posibles patrones estacionales en las playas a causa de las diferentes presiones turísticas

III. Establecer la presencia los filtros UV orgánicos seleccionados en organismos marinos (macrofitas y consumidores primarios), establecer la posible relaciones entre ellos y evaluar el impacto ambiental en estos organismos debido a su relevancia ecológica.

h. Aplicar el método de extracción desarrollado a muestras de macrofitas marinas provenientes de las mismas playas antes mencionadas
i. Establecer la posible transferencia de los analitos de interés desde el agua de mar hacia las macrofitas
j. Determinar la presencia de los compuestos objetivo en organismos marinos consumidores primarios procedentes de las mismas playas, usando el método desarrollado para ello
k. Evaluar la posible transferencia de los contaminantes elegidos desde el agua de mar hacia los organismos consumidores primarios
l. Estimar la posible biomagnificación desde el alimento (macrofitas) hacia los organismos consumidores primarios

CAPÍTULO 3.
PARTE EXPERIMENTAL Y RESULTADOS

El creciente uso de compuestos de cuidado personal, en particular de aquellos que contienen filtros UV orgánicos, ha traído como consecuencia un significativo aumento de su introducción en el medio acuático, bien por entrada directa, por actividades recreativas acuáticas, o bien por entrada indirecta, a través de aguas residuales. Existe poca información de los efectos adversos que la exposición a estos compuestos puede causar en organismos vivos.

Por ellos, es fundamental determinar la presencia y destino de estos contaminantes en el medio acuático, en muestras de agua de mar y aguas residuales, y evaluar el impacto antropogénico que

la entrada de estos contaminantes ejerce sobre diferentes organismos en las áreas estudiadas.

En este capítulo se presentarán los resultados de los diferentes trabajos experimentales incluidos en la presente Tesis Doctoral, donde se abordará su presencia y distribución en muestras de aguas residuales y costeras, y posteriormente nos centraremos también en su presencia y efecto en biota marina. Además, se discute el efecto sobre la contaminación por estos compuestos en macrofitas marinas (algas y fanerógamas) así como en consumidores primarios marinos.

Se presentan también las metodologías analíticas que han sido desarrolladas para el análisis de filtros UV orgánicos seleccionados, en las diferentes matrices consideradas. Estas metodologías de análisis están basadas en la cromatografía liquida de ultra resolución con detección por espectrometría de masas en tándem (UHPLC-MS/MS), para su separación y detección, respectivamente. La extracción se llevó a cabo usando las técnicas de extracción en fase sólida (SPE, por sus siglas en inglés) para las muestras líquidas y la extracción asistida por microondas (MAE, por sus siglas en inglés) para las muestras sólidas.

La Figura 7 esquematiza el procedimiento experimental llevado a cabo para las diferentes muestras en las que se han analizado los filtros UV orgánicos seleccionados.

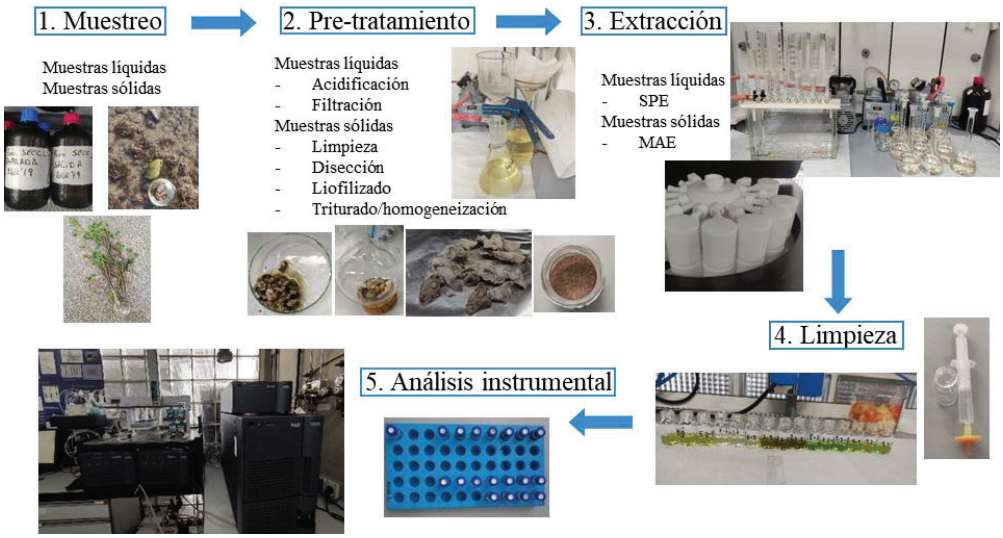

Figura 7: Diagrama del proceso de análisis de las muestras ambientales analizadas en la presente Tesis

Los parámetros de detección por MS/MS de los ocho filtros UV orgánicos seleccionados están recogidos en la Tabla 2. Los cuales son: benzofenona-3 (BP3), homosalato (HMS), p-metoxicinamato de isoamilo (IMC), alcanfor 4-metilbencilideno (4MBC), drometrizol trisiloxano (DTS), metileno bis-benzotriazolil tetrametilbutilfenol (MBP), butil metoxidibenzoilmetano (BMDBM) y octocrileno (OC).

Tabla 2: Parámetros de MS/MS empleado

Compuesto	Ion precursor (m/z)	Voltaje de cono (V)	Ion de cuantificación (m/z)	Potencial de colisión (V)	Ion de confirmación (m/z)	Potencial de colisión (V)
4MBC	255.4	25	105.0	27	171.0	19
BP3	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	332.0	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
MBP	659.8	40	336.2	25	224.2	35

Para la separación cromatográfica se empleó un método en gradiente, utilizando dos fases móviles, agua (A) y metanol (B) a un flujo de 0.3 $mL \cdot min^{-1}$. El gradiente empleado consistió en comenzar con 25% de A y 75% de B, el cual es mantenido durante 3 minutos. Luego la fase B es aumentada a un 100% durante 2 minutos y mantenida por 1 minuto. Por último, la fase A es aumentada a un 25% durante 1 y se mantiene esta composición por otro minuto antes de la siguiente inyección. El resultado de la separación cromatográfica está presentada en la Figura 8. En este método se obtuvieron bajos límites de detección y altas reproducibilidades, de acuerdo con la sensibilidad y selectividad necesaria para el análisis de muestras ambientales.

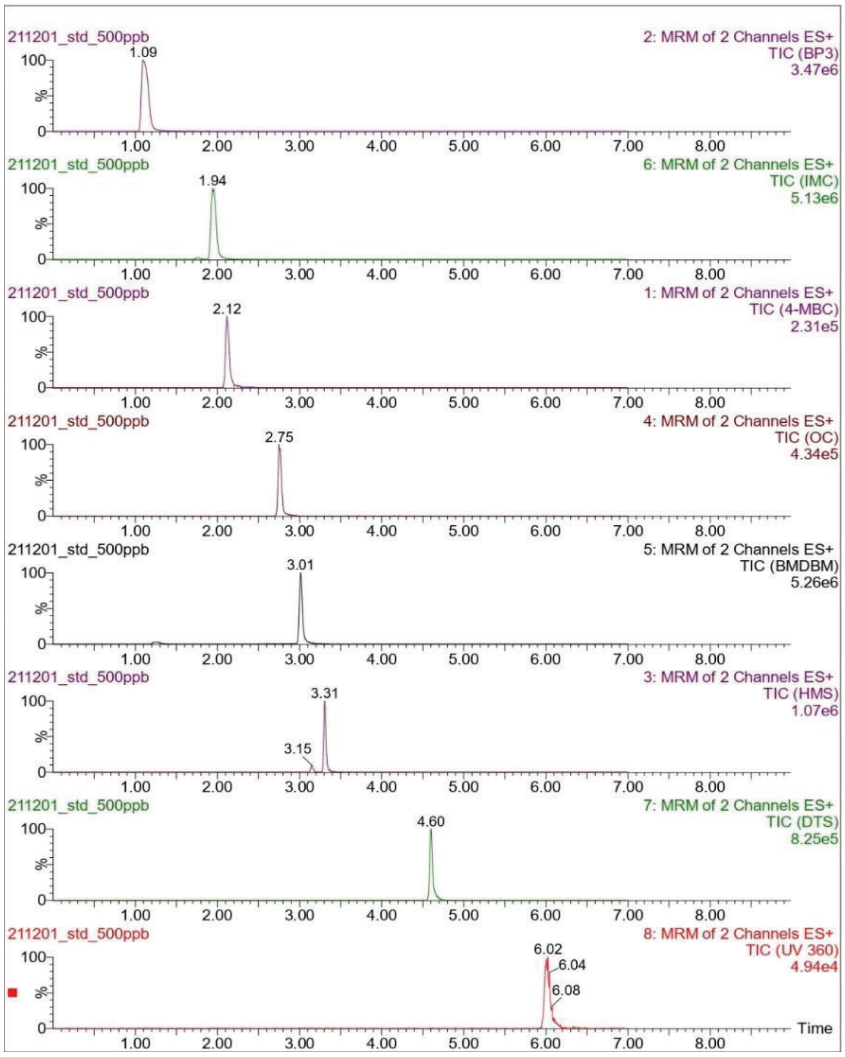

Figura 8: Separación cromatográfica de los ocho filtros UV orgánicos estudiados

3.1. Análisis de muestras líquidas

Como ya se ha comentado previamente, la presencia de filtros UV orgánicos en el medio acuático es de gran preocupación por el impacto que pueden ocasionar. Por ello, para comprender

mejor su destino en el medio ambiente, es necesario obtener datos representativos que faciliten una mejor comprensión de sus tendencias espaciales y temporales. Así, el desarrollo de métodos analíticos que permitan una determinación segura y confiables son necesarios.

En la presente Tesis Doctoral se han analizados muestras líquidas que incluyen agua de mar y aguas residuales. Se han desarrollado nuevos métodos analíticos para identificar los compuestos seleccionados en estos compartimentos ambientales, lo que permite identificarlos, cuantificarlos y evaluar el nivel de contaminación ambiental. Los métodos analíticos desarrollados muestran una buena reproducibilidad y repetibilidad, y bajos límites de detección necesarios en muestras ambientales.

3.1.1. Presencia y riesgo ambiental de filtros UV orgánicos en agua de mar y aguas residuales de la isla de Gran Canaria (Islas Canarias, España)

Los filtros UV orgánicos son mayoritariamente usados en productos de cuidado personal, aunque también son usados en productos industriales. Estos compuestos entran en el ambiente marino directamente por las actividades que se desarrollan en este medio o indirectamente por descargas de las aguas residuales.

En este estudio se analizó la presencia de 8 filtros UV orgánicos ampliamente utilizados en agua de mar de tres playas de la isla de Gran Canaria (España) y en tres estaciones depuradoras de aguas residuales (EDAR), tanto en muestras de influentes como de efluentes. Las tres playas son; playa de Las Canteras, playa de Arinaga y Playa del Inglés.

La playa de Las Canteras está situada en la parte noreste de la isla de Gran Canaria, su característica principal es la presencia de una barra paralela a su costa, la cual crea una zona de calma durante la bajamar. Esta playa es utilizada principalmente por ciudadanos locales y moderadamente por turismo nacional y extranjero todo el año, donde la máxima actividad se da en verano.

Por otro lado, la playa de Arinaga está situada al sureste de la isla de Gran Canaria y se caracteriza por la intensa acción de los vientos Alisios y la Corriente de Canarias, la cuales favorecen la renovación del agua. Esta es una playa abierta usada principalmente por ciudadanos locales y apenas visitada por turistas.

Playa del Inglés se encuentra al sur de la isla de Gran Canaria, la cual se caracteriza por la presencia de barreras artificiales perpendiculares a su costa y la suave acción de los vientos Alisios y la Corriente de Canarias. Esta es una playa abierta utilizada durante todo el año por numerosos turistas internacionales, esencialmente del norte de Europa, según la Agencia de Turismo

de Gran Canaria, así como, por los turistas nacionales y locales con su máxima actividad en verano.

Puesto que las aguas residuales y el agua de mar tienen una complejidad diferente, es necesario el desarrollo de una metodología sensible y selectiva que permita la extracción y preconcentración de los analitos de interés en cada matriz y, además, elimine la mayor cantidad posible de interferencias. En este sentido, la extracción de los compuestos se ha llevado a cabo mediante la extracción en fase sólida (SPE, por sus siglas en inglés) seguida por su determinación por cromatografía líquida de ultra resolución acoplada a la espectrometría de masas en tándem (UHPLC-MS/MS, por sus siglas en inglés).

La SPE es una de las técnicas de extracción más aplicadas ya que integra la extracción y la preconcentración en un solo paso. En este procedimiento, es necesario optimizar aquellos parámetros que afectan al proceso de extracción según la naturaleza y características fisicoquímicas de los analitos, así como el tipo de muestra, para obtener la mayor eficacia en la extracción. Estas variables son; el tipo de polímero (cartucho), el pH de la muestra, el volumen y la fuerza iónica de la muestra, así como el volumen y tipo de extractante (metanol, MeOH; acetonitrilo, ACN).

En primer lugar, se probaron los diferentes adsorbentes empleados en SPE, para cada tipo de muestra. Una vez

seleccionado el cartucho, se optimizaron los parámetros de extracción y desorción mediante un diseño factorial que permite determinar no solo la influencia de cada variable sino también las relaciones entre ellas. Como resultado se obtuvieron dos procedimientos de SPE, con un cartucho C18, pero diferentes condiciones experimentales para agua de mar y aguas residuales. En la Tabla 3 se muestran las condiciones óptimas para la extracción de filtros UV orgánicos en agua de mar y aguas residuales.

Tabla 3: Condiciones de extracción para agua de mar y aguas residuales.

Tipo de muestra	Volumen de muestra (mL)	pH de la muestra	Tipo de extractante	Volumen del extractante (mL)
Agua de mar	700	3	MeOH:ACN (1:1, *v,v*)	5
Aguas residuales	250	7	MeOH	5

Una vez optimizados los métodos, se evaluó la linealidad, recuperación, precisión, límites de detección y límites de cuantificación para cada tipo de agua para una mezcla de soluciones estándar de los analitos. En ambos tipos de muestras se obtuvo una linealidad satisfactoria (>0.99) en el rango de concentración de concentraciones estudiado, entre 0.025 $\mu g \cdot L^{-1}$ – 250 $\mu g \cdot L^{-1}$ en el caso del agua de mar y entre 0.05 $\mu g \cdot L^{-1}$ – 250 $\mu g \cdot L^{-1}$ en el caso de

las aguas residuales. Finalmente, se obtuvieron límites de detección entre 10.8 $ng \cdot L^{-1}$ – 36.4 $ng \cdot L^{-1}$ en agua de mar y entre 24.6 $ng \cdot L^{-1}$ – 555 $ng \cdot L^{-1}$ en aguas residuales.

Se comprobó la eficacia de extracción del método que varía entre 43.8 % – 100 % para el agua de mar y 19.3 % – 98.5 % para las aguas residuales, los cuales son adecuados para el análisis de muestras ambientales. Así mismo, se comprobó la reproducibilidad y repetibilidad del método, que varió de 0.02 a 13.9 % para agua de mar, y de 0.50 a 13.9 % para aguas residuales.

Los métodos desarrollados se usaron para la determinación de los analitos de interés en muestras ambientales reales procedentes de las tres playas y tres EDAR seleccionadas de la isla de Gran Canaria. Las muestras de aguas residuales fueron tomadas en la entrada, salida del tratamiento secundario y salida del tratamiento terciario en caso de tenerlo. Así mismo, se tomaron muestras de agua de mar a 2 metros de la costa en el centro de la zona de baño y aproximadamente a 50 centímetros por debajo de la superficie del agua en las tres playas. Se realizó un monitoreo durante 6 meses en ambos casos. Todas las muestras fueron tomadas en botellas de cristal ámbar para evitar la fotodegradación y fueron acidificadas para inhibir la actividad microbiana.

Como resultado de estos estudios, se determinaron todos los analitos de interés tanto en las muestras de agua de mar como en las de aguas residuales.

En cuanto a las muestras de agua de mar, todos los compuestos estudiados fueron detectados con distintas frecuencias en las diferentes playas. La BP3 fue el compuesto más frecuentemente encontrado, se detectó en el 83% de las muestras analizadas, sin embargo, el compuesto que presentó mayor concentración fue el OC (172 $\mu g \cdot L^{-1}$). Las diferencias entre el tipo de filtro UV orgánico encontrado y las concentraciones observadas parecen indicar que la acumulación en el agua de mar depende no solo del tipo de usuario, sino también de la tasa de remoción de agua, la estación del año y las características geomorfológicas del lugar de muestreo.

Por otro lado, en las muestras de aguas residuales también se detectaron todos los compuestos objetivos. La BP3 y el BMDBM se detectaron en todas las muestras tanto de influentes como de efluentes del tratamiento secundario durante todo el período de muestreo. Para el BMDBM se obtuvo el rango de eficiencia de eliminación más amplio (83 – 99 %), seguido de OC (50 – 100 %). En general se observó que las eficiencias de eliminación de los distintos tratamientos de las aguas residuales fueron superiores al 50 % para la mayoría de los compuestos. Como algunos

compuestos no se eliminan por completo durante el tratamiento de aguas residuales, esto implica que son liberados continuamente al medio ambiente.

Por último, se evaluó el cociente de riesgo asociado con la presencia de estos analitos en agua de mar para los organismos expuestos a ellos. Los cocientes de riesgo asociados a las concentraciones medidas mostraron un riesgo potencial para las especies marinas en todos los lugares donde se encontró OC (peligro ambiental superior a 1), mientras que BMDBM presentó un peligro medio-alto y BP3 mostró valores muy variables.

Este trabajo fue publicado en la revista *Environmental Pollution* en el año 2022, ésta es una revista internacional dedicada a publicar revisiones bibliográficas y trabajos experimentales en el campo de la contaminación ambiental, sus efectos en ecosistemas y en la salud humana. A pesar de que las métricas del año 2022 aún no están disponibles, esta revista se ha encontrado en el primer cuartil del área *Environmental Sciences* durante los últimos 5 años, con un factor de impacto entre 5.291 y 9.988 según *Journal Citation Reports*.

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Occurrence and environmental hazard of organic UV filters in seawater and wastewater from Gran Canaria Island (Canary Islands, Spain)☆

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ABSTRACT

Organic ultraviolet (UV) filters are used in personal care products, but they are also added to industrial products and are constantly released to the environment. This study analyses the occurrence of 8 widely used organic UV filters in seawater from three beaches on the Gran Canaria Island (Spain) and in three wastewater treatment plants (WWTPs) by taking samples from influents and effluents. It also discusses the target compounds' post-treatment removal efficiencies. Sampling was carried out for 6 months and analytes were extracted by solid phase extraction with Sep-pak C18 cartridges. They were determined by ultra-high performance liquid chromatography coupled to mass spectrometry in tandem. The potential environmental hazard associated with the found concentrations was also assessed for marine organisms.

Different target compounds were detected on the analysed beaches and in the wastewater. Benzophenone-3 (BP3) was the most recurrent compound in the seawater samples (frequency detection of 83%) and also in wastewater influents and effluents (measured in all the samples). However, the highest concentrations for seawater (172 μg L^{-1}) and influent wastewater (208 μg L^{-1}) corresponded to octocrylene, while methylene bis-benzotriazolyltetramethylbutylphenol was the compound most concentrated in secondary treatment effluent (34.0 μg L^{-1}) and BP3 in tertiary treatment effluent (8.07 μg L^{-1}). All the analysed samples showed that at least one target UV filter was present.

Regarding the removal efficiencies of these compounds in the studied WWTPs, consistent differences between the target compounds were observed in influent concentration terms, where the average removal rates were higher than 50% for most of the compounds. Conventional treatment is unable to completely remove many studied compounds, while tertiary treatment acts as an additional elimination for some of them.

An environmental hazard quotient above 1 was found for octocrylene, benzophenone-3 and 4-methylbenzylidene camphor, which indicates a potential high hazard for living species if these compounds are present.

1. Introduction

Ultraviolet (UV) filters are used to protect skin from harmful UV radiation effects, and they are added to different personal care products (PCPs) and industrial goods. However, some UV filters cause undesired dermatological effects, such us dermatitis or allergies (Giokas et al., 2007). The maximum concentration of each UV filter is controlled in the European Union by Regulation no. 1223/2009 (EC, 2009), and ranges between 4% and 15% for organic UV filters and is approximately 25% for inorganic UV filters. Combinations of filters are used to gain protection for both solar radiation regions: UVA and UVB. Eleven families of organic UV filters have been established according to their main physico-chemical properties (Ramos et al., 2015). Given their extensive use, hundreds of tonnes of organic UV filters are released to the environment annually (Danovaro et al., 2008), and means that they are considered a new kind of environmental pollutant (Emmanouil et al., 2019). In addition, most exhibit some priority organic pollutant characteristics, such as high octanol-water coefficients (Log K_{ow} >3) and stability against biotic degradation (Vila et al., 2017).

Organic UV filters follow two main pathways to reach the aquatic environment: i) by being directly washed off from skin and clothing during recreational activities; ii) by being indirectly released in treated

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wastewater from domestic use (showering, washing, etc.), industrial discharge and runoff (Molins-Delgado et al., 2014). UV filters are detected worldwide in several matrices: fresh (Ramos et al., 2015; Sereshti et al., 2020; Nouri et al., 2020) and marine environments (Cadena-Aizaga et al., 2020), sludges (Ramos et al., 2016) and even tap water (Díaz-Cruz et al., 2012). The study performed by Downs et al. (2016) reports concentrations in seawater of up to mg·L^{-1} level, in which the most obvious input is the direct one. Other inputs to the marine environment are presented in Fig. 1. In recent years, organic UV filters have become an increasing concern because they show a tendency to bioaccumulate at different trophic levels (Cadena-Aizaga et al., 2020). These compounds have already been reported in marine biota (Ramos et al., 2015), and even in humans (Fivenson et al., 2020). Some organic UV filters like 4-methylbenzylidene camphor (4MBC) caused impaired reproduction, increased mortality in benthic organisms (Schmitt et al., 2008), and they produce coral bleaching (Danovaro et al., 2008) and induce malformation and mortality in early fish stages (Araújo et al., 2018). Benzophenone-3 (BP3) and 4MBC have a reported similar toxicity to metals to marine organisms (Paredes et al., 2014) so it is important to understand their fate and behaviour in the environment.

Different methodologies for extracting and determining organic UV filters from environmental samples have been used (Ramos et al., 2015; Cadena-Aizaga et al., 2020). Solid phase extraction (SPE) technique is one of the most widely applied techniques as it integrates both preconcentration and extraction in one step (Gago-Ferrero et al., 2013a). Organic UV filters analyses are performed by gas (GC) or liquid chromatography (LC) coupled to mass spectrometry detectors (MS). Often LC coupled to MS detection in tandem (MS/MS) is the best option because it yields high sensitivity for a wide range of compounds (Ramos et al., 2015; Cadena-Aizaga et al., 2020). Moreover, some organic UV filters cannot be determined by GC for their low volatility and thermal stability (Sánchez-Brunete et al., 2011).

The Gran Canaria Island is part of Canary archipelago (Spain) located in the Atlantic Ocean. This is the perfect scenery to carry out environmental studies about these compounds because tourism (both national and international (de Turismo, 2021)) is one of the mainstays of its economy and its beaches are used almost all year long. Therefore, its coast is subjected to the intense and continuous direct input of organic UV filters. However, only a few works (García-Guerra et al., 2016; Sánchez Rodríguez et al., 2015; Montesdeoca-Esponda et al., 2012; Montesdeoca-Esponda et al., 2013) have been performed on their occurrence in and impact on the aquatic systems in this geographical area, and have focused mostly on benzotriazole UV stabilisers.

Hence the aim of this work was to study the presence of eight organic UV filters in seawater and wastewater samples taken from the Gran Canaria Island. Three beaches and three WWTPs were monitored for 6 months (May–October 2019) to evaluate spatio-temporal variation and the efficiency of the elimination achieved with the sewage treatments for each target compound was discussed. Finally, the environmental hazard associated with the found concentrations was assessed for different aquatic organisms.

2. Materials and methods

2.1. Reagents and materials

Eight analytical-grade (purity ≥99%) organic UV filters (Table 1), which ranges of concentration are shown in Table S1, namely homosalate (HMS), 4-MBC, BP3, drometrizole trisiloxane (DTS), octocrylene (OC), butyl methoxydibenzoylmethane (BMDBM), isoamyl *p*-methoxicinnamate (IMC), and methylene bis-benzotriazolyltetramethyl butylphenol (MBP) were purchased from Sigma-Aldrich (Madrid, Spain). Methanol (MeOH), acetone, acetonitrile (ACN), water and formic acid (LC-MS grade) were supplied by Panreac Química (Barcelona, Spain). Stock solution (250 mg L^{-1}) was prepared in acetone and stored in amber glass bottles in a freezer until used. Working solutions were prepared in MeOH daily. Membrane filters (0.22 and 0.45 μm) were purchased from Millipore (Cork, Ireland). For the SPE technique, three cartridges were tested: 200 mg Oasis HLB; 500 mg Sep-pak C18 from Waters (Madrid, Spain); 500 mg Strata-X from Phenomenex (Madrid, Spain).

2.2. Sample collection

Three different beaches were selected for their particular geomorphological characteristics, their level of tourist pressure and type of users: Las Canteras, Arinaga and Playa del Inglés. Sampling lasted 6 months (May–October 2019) at low tide around the noon; these months

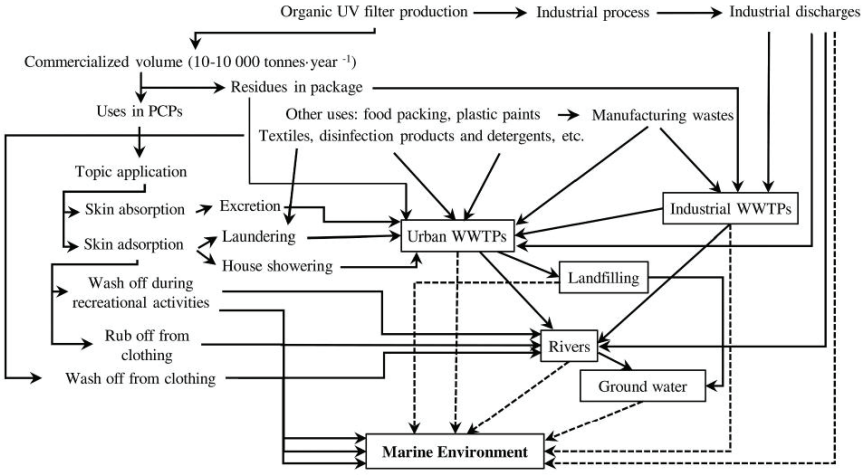

Fig. 1. Organic UV filters inputs to the marine environment. Dotted line refers to indirect inputs.

Table 1
Main characteristics and structure of the eight organic UV filters subjected to study.

Family	INCI name[a]/Other common names	Abbreviations	Structure	CAS number	Molecular formula	Molecular weight	Log K_{ow}	pKa	Solubility ($g\,L^{-1}$)[g]	EU production[h]
Benzophenones	Benzophenone-3/Oxybenzone	BP3/B23/HMB/OBZ		131-57-7	$C_{14}H_{12}O_3$	228,24	3.79[b]	7.56[d]	0.21	LPV
Salicylates	Homosalate	HMS/HS		118-56-9	$C_{16}H_{22}O_3$	262,34	6.16[c]	8.09[e]	0.02	HPV
Cinnamates	Isoamyl *p*-methoxycinnamate/Amiloxate	IMC/IAMC		71 617-10-2	$C_{15}H_{20}O_3$	248.32	4.33[c]	–	0.06	LPV
Camphor derivatives	4-methylbenzylidene camphor/Enzacumene	4MBC/MBC		36 861-47-9/ 38 102-62-4	$C_{18}H_{22}O$	254,37	4.95[c]	–	5.1×10^{-3}	LPV
Benzotriazoles	Drometrizole trisiloxane	DTS		155 633-54-8	$C_{24}H_{39}N_3O_3Si_3$	501,84	10.82[d]	9.72[f]	1.3×10^{-5}	–
	Methylene bis-benzotriazolyltetramethylbutylphenol/ Bisoctrizole	MBP/UV 360/MBBT/ MBT		103 597-45-1	$C_{41}H_{50}N_6O_2$	658,87	12.46[d]	7.56[f]	3×10^{-9}	LPV
Dybenzoyl methane derivatives	Butyl methoxydibenzoylmethane/Avobenzone	BMDBM/BDM/ BMDM/BMBM/AVO/ AVB		70 356-09-1	$C_{20}H_{22}O_3$	310,39	4.51[c]	9.74[e]	0.037	HPV
Crylenes	Octocrylene	OC/OCR/OCT		6197-30-4	$C_{24}H_{27}NO_2$	361,48	6.88[c]	–	2×10^{-4}	HPV

[a] INCI International Nomenclature for Cosmetic Ingredients.
[b] Experimental value from Syracuse Research Corporation database.
[c] Estimated values from Syracuse Research Corporation database.
[d] Calculated by use of Estimation Program Interface (EPI) suite v4.11 (2012).
[e] Software calculated value, from SciFinder Scholar Database 2006.
[f] Values obtained from Chemizalize website.
[g] From Díaz-cruz et al. (2012) in water at 25 °C.
[h] From European Chemicals Agency (ECHA), low production volume (LPV) between 10 and over 100 tonnes $year^{-1}$ and high production volume (HPV) between 1000 and 10 000 tonnes $year^{-1}$ of chemicals produced or imported in the European economic area.

were selected to find possible seasonal variation during pre-summer (May–June), summer (July–August) and post-summer (September–October) periods. The seawater samples were collected in 2-L amber glass bottles using gloves, at 2 m from the coast in the middle of the bathing zone and approximately at 50 cm below the water surface (Fagervold et al., 2019).

Las Canteras beach is located on the northeast coast of the Gran Canaria Island (sample location 1, SL1, Table S2). It is an urban beach used mainly by locals and moderately by international tourists approximately all year long (de Turismo, 2021), where the most intense tourism takes place in the summer. The main characteristic of this beach is the presence of a natural barrier running in parallel to the coast, which leads to a lower water renovation rate at low tide than at high tide given the almost null wave action (Perez-Torrado and Mangas, 1994). For this reason, local fauna might be affected by pollutants' long residence time.

The Arinaga beach is located on the southeast coast of the Gran Canaria Island (SL2, Table S2). It is principally used by locals and barely used by international tourists (de Turismo, 2021). It is an open beach with intense wind and a strong swell influence due to the north-northeast effect of Trade winds and the Canary Current (Alonso et al., 2001), which make water renewal easy.

The Playa del Inglés beach is located on the south coast of the Gran Canaria Island (SL3, Table S2). It is an open beach characterised by mass international tourism formed essentially by northern Europeans according to the Tourism Agency of Gran Canaria (de Turismo, 2021). These tourists often use sunscreens with a high sun protection factor. On this beach, trade winds and the Canary Current effect are less pronounced (Alonso et al., 2001), and this creates a peaceful zone with light swells. This beach has artificial barriers. SL3 is used almost all year, and more intensely by international tourists than locals in winter, but more intensely by national tourists than international ones in summer. Moreover, this beach could be influenced by treated sewage discharges (de Canarias, 2021).

The wastewater samples were taken from the influents and effluents in three different WWTPs on the Gran Canaria Island, namely WWTP1, WWTP2 and WWTP3 (Table 2), located in the Las Palmas city, in the Arinaga village and in the San Bartolomé de Tirajana municipality, respectively. Facilities comprise primary and secondary treatments, with the latter based on conventional activated sludge. The tertiary treatment, performed by microfiltration, is only available in WWTP2. Samples were collected by the WWTP staff at the same hour every month in 2-L amber glass bottles. More detailed information on the WWTPs treatments and characteristics is available in Table 2.

2.3. Pre-treatment and extraction procedures

Seawater and wastewater samples were acidified with formic acid to pH = 3 and pH = 2 respectively to inhibit microbial activity and were stored at fridge in amber glass bottles until their analysis in the maximum period of one month. Seawater samples were filtered through 0.22 μm membrane filters and wastewater samples by 0.45 μm cellulose filters.

Sample extraction was done by the SPE procedure. C18 cartridges were conditioned before each extraction with 5 mL of MeOH followed by 5 mL of Milli-Q water. For seawater, 700 mL of seawater at pH 3 were passed through a cartridge, while 250 mL were used for wastewater at pH 7. A cleaning step (salt or impurity elimination) was carried out with 5 mL of Milli-Q water. Then cartridges were dried in a vacuum for 1 min and the retained analytes were eluted with 5 mL of MeOH:ACN (1:1, *v/v*) for seawater and 5 mL of MeOH for wastewater.

2.4. Instrumental analysis

The selected organic UV filters were determined in an ACQUITY UHPLC system equipped with a binary solvent manager, a thermostated autosampler, a BEH C18 column (50 × 2.1 mm, 1.7 μm particle size) and a tandem triple quadrupole mass spectrometer detector (MS/MS) with electrospray ionisation (ESI). All the components were controlled by the MassLynx Mass Spectrometry software (Waters Chromatography, Barcelona, Spain). The ESI parameters were fixed as follows: capillary voltage at 4 kV, 15 V cone voltage, 120 °C source temperature, 450 °C desolvation temperature and 500 L h^{-1} desolvation gas at. Nitrogen and argon gases were used for desolvation and collision, respectively. Detailed MS/MS conditions are found in the Supplementary Material (Table S3).

The mobile phase consists in MeOH (A) and water (B) of LC-MS grade with 0.1% (*v/v*) formic acid, each at a flow rate of 0.3 mL min^{-1}. To separate analytes, the following gradient was employed; starting with 25% A: 75% B, which was left for 3 min and then lowered to 0% of A in 2 min and held for 1 min. Finally, A was increased to 25% for 1 min and held for 1 min for the next injection. The injected extract volume was 10 μL.

2.5. Environmental hazard

Toxicological data for the target compounds in marine species are necessary for an environmental hazard quantification. Nevertheless, toxic effects studies are not available for several organic UV filters. All the existing harmful data on target compounds for marine organisms belonging to different trophic levels are shown in Table 3. A marine gram-negative bioluminescent bacterium (*Photobacterium phosphoreum*), which usually lives in symbiosis with marine organisms, has been studied for the toxic effect of BP3 (Liu et al., 2015). Two microalgae (*Isochrysis galbana* and *Skeletonema pseudocostatum*) of the marine plankton have been used to test the toxicity effects of 4MBC, BP3 and OC (Paredes et al., 2014; Giraldo et al., 2017; Petersen et al., 2014). A copepod (crustacean) was exposed to 4MBC for four generations, which reports toxicity in development and reproductive (Chen et al., 2018). Two bivalve molluscs, a mussel (*Mytilus galloprovincialis*) and a clam (*Ruditapes philippinarum*), have also been investigated to analyse the effects of OC, 4MBC and BP3, and 4MBC, respectively (Giraldo et al., 2017; Santonocito et al., 2020). One echinoderm, the sea urchin *Paracentrotus lividus*, have been exposed to BP3, 4MBC and OC to know its toxic effects on larval stages (Giraldo et al., 2017; Petersen et al., 2014). The carnivore arthropod crustacean *Siriella armata* has also been exposed to 4MBC and BP3 (Paredes et al., 2014). Finally, fertilised eggs of a flatfish (*Solea senegalensis*) have been exposed to 4MBC to analyse mortality, malformations, length, behaviour and biochemical markers in the larval stage (Araújo et al., 2018).

However, as compounds like BMDBM, DTS, HMS and MBP have a

Table 2
Main characteristics of studied WWTPs.

WWTPs	Treatments[a]		Inhabitants equivalents[b]	Secondary effluent characteristics[a]		
	Secondary	Tertiary		Discharge level (m)	Emissary length (m)	Emissary flow ($m^3 \cdot h^{-1}$)
WWTP1	Activated sludge	–	200 749	- 41	2090	540
WWTP2	Activated sludge	Microfiltration	134 000	- 27	930	355
WWTP3	Activated sludge	–	103 315	- 19	350	147

[a] Data obtained from Gobierno de Canarias (https://www.pilotajelitoralcanario.es).
[b] Data obtained from iagua (https://www.iagua.es).

Table 3
Normalized target organic UV filters concentrations measured in the three studied WWTPs (μg·d^{-1}·1000 inhabitant^{-1}).

Date	UV filters	WWTP 1		WWTP 2			WWTP 3	
		Influent	Secondary	Influent	Secondary	Tertiary	Influent	Secondary
May-19	4MBC	311 ± 16.9	76.5 ± 5.40	236 ± 4.88	96.8 ± 1.77	49.2 ± 5.36	596 ± 77.8	44.4 ± 4.16
	BP3	2582 ± 241	474 ± 14.6	5266 ± 354	791 ± 90.4	565 ± 4.41	8572 ± 535	263 ± 5.77
	HMS	nd	nd	437 ± 31.5	37.2 ± 0.72	20.2 ± 2.41	2629 ± 124	nd
	DTS	315 ± 44.7	10.1 ± 1.33	110 ± 15.1	48.1 ± 1.68	37.2 ± 2.82	205 ± 24.7	nd
	OC	217 ± 27.6	nd	2396 ± 138	95.7 ± 7.72	nd	12 327 ± 461	84.7 ± 10.5
	BMDBM	4804 ± 413	140 ± 10.3	2349 ± 172	410 ± 1.10	nd	7423 ± 296	125 ± 3.25
	IMC	53.7 ± 8.37	38.2 ± 3.78	97.5 ± 2.48	74.3 ± 11.3	38.0 ± 2.56	92.0 ± 6.27	11.4 ± 0.94
	MBP	nd	nd	nd	nd	nd	1293 ± 80.0	nd
June-19	4MBC	nd	nd	99.5 ± 14.4	29.7 ± 4.48	18.2 ± 1.10	623 ± 65.6	42.8 ± 5.57
	BP3	4490 ± 654	338 ± 27.0	3435 ± 467	791 ± 50.4	821 ± 58.0	6575 ± 250	259 ± 24.0
	HMS	241 ± 28.2	nd	28.3 ± 3.62	nd	138 ± 3.27	1822 ± 215	nd
	DTS	213 ± 27.1	25.2 ± 2.65	22.4 ± 2.21	15.1 ± 1.72	nd	124 ± 18.2	nd
	OC	1184 ± 109	118 ± 16.0	634 ± 38.2	148 ± 22.4	144 ± 16.4	9335 ± 706	72.4 ± 8.77
	BMDBM	3687 ± 296	216 ± 31.8	3454 ± 356	251 ± 15.5	162 ± 11.7	6371 ± 697	165 ± 24.3
	IMC	55.3 ± 8.30	26.6 ± 2.17	74.0 ± 8.11	56.5 ± 8.87	34.3 ± 3.59	96.3 ± 1.55	10.8 ± 0.59
	MBP	nd	nd	1327 ± 154	826 ± 117	nd	nd	nd
July-19	4MBC	85.0 ± 11.7	34.3 ± 4.80	239 ± 25.1	16.2 ± 0.92	155 ± 16.3	474 ± 35.8	nd
	BP3	3004 ± 209	324 ± 29.8	2786 ± 98.8	903 ± 77.1	890 ± 28.9	7838 ± 93.1	200 ± 5.24
	HMS	172 ± 24.5	nd	148 ± 18.8	98.5 ± 10.6	16.9 ± 0.18	2590 ± 74.1	nd
	DTS	104 ± 12.2	nd	177 ± 14.3	nd	139 ± 8.30	234 ± 31.6	24.0 ± 0.59
	OC	927 ± 62.0	144 ± 18.5	2984 ± 128	189 ± 11.0	35.2 ± 2.23	8877 ± 308	21.0 ± 2.30
	BMDBM	3965 ± 276	292 ± 30.1	390971.0	288 ± 33.1	233 ± 2.42	6632 ± 493	100 ± 10.5
	IMC	74.6 ± 6.39	18.5 ± 1.73	28.2 ± 1.81	31.3 ± 1.53	25.5 ± 2.87	113 ± 4.80	5.03 ± 0.80
	MBP	1847 ± 222	1091 ± 144	nd	nd	nd	1207 ± 98.2	nd
August-19	4MBC	nd	nd	317 ± 13.1	nd	nd	386 ± 44.0	43.9 ± 6.28
	BP3	3444 ± 325	294 ± 26.2	2682 ± 318	825 ± 14.2	740 ± 29.0	5882 ± 266	385 ± 26.3
	HMS	318 ± 45.7	nd	54.2 ± 6.87	216 ± 33.0	nd	1688 ± 77.6	26.1 ± 3.12
	DTS	nd	nd	147.8 ± 16.0	nd	93.4 ± 11.1	205 ± 29.2	nd
	OC	913 ± 126	88.6 ± 3.65	436 ± 32.4	217 ± 11.6	200 ± 15.0	7518 ± 675	22.9 ± 2.04
	BMDBM	4199 ± 590	132 ± 19.5	3982 ± 576	190 ± 12.1	107 ± 5.0	5319 ± 79.4	136 ± 18.2
	IMC	100 ± 8.09	19.5 ± 1.26	56.8 ± 1.22	42.6 ± 5.20	29.0 ± 0.97	123 ± 8.07	nd
	MBP	nd	nd	nd	nd	nd	1596 ± 28.6	1325 ± 51.1
September-19	4MBC	nd	nd	nd	nd	nd	454 ± 29.5	nd
	BP3	2330 ± 79.3	488 ± 27.2	2828 ± 300	479 ± 16.4	432 ± 35.5	6951 ± 307	244 ± 4.64
	HMS	nd	nd	140 ± 10.4	nd	72.5 ± 10.2	1345 ± 85.0	nd
	DTS	nd	nd	223 ± 26.7	nd	nd	36.8 ± 6.31	nd
	OC	780 ± 17.8	99.9 ± 6.60	3219 ± 489	224 ± 1.10	nd	5549 ± 119	nd
	BMDBM	3423 ± 456	173 ± 7.78	3914 ± 100	220 ± 22.1	nd	5161 ± 524	168 ± 1.87
	IMC	55.4 ± 6.71	41.5 ± 6.48	53.4 ± 8.48	41.3 ± 4.82	nd	87.4 ± 13.5	3.40 ± 0.45
	MBP	nd	nd	nd	nd	nd	2637 ± 182	2013 ± 13.3
October-19	4MBC	98.9 ± 14.9	nd	118 ± 3.89	16.4 ± 3.21	61.3 ± 0.78	349 ± 17.3	nd
	BP3	2189 ± 95.8	308 ± 17.4	2717 ± 331	504 ± 34.5	483 ± 1.68	5215 ± 316	187 ± 20.9
	HMS	133 ± 21.3	nd	87.7 ± 11.2	nd	47.1 ± 3.05	540 ± 60.0	nd
	DTS	117 ± 17.5	nd	210 ± 30.0	31.2 ± 3.58	91.7 ± 4.36	nd	nd
	OC	1120 ± 104	72.1 ± 8.72	1842 ± 139	129 ± 4.47	69.9 ± 6.12	1277 ± 151	42.9 ± 5.31
	BMDBM	4003 ± 419	83.2 ± 6.93	3632 ± 517	242 ± 19.9	nd	3021 ± 435	86.7 ± 12.1
	IMC	22.2 ± 2.89	10.4 ± 0.65	66.0 ± 2.33	21.3 ± 0.60	19.1 ± 1.46	67.6 ± 1.25	nd
	MBP	nd	nd	1641 ± 155	967 ± 17.1	215 ± 22.7	2041 ± 164	nd
Detection frequencies (%)	4MBC	50	33	83	67	67	100	50
	BP3	100	100	100	100	100	100	100
	HMS	67	0	100	50	83	100	17
	DTS	67	33	100	50	67	83	17
	OC	100	83	100	100	67	100	83
	BMDBM	100	100	100	100	50	100	100
	IMC	100	100	100	100	83	100	67
	MBP	17	17	33	33	17	83	33
Percentage of positive samples (%)		**75**	**58**	**90**	**75**	**67**	**96**	**58**

nd: not detected.

high Log K_{ow} (>4.51), they could affect aquatic organisms at lower concentrations (Sánchez Rodríguez et al., 2015). In addition, the joint effects of several additives, metabolites, and their degradation products, should be considered towards a more realistic approach to deal with the environmental hazard because a mixture of these organic UV filters is found in seawater and marine organisms (Cadena-Aizaga et al., 2020; Molins-Delgado et al., 2018).

Environmental hazard associated with the concentrations measured in seawater were quantified for those compounds for which toxic data are available (BP3, 4MBC and OC). The hazard quotient (HQ) was quantified by the following expression (Paredes et al., 2014):

$$HQ = MEC/PNEC$$

where MEC is the measured environmental concentration in seawater and PNEC is the predicted non-effect concentration. PNEC is established on the non-observed effect concentration (NOEC), the median lethal

concentration (LC_{50}) or the median effective concentration (EC_{50}), which are divided by an appropriate assessment factor (AF) according to the Technical Guidance Document of the European Commission of Risk Assessment (Commission, 2003). In this case, and based on the available information for the target compounds, the chosen AF was 50 (Commission, 2003; Carve et al., 2021). HQs were calculated for each marine species and location using a mean value for each period (pre-summer, summer and post-summer).

3. Results and discussion

3.1. Extraction process

The extraction and elution parameters that potentially affected the SPE process were optimised for both matrices (seawater and wastewater) to achieve the best extraction efficiencies for the target UV filters. Firstly, the different sorbents employed in SPE were tested. Once the cartridge was selected, the extraction and desorption parameters were optimised by an experimental design in the statistical Minitab 17 software, in which the influence of each variable and their possible correlations were studied.

3.2. Extracting organic UV filters from seawater

Due to the target compounds' different physico-chemical characteristics, three frequently used cartridges to extract organic UV filters from seawater were tested: OASIS HLB (Paredes et al., 2014), Strata-X (Sánchez Rodríguez et al., 2015) and Sep-pak C18 (Goksøyr et al., 2009). The initial conditions employed to test cartridges were: sample volume, 250 mL; extractant volume and type; 5 mL of MeOH; two pH values of 3 and 7. After comparing the results obtained with each combination, the best recoveries were obtained for pH 3. Then different elution organic solvents were examined, i.e., MeOH, ACN and an MeOH:ACN mixture (1:1, *v/v*). The best recoveries for most compounds were achieved with a C18 cartridge and the MeOH:ACN (1:1, *v/v*) mixture as the eluent (Figure S1). Therefore, the conditions chosen from this step were a C18 cartridge, pH 3 and MeOH:ACN (1:1, *v/v*) as the elution solvent.

In a second stage, other extraction parameters were optimised by a 2^3 experimental design (three variables, two levels). The following conditions were tested: 100 mL and 400 mL of the sample volume, 1 mL and 5 mL of MeOH:ACN (1:1, *v/v*) as eluents, and 0% and 3% of salt addition. A Pareto chart of the standardised effects was built (an example of BMDBM in Figure S2, where the most influential variable is marked in blue). The correlations between the different variables were analysed, where 0 means no effect and 1 is the maximum positive effect. Solvent volume and sample volume led to the highest correlation with between 0.66 and 0.88 and between 0.18 and 0.53, respectively. Regarding the eluent volume influence, 1 mL did not suffice to recover analytes, while better recoveries were obtained for 5 mL. The same behaviour was observed for sample volume as bigger volumes provided higher recoveries. Low or negative effects were obtained for ionic strength.

Ionic strength was ruled out for the second experimental design. Then the two most influential variables were studied in-depth using a 3^2 factorial design (two variables, three levels) for sample volume (250, 500, 700 mL) and eluent volume (4, 5, 6 mL). The best recoveries were gained by using 700 mL of the sample volume and 5 mL of eluent. The response surfaces for the effect of the variables on the extraction of BMDBM are seen in Figure S3, which was comparable for all the target compounds. Based on all these results, the following seawater extraction conditions were chosen: 700 mL of sample volume, 5 mL of MeOH:ACN (1:1, *v/v*) as the eluent, pH 3 and 0% ionic strength. Under these conditions, a preconcentration factor of 140 times was achieved.

3.3. Extracting organic UV filters from wastewater

As wastewater is a different and more complex matrix than seawater, the extraction conditions were also optimised for this kind of matrix. The same cartridges (HLB, Strata-X and Sep-pak C18) were tested. The fixed conditions of pH, sample volume, and eluent for this first attempt were 3, 250 mL and 5 mL of MeOH, respectively. As expected, the best recoveries were obtained with the C18 cartridge (Figure S4).

After selecting the cartridge, a 2^3 experimental design was followed. The three studied variables were pH, sample volume and ionic strength, and the two levels were 3 and 7, 100 mL and 250 mL and 0% and 5%, respectively. A Pareto chart analysis was performed for all the target compounds (an example of BMDBM in Figure S5). From the obtained results, the most significant variable for analytes' responses was ionic strength. The effect was clearly negative (between −0.8 and −0.9), except for MBP, which was slightly positive (0.3). Sample volume (<0.27) and pH (<0.19) did not show any significant effect for most compounds. Given the negative effects of ionic strength, this variable was set at 0%. The selected pH was 7 because this condition reported slightly better recoveries for BP3, IMC and HMS. Sample volume was established at 250 mL to obtain the highest possible preconcentration. No bigger volumes were studied because large volumes can clog cartridges. Thus the fixed conditions were: a C18 cartridge, 0% ionic strength, 250 mL of sample volume and pH 7.

After setting the extraction conditions, the elution conditions were optimised and, therefore, a 3^2 factorial design was run. The variables under study were eluent volume and eluent solvent: 2, 4 and 6 mL of MeOH, and ACN and MeOH:ACN (1:1, *v/v*) mixtures, were studied. Regarding the eluent volume, 2 mL gave the lower recoveries for all the tested eluents, and 5 mL led to satisfactory results. As for eluent type, ACN obtained the lowest recoveries for all the tested volumes (Figure S6). Using MeOH and MeOH:ACN (1:1, *v/v*), five compounds (4MBC, BP3, BMDBM, IMC, MBP) resulted in better or comparable recoveries using only MeOH. Thus, MeOH was chosen to achieve the simplest and fastest method. According to the results of the experimental designs, the optimum conditions for extracting target UV filters from wastewater were: 250 mL of sample, pH 7, 0% ionic strength and 5 mL of MeOH as the extractant, which gave a concentration factor of 50.

3.4. Quality assurance

The linearity, recovery, precision, limits of detection and limits of quantification were evaluated under the optimum extraction conditions for each water type for a mixture of standard solutions. Each value corresponded to the mean of three replicates.

Clean seawater was used to build calibration curves by the matrix match calibration method at eight concentration levels of a mixture of the target UV filters within the 0.025–250 μg L^{-1} Range. The linear correlation coefficient obtained for each compound within this range was >0.99 (Table S4). For wastewater, as the target compounds were present in the influent, secondary and tertiary effluents, a standard additions method was followed to build the calibration curves in each water type. Eight concentration levels of a mixture of the target compounds within the 0.05–250 μg L^{-1} range were employed. Satisfactory linear range coefficients (>0.99) were reached for each compound in the three wastewater types (Table S4).

Extraction efficiencies were studied for seawater and for the three wastewater types (influent, and secondary and tertiary effluents) at two concentration levels (Table S5). In the case of seawater the concentrations used were 0.05 μg L^{-1} and 200 μg L^{-1}, while for the influent samples 0.3 μg L^{-1} and 200 μg L^{-1}, and for secondary and tertiary treatment effluent were 0.1 μg L^{-1} and 10 μg L^{-1}. Recoveries ranged from 43.8% to 100% for seawater. In the influent and secondary effluent samples from WWTPs, values were above 50.6% and 65.1%, respectively (except for MBP, which was around 20%). In the samples from the tertiary effluent, recoveries were between 26.0% and 98.5%.

The intraday (n = 9) and interday (k = 3) repeatability of the developed method were expressed as relative standard deviation and were performed for each water type at the two concentration levels mentioned above (Table S6). Intraday and interday precision ranged from 0.02 to 13.9% for seawater, from 0.50 to 13.9 for influent, from 2.30 to 12.5 for the secondary effluent and from 4.49 to 12.4 for the tertiary effluent.

Method limits of detection (MLODs) and quantification (MLOQ) were calculated for each compound from the signal to noise (S/N) by assuming a minimum detectable limit of 3 and 10 times the S/N ratio, respectively. MLODs ranged from 11.3 ng L^{-1} to 36.4 ng L^{-1} and the MLOQs between 35.9 and 121.3 ng L^{-1} for the eight target compounds in seawater, while the MLODs ranged from 24.6 ng L^{-1} to 555.6 ng L^{-1} and the MLOQs between 52.1 ng L^{-1} and 1851.9 ng L^{-1} for wastewater samples (Table S7).

3.5. Occurrence of organic UV filters in seawater and wastewater

The developed method was applied to determine the target analytes in the seawater and wastewater from the Gran Canaria Island. Samples were collected from three different beaches and in the influents and effluents of three WWTPs, for 6 months (May–October 2019). The found concentrations and detection frequencies for all the organic UV filters analysed in seawater and wastewater are detailed in Table S8 and Table S9, respectively.

3.5.1. Seawater

Seven of the eight compounds were detected with different frequencies on several beaches (Table S8), while MBP was detected only in one location and in one sample. Detection frequencies ranged from 6% for MBP to 83% for BP3, with concentrations levels between 0.07 μg L^{-1} and 172 μg L^{-1}. BP3 and IMC were the most frequently detected (83% and 78%, respectively) with concentration ranges from 0.16 μg L^{-1} to 20.5 μg L^{-1} and from 0.07 μg L^{-1} to 4.27 μg L^{-1}, respectively. At least one compound was detected in each sample (Table S8).

The high detection frequency of BP3 and IMC could be explained by these compounds presenting the lowest Log K_{ow} (3.79 and 4.33, respectively) and the highest water solubility of all the studied compounds (Table 1). BP3 is one of the most widely used UV filters, and is allowed in all countries (Tarazona et al., 2010). It also has a slower photodegradation rate than other organic UV filters (Santos et al., 2012). In the study by Tsui et al. (2014a), BP3 was the most widely detected compound in the different sampled places, including the Arctic. In a recent review, a recurrent compound was also reported in seawater, with a concentration up to the mg·L^{-1} level in the samples taken in summer, which demonstrates its worldwide distribution and occurrence (Cadena-Aizaga et al., 2020). Furthermore, the highest concentration corresponded to OC (172 μg L^{-1}), a compound that is also commonly used in PCPs formulations. A similar concentration (171 μg L^{-1}) has been detected in seawater on the eastern Spanish coast sampled in summer (Vila et al., 2016a). In contrast, the IMC in that study had the lowest concentrations, between 0.07 μg L^{-1} and 4.27 μg L^{-1}. IMC is also often used in PCPs formulations (Vila et al., 2016b), but scarce information about its occurrence is available.

According to concentration per location and seasonality, SL1 shows marked temporal variation (Fig. 2), which can be attributed to locals' seasonal habits (Sánchez Rodríguez et al., 2015). The high concentrations of target UV filters in summer at this site can be explained by this beach being more widely used in summer than in winter, and because water remains longer as a result of the natural barrier.

At SL2, the beach also displayed marked seasonal variation, and the August sample had higher concentrations than the post-summer samples. MBP was detected only in October and presented the highest concentration at this site (146 μg L^{-1}).

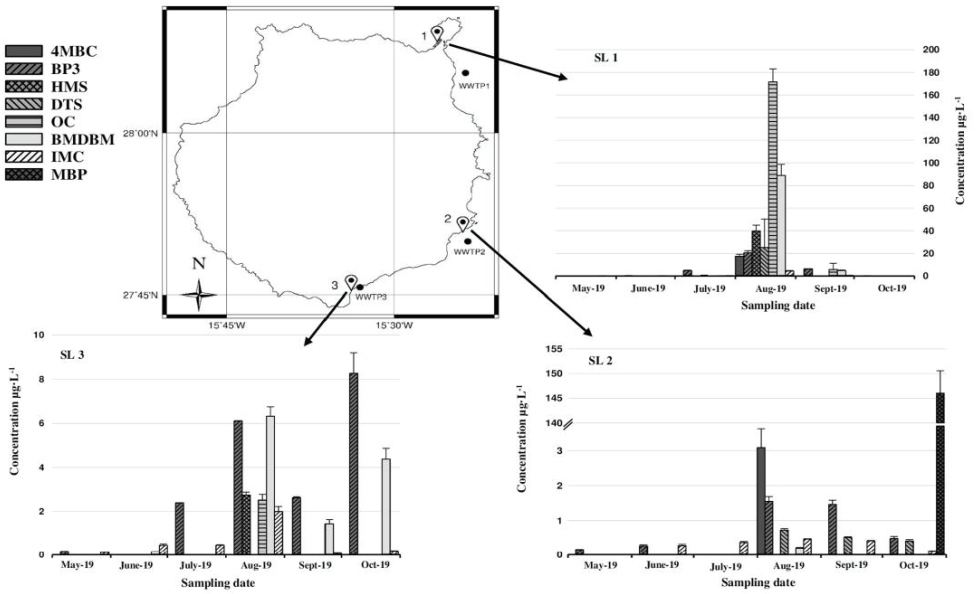

Fig. 2. Measured concentrations of target organic UV filters in seawater samples. Las Canteras beach (SL1), Arinaga beach (SL2), Playa del Inglés beach (SL3). Black points indicate the marine outfall of the three WWTPs.

SL3 receives international tourists all year round. On this beach, a different seasonal variation pattern was observed (Table S8). The second increase during the post-summer period can be explained by this beach being well used by international tourists (mainly north Europeans) during this period. The concentrations measured on this beach are comparable to a "semiclosed" beach in Gran Canaria south, which also has an artificial barrier (Mogán beach) where no seasonal variation is described (Sánchez Rodríguez et al., 2015).

In short, the found organic UV filters and their concentrations seemed to be associated with user type and the water removal rate. Only two studies have been performed on the Canteras beach (SL1) as regards organic UV filters (Sánchez Rodríguez et al., 2015; Montesdeoca-Esponda et al., 2021). By comparing the herein found concentrations to those reported by a study in 2011 (Sánchez Rodríguez et al., 2015), this work detected higher concentrations for OC, BP3, 4MBC, HMS and BMDBM. These variations can be explained by a larger number of tourists in 2019 than in 2011 (25%) (de Turismo, 2021). SL1 appears to be the most contaminated by organic UV filters among the three sampling beaches. This can be attributed to geomorphological characteristics, such as the presence of the natural barrier parallel to its coast that acts as a calm zone where pollutants can be retained. The same behaviour has been described in the same zone in another kind of study, with narrow variation in the micro-meso debris as a result of a less marked marine dynamics influence (McKnight and Rodríguez, 2017). In addition, the concentrations found for BMDBM and BP3 at SL1 were comparable to those reported in other studies carried out in other coastal areas of Spain in summer (Vila et al., 2016b) and in other areas like Hawaii (Downs et al., 2016).

This is the first time that 4MBC, BP3, DTS, BMDBM, IMC and MBP have been studied on the Arinaga (SL2) and Playa del Inglés (SL3) beaches. For SL2, the concentrations found for all the compounds were lower than for the other beaches (Fig. 2). This can be explained because Arinaga is an open beach that is the most affected by trade winds, which facilitate water exchange, and this could demonstrate that the concentration of organic UV filters depends not only on sunscreen users, but also on the water removal rate (Chisvert et al., 2017). According to this study, SL3 is the second most contaminated point by the target organic UV filters, and the observed variability seems related to the different kind of users.

The relatively high concentrations in seawater reported in this study are attributed to its sampling period (higher concentration in summer) and because beaches were sampled at low tide around noon when high sunscreens are expected to be applied (Tovar-Sánchez et al., 2013).

3.5.2. Wastewater

As mentioned above, the mass production and usage of organic UV filters results in them being extensively released to the aquatic environment from WWTPs, which are often not efficient in removing these emerging pollutants.

In order to compare the found concentrations of the target organic UV filters in the different WWTPs, they were normalized to $\mu g \cdot d^{-1} \cdot 1000\ inhabitants^{-1}$ by considering the treated wastewater volume and the population served by each WWTP (Table 2). The normalized loads for influent, the secondary and tertiary effluents, as well as the detection frequencies of each compound, are presented in Table 3.

The WWTP2 influent had the highest percentage of detected compounds (90%), followed by WWTP1 (75%) and WWTP3 (67%). BP3, OC, BMDBM and IMC were detected in all the influent samples. OC had the highest input load (12 327 $\mu g\ d^{-1} \cdot 1000\ inhabitants^{-1}$), followed by BP3 (8572 $\mu g\ d^{-1} \cdot 1000\ inhabitants^{-1}$) and BMDBM (7423 $\mu g\ d^{-1} \cdot 1000\ inhabitants^{-1}$). Even though IMC was measured in all the influent samples, it had the lowest mass load (22.2–123 $\mu g\ d^{-1} \cdot 1000\ inhabitants^{-1}$). MBP showed the most variable frequency in the influent samples, with a range from 17% to 83% depending on the sampling date, and an input load range of 1207–2637 $\mu g\ d^{-1} \cdot 1000\ inhabitants^{-1}$.

Among the results obtained for the secondary treatment effluent, BP3 and BMDBM were present in all the WWTPs during the sampling period, with loads ranges from 200 to 903 $\mu g\ d^{-1} \cdot 1000\ inhabitants^{-1}$ and between 83.2 and 410 $\mu g\ d^{-1} \cdot 1000\ inhabitants^{-1}$, respectively. The highest load went to MBP (2013 $\mu g\ d^{-1} \cdot 1000\ inhabitants^{-1}$) although this compound presents a wide variation in its detection frequency (17–33%). The percentage of target compounds detected in the secondary effluents of both WWTP1 and WWTP3 was 58%, and was 75% for WWTP2.

By comparing the results obtained in these two wastewater types (influent and effluent from the secondary treatment), BP3 was present in them all throughout the sampling period. This could be explained by BP3 being one of the most hydrophilic compounds (Ramos et al., 2016). BMDBM was also detected in all the influents and secondary effluents. Regarding the most contaminated influent, WWTP3 showed the highest mass loads for all the compounds, with values falling within the range of 36.8–12327 $\mu g\ d^{-1} \cdot 1000\ inhabitants^{-1}$.

While observing the WWTP effluents discharge into the marine environment (indirect input), WWTP1 has a long deep outfall (de Canarias, 2021). Thus, the released water was vastly dilution before reaching the beach. Moreover, its waters from the secondary treatment had the lowest concentration of the studied WWTPs for almost all the compounds, except IMC and MBP.

Previous studies have demonstrated the presence of MBP in marine fish (Montesdeoca-Esponda et al., 2021) and sediment (Montesdeoca-Esponda et al., 2019) taken close to the WWTP2 outfall. This agrees with the results found for this compound in the secondary treatment effluent (4.17–9.78 $\mu g\ L^{-1}$). Because of its high lipophilicity (Log K_{ow} 7.56), this compound tends to be accumulate in solid samples like sediment (Montesdeoca-Esponda et al., 2019) or is bioaccumulated by fish (Peng et al., 2015). This WWTP presents the highest concentrations in the effluent after the secondary treatment for seven compounds (except MBP) and presented the highest positive samples (75%) of all the secondary effluents. However, this marine outfall should not affect the beach because it is located 1.4 km south, and also due to the direction of the current.

The WWTP3 outfall is a shallow emissary (de Canarias, 2021) located north of SL3 and, thus, currents may carry pollutants to the coast. Therefore, the organic UV filters found in its effluent can affect this area and the WWTP3 secondary effluent may be considered a source of such contamination.

BP3 has been the most reported compound in the influent samples from various WWTPs in different cities of Portugal (Cunha et al., 2015), Hong Kong (Tsui et al., 2014b), Italy (Magi et al., 2013) and Spain (Gago-Ferrero et al., 2013b). BMDBM has also been presented in all the influent samples taken in Hong Kong (Tsui et al., 2014b). This could be explained by the relatively low Log K_{ow}, which implies a marked tendency to remain in water (Ramos et al., 2016) and $mg \cdot L^{-1}$ (Kasprzyk-Hordern et al., 2009) have been found in European countries for influents and effluents, respectively.

In addition, the samples from the WWTP2 tertiary treatment were analysed (Table S9). These samples presented BP3 with a 100% frequency during the sampling period, followed by HMS and IMC with 83%, where the highest concentrations corresponded to BP3 and BMDBM (Table 3). Although the tertiary treatment waters are not released to the marine environment, the presence of organic UV filters should be taken into account because they are used for agricultural purposes. A recent study demonstrates that irrigation water containing four organic UV filters (BP3, BMDBM, OC, octinoxate) inhibit cucumber plant growth and decrease both photosynthesis and plant respiration (Zhong et al., 2020). Three compounds reported by that study in tertiary treatment samples (4MBC, OC and DTS) have also been found in market tomatoes at concentrations up to 45 ng g^{-1} dry weight. The authors suggest possible contamination coming from irrigation water, although the agricultural conditions for these tomatoes were unknown (Ramos et al., 2020).

3.6. Removal of organic UV filters in WWTP

Removal in conventional WWTPs is variable and depends on substance properties and the applied treatment process. The three studied WWTPs have the same secondary treatment by activated sludge. As mentioned above, the concentrations of organic UV filters found in this study are generally lower by 1–2 orders of magnitude in effluents than in influents. Removal rates were calculated by comparing the concentrations in the influent and the effluent from the secondary treatment. In WWTP2, the removal efficiencies after the tertiary treatment were also calculated (Table S10).

All the target compounds showed different elimination rates after the secondary treatment (Table S10), which agrees with previous works (Ramos et al., 2016; Cunha et al., 2015). Two compounds (OC and 4MBC) had a removal rate between 50% and 100%, and these results agree with those reported in different studies for OC (Balmer et al., 2005; Kupper et al., 2006) and 4MBC (Kupper et al., 2006) by applying the same technology of activated sludge.

Two other compounds (BP3 and BMDBM) obtained a removal rate of 68–99%, which agrees with other studies (68–93%) for BP3 (Balmer et al., 2005). However, some works report lower removal efficiencies for BMDBM. Li et al. (2018) report elimination to be lower than 80% and Tsui et al. (2014b) name one of 34% after activated sludge. As BP3 was present in all the analysed wastewater matrices, this compound was selected to highlight removal efficiencies at the different WWTPs (Fig. 3A and B).

Regarding HMS and DTS, a variation in the removal rates between 33% and 100% was observed and these results are comparable to those found in other studies for the same compounds, HMS (>70%) (Tsui et al., 2014b) and DTS (52–76%) (Ramos et al., 2019). The widest variations found in this study were for IMC and MBP (17–100%). A removal rate of 44% was noted in Hong Kong (Tsui et al., 2014b) for IMC and Montesdeoca-Esponda et al. study (Montesdeoca-Esponda et al., 2019) report that part of MBP elimination could be due to its adsorption in particles during treatment because of its high Log K_{ow}.

Although activated sludge is a widely used conventional secondary treatment for wastewater, it shows incomplete removal for organic UV filters and their metabolites, which can prove more toxic than parents (Ramos et al., 2016). Organic UV filters are not easily degraded in WWTPs due to their physicochemical properties, and they are present in both influent and effluent of WWTPs. This means a low removal efficiency of the wastewater treatments. However, because of the lipophilic character of these compounds (log K_{ow}>5), many of them may be probably sorbed onto sludge (Ramos et al., 2016). Therefore, as some compounds exhibit poor removal rates after secondary treatment process, a tertiary treatment can be employed. To improve the removal efficiency of WWTPs, the implementation of advanced treatments, such as membrane microfiltration, is a possible solution to obtain high-quality water. As the WWTP2 tertiary treatment is performed by microfiltration, these samples were also analysed. Table S10 shows the average removal rates that vary from 10% to 100% for the different compounds. In addition, another tertiary treatment consisting in filtering fine suspended solids, followed by UV disinfection, performing better removal efficiencies for those compounds with a relatively high Log K_{ow} (Tsui et al., 2014b).

In summary, of the removal efficiencies herein calculated, four compounds obtained removal rates above 50% (4MBC, BP3, BMDBM, OC) and the other compounds (HMS, DTS, IMC, MBP) had more variable removal rates (17–100%) after secondary treatment. Removal capacity of WWTPs to eliminate UV filters from water and sludge at some extent strongly depends on the technology implemented in the WWTP and the physicochemical properties of the compounds. It is expected that UV filters can be removed from the water line by sorption onto sludge. Compounds with low water solubility and high log K_{ow} are especially prone to this phenomenon.

3.7. Organic UV filters environmental hazard assessment

The HQs for the measured target organic UV filters in seawater are presented in Table 4. The hazard classification is based on the Hernando et al. criteria (Hernando et al., 2006), where HQ < 0.01 corresponds to an unlikely hazard, and an HQ between 0.01 and < 0.1 poses a low hazard, an HQ between 0.1 and < 1 denotes a medium hazard and an HQ > 1 indicates a potential high hazard. This classification is pointed out without asterisks (*) for unlikely and low hazard, one asterisk for a medium hazard and two asterisks for a high hazard in Table 4.

According to these results, OC had HQs higher than 1 in all the locations where it was measured (SL1 and SL3), which indicates a high

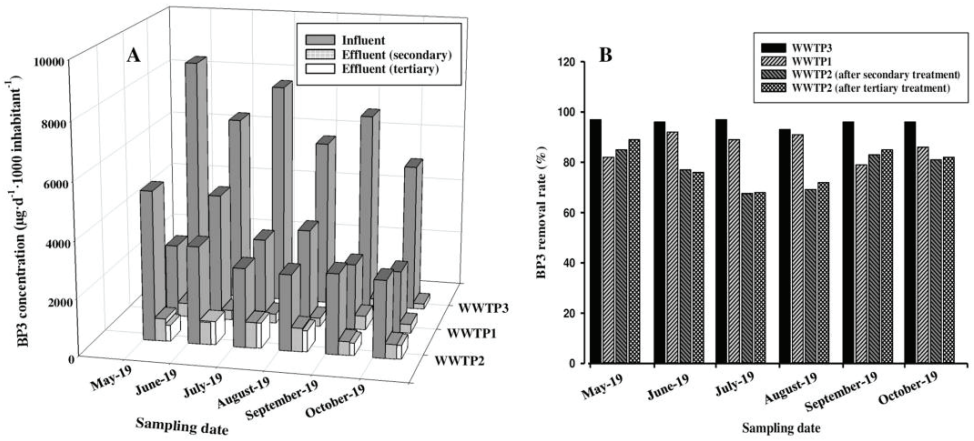

Fig. 3. A: standarized concentration of BP3 in wastewater for the three studied WWTPs. B: removal rates of BP3 in the three WWTPs.

Table 4
Harmful data and HQ values for target UV filters in seawater samples.

Compound	Sampling place	MEC (μg·L^{-1})			Species	Organism type	EC_{50}/ LC_{50}	NOEC	PNEC	HQ[b]		
		Pre-summer	Summer	Post-summer						Pre-summer	Summer	Post-summer
OC	SL 1	–	172 ± 11.4	5.64 ± 0.85	*Isochrysis galbana*[a]	Microalgae	>150	40	0.8	–	215 ± 14.3**	7.05 ± 1.06**
					Mytilus galloprovincialis[a]	Mussel	>650	20	0.4		430 ± 28.5**	14.1 ± 2.13**
					Paracentrotus lividus[a]	Sea urchin	737	20	0.4		430 ± 28.5**	14.1 ± 2.13**
	SL 3	–	2.52 ± 0.26	–	*Isochrysis galbana*[a]	Microalgae	>150	40	0.8	–	3.15 ± 0.33**	–
					Mytilus galloprovincialis[a]	Mussel	>650	20	0.4		6.3 ± 0.65**	
					Paracentrotus lividus[a]	Sea urchin	737	20	0.4		6.3 ± 0.65**	
4MBC	SL 1	–	17.5 ± 1.70	–	*Isochrysis galbana*[b]	Microalga	171.45	18	0.36	–	48.6 ± 4.72**	–
					Mytilus galloprovincialis[b]	Mussel	587.17	300	6		2.92 ± 0.28**	
					Paracentrotus lividus[b]	Sea urchin	853.74	300	6		2.92 ± 0.28**	
					Siriella armata[b]	Crustacean	192.63	37.04	0.74		23.7 ± 2.30**	
					Solea senegalensis[c]	Flatfish malformation	372	235	4.7		3.72 ± 0.36**	
						Flatfish length	–	229	4.58		3.82 ± 0.37**	
						Flatfish behaviour	–	68	1.36		12.9 ± 1.25**	
						Flatfish mortality	439	–	8.78		1.99 ± 0.19**	
					Ruditapes philippinarum[d]	Clam	/7.71	–	0.154		113.5 ± 11.0**	
					Tigriopus japonicus[e]	Copepod	–	0.5	0.01		1750 ± 170**	
	SL 2	–	3.08 ± 0.54	–	*Isochrysis galbana*[b]	Microalga	171.45	18	0.36	–	8.56 ± 1.50**	–
					Mytilus galloprovincialis[b]	Mussel	587.17	300	6		0.51 ± 0.09*	
					Paracentrotus lividus[b]	Sea urchin	853.74	300	6		0.51 ± 0.09*	
					Siriella armata[b]	Crustacean	192.63	37.04	0.74		4.16 ± 0.73**	
					Solea senegalensis[c]	Flatfish malformation	372	235	4.7		0.66 ± 0.11*	
						Flatfish length	–	229	4.58		0.67 ± 0.12*	
						Flatfish behaviour	–	68	1.36		2.27 ± 0.40**	
						Flatfish mortality	439	–	8.78		0.35 ± 0.06*	
					Ruditapes philippinarum[d]	Clam	/7.71	–	0.154		20.0 ± 3.50**	
					Tigriopus japonicus[e]	Copepod	–	0.5	0.01		308 ± 54.0**	
BP3	SL 1	0.42 ± 0.06	12.7 ± 9.11	3.43 ± 3.48	*Photobacterium phosphoreum*[f]	Bacterium	14 270	–	285.4	0.001 ± 0.0002	0.04 ± 0.03	0.01 ± 0.01
					Skeletonema pseudocostatum[g]	Diatom	250	–	5	0.08 ± 0.01	2.53 ± 1.82**	0.69 ± 0.70*
					Isochrysis galbana[b]	Microalgae	13.87	30	0.6	0.70 ± 0.10*	21.1 ± 15.2**	5.72 ± 5.80**
					Mytilus galloprovincialis[b]	Mussel	3472.59	30	0.6	0.70 ± 0.10*	21.1 ± 15.2**	5.72 ± 5.80**
					Paracentrotus lividus[b]	Sea urchin	3280	1920	38.4	0.01 ± 0.002	0.33 ± 0.24*	0.09 ± 0.09
					Siriella armata[b]	Crustacean	710.76	375	7.5	0.06 ± 0.01	1.69 ± 1.21**	0.46 ± 0.46*
	SL 2	0.22 ± 0.07	1.55 ± 0.14	0.97 ± 0.57	*Photobacterium phosphoreum*[f]	Bacterium	14 270	–	285.4	0.001 ± 0.0002	0.01 ± 0.0005	0.003 ± 0.002
					Skeletonema pseudocostatum[g]	Diatom	250	–	5	0.04 ± 0.01	0.31 ± 0.03*	0.19 ± 0.11*
					Isochrysis galbana[b]	Microalgae	13.87	30	0.6	0.36 ± 0.12*	2.58 ± 0.23**	1.62 ± 0.95**
						Mussel	3472.59	30	0.6			

(*continued on next page*)

Table 4 (*continued*)

Compound	Sampling place	MEC (μg·L^{-1})			Species	Organism type	EC_{50}/ LC_{50}	NOEC	PNEC	HQ[h]		
		Pre-summer	Summer	Post-summer						Pre-summer	Summer	Post-summer
					Mytilus galloprovincialis[b]					0.36 ± 0.12*	2.58 ± 0.23**	1.62 ± 0.95**
					Paracentrotus lividus[b]	Sea urchin	3280	1920	38.4	0.01 ± 0.002	0.04 ± 0.004	0.03 ± 0.01
					Siriella armata[b]	Crustacean	710.76	375	7.5	0.03 ± 0.01	0.21 ± 0.02*	0.13 ± 0.08*
	SL3	0.17 ± 0.02	4.25 ± 2.14	5.45 ± 3.30	*Photobacterium phosphoreum*[f]	Bacterium	14 270	–	285.4	0.001 ± 0.0001	0.01 ± 0.01	0.02 ± 0.01
					Skeletonema pseudocostatum[g]	Diatom	250	–	5	0.03 ± 0.004	0.85 ± 0.43*	1.09 ± 0.66**
					Isochrysis galbana[b]	Microalgae	13.87	30	0.6	0.28 ± 0.03*	7.08 ± 3.57**	9.08 ± 5.50**
					Mytilus galloprovincialis[b]	Mussel	3472.59	30	0.6	0.28 ± 0.03*	7.08 ± 3.57**	9.08 ± 5.50**
					Paracentrotus lividus[b]	Sea urchin	3280	1920	38.4	0.004 ± 0.001	0.11 ± 0.06*	0.14 ± 0.09*
					Siriella armata[b]	Crustacean	710.76	375	7.5	0.02 ± 0.003	0.57 ± 0.29*	0.73 ± 0.44*

[a] Data from Giraldo et al. (2017)
[b] Data from Paredes et al. (2014).
[c] Data from Araújo et al. (2018).
[d] Data from Santonocito et al. (2020).
[e] Data from Chen et al. (2018).
[f] Data from Liu et al. (2015).
[g] Data from Petersen et al. (2014).
[h] Based on the Hernando et al. (2006) risk criteria. No asterisk (*) means unlikely and low risk, one asterisk means medium risk and two asterisk means high risk.

hazard for marine species. For 4MBC, the HQs presented a medium to very high hazard for species depending on sampling places/period, where a higher hazard was found for both copepod and clam.

The calculated HQs for BP3, which was found at all the sampling locations, showed wide variation. In general, medium and high hazard were obtained for this compound in summer, which could be related to the extensive use of sunscreens.

The environmental hazard for 4MBC and BP3 has already been reported on beaches on the Gran Canaria island, but a fresh water crustacean (*Daphnia magna*) and an AF value of 1000 were used to calculate the HQs (Sánchez Rodríguez et al., 2015). The study of Sánchez-Rodríguez et al. found a high hazard for 4MBC (HQ > 2.7) at SL1, which agrees with the HQs stated in this study.

4. Conclusions

Knowledge of the presence of UV filters in seawater and wastewater is very limited. An analytical SPE-UHPLC-MS/MS method for the quantitative analysis of eight widely used organic UV filters was successfully applied to the samples taken on beaches and three WWTPs from the Gran Canaria Island, during a 6-month sampling period in 2019.

Despite the Gran Canaria Island beaches being used almost all year round, the three studied beaches showed seasonal variation for the occurrence of the target organic UV filters, with the highest concentrations in summer than for the pre-summer and post-summer periods. All the analysed seawater samples presented at least one target compound throughout the sampling period. BP-3) was detected in 83% of the samples and the highest concentration was found for OC (172 μg L^{-1}). The differences between the kind of organic UV filter found and the observed concentrations seems to indicate that accumulation in seawater depends not only on the user type, but also on the water removal ratio, the season and the geomorphological characteristics of the sampling place.

At the studied WWTPs, OC (12 327 μg d^{-1}·1000 inhabitants^{-1}) presented the highest mass load in all the influent samples. BP-3 and BMDBM were detected in all the influents and secondary treatment effluent throughout the sampling period. BMDBM obtained the widest elimination efficiencies range (83–99%) followed by OC (50–100%). As some compounds are not completely removed during wastewater treatment, they are continuously released to the environment.

Likewise, and comparing the results obtained for beaches with those from secondary effluent, the direct input appears to be the most important source of such pollutants. Even though the secondary wastewater releases from WWTP3 contained the maximum MBP concentration, this compound was not detected in any seawater sample. This could be explained by dilution and its high lipophilicity, which could avoid the transport to beach by currents.

The hazard quotients associated with the measured concentrations showed a potential hazard for the marine species in all the locations where OC was found, while BMDBM presented a medium-high hazard and BP-3 showed widely varying values.

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Author statement

M. Isabel Cadena-Aizaga: Methodology, Validation; Formal analysis; Investigation; Data curation; Writing – original draft. **Sarah Montesdeoca-Esponda:** Conceptualization; Validation; Visualization; Writing – review & editing; Supervision. **Zoraida Sosa-Ferrera:** Conceptualization; Writing – review & editing; Supervision; Resources; Funding acquisition. **José Juan Santana-Rodríguez:** Writing – review & editing; Resources; Funding acquisition.

Declaration of competing interest

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

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Appendix A. Supplementary data

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3.2. Análisis de muestras sólidas

La existencia de filtros UV orgánicos tiene un impacto negativo en el medio acuático y en los organismos presentes en el mismo (flora y fauna), ya que son persistentes, bioactivos y bioacumulativos. Incluso si están presentes en pequeñas concentraciones, pueden afectar y perturbar el normal funcionamiento de los organismos. Estos efectos dependen en gran medida del tiempo de exposición y de los mecanismos de transformación de los compuestos, así como de su naturaleza lipofílica, la cual facilita su acumulación.

Debido a los efectos adversos que la exposición a los filtros UV orgánicos puede producir en los organismos, es necesario el desarrollo de tecnologías altamente eficientes para determinar su presencia en biota.

En esta Tesis Doctoral se evaluará la presencia de los filtros UV orgánicos seleccionados en muestras de macrofitas (algas y plantas marinas) y consumidores primarios marinos.

La extracción de analitos de este tipo de muestras sólidas es compleja, debido a las interacciones soluto-matriz que son muy difíciles de predecir y superar. La extracción en ambos casos se llevó a cabo usando la técnica de extracción asistida por microondas (MAE, por sus siglas en inglés). Ésta es una técnica

simple y rápida que permite la extracción de varias muestras a la vez, además tiene un bajo consumo de disolvente orgánico.

3.2.1. Evaluación de la contaminación antropogénica de filtros UV orgánicos usando macrofitas como bioindicadores

Debido a la contante y exhaustiva entrada de contaminantes antropogénicos al medio marino, tanto la flora como la fauna que allí habitan pueden verse afectados al estar continuamente expuestos a ellos. La flora marina en general son organismos sésiles (*i.e.* viven fijos a un sustrato o estructura) que pueden acumular los contaminantes disueltos y reflejar sus cambios, pudiendo ser indicadores de contaminación local. Las macrofitas marinas son parte de la flora, las cuales pueden ser definidas como vegetación marina visible a simple vista, entre ellas se encuentran las macroalgas y las fanerógamas marinas (plantas).

En la actualidad, la contaminación antropogénica por la entrada de filtros UV orgánicos se ha visto incrementada en el entorno marino, por lo que es indispensable el análisis de los organismos que están expuestos. En esta línea, las macrofitas marinas son organismos ideales para monitorizar la posible contaminación.

La isla de Gran Canaria es uno de los principales destinos turísticos de las Islas Canarias, siendo sus playas uno de sus atractivos más importantes. Sus playas se utilizan casi todo el año, lo que puede tener un marcado impacto en el ecosistema acuático. Miles de turistas que visitan sus playas cada año, usan protector solar, el cual es descargado directamente al ambiente acuático. Esto convierte sus costas en un escenario idóneo para realizar estudios sobre la influencia de la presencia de los filtros UV orgánicos en diferentes matrices marinas.

Se han estudiado tres playas de la isla de Gran Canaria que tienen diferentes características y frecuencia de uso. Estas son la playa de Las Canteras, playa de Arinaga y Playa del Inglés.

Debido a la barrera natural de la playa de Las Canteras hay una menor renovación del agua durante la marea baja, por lo que tiempo de residencia de los contaminantes aumenta, pudiendo afectar a la fauna local (Cadena-Aizaga et al., 2022a). Esta playa tiene un sustrato arenoso donde las algas del género Ochrophyta son predominantes.

La playa de Arinaga presenta un sustrato rocoso-arenoso, donde dominan las algas del género Rhodophyta y Ochrophyta. Debido a que se trata de una playa abierta, la renovación del agua es mayor comparado con la playa de Las Canteras.

Respecto a la Playa del Inglés tiene un sustrato arenoso, donde predominan las praderas de fanerógamas marinas, como la *Cymodocea nodosa*. En esta playa hay un oleaje suave, lo cual favorece la renovación del agua.

En el trabajo anterior se estableció la presencia de ocho filtros UV orgánicos en agua de mar (apartado 3.1.1.) de tres playas de la isla de Gran Canaria. En este trabajo, se analizaron las macrofitas marinas de las mismas tres playas, con el objetivo de establecer la posible asimilación y bioacumulación de estos compuestos desde el agua, y consecuentemente, determinar si estos organismos pueden ser bioindicadores de contaminación antropogénica por filtros UV orgánicos.

En este trabajo se desarrolló un método de extracción basado en la técnica MAE, donde la determinación de los analitos se realizó con el método UHPLC-MS/MS optimizado previamente. El desarrollo del método de extracción se llevó a cabo optimizando las variables que pueden afectar a la extracción (temperatura, tiempo de extracción, volumen y tipo de extractante) por medio de diseños factoriales. Con esto se consigue la combinación más adecuada de los parámetros experimentales que obtiene los mejores resultados. El diseño factorial se realizó en dos etapas diferentes, el tiempo y el volumen de extractante fueron las variables que tenían una mayor influencia en la eficiencia de extracción. Las condiciones

experimentales del método optimizado consisten en dos extracciones consecutivas a 50 ºC durante 5 minutos con 2 mL de acetona en cada paso. El método global optimizado (MAE-HPLC-MS/MS) presenta unas eficiencias de extracción entre 39.8 – 98.3 % y una repetibilidad (tanto en el mismo día como entre días) expresada como la desviación estándar, inferior al 11.87 %.

Las tres playas anteriormente mencionadas fueron monitorizadas durante seis meses, de mayo a octubre de 2019, recolectándose un total de 76 muestras de macrofitas correspondiente a 13 especies de macroalgas y una especie de fanerógama. Dado el elevado número de especies diferentes, una curva de calibración externa fue usada para la cuantificación de los analitos y las concentraciones fueron ajustadas a su correspondiente eficiencia de extracción.

Las muestras fueron tomadas en marea baja y solo las algas provenientes de arribazones fueron recolectadas. Por lo tanto, las mismas especies no fueron recolectadas en todos los muestreos, por ese motivo fueron agrupadas por tipo (rojas, pardas y verdes) para realizar el análisis estadístico. En la playa de Playa del Inglés, la fanerógama *Cymodocea nodosa* se sometió a un análisis estadístico sola porque no se puede agrupar con las algas y además estuvo presente durante todo el muestreo en esta playa.

Todos los analitos fueron detectados con frecuencias de detección que varían entre el 16 % y 100 %, siendo el OC el único compuesto que fue encontrado en todas las muestras de las tres playas durante todo el periodo de muestreo. Este mismo analito también mostró la concentración más alta en la fanerógama marina *Cymodocea nodosa* (19 369 $ng \cdot g^{-1}dw$). Su alta concentración y frecuencia de detección puede ser explicada por su alto Log K_{ow} (>6) y su baja solubilidad (<0,02 $g \cdot L^{-1}$), lo que hace que se más probable encontrarlo en estas matrices. Esto también puede estar relacionado con el hecho de que este compuesto se usa ampliamente en PCP y es permitido en todos los países. Por el contrario, 4MBC, IMC y BP3 presentaron las frecuencias más bajas (16 – 25%), esto puede ser debido a que son más hidrofílicos y presentan mayor solubilidad. Las concentraciones más altas encontradas por playa fueron para el alga verde *Cymopolia barbata* en la playa de Las Canteras, para el alga verde *Codium decorticatum* en la playa de Arinaga y para la fanerógama *Cymodocea nodosa* en Playa del Inglés.

Los resultados revelaron que, aunque las algas verdes recolectadas eran menos comunes, contenía las concentraciones más altas. Lo que sugiere que este tipo de alga es un excelente indicador de la contaminación de los filtros UV orgánicos. Los altos niveles de filtros UV orgánicos acumulado en macrofitas refleja la biodisponibilidad de los contaminantes en el área de estudio y la

capacidad de éstas para asimilarlos desde el entorno. Así, los resultados obtenidos sugieren que las macrofitas pueden ser usadas como bioindicadores para monitorizar la contaminación antropogénica por filtros UV orgánicos.

Por otro lado, también se determinó la relación de bioconcentración (BCR) para las macroalgas agrupadas por tipo (pardas, rojas y verdes), usando las concentraciones previamente obtenidas en agua de mar en las mismas playas. La relación de bioconcentración mide la capacidad de un organismo de asimilar un contaminante desde su entorno, y es usado para demostrar la fiabilidad de las macrofitas como bioindicadores. Cuando BCR es superior a 1, se considera que hay bioacumulación, mientras que valores superiores a 1 000 indican que se produce una bioacumulación significativa.

Se obtuvieron diferentes grados de bioconcentración de los compuestos estudiados en todos los tipos de algas. Esto refleja que, aunque su disponibilidad es baja en agua de mar, se produce asimilación (bioconcentración). Teniendo en cuenta el tipo de alga, el BCR siguió este orden; alga verde> alga roja> alga parda. Si consideramos los valores medios de BCR para todos los tipos de algas, playas y compuesto, el valor más alto fue para OC y el más bajo para MBP.

Los resultados obtenidos sugieren que las algas marinas acumulan los filtros UV orgánicos en gran medida en todas las playas estudiadas, porque los BCR obtenidos generalmente fueron superiores a 1 000, lo que sugiere posibles efectos nocivos en estos organismos. Además, estos resultados sugieren posibles efectos de biomagnificación en organismos superiores que se alimentan de estas macroalgas.

Este trabajo fue publicado en la revista *Science of the Total Environment* en el año 2022, la cual está dedicada a publicar investigaciones sobre el impacto en el medioambiente y las interconexiones con la atmósfera, la litosfera, la hidrosfera, la biosfera y la antroposfera. Esta revista se encuentra en el primer cuartil del área *Environmental Sciences*, posición que ha mantenido en los últimos 5 años de los que se han publicado métricas, con un factor de impacto entre 4.984 y 10.753 según *Journal Citation Reports*.

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Assessment of anthropogenic pollution by UV filters using macrophytes as bioindicators

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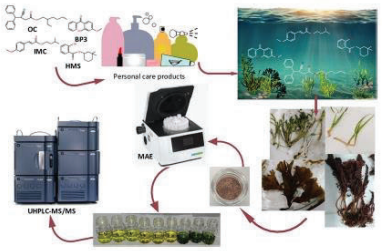
HIGHLIGHTS

- An analytical method for eight organic UV filters was optimized for macrophytes.
- All target compounds have been detected in different frequencies.
- Octocrylene was detected in all samples and it was found in the highest concentration.
- First monitoring of organic UV filters and bioconcentration assessment on macrophytes
- Detection of target compounds in macrophytes indicates their potential as bioindicators.

GRAPHICAL ABSTRACT



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ABSTRACT

Marine environment pollution has increased in recent decades as a result of anthropogenic activities. Macrophytes can assimilate the compounds dissolved in the water and respond to changes in surround conditions, for that, they can be used as bioindicators of pollution in aquatic environments.

Currently organic ultraviolet (UV) filters have shown ever-increasing in pollution levels in marine ecosystems. The anthropogenic pollution produced by eight organic ultraviolet (UV) filters in coastal macrophytes was studied. A microwave-assisted extraction (MAE), followed by ultrahigh-performance liquid chromatography with tandem mass spectrometry (UHPLC-MS/MS) was applied to 76 macrophyte (seaweeds and seagrass) samples from three different beaches on the Gran Canaria Island (Spain), collected for 6 months. All studied UV filters were found with different detection frequencies from 16% to 100% in macrophyte samples. Octocrylene (OC) was detected in all the analysed samples throughout the sampling period. The highest concentration, 19,369 ng g^{-1} dry weight (dw), was for this compound in the seagrass *Cymodocea nodosa*.

The bioconcentration ratio was determined for several seaweed groups (red, brown, green). Different bioconcentration grades were obtained. Those above 1000 indicated significant accumulation, which increases the possibility of chronic effects on seaweed and at upper tropic levels.

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1. Introduction

Seaweeds and seagrass are altogether known as macrophytes, which are multicellular photoautotrophic organisms with a wide geographical distribution. Seaweeds comprise the Genus Rhodophyta (red seaweed), Ochrophyta (brown seaweed) and Chlorophyta (green seaweed), and seagrass is a grass-like marine plant. They are deemed a useful tool for environmental monitoring as bioindicators of pollution given their sessile nature in a dynamic habitat where pollutants settle or resuspend due to tidal action. (Ruiz Chancho et al., 2010; Chaudhuri et al., 2007).

Seaweeds are used for identifying heavy metal pollution in marine environments because they are easy to identify, and also for their availability in some areas (Chakraborty et al., 2014). Seaweeds can be employed to monitor organic pollution because their diversity is strongly impacted by the presence of organic compounds (Sabri et al., 2020). As seaweeds are also the basis of several marine food webs, understanding their pollution by anthropogenic compounds is essential for their environmental importance.

Several pollutants constantly enter marine ecosystems, of which organic ultraviolet (UV) filters have increased in the last few decades. These compounds are used in different products, such as personal care products (PCPs), including sunscreen, soaps, makeup, lotions and toothpaste, to protect skin from harmful UV radiation effects (Díaz-Cruz and Barceló, 2015). The maximum concentration of each compound in cosmetics is controlled in the European Union by Regulation no. 1223/2009.

Organic UV filters reach the environment both directly (washed off skin and clothes) and indirectly (treated wastewater, industrial discharges, runoff) (Molins-Delgado et al., 2014). Given their extensive use, hundreds of tonnes of these compounds are released to the environment (Danovaro et al., 2008) and are considered a new pollutant type (Emmanouil et al., 2019). PCPs generally do not undergo structural changes and, consequently, unaltered compounds are released to the environment (Brausch and Rand, 2011).

The occurrence of organic UV filters in the environment may have negative effects on the aquatic biota (marine and fresh waters) because of their accumulation or long-term exposure (Carve et al., 2021). In fact some organic UV filters like benzophenone-3 (BP3), 4-methylbenzylidene camphor (4MBC) and octocrylene (OC) produce coral bleaching, impaired reproduction, malformation and increased mortality for some marine organisms (Danovaro et al., 2008; Schmitt et al., 2008; Araújo et al., 2018).

Their presence has been globally reported in several matrices, such as wastewater (Ramos et al., 2016), seawater, marine sediments, marine organisms (Cadena-Aizaga et al., 2020), lakes and rivers (Ramos et al., 2015). These environmental pollutants can affect coastal waters' ecological integrity. Therefore, biological indicators like seaweeds can be globally used to assess water pollution. However, to the best of our knowledge, only one work has previously reported the occurrence of such compounds in seaweeds (Pacheco-Juárez et al., 2019).

Coastal tourism is one of the main reasons for visiting the Canary Islands (Spain) and, as such, it is one of the mainstays of its economy. Beaches there are used almost all year long, which can have a marked impact on the aquatic ecosystem. This makes the Gran Canaria Island coast a suitable scenario for carrying out studies about the presence of organic UV filters in different marine matrices.

Hence the aim of this work is to assess the use of macrophytes as bioindicators of UV filters pollution. To that end, an analytical approach based on microwave-assisted extraction (MAE), followed by ultra-high-performance liquid chromatography with tandem mass spectrometry (UHPLC-MS/MS), was applied to determine the presence of eight commonly used organic UV filters in coastal macrophytes. One of the main advantages of the MAE technique is that it requires small volumes and amounts of solvent and sample. It is also is easy to perform and many samples can be extracted at the same time.

Three beaches on the Gran Canaria Island (Spain) were monitored for 6 months (May – October 2019). Seventy-six macrophytes (seaweeds and seagrass) samples from 14 species were analysed to demonstrate if they were suitable indicators of pollution by emerging pollutants like organic UV filters. As far as we are aware, only one of the studied compounds has been reported in seaweed samples by Pacheco et al. (Pacheco-Juárez et al., 2019) in the Canary Islands. The bioconcentration ratio was also calculated for the different seaweed groups (red, brown, green) and for seagrass which is based on the results obtained for in seawater in the same beaches and periods (Cadena-Aizaga et al., 2021).

2. Materials and methods

2.1. Reagents

Eight organic UV filters, namely homosalate (HMS), 4MBC, BP3, drometrizole trisiloxane (DTS), octocrylene (OC), butyl methoxydibenzoylmethane (BMDBM), isoamyl p-methoxicinnamate (IMC) and methylene bis-benzotriazolyltetramethylbutylphenol (MBP) of analytical grade (purity ≥ 99%), were purchased from Sigma-Aldrich (Madrid, Spain). Methanol (MeOH), acetone, acetonitrile (ACN), hexane (Hex), water and formic acid, of LC-MS grade, were supplied by Panreac Química (Barcelona, Spain). Main characteristics of the target organic UV filters analysed in macrophytes are summarised in the Supplementary Material (Table S1).

Stock solution (250 $mg{\cdot}L^{-1}$) was prepared in acetone and stored in amber glass bottles in a freezer until used. Working solutions were prepared daily in MeOH.

2.2. Characteristics of sampling sites, sample collection and pre-treatment

The Gran Canaria Island was selected as a study site because of the many tourists that arrive there throughout the year. Three beaches with different tourism pressures and characteristics were compared (Fig. 1). The geographic coordinates of the sampled beaches are reported in the Table 1.

The Las Canteras beach is located in the northeast part of the island and is characterised by the presence of a natural barrier that runs parallel to its coast. This implies a lower renovation ratio at low tide due to almost null wave action (Perez-Torrado and Mangas, 1994). Ochrophyta seaweed dominates as a rocky-sandy substratum is present on this beach (Tabraue et al., 2009). Due to low water renovation, the long residence time of pollutants can affect the local fauna. This beach is used mainly by locals and moderately by foreigners all year round, where the maximum activity takes place in summer.

The Arinaga beach is located southeast of the Gran Canaria Island and its principal characteristic is the intense influence of wind and swell due to trade winds and the Canary Current (Alonso et al., 2001), which make water renewal easy. It is an open beach employed principally by locals, but barely by international tourists. Here, like the Las Canteras beach, a rocky-sandy substratum is present, where Rhodophyta and Ochrophyta seaweed dominate (Tabraue et al., 2009).

The Playa del Inglés beach lies to the south of the Gran Canaria Island and presents artificial barriers. The effect of trade winds and the Canary Current is milder (Alonso et al., 2001), which creates a calm zone with a light swell. In this case a sandy substratum is found, where seagrass meadows are typical and *Cymodocea nodosa* is one of the main phanerogams present (Tabraue et al., 2009). This open beach is used all year long by numerous international tourists, essentially northern Europeans, according to the Gran Canaria Tourism Agency (G.C.P. de Turismo Estadísticas - Web Oficial de Turismo de Gran Canaria, n.d.). National tourists also prevail in summer.

Macrophyte samples of both seaweed and seagrass species were taken monthly from May to October 2019. The sampling time was selected due to the tourist affluence in this period. Number of the collected samples per beach and month are presented in Table S2. They were collected at low tide along the beach and only the seaweeds washed ashore were picked up. For this reason, different species were taken during each sampling. The seaweed species grouped according to type (red, brown, green) and the seagrass are presented in Table 1. Some species were repeatedly collected. For the Las Canteras beach, *Cymopolia barbata* (green seaweed), *Lobophora*

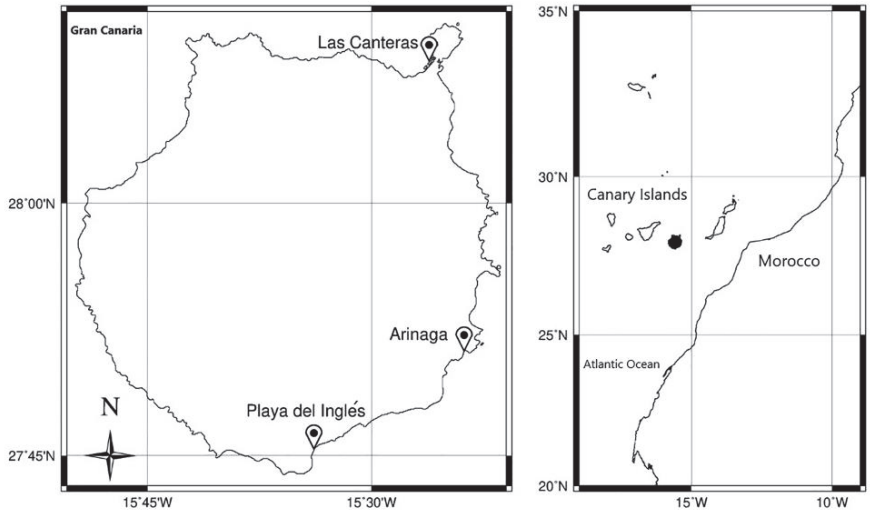

Fig. 1. Geographical location of the Canary Islands, Gran Canaria Island and the sampling sites.

variegata and *Dictyota dichotoma* (brown seaweed) were present during each sampling. On the Arinaga and Playa del Ingles beaches, only *Asparagopsis taxiformis* (red seaweed) and *Cymodocea nodosa* (seagrass) were respectively found during all the samplings. After collection, samples were transported to the laboratory in glass bottles in a portable fridge, where they were rinsed with deionised water to remove sand and salt. Then clean seaweeds were identified and frozen at − 20 °C to be subjected to freeze-drying. To obtain a homogenous sample, whole tissues of each species were sifted through a < 300 μm particle size and stored in the dark in a fridge until analysed.

Table 1
Macrophytes species collected in the three beaches.

Sampling Place	Phylum	Scientific name
Las Canteras beach (28°8′27.982″N, 15°26′8.237″W)	Rhodophyta	*Asparagopsis taxiformis*
		Corallina elongata
		Laurencia sp.
		Liagora sp.
		Lophocladia trichoclados
	Ochrophyta	*Lobophora variegata*
		Sporochnus pedunculatus
		Dictyota dichotoma
		Sargassum sp.
		Stypocaulon scoparium
	Chlorophyta	*Cymopolia barbata*
Arinaga beach (28°8′27.982″N, 15°26′8.237″W)	Rhodophyta	*Asparagopsis taxiformis*
		Corallina elongata
		Laurencia sp.
		Liagora sp.
		Lophocladia trichoclados
	Ochrophyta	*Taonia atomaria*
		Stypocaulon scoparium
		Dictyota dichotoma
	Chlorophyta	*Codium decorticatum*
Playa del Inglés beach (27°45′23.579″N, 15°33′51.2809″W)	Rhodophyta	*Corallina elongata*
		Liagora sp.
		Lophocladia trichoclados
	Ochrophyta	*Stypocaulon scoparium*
		Dictyota dichotoma
	Chlorophyta	*Cymopolia barbata*
	Tracheophyta	*Cymodocea nodosa*

2.3. Sample preparation and extraction

In order to obtain a representative sample, a mixture of seaweeds from the Genus Ochrophyta, Chlorophyta and Rhodophyta was employed for extraction optimisation purposes. It was spiked with the target compounds, stirred and air-dried at room temperature in the dark for 24 h to obtain a homogeneous dry sample.

Organic UV filter extraction was carried out in a Titan MPS microwave oven equipped with 16 TFM vessels (Perkin Elmer, Madrid, Spain). The MAE procedure was performed using a factorial design strategy in order to achieve the most suitable combination of the tested values for the different variables that affect the extraction procedure. The factorial design was conducted in two different stages, and time and volume were that variables that have a greater influence on the extraction efficient. In the optimized conditions, one hundred milligrams of the spiked mixture were transferred to the MAE vessels and 2 mL of acetone were added to the mixture. Then vessels were closed and subjected to the optimized MAE process, which consisted in applying 50 °C for 5 min. Once extraction was done, the extract was carefully filtered through a 0.2 μm syringe filter. Then another extraction process was performed with the same sample under the same conditions. The second extract was also filtered, and both were combined to be dried under a nitrogen stream and reconstituted in 2 mL of MeOH.

2.4. Instrumental analysis

Determination was performed by an ACQUITY UHPLC system equipped with a binary solvent manager, a thermostated autosampler, a BEH C18 column (50 × 2.1 mm, 1.7 μm particle size) and a tandem triple quadrupole mass spectrometer detector (MS/MS) with electrospray ionization (ESI). All the components were controlled by the MassLynx Mass Spectrometry software (Waters Chromatography, Barcelona, Spain). The mobile phase consisted of MeOH (A) and water (B), of LC-MS grade, with 0.1% (*v*/*v*) formic acid, and each one at a flow rate of 0.3 mL·min^{-1}. The following

gradient was employed for analytes separation: starting with 25% A: 75% B, which was kept for 3 min, then decreased to 0% of A for 2 min and held for 1 min. Finally, A was increased to 25% in 1 min and held for 1 min for the next injection. The injected extract volume was 10 μL. The MS/MS conditions were previously established (Cadena-Aizaga et al., 2021) and are summarised in Table S1. In brief, the ESI parameters were fixed as follows: capillary voltage at 4 kV, cone voltage 15 V, source temperature at 120 °C, desolvation temperature at 450 °C, and desolvation gas at 500 L h^{-1}. Nitrogen and argon gases were used for desolvation and collision, respectively.

2.5. Statistical analysis

As most seaweed species were not present in all the samplings, they were grouped per type (red, brown, green) to perform the statistical analysis. On the Playa del Inglés beach, the phanerogam *Cymodocea nodosa* was subjected to a statistical analysis alone because it is a seagrass and cannot be grouped with seaweeds.

For the statistical analysis, concentrations were compared by the combined effect of beach for each seaweed type and compound (the Las Canteras, Arinaga and Playa del Inglés beaches) and seasonal period: pre-summer (May and June), summer (July and August) and post-summer (September and October). Given lack of normality within groups, the Kruskal-Wallis test was run to assess the significance of the differences associated with beach-period, for which differences with *p*-values (p) below 0.05 are considered significant. When this test was not significant for the combined effect, the same test was used to look for individual effects. When an individual test was significant, *post hoc* comparisons were made by the Conover test. This test was utilised because it establishes the exact groups within which significant differences can be found, whereas the Kruskall-Wallis test only allows the presence or lack of significant differences to be evaluated. Version 4.1.1 of the statistical R software was used for this purpose (R.C. Team, 2021).

2.6. Bioconcentration ratio (BCR)

Seaweeds and seagrass are potential biomonitors due to limited mobility, the potential to absorb organic substances (Pavoni et al., 2003) and abundance in marine environments. Bioconcentration is the process by which the aquatic organism absorbs a pollutant from the environment *via* non-dietary uptake (Ismail and Ismail, 2017), and is a quantitative measure of its accumulative capacity (Jahan and Strezov, 2019). In order to assess the ability of the studied macrophytes as organic UV filters bioindicators, the bioconcentration ratio (BCR) was determined. BCR is the concentration (accumulation) of a pollutant in an aquatic organism in relation to this pollutant in the surrounding environment. The BCR is calculated by the following formula (Arnot and Gobas, 2006):

$$BCR = \frac{C_{Macrophyte}}{C_{water}}$$

where $C_{Macrophyte}$ is the concentration of a pollutant in seaweed or seagrass (expressed as mg·kg^{-1}) and C_{water} is the concentration of the same pollutant in water (Table S3) (Cadena-Aizaga et al., 2021) expressed as mg·L^{-1}). When the BCR is above 1, the bioaccumulation process is considered to take place. A BCR higher than 1000 indicates significant bioaccumulation (Jahan and Strezov, 2019).

3. Results and discussion

3.1. MAE optimisation

The variables that can affect extraction efficiency in the MAE technique were optimized. A 2^4 experimental design was built with the MiniTab software as the first approach. This consisted in four variables at two levels: temperature (50 °C and 60 °C); extraction time (3 and 6 min); extractant volume (2.5 and 5 mL); solvent type (MeOH and ACN). With the results, a Pareto Chart analysis was performed to see which variables most affected extraction. They are denoted in blue in the Supplementary Material in Fig. S1 for 4MBC. Any correlations between the variables were also analysed, where 0 means no influence, −1 is a maximum negative effect and 1 represents a maximum positive effect. The variables showing the strongest effect were extractant volume and solvent type. A marked combined effect was noted between them (Fig. S1). MeOH performed better recoveries than ACN for each volume, temperature and extraction time. Regarding correlations, the extractant volume obtained the highest values for all the compounds, but was negative (−0.84 to −0.96), while the extraction time presented a correlation between −0.01 and 0.07. The lowest correlation was for temperature (0.01–0.02). The strong negative effect on the extractant volume means that the higher the volume, the more negative the influence on recoveries (Fig. S1). For extraction time, similar results were obtained at 3 min and 6 min, but slightly better results were obtained at 3 min. Regarding the temperature results, this parameter had no significant influence (similar results were obtained at 50 °C and 60 °C). For this reason, temperature was set at 50 °C. Therefore, extractant type (MeOH) and temperature (50 °C) were fixed, while extraction time and extractant volume were analysed in more depth.

In a second stage, 3^2 (two variables at three levels), a factorial design was applied with the aforementioned fixed variables. The two target variables extractant volume and extraction time were analysed at 2, 3 and 4 mL, and at 3, 4 and 5 min, respectively. The OC surface response obtained from this design appears in Fig. S2. The best recoveries were obtained at 2 mL of extractant and for a 5-min extraction time, which were observed for all the compounds.

Later other organic solvents were tested to give the best recoveries. The employed organic solvents were acetone, MeOH:acetone (1:1, *v*,*v*) and hexane (Fig. S3). Similar results were obtained using all the extractants. However, acetone gave generally better recoveries for most compounds. This was why acetone was chosen for the extraction as a compromise in a multicompound analysis.

Finally, a second sample extraction was implemented using another lot of 2 mL of acetone, which resulted in significantly better recoveries. Thus, the optimal conditions were two extractions lasting 5 min at 50 °C with 2 mL of acetone. Both extracts were combined and dried under a nitrogen stream and reconstituted in the 2 mL of MeOH to be injected into the UHPLC-MS/MS system.

3.2. Quality assurance

The linearity, recovery, precision, limits of detection (LODs) and limits of quantification (LOQs) were evaluated under the optimum extraction conditions for the mixture of seaweeds. Each value corresponded to the mean of three replicates.

An external calibration curve was built in MeOH within the 100 ng·L^{-1} to 250 μg·L^{-1} range. Satisfactory linear range coefficients (>0.99) were obtained for each compound.

The instrumental limits of detection (ILODs) and quantification (ILOQs) were calculated from the signal to noise (S/N) of each compound by assuming a minimum detectable limit of 3- and 10-fold the S/N, respectively. The ILODs ranged between 6.84 ng·L^{-1} and 140.34 ng·L^{-1}, while the ILOQs went from 22.79 ng·L^{-1} to 467.81 ng·L^{-1}.

The extraction efficiencies and precision of the method for each compound were calculated considering the application of the whole method. For that, 100 mg of dry sample were spiked to a final concentration of 5, 2000, 10,000 ng·g^{-1} of the mixture of target compounds, which were extracted with 2 mL of MeOH, resulting in final concentrations of 250 ng·L^{-1}, 100 μg·L^{-1} and 500 μg·L^{-1}, respectively.

Extraction efficiencies for each compound were calculated by comparing the signal obtained after applying optimized extraction method to the spiked samples. The obtained recoveries range was 39.8–98.3% (Table 2).

The method's repeatability (intraday precision, $n = 3$) and reproducibility (interday precision, $k = 3$) were expressed as relative standard

Table 2
Analytical parameters: recoveries, intra, inter-day at three levels of concentration (expressed in dw), and ILODs and ILOQs for the developed MAE-UHPLC-MS/MS method.

Compounds	Recoveries (%)[a]			Intra-day precision (%)[a]			Inter-day precision (%)[b]			ILODs[c]	ILOQs[d]
	5 ng·g^{-1}	2000 ng·g^{-1}	10,000 ng·g^{-1}	5 ng·g^{-1}	2000 ng·g^{-1}	10,000 ng·g^{-1}	5 ng·g^{-1}	2000 ng·g^{-1}	10,000 ng·g^{-1}	ng·L^{-1}	ng·L^{-1}
4MBC	–	85.4	89.4	–	3.25	2.42	–	7.00	3.53	51.41	171.35
BP3	51.8	60.7	65.4	8.91	2.66	7.31	10.44	4.22	7.23	22.81	76.05
HMS	39.8	44.0	44.2	0.65	6.55	6.31	11.87	8.91	4.93	11.39	37.97
DTS	44.8	50.6	52.3	4.93	3.57	3.86	8.39	8.24	5.09	6.84	22.79
OC	45.6	78.8	83.2	8.03	2.40	5.56	8.46	6.50	4.31	20.78	69.25
BMDBM	55.6	59.2	65.9	–	11.73	8.44	–	7.47	6.93	40.43	134.77
IMC	56.0	65.4	67.6	7.88	3.91	6.26	8.42	4.20	6.42	16.30	54.35
MBP	–	92.8	98.3	–	2.78	4.76	–	5.59	7.31	140.34	467.81

[a] Mean of three replicates (n = 3).
[b] Mean of three replicates performed for three days (k = 3).
[c] Calculated from the signal to noise (S/N) assuming a minimum detectable limit of three times the S/N.
[d] Calculated from the S/N assuming a minimum detectable limit of ten times the S/N.

deviation. Intraday precision ranged from 0.65% to 11.73%, and interday precision between 3.53% and 11.87% (Table 2).

3.3. Environmental occurrence of organic UV filters in macrophytes

The MAE-UHPLC-MS/MS method was applied to determine the target analytes in 76 macrophyte samples taken from the Gran Canaria Island. They were collected from three different beaches for 6 months (May – October 2019). The detailed concentrations and detection frequencies for all the organic UV filters analysed in macrophytes are summarised in the Supplementary Material (Table S2).

All the target compounds were found, with different detection frequencies ranging between 16% and 100% in the macrophyte samples. The sum of the measured concentrations in the different species for each compound is represented for seasonal period and beach in Fig. 2. OC was detected in all the analysed samples, while HMS was present in 91% of them (Table S2). The highest concentration corresponded to OC (19,369 ng·g^{-1} dw) in the seagrass *Cymodocea nodosa* on the Playa del Inglés beach in October, and in the green seaweed *Cymopolia barbata* (8128 ng·g^{-1} dw) on the Las Canteras beach in September.

OC was the most frequently found compound and the most concentrated one (107–19,369 ng·g^{-1} dw). Its high Log K_{ow} (>6) and low solubility (<0.02) might explain it being highly detected in such a matrix. This may also be related to the fact that this compound is widely used in PCPs formulations and allowed in all countries (Fivenson et al., 2020; Al-Jamal et al., 2014). Conversely, 4MBC, IMC and BP3 presented the lowest frequencies (16–25%), which can be explained by these compounds presenting low Log K_{ow} (<5).

Regarding concentration per beach, 37 seaweed samples were examined at Las Canteras, and the target compounds were detected several times. All the analysed seaweeds presented OC within a concentration range of 126–6372 ng·g^{-1} dw. HMS was present in 97% of the samples, with a concentration range between 4.64 and 8128 ng·g^{-1} dw (Table S2). Three seaweed species were found during all the samplings on this beach: *Cymopolia barbata* (green seaweed), *Lobophora variegata, Dictyota dichotoma* (both brown seaweeds). All the target compounds were detected in *Cymopolia barbata*. HMS and OC were present throughout the sampling period and had the highest concentrations (8128 ng·g^{-1} dw and 6372 ng·g^{-1} dw, respectively, in September). In *Lobophora variegata,* BMDBM and OC were detected in all the samples (maximum concentrations of 3663 and 2077 ng·g^{-1} dw, respectively). Lastly in *Dictyota dichotoma,* HMS and OC were detected in all the samples, and OC showed the highest concentration (5971 ng·g^{-1} dw) in August. Two of these species (*Dictyota dichotoma* and *Lobophora variegate*), along with *Asparagopsis taxiformis*, have been reported to contain MBP (also called UV 360) on the Las Canteras beach in another study (Pacheco-Juárez et al., 2019), with concentrations between 42.5 and 115 ng·g^{-1} dw were found. They are in the same order as those measured in our study (29.69–78.19 ng·g^{-1} dw).

On the Arinaga beach, 26 seaweed samples were analysed, in which all the compounds were detected at least once. All the samples presented OC at concentrations between 107 and 7163 ng·g^{-1} dw, and its maximum concentration appeared in the green seaweed *Codium decorticatum* in June. Only one species was present throughout the sampling period, the red seaweed *Asparagopsis taxiformis*. In this species, OC, DTS and HMS were present at more than 67% of the samples during the whole period.

On the Playa del Inglés beach, all the compounds were detected at least once in the 13 macrophyte samples. OC and HMS were detected in 100% samples, while BMDBM was found in 85% of them. The highest concentration corresponded to OC (19,369 ng·g^{-1} dw) in the seagrass *Cymodocea nodosa* in October. Only this species was picked up during all the samplings. The frequency of detecting the target compounds was lower in the other analysed species (Table S2).

The results revealed that although the collected green seaweeds were less common, they contained the highest concentrations (Table S2). In this context, the studied green seaweeds suggest being an excellent indicator of organic UV filters pollution. The results of the three beaches suggest a different seasonal behaviour for each species. Some studies indicate that seasonal variation can be explained by solar radiation effects on seaweed growth because metabolic rates slow down in winter due to less light and lower temperatures (Villares et al., 2002). Nevertheless on the Gran Canaria Island, solar radiation on the three beaches is almost the same during the three analysed periods (20–30 MJ·m^{-2}·day^{-1}) (Stackhouse, 2020). The high levels of organic UV filters accumulated in macrophytes reflects the bioavailability of the pollutants in the studied area and the capacity of them to take the pollutants from the surrounding.

Detection frequencies were compared using the data obtained with the seawater analysis from the same beaches during the same period (Cadena-Aizaga et al., 2021). According to the overall frequency in seawater and macrophytes, a tendency was observed: BP3 and IMC were the most frequently found compounds in seawater (>78%), but they were detected in less than 25% of the samples in macrophytes. This can be explained by them presenting the highest solubility and lowest Log K_{ow} of all the target compounds, so they can be more reliably found in seawater. With HMS and OC, they were detected in more than 91% of the analysed samples, while the detection frequency in seawater went below 17%. This can be explained by their high Log K_{ow} (>6.16) and poor solubility (<0.02), so they tend to accumulate in solids. MBP and DTS were barely found in seawater (<28%) and were reported in macrophytes at more than 37%. This relation can be explained by these compounds having the highest Log K_{ow} and lowest solubility of all the compounds. Hence despite their low availability in seawater, they tend to accumulate in solids. 4MBC was scarcely detected in both matrices, which can be justified by this compound having the lowest allowed maximum concentration (4%) for cosmetics in the European Union (EC, 2009).

In addition, by-products (transformation products, metabolites, photodegradation products and conjugates) should be taken into consideration. For example, BP3 (which was reported herein just in the 25% of the

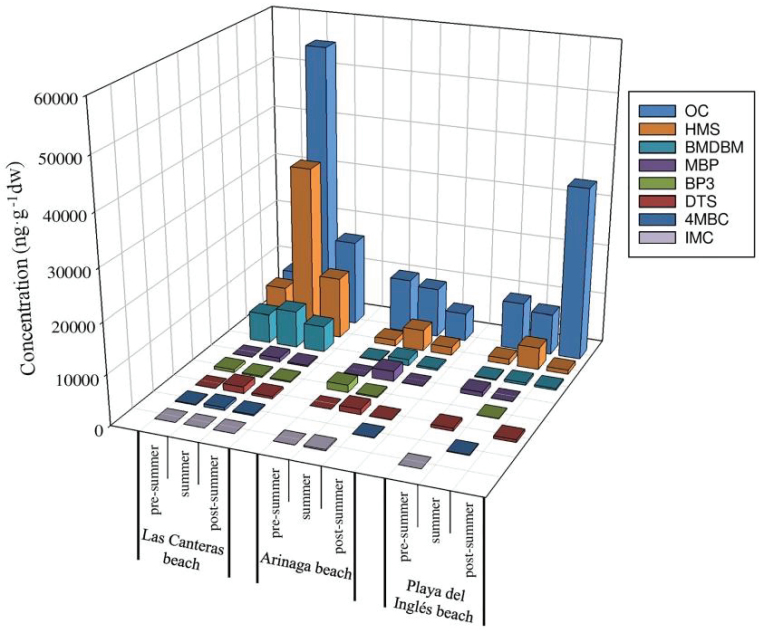

Fig. 2. Organic UV filters detected in the analysed macrophytes.

samples) was reported biodegraded by organic matter in seawater (Li et al., 2016). In fact, a recent study reported BP3 metabolites in seaweed samples (Chiriac et al., 2021). Therefore, for a more reliable approach of the target compounds concentration, their metabolites should be estimated as well as the parents.

3.4. Statistical study

A statistical analysis was performed of the grouped species (red, brown and green seaweed) collected on each beach to see the possible variation in the concentration of the target compounds depending on beach or season (pre-summer, summer, post-summer), or given the combined beach-period effect. The combined beach-period effect per seaweed type was firstly analysed. The obtained results are presented in Table S4 for the red seaweeds and in Table S5 for the brown seaweeds. The individual beach-period effects appear in Table S6A and Table S6B, respectively. Each table contains the median value of the total data, the first quartile (Q1, which is the value under which 25% of data were found) and the median of the third quartile (Q3, which is the value under which 75% of data were found).

For the red seaweeds, differences were significant for the combined beach-period effect on the concentration in BP3 ($p = 0.0155$), IMC ($p = 0.0254$) and OC ($p = 0.0378$), (Table S4). Therefore, the statistical analysis demonstrated that the concentration of the target compounds depended on beach and period. When no significance was observed in the combined beach-period effect, it meant that the statistical test did not have enough sensitivity to define differences between periods for beach or between beaches during the same period. Hence there was no evidence for any beach-period interaction. However, each factor on its own (beach or period) can show significant differences. This occurred with HMS (Table S6A), whose concentration on the Las Canteras beach was always higher than at other locations, and was also higher in summer for all the beaches.

Following the brown seaweeds statistical results, in the beach-period interaction compounds DTS ($p = 0.0046$), HMS ($p = 0.0465$) and OC ($p = 0.0048$) were significantly different (Table S5). For the brown seaweeds, the 4MBC concentration significantly differed for only period (Table S6B) and was detected only in summer. Detailed information about the p-values of each comparison are provided in the Supplementary Material. The present results suggest that the compound concentration mainly depended on the combined beach-period effect. This agrees with the fact that the three beaches presented different tourism pressures depending on the period, water removal rates and geomorphological characteristics. For these reasons, the three beaches did not display the same behaviour during the analysed periods. For example, mainly local tourists use the Las Canteras beach in summer (Sánchez Rodríguez et al., 2015), while the Playa del Inglés beach has two tourism peaks: summer with local tourists and post-summer with international tourists. According to these reasons, this agrees with the fact that compounds' concentration depends mainly on the combined beach-period effect as these factors interact.

The green seaweeds showed no significance in any compound. This can be explained by lack of data to not identify significant differences.

Given the Playa del Inglés results, and as seagrass was collected throughout the sampling period, a Kruskal-Wallis test was done with only this species. Only DTS, whose highest concentration was found in post-summer (135 $ng \cdot g^{-1}$ dw), showed a significant difference in relation to the other periods ($p < 0.0223$).

3.5. Assessment of bioconcentration ratios

The BCRs for the target pollutants were calculated using the concentrations herein obtained (expressed as $mg{\cdot}kg^{-1}$) and the data acquired for the same compounds in seawater (expressed as $mg{\cdot}L^{-1}$) (Cadena-Aizaga et al., 2021) for each seaweed and seagrass group at the same locations and times. The minimum and maximum values measured in the seawater samples were used for the BCR estimations (Table 3). The higher the BCR, the higher the concentration in seaweed in relation to seawater. The obtained BCR values indicated the grade of bioconcentration, thus is used to prove the reliability of macrophytes as bioindicators (Ismail and Ismail, 2017) (values over 1 are considered accumulation and those over 1000 indicate significant accumulation).

All the target compounds were detected in macrophytes, but some were absent in seawater. This can be explained by macrophyte uptake from their surroundings because they are exposed to the pollutant while they grew.

The maximum and minimum BCR values for the grouped seaweeds (red, brown, green) per beach are presented in Table 3. All the target compounds showed different grades of bioconcentration in all the seaweed types. This reflects that, although their availability is low in seawater, they are bioconcentrated.

Taking into account seaweed type, the BCR followed this order: green>red>brown. All the target compounds accumulated in the three analysed seaweed types, which indicates their availability in the aquatic phase.

When considering the BRC per beach, the highest values corresponded to BP3 on the Arinaga beach in the green seaweed, followed by OC on the Playa del Inglés beach and BMDBM on the Las Canteras beach in the brown seaweed (Table 3). In contrast, the highest BCR per seaweed type corresponded to BMDBM in the red seaweeds, to OC in the brown ones and BP3 in the green ones.

For the average BCR of all the seaweed types and beaches per compound, the highest values were for OC and the lowest for MBP. However, the highest BCR was calculated for OC in the seagrass *Cymodocea nodosa* on the Playa del Inglés beach.

The obtained results suggest that seaweeds greatly accumulate on all the studied beaches because the generally obtained BCRs were higher than 1000, which could increase the possibility of chronic effects on marine organisms due to biomagnification through the whole food web at the highest tropic levels (Jahan and Strezov, 2019). There was no specific pattern for organic UV filters bioconcentration, since the obtained BCR values varies according to compound, macrophyte and study area.

Seaweeds form an underwater forest that provides habitats and breeding areas for several organisms. They are also an important food source for organisms like sea urchins and gastropods. Nevertheless, the degraded biomass and released spores from seaweeds feed detritivore organisms like filter feeders and zooplankton. Hence seaweed bioaccumulation not only affects direct consumers, but also other organisms, which spells ecological concern (Wiencke and Bischof, 2012).

4. Conclusion

Macrophytes have been used as bioindicators for anthropogenic pollution in the marine environment (both organic and inorganic) because other than biomonitoring, they provide an approach to study the indirect effects

Table 3
Bioconcentration ratios for the grouped seaweeds (red, brown and green algae) and seagrass in the three beaches.[c]

Sampling place	BCR						
	Compounds	Red seaweeds		Brown seaweeds		Green seaweeds	
		min[a]	max[b]	min[a]	max[b]	min[a]	max[b]
Las Canteras beach	4MBC	–	2,954,277	–	5,091,942	–	13,549,300
	BP3	<0.0001	<0.0001	18,686,463	15,585,306	161,214,946	11,894,887
	HMS	–	70,918,586	–	90,636,320	–	204,234,061
	DTS	20,328,206	15,754,142	10,415,351	10,020,673	35,403,056	9,580,505
	OC	108,655,838	28,525,247	22,371,274	34,792,732	46,241,998	37,129,302
	BMDBM	322,935,014	4,600,285	515,874,305	41,208,303	518,339,458	4,104,916
	IMC	8,229,375	828,440	7,897,248	795,005	29,706,937	4,720,496
	MBP	–	–	–	–	–	–
Arinaga beach	4MBC	–	29,932,490	–	<0.0001	–	<0.0001
	BP3	197,072,700	117,624,342	169,868,443	72,925,641	7,207,019,289	743,950,378
	HMS	–	–	–	–	–	–
	DTS	12,331,795	907,788,921	<0.0001	<0.0001	<0.0001	<0.0001
	OC	–	–	–	–	–	–
	BMDBM		3,759,494,178		859,718,048		727,870,984
	IMC	28,957,348	395,798,243	92,954,408	56,311,111	<0.0001	<0.0001
	MBP	–	6,635,749	–	1,132,012	–	<0.0001
Playa del Inglés beach	4MBC	–	–	–	–	–	–
	BP3	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	10,673,247
	HMS	–	41,003,641		432,568,947	–	889,739,510
	DTS	–	–	–	–	–	–
	OC	–	2,187,817,967	–	2,274,016,027	–	967,550,768
	BMDBM	134,126,688	9,957,330	251,294,055	41,058,878	<0.0001	<0.0001
	IMC	<0.0001	<0.0001	60,361,334	2,261,972	<0.0001	<0.0001
	MBP	–	–	–	–	–	–
	Compounds	Seagrass					
		min[a]				max[b]	
	4MBC	–				–	
	BP3	<0.0001				<0.0001	
	HMS	–				224,728,489	
	DTS	–				–	
	OC	–				7,686,738,250	
	BMDBM	173,530,188				29,446,372	
	IMC	<0.0001				<0.0001	
	MBP	–				–	

[a] Calculated using the minimum value obtained in seaweed and seawater.
[b] Calculated using the maximum value obtained in seaweed and seawater.
[c] Indicated just for one specie in Playa del Inglés beach (*Cymopolia barbata*). The hyphen indicates that the compound was not detected in seawater, hence was not possible to calculate the ratio.

of pollutants on the complete food web. Of all the different pollutants in the marine environment, organic UV filters are becoming a cause of emerging concern as they are widely used in a variety of personal care products. Hence they are constantly released to the environment, which renders them persistent and they accumulate. Despite these pollutants having been reported in several matrices, they have not been profoundly studied in macrophytes to date.

Therefore, this study presents the assessment of using macrophytes as bioindicators of UV filter pollution. Eight widely used organic UV filters were detected at least once among the 76 studied samples, and belonged to 14 macrophyte species (both seaweeds and seagrass) on three beaches. OC was found in all the samples throughout the sampling period all the three studied beaches. The highest concentration (19,369 ng·g^{-1} dw) was for the *Cymodocea nodosa* seagrass species.

Seasonal variation was detected, despite the beaches on the Gran Canaria Island being used almost all year round. However, this variation very much depended on the seaweed species.

The detection of all the target compounds in all seaweed types (red, brow, green) suggests that they can be used as bioindicators to monitor organic UV filter pollution over time.

BP3, OC and BMDBM were related to the highest bioconcentration ratios. Although different bioconcentration ranges were found, they were generally above 1000, which indicates a significant possibility of causing chronic effects on seaweed and other organisms at upper trophic levels.

CRediT authorship contribution statement

M. Isabel Cadena-Aizaga:: Experimental part, research, writing original draft

Sarah Montesdeoca-Esponda: Reviewing, discussion of results and editing

Ángelo Santana-Del Pino: Statistical analysis, Validation

Zoraida Sosa-Ferrera: Conceptualization, supervision, discussion of results, reviewing and editing; Funding adquisition

José Juan Santana-Rodríguez: Conceptualization, supervision, discussion of results, reviewing and editing; Funding adquisition

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Zoraida Sosa-Ferrera reports financial support was provided by University of Las Palmas de Gran Canaria. Sarah Montesdeoca-Esponda reports financial support was provided by University of Las Palmas de Gran Canaria. M. Isabel Cadena-Aizaga reports financial support was provided by University of Las Palmas de Gran Canaria. Angelo Santana-Del Pino reports financial support was provided by University of Las Palmas de Gran Canaria. Jose Juan Santana-Rodriguez reports financial support was provided by University of Las Palmas de Gran Canaria.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2022.155012.

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3.2.2. Presencia y bioconcentración de filtros UV orgánicos en organismos consumidores primarios marinos

Debido a la preocupación actual sobre los filtros UV orgánicos en el medio ambiente se están realizando estudios para revelar su potencial de alteración endocrina y posibles efectos tóxicos en los organismos. Sin embargo, para realizar un seguimiento realista de sus efectos, se requieren estudios sobre las cantidades a las que están siendo expuestos tanto por el medio circundante como a través de su dieta. Para ello, los pequeños organismos marinos pueden servir como centinelas de los niveles de contaminación en ambientes marinos y sugerir el estado ambiental del medio acuático.

La contaminación en agua de mar y en macrofitas por filtros UV orgánicos, ha sido establecida en las tres playas en estudio de la isla de Gran Canaria en trabajos anteriores. Por tanto, los organismos consumidores primarios presentes en tales playas, también están expuestos a estos contaminantes a través de su dieta y desde el medioambiente, y pueden ser utilizados como centinelas de la contaminación en ambientes marinos.

Así pues, en este estudio, se realizó la determinación de los mismos analitos en organismos considerados como consumidores primarios recolectados en las mismas tres playas, con el fin de

establecer las posibles relaciones entre los distintos niveles tróficos (posible biomagnificación). Para ello, se estudiaron cinco especies diferentes de consumidores primarios marinos con varios hábitos alimenticios. Se estudiaron dos especies de caracoles (herbívoros y carnívoros), liebre de mar (herbívoros), esponja marina (filtrador) y pepino de mar (detritívoros).

Los analitos fueron extraídos usando la técnica MAE, la separación y determinación fueron realizadas por la metodología de UHPLC-MS/MS optimizada en el primer trabajo experimental. El desarrollo del método de extracción para estos organismos se llevó a cabo optimizando las variables experimentales que pueden afectar a la extracción (temperatura, tiempo de extracción, volumen y tipo de extractante) por medio de diseños factoriales. Las variables que mostraron un mayor efecto sobre la extracción fueron el volumen y tipo de disolvente. El método optimizado consiste en una extracción a 50 ºC durante 3 minutos con 5 mL de acetona.

La linealidad, los límites de detección y cuantificación del método, la precisión y la eficiencia de extracción se evaluaron bajo las condiciones óptimas de extracción. Para ello se usó como matriz una mezcla de caracoles, ya que fue el organismo más abundante durante los muestreos. Posteriormente, el método fue validado para los otros organismos (caracol carnívoro, libre de mar, pepino de mar y esponja marina). En este caso, la cuantificación de los

analitos se llevó a cabo mediante una calibración interna, la cual presentó una linealidad satisfactoria (>0.99) para todos los analitos en el rango de concentración entre 7.5 y 25 000 $ng \cdot g^{-1}$ (dw). De la aplicación de este método se obtuvieron unas eficiencias de extracción entre el 31.5 % y el 94.4 %, unos límites de detección inferiores a 7.13 $ng \cdot g^{-1}$ (dw) y una reproducibilidad (en el mismo día y entre diferentes días) expresada como la desviación estándar inferiores al 12.45%. Para el resto de los organismos se obtuvieron eficiencias de extracción similares y las concentraciones encontradas en estos organismos fueron reajustadas consecuentemente.

Los organismos analizados en este trabajo fueron muestreados durante 4 meses, en las tres playas, obteniéndose un total de 20 muestras de 5 especies diferentes. En todas las muestras se detectó al menos uno de los filtros UV orgánico analizados, además de ser detectados todos ellos al menos una vez. Las frecuencias de detección variaron entre 10 % y 55 %. Los compuestos con la frecuencia de detección más alta fueron el BMDBM (55 %) y el OC (40 %), con rangos de concentraciones entre 9.74 a 88.2 $ng \cdot g^{-1}$ (dw) y de 33.1 a 1 735 $ng \cdot g^{-1}$ (dw), respectivamente. Las concentraciones más altas obtenidas correspondieron a OC (1 735 $ng \cdot g^{-1}$, dw) en la liebre de mar (*Aplysia dactylomela*) y a HMS (1 113 $ng \cdot g^{-1}$, dw) en el pepino de mar (*Holothuria santori*).

La alta concentración encontrada para OC puede explicarse porque este compuesto no es fácilmente biodegradable (apartado 1.2.2.). Tiene un alto Log K_{ow} y baja solubilidad, lo que puede contribuir a su bioacumulación. Además, se usa ampliamente en formulaciones de PCP y está permitido en todos los países. Por el contrario, la baja frecuencia de detección de la BP3 (5 %) en los organismos marinos podría explicarse porque tiene el Log K_{ow} más bajo y la solubilidad más alta de todos los compuestos estudiados.

Teniendo en cuenta las concentraciones encontradas en caracoles (*Phorcus atratus*) en todas las playas y para todos los contaminantes, en Playa del Inglés se obtuvieron las concentraciones más altas, seguido de la playa de Las Canteras y por último la playa de Arinaga.

Comparando los resultados obtenidos en este trabajo para consumidores primarios marinos con los encontrados para muestras de agua de mar y macrofitas de las mismas playas, se observa que, en los tres estudios, el OC tuvo las concentraciones más altas tanto en agua de mar, como en macrófitos y en los consumidores primarios marinos. En cuanto a la frecuencia de detección en las tres matrices, se observó que BMDBM, HMS y OC fueron los compuestos más comúnmente encontrados en consumidores primarios marinos y macrofitas, mientras que se detectaron en menos del 56 % de las muestras en agua de mar. Por el contrario,

los compuestos BP3 e IMC, se detectaron en más del 78 % de las muestras de agua de mar, pero este porcentaje baja hasta el 25 % en las muestras de los organismos analizados.

Por último, se realizó una evaluación preliminar de los factores de bioconcentración (BCF) y bioacumulación (BMF) en los organismos consumidores analizados, para ello se usaron las concentraciones obtenidas en agua de mar y macroalgas en las mismas playas. Cuando el valor de BCF de un compuesto es superior a 5 000 o su logaritmo mayor a 3.7, se considera como muy acumulativo. Por otro lado, valores superiores a 1 de BMF sugieren biomagnificación.

Se calculó el BCF utilizando el valores mínimos y máximos de los compuestos seleccionados en agua de mar, y en cada organismo. Para el cálculo de BMF, los valores mínimos y máximos empleados se basaron en las concentraciones obtenidas de los analitos objetivo de las posibles especies de algas consumidas por caracoles (*Phorcus atratus*) y liebre de mar (*Aplysia dactylomela*).

El resultado del Log BCF fue superior a 3.7 para todos los compuestos en los que se pudo calcular este factor, lo que sugiriere una posible bioacumulación en estos consumidores primarios marinos.

Respecto al factor BMF, solo para los compuestos 4MBC y DTS se obtuvieron valores superiores a 1 en los caracoles (*Phorcus atratus*), lo que indica una posible biomagnificación en niveles tróficos superiores. Para el resto de los analitos, los valores obtenidos fueron inferiores a 1.

De los estudios realizados podemos concluir que, la presencia de filtros UV orgánicos en los consumidores primarios marinos analizados se puede atribuir a la absorción por la exposición al entorno, y por la ingesta de alimentos que contienen estos contaminantes.

Este trabajo fue publicado en la revista *Microchemical Journal* en el año 2022, la cual está dedicada a publicar investigaciones sobre Química Analítica. Esto incluye aspectos fundamentales, en instrumentación, nuevos desarrollos de métodos y aplicaciones innovadoras y novedosas, incluido el medio ambiente. Esta revista se ha encontrado en el primer cuartil del área *Analytical Chemistry*, posición que ha mantenido en los últimos 5 años de los que se han publicado métricas, con un factor de impacto entre 2.867 y 5.304 según *Journal Citation Reports*.

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Occurrence and bioconcentration of organic UV filters in primary marine consumers

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ABSTRACT

Organic ultraviolet (UV) filters are added in different products to absorb UV radiation, whose use has been voiced due to increasing concerning about skin damage. Given their extensive production, these compounds are continuously released to the aquatic environment, which makes them an important family of emerging pollutants. Their presence in the marine environment poses a hazard to the living organisms exposed to them.

Primary marine consumers can be recognised as sentinels of pollution in marine environments. In this study, the occurrence of eight widely used organic UV filters was analysed in five different primary marine consumers from three beaches on the Gran Canaria Island (Spain) collected for 4 months. For that, a new method, based on microwave-assisted extraction and ultrahigh-performance liquid chromatography coupled to mass spectrometry in tandem, was optimized and validate. The developed method presented detection limits between 0.7 ng·g^{-1} dry weight (dw) and 7.1 ng·g^{-1} dw and intraday and interday precision with ranges from 0.2 % to 9.9 % and from 1.9 % to 12.4 %, respectively.

The method was applied to 20 samples comprising five different types of organisms. All the analysed samples revealed the presence of organic UV filters, in all samples at least one analyte was determined. The highest detection frequency corresponded to butyl methoxydibenzoylmethane (BMDBM) (55 %), while octocrylene (OC) was found at the highest concentration (1,735 ng·g^{-1} dw) in the sea hare *Aplysia dactylomela*.

At the same time, a preliminary bioconcentration and biomagnification assessment was made for the UV filters found in the studied marine organisms. Bioconcentration factors (Log values) over 3.7 were obtained in some cases, which suggests possible bioaccumulation. 4-methylbenzylidene camphor (4MBC) and drometrizole trisiloxane (DTS) obtained a biomagnification factor over 1, which implies potential biomagnification for these compounds.

1. Introduction

The use of organic ultraviolet (UV) filters has increased in the last century because of awareness of sun radiation effects on skin. These compounds are mainly added in personal care products (PCPs), but are also used for other purposes, such as food packaging, paints, textiles, industrial goods, etc. [1]. Given their extensive use, they are continuously released to terrestrial [2] and aquatic environments [2,3].

Organic UV filters enter marine aquatic media via two pathways; direct input, which takes place from being washed off from skin during recreational activities; indirect input, associated with the release of wastewater outfall and river discharge [2] (Fig. 1). Because of their uninterrupted input to the aquatic environment, they are considered an important group of emerging pollutants. Therefore, biota is continuously exposed to organic UV filters. The inputs to the marine environment are presented in Fig. 1. In fact several studies have already reported their presence in different organisms [3,4].

Research into hazardous effects on marine species have increased in the last decade [5,6]. Some studies suggest adverse effects on different marine organisms for short exposures to organic UV filters, such as coral bleaching, mortality, endocrine disruption or diminished reproduction [5,6]. Given these adverse effects, Hawaii, the Republic of Palau and the US Virgin Islands have banned the use of benzophenone-3 (BP3) and octocrylene (OC), while the European Union has lowered the BP3 concentration allowed in cosmetics [7]. Nevertheless, long-term effects could result in greater damage to the marine biota besides the

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biomagnification effect of xenobiotics [8]. Coastal species are especially subjected to the anthropogenic impact [9].

The study of the occurrence of organic UV filters has focused mostly on fish [2] due to the concern of them reaching humans beings [5]. However, small organisms may be more likely affected by the presence of these compounds [6]. Higher concentrations of organic UV filters have been reported in the marine biota than in the fresh biota. Hence it is important to determine their presence and possible associated negative impacts on marine species [8].

In aquatic organisms, the potential uptake mechanisms of contaminants can follow two pathways. The direct uptake consists in passive absorption from the environment to exposed surfaces of organisms (*i.e.* respiratory and dermal surfaces). The indirect uptake is related to diet [10]. Direct absorption involves bioconcentration and indirect absorption entails biomagnification processes [11]. Approaches to estimate these mechanisms are important for reducing the uncertainty about the hazards and risks that those compounds pose to organisms.

In this context, primary marine consumers can be recognised as sentinels of pollution in marine environments. Thus, the aims of this work were, on the one hand, to develop a new method based on microwave-assisted extraction and ultrahigh-performance liquid chromatography coupled to mass spectrometry in tandem for the determination of eight organic UV filters in different species of primary marine consumers, and on the other hand, make a preliminary assessment of their possible bioconcentration and biomagnification through the trophic chain.

This study included five different species of primary marine consumers (two sea snails, the detritivore sea cucumber, an algae feeder sea hare, and the filtering sponge), which were recovered on three beaches of the Gran Canaria Island (Canary Islands) with different tourism pressures and characteristics.

The Gran Canaria Island (Spain) was selected as an interesting study site because of the many visitors that arrive there all year long. Moreover, previous studies have determined the target compounds in seawater [12], sediment [13] and macrophytes [14] from the beaches included in this work. Some of these compounds were also found in fish from Canary Islands [15], however, for the best of our knowledge, primary consumers from this region have not been investigated regarding the presence of organic UV filters. Since there is no available information about the levels of organic UV filter contaminations in this type of organisms, this work represents an opportunity to estimate bioconcentration processes for first time.

Given the detection of organic UV filters in different matrices, it is important to determine them in primary marine organisms to identify possible accumulation through the food web. In this sense, the extraction method developed in this work can be used to determine the anthropogenic pollution of organic UV filters of a wide range of physicochemical characteristic, in primary marine consumers.

2. Materials and methods

2.1. Reagents

Eight organic UV filters, namely homosalate (HMS), 4-methylbenzylidene camphor (4MBC), benzophenone-3 (BP3), drometrizole trisiloxane (DTS), octocrylene (OC), butyl methoxydibenzoylmethane (BMDBM), isoamyl p-methoxicinnamate (IMC) and methylene bisbenzotriazolyltetramethylbutylphenol (MBP) of analytical grade (purity $\geq$ 99 %), were purchased from Sigma-Aldrich (Madrid, Spain). Panreac Química (Barcelona, Spain) supplied methanol (MeOH), acetone, hexane (Hex), water and formic acid of LC-MS grade.

The stock solution of the target compounds (250 $mg{\cdot}L^{-1}$) was prepared in acetone and stored in amber glass bottles in a freezer until used. Working solutions were prepared daily in MeOH.

2.2. Study area, sample collection and pretreatment

The samples of organisms to be analysed were collected from three beaches on the Gran Canaria Island (Canary Islands, Spain), namely Las Canteras, Arinaga and Playa del Inglés.

Las Canteras beach is located in the northeast part of the Gran Canaria Island (28°8′27.982″N, 15°26′8.237″W), and is characterised by the presence of a rocky-sandy substratum [16] and a natural barrier that runs in parallel to its coast. This leads to lower water renovation at low tide because of almost no wave action [17], which might affect the local fauna due to the long residence time of pollutants. This beach is used mainly by locals, but also by foreigners, almost all year long, although the most intense tourism activity takes place in summer.

The Arinaga beach lies in the southeast part of the Gran Canaria Island (28°8′27.982″N, 15°26′8.237″W). It is an open beach characterised by the intense influence of wind and swell because of Trade winds and the Canary Current effect [18], which implies easy water renewal. It is

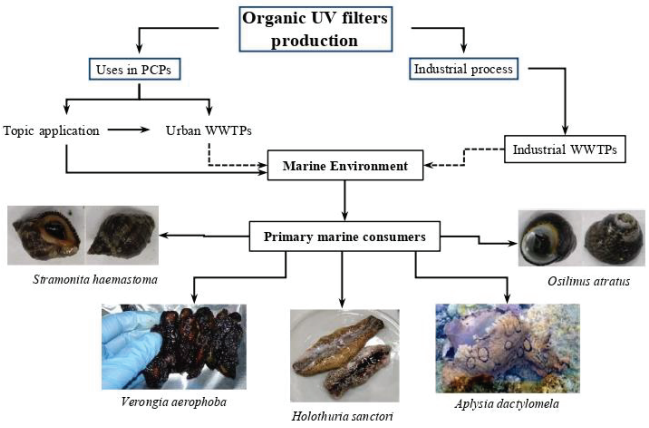

Fig. 1. Direct and indirect inputs to the marine environment. Indirect inputs are denoted by the dotted line.

used principally by locals, and scarcely by foreigners. This beach also presents a rocky-sandy substratum [16].

The Playa del Inglés beach is situated to the south of the Gran Canaria Island (27°45′23.579″N, 15°33′51.2809″W). This is an open beach with artificial barriers where the effect of Trade winds and the Canary Current is milder [18]. It is a quiet zone with a light swell that also presents a sandy substratum [16]. This beach is used all year round by international tourists, essentially northern Europeans in winter and national tourists in summer, according to the Gran Canaria Tourism Agency [19].

Primary marine consumers of five different species were taken monthly from October 2019 to January 2020. These organisms correspond to two sea snails, the herbivore *Phorcus atratus* (previously identified as *Osilinus atratus*) and the carnivorous *Stramonita haemastoma*, the detritivore sea cucumber (*Holothuria sanctori*), the algae feeder sea hare (*Aplysia dactylomela*), and the filtering sponge (*Aplysina aerophoba* that has been previously identified as *Verongia aerophoba*). This study examined 20 samples from the different organisms.

In order to compare the presence of organic UV filters between the different locations, sea snails (*Phorcus atratus*) of a similar size (1.8 – 2.9 cm length) were collected during the 4-month period at the three studied beaches in the rocky zone at low tide. On the Las Canteras beach, only *Phorcus atratus* was collected, while the two sea snail types (*Phorcus atratus* and *Stramonita haemastoma*) were collected on Playa del Inglés. On the Arinaga beach, four species were collected: *Phorcus atratus*, the sea cucumber, the sea hare, and the sponge. These organisms were collected at low tide, and only the organisms washed ashore were picked up. Therefore, different species were collected during each sampling.

After collection, samples were transported to the laboratory in glass bottles in a portable fridge. Upon arrival, they were rinsed with deionised water to remove sand and salt. The cleaned organisms were then identified, measured and frozen at –20 °C to be subjected to freeze-drying. The flesh of sea snails was separated from shells before the freeze-drying, while the whole body of the other organisms (sea cucumber, sea hare and sponge) was used. To obtain a homogenous sample, the freeze-dried tissues of each species were sifted through a < 300 μm particle size and stored in a fridge in the dark until analysed.

2.3. Preparing spiked samples and MAE extraction

The sea snail *Phorcus atratus* was employed for extraction optimisation purposes because this species was present on all the sampled beaches throughout the sampling period. The batch sample was spiked with a mixture of the target compounds, stirred, and air-dried at room temperature in the dark for 24 h to obtain a homogeneous dry sample.

One hundred milligrams of the spiked mixture were transferred to MAE vessels and 5 mL of acetone were added as an extractant. Then vessels were closed and sonicated for 2 min to homogenise the sample and extractant. The MAE process consisted in applying 50 °C for 3 min. Having completed extraction, the extract was carefully filtered through a 0.2 μm syringe filter. Then the filtered extract was transferred to LC vials and 10 μL was injected.

2.4. Instrumental analysis

Organic UV filters extraction was carried out in a Titan MPS microwave oven equipped with 16 TFM vessels (Perkin Elmer, Madrid, Spain).

Determination was performed by an ACQUITY UHPLC system equipped with a binary solvent manager, a thermostated autosampler, a BEH C18 column (50 × 2.1 mm, 1.7 μm particle size) and a tandem triple quadrupole mass spectrometer detector (MS/MS) with electrospray ionisation (ESI). The MassLynx Mass Spectrometry software (Waters Chromatography, Barcelona, Spain) controlled all the components.

Chromatographic conditions were previously optimised [12]. Briefly, the mobile phase consisted of MeOH (A) and water (B) LC-MS grade, each with 0.1 % (*v*/*v*) formic acid, at a flow rate of 0.3 $mL{\cdot}min^{-1}$. Detailed information about the mass conditions is reported in the Supplementary Material (Table S1).

2.5. Bioconcentration and biomagnification calculation

The bioconcentration factor (BCF) is calculated as the ratio between the pollutant concentration detected in the organisms and the pollutant concentration in the surrounding environment using the following formula [20]:

$$BCF = \frac{C_{organisms}}{C_{water}}$$

where $C_{organisms}$ is the concentration of the pollutant found in this study for the different target organisms (expressed as $mg{\cdot}kg^{-1}$ dry weight, dw) and C_{water} is the concentration (expressed as $mg{\cdot}L^{-1}$) measured in the seawater on the same beaches [12]. According to the European Commission, a substance is considered "very bioaccumulative" when the BCF is higher than 5,000 or Log BCF > 3.7 [20].

The bioaccumulation factor (BMF) is calculated as the ratio of the contaminant in the consumer to its concentration in food or prey by the following formula [21]:

$$BMF = \frac{C_{consumer}}{C_{food}}$$

where $C_{consumer}$ is the concentration (expressed as $ng{\cdot}g^{-1}$ dw) of the pollutant found in this study for the target marine organisms and C_{food} is the concentration in the consumer food (expressed as $ng{\cdot}g^{-1}$ dw) [22], taken from the data acquired for the same compounds in the seaweeds on the same beaches [14]. A BMF above 1 suggests the biomagnification of the contaminant from lower trophic chain levels [4,21].

3. Results and discussion

3.1. Microwave-assisted extraction

The impacts of temperature, extraction time, extractant volume and solvent type on the extraction efficiency of the target analytes were assessed with a 2^4 experimental design (four variables at two levels) built with the MiniTab software as a first approach. This consisted in 16 runs that combined temperatures at 50 °C and 60 °C; extraction time at 3 and 6 min; extractant volume at 2.5 and 5 mL; MeOH and acetone as extractants. With the obtained results, a Pareto Chart analysis was performed to see which variables affected extraction the most. They are denoted in blue in Fig. 2 for IMC. The variables showing the strongest effect were extractant volume and solvent type. Acetone performed better recoveries than MeOH for five compounds. The correlations between the variables were also analysed by Pearson's coefficient (0 means no influence; –1 is the maximum negative effect; 1 represents the maximum positive effect). The extractant volume obtained the highest values, with positive correlations between 0.1 and 0.7 for all the compounds, while temperature presented a negative correlation (except for BP3), which varied between –0.6 and –0.3. The lowest correlation was for the extraction time (from –0.3 to –0.1). The positive effect on the extractant volume means that the higher the volume, the more positive the influence on recoveries. The negative effect on both temperature and extraction time means that the higher the temperature and the longer the time, the more negative the influence on recoveries. For this reason, temperature was set at 50 °C and the extraction time was 3 min. Therefore, extractant type and volume were analysed in more depth.

In a second stage, a 3^2 factorial design (two variables at three levels) was applied with the aforementioned fixed variables. The two-target variables, namely extractant volume (5, 7.5 and 10 mL) and solvent type (acetone, hexane and MeOH), were studied. The best recoveries were obtained with 5 mL of acetone. As an example of the general observed trend, the surface response obtained for the DTS compound

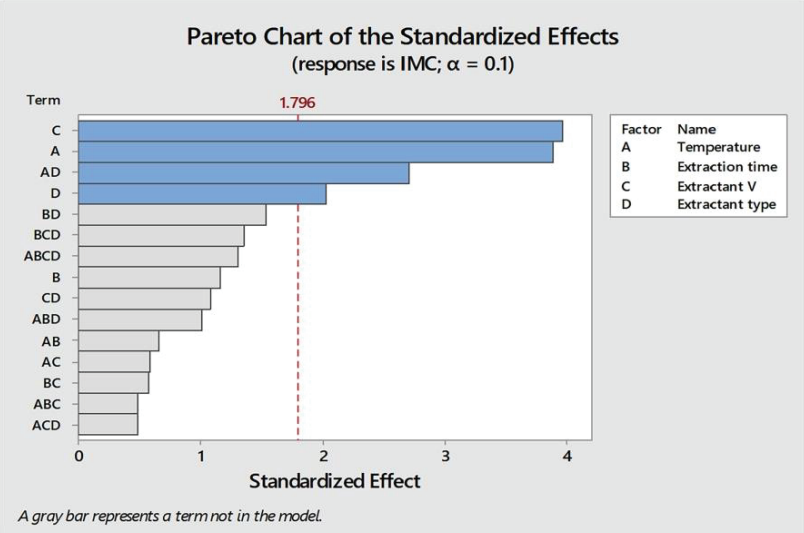

Fig. 2. Pareto chart of the standardised effects for the factors studied in the 2^4 experimental design on compound IMC.

from this design is shown in Fig. 3.

Therefore, the optimised conditions were: 5 mL of acetone as the extractant by applying 50 °C for 3 min.

3.2. Quality assurance and method validation

The linearity, method limits of detection (MLODs), method limits of quantification (MLOQs), precision and extraction efficiencies were evaluated under the optimum extraction conditions for the batch of sea

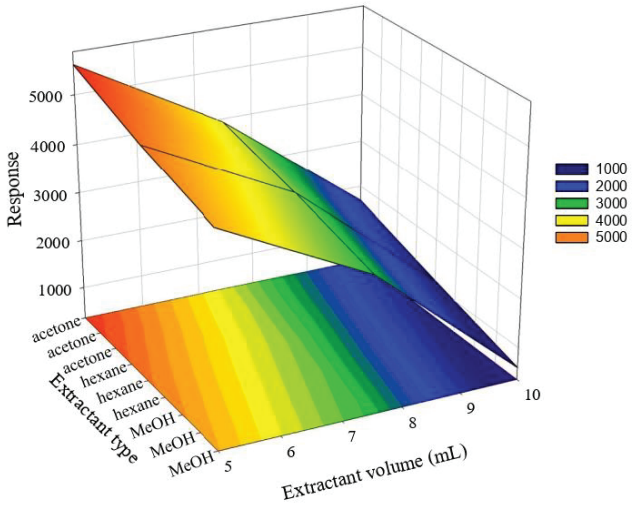

Fig. 3. Response surface for the effect of the extractant volume and type in compound DTS.

snails (*Phorcus atratus*). Each value corresponded to the mean of three replicates.

Calibration curves were built by means of the matrix matched calibration method at eight concentration levels of a mixture of the target compounds within the range from 7.5 ng·g^{-1} dw to 25,000 ng·g^{-1} dw. The linear correlation coefficient obtained for each compound within this range was > 0.99.

MLODs and MLOQs were calculated from the signal-to-noise (S/N) of each compound by assuming a minimum detectable limit of 3 and 10-fold the S/N, respectively. MLODs ranged between 0.7 ng·g^{-1} dw and 7.1 ng·g^{-1} dw, while MLOQs varied from 2.3 ng·g^{-1} dw to 23.8 ng·g^{-1} dw (Table 1).

The precision and extraction efficiencies were calculated at three concentrations levels (37.5, 250, 1,250 ng·g^{-1} dw) by comparing the signal from the standard solution to those obtained after applying the complete extraction method to the spiked samples.

The intraday (n = 3) and interday (k = 3) precisions of the developed method were estimated as relative standard deviation (RSD, %), which ranged from 0.2 % to 9.9 % and from 1.9 % to 12.4 %, respectively (Table 1).

Extraction efficiencies fell within the range from 31 % to 94 % (Table 1). The optimised method was validated for the other organisms. It gave similar recoveries and concentrations were adjusted to each obtained efficiency.

3.3. Environmental occurrence of organic UV filters in primary marine consumers

The developed analytical method was applied to determine the target analytes in five species of primary marine consumers and comprised 20 samples taken from three beaches of the Gran Canaria Island for 4 months. The measured concentrations and detection frequencies are summarised and presented in Table S2.

At least one compound was identified in each analysed marine organism (Fig. 4). Seven compounds presented detection frequencies between 10 % and 55 %, while BP3 was detected in only one sample. BMDBM (55 %) and OC (40 %) were the most frequently detected compounds, and fell within concentration ranges from 9.7 to 88.2 ng·g^{-1} dw and from 33.1 to 1,735 ng·g^{-1} dw, respectively. The highest detected concentrations corresponded to OC (1,735 ng·g^{-1} dw) in sea hare (*Aplysia dactylomela*) and to HMS (1,113 ng·g^{-1} dw) in sea cucumber (*Holothuria sanctori*).

The scarce detection frequency of BP3 in the marine organisms could be due to its lowest octanol–water coefficient (Log K_{ow}) value and the greatest water solubility among the target compounds (Table S1). This compound is considered readily biodegradable [23]. BP3 was found in a degraded state in the seawater enriched with dissolved organic matter [24] and some ligands [25]. Furthermore based on the Log K_{ow} approach, a passively partition according to their chemical affinity was assumed that did not take into account the metabolic biotransformation of organisms [26]. For example, BP3 can be degraded by microalgae into less toxic intermediates, which has been reported for *Scenedesmus obliquus* in freshwater [27]. However, BP3 has not been detected in a freshwater mussel (*Dreissena polymorpha*), which did accumulate other organic UV filters [28]. This falls in line with the scarce detection of BP3 in this study, which also agrees with its low bioaccumulation reported in the marine mussel *Mytilus galloprovincialis* [26].

The highest found concentration for OC can be explained by this compound being considered not easily biodegradable [23]. It had a high Log K_{ow} and low solubility (Table S1), which contribute to its bioaccumulation. This compound is extensively used in PCPs formulations [29] and is allowed in all countries [30,31]. The high OC concentration herein detected agrees with the found marine mussels *Mytilus galloprovincialis*, for which rapid uptake and a low depuration rate have been reported [26]. Nevertheless, the concentration of lipophilic compounds can be underestimated due to biotransformation products, as demonstrated for OC in marine corals [32] and a marine sediment worm species [33] for being transformed into fatty acid conjugates. Hence the actual accumulation of some compounds in the food web could be greater.

According to the concentrations found per location, on the Las Canteras beach BMDBM was the only target compound detected in all the samples (Table S2), which also presented the highest concentration (61.8 ng·g^{-1} dw). OC was present in 50 % of the samples and also at a high concentration (43.7 ng·g^{-1} dw) for *Phorcus atratus*. On the Arinaga Beach, almost all the compounds were reported, except MBP. OC (1,735 ng·g^{-1} dw) and HMS (1,113 ng·g^{-1} dw) had the highest concentrations for *Aplysia dactylomela* and *Holothuria sanctori*, respectively. Finally on the Playa Inglés beach, BMDBM was present in 50 % of the samples. On this beach HMS was measured at the highest concentration (1,003 ng·g^{-1} dw) for *Stramonita haemastoma*.

Taking into account the concentrations found in *Phorcus atratus* on all the beaches, Playa del Inglés was the location most contaminated by the target compounds, where the cumulative concentration of all the pollutants was 1,085 ng·g^{-1} dw, followed by the Las Canteras beach (260 ng·g^{-1} dw) and the Arinaga beach (248 ng·g^{-1} dw).

After considering the presence of the target analytes in all studied primary marine consumers, Playa del Inglés obtained the most contaminants (Fig. 4). In addition, the maximum concentrations appeared in the largest organisms (*i.e.* sea hare and sea cucumber), and also in the carnivorous sea snail (*Stramonita haemastoma*). These variations in the measured concentrations might be related to the potential species-specific differences in the uptake, accumulation, metabolism [4,34] and depuration rates [26] of the different marine organisms.

The results obtained in this work for primary marine consumers were compared to those found in previous studies for seawater [12] and

Table 1
Analytical parameters for the MAE-UHPLC-MS/MS method (concentrations expressed in dw).

Compounds	Intra-day precision (%)[a]			Inter-day precision (%)[b]			Recoveries (%)[c]			MLODs[d]	MLOQs[e]
	37.5 ng·g^{-1}	250 ng·g^{-1}	1250 ng·g^{-1}	37.5 ng·g^{-1}	250 ng·g^{-1}	1250 ng·g^{-1}	37.5 ng·g^{-1}	250 ng·g^{-1}	1250 ng·g^{-1}	ng·g^{-1}	ng·g^{-1}
4MBC	–	6.7	5.2	–	12.4	8.1	–	89	94	7.1	23.8
BP3	9.5	2.0	5.1	10.2	6.9	6.3	41	52	63	1.1	3.7
HMS	5.6	4.8	3.9	10.6	8.2	6.8	43	52	80	1.8	6.0
DTS	9.9	8.1	0.9	11.7	9.5	9.1	31	41	51	1.3	4.4
OC	9.3	5.7	1.0	9.8	5.2	1.9	65	68	93	1.9	6.3
BMDBM	3.6	3.1	0.2	5.2	6.0	4.8	84	88	91	1.4	4.6
IMC	5.2	4.8	1.9	11.5	8.5	8.7	59	62	73	0.7	2.3
MBP	–	6.1	4.9	–	10.4	9.5	–	64	82	7.0	23.3

[a] Mean of three replicates (n = 3).
[b] Mean of three replicates performed for three days (k = 3).
[c] Extraction efficiencies using *Phorcus atratus*.
[d] Calculated from the signal to noise (S/N) assuming a minimum detectable limit of three times the S/N.
[e] Calculated from the S/N assuming a minimum detectable limit of ten times the S/N.

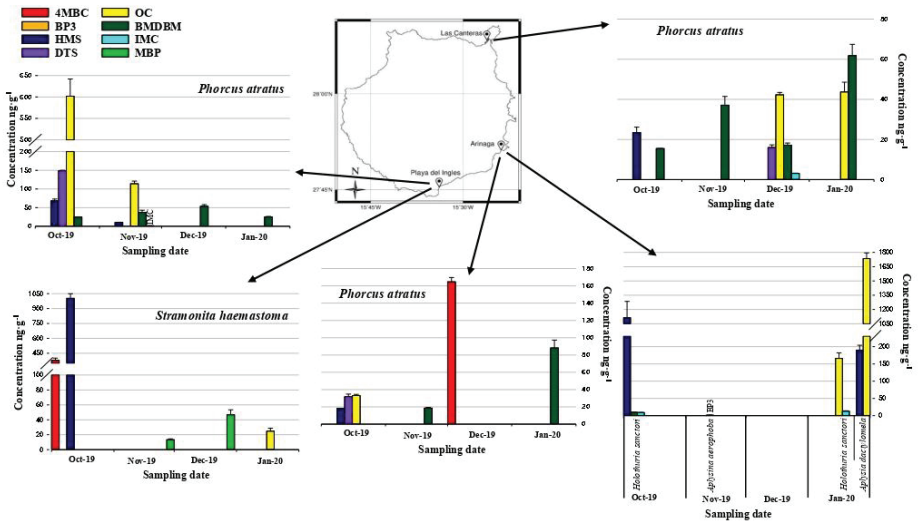

Fig. 4. Occurrence of organic UV filters in primary marine consumers from selected locations.

macrophytes samples [14] from the same beaches. In three studies, OC had the highest concentrations (172 $\mu g \cdot L^{-1}$ in seawater, 19,369 $ng \cdot g^{-1}$ dw in macrophytes and 1,735 $ng \cdot g^{-1}$ dw in primary marine consumers). According to the overall detection frequency in the three matrices, a tendency was observed: BMDBM, HMS and OC were the most commonly found compounds in primary marine consumers and macrophytes, while they were detected in<56 % of the samples in seawater. This can be explained by their high Log K_{ow} (>4.5) and poor solubility (<0.04) that, therefore, allow these compounds to be more easily distributed in solid matrices. The comparison of the concentrations found in this study to those reported in seawater demonstrated accumulation in solid matrices.

Otherwise in compounds BP3 and IMC, a contrary trend in their frequencies appeared because they were detected in over 78 % of the seawater samples, but this percentage was below 25 % in the organism samples. Such behaviour can be explained because these compounds presented the highest solubility and the lowest Log K_{ow} (Table S1) of the target compounds.

The detection of the target compounds in macrophytes and marine animals and their concentration levels indicated that these organisms could be used as bioindicators of organic UV filters contamination in coastal areas.

3.4. Global comparison

Organic UV filters have been registered in aquatic systems since the early 1980 s, but mainly in freshwater environments [35]. However, high concentrations are presently reported in marine ecosystems as a consequence of recreational activities and wastewater release to these media [3]. As all the target compounds were detected at least once in the different analysed primary marine consumers (Table S2), these concentrations will be discussed in relation to other wild primary marine organisms.

In this study, OC was detected at concentrations up to 1,735 $ng \cdot g^{-1}$ dw in sea hare. This level is comparable to those found for mussel on the French Mediterranean coast [36] and in coral in Hawaii [37], where samples were collected in areas impacted by human activities. This compound has been analysed in several mussel species, mainly from European countries by measuring concentrations generally within the 1.4 – 3,992 $ng \cdot g^{-1}$ dw range [8,29,35,38–42]. However in the study of Bachelot et al. [35], OC is reported in mussels from the French coast at a higher concentration (7,112 $ng \cdot g^{-1}$ dw) in August. Furthermore, OC has been reported in other organisms like clams, conchs, shrimps, sea urchin, oysters [8,29,38,43], corals [34], crabs [44] and squids [21] from Spain, China, Norway, and the USA.

The values of the HMS concentrations found in this study were also high (1,113 $ng \cdot g^{-1}$ dw), which is higher than those reported for oysters (56.1 – 211 $ng \cdot g^{-1}$ dw) [38,43] collected in the USA. This compound has also been detected in mussels and corals from different European countries, Hawaii and the USA within the range from 24.2 to 611.2 $ng \cdot g^{-1}$ dw [37,38,42].

The same case occurred for 4MBC. The concentrations reported in this study (165 – 379 $ng \cdot g^{-1}$ dw) are higher than those indicated for sea snails (whelk), mussels, clams, conchs, shrimps, sea urchins, octopus and crabs (0.2 – 102 $ng \cdot g^{-1}$ dw) from China and other European countries [8,40,42,45,46]. 4MBC has also been reported in squids, prawns, shrimps and crabs [21] from China within the 2 – 38.9 $ng \cdot g^{-1}$ lw range.

BMDBM was detected within the concentration 9.7 – 88.2 $ng \cdot g^{-1}$ dw range, which is lower than those reported for corals in Hawaii (4.8 – 291.3 $ng \cdot g^{-1}$ dw) [37]. This compound has also been found in stone crabs at 21 $ng \cdot g^{-1}$ lw from China [21].

Compound IMC was detected at concentrations from 1.5 to 12.8 $ng \cdot g^{-1}$ dw. Higher concentrations have been observed for mussels from Portugal (43.1 $ng \cdot g^{-1}$ dw) [46] and of other European origins (37.3 $ng \cdot g^{-1}$ dw) [42].

BP3 was detected only once in sponge (*Aplysina aerophoba*) in this study, but it could not be not quantified. It has also gone undetected in mussels from Spanish and Italian coasts [29]. Nevertheless, this compound has been quantified in several marine organisms [3] from

different places around the world, even in Antarctic clams (at 112 ng·g^{-1} dw) [47]. In mollusc bivalves (mussels, oysters, clams, conchs), levels of 0.9 – 622.1 ng·g^{-1} dw have been reported from China [8], the USA [38,43] and some European countries [40,42,46]. In echinoderms (sea cucumber and sea urchin), it has been recorded in the Antarctic [47], China [8] and Spain [48]. BP3 has been reported in arthropods (shrimps and Squilla) [8,42,45] and in cephalopods (squids) [45] from Europe and China. This compound has also been reported in corals from Hawaii [37], and in shrimps, crabs and corals [34,44] from Norway and China. The study of Peng et al. [21] has reported BP3 in squids, prawns, shrimps and crabs from China.

Finally, MBP was found in two samples in this study, at 13.3 and 46.7 ng·g^{-1} dw, and has not been reported in other primary marine consumers, only in fish [13,49].

In summary, organic UV filters have been reported in many primary marine consumers worldwide, and seem to accumulate by following similar patterns to polychlorinated biphenyls [50], which persist in the environment [51] and potentially reach upper trophic levels, such as marine mammals [52] and marine birds [28]. Rodil et al. [40] reported greater abundance for some organic UV filters than polycyclic aromatic hydrocarbons in mussels from Spain.

Transformation products, metabolites, photodegradation products and disinfection by-products should be determined because the biological process may be stereoselective (preferential accumulation for one structural form over others) [4], as suggested for 4MBC in lake fish [53]. Therefore, to reliably estimate organic UV filter bioavailability, bioaccumulation and biomagnification through the food web, these products should be taken into account [4].

A recent study has reported BP3 biodegradation products in seawater, sediment and two green seaweeds, and some have been detected in 100 % samples [54]. Nevertheless, depuration rates, metabolism, and excretion of organic UV filters for marine organisms are scarcely reported. The study by Cleargeaud et al. [33] suggests that the determination of only parent organic UV filters may underestimate the real exposure of organisms to xenobiotics and their metabolites. Further studies should be conducted in this field because some organic UV filters show similar toxicity to trace metals, such as copper, mercury, cadmium and zinc, and can reach different marine organisms [55].

3.5. Preliminary bioconcentration and biomagnification assessment

The presence of organic UV filters in previous studies in seaweed and seawater suggests that marine organisms may be exposed to these pollutants through diet and from the environment. A preliminary assessment of their possible bioconcentration and biomagnification in different organisms was performed with the concentrations that we obtained and those found before in seaweed [14] and seawater [12] on the same beaches. To do so, BCF was calculated using the minimum and maximum values of the target compounds in not only seawater, but also in each organism. For the BMF, the employed minimum and the maximum values were based on the possible seaweed species subjected to be eaten by *Phorcus atratus* [56] and *Aplysia dactylomela* [57–59]. The Log BCF and BMF results are summarised in Table 2.

The Log BCFs of all the found organic UV filters were above 3.7 (Table 2), which suggests bioaccumulation in the analysed primary marine consumers. The maximum BCF value was calculated for BMDBM on the Arinaga beach (Log BCF 8.6) for *Phorcus atratus*. The OC values are comparable to those reported in Hawaii for coral (Log BCF 3.4 – 6.1) [37], but higher than those reported in China (Log BCF 2.2 – 3.0) for coral [34] and mussels [26].

Lack of BP3 in marine organisms is explained because it can be eliminated by organisms, as Vidal-Liñá et al. [26] reported a quick elimination from mussels. Peng et al. [21] stated that this compound was not bioaccumulative because the concentration in carnivorous fish was lower than in detritivores ones. Nevertheless, BP3 accumulation has been reported in sea cucumber (*Holothuria tubulosa*) [48].

Regarding the BMF, only 4MBC and DTS obtained values above 1 for *Phorcus atratus*, which indicates possible biomagnification. The high BMF reported for 4MBC falls in line with the findings of benzophenone-4 in mussels, whose bioaccumulation was much greater than that predicted from its Log K_{ow} [26]. In addition, OC and HMS presented the lowest BMF (<0.3). Peng et al. [21] reported a BMF above 1 for OC in some marine organisms from the Pearl River (China). This difference could be attributed to the tendency of OC to form OC-fatty acids conjugated in some organisms, as previously mentioned.

The fate of organic UV filters at high trophic levels has been barely reported [9]. A study by Alonso et al. [60] found a higher concentration of organic UV filters and insecticides in a dolphin foetus than in the mother. Organic UV filters were found at higher concentrations than insecticides. These results suggest biomagnification at high trophic levels in the marine food web.

4. Conclusions

An analytical MAE-UHPLC-MS/MS method was successfully developed, validate, and applied to determine eight organic UV filters in five different primary marine consumers.

The highest concentration level was for OC (1,735 ng·g^{-1} dw) in sea hare (*Aplysia dactylomela*) in the Arinaga beach. This concentration corresponds to the largest studied organism, which can be attributed to

Table 2
Bioaccumulation for the target organic UV filters.

Bioconcentration factor (Log BCF)									
Sample location	**Organisms**	**Compounds**							
		4-MBC	**BP-3**	**HMS**	**DTS**	**OC**	**BMDBM**	**IMC**	**MBP**
Las Canteras beach	*Phorcus atratus*	–*	–	5.8	7.6–5.8	6.9–5.4	8.2–5.8	5.9	–
Arinaga beach	*Phorcus atratus*	7.7	–	–	7.9–7.6	–	8.6	–	–
	Holothuria sanctori	–	–	–	–	–	7.7	7.9–7.4	–
Playa del Inglés beach	*Phorcus atratus*	–	–	7.4	–	8.4	6.9	5.9	–
	Stramonita haemastoma	–	–	8.6	–	7.0	–	–	–
Biomagnification factor (BMF)									
Sample location	**Organisms**	**Compounds**							
		4-MBC	**BP-3**	**HMS**	**DTS**	**OC**	**BMDBM**	**IMC**	**MBP**
Las Canteras beach	*Phorcus atratus*	–	–	0.01	1.1–0.1	0.05–0.01	0.3–0.1	0.9	–
Arinaga beach	*Phorcus atratus*	1.8	–	0.02	0.05	0.01	0.5	–	–
	Aplysia dactylomela	–	–	0.2	–	0.3	–	–	–
Playa del Inglés beach	*Phorcus atratus*	–	–	0.1	0.4	0.1	0.3	0.3	–

* The hyphen indicates that it was not possible to calculate the BCF and BMF.

its greater feeding behaviour *versus* the other analysed organisms. BMDBM showed the highest detection frequency of the target compounds. In contrast, BP3 was detected only once. The differences in the detection frequencies between these compounds can be attributed to their hydrophobicity behaviour, besides their different uses in PCPs, because BP3 presented a higher affinity for the aqueous phase than BMDBM.

According to the comparison made of the different marine matrices (seawater, macrophytes, primary marine consumers) in the same locations, OC obtained the highest concentration of all the target compounds. The frequency of detection of this compound was at its lowest in the aqueous phase (17 %), and its detection in the solid phases increased to>40 %. This fate can be explained by its high Log K_{ow} (6.88), which indicates a high affinity for solids. These results seem to indicate a pollution concern for OC in different marine compartments.

A preliminary bioconcentration (through BCF) and biomagnification (by means of the BMF) assessment was performed using previous data about the target compounds in seawater and seaweed, respectively. The reported Log BCF was over 3.7 for the quantified target compounds, which suggests their bioaccumulation in the studied marine organisms. Furthermore, the BMF found for 4MBC and DTS indicated possible biomagnification through the food web. Hence, the presence of organic UV filters in the analysed primary marine consumers can be attributed to the net absorption of compounds via all routes, which entails exposure from the surroundings and intake by the presence of pollutants in food.

Comprehensive research into the occurrence, bioaccumulation and biomagnification of these compounds is imperative to support adequate environmental management.

Due to the ecological relevance, further studies should be carried out in upper trophic organisms to a better understanding of the biomagnification of the target compounds. In addition, the possible metabolites should be considered to a real exposure evaluation.

CRediT authorship contribution statement

M. Isabel Cadena-Aizaga: Investigation, Methodology, Validation, Visualization, Writing – original draft. **Sarah Montesdeoca-Esponda:** Conceptualization, Supervision, Validation, Writing – review & editing. **Zoraida Sosa-Ferrera:** Conceptualization, Supervision, Validation, Resources. **José Juan Santana-Rodríguez:** Conceptualization, Writing – review & editing, Resources, Project administration.

Declaration of Competing Interest

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

Data availability

No data was used for the research described in the article.

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Appendix A. Supplementary data

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CAPÍTULO 4. CONCLUSIONES

Los resultados de los estudios obtenidos en la presente Tesis Doctoral nos permiten extraer las siguientes conclusiones:

I. De la revisión bibliográfica se concluye lo siguiente:
    a. Existe una problemática global por contaminación de filtros UV orgánicos en el medio marino, si bien existe poca información disponible acerca de sus efectos adversos.
    b. La presión antropogénica y la incompleta eliminación de estos compuestos en las EDAR suponen las principales vías de entrada al medio marino

c. Se han discutido también los riesgos ambientales de los filtros UV orgánicos en el medio marino para ciertas especies.
d. Las metodologías de análisis para su determinación deben ser sensibles y selectivas para determinar las bajas concentraciones presentes de estos contaminantes en muestras ambientales.

II. Ha sido necesario el desarrollo de diversos métodos de análisis, basados en diferentes técnicas de extracción, dependiendo de la naturaleza de la matriz sujeta a estudio. Así mismo, de la optimización de la determinación por cromatografía líquida de ultra resolución con detección por espectrometría de masas en tándem (UHPLC-MS/MS).
    a. Empleando la UHPLC, se obtuvo una excelente separación cromatográfica de los analitos de interés, a pesar de tener un rango de características fisicoquímicas amplias.
    b. Del uso de la MS/MS que es una técnica altamente sensible y selectiva, se obtuvieron límites de detección excelentes, capaces de detectar concentraciones tan bajas como partes por trillón ($ng \cdot L^{-1}$). Por lo tanto, la combinación de las dos técnicas ofreció capacidad de identificación y sensibilidad idónea para la determinación de filtros UV orgánicos seleccionados.

III. En el caso de las muestras líquidas, se establecieron dos métodos de extracción, uno para muestras de agua de mar y otro para aguas residuales. En ambos casos se usó la técnica de extracción en fase sólida (SPE), y se concluyó que:

a. Los métodos de extracción basado en SPE para los ocho filtros UV orgánicos seleccionados presentan parámetros analíticos adecuados para la extracción y preconcentración desde agua de mar y aguas residuales.

i. Empleando los métodos SPE desarrollado se consiguieron factores de preconcentración de 140 y 50; en agua de mar y aguas residuales, respectivamente. Esto demuestra que esta técnica es adecuada para extraer estos contaminantes desde muestras ambientales.

ii. En términos de eficiencia de extracción, se obtuvieron buenas recuperaciones, superiores al 50 % para la mayoría de los compuestos, en los dos tipos de aguas.

iii. Respecto a la repetibilidad, expresada como el porcentaje desviación estándar, se obtuvieron valores inferiores al 15 % en ambos casos, demostrándose que los métodos son altamente reproducibles.

iv. Los límites de detección de los métodos en los dos tipos de agua varían entre 11.3 $ng \cdot L^{-1}$ y 24.6 $ng \cdot L^{-1}$. Estos son suficientemente bajos para determinar estos contaminantes en muestras complejas, como lo son el agua de mar y las aguas residuales.

v. En los dos casos, las metodologías analíticas desarrolladas han demostrado ser sensibles, rápidas y selectivas, y presentan mejores límites de detección y cuantificación respecto a otras metodologías previamente descritas en la bibliografía.

b. De la aplicación de los métodos de extracción y determinación a muestras ambientales reales de agua de mar y aguas residuales:

i. Se cuantificaron todos los analitos de interés en agua de mar procedentes de tres playas de Gran Canaria: Playa de las Canteras, playa de Arinaga y Playa del Inglés. Las concentraciones encontradas estuvieron entre 0.07 $\mu g \cdot L^{-1}$ y 172 $\mu g \cdot L^{-1}$, con unas frecuencias de detección entre el 6 % y el 83 %. En la playa de Arinaga se cuantificaron estos compuestos por primera vez.

ii. Las mayores frecuencias de detección fueron para la BP3 (83 %) y el IMC (78 %). Siendo el OC el que presenta mayor concentración (172 $\mu g \cdot L^{-1}$) en la playa de Las Canteras.

iii. Se observa una variación temporal en la presencia de estos filtros UV orgánicos, reportándose las concentraciones más altas en los meses de verano.

iv. Por primera vez se estableció la presencia de filtros UV orgánicos en aguas residuales de tres estaciones depuradores de aguas en Gran Canaria. Los niveles de concentraciones detectados varían en el rango 0.20 – 207.9 $\mu g \cdot L^{-1}$ en aguas sin tratar del influente; entre 0.06 – 34.0 $\mu g \cdot L^{-1}$ en la salida del tratamiento secundario y entre 0.15 – 8.07 $\mu g \cdot L^{-1}$ en la salida del tratamiento terciario.

v. Se comprobó que hay una eliminación parcial de estos compuestos, tanto después del tratamiento secundario como del tratamiento terciario.

vi. En general se observó que las eficiencias de eliminación de los distintos tratamientos de las aguas residuales fueron superiores al 50 %.

vii. Debido a la presencia de estos contaminantes, se obtuvo el riesgo ambiental (HQ) asociado a los organismos expuestos a las concentraciones detectadas. Se destaca el alto HQ encontrado para el compuesto OC, mientras que BMDBM presentó un riesgo medio-alto y BP3 mostró valores muy variables.

IV. En el caso de las muestras sólidas, se desarrollaron dos métodos de extracción basados en la técnica de extracción asistida por ondas microondas (MAE). Uno para muestras de macrofitas y otro para muestras de organismos consumidores primarios. Usando esta técnica:

a. Los métodos de extracción basado en MAE presentan parámetros analíticos adecuados para la extracción desde macrofitas y organismos consumidores primarios, usando una pequeña cantidad de muestra (100 mg)

i. En el caso de macrofitas, se obtuvieron eficiencias de extracción superiores al 40 % para todos los compuestos. Además, tiene una excelente reproducibilidad, siendo esta menor del 12 %. Este método demostró ser aplicable a varias especies de algas.

ii. En el caso de los organismos consumidores primarios, las eficiencias de extracción varían entre 32 % y el 94 %, las cuales son adecuadas considerando la complejidad de la matriz. Respecto a la reproducibilidad, también se obtuvieron valores excelentes, siendo estos menores al 13 % en todos los compuestos analizados. Además, se comprobó que el método es válido para varios tipos de organismos consumidores primarios.

b. De la aplicación del método MAE desarrollado para macrofitas, en muestras reales:
   i. Las macrofitas parecen ser organismos ideales para monitorizar la contaminación antropogénica por filtros UV orgánicos.
   ii. Por primera vez se determinó la concentración de los analitos en macrofitas de las playas de Arinaga y Playa del Inglés.
   iii. Se extrajeron y cuantificaron todos los compuestos de interés, con frecuencias de detección entre 16 % y el 100 % y un rango de concentración entre 3.50 $ng \cdot g^{-1}$ y 19 369 $ng \cdot g^{-1}$.
   iv. OC fue detectado en todas las muestras de macrofitas analizadas, seguido por el

compuesto HMS que estuvo presente en el 91 % de las muestras.

v. Se destaca que, en estas muestras, el compuesto que tuvo la concentración más alta fue OC (19 369 $ng \cdot g^{-1}$), al igual que en las muestras de agua de mar y aguas residuales.

vi. El estudio de la relación de bioconcentración (BCR) muestra diferentes grados, dependiendo del tipo de alga, siguiendo el orden; alga verde> alga roja> alga parda.

vii. Considerando los valores medios de BCR para todos los tipos de algas, playas y compuesto, el valor más alto fue para OC y el más bajo para MBP

viii. Se obtuvieron valores de bioconcentración superiores a 1 000 para varios compuestos, lo que indica una gran posibilidad de causar efectos adversos en organismos superiores que consumen estas macrofitas.

c. De la aplicación del método MAE desarrollado para organismos consumidores primarios, en muestras ambientales reales:

i. Por primera vez en Gran Canaria, se estableció la presencia de filtros UV orgánicos en este tipo de organismos.
ii. Los compuestos de interés presentaron una frecuencia de detección entre el 10 % y el 55 %.
iii. Los compuestos con la frecuencia de detección más alta fueron el BMDBM (55 %) y el OC (40 %)
iv. La concentración más alta detectada fue para el OC (1 735 $ng \cdot g^{-1}$), al igual que en las otras matrices estudiadas (agua de mar, aguas residuales y macrofitas).
v. La presencia de estos compuestos en los organismos estudiados puede ser consecuencia de la transferencia del contaminante desde el medio (bioconcentración) o por la ingesta (biomagnificación) de otros organismos contaminados. Por lo que se calcularon los índices de bioconcentración (BCF) y biomagnificación (BMF).
vi. El BCF se calculó usando las concentraciones de agua de mar en las mismas playas y compuestos. Se obtuvieron valores que indican

una posible bioacumulación desde el medio al estar expuestos al contaminante.

vii. Se determinó el BMF usando las concentraciones de estos compuestos en las algas, ya que se realizó el estudio en las mismas playas. Se usaron los valores de las algas que pueden ser consumidas por estos organismos. Los resultados de este índice indican una posible biomagnificación hacia niveles superiores de la cadena trófica.

V. Con los resultados aportados en esta Tesis, se estableció la contaminación antropogénica por filtros UV orgánicos en varias matrices marinas de tres playas de la isla de Gran Canaria. Se demostró que estos compuestos entran al medio marino tanto por via directa como por vía indirecta. Además, los organismos expuestos a estos compuestos los bioacumulan, representando un riesgo para ellos. Asimismo, en niveles superiores se puede dar efecto de biomagnificación, llegando en última instancia a ser parte de la dieta humana.

Como se ha expuesto a lo largo de los capítulos de la presente Tesis, la contaminación por filtros UV orgánicos tiene una extensión global y presentan un problema a largo plazo para los organismos que están expuestos a ellos.

Teniendo esto en cuenta, el desarrollo de nuevas técnicas de determinación son necesarias para incluir estos contaminantes en programas de monitoreo, promoviendo cambios en la legislación que controle las concentraciones que pueden ser liberadas en el medioambiente marino. Finalmente, para que estos contaminantes puedan ser incluidos en la Lista de Vigilancia de la Unión Europea y controlar su presencia en el medio ambiente.

CHAPTER 4. CONCLUSIONS

Based on the results obtained in this Thesis, the following conclusions can be drawn:

I. From the bibliographic review the following is concluded:
    a. There is a global contamination by organic UV filters in the marine environment nevertheless, few information is available about their harmful effects
    b. Intensive human activities and incomplete elimination during wastewater treatment are the main inputs into the marine environment.

c. The environmental risk of organic UV filters in the marine environment are also discussed.
d. The techniques used to determine these pollutants must be sensitive and selective due to their low concentrations in environmental samples.

II. New analytical methods were developed, they were based on different extraction techniques and the type of matrix. Furthermore, the analytes determination was optimized based on the ultra-resolution liquid chromatography with detection by tandem mass spectrometry (UHPLC-MS/MS).
    a. Applying the UHPLC, excellent chromatographic separation of the analytes was obtained, despite they have a wide range of physicochemical characteristics.
    b. Using MS/MS which is a highly sensitive and selective technique, very low limits of detection were achieved that are capable of detecting concentrations as low as parts per trillion ($ng \cdot L^{-1}$). Therefore, the combination of both techniques offered an ideal sensibility for the determination of the selected organic UV filters.

III. In the case of the liquid samples, two extraction methods were established, one for the seawater samples and the other for wastewater samples. In both cases, the solid phase extraction (SPE) technique was used, and it was concluded:

a. The SPE-based extraction methods presented suitable analytical parameters for the extraction and pre-concentration for the selected organic UV filters from seawater and wastewater
    i. Preconcentration factors of 140 and 50 were obtained using the methods developed using SPE for seawater and wastewater, respectively. This shows the suitability of this technique to extract these pollutants from environmental samples.
    ii. Good extraction efficiencies were obtained, which were above 50 % for most of the analytes in the two water types.
    iii. The reproducibility expressed as the standard deviation were below 15 % in both cases, thereby, the two developed methods are highly reproducible.
    iv. The limits of detection ranged from 11.3 $ng \cdot L^{-1}$ y 24.6 $ng \cdot L^{-1}$ in the two water types. Which are low enough to determine these pollutants in complex matrices such as seawater and wastewater.
    v. In both cases, the analytical methods developed are sensitive, fast, selective, and present better

detection limits of detection and quantification respect to some other methods previously described in the bibliographic work.

b. When the developed methods were applied to environmental seawater and wastewater samples:
    i. All analytes were quantified in seawater from the three beaches of Gran Canaria Island, Las Canteras beach, Arinaga beach and Playa del Inglés beach. The concentrations found were between 0.07 $\mu g \cdot L^{-1}$ y 172 $\mu g \cdot L^{-1}$ with detection frequencies between 6 % and 83 %. In Arinaga beach these pollutants were determined for the first time.
    ii. The most frequently detected compounds were BP3 (83 %) and IMC (78 %). Furthermore, the highest concentration was detected for OC (172 $\mu g \cdot L^{-1}$) at Las Canteras beach.
    iii. A seasonal variation was detected, highest concentrations were reported in summer periods.
    iv. For the first time the presence of organic UV filters was established in wastewater from three wastewater treatment plants from Gran Canaria. The found concentrations ranged between 0.20

– 207.9 $\mu g \cdot L^{-1}$ in the influent; between 0.06 – 34.0 $\mu g \cdot L^{-1}$ in the secondary treatment effluent and between 0.15 – 8.07 $\mu g \cdot L^{-1}$ in the tertiary treatment effluent.

v. It was verified a partial elimination of these pollutants was found, after both secondary and tertiary treatment.

vi. In general, removal efficiencies over 50 % were observed in the different wastewater treatments.

vii. The environmental hazard (HQ) associated to the presence of these pollutants for different marine organisms was determined using the found concentrations. The highest HQ found correspond to OC, while BMDBM presented a medium-high risk and BP3 reported variable values.

IV. In the case of solid samples, two analytical methods were developed, based on the microwave assisted extraction (MAE) technique. One of them was established for macrophytes and the other one for primary marine consumers. Using these methods:

a. MAE-based extraction methods presented suitable analytical parameters to extract the analytes from

macrophytes and primary marine consumers using a small amount of sample (100 mg).

i. Extraction efficiencies over 40 % were obtained for all compounds in macrophytes. In addition, it has an excellent reproducibility, being less than 12 %. This method demonstrated to be applicable to several seaweed species.

ii. For the primary marine consumers, the extraction efficiencies ranged from 32 % to 94 %, which are adequate considering the complexity of this matrix. Regarding the reproducibility, excellent values were obtained, being these below 13 % for all analysed compounds. In addition, the method was validated for different primary marine consumers.

b. When the MAE method was applied to environmental macrophytes samples:

i. Macrophytes seem to be ideal organisms to monitor the pollution of organic UV filters.

ii. It was determined the presence of the target analytes in macrophytes of Arinaga and Playa del Inglés beach for the very first time.

iii. All analytes were extracted and quantified with detection frequencies between 16 % and 100 %, and concentration ranges between 3.50 $ng \cdot g^{-1}$ and 19,369 $ng \cdot g^{-1}$.

iv. OC was detected in all macrophytes samples analysed, while HMS was present in the 91 % of them.

v. It is highlighted that OC presented the highest concentration, as was reported in seawater and wastewater samples.

vi. The bioconcentration ratio (BCR) was assessed obtaining different grades, considering the seaweed type followed the order: green>red>brown.

vii. The highest BCR average value by seaweed type, beach and compound correspond to OC and the lowest to MBP.

viii. BCR values over 1,000 were obtained for several compounds, which indicates a high potential of causing adverse effects in higher trophic organisms that feeds on macrophytes.

c. Applying the MAE method developed for primary marine consumers to environmental samples:

i. For the first time in Gran Canaria, the presence of organic UV filters was established in this type of organisms.
ii. Target analytes presented a detection frequency between 10 % and 55 %.
iii. BMDBM (55 %) and OC (40 %) were the most frequently detected compounds.
iv. The highest concentration was found for OC (1,735 $ng \cdot g^{-1}$), as in the other analysed matrices (seawater, wastewater and macrophytes).
v. The presence of the target analytes in these organisms can be attributed to the absorption of the pollutant from the surroundings (bioconcentration) and to the intake by the polluted food (biomagnification). Thus, bioconcentration factor (BCF) and bioaccumulation factor (BMF) were determined.
vi. BCF was calculated using the seawater concentrations previously obtained for the same compounds in the same beaches. The obtained values indicate a possible bioaccumulation from the surrounding environment when the organisms are exposed to the pollutant.

vii. BMF was determined using the concentrations obtained for the same compounds in the same beaches in the seaweeds. the values used correspond to the seaweed subjected to be consumed by these organisms. The obtained BMF values suggest a possible biomagnification to upper trophic levels of the food chain.

V. The obtained results from this Thesis established anthropogenic pollution due to organic UV filters in different marine matrices from three beaches of Gran Canaria. It was verified that these compounds reach the marine environment by direct and indirect inputs. Furthermore, the organisms exposed to these pollutants bioaccumulate them, which present a risk to the organisms. Additionally, at higher trophic levels biomagnification may be taking place and they may ultimately become part of the human diet.

As has been exposed throughout the chapters of this Thesis, the pollution by organic UV filters has a global extension and represents a long-term risk to the marine ecosystem.

Taking this into consideration, the development of new detection techniques is necessary to include them in monitoring programs, promoting changes in the legislation that controls the

concentrations that can be released to the marine environment. Finally, in order to include these pollutants in the European Watching list.

Anexo I. Índice de tablas y figuras

Tablas:

Figuras:

Anexo II. Publicaciones de la Tesis Doctoral

1. **Autores:** M. Isabel Cadena-Aizaga, Sarah Montesdeoca-Esponda, María Esther Torres-Padrón, Zoraida Sosa-Ferrera, José Juan Santana-Rodríguez

   Título: Organic UV filters in marine environments: An update of analytical methodologies, occurrence and distribution

   Revista: Trends in Environmental Analytical Chemistry

   Volumen: 25

   Páginas: e00079

   Fecha: 2020

2. **Autores:** M. Isabel Cadena-Aizaga, Sarah Montesdeoca-Esponda, Zoraida Sosa-Ferrera, José Juan Santana-Rodríguez

   Título: Occurrence and environmental hazard of organic UV filters in seawater and wastewater from Gran Canaria Island (Canary Islands, Spain)

   Revista: Environmental Pollution

   Volumen: 300

   Páginas: 118843

   Fecha: 2022

3. **Autores:** M. Isabel Cadena-Aizaga, Sarah Montesdeoca-Esponda, Ángelo Santana-Del Pino, Zoraida Sosa-Ferrera, José Juan Santana-Rodríguez
   Título: Assessment of anthropogenic pollution by UV filters using macrophytes as bioindicators
   Revista: Science of the Total Environment
   Volumen: 832
   Páginas: 155012
   Fecha: 2022

4. **Autores:** M. Isabel Cadena-Aizaga, Sarah Montesdeoca-Esponda, Zoraida Sosa-Ferrera, Jose Juan Santana-Rodríguez
   Título: Occurrence and bioconcentration of organic UV filters in primary marine consumers
   Revista: Microchemical Journal
   Volumen: 181
   Páginas: 107807
   Fecha: 2022

Anexo III. Material suplementario de las publicaciones

Publicación: Organic UV filters in marine environments: An update of analytical methodologies, occurrence and distribution

Supplementary Material.

Table S1. UV filters occurrence in seawater. Chronological order.

Kind of matrices	Location	Compounds	Concentration ($ng \cdot L^{-1}$)	Reference
Seawater (coastal areas and fjord)	Norway (Bærum)	BP-3 4-MBC OC OMC	n.d- 439.9 n.d- 798.7 n.d- 7301.0 n.d- 389.9	[74]
Seawater (0, 10 and 100 m off a WWTP discharge)	Norway (Oslo Fjord)	BP-3 4-MBC OC OMC	n.d., 15.5-22.5, 13.7-35.5 n.d., n.d.- 17.2, 2.6-5.3 n.d., n.d.- 31.2, n.d.-24.8 32.6- 164.1, n.d.-189.3, n.d.- 178.9	
Seawater (beach site)	Spain (Galicia)	BP-3 BP-4 IMC 4-MBC OC OD-PABA BM-DBM PMDSA DPDT	<LOD 38-138 <LOD <LOD <LOD <LOD <LOD <LOD-42 <LOD	[42]
Seawater (ocean water)	Pacific Ocean (crossed from Peru to Polynesia)	BP-3 4-MBC E-OMC Z-OMC	(pg/SPMD) <LOD- 34310 <LOD 11464- 27058 3432- 8484	[50]

Seawater (surface microlayer)	Pacific Ocean (near to Polynesia)	PB-3 4-MBC E-OMC Z-OMC	5- 6 18- 30 7- 55 6- 37	
Seawater (Ria water)	Spain (A Coruña)	BP-3 BP-4 IMC 4-MBC OC OMC OD-PABA PMDSA	n.d.***	[76]
Seawater (beach sites)	Spain (Valencia and Alicante)	BP-3 IMC 4-MBC OC OMC OD-PABA	n.d.***	[89]
Seawater (beach sites)	Spain (Murcia and Alicante)	BP-3	1340- 3300	[86]
Seawater (beach site)	Spain (Alicante)	BP-3 IMC 4-MBC OC OMC OD-PABA EHS HMS	254- 879 245- 645 358- 758 <LOQ- 440 409- 774 682- 1187 792- 1222 625- 1030	[48]
Seawater (coastal areas)	Italy (Liguria)	BP-3 OMC	<LOQ- 118 <LOQ- 83	[49]
Seawater (coastal areas)	United States (South Carolina)	BP-3 BP-4 OC OMC OD-PABA BM-DBM	10-2013 <1 <25-1409 30-264 <1-111 62-303	[44]
Seawater (beach site)	Italy (Genoa)	BP-3 OC	8-13 19-32	[43]

Seawater (beach sites)	Spain (Gran Canaria Island)	MBP	<LOD-5.2†	[39]
Seawater (surface water)	Spain (Cádiz)	BP-3 OC	70 100	[38]
Seawater (beach sites)	Spain (Majorca Island, Palmira beach)	BP-3 4-MBC	143.6 62.5	[11]
	Spain (Majorca Island, Santa Ponça beach)	BP-3 4-MBC	76.2- 314.8 47.5- 65	
	Spain (Majorca Island, Ses Salines Cape)	BP-3 4-MBC	36.3 26.6	
Seawater	Portugal (Costa de Caparica)	BP-3	<LOD	[82]
Seawater (beach sites)	Japan (Okinawa Island)	BP-3 OC OMC OD-PABA EHS HMS	n.d.- 1258 n.d.- 79 n.d.- 143 n.d.- 0.8 n.d.- 10 n.d.- 214	[45]
Seawater (river and reef sites)	Japan (Okinawa Island)	BP-3 OC OMC OD-PABA EHS HMS	n.d.- 9.0 n.d.- 8.1 n.d.- 3.9 n.d. n.d.- 1.8 n.d.- 3.2	
Seawater (beaches sites)	Spain (Galicia, Coira beach)	BP-3 BP-4 4-MBC OMC	68.6 164.4 84.6 52.5	[27]
	Spain (Galicia,	BP-3 BP-4 4-MBC	21.7 58.8 -	

	Toralla beach)	OMC	35.7	
Surface samples	Slovenia (Novigrad)	BP-3	96	[54]
	Slovenia (Ankaran)		340	
	Slovenia (Portorož)		380	
Surface samples	Spain (Cádiz)	BP-3 4-MBC OC OMC EHS HMS	60 46 49 36 <LOD 9	[77]
Seawater (surface water)	China (Hong Kong)	BP-3 BP-4 IMC 4- MBC OC OMC OD-PABA EHS HMS BM-DBM	39- 5429 54- 389 63- 173 173- 379 103- 6812 89- 4043 95- 182 61- 1030 66- 2812 24- 721	[29]
	Japan (Tokyo Bay)	BP-3 BP-4 IMC 4- MBC OC OMC OD-PABA EHS HMS BM-DBM	24- 86 71- 136 <LOD <LOD 87- 108 46- 95 <LOD 71- 95 65- 110 78- 104	
	United States (New York)	BP-3 BP-4 IMC 4- MBC OC OMC OD-PABA	23- 178 89- 574 <LOD <LOD 117- 128 89- 150 <LOD	

		EHS HMS BM-DBM	<LOD 91- 114 70- 87	
	United States (Los Angeles)	BP-3 BP-4 IMC 4- MBC OC OMC OD-PABA EHS HMS BM-DBM	227- 601 <LOD <LOD <LOD 145- 377 91- 138 <LOD 53- 120 142- 270 67- 109	
	China (Shantou)	BP-3 BP-4 IMC 4- MBC OC OMC OD-PABA EHS HMS BM-DBM	55- 188 <LOD <LOD <LOD 75- 107 52- 78 <LOD <LOD <LOD 53- 100	
	China (Chaozhou)	BP-3 BP-4 IMC 4- MBC OC OMC OD-PABA EHS HMS BM-DBM	37- 49 <LOD- 49 <LOD <LOD 36- 102 <LOD- 79 <LOD 121- 128 <LOD <LOD	
	Arctic (Arctic Ocean and Chukchi Sea between 65 and 75ºN)	BP-3 BP-4 IMC 4- MBC OC OMC OD-PABA EHS HMS	17- 33 <LOD <LOD <LOD 26- 31 25- 66 <LOD <LOD <LOD	

		BM-DBM	18- 70	
Seawater (beach sites)	Spain (Majorca Island, Palmira beach)	BP-3 IMC 4-MBC OC OMC OD-PABA EHS HMS	308 280 192 260 260 246 880 310	[46]
Seawater (beach sites)	Spain (Valencia, Malvarrosa beach)	BP-3 IMC 4-MBC OC OMC OD-PABA EHS HMS	200 251 220 317 250 390 750 280	
Seawater (beach sites)	Spain (Valencia, Pineda beach)	BP-3 IMC 4-MBC OC OMC OD-PABA EHS HMS	<LOQ 118 <LOD <LOQ 91 163 440 157	
Seawater (beach sites)	Spain (Gran Canaria Island, Maspalomas-Los Ingleses beach)	BP-3 4-MBC OC OMC HMS BM-DBM DHHB	<LOD- 27.1 <LOD- 7.2 <LOQ- 359.1 <LOD- 16.1 <LOD- 51.5 <LOD- 188.4 <LOD- <LOQ	[40]
	Spain (Gran Canaria Island, Puerto Rico beach)	BP-3 4-MBC OC OMC	32.7- 979.8 4.1- 219.5 61.2- 973.1 <LOD- 756.2	

		HMS BM-DBM DHHB	9.2- 536.2 35.6- 1163.2 <LOQ- 228.7	
	Spain (Gran Canaria Island, Amadores beach)	BP-3 4-MBC OC OMC HMS BM-DBM DHHB	12.7- 2675.7 <LOD- 104.8 30.7- 766.7 <LOD- 276.8 <LOD- 319.0 <LOQ- 792.0 <LOD- 163.5	
	Spain (Gran Canaria Island, Mogán beach)	BP-3 4-MBC OC OMC HMS BM-DBM DHHB	54.2- 3316.7 <LOQ- 346.3 37.8- 1324.9 <LOQ- 260.2 10.8- 526.1 19.8- 1770.3 <LOQ- 144.4	
	Spain (Gran Canaria Island, Las Alcaravaneras beach)	BP-3 4-MBC OC OMC HMS BM-DBM DHHB	<LOD- 158.0 <LOD- 29.7 <LOD- 183.2 <LOD- 65.4 <LOD- 84.8 <LOD- 314.3 <LOD- 34.7	
	Spain (Gran Canaria Island, Las Canteras beach)	BP-3 4-MBC OC OMC HMS BM-DBM DHHB	<LOD- 182.6 <LOD- 1043.4 <LOD- 768.5 <LOD- 109.9 <LOD- 102.2 <LOD- 737.1 <LOD- 176.3	
Seawater (beach sites)	United states (South Carolina)	BP-3 OC OMC OD-PABA BM-DBM	37.6- 591 41.1- 711 10.7- 96.9 n.d- 36.7 31.9- 234	[47]
Ocean seawater	Antarctic (Cape Armitage, Winter Quarters Bay, Scott Base,	BP-3 4-MBC OMC	12- 88.4 n.d- 47.5 <LOQ- 41.7	[10]

	and Cape Evans during 2009-2010)			
Ocean seawater	Antarctic (Cape Armitage, Winter Quarters Bay, Scott Base, and Cape Evans during 2012-2013)	BP-3 4-MBC OMC	<LOQ- 3.7 <LOQ- 5.8 <LOQ- 4.3	
Thawed sea ice	Antarctic (Cape Armitage, Winter Quarters Bay, Scott Base, and Cape Evans during 2012-2013)	BP-3 4-MBC OMC	<LOQ- 4.2 <LOQ- 4.3 <LOQ- 4.8	
Seawater (beach sites)	Japan (Kumamoto, winter)	OMC EHS	11-20 2.0-3.8	[84]
	Japan (Kumamoto, summer)	OMC EHS	210-1080 4.3-23.1	
Seawater (surface water)	United States (St. John Island)	BP-3	75000 (ng/L)- 1.395 (mg/L)	[31]
Seawater (surface water)	Hawaii (Oahu Island)	BP-3	<LOQ- 19200	
Seawater (surface water)	Hawaii (Maui Island)	BP-3	<LOQ	
Seawater (beach sites)	Spain (Valencia, Patacona beach)	BP-3 IMC 4-MBC OC	603 174 169 406	[79]

		OMC OD-PABA EHS HMS	691 212 914 369	
Seawater	Spain	BP-3 OC BM-DBM	692000 30000 72000	[70]
Seawater (beach sites)	Spain (Gran Canaria Island)	MBP	41.12- 544.9	[73]
Seawater	Spain	IMC 4-MBC OC OMC EHS HMS	88 <LOD 1100- 171000 1200 420 720	[69]
Seawater	Spain	OC OMC EHS HMS	14- 79000 10 34- 2500 1300	[16]
Seawater (coral ambient)	China (Hong Kong, Ung Kong, wet season)	BP-3 4-MBC OC OMC OD-PABA	25.5- 26.1 <LOD 13.1- 13.2 <LOD 15.1- 15.2	[32]
	China (Hong Kong, Wu Pai, wet season)	BP-3 4-MBC OC OMC OD-PABA	13.9- 14.0 <LOD 11.8- 11.9 <LOD 13.2	
	China (Hong Kong, Sharp Island, wet season)	BP-3 4-MBC OC OMC OD-PABA	23.2- 25.6 <LOD 9.6- 9.8 <LOD 22.6 -22.7	
	China (Hong Kong, Sung Kong, wet season)	BP-3 4-MBC OC OMC OD-PABA	12.9- 13.5 <LOD 8.7- 9.0 <LOD 14.8- 14.9	

	China (Hong Kong, Ung Kong, dry season)	BP-3 4-MBC OC OMC OD-PABA	28.9- 29.2 <LOD 14.1- 14.2 <LOD <LOD	
	China (Hong Kong, Wu Pai, dry season)	BP-3 4-MBC OC OMC OD-PABA	13.7- 13.8 <LOD 10.7- 10.8 <LOD <LOD	
	China (Hong Kong, Sharp Island, dry season)	BP-3 4-MBC OC OMC OD-PABA	31.5- 31.9 <LOD 13.2 <LOD <LOD	
Seawater (beach sites)	Korea (Gwangalli)	BP-3 4-MBC OMC OD-PABA EHS	n.d.- 17.3 n.d.- 4.70 15.1- 70.5 n.d. n.d.- 16.7	[41]
	Korea (Songjeong)	BP-3 4-MBC OMC OD-PABA EHS	13.5- 87.8 n.d.- 3.60 2.11- 10.9 n.d. n.d.- 11.7	
	Korea (Haeundae)	BP-3 4-MBC OMC OD-PABA EHS	8.48- 72.7 n.d.- 10.6 3.56- 15.6 n.d. 4.25- 19.6	
Seawater (beach sites)	China (Hong Kong, winter)	BP-3 4-MBC OC OMC OD-PABA	13.08- 70.55 24.38- 74.50 13.50- 53.86 34.71- 167.72 <LOQ- 41.68	[24]
Seawater (beach sites)	China (Hong Kong, summer)	BP-3 4-MBC OC OMC OD-PABA	27.36- 82.35 26.04- 67.78 15.50- 63.63 99.05- 191.67 <LOQ- 46.14	

Seawater (coastal areas)	China (Hong Kong, winter)	BP-3 4-MBC OC OMC OD-PABA	19.86- 32.47 20.39- 41.89 11.54- 43.95 34.15- 148.81 <LOQ- 25.42	
Seawater (coastal areas)	China (Hong Kong, summer)	BP-3 4-MBC OC OMC OD-PABA	26.03- 41.17 27.26- 46.26 12.72- 46.44 81.64- 182.12 <LOQ- 28.82	
Seawater (beach sites)	Spain (Puzol beach, Valencia)	BP-3 IMC 4-MBC OC OMC OD-PABA EHS HMS	148 73 105 745 349 187 553 257	[78]
	Spain (Patacona beach, Valencia)	BP-3 IMC 4-MBC OC OMC OD-PABA EHS HMS	405 103 144 149 436 201 731 497	
Seawater (surface water)	Taiwan (Kenting National Park)	BP-3 4-MBC	18.8- 1233 2.40- 7.93	[87]
Seawater (beach sites)	Netherlands (Lac Bay)	BP-3 4-MBC OC	<10- 1540 <10 <20- 1950	[33]

n.d. Not detected

*** All compounds were not detected

† Performed using on-line SPE and UPLC-MS/MS

Table S2. UV filters occurrence in sediments and sand. Chronological order.

Kind of matrices	Location	Compounds	Concentration ($ng \cdot g^{-1}$ d.w.)	Reference
Coastal sediments	Spain (Valencia)	BP-3 EHS HMS	n.d. 13.3 n.d.	[53]
Coastal sediments	Lebanon (sewage outfalls along the El-Mina coastline)	OC OMC OD-PABA	79.0 9.0 9.0	[51]
Coastal sediments	Lebanon (commercial harbour and fishing harbour on the El-Mina coastline)	OC OMC OD-PABA	51.0 9.0 6.0	
Coastal sediments	Chile (Concepción Bay, San Vicente Bay and Coronel Bay)	BP-3 4-MBC OC OMC OD-PABA	n.d.- 1.42 n.d. - n.d -	[22]
Coastal sediments	Colombia (West coastline)	BP-3 4-MBC OC OMC OD-PABA	n.d.- 2.52 n.d.- 7.90 - n.d.- 17.8 -	
Sediments from 0, 10 and 20 cm depths	Spain (Cadiz Bay)	BP-3 OC	47, 26 and 38 53, 20 and 41	[38]
Coastal sediments (beach sediments)	Spain (Gran Canaria Island)	MBP	<LOD	[114]

Sediments close to marine outfalls at different distances from the coast		MBP	<LOD- 0.33	
Top 10 cm sediment layer	Slovenia (Novigrad)	BP-3	2.0	[54]
	Slovenia (Ankaran)		<LOD	
	Slovenia (Portorož)		<LOD	
Fjord sediments	Norway (along a transect from close to a WWTP discharge and southward)	BP-3 OC OMC OD-PABA	<LOD <LOD- 82.1 8.5- 16.4 <LOD	[61]
Different depths marine sediments	China (Hong Kong in the Victoria Harbour and Sai Kung)	BP-3 IMC 4-MBC OC OMC OD-PABA EHS HMS BM-DBM	0.05- 39.8 <LOD <LOD 0.04- 15.6 0.6- 447 1.5- 150 <LOD <LOD 4.3- 42.9	[57]
	Japan (Tokyo Bay)	BP-3 IMC 4-MBC OC OMC OD-PABA EHS HMS BM-DBM	<LOD <LOD <LOD <LOD 0.3- 54.5 0.8- 13.9 <LOD <LOD 2.5- 64.5	

Surface sediments	China (Pearl River estuary)	4-MBC OC OMC	0.36- 3.68 6.26- 27.8 14.5- 81.6	[52]
	China (fishing harbour)	4-MBC OC OMC	2.16- 31.3 18.1- 551 36.4- 456	
Surface and deep sea regions sediments	Italy (along the Adriatic Sea, Northern Adriatic)	BP-3 OC OMC	<LOD- 0.23 4.0- 40.7 1.0- 10.4	[93]
	Italy (along the Adriatic Sea, Central Adriatic)	BP-3 OC OMC	<LOD- 0.1 0.8- 33.7 0.9- 6.9	
	Italy (along the Adriatic Sea, Southern Adriatic)	BP-3 OC OMC	<LOD- 0.18 0.9- 19.0 1.3- 10.0	
Different surface sediments	Spain (Huelva estuary, Cadiz Bay and Almeria coast)	BP-3 OC OMC EHS HMS	0.45- 1.5 0.73- 25.1 <LOQ- 26.2 2.3- 6.8 <LOQ- 9.7	[94]
Surface sediments	China (along the Pearl River Estuary)	BP-3 4-MBC OC OMC EHS HMS	n.d.- 4.0 n.d.- 25.4 6.2- 105.2 n.d.- 30.1 n.d.- 13.7 n.d.- 10.7	[95]
Surface sediments	China (along the Pearl River Estuary)	BP-3 OC OMC OD-PABA	0.16- 1.07 91.7 22.4 <LOQ	[35]

Surface sediments (coral ambient)	China (Hong Kong, Ung Kong, wet season)	BP-3 4-MBC OC OMC OD-PABA	6.1 <LOD 2.0- 2.2 <LOD 3.4	[32]
	China (Hong Kong, Wu Pai, wet season)	BP-3 4-MBC OC OMC OD-PABA	9.7- 9.9 <LOD 2.5- 2.6 <LOD 4.3- 4.5	
	China (Hong Kong, Sharp Island, wet season)	BP-3 4-MBC OC OMC OD-PABA	6.5- 6.6 <LOD 2.7 <LOD 4.9	
	China (Hong Kong, Sung Kong, wet season)	BP-3 4-MBC OC OMC OD-PABA	8.0- 9.0 <LOD 3.0- 3.1 <LOD 8.0	
	China (Hong Kong, Ung Kong, dry season)	BP-3 4-MBC OC OMC OD-PABA	3.4- 4.9 <LOD <LOD <LOD <LOD	
	China (Hong Kong, Wu Pai, dry season)	BP-3 4-MBC OC OMC OD-PABA	16.9- 17.1 <LOD <LOD <LOD <LOD	
	China (Hong Kong, Sharp Island, dry season)	BP-3 4-MBC OC OMC OD-PABA	8.1 <LOD <LOD <LOD <LOD	
Superficial sediments	Northwest Pacific Ocean (Laizhou Bay)	OC OMC OD-PABA EHS HMS	<LOD- 25 <LOD- 0.22 <LOD <LOD- 1.28 <LOD	[30]

	Northwest Pacific Ocean (Bohai Sea)	OC OMC OD-PABA EHS HMS	<LOD- 0.36 <LOD- 0.24 <LOD <LOD <LOD- 0.06	
	Northwest Pacific Ocean (Yellow Sea)	OC OMC OD-PABA EHS HMS	<LOD- 4.25 <LOD- 0.08 <LOD- 0.004 <LOD- 1.35 <LOD- 0.94	
Beach sand	Spain (Valencia, Malvarrosa beach)	BP-3 IMC 4-MBC OC OMC OD-PABA EHS HMS	1.0 1.3 0.9 8 2.1 <LOQ 5.3 1.8	[55]
	Spain (Valencia, Pinedo beach)	BP-3 IMC 4-MBC OC OMC OD-PABA EHS HMS	<LOQ <LOQ <LOQ 1.7 0.9 <LOQ 2.6 1.06	
	Spain (Valencia, Patacona beach)	BP-3 IMC 4-MBC OC OMC OD-PABA EHS HMS	<LOQ <LOQ <LOQ 5.2 <LOQ <LOQ 1.8 <LOQ	
	Spain (Gran Canaria Island, Los Ingleses beach)	BP-3 IMC 4-MBC OC OMC OD-PABA EHS HMS	<LOQ 1.2 2.0 25 10 <LOQ 12 4.9	

Beach sand	Spain (Patacona beach, Valencia)	BP-3 IMC 4-MBC OC OMC OD-PABA EHS HMS	<LOD <LOD 4.9 2.4 1.3 0.52 4.7 4.8	[100]
	Spain (El Saler beach, Valencia)	BP-3 IMC 4-MBC OC OMC OD-PABA EHS HMS	3.3 1.1 6.7 4.6 7.0 1.7 6.9 7.1	
	Spain (Javea beach, Alicante)	BP-3 IMC 4-MBC OC OMC OD-PABA EHS HMS	9.2 6.9 16.2 8.2 14.0 10.2 7.5 10.1	
	Spain (Maspalomas beach, Gran Canaria Island)	BP-3 IMC 4-MBC OC OMC OD-PABA EHS HMS	10.2 6.5 13.8 11.0 5.5 5.8 5.9 7.4	
Beach sand	Spain (Galicia)	BP-3 IMC 4-MBC OC OMC EHS HMS	<LOD- 33 <LOD- 0.090 2.2- 206 31- 454 0.21- 2.7 0.93- 609 1.6- 149	[99]
	Portugal	BP-3 IMC 4-MBC OC	<LOD- 2.2 <LOD- 0.14 0.1- 1.2 13- 35	

		OMC EHS HMS	0.46- 3.5 0.67- 1.8 0.34- 1.1	
	Spain (Gran Canaria Island)	BP-3 IMC 4-MBC OC OMC EHS HMS	7.5 2.6 87 670 54 83 34	
	Spain (Mallorca Island)	BP-3 IMC 4-MBC OC OMC EHS HMS	<LOD- 0.85 <LOD 0.066- 1.0 2.9- 20 0.45- 1.4 2.7- 6.9 3.5- 6.8	

Table S3. UV filters occurrence in marine biota. Chronological order.

Kind of matrices	Location	Compounds	Concentration ($ng \cdot g^{-1}$ d.w.)	Reference
Mussel (*M. galloprovinciali*)	France (Atlantic coast)	OC OMC	n.d.- 23 5- 45	[64]
Mussel (*M. edulis*)	France (Mediterranean coast)	OC OMC	n.d.- 7112 3- 256	
Mussels (*Mylitus galloprovincialis*)	Spain (Galicia)	OC	15- 20	[63]
Mackerel (*Scomber scombrus*)			18	
Dolphin liver (*Pontoporia blainvillei*)	Brazil (Espirito Santo)	OC	n.d.- 712 ($ng \cdot g^{-1}$ l.w.)	[65]
	Brazil (Rio de Janeiro)	OC	n.d.	
	Brazil (São Paulo)	OC	n.d.- 524 ($ng \cdot g^{-1}$ l.w.)	
	Brazil (Paraná)	OC	n.d.- 129 ($ng \cdot g^{-1}$ l.w.)	
	Brazil (Santa Carina)	OC	n.d.- 401 ($ng \cdot g^{-1}$ l.w.)	
	Brazil (Rio Grande do Sul)	OC	n.d.- 782 ($ng \cdot g^{-1}$ l.w.)	
Fish (*Striped bass*, marketed fish)	Taiwan	BP-3 EHS HMS	5.7 2.9 n.d.	[102]
Fish (Cod, marketed fish)		BP-3 EHS HMS	3.3 0.8 n.d.	
Fish (Salmon, marketed fish)		BP-3 EHS HMS	6.9 3.9 0.7	
Mussels (*M. galloprovincialis*)	Portugal (south of Portugal)	OC OMC OD-PABA	3992 1765 833	[67]

Antarctic clams (*Laternula elliptica*)	Antarctic (Winter Quarters Bay)	BP-3	9.2- 112	[10]
Sea urchin (*Sterichinus neumayeri*)	Antarctic (Cape Armitage)	BP-3	8.6	
Fish (*Trematomus bernachii*)	Antarctic (Cape Evans)	BP-3	<6.6- 14.1 (265-1450 $ng \cdot g^{-1}$ l.w.)	
Fish liver (*Trematomus bernachii*)		BP-3	41.0 (1690 $ng \cdot g^{-1}$ l.w.)	
Fish (Red snapper, farmed fish, fillet)	China (Pearl River estuary)	BP-3 4-MBC OD-PABA BM-DBM	0.59 14.7 0.239 33	[62]
Fish (Red snapper, farmed fish, fish belly)		BP-3 4-MBC OD-PABA BM-DBM	0.80 41.5 0.36 52	
Fishes (Pomfret, Flounder and Osteomugi, tissues)		BP-3 4-MBC OD-PABA BM-DBM	n.d.***	
Fish (Goby, tissues)		BP-3 4-MBC OD-PABA BM-DBM	0.276 n.d. n.d. n.d.	
Fish (Hairtail, tissues)		BP-3 4-MBC OD-PABA BM-DBM	0.106 n.d. n.d. n.d.	
Squid (Sleeve- fish, tissues)		BP-3 4-MBC OD-PABA BM-DBM	0.408 n.d. n.d. n.d.	
Crustacean (Squilla, deshelled)		BP-3 4-MBC OD-PABA BM-DBM	1.520 n.d. n.d. n.d.	

Sea snail (Whelk, whole body)		BP-3 4-MBC OD-PABA BM-DBM	n.d. 0.2 n.d. n.d.	
Fish liver (*Gadus morhua*)	Norway (Oslofjord)	BP-3 OC OMC OD-PABA	($ng \cdot g^{-1}$ w.w.) <LOQ- 1037 <LOQ- 11875 <LOQ- 36.9 <LOQ- 21.3	[61]
Shrimp (*Pandalus borealis*)		BP-3 OC OMC OD-PABA	($ng \cdot g^{-1}$ w.w.) <30- 68.9 <10- 23.1 <20 <20	
Crab (*Carcinus meanas*)	Norway (north of WWTP in Sjøstrand)	BP-3 OC OMC OD-PABA	($ng \cdot g^{-1}$ w.w.) <30 <10 <10 <20	
Mussels (*Mytilus edulis* and *Mytilus galloprovincialis* meat and intervalvular fluid) and fish (*Platichthys fesus*)	Portugal (Tagus estuary) and Italy (Po estuary)	BP-3 IMC 4-MBC OC OMC OD-PABA EHS HMS DHHB	n.d***	[104]
Mussels (*Mytilus edulis* and *Mytilus galloprovincialis,* meat and intervalvular fluid)	Spain (Ebro delta)	BP-3 IMC 4-MBC OC OMC OD-PABA EHS HMS DHHB	n.d. n.d. n.d. <LOQ <LOQ n.d. n.d. n.d. n.d.	
Fish (*Liza aurata*)	Portugal (Tagus estuary)	BP-3 IMC 4-MBC OC OMC	<LOQ n.d. n.d. n.d. n.d.	

		OD-PABA EHS HMS DHHB	n.d. n.d. n.d. n.d.	
Clams (*Chamelea gallina*, meat and intervalvular fluid)	Spain (Ebro delta)	BP-3 IMC 4-MBC OC OMC OD-PABA EHS HMS DHHB	n.d. n.d. n.d. <LOQ <LOQ n.d. n.d. n.d. n.d.	
Dolphin (*Pontoporia blainvillei*, mother, blubber)	Brazil (Rio de Janeiro, Sao Paulo and Ceará state)	4-MBC OC OMC OD-PABA	($ng \cdot g^{-1}$ l.w.) n.d.- 47.5 n.d.- 113 n.d.- 85.0 n.d.- 3.15	[60]
Dolphin (*Pontoporia blainvillei*, mother, muscle)		4-MBC OC OMC OD-PABA	($ng \cdot g^{-1}$ l.w.) n.d.- 855 n.d. 54- 67.5 n.d.	
Dolphin (*Pontoporia blainvillei*, mother, milk)		4-MBC OC OMC OD-PABA	($ng \cdot g^{-1}$ l.w.) 17.5- 20.0 n.d. n.d.- 120 n.d.- 8.5	
Dolphin (*Pontoporia blainvillei*, mother, placenta)		4-MBC OC OMC OD-PABA	($ng \cdot g^{-1}$ l.w.) n.d. n.d. n.d. 1385	
Dolphin (*Pontoporia blainvillei*, calf, blubber)		4-MBC OC OMC OD-PABA	($ng \cdot g^{-1}$ l.w.) n.d. n.d. 67.0 n.d.	
Dolphin (*Pontoporia blainvillei*, calf, muscle)		4-MBC OC OMC	($ng \cdot g^{-1}$ l.w.) 250 925 133	

		OD-PABA	36.5	
Dolphin (*Pontoporia blainvillei*, fetus, blubber)		4-MBC OC OMC OD-PABA	($ng \cdot g^{-1}$ l.w.) n.d.- 97.0 n.d.- 50.0 n.d.- 117 n.d.- 67.5	
Dolphin (*Pontoporia blainvillei*, fetus, muscle)		4-MBC OC OMC OD-PABA	($ng \cdot g^{-1}$ l.w.) n.d.- 170 n.d.- 11130 69.0- 250 n.d.- 155	
Dolphin (*Sotalia guianensis*, mother, blubber)		4-MBC OC OMC OD-PABA	($ng \cdot g^{-1}$ l.w.) n.d.- 48.0 n.d.- 220 n.d.- 205 n.d.- 34.0	
Dolphin (*Sotalia guianensis*, mother, muscle)		4-MBC OC OMC OD-PABA	($ng \cdot g^{-1}$ l.w.) 230- 570 970- 8310 70- 545 n.d.- 1050	
Dolphin (*Sotalia guianensis*, fetus, blubber)		4-MBC OC OMC OD-PABA	($ng \cdot g^{-1}$ l.w.) n.d.- 34.0 n.d. n.d. n.d.	
Dolphin (*Sotalia guianensis*, fetus, muscle)		4-MBC OC OMC OD-PABA	($ng \cdot g^{-1}$ l.w.) 60.0- 80.0 115- 240 40.0- 85.0 17.0- 26.0	
Fish (*Lutjanus argentimaculatus*, *Lutjanus stellatus* and *Epinephelus lanceolatus*. Farmed fishes)	China (Hong Kong)	BP-3 4-MBC OC OMC OD-PABA	<LOD- 3.1 <LOD <LOD- 5.4 <LOD- 12.7 <LOD- 10.3	[58]
Mussels (*Perna viridis*)		BP-3 4-MBC OC OMC	<LOD- 10.3 <LOD <LOD- 8.8 <LOD- 51.3	

		OD-PABA	<LOD- 24.1	
Clams (*Mactra antiquata* and *Corbicula sp.)*		BP-3 4-MBC OC OMC OD-PABA	9.7- 12.4 <LOD <LOQ- 11.6 24.6- 33.1 18.7- 22.6	
Conch (*Babylonia sp.*)		BP-3 4-MBC OC OMC OD-PABA	<LOD- <LOQ <LOD <LOD <LOQ <LOQ	
Shrimp (*Penaeus monodon*)		BP-3 4-MBC OC OMC OD-PABA	<LOD <LOD <LOD <LOD <LOD	
Sea urchin (*Anthocidaris crassispina*)		BP-3 4-MBC OC OMC OD-PABA	<LOD <LOD <LOD <LOD <LOD	
Golden pompano (*Trachinotus ovatus*)	China (Pearl River estuary)	BP-3 4-MBC OC	($ng \cdot g^{-1}$ l.w.) 5.04 8.0 20.0	[66]
Bigeye herring (*Harengula ovalis*)		BP-3 4-MBC OC BM-BMD	($ng \cdot g^{-1}$ l.w.) 5.82 13.4 17.4 2	
Gray's grenadier anchovy (*Coilia grayii*)		BP-3 4-MBC OC	($ng \cdot g^{-1}$ l.w.) 4.19 10.7 7.9	
Black pomfret (*Formio niger*)		BP-3 4-MBC OC	($ng \cdot g^{-1}$ l.w.) 1.62 5.4 11.5	

Bombay duck (*Harpadon nehereus*)		BP-3 4-MBC OC	($ng \cdot g^{-1}$ l.w.) 1.77 8.7 10.4	
Yellow drum (*Nibea albiflora*)		BP-3 4-MBC OC	($ng \cdot g^{-1}$ l.w.) 2.96 13.9 13.7	
Bighead croaker (*Collichthys lucidus*)		BP-3 4-MBC OC BM-DBM	($ng \cdot g^{-1}$ l.w.) 5.11 9.3 13.7 3	
Smallhead hairtail (*Eupleurogrammus muticus*)		BP-3 4-MBC OC	($ng \cdot g^{-1}$ l.w.) 2.12 8.9 27.2	
Bigeye snapper (*Lutjanus lutjanus)*		BP-3 OC	($ng \cdot g^{-1}$ l.w.) 2.14 20	
Shortnose ponyfish (*Leiognathus brevirostris*)		BP-3 4-MBC OC	($ng \cdot g^{-1}$ l.w.) 0.68 8.4 25.2	
Taileyed goby (*Parachaeturichthys polynema)*		BP-3 4-MBC OC	($ng \cdot g^{-1}$ l.w.) 2.26 16.9 5.3	
Silver sillago (*Sillago sihama*)		BP-3 4-MBC OC	($ng \cdot g^{-1}$ l.w.) 2.94 10.9 30.5	
Half-smooth golden pufferfish (*Lagocephalus spadiceus*)		BP-3 4-MBC OC	($ng \cdot g^{-1}$ l.w.) 2.22 5.9 12.8	
Pike conger (*Muraenesox cinereus*)		BP-3 4-MBC	($ng \cdot g^{-1}$ l.w.) 8.88 5.7	

Rice-paddy eel (*Pisodonophis boro*)		BP-3 4-MBC OC BM-DBM	(ng·g^{-1} l.w.) 3.97 4.7 20.2 3	
Macao tonguesole (*Cynoglossus sinicus*)		BP-3 4-MBC OC	(ng·g^{-1} l.w.) 5.26 12.0 31.8	
Bluespot mullet (*Moolgarda seheli)*		BP-3 OC	(ng·g^{-1} l.w.) 9.99 18.6	
Musket squid (*Loliolus beka*)		BP-3 4-MBC OC OMC	(ng·g^{-1} l.w.) 2.40 6.0 10.4 13	
Bigfin reef squid (*Sepioteuthis lessoniana*)		BP-3 4-MBC OC	(ng·g^{-1} l.w.) 9.04 38.9 28.1	
Sword prawn (*Parapenaeopsis hardwickii*)		BP-3 4-MBC OC	(ng·g^{-1} l.w.) 1.24 2.0 3.3	
Kuruma prawn (*Marsupenaeus japonicus*)		BP-3 4-MBC OC	(ng·g^{-1} l.w.) 2.93 3.3 5.0	
Japanese stone crab (*Charybdis japonica*)		BP-3 4-MBC OC BM-BDM	(ng·g^{-1} l.w.) 43.40 2.3 5.8 21	
Blue swimming crab (*Portunus pelagicus*)		BP-3 4-MBC OC	(ng·g^{-1} l.w.) 0.94 3.5 2.4	
Mantis shrimp (*Oratosquilla oratoria*)		BP-3 4-MBC	(ng·g^{-1} l.w.) 2.30 12.2	

		OC	16.6	
Coral tissues (*Favites abdita*)♦	China (Hong Kong, Ung Kong, wet season)	BP-3 4-MBC OC OMC OD-PABA	8.0- 14.3 <LOD 1.5- 2.1 <LOD <LOD	[32]
	China (Hong Kong, Wu Pai, wet season)	BP-3 4-MBC OC OMC OD-PABA	14.1- 21.8 <LOD 2.0- 4.3 <LOD <LOD	
	China (Hong Kong, Sharp Island, wet season)	BP-3 4-MBC OC OMC OD-PABA	14.1- 21.8 <LOD 3.1- 4.9 <LOD <LOD	
	China (Hong Kong, Sung Kong, wet season)	BP-3 4-MBC OC OMC OD-PABA	9.5- 11.2 <LOD 1.8- 2.6 <LOD <LOD	
Coral tissues (Porites sp)♦	China (Hong Kong, Ung Kong, wet season)	BP-3 4-MBC OC OMC OD-PABA	10.6- 22.7 <LOD 2.9- 6.3 <LOD 6.0- 17.1	
	China (Hong Kong, Wu Pai, wet season)	BP-3 4-MBC OC OMC OD-PABA	9.4- 15.7 <LOD <LOD <LOD <LOD	
	China (Hong Kong, Sharp Island, wet season)	BP-3 4-MBC OC OMC OD-PABA	22.1- 38.4 <LOD 6.2- 7.0 <LOD 8.4- 14.8	
	China (Hong Kong, Sung Kong, wet season)	BP-3 4-MBC OC OMC OD-PABA	11.3- 24.2 <LOD 6.5- 8.7 <LOD 4.4- 14.7	

	China (Hong Kong, Ung Kong, dry season)	BP-3 4-MBC OC OMC OD-PABA	5.6- 14.7 <LOD <LOD <LOD <LOD	
	China (Hong Kong, Wu Pai, dry season)	BP-3 4-MBC OC OMC OD-PABA	10.3- 11.3 <LOD <LOD <LOD <LOD	
	China (Hong Kong, Sharp Island, dry season)	BP-3 4-MBC OC OMC OD-PABA	4.7- 14.0 <LOD <LOD <LOD <LOD	
Coral tissues (*Pavona decussat*)♦	China (Hong Kong, Ung Kong, wet season)	BP-3 4-MBC OC OMC OD-PABA	2.3- 5.1 <LOD <LOD <LOD <LOD	
	China (Hong Kong, Wu Pai, wet season)	BP-3 4-MBC OC OMC OD-PABA	9.4- 15.7 <LOD <LOD <LOD <LOD	
	China (Hong Kong, Sharp Island, wet season)	BP-3 4-MBC OC OMC OD-PABA	13.9- 26.6 <LOD <LOD <LOD <LOD	
	China (Hong Kong, Sung Kong, wet season)	BP-3 4-MBC OC OMC OD-PABA	3.9- 16.4 <LOD <LOD <LOD <LOD	
	China (Hong Kong, Ung Kong, dry season)	BP-3 4-MBC OC OMC OD-PABA	2.1- 7.8 <LOD <LOD <LOD <LOD	

	China (Hong Kong, Sharp Island, dry season)	BP-3 4-MBC OC OMC OD-PABA	1.0- 5.6 <LOD <LOD <LOD <LOD	
Coral tissues (*Acropora valida*)♦	China (Hong Kong, Ung Kong, dry season)	BP-3 4-MBC OC OMC OD-PABA	9.9- 12.3 <LOD <LOD <LOD <LOD	
Coral tissues (*Platygyra acuta*)♦	China (Hong Kong, Ung Kong, dry season)	BP-3 4-MBC OC OMC OD-PABA	1.0- 5.7 <LOD <LOD <LOD <LOD	
	China (Hong Kong, Wu Pai, dry season)	BP-3 4-MBC OC OMC OD-PABA	4.8- 6.1 <LOD <LOD <LOD <LOD	
	China (Hong Kong, Sharp Island, dry season)	BP-3 4-MBC OC OMC OD-PABA	2.2- 6.0 <LOD <LOD <LOD <LOD	
Mussels (*Mytilus galloprovincialis*)♥	Spain (Galicia)	BP-3 BP-4 4-MBC OC OD-PABA	<LOQ- 80 6- 739 <LOQ- 801 <LOQ- 833 <LOQ- 46	[115]
Fish liver (*Mugil liza*)	Brazil (Ipiranga)	BP-3 4-MBC OC OMC OD-PABA	11.8- 74.4 7.16- 13.7 <LOQ- 25.9 <LOQ- 9.53 <LOQ	[59]
	Brazil (Itaipu)	BP-3 4-MBC OC OMC OD-PABA	7.55- 50.6 <LOQ- 11.7 <LOQ- 11.6 <LOQ- 14.0 n.d.- <LOQ	

Fish (*Mugil liza*, fillet)	Brazil (Ipiranga)	BP-3 4-MBC OC OMC OD-PABA	3.5- 15.4 <LOQ- 23.4 <LOQ- 57.8 <LOQ- 49.4 <LOQ	
	Brazil (Itaipu)	BP-3 4-MBC OC OMC OD-PABA	<LOQ- 4.84 n.d.- 16.4 n.d.- 22.3 <LOQ <LOQ	
Fish (*Mugil liza*, gills)	Brazil (Ipiranga)	BP-3 4-MBC OC OMC OD-PABA	<LOQ- 6.62 <LOQ- 7.47 <LOQ- 9.96 <LOQ <LOQ	
	Brazil (Itaipu)	BP-3 4-MBC OC OMC OD-PABA	<LOQ- 24.0 4.42- 14.5 <LOQ- 16.8 <LOQ- 7.27 <LOQ	
Fish (Mackerel, canned)	Portugal	BP-3 IMC 4-MBC OC OMC OD-PABA EHS HMS DHHB	n.d.- 5.0 5.0- 43.9 5.0- 17.5 n.d.- 18.5 n.d.- 2.5 n.d. n.d.- 48.1 n.d.- 5.1 n.d.	[103]
Fish (Tuna, canned)	Portugal	BP-3 IMC 4-MBC OC OMC OD-PABA EHS HMS DHHB	n.d.- 27.6 n.d.- 5,5 5,0-5,0 n.d.- 57.6 n.d.- 65.4 n.d. n.d.- 13.8 n.d.- 10.4 n.d.	
Fish (Sardine, canned)	Portugal	BP-3 4-MBC OD-PABA DHHB	55.72 14.09 n.d. n.d.	

Fish (Salmon, aquaculture, fish fillet)	Denmark	BP-3 IMC 4-MBC OC OMC OD-PABA EHS HMS DHHB	n.d.- 2,5 n.d.- 5 5,0-5,0 n.d.- 5 n.d.- 2.5 n.d. n.d.- 23 n.d.- 15.3 n.d.	
Fish (Seabream, aquaculture, fish fillet)	Italy and other origins	BP-3 IMC 4-MBC OC OMC OD-PABA EHS HMS DHHB	n.d.- 5.0 5- 66.7 n.d.- 8 30- 103.3 n.d.- 2.5 n.d. n.d.- 42.9 n.d.- 33.4 n.d.	
Mussel (soft tissues)	Italy, Netherlands, Spain, Denmark, France and Ireland	BP-3 IMC 4-MBC OC OMC OD-PABA EHS HMS DHHB	n.d.- 85.5 n.d.- 37.3 n.d.- 56.2 n.d.- 56.0 n.d.- 34.2 n.d. n.d.- 72.1 n.d.- 19.1 n.d.	
Octopus	Mediterranean	4-MBC OD-PABA DHHB	5,0- 5,0 n.d. n.d.	
Crab	Netherlands	4-MBC OD-PABA DHHB	5,0- 5,0 n.d. n.d	
Fish (Cod, fish fillet)	Denmark, Pacific	4-MBC OC OD-PABA EHS HMS DHHB	5,0- 5,0 n.d.- 39.1 n.d. n.d.- 26.7 n.d.- 2.5 n.d.	
Fish (Mackerel, fish fillet)	Italy, North Sea, Spain and Denmark	BP-3 IMC 4-MBC	n.d.- 82.2 n.d.- 55.5 n.d.- 15.7	

		OC OMC OD-PABA EHS HMS DHHB	n.d.- 43.2 n.d.- 28.7 n.d. n.d.- 49.1 n.d.- 6.4 n.d.	
Fish (Monkfish, fish fillet)	Portugal	BP-3 IMC 4-MBC OC OMC OD-PABA EHS HMS DHHB	5.0- 98.7 n.d.- 5.0 5.0- 20.4 n.d.- 19.3 2.5- 74.4 n.d. n.d.- 15.3 n.d.- 54 n.d.	
Fish (Plaice/Sole, fish fillet)	Italy and North Sea	4-MBC OD-PABA DHHB	5,0- 5,0 n.d. n.d.	
Fish (Tuna, fish fillet)	Pacific	BP-3 IMC 4-MBC OC OMC OD-PABA EHS HMS DHHB	n.d.- 2,5 n.d.- 5.0 n.d.- 5,0 n.d.- 5.0 n.d.- 2.5 n.d. n.d.- 5.0 n.d.- 58.5 n.d.	

♦ Expressed in $ng \cdot g^{-1}$ ww.

˜Concentration measured after 30 days of exposition

Publicación: Occurrence and environmental hazard of organic UV filters in seawater and wastewater from Gran Canaria Island (Canary Islands, Spain)

Supplementary material

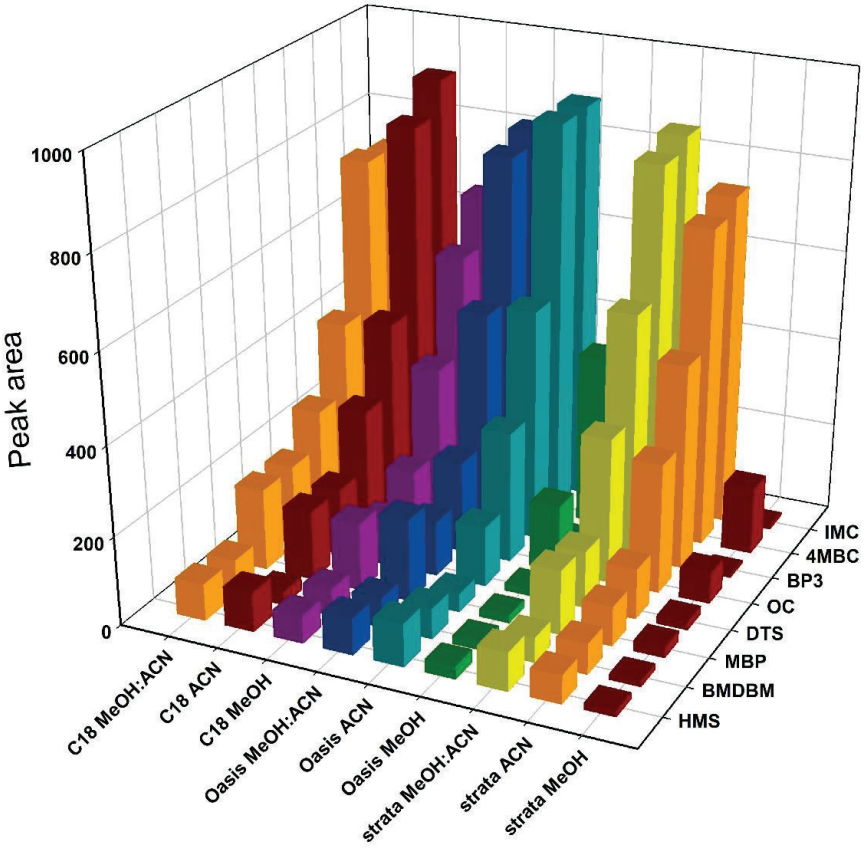

Figure S1. Responses obtained using different SPE sorbents and eluents for the extraction of target organic UV filters from seawater.

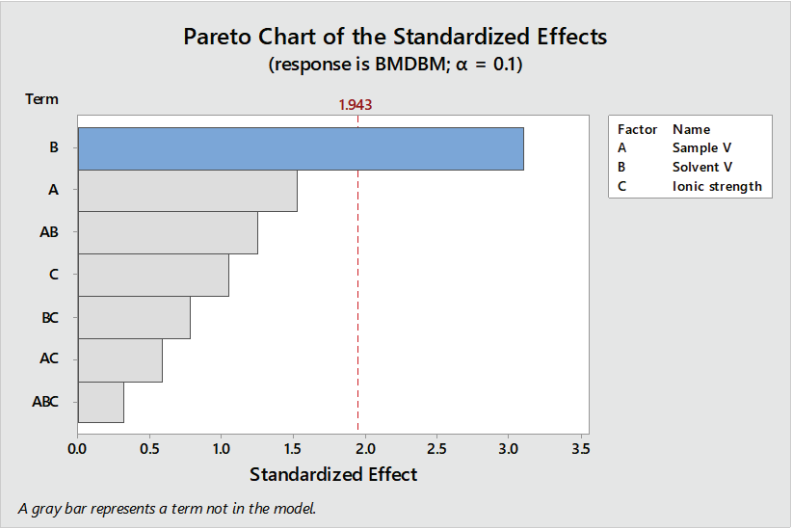

Figure S2. Pareto chart of the standardized effects for the factors studied in the 2^3 experimental design for BMDBM in seawater.

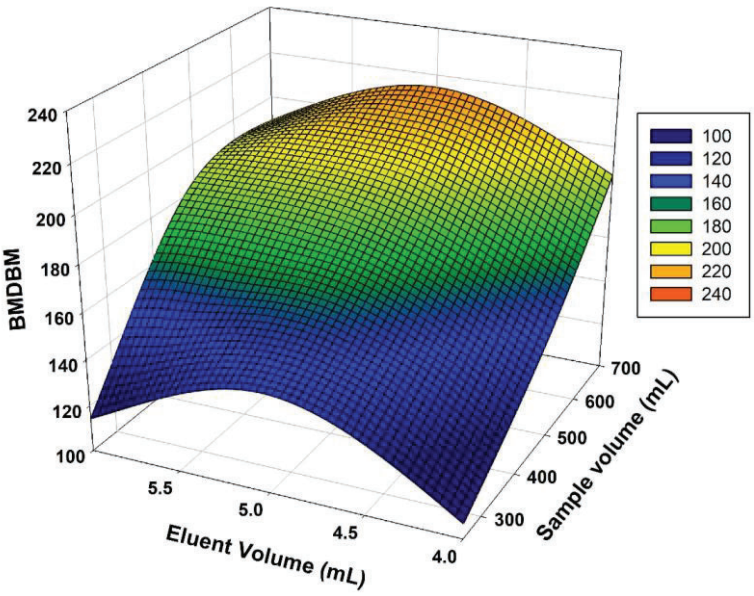

Figure S3. Response surface for the effect of the sample and eluent volumes in the extraction of BMDBM from seawater.

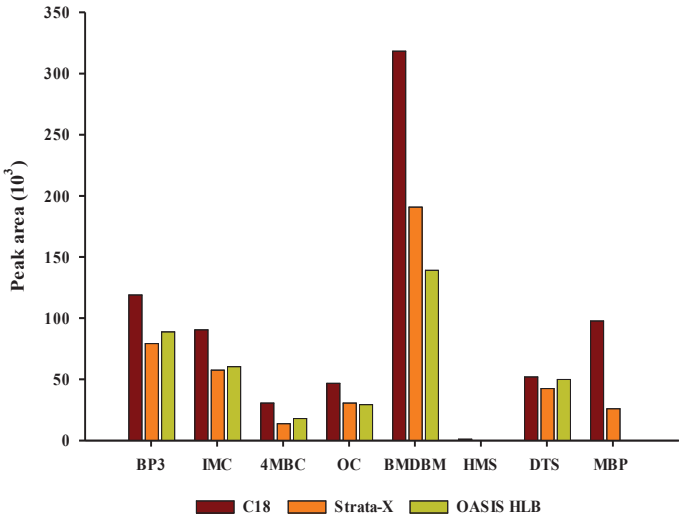

Figure S4. Responses obtained using different SPE sorbents for the extraction of target organic UV filters from wastewater.

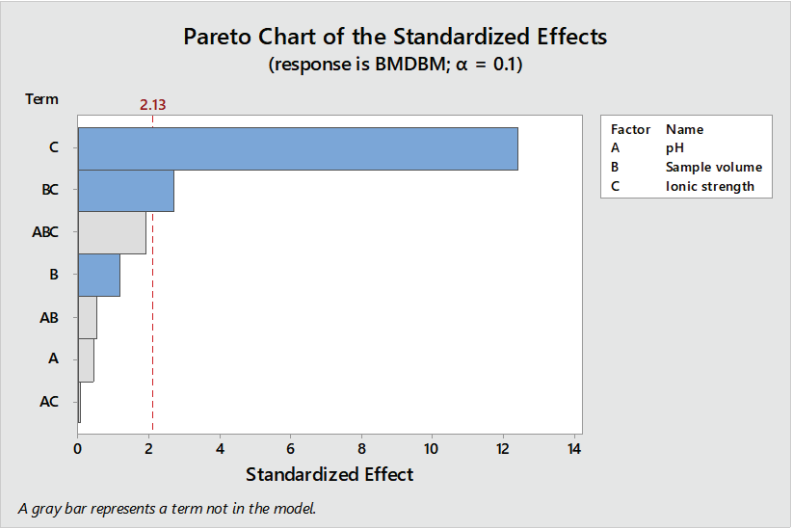

Figure S5. Pareto chart result of the standardized effects for the factor studied in the 2^3 experimental design for BMDBM in wastewater.

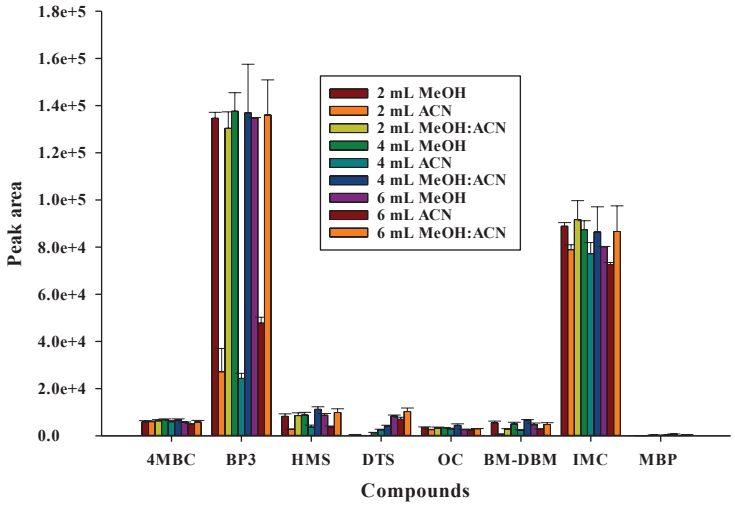

Figure S6. Responses obtained using different organic solvents and volumes to elute organic UV filters from SPE cartridges (wastewater samples).

Table S1. Maximum concentration in the ready to use preparation of PCPs according the European Union.

INCI name[a]	Abbreviation	CAS number	EC number	Maximum concentration (%)
Benzophenone-3/ Oxybenzone	BP3	131-57-7	205-031-5	6
Homosalate	HMS	118-56-9	204-260-8	10
Isoamyl *p*-methoxycinnamate/ Amiloxate	IMC	71617-10-2	275-702-5	10
4-methylbenzylidene camphor/Enzacamene	4MBC	36861-47-9/ 38102-62-4	253-242-6	4
Drometrizole trisiloxane	DTS	155633-54-8	-	15
Methylene bis-benzotriazolyltetramethylbutylphenol/ Bisoctrizole	MBP	103597-45-1	403-800-1	10
Butyl methoxydibenzoylmethane/ Avobenzone	BMDBM	70356-09-1	274-581-6	5
Octocrylene	OC	6197-30-4	228-250-8	10 (as acid)

[a] INCI: International Nomenclature for Cosmetic Ingredients.

Table S2. Detailed information of the seawater sampling places and marine outfall locations of the 3 WWTPs.

Sampling place	GPS coordinates
Las Canteras beach	28°8'27.982"N, 15°26'8.237"W
Arinaga beach	27°51'24.709"N, 15°23'49.5546"W
Playa del Inglés beach	27°45'23.579"N, 15°33'51.2809"W
WWTP1 outfall	28º 05' 34.13" N, 15º 23' 35.48"W
WWTP2 outfall	27º 50' 18.80" N, 15º 23' 30.27"W
WWTP3 outfall	27º 45' 47.88" N, 15º 33' 28.38"W

Table S3. Mass parameters conditions for organic UV filters determination.

Compounds	Precursor 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	332.0	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
MBP	659.8	40	336.2	25	224.2	35

Table S4. Linearity of the calibration curves for each studied matrix.

Concentration range	0.025 µg·L^{-1}- 250 µg·L^{-1}		0.05 µg·L^{-1}- 250 µg·L^{-1}					
	Seawater		Influent		Secondary treatment effluent		Tertiary treatment effluent	
Compounds	**Equation**	**R^2**	**Equation**	**R^2**	**Equation**	**R^2**	**Equation**	**R^2**
4-MBC	8.171x+15.59	0.993	7.837x-0.0003	0.999	33.034x-0.0003	0.996	36.24x+0.0006	0.997
BP-3	126.5x+32.68	0.991	233.4x+0.0902	0.998	528.33x-0.0799	0.997	575.1x+0.0165	0.997
HMS	10.82x+3.452	0.992	14.87x-0.0064	0.993	17.77x-0.0024	0.998	30.76x+0.0021	0.997
DTS	2.607x+1.658	0.992	30.07x-0.0018	0.999	34.47x-0.0003	0.999	46.34x+0.0002	0.998
OC	5.297x+5.720	0.990	27.18x+0.0092	0.987	38.44x-0.0001	0.999	49.78x-0.0027	0.998
BMDBM	24.98x+14.23	0.996	34.79x+0.0208	0.997	163.22x-3.776	0.999	171.25x-0.0043	0.996
IMC	95.89x+9.781	0.992	142.2x+0.0199	0.994	340.77x-0.0083	1.000	476.19x-0.0552	0.996
MBP	0.947x+0.587	0.991	4.173x+0.0009	1.000	4.9037x+0.0071	0.998	7.7124x+1.476	0.998

Table S5. Recoveries obtained for the target organic UV filters in seawater and three kinds of wastewater for two concentrations levels.

Compounds	Seawater recoveries (%)		Influent recoveries (%)		Secondary recoveries (%)		Tertiary recoveries (%)	
	0.05 $\mu g \cdot L^{-1}$	200 $\mu g \cdot L^{-1}$	0.3 $\mu g \cdot L^{-1}$	200 $\mu g \cdot L^{-1}$	0.1 $\mu g \cdot L^{-1}$	10 $\mu g \cdot L^{-1}$	0.1 $\mu g \cdot L^{-1}$	10 $\mu g \cdot L^{-1}$
4MBC	95.8	100	71.7	78.9	84.7	84.9	80.0	89.7
BP3	99.0	99.3	78.9	81.8	89.5	90.4	90.0	98.5
HMS	92.0	98	53.9	62.3	71.4	80.2	89.0	95.7
DTS	86.0	91.1	56.5	65.1	73.1	77.4	73.0	87.9
OC	84.0	89.5	50.6	60.1	71.5	75.5	83.0	85.2
BMDBM	80.0	89.9	59.9	64.6	66.6	71.7	78.5	80.3
IMC	96.0	98.4	58.0	74.6	65.1	88.3	90.0	97.1
MBP	-	43.8	19.3	28.5	20.0	33.3	26.0	39.0

Table S6. Intra-day and inter-day precision for the developed SPE-UHPLC-MS/MS method at two concentration levels for seawater and the three wastewater types.

Compounds	Seawater intra-day precision (%)		Seawater inter-day precision (%)		Influent intra-day precision (%)		Influent inter-day precision (%)		Secondary intra-day precision (%)		Secondary inter-day precision (%)		Tertiary intra-day precision (%)		Tertiary inter-day precision (%)	
	0.05 $\mu g \cdot L^{-1}$	200 $\mu g \cdot L^{-1}$	0.05 $\mu g \cdot L^{-1}$	200 $\mu g \cdot L^{-1}$	0.3 $\mu g \cdot L^{-1}$	200 $\mu g \cdot L^{-1}$	0.3 $\mu g \cdot L^{-1}$	200 $\mu g \cdot L^{-1}$	0.1 $\mu g \cdot L^{-1}$	10 $\mu g \cdot L^{-1}$	0.1 $\mu g \cdot L^{-1}$	10 $\mu g \cdot L^{-1}$	0.1 $\mu g \cdot L^{-1}$	10 $\mu g \cdot L^{-1}$	0.1 $\mu g \cdot L^{-1}$	10 $\mu g \cdot L^{-1}$
4MBC	1.70	2.69	9.80	9.11	5.90	6.95	9.22	5.00	7.25	9.49	8.98	5.26	7.81	7.14	12.0	9.14
BP3	3.30	0.02	11.8	13.0	1.65	3.23	5.04	3.72	2.30	9.78	11.9	8.07	8.70	5.93	8.02	5.17
HMS	5.10	7.50	13.5	5.43	8.09	7.52	9.03	7.01	9.81	6.51	8.80	8.73	6.10	11.9	4.49	7.12
DTS	4.00	4.01	6.10	5.69	6.19	3.63	11.8	13.9	12.0	6.55	12.5	8.87	5.79	12.4	14.9	9.25
OC	13.9	10.7	11.8	6.68	9.02	1.13	11.5	8.50	9.81	7.54	9.02	12.5	9.00	8.79	7.00	13.6
BMDBM	0.10	0.59	9.40	2.59	9.30	4.80	9.32	12.1	6.55	11.0	12.8	10.9	13.5	11.9	11.3	11.5
IMC	3.80	11.4	5.20	11.0	13.2	0.50	8.75	4.04	10.9	12.2	9.52	10.0	9.83	1.68	7.26	4.80
MBP	-	0.77	-	13.5	6.26	12.1	12.8	11.5	3.48	9.41	10.9	9.83	10.2	12.1	9.37	11.9

Table S7. Method limits of detection (MLODs) and method limits of quantification (MLOQs) for the developed SPE- UHPLC-MS/MS method.

Compounds	Seawater		Influent		Tertiary	
	MLODs ($ng \cdot L^{-1}$)	MLOQs ($ng \cdot L^{-1}$)	MLODs ($ng \cdot L^{-1}$)	MLOQs ($ng \cdot L^{-1}$)	MLODs ($ng \cdot L^{-1}$)	MLOQs ($ng \cdot L^{-1}$)
4MBC	12.9	43.1	96.5	321.5	34.1	113.5
BP3	11.9	39.8	29.1	97.1	24.6	82.1
HMS	11.3	37.7	66.8	222.7	45.1	150.2
DTS	12.1	40.4	60.2	200.6	45.3	151.1
OC	12.7	42.4	45.6	152.0	33.7	112.4
BMDBM	10.8	35.9	32.1	106.8	26.2	87.3
IMC	13.7	45.6	52.9	176.5	44.0	146.8
MBP	36.4	121.3	555.6	1851.9	72.7	242.5

Table S8. Target organic UV filters concentrations measured in seawater samples. Each value corresponds to the mean of three replicates (n=3).

Sampling place	Date	Compound concentration (μg·L^{-1})							
		4MBC	BP3	HMS	DTS	OC	BMDBM	IMC	MBP
SL1	May-19	nd	nd	nd	nd	nd	0.19±0.01	nd	nd
	June-19	nd	0.42±0.06	nd	nd	nd	0.33±0.03	nd	nd
	July-19	nd	4.81±0.49	nd	0.44±0.02	nd	0.10±0.01	0.43±0.06	nd
	August-19	17.5±1.70	20.5±1.78	39.8±5.22	25.2±1.36	172±11.4	88.9±9.94	4.27±0.58	nd
	September-19	nd	6.45±0.08	nd	nd	5.64±0.85	4.82±0.58	0.64±0.06	nd
	October-19	nd	0.41±0.01	nd	nd	nd	nd	nd	nd
	Detection frequencies (%)	17	83	17	33	33	83	50	0
SL2	May-19	nd	0.16±0.01	nd	nd	nd	nd	nd	nd
	June-19	nd	0.27±0.03	nd	nd	nd	nd	0.28±0.04	nd
	July-19	nd	nd	nd	nd	nd	nd	0.37±0.03	nd
	August-19	3.08±0.54	1.55±0.14	nd	0.73±0.04	nd	0.21±0.02	0.47±0.01	nd
	September-19	nd	1.46±0.12	nd	0.51±0.02	nd	nd	0.42±0.01	nd
	October-19	nd	0.48±0.06	nd	0.41±0.04	nd	nd	0.12±0.01	146±4.54
	Detection frequencies (%)	17	83	0	50	0	17	83	17
SL3	May-19	nd	0.17±0.02	nd	nd	nd	nd	0.12±0.02	nd
	June-19	nd	nd	nd	nd	nd	0.16±0.01	0.46±0.06	nd
	July-19	nd	2.39±0.01	nd	nd	nd	nd	0.47±0.02	nd
	August-19	nd	6.10±0.02	2.75±0.13	nd	2.52±0.26	6.32±0.43	2.00±0.23	nd

September-19	nd	2.62±0.04	nd	nd	nd	1.44±0.20	0.07±0.01	nd
October-19	nd	8.27±0.93	nd	nd	nd	4.37±0.49	0.19±0.02	nd
Detection frequency (%)	0	83	17	0	17	67	100	0
Total detection frequency (%)	**11**	**83**	**11**	**28**	**17**	**56**	**78**	**6**

nd Not detected.

Table S9. Target organic UV filters concentrations measured in the three studied WWTPs.

Date	UV filters	WWTP 1		WWTP 2			WWTP 3	
		Influent ($\mu g \cdot L^{-1}$)	Secondary ($\mu g \cdot L^{-1}$)	Influent ($\mu g \cdot L^{-1}$)	Secondary ($\mu g \cdot L^{-1}$)	Tertiary ($\mu g \cdot L^{-1}$)	Influent ($\mu g \cdot L^{-1}$)	Secondary ($\mu g \cdot L^{-1}$)
May-19	4MBC	2.78±0.15	0.68±0.05	2.13±0.04	0.88±0.02	0.45±0.05	10.1±1.31	0.75±0.07
	BP3	23.0±2.15	4.23±0.13	47.7±3.21	7.17±0.82	5.11±0.04	145±9.02	4.44±0.10
	HMS	nd	nd	3.96±0.29	0.34±0.01	0.18±0.02	44.4±2.10	nd
	DTS	2.81±0.40	0.09±0.01	1.00±0.14	0.44±0.02	0.34±0.03	3.46±0.42	nd
	OC	1.94±0.25	nd	21.7±1.25	0.87±0.07	nd	208±7.78	1.43±0.18
	BMDBM	42.9±3.69	1.25±0.09	21.3±1.56	3.71±0.01	nd	125±4.99	2.11±0.05
	IMC	0.48±0.07	0.34±0.03	0.88±0.02	0.67±0.10	0.34±0.02	1.55±0.11	0.19±0.02
	MBP	nd	nd	nd	nd	nd	21.8±1.35	nd
June-19	4MBC	nd	nd	0.90±0.13	0.27±0.04	0.16±0.01	10.5±1.11	0.72±0.09
	BP3	40.1±5.83	3.01±0.24	31.1±4.23	7.16±0.46	7.43±0.53	111±4.21	4.36±0.40
	HMS	2.15±0.25	nd	0.26±0.03	nd	1.25±0.03	30.7±3.62	nd
	DTS	1.90±0.24	0.22±0.02	0.20±0.02	0.14±0.02	nd	2.09±0.31	nd
	OC	10.6±0.97	1.06±0.14	5.74±0.35	1.34±0.20	1.31±0.15	157±11.9	1.22±0.15
	BMDBM	32.9±2.64	1.93±0.28	31.3±3.22	2.27±0.14	1.47±0.11	107±11.8	2.78±0.41
	IMC	0.49±0.07	0.24±0.02	0.67±0.07	0.51±0.08	0.31±0.03	1.62±0.03	0.18±0.01
	MBP	nd	nd	12.0±1.39	7.48±1.06	nd	nd	nd
July-19	4MBC	0.76±0.10	0.31±0.04	2.16±0.23	0.15±0.01	1.40±0.15	8.00±0.60	nd
	BP3	26.8±1.86	2.89±0.27	25.2±0.90	8.18±0.70	8.07±0.26	132.±1.57	3.38±0.09
	HMS	1.54±0.22	nd	1.34±0.17	0.89±0.10	0.15±0.01	43.7±1.25	nd
	DTS	0.93±0.11	nd	1.60±0.13	-	1.26±0.08	3.94±0.53	0.41±0.01
	OC	8.27±0.55	1.28±0.17	27.0±1.16	1.72±0.10	0.32±0.02	150±5.19	0.35±0.04
	BMDBM	35.4±2.47	2.61±0.27	35.4±0.64	2.61±0.30	2.11±0.02	112±8.31	1.64±.18
	IMC	0.67±0.06	0.17±0.02	0.26±0.02	0.28±0.01	0.23±0.03	1.91±0.08	0.08±0.01

	MBP	16.5±1.98	9.73±1.29	nd	nd	nd	20.4±1.66	nd
August-19	4MBC	nd	nd	2.87±0.12	nd	nd	6.52±0.74	0.74±0.11
	BP3	30.7±2.90	2.62±0.23	24.3±2.88	7.48±0.13	6.70±0.26	99.2±4.49	6.50±0.44
	HMS	2.84±0.41	nd	0.49±0.06	1.95±0.30	nd	28.5±1.31	0.44±0.05
	DTS	nd	nd	1.34±0.14	nd	0.85±0.10	3.45±0.49	nd
	OC	8.15±1.12	0.79±0.03	3.95±0.29	1.96±0.10	1.82±0.14	127±11.4	0.39±0.03
	BMDBM	37.5±5.26	1.18±0.17	36.1±5.22	1.72±0.11	0.97±0.05	89.7±1.34	2.25±0.31
	IMC	0.90±0.07	0.17±0.01	0.51±0.01	0.39±0.05	0.26±0.01	2.07±0.14	nd
	MBP	nd	nd	nd	nd	nd	26.9±0.48	22.4±0.86
September-19	4MBC	nd	nd	nd	nd	nd	7.66±0.50	nd
	BP3	20.8±0.71	4.35±0.24	25.6±2.72	4.34±0.15	3.91±0.32	117±5.17	4.12±0.08
	HMS	nd	nd	1.27±0.09	nd	0.66±0.09	22.7±1.43	nd
	DTS	nd	nd	2.02±0.24	nd	nd	0.62±0.11	nd
	OC	6.96±0.16	0.89±0.06	29.2±4.43	2.03±0.01	nd	93.6±2.01	nd
	BMDBM	30.5±4.07	1.54±0.07	35.5±0.91	1.99±0.20	nd	87.1±8.85	2.79±0.03
	IMC	0.49±0.06	0.37±0.06	0.48±0.08	0.37±0.04	nd	1.47±0.23	0.06±0.01
	MBP	nd	nd	nd	nd	nd	44.5±3.06	34.0±0.22
October-19	4MBC	0.88±0.13	nd	1.07±0.04	0.15±0.03	0.56±0.01	5.88±0.29	nd
	BP3	19.5±0.86	2.75±0.16	24.6±3.00	4.56±0.31	4.37±0.02	88.0±5.34	3.16±0.35
	HMS	1.19±0.19	nd	0.79±0.10	nd	0.43±0.03	9.10±1.01	nd
	DTS	1.04±0.16	nd	1.90±0.27	0.28±0.03	0.83±0.04	nd	nd
	OC	9.99±0.93	0.64±0.08	16.7±1.26	1.16±0.04	0.63±0.06	21.6±2.54	0.72±0.09
	BMDBM	35.7±3.74	0.74±0.06	32.9±4.68	2.20±0.18	nd	51.0±7.34	1.42±0.20
	IMC	0.20±0.03	0.09±0.01	0.60±0.05	0.19±0.01	0.17±0.01	1.14±0.02	nd
	MBP	nd	nd	14.9±1.40	8.76±0.15	1.95±0.21	34.4±2.76	nd

nd Not detected. Mean concentration and standard deviation of n=3 replicates.

Table S10. Removal efficiencies of the target UV filters for the three WWTPs.

Date	UV filters	Removal efficiencies (%)			
		WWTP 1	WWTP 2		WWTP 3
			Influent-secondary	Influent-tertiary	
May-19	4MBC	75	59	79	93
	BP3	82	85	89	97
	HMS	-	91	95	100
	DTS	97	56	66	100
	OC	100	96	100	99
	BMDBM	97	83	100	98
	IMC	29	24	61	88
	MBP	-	-	-	100
June-19	4MBC	-	70	82	93
	BP3	92	77	76	96
	HMS	100	100	-	100
	DTS	88	33	100	100
	OC	90	77	77	99
	BMDBM	94	93	95	97
	IMC	52	24	54	89
	MBP	-	38	100	-
July-19	4MBC	60	93	35	100
	BP3	89	68	68	97
	HMS	100	33	89	100
	DTS	100	100	21	90
	OC	85	94	99	100
	BMDBM	93	93	94	99
	IMC	75	-	10	96
	MBP	41	-	-	100
August-19	4MBC	-	100	100	89
	BP3	91	69	72	93
	HMS	100	-	100	98
	DTS	-	100	37	100
	OC	90	50	54	100
	BMDBM	97	95	97	97
	IMC	81	25	49	100
	MBP	-	-	-	17
September-19	4MBC	-	-	-	100
	BP3	79	83	85	96
	HMS	-	100	48	100
	DTS	-	100	100	100
	OC	87	93	100	100
	BMDBM	95	94	100	97
	IMC	25	23	100	96

	MBP		-	-	24
October-19	4MBC	100	86	48	100
	BP3	86	81	82	96
	HMS	100	100	46	100
	DTS	100	85	56	-
	OC	94	93	96	97
	BMDBM	98	93	100	97
	IMC	53	68	71	100
	MBP	-	41	87	100

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Supplementary material

Figure S1. Pareto chart of the standardized effects for the factors studied in the 2^4 experimental design for 4MBC in the mixture of seaweed.

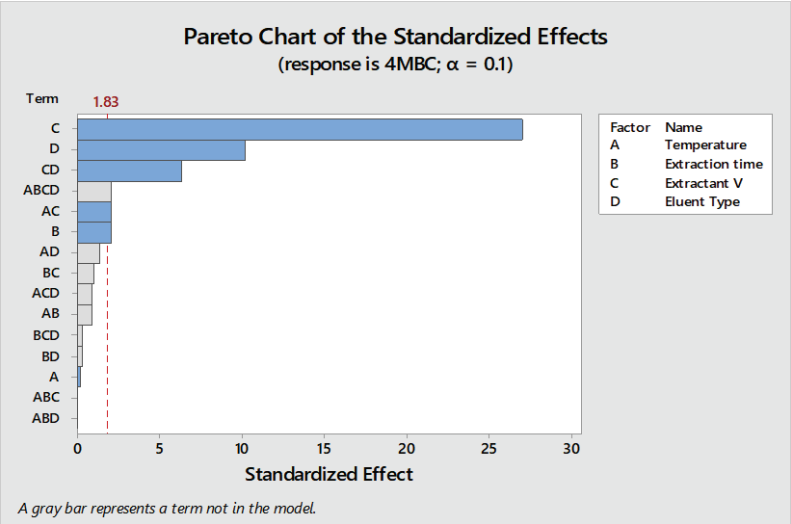

Figure S2. Response surface for the effect of the extractant volume and extraction time in OC.

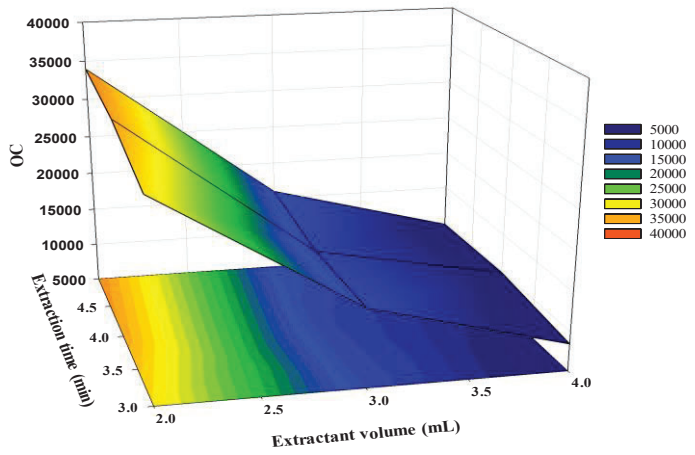

Figure S3. Recoveries of target UV filters using different extractants.

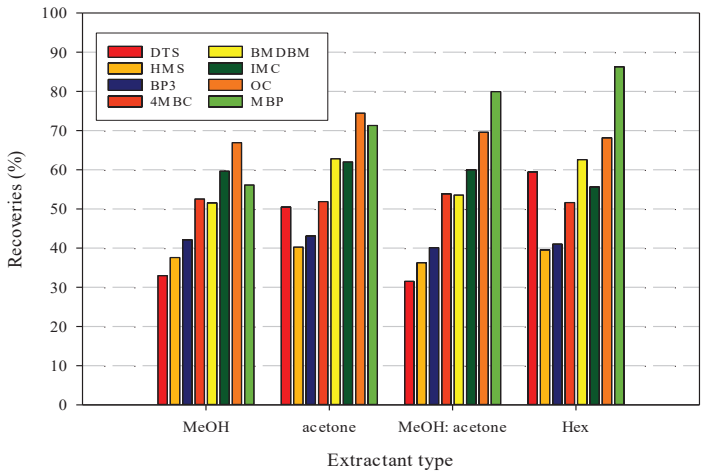

Table S1. Main characteristics of the eight target compounds and mass spectrometer conditions for their determination.

Organic UV filters characteristics							Mass spectrometer detection parameters					
Family	**INCI name[a]**	**Abbreviation**	**CAS number**	**Log K_{ow}**	**Solubility ($g \cdot L^{-1}$)[e]**	**EU product ion[f]**	**Precursor ion (m/z)**	**Cone voltage (V)**	**Quantification ion (m/z)**	**Collision potential (V)**	**Confirmation ion (m/z)**	**Collision potential (V)**
Benzophenones	Benzophenone-3	BP-3	131-57-7	3.79[b]	0.21	LPV	229.0	32	151.0	20	105.0	25
Salicylates	Homosalate	HMS	118-56-9	6.16[c]	0.02	HPV	263.1	12	139.0	10	121.0	30
Cinnamates	Isoamyl p-methoxycinnamate	IMC	71617-10-2	4.33[c]	0.06	LPV	249.1	15	161.2	15	179.2	9
Camphor derivatives	4-methylbenzylidene camphor	4-MBC	36861-47-9/ 38102-62-4	4.95[c]	5.1×10^{-3}	LPV	255.4	25	105.0	27	171.0	19
Benzotriazoles	Drometrizole trisiloxane	DTS	155633-54-8	10.82[d]	1.3×10^{-5}	-	502.0	12	412.2	15	396.2	25
	Methylene bis-benzotriazolyltetramethylbutylphenol	MBP	103597-45-1	12.46[d]	3×10^{-8}	LPV	659.8	40	336.2	25	224.2	35
Dybenzoyl methane derivatives	Butyl methoxydibenzoyl methane	BMDBM	70356-09-1	4.51[c]	0.037	HPV	311.2	30	161.2	23	135.1	23
Crylenes	Octocrylene	OC	6197-30-4	6.88[c]	2×10^{-4}	HPV	362.4	28	250.0	12	332.0	20

[a] INCI International Nomenclature for Cosmetic Ingredients. [b] Experimental value from Syracuse Research Corporation database. [c] Estimated values from Syracuse Research Corporation database. [d] Calculated by use of Estimation Program Interface (EPI) suite v4.11 (2012). [e] In water at 25 ºC, from Díaz-Cruz et al., [1]. [f] From European Chemicals Agency (ECHA), low production volume (LPV) between 10 and over 100 tonnes·year^{-1} and high production volume (HPV) between 1000 and 10000 tonnes·year^{-1} of chemicals produced or imported in the European economic area.

Table S2. Target UV filters concentrations measured in macrophytes samples.

Sampling place	Date	Specie	Compounds concentration (ng·g^{-1}, dw)							
			4-MBC	BP-3	HMS	DTS	OC	BMDBM	IMC	MBP
Las Canteras beach	05/2019	*Cymopolia barbata*	nd	nd	483±43.8	nd	261±29.8	365±19.2	nd	nd
		Lobophora variegata	nd	nd	nd	nd	151±9.37	3663±255	nd	nd
		Sporochnus pedunculatus	nd	319±27.5	914±67.6	nd	293±16.7	nd	nd	nd
		Dictyota dichotoma	nd	Nd	479±58.5	nd	350±13.4	nd	nd	nd
	06/2019	*Sporochnus pedunculatus*	nd	nd	2,162±49.1	4.63±0.57	1,522±77.5	nd	<LOQ	nd
		Cymopolia barbata	165±16.3	244±11.3	2,087±23.8	nd	1,041±92.9	nd	12.8±0.70	nd
		Sargassum sp.	nd	7.73±0.38	82.1±9.45	nd	357±21.4	nd	nd	nd
		Lobophora variegata	nd	21.5±1.07	59.7±1.86	8.93±0.17	938±13.1	1724±138	<LOQ	nd
		Stypocaulon scoparium	nd	nd	100±9.61	20.2±2.33	910±89.5	nd	<LOQ	36.5±0.24
		Asparagopsis taxiformis	nd	nd	252±32.7	14.0±0.46	1,480±8.35	46.4±4.57	nd	nd
		Dictyota dichotoma	nd	nd	1,886±91.0	nd	1,679±75.9	nd	nd	nd
	07/2019	*Liagora sp.*	nd	nd	463±45.5	54.7±6.30	1,577±10.3	nd	nd	<LOQ
		Sporochnus pedunculatus	nd	nd	1,874±78.9	252±28.2	5,249±114	52.1±3.97	nd	134±16.8

		Dictyota dichotoma	nd	nd	2,340±86.5	44.9±1.10	4,180±381	nd	nd	37.9±2.6
		Corallina elongata	nd	nd	2,097±141	397±51.7	4,742±171	nd	nd	315±1.10
		Laurencia sp.	14.9±1.10	nd	1,568±60.9	47.8±4.80	3,320±194	54.4±3.10	3.5±0.20	nd
		Cymopolia barbata	120±1.50	158±7.90	5,479±515	37.7±2.33	2,493±27.8	nd	nd	71.0±6.90
		Lobophora variegata	17.9±1.30	11.2±0.30	357±34.2	28.4±1.70	1,498±72.3	818±38.1	nd	47.8±2.60
	08/2019	*Sporochnus pedunculatus*	nd	nd	3,607±161	73.2±1.90	5,068±140	439±20.7	nd	<LOQ
		Stypocaulon scoparium	36.2±0.95	nd	1,977±138	102±5.40	5,050±141	577±65.4	nd	59.3±8.30
		Liagora sp.	51.7±6.57	nd	1,280±126	9.04±0.20	2,192±16.9	141±0.85	nd	nd
		Sargassum sp.	80.6±7.70	nd	1,508±148	24.5±1.4	4,322±278	486±18.4	nd	nd
		Dictyota dichotoma	nd	nd	3,229±65.9	nd	5,971±483	1,679±64.2	nd	nd
		Asparagopsis taxiformis	nd	nd	2,822±46.2	227±23.3	4,895±480	409±54.0	nd	78.2±1.90
		Cymopolia barbata	165±3.60	66.7±8.3	4,873±449	15.7±1.40	3,012±296	52.4±2.40	nd	nd
		Lobophora variegata	1±1.00	24.0±1.10	469.6±8.30	28.8±1.30	2,078±50.7	2617±123	nd	37.9±2.50
	09/2019	*Lobophora variegata*	nd	19.8±1.20	147±19.4	14.1±0.72	679±64.0	1,885±130	nd	nd

		Sargassum sp.	nd	nd	239±29.5	17.1±0.83	998±85.9	195±8.34	3.40±0.22	<LOQ
		Asparagopsis taxiformis	nd	nd	363±5.10	63.6±0.59	1,570±36.5	102±4.58	nd	51.8±3.83
		Lophocladia trichoclados	nd	nd	191±26.5	45.5±2.30	1,654±22.9	nd	nd	55.4±4.11
		Cymopolia barbata	237±11.9	180±17.4	8,128±37.1	241±20.4	6,372±183	89.3±2.94	20.2±1.66	96.9±12.0
		Dictyota dichotoma	nd	nd	562±30.6	40.3±3.24	1,485±72.1	65.3±0.73	nd	29.6±2.87
	10/2019	*Lophocladia trichoclados*	nd	nd	139±3.31	12.7±0.63	612±54.2	32.6±3.87	nd	<LOQ
		Asparagopsis taxiformis	nd	nd	200±14.9	19.1±2.61	1,317±6.17	nd	nd	31.2±2.15
		Cymopolia barbata	nd	nd	1,113±32.8	nd	505±40.5	nd	nd	nd
		Lobophora variegata	nd	22.7±0.48	4.64±0.07	nd	126±13.4	2,859±21.6	nd	nd
		Dictyota dichotoma	nd	nd	1,124±16.7	nd	1,713±42.3	nd	nd	nd
	Detection frequencies (%)		27	30	97	70	100	59	11	38
Arinaga beach	05/2019	*Asparagopsis taxiformis*	nd	31.5±0.36	192±19.2	nd	229±14.8	nd	12.2±0.38	nd
	06/2016	*Taonia atomaria*	nd	nd	nd	nd	229±22.7	<LOQ	<LOQ	nd
		Stypocaulon scoparium	nd	27.2±0.84	236±10.8	<LOQ	844±63.9	nd	11.2±0.74	nd

		Liagora sp.	<LOQ	182±8.89	347±4.24	16.7±7.35	1,107±47.7	nd	7.03±0.47	26.5±0.16
		Asparagopsis taxiformis	nd	92.7±10.6	299±1.82	nd	1,240±37.0	nd	3.47±0.34	39.2±3.51
		Codium decorticatum	<LOQ	1,153±70.3	180±10.2	nd	7,163±332	150±4.88	nd	nd
	07/2019	*Asparagopsis taxiformis*	nd	124±18.5	776±42.4	388±6.52	5234±579	<LOQ	4.52±0.47	172±18.1
		Laurencia sp.	nd	nd	1,008±10.6	663±48.0	1,762±94.7	168±15.5	41.2±5.23	969±78.0
	08/2019	*Corallina elongata*	nd	nd	819±52.5	nd	722±87.8	775±53.9	186±29.4	721±31.8
		Stypocaulon scoparium	nd	113±6.92	614±42.3	nd	395±45.2	177±5.26	26.5±0.45	165±17.3
		Dictyota dichotoma	nd	nd	646±18.6	<LOQ	970±6.37	<LOQ	nd	nd
		Asparagopsis taxiformis	nd	nd	74.2±6.30	23.3±0.37	248±16.9	nd	nd	nd
		Taonia atomaria	nd	nd	297±0.60	nd	377±23.3	90.1±1.69	nd	nd
		Codium decorticatum	nd	nd	<LOQ	nd	107±11.8	19.3±2.42	nd	nd
	09/2019	*Laurencia sp.*	nd	nd	412±48.9	11.5±1.72	989±25.9	49.2±1.71	nd	27.0±0.21
		Corallina elongata	nd	nd	81.9±8.68	9.0±0.14	209±1.33	14.1±0.07	nd	22.3±1.32
		Codium decorticatum	nd	nd	nd	nd	176±2.55	nd	nd	nd

		Taonia atomaria	nd	nd	92.2±2.19	nd	265±6.29	45.8±4.5	nd	nd
		Asparagopsis taxiformis	nd	nd	nd	31.5±1.67	169±1.20	33.4±0.05	nd	15.8±1.15
		Dictyota ciliolata	nd	nd	196±7.37	nd	778±31.8	nd	nd	nd
		Dictyota cervicornis	nd	nd	229±10.7	nd	458±0.86	nd	nd	nd
	10/2019	*Lophocladia trichoclados*	nd	nd	38.9±1.79	5.06±0.66	224±3.70	19.3±2.41	nd	nd
		Asparagopsis taxiformis	nd	nd	nd	22.3±1.75	185±1.33	43.7±5.12	nd	nd
		Laurencia sp.	92.2±1.70	nd	349±20.4	9.28±1.12	1,325±14.4	93.8±11.6	nd	<LOQ
		Taonia atomaria	nd	nd	nd	nd	401±4.96	51.0±3.80	nd	nd
		Dictyota dichotoma	nd	nd	206±4.94	nd	374±42.2	23.4±0.82	nd	nd
	Detection frequencies (%)		4	27	77	38	100	58	31	35
Playa del Inglés beach	05/2019	*Cymodocea nodosa*	nd	nd	201±9.35	4.51±0.06	1,229±24.5	nd	nd	nd
	06/2019	*Corallina elongata*	nd	nd	84.7±8.65	183±11.0	461±37.3	22.1±2.80	<LOQ	170±24.2
		Stypocaulon scoparium	nd	nd	600±45.9	389±12.0	5,730±492	154±1.15	4.52±0.25	681±12.6
		Cymodocea nodosa	nd	nd	241±21.3	<LOQ	2,092±167	28.5±1.62	<LOQ	2.69±0.25

	07/2019	*Cymodocea nodosa*	nd	<LOQ	71.4±8.82	nd	1,418±28.6	47.0±6.97	nd	23.3±2.28
	08/2019	*Cymodocea nodosa*	nd	nd	618±38.4	nd	1,637±147	141±6.58	nd	9.46±1.36
		Cymopolia barbata	131±2.71	88.3±5.58	2,446±45.2	nd	2,438±165	nd	nd	nd
		Dictyota dichotoma	nd	nd	1,189±23.7	nd	2,315±205	260±5.26	nd	nd
		Liagora sp.	nd	<LOQ	88.0±6.66	<LOQ	335±21.3	27.1±2.56	nd	nd
	09/2019	*Cymodocea nodosa*	nd	<LOQ	113±10.3	44.6±1.01	3,971±21.0	64.1±3.22	nd	nd
	10/2019	*Lophocladia trichoclados*	nd	nd	113±8.92	134±7.09	5,513±29.9	62.9±5.82	nd	nd
		Cymodocea nodosa	nd	nd	219±4.32	225±24.7	19,369±566	186±24.8	nd	<LOQ
		Dictyota dichotoma	nd	nd	396±18.6	131±1.32	5,507±196	41.3±1.77	nd	nd
	Detection frequencies (%)		8	8	100	54	100	85	8	38
Total macrophytes detection frequencies (%)[a]			**16**	**25**	**91**	**57**	**100**	**63**	**17**	**37**

[a] n= 76

nd means not detected

Table S3. Target organic UV filters concentrations measured in seawater samples, from Cadena-Aizaga et al. [2].

Sampling place	Date	Compound concentration (μg·L^{-1})							
		4MBC	BP3	HMS	DTS	OC	BMDBM	IMC	MBP
SL1	May-19	nd	nd	nd	nd	nd	0.19±0.01	nd	nd
	June-19	nd	0.42±0.06	nd	nd	nd	0.33±0.03	nd	nd
	July-19	nd	4.81±0.49	nd	0.44±0.02	nd	0.10±0.01	0.43±0.06	nd
	August-19	17.5±1.70	20.5±1.78	39.8±5.22	25.2±1.36	171±11.4	88.9±9.94	4.27±0.58	nd
	September-19	nd	6.45±0.08	nd	nd	5.64±0.85	4.82±0.58	0.64±0.06	nd
	October-19	nd	0.41±0.01	nd	nd	nd	nd	nd	nd
	Detection frequencies (%)	17	83	17	33	33	83	50	0
SL2	May-19	nd	0.16±0.01	nd	nd	nd	nd	nd	nd
	June-19	nd	0.27±0.03	nd	nd	nd	nd	0.28±0.04	nd
	July-19	nd	nd	nd	nd	nd	nd	0.37±0.03	nd
	August-19	3.08±0.54	1.55±0.14	nd	0.73±0.04	nd	0.21±0.02	0.47±0.01	nd
	September-19	nd	1.46±0.12	nd	0.51±0.02	nd	nd	0.42±0.01	nd
	October-19	nd	0.48±0.06	nd	0.41±0.04	nd	nd	0.12±0.01	146±4.54
	Detection frequencies (%)	17	83	0	50	0	17	83	17
SL3	May-19	nd	0.17±0.02	nd	nd	nd	nd	0.12±0.02	nd
	June-19	nd	nd	nd	nd	nd	0.16±0.01	0.46±0.06	nd
	July-19	nd	2.39±0.01	nd	nd	nd	nd	0.47±0.02	nd
	August-19	nd	6.10±0.02	2.75±0.13	nd	2.52±0.26	6.32±0.43	2.00±0.23	nd
	September-19	nd	2.62±0.04	nd	nd	nd	1.44±0.20	0.07±0.01	nd

October-19	nd	8.27±0.93	nd	nd	nd	4.37±0.49	0.19±0.02	nd
Detection frequency (%)	0	83	17	0	17	67	100	0
Total detection frequency (%)	**11**	**83**	**11**	**28**	**17**	**56**	**78**	**6**

nd Not detected.

Table S4. Combined effect of beach-period for red seaweeds.

Compounds	Pre-summer			Summer			Post-summer			P-value
	Arinaga beach	Las Canteras beach	Playa del Inglés beach	Arinaga beach	Las Canteras beach	Playa del Inglés beach	Arinaga beach	Las Canteras beach	Playa del Inglés beach	
4MBC	0.00 (0.00;0.00)	0.00 (0.00;0.00)	0.00 (0.00;0.00)	0.00 (0.00;0.00)	0.00 (0.00;14.93)	0.00 (0.00;0.00)	0.00 (0.00;0.00)	0.00 (0.00;0.00)	0.00 (0.00;0.00)	0.7027
BMDBM	0.00 (0.00;0.00)	46 (46;46)	22.06 (22.06;22.1)	84 (0;320)	54 (0;141)	27.05 (27.05;27.1)	39 (23;48)	16.32 (0.00;49.99)	63 (63;63)	0.6535
BP3	93 (62;138)	0.00 (0.00;0.00)	0.00 (0.00;0.00)	0.00 (0.00;31.1)	0.00 (0.00;0.00)	0.00 (0.00;0.00)	0.00 (0.00;0.00)	0.00 (0.00;0.00)	0.00 (0.00;0.00)	0.0155
DTS	0.00 (0.00;8.35)	14.0 (14.0;14.0)	183 (183;183)	206 (17;457)	55 (48;227)	0.00 (0.00;0.00)	10.37 (9.07;19.6)	32 (17;50)	134 (134;134)	0.1489
HMS	299 (245;323)	252 (252;252)	85 (85;85)	798 (601;866)	1568 (1281;2097)	88 (88;88)	60 (10;282)	196 (178;241)	113 (113;113)	0.0562
IMC	7.03 (5.25;9.63)	0.00 (0.00;0.00)	0.00 (0.00;0.00)	22.87 (3.39;77.4)	0.00 (0.00;0.00)	0.00 (0.00;0.00)	0.00 (0.00; 0.00)	0.00 (0.00;0.00)	0.00 (0.00;0.00)	0.0254
MBP	26.47 (13.3;32.8)	0.00 (0.00;0.00)	170 (170;170)	447 (129;783)	0.00 (0.00;78.19)	0.00 (0.00;0.00)	7.91 (0.00;20.7)	41 (23;53)	0.00 (0.00;0.00)	0.3471
OC	1107 (668;1174)	1480 (1480;1480)	461 (461;461)	1242 (604;2630)	3320 (2192;4742)	335 (335;335)	216 (191;798)	1443 (1141;1591)	5513 (5513;5513)	0.0378

Significant p-values are market in red.

Table S5. Combined effect of beach-period for brown seaweeds

Compounds	Pre-summer			Summer			Post-summer			P-value
	Arinaga beach	Las Canteras beach	Playa del Inglés beach	Arinaga beach	Las Canteras beach	Playa del Inglés beach	Arinaga beach	Las Canteras beach	Playa del Inglés beach	
4MBC	0.00 (0.00;0.00)	0.00 (0.00;0.00)	0.00 (0.00;0.00)	0.00 (0.00;0.00)	8.97 (0.00;47.29)	0.00 (0.00;0.00)	0.00 (0.00;0.00)	0.00 (0.00;0.00)	0.00 (0.00;0.00)	0.076
BMDBM	0.00 (0.00;0.00)	0.00 (0.00;431)	154 (154; 154)	90 (45;134)	532 (343;1033)	260 (260; 260)	23.40 (0.00;45.77)	195 (65;1885)	41 (41;41)	0.1968
BP3	13.59 (6.80;20.4)	0.00 (0.00;11.17)	0.00 (0.00;0.00)	0.00 (0.00;56.5)	0.00 (0.00;2.79)	0.00 (0.00;0.00)	0.00 (0.00;0.00)	0.00 (0.00;19.8)	0.00 (0.00;0.00)	0.8067
DTS	0.00 (0.00;0.00)	0.00 (0.00;5.71)	389 (389; 389)	0.00 (0.00;0.00)	37 (27;80)	0.00 (0.00;0.00)	0.00 (0.00;0.00)	14.11 (0.00;17.08)	131 (131;131)	0.0046
HMS	118 (59;177)	290 (76;1157)	600 (600;600)	614 (456;631)	1925 (1249;2563)	1189 (1189; 1189)	196 (92;206)	239 (147;562)	396 (396; 396)	0.0465
IMC	5.58 (2.79;8.37)	0.00 (0.00;0.00)	4.52 (4.52;4.52)	0.00 (0.00;13.23)	0.00 (0.00;0.00)	0.00 (0.00;0.00)	0.00 (0.00;0.00)	0.00 (0.00;0.00)	0.00 (0.00;0.00)	0.0688
MBP	0.00	0.00 (0.00;0.00)	681 (681;681)	0.00	38 (0.00;51)	0.00 (0.00;0.00)	0.00	0.00 (0.00;0.00)	0.00 (0.00;0.00)	0.0773

	(0.00;0.00)			(0.00;82.65)			(0.00;0.00)			
OC	537 (383;690)	633 (336;1084)	5730 (5730;5730)	395 (386;682)	4686 (3654;5113)	2315 (2315;2315)	401 (374;458)	998 (679;1485)	5507 (5507;5507)	0.0048

Significant p-values are market in red.

Table S6. Comparison (A) by beach and (B) by period for each seaweed type.

Compounds	A) Comparison by beach							
	Red seaweeds				Brown seaweeds			
	Arinaga beach	Las Canteras beach	Playa del Inglés beach	p-value	Arinaga beach	Las Canteras beach	Playa del Inglés beach	p-value
4MBC	0.00 (0.00;0.00)	0.00 (0.00;0.00)	0.00 (0.00;0.00)	0.5890	0.00 (0.00;0.00)	0.00 (0.00;0.00)	0.00 (0.00;0.00)	0.2579
BMDBM	19.30 (0.00;49.2)	40 (0;90)	27.05 (24.6;45.0)	0.8656	11.70 (0.00;49.7)	195 (0;1679)	154 (98;207)	0.1395
BP3	0.00 (0.00;31.5)	0.00 (0.00;0.00)	0.00 (0.00;0.00)	0.1051	0.00 (0.00;0.00)	0.00 (0.00;11.2)	0.00 (0.00;0.00)	0.5017
DTS	11.45 (5.06;23.3)	47 (15;61)	134 (67;158)	0.2317	0.00 (0.00;0.00)	14.11 (0.00;28.79)	131 (65;260)	0.0048
HMS	299 (74;412)	413 (213;1496)	88 (86;100)	0.0484	217 (118;282)	562 (147;1886)	600 (498;895)	0.0872
IMC	0.00 (0.00;7.03)	0.00 (0.00;0.00)	0.00 (0.00;0.00)	0.0740	0.00 (0.00;0.00)	0.00 (0.00;0.00)	0.00 (0.00;2.26)	0.2140
MBP	22.34	15.59	0.00	0.8751	0.00	0.00	0.00	0.4486

	(0.00;39.2)	(0.00;54.53)	(0.00;84.8)		(0.00;0.00)	(0.00;36.48)	(0.00;340.6)	
OC	722 (224;1240)	1616 (1502;3038)	461 (398;2987)	0.0297	398 (2255)	1498 (679;4180)	5507 (3911;5619)	0.0051
Compounds	B) Comparison by period							
	Red seaweeds				Brown seaweeds			
	Pre-summer	Summer	Post-summer	p-value	Pre-summer	Summer	Post-summer	p-value
4MBC	0.00 (0.00;0.00)	0.00 (0.00;0.00)	0.00 (0.00;0.00)	0.5459	0.00 (0.00;0.00)	0.00 (0.00;22.5)	0.00 (0.00;0.00)	0.0181
BMDBM	0.00 (0.00;22.1)	41 (0;162)	33 (17;56)	0.2884	0.00 (0.00;77.0)	350 (81;637)	46 (12;130)	0.0714
BP3	32 (0;93)	0.00 (0.00;0.00)	0.00 (0.00;0.00)	0.0104	0.00 (0.00;14.6)	0.00 (0.00;2.79)	0.00 (0.00;0.00)	0.5916
DTS	14.01 (0.00;16.7)	51 (13;348)	19.07 (10.4;38.5)	0.2950	0.00 (0.00;6.78)	26.48 (0.00;52.01)	0.00 (0.00;15.6)	0.2640
HMS	252 (192;299)	914 (541;1496)	139 (60;274)	0.0105	236 (71;757)	1349 (578;2068)	206 (120;317)	0.0026
IMC	3.48 (0.00;7.03)	0.00 (0.00;4.28)	0.00 (0.00;0.00)	0.0315	0.00 (0.00;0.00)	0.00 (0.00;0.00)	0.00 (0.00;0.00)	0.7311
MBP	26.47 (0.00;39.2)	39 (0;279)	15.82 (0.00;29.09)	0.6021	0.00 (0.00;0.00)	18.93 (0.00;50.68)	0.00 (0.00;0.00)	0.0505
OC	1107 (461;1240)	1977 (936;4386)	989 (216;1448)	0.0967	844 (322;1230)	3247 (1366;5054)	679 (388;1241)	0.0189

Significant p-values are market in red.

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Publicación: Occurrence and bioconcentration of organic UV filters in primary marine consumers

Supplementary material

Table S1. Main characteristics of the eight target compounds and mass spectrometer conditions for their determination.

Organic UV filters characteristics					Mass spectrometer detection parameters					
INCI name[a]	**Abbreviation**	**CAS number**	**Log K_{ow}**	**EU production[e]**	**Precursor ion (m/z)**	**Cone voltage (V)**	**Quantification ion (m/z)**	**Collision potential (V)**	**Confirmation ion (m/z)**	**Collision potential (V)**
Benzophenone-3	BP-3	131-57-7	3.79[b]	LPV	229.0	32	151.0	20	105.0	25
Homosalate	HMS	118-56-9	6.16[c]	HPV	263.1	12	139.0	10	121.0	30
Isoamyl p-methoxycinnamate	IMC	71617-10-2	4.33[c]	LPV	249.1	15	161.2	15	179.2	9
4-methylbenzylidene camphor	4-MBC	36861-47-9/ 38102-62-4	4.95[c]	LPV	255.4	25	105.0	27	171.0	19
Drometrizole trisiloxane	DTS	155633-54-8	10.82[d]	-	502.0	12	412.2	15	396.2	25
Methylene bis-Benzotriazolyl tetramethyl butylphenol	MBP	103597-45-1	12.46[d]	LPV	659.8	40	336.2	25	224.2	35

Butyl methoxydibenzoyl methane	BMDBM	70356-09-1	4.51[c]	HPV	311.2	30	161.2	23	135.1	23
Octocrylene	OC	6197-30-4	6.88[c]	HPV	362.4	28	250.0	12	332.0	20

[a] INCI International Nomenclature for Cosmetic Ingredients. [b] Experimental value from Syracuse Research Corporation database. [c] Estimated values from Syracuse Research Corporation database. [d] Calculated by use of Estimation Program Interface (EPI) suite v4.11 (2012). [e] From European Chemicals Agency (ECHA): low production volume (LPV) between 10 and over 100 tonnes·year^{-1} and high production volume (HPV) between 1000 and 10000 tonnes·year^{-1} of chemicals produced or imported in the European economic area.

Table S2. Concentrations measured for target organic UV filters in the marine organisms.

Sampling place	Date	Specie	Compound concentration (ng·g^{-1}, dw)							
			4-MBC	BP-3	HMS	DTS	OC	BMDBM	IMC	MBP
Las Canteras beach	10/2019	*Phorcus atratus*	nd	nd	23.5±2.7	nd	nd	15.5±0.05	nd	nd
	11/2019		nd	nd	nd	nd	nd	37.1±4.4	nd	nd
	12/2019		nd	nd	nd	16.0±1.3	42.3±1.2	17.2±1.06	3.10±0.14	nd
	01/2020		nd	nd	nd	nd	43.7±4.9	61.8±5.66	nd	nd
	Detection frequencies (%)		0	0	25	25	50	100	25	0
Arinaga beach	10/2019	*Phorcus atratus*	nd	nd	18.1±0.28	31.7±3.11	33.1±1.34	nd	nd	nd
		Holothuria sanctori	nd	nd	1113±172	nd	nd	9.74±0.52	9.01±0.59	nd
	11/2019	*Phorcus atratus*	nd	nd	nd	nd	nd	18.6±0.85	nd	nd
		Aplysina aerophoba	nd	<LOQ	nd	nd	nd	nd	nd	nd
	12/2019	*Phorcus atratus*	165±4.91	nd	nd	nd	nd	nd	nd	nd
	01/2020	*Phorcus atratus*	nd	nd	nd	nd	nd	88.2±9.10	nd	nd
		Holothuria sanctori	nd	nd	nd	nd	166±16.2	nd	12.8±1.4	nd
		Aplysia dactylomela	nd	nd	190±14.2	nd	1735±59.5	nd	nd	nd
	Detection frequencies (%)		13	13	38	13	38	38	25	0

Playa del Inglés beach	10/2019	*Phorcus atratus*	nd	nd	68.2±4.99	149±1.24	602±40.1	24.8±0.28	nd	nd
		Stramonita haemastoma	379±21.9	nd	1003±45.7	nd	nd	nd	nd	nd
	11/2019	*Phorcus atratus*	nd	nd	10.3±0.67	nd	114±7.28	37.3±5.87	1.53±0.18	nd
		Stramonita haemastoma	nd	nd	nd	nd	nd	nd	nd	13.3±1.24
	12/2019	*Phorcus atratus*	nd	nd	nd	nd	nd	53.6±4.56	nd	nd
		Stramonita haemastoma	nd	nd	nd	nd	nd	nd	nd	46.7±6.72
	01/2020	*Phorcus atratus*	nd	nd	nd	nd	nd	24.9±1.59	nd	nd
		Stramonita haemastoma	nd	nd	nd	nd	24.8±3.92	nd	nd	nd
	Detection frequencies (%)		13	0	38	13	38	50	13	25
Total detection frequencies (%)[a]			**10**	**5**	**35**	**15**	**40**	**55**	**20**	**10**

[a] n= 20

nd: means not detected

Anexo IV. Comunicaciones a congresos

1. **Autores:** M. Isabel Cadena-Aizaga, Sarah Montesdeoca-Esponda, Ángelo Santana-Del Pino, Zoraida Sosa-Ferrera, José Juan Santana-Rodríguez
   Título: Assessment of anthropogenic pollution by organic uv filters using macrophytes as bioindicators
   Congreso: VIII International Symposium on Marine Sciences
   Tipo de participación: Comunicación oral
   Lugar de celebración: Las Palmas de Gran Canaria (España)
   Fecha: Julio 2022

2. **Autores:** M. Isabel Cadena-Aizaga, Sarah Montesdeoca-Esponda, Zoraida Sosa-Ferrera, José Juan Santana-Rodríguez
   Título: Occurrence and environmental hazard of organic UV filters in seawater and wastewater from Gran Canaria (Spain)
   Congreso: 33nd International Symposium on Chromatography
   Tipo de participación: Póster
   Lugar de celebración: Budapest (Hungría)
   Fecha: Septiembre 2022

3. **Autores:** M. Isabel Cadena-Aizaga, Sarah Montesdeoca-Esponda, Zoraida Sosa-Ferrera, José Juan Santana-Rodríguez

   Título: Occurrence and bioconcentration of organic UV filters in primary marine consumers from Gran Canaria (Spain)

   Congreso: 33nd International Symposium on Chromatography

   Tipo de participación: Póster

   Lugar de celebración: Budapest (Hungría)

   Fecha: Septiembre 2022

VIII International Symposium on Marine Sciences (ISMS)

Las Palmas de Gran Canaria (España), julio 2022

Occurrence and environmental hazard of organic UV filters in seawater and wastewater from Gran Canaria (Spain)

M. Isabel Cadena-Aizaga[a]*, Sarah Montesdeoca-Esponda[a], Zoraida Sosa-Ferrera[a], José Juan Santana-Rodríguez[a]
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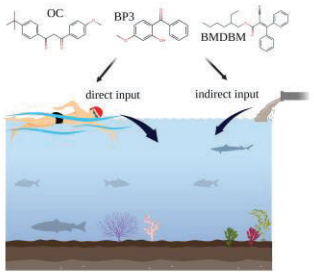
INTRODUCTION

Organic ultraviolet (UV) filters are added to different personal care products to protect the skin from harmful UV radiation effects. Moreover, they can be found in industrial goods. Given their extensive use, hundreds of tonnes are released to the marine environment annually. These compounds follows two pathways to reach the aquatic environment : directly through the wash off from the skin and indirectly by the release of wastewater, industrial discharges and runoffs.

Compounds name	Abbreviation
benzophenone-3	BP3
homosalate	HMS
isoamyl p-methoxycinnamate	IMC
4-methylbenzylidene camphor	4MBC
drometrizole trisiloxane	DTS
bisoctrizole	MBP
avobenzone	BMDBM
octocrylene	OC



OBJECTIVES

The aims of this work are:

1. Stablish the **presence of eight organic UV filters in seawater and wastewater** from the Gran Canaria Island.
2. Evaluate the **spatio-temporal variation and effiency of elimination** of sewage treatment.
3. Evaluate the associated **environmental hazard**.

METHODS

Sampling during six months, May-October 2019
Extraction process was developed using solid phase extraction (SPE) and determination by UHPLC-MS/MS

Sample type	Sample volume (mL)	Sample pH	Extractant type	Extractant volume (mL)
seawater	700	3	MeOH:ACN (1:1)	5
wastewater	250	7	MeOH	5

Environmental hazard quotient (HQ) was quantified following the expression:

$$HQ = MEC/PNEC$$

MEC is the measured environmental concentration in seawater and PNEC is the predicted no effect concentration. HQ > 1 indicates a potential high hazard

RESULTS

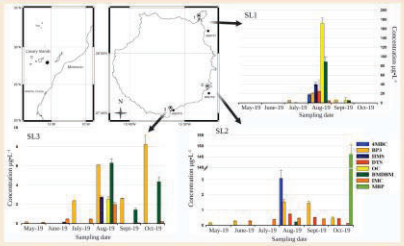


Figure 1. Measured concentration of target organic UV filters in seawater in the three beaches. Las Canteras beach (SL1), Arinaga beach (SL2) and Playa del Inglés beach (SL3). Black points indicate the wastewater treatment plants (WWTPs) outfalls.
Sampling was divided in pre-summer (May-June), summer (July-August) and post-summer (September-October).
BP3 was detected in 83% of the seawater samples
All beaches showed temporal variation, where SL1 and SL2 presented higher concentrations in summer, and SL3 in post-summer.

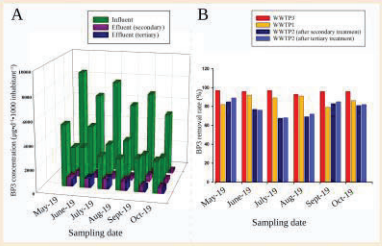


Figure 2. A: standardized concentration of BP3 in wastewater for the three studied WWTPs. B: removal rates of BP3 in the three WWTPs.
All target compounds were determined in the three WWTPs
Any seasonal patter was observed in the wastewater mass loads
BP3 was detected in 100% of the influent and secondary effluent samples
OC presented the highest input load in all the influent (12,327 μg•d^{-1}•1,000 inhabitant^{-1})
Target analytes removal rates ranged between 17-100 % in the three WWTPs

The highest concentration in seawater **correspond to OC (172±11 μg•L-1)** in SL1 and had **HQs higher than 1** in all the locations where it was measured (SL1 and SL3), which indicates a high hazard for marine species

CONCLUSIONS

- An analytical SPE-UHPLC-MS/MS method was applied to extract eight widely used organic UV filters from seawater and wastewater
- Dispite Gran Canaria Island is used all year round, the three beaches showed seasonal variation, with highest concentrations in summer
- Removal efficiencies reported an average of >50 % for most compounds
- Incomplete elimination of taget analytes was observed in all WWTPs, thus, they are released to the marine environment
- The HQ showed a potential hazard for OC, while BMDBM presented a medium high hazard and BP3 showed a widely varying values

ACKNOWLEDGEMENTS

M. Isabel Cadena-Aizaga would like to thank to University of Las Palmas de Gran Canaria for this Ph.D. student grant.

33nd International Symposium on Chromatography (ISC)

Budapest (Hungría), septiembre 2022

Occurrence and bioconcentration of organic UV filters in primary marine consumers from Gran Canaria (Spain)

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INTRODUCTION

Organic ultraviolet (UV) filters use has been increasing in the last century, they are used to absorb UV radiation to protect the skin and the polymers from degradation. Due to their extensive production, they are continuously released into the aquatic environment posing a hazard to living organisms. In aquatic organisms, the potential uptake mechanisms of pollutants can follow two pathways: the direct uptake consists in passive absorption from the environment and the indirect uptake is related to diet.

Compounds name	Abbreviation
benzophenone-3	BP3
homosalate	HMS
isoamyl p-methoxycinnamate	IMC
4-methylbenzylidene camphor	4MBC
drometrizole trisiloxane	DTS
bisoctrizole	MBP
avobenzone	BMDBM
octocrylene	OC

OBJETIVES

The aims of this work are:

1. Determine the concentration of organic UV filters in primary marine consumers.
2. Determine the possible bioaccumulation and biomagnification.

METHODS

Primary marine consumers were collected from October 2019 to January 2020, which were recovered on three beaches of the Gran Canaria Island (Canary Islands).
The extraction process was optmized based on microwave-assisted extraction and the determination by ultrahigh-performance liquid chromatography coupled to mass spectrometry in tandem (MAE-UHPLC-MS/MS). Optimized MAE process consisted in applying 50 ºC for 3 min with 5 mL of acetone.
The method was applied to the five species that comprised 20 samples

Bioconcentration (BCF) and biomagnification (BMF) calculation:

$$BCF = C_{organism}/C_{water}$$

$$BMF = C_{consumer}/C_{food}$$

Log BCF >3.7 the substance is very bioaccumulative and when BMF >1 there is a possible biomagnification

RESULTS

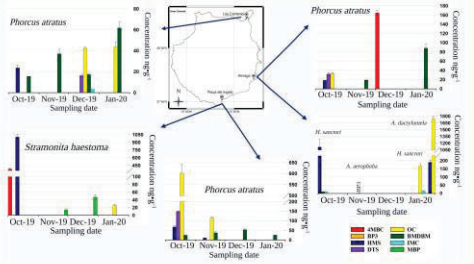
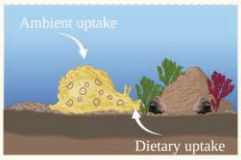


Figure 1. Ocurence of organic UV filters in primary marine consumers from the three beaches: Las Canteras beach, Arinaga beach and Playa del Inglés beach.

At least one compound was identified in each analysed marine organism
The highest detected concentrations corresponded to OC (1,735 ng·g^{-1} dw) in sea hare and to HMS (1,113 ng·g^{-1} dw) in sea cucumber
BMDBM (55 %) and OC (40 %) were the most frequently detected compounds
The Log BCFs of all the found organic UV filters were above 3.7, which suggests bioaccumulation in the analysed primary marine consumer
The maximum BCF was found for BMDBM on the Arinaga beach (Log BCF 8.63)
Only 4MBC and DTS obtained values of BMF above 1 for sea snail, which indicates possible biomagnification to upper thropic levels



CONCLUSIONS

1. The analytical method was successfully developed, validate and applied in five different primary marine consumers
2. Highest concentration level was for OC (1,735 ng·g-1 dw) in sea hare
3. BMDBM showed the highest detection frequency of the target compounds
4. Log BCF was over 3.7 for the quantified target compounds, which suggests their bioaccumulation
5. BMF found for 4MBC and DTS indicated possible biomagnification through the food web

ACKNOWLEDGEMENTS

M. Isabel Cadena-Aizaga would like to thank to University of Las Palmas de Gran Canaria (Spain) for Ph.D. student grant.

33nd International Symposium on Chromatography (ISC)

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M. Isabel Cadena Aizaga

Las Palmas de Gran Canaria

Septiembre 2022

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