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

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ABSTRACT

The release of chemicals into marine environments from coastal human activities has raised growing concern about pollution. Among these chemicals, organic ultraviolet filters (oUVFs), widely used in personal care products and industrial applications, have recently been identified as pollutants of emerging concern. Their extensive use and persistence highlight the need to assess their occurrence and potential impacts on aquatic ecosystems. This study aimed to optimize and apply an analytical methodology for the determination of eleven oUVFs in zooplankton matrices. Microwave-assisted extraction (MAE) was employed for sample preparation, while ultra-high-performance liquid chromatography coupled with tandem mass spectrometry (UHPLC-MS/MS) enabled the identification and quantification of the target compounds. Extraction parameters, including solvent, temperature, and time, were systematically optimized to enhance recovery and ensure accuracy and precision in complex biological samples. The method achieved limits of detection (MLOD) between 1.47 and 5.98 ng g^{-1} dry weight (d.w.) and method limits of quantification (MLOQ) between 4.900 and 19.92 ng g^{-1} d.w. Recovery efficiencies were low, ranging from 28 to 63 %, reflecting the diverse physicochemical properties of oUVFs and the strong matrix effects associated with zooplankton heterogeneity. Application of the validated method to zooplankton collected around Madeira Island (Portugal) revealed the presence of six oUVFs. Homosalate was the most frequently detected compound (53 % of samples), while octocrylene exhibited the highest concentrations, ranging from 24.01 to 1029 ng g^{-1} d.w. These findings demonstrate the relevance of zooplankton as bioindicators of oUVF contamination and support the need for regulatory monitoring and ecological risk assessments in coastal ecosystems.

1. Introduction

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

Both organic (oUVFs) and inorganic (iUVFs) ultraviolet filters are used extensively in PCPs to prevent skin damage, as well as in food packaging and industrial products like paints to protect against degradation caused by UV radiation (Huang et al., 2021). These UVFs act in the wavelength ranges of 320–400 nm (UVA) and 280–320 nm (UVB) (Tovar-Sánchez et al., 2019; Caloni et al., 2021). Currently, 33 UVFs are accepted by the European Union (European Commission, 2024). Among these, only two iUVFs, zinc oxide (ZnO) and titanium dioxide (TiO_2), are added in both micrometric and nanometric forms (Fastelli and Renzi, 2019; Caloni et al., 2021). The oUVFs are classified into eleven distinct

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families characterised by simple or multiple aromatic ring structures linked to hydrophobic groups (Caloni et al., 2021). The use of these oUVFs in PCPs is governed by regulatory frameworks such as REACH (Registration, Evaluation, Authorisation and Restriction of Chemicals) in Europe (Council of the European Union, 2007), which limits their concentration in PCP formulations to between 2 and 25 % of the total product (European Parliament and Council, 2009). According to their physicochemical properties, oUVFs typically exhibit high lipophilicity, as measured by the n-octanol-water partition coefficient (K_{ow}), and low water solubility (Vila et al., 2016). They are characterised by exhibiting good environmental stability due to their poor degradability and photostability, which tend to accumulate in solid matrices and organisms (Barón et al., 2013). Marine organisms can absorb oUVFs through two primary mechanisms: directly by ingestion or indirectly by absorption *via* exposed surfaces (Rani et al., 2017). Once absorbed, marine organisms can degrade, metabolize, or accumulate oUVFs in their tissues or organs (Jentzsch et al., 2023).

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

Research on the risks associated with these compounds has increased significantly over the past few decades (Daughton, 2013; González et al., 2022; Pawlowski et al., 2023). Numerous harmful physiological effects on marine organisms, such as impaired reproduction, physical deformities, and increased mortality rates, have been previously observed under laboratory conditions (Danovaro et al., 2008; Schmitt et al., 2008; Araujo et al., 2018). These studies often rely on exposure concentrations exceeding those typically detected in the natural environment (Thorel et al., 2020). However, some effects have already been described *in situ*, notably coral bleaching on tourist beaches (Mitchelmore et al., 2021), which has led to a ban on sunscreen use in some coastal areas (Downs et al., 2016). Hence, in Europe, three sunscreen agents (avobenzone, octocrylene, and benzophenone-3) were already included in the European “Watch List” tool in July 2022 (European Commission, 2022). The updated list of 2025 has also included a fourth UVF, the octisalate (2-ethylhexyl salicylate) (European Commission, 2025).

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

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

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

In this context, the present study aims to focus on the development of an analytical methodology for quantifying eleven oUVFs in zooplankton samples, using microwave-assisted extraction (MAE) coupled with ultra-high-performance liquid chromatography-tandem mass spectrometry (UHPLC-MS/MS). MAE, though less commonly applied, is particularly suited for solid or semi-solid samples. It offers several advantages, including enhanced extraction efficiency, reduced extraction time, lower solvent consumption, and improved analyte recovery compared to conventional solid-sample preparation methods (Cadena-Aizaga et al., 2020; Oubahmane et al., 2023; Nieddu et al., 2024). These benefits result from the direct heating of the sample by microwaves, which accelerates extraction and enables effective analyte release using smaller volumes of solvent (Narloch and Wejnerowska, 2021). To achieve optimal performance, parameters such as extraction temperature, solvent type, and extraction time must be carefully optimized in accordance with the specific matrix involved (Ferrara et al., 2023). Given these attributes, MAE represents a promising approach within the framework of green analytical chemistry compared to conventional solid-sample preparation methods such as extraction by ultrasound or Soxhlet (Destandau and Michel, 2022). To assess the environmental sustainability of the sample preparation process, the AGREEprep metric was applied to evaluate its overall greenness (Pena-Pereira et al., 2022).

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

2. Materials and methods

2.1. Study area, sampling, and pre-treatment

Thirty-six zooplankton samples were collected in six different stations during two distinct seasons in 2023 around Madeira and Desertas Islands (Portugal) (Table SM1; Fig. 1). These islands, located in the northeast Atlantic Ocean, are characterised by oligotrophic waters and subtropical temperatures ranging from 17 to 24 °C (Santos et al., 2004; Spalding et al., 2007).

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

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

2.2. Reagents and consumables

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

The stock solution of the target compounds was prepared in ACE at

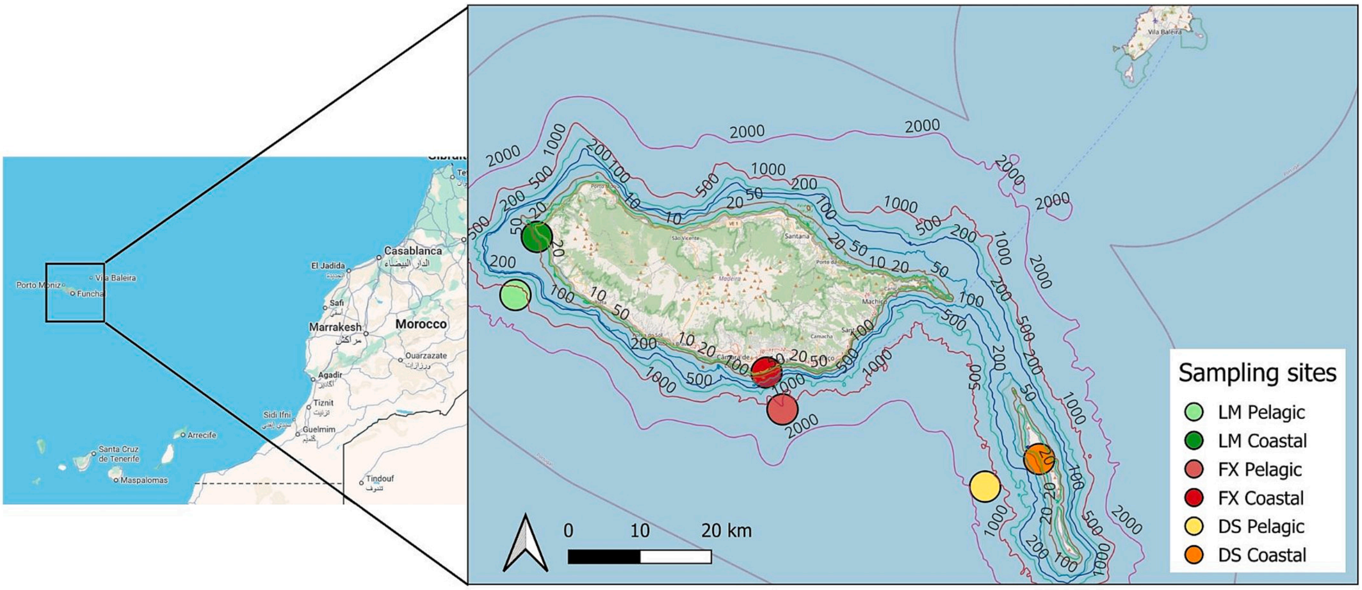

Fig. 1. Location of Madeira and the Desertas Islands. The dots represent the sampling sites: Lombada dos Marinheiros (LM): LM_pelagic (32° 73.296 N, 17° 30.542 W), LM_coastal (32° 78.771 N, 17° 25.797 W); Funchal (FX): FX_pelagic (32° 35.545 N, 16° 53.605 W), FX_coastal (32° 38.210 N, 16° 52.010 W);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

250 μg·mL^{-1} and stored in capped glass vials at −20 °C in the dark. Daily intermediate standards were freshly prepared in MeOH from the stock solution.

2.3. Instrumental analysis

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

2.4. Chromatography and detection conditions

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

2.5. Quality control

The linearity, method limit of detection (MLOD), and method limit of quantification (MLOQ), as well as instrumental limit of detection (ILOD) and instrumental limit of quantification (ILOQ), were evaluated for each compound under optimal extraction conditions from the matrix. Calibration curves using the IS approach were prepared using eight concentration points ranging from 1 to 500 ng mL^{-1} for each compound (with estimated concentrations between 20 and 10,000 ng g^{-1} d.w. in the zooplankton samples). ILOD and ILOQ were determined based on the signal-to-noise ratio (S/N) of individual compound responses at the lowest point of the calibration curve, assuming minimum detectable S/N levels of 3 and 10, respectively.

To evaluate the extraction efficiencies, recoveries at theoretical concentrations of 25 and 250 ng mL^{-1} in the final extract were determined by comparing spiked samples before and after extraction ($n = 6$ for each level). Repeatability expressed as inter-day precision of six replicates was also calculated for both concentration levels (25 and 250 ng mL^{-1} in the final extract). This assessment was performed by adding known amounts of a standard mixture to 50 mg of the sample to achieve these concentrations in the final theoretical extract. The IS-BP-d$_{10}$ was added at a final concentration of 200 ng mL^{-1} in all samples and the calibration curve before injection. It was chosen to account for instrumental variability and matrix effects, as it shares chemical and chromatographic behaviour with the target compounds. Using a single IS simplifies analysis, reduces costs, and ensures reproducibility across matrices, as demonstrated by Van Den Houwe et al. (2014). The matrix effect is calculated as the ratio between the analyte signal in the solvent after extraction of a blank matrix, and the signal of the analyte prepared in a pure solvent, multiplied by 100 to express it as a percentage. A value of 100 % indicates the absence of a matrix effect, whereas values below or above this threshold indicate signal suppression or enhancement, respectively.

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

2.6. Software

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

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

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

3. Results and discussion

3.1. MAE optimization

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

The first experimental design consisted of 2^3 runs based on a 2-level factorial design (Table SM4). The variables tested were extraction temperatures of 50 °C and 55 °C, extraction times of 5 and 10 min., and two solvents: MeOH and ACN. This first experimental design was conducted to determine which variables had the most significant impact on the recovery area of the target analytes, and to assess whether temperature and time exhibited positive or negative correlations with extraction efficiency. For that, Pareto chart analysis (Fig. 2 and Fig. SM2) was conducted to prioritise and determine the most influential variables impacting the extraction results. It was observed that the peak areas obtained for the main target compounds (4MBC, BP-3, DTS, BMDBM, UV-360, and OMC) were significantly influenced by both temperature and solvent type, either independently, as in the case of DTS and UV-360, or through the interaction of both factors, as observed for OMC, OD-PABA, and BP-3. In contrast, extraction time did not show a significant effect on the recovery areas, except for BMDBM, where a combined effect with temperature was observed (Fig. 2 and Fig. SM2).

Additionally, Pearson correlation coefficients were calculated to evaluate the experimental results and to identify potential linear relationships between the tested variables and the extraction efficiency. These correlations enable us to observe the trend of the variables' effects and establish them for subsequent experimental designs. When the result of the test is 0, it indicates no variable influence. -1 represents the maximum adverse effect of the variable, and 1 represents the maximum positive effect of the variable. Correlation analysis revealed that most compounds exhibited higher recovery at higher temperatures (except EHS) (Table 1). Time was excluded from this design due to the absence of an impact, as indicated by the Pareto chart test. Furthermore, ACN consistently yielded higher peak areas than MeOH (Fig. 3).

Based on the findings of the first experimental design, which used ACN as the extraction solvent, the second experimental design focused

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

Compound	Temperature (°C)
4MBC	0.712
BP3	0.828
HMS	0.027
DTS	0.152
OC	0.339
BMDBM	0.716
IMC	0.599
UV-360	0.807
OD-PABA	0.908
OMC	0.784
EHS	−0.020

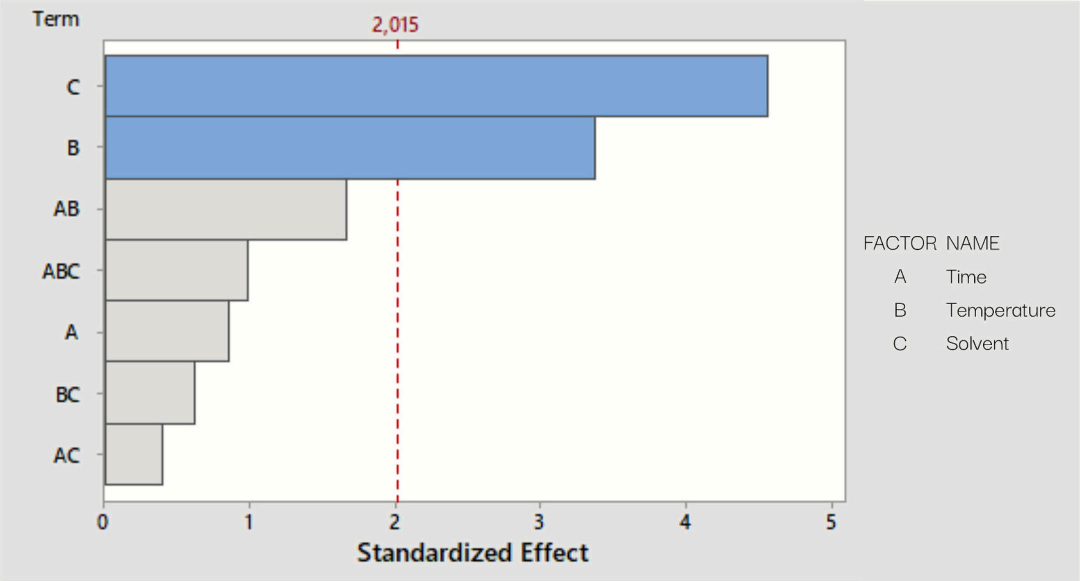

Fig. 2. Pareto chart of the standardized effects of the three variables, solvent, temperature and time for UV-360, as an example. The Pareto chart for all the target compounds is available in Fig. SM2. The red dashed line corresponds to the value at which the factor has a significant effect. The blue bars correspond to factors that exceed the significance level, and the grey bars to those that do not. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

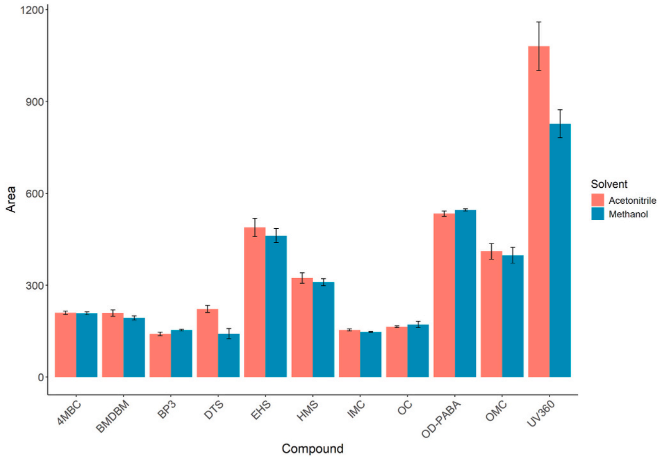

Fig. 3. Comparison of the chromatographic peak areas and standard deviation (black bars) of target compounds obtained with two organic solvents during the first experimental design, highlighting the influence of solvent selection on compound response. Wilcox paired text *p-value* > 0.05. Peak area values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

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

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

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

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

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

3.2. Method performance

Analytical parameters of the optimized MAE procedure followed by UHPLC-MS/MS are shown in Table 2. The linearity coefficients were greater than 0.99 for all target compounds. The ILODs ranged from 0.073 to 0.299 ng mL^{-1} while ILOQs ranged from 0.245 to 0.996 ng mL^{-1}. The MLODs were between 1.470 and 5.976 ng g^{-1} d.w. MLOQs ranged from 4.900 to 19.92 ng g^{-1} d.w. These values are generally in line with those reported in previously developed UHPLC-MS/MS-based methods. For instance, Bachelot et al. (2012) reported MLODs of 2 ng g^{-1} d.w. and MLOQs of 5 ng g^{-1} d.w. for EHMC, OC, and OD-PABA in mussel tissue. Similarly, Tsui et al. (2017) described MLODs ranging from 0.11 to 7.05 ng g^{-1} d.w. in coral tissues, while Peng et al. (2015) reported LOQs from 0.004 to 10 ng g^{-1} across various fish tissues. Higher MLOQ values were observed for BMDBM, BP-3, and EHS when compared with those reported in previous studies. This may be due to the physicochemical properties and behaviour of these analytes in zooplankton samples, which can lead to greater matrix interferences or lower extraction efficiency, thus requiring more extensive clean-up procedures.

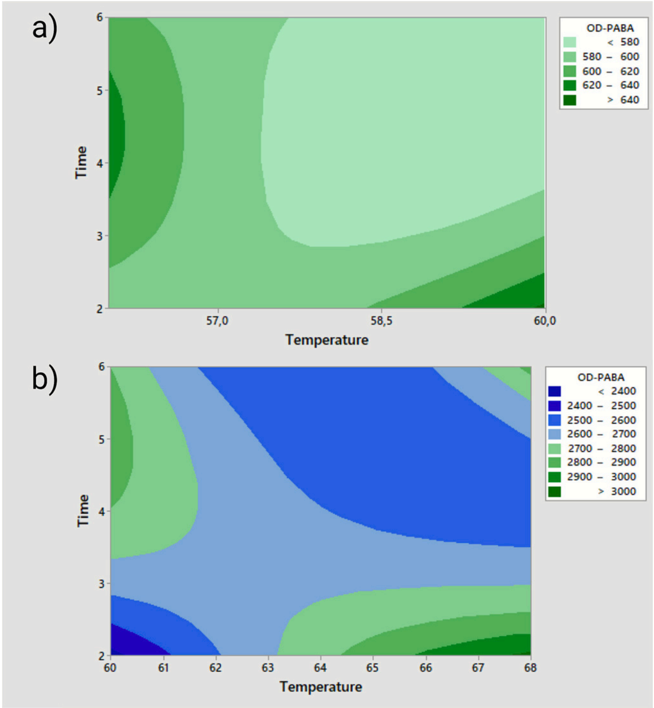

Fig. 4. Contour plots as examples of the response areas showing the effect of temperature and extraction time on the extraction efficiency for two different experimental designs: (a) the second experimental design extraction for OD-PABA and (b) the third experimental design extraction for OD-PABA, both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

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

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

Table 2

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

Compounds	Recovery (%)		Intra-day precision (%)		Matrix effect	ILOD	ILOQ	MLOD	MLOQ
	25 ng mL^{-1} *	250 ng mL^{-1} *	25 ng mL^{-1} *	250 ng mL^{-1} *	After extraction**	(ng mL^{-1})	(ng mL^{-1})	(ng mL^{-1})	(ng mL^{-1})
4-MBC	46.01	40.10	20.61	11.61	96.46	0.138	0.46	2.757	9.191
BP3	27.64	26.61	10.95	15.69	95.83	0.269	0.895	5.372	17.91
HMS	47.37	41.30	14.91	7.910	93.03	0.101	0.337	2.024	6.745
DTS	45.54	38.71	17.75	5.250	84.92	0.091	0.303	1.818	6.059
OC	63.32	51.61	9.380	6.680	93.29	0.149	0.498	2.988	9.96
BMDBM	43.48	35.41	9.540	6.460	89.37	0.270	0.901	5.405	18.02
IMC	48.27	42.80	15.77	10.05	94.13	0.158	0.527	3.16	10.53
UV-360	51.25	26.76	10.75	3.190	119.8	0.094	0.314	1.886	6.288
OD-PABA	41.06	41.40	13.61	8.350	103.1	0.073	0.245	1.470	4.900
OMC	49.98	49.62	18.80	13.98	93.65	0.125	0.416	2.495	8.316
EHS	50.67	31.21	9.220	10.43	105.5	0.299	0.996	5.976	19.92

[*] Theoretical concentration in the final extract; The respective spiking-level concentrations in mass–mass units are 500 ng g^{-1} and 5000 ng g^{-1}.

[**] Samples spiked after the extraction (100 ng mL^{-1}); ILOD: Instrumental Limit of Detection; ILOQ: Instrumental Limit of Quantification; MLOD: Method Limit of Detection; MLOQ: Method Limit of Quantification.

resulting in RSD ranging from 3.19 to 20.61 %.

The recovery efficiencies obtained for the target compounds in the zooplankton matrix were lower than those reported in previous studies using the same extraction methods on other sample matrices. For instance, Bachelot et al. (2012) and Gomez et al. (2012) reported recovery efficiencies above 85 % in mussels. However, these values were achieved using larger sample quantities (3 g) and longer extraction processes at higher temperatures. Hence, the analytes were detected and quantified by GC–MS/MS, but only for three compounds: OMC, OC, and OD-PABA. Similarly, Cadena-Aizaga et al. (2022) reported recovery values ranging from 31 to 94 % for oUVFs in primary producers. The wide variability observed in the present study, as well as in previous research (Cadena-Aizaga et al., 2022), may be attributed to the diverse chemical structures and physicochemical properties of the target compounds. Differences in polarity, functional groups, and molecular weight lead to distinct extraction behaviors, making the optimization process complex (Nitulescu et al., 2023). Taken together, these findings support the interpretation that the relatively low recovery efficiencies observed could be linked to the matrix effect due to the complexity of the zooplankton matrix (Sørensen et al., 2023). This variability can be observed in the matrix effects results, where 4-MBC and OD-PABA show the lowest matrix effects, values cosest to the ideal 100% (96.46 and 103.1, respectively). HMS, DTS, OC, BMDBM, IMC, and OMC showed noticeable ion suppression (in the range 89.37–94.13) while UV-360 and EHS showed ion enhancement (119.8–105.5) (Table 2). Zooplankton is typically composed of multiple species from various taxa, including gelatinous specimens, such as jellyfish, crustaceans, molluscs, and fish larvae, among others, with a constantly shifting community composition (Kléparski et al., 2021; Bucklin et al., 2021, 2022). Each group exhibits distinct accumulation capacities influenced by lipid content, feeding behaviour, and habitat (Sørensen et al., 2023). This biodiversity could contribute to variability in analyte extraction and quantification, potentially influencing residual signals and, consequently, the MLOD and MLOQ, due to the different nature and composition of the various species. For example, the high lipophilicity of certain compounds may lead to preferential accumulation in lipid-rich species within the zooplankton assemblage, such as copepods (Connelly et al., 2012). Moreover, zooplankton have been collected in subtropical areas, mainly consisting of omnivorous species that present smaller lipid reserves (Lee et al., 2006). Considering the lipophilic behaviour of the target compounds, low quantities of lipid content in the matrix could affect the observed recovery rates (Nieddu et al., 2024).

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

3.3. *Greenness of the developed methodology*

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

3.4. *Monitoring the presence of organic UVFs in the zooplankton matrix*

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

The measured analytes were BP-3, DTS, EHS, HMS, OC, and OD-

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

PABA (Table 3). HMS had the highest frequency of quantification (FQ) (52.8 %), followed by OC, OD-PABA, and BP-3. OC presented the highest concentration, followed by BP-3, HMS, and OD-PABA (Table 3). The compounds DTS and EHS were found to be the least FQ, in 8.33 % and 5.56 % of the samples, respectively, and presented the lowest quantified concentrations. BP-3, EHS, HMS, OC, and OD-PABA, at concentrations ranging from 4.2 to 8.9, 15.5 to 20.5, 3.3 to 25.5, 5.6 to 10.9, and 4.6 to 19.5 ng g^{-1} (wet weight), respectively, together with six additional oUVFs (some optimized in the present study), have previously been reported in aquatic zooplankton from urban river systems in China (Yang et al., 2020). Although concentrations observed in Madeira appear higher, the values reported by Yang et al. (2020) were expressed on a wet weight basis, which likely underestimates values compared to d.w. based on measurements. This difference may be particularly relevant considering that the Chinese samples were collected in areas with greater human influence (urban rivers). In addition, the Madeira concentrations were corrected for recovery efficiencies, which may slightly overestimate the values (Table 2). Regardless of concentration, similar oUVF profiles were observed in both ecosystems, indicating a high release rate of these compounds and suggesting their widespread occurrence in aquatic environments. These results also imply that zooplankton at lower trophic levels are particularly susceptible to exposure and accumulation of organic contaminants, including oUVFs, and highlight the global presence and ecological impact of these compounds in aquatic and marine biota. Considering that zooplankton, together with phytoplankton, constitute the base of the aquatic trophic chain, the presence of CECs in these organisms must be considered. Previous studies have already demonstrated the trophic transfer potential of BP-3, OC, HMS, and OMC from plankton to higher trophic levels (Yang et al., 2020).

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

Compounds	Range (ng g $^{-1}$ d. w)	Mean (ng g $^{-1}$ d.w)	Median (ng g $^{-1}$ d.w)	FQ (%)
BP3	101.3–658.5	336.5	289.4	19.44
DTS	93.76–193.2	134.5	116.4	8.33
EHS	38.16–51.31	44.73	44.7	5.56
HMS	9.503–350.4	117.7	51.8	52.78
OC	24.01–1029	249.7	72.6	41.67
OD-PABA	39.10–287.4	191.2	221.6	16.67

Relative to the presence of the different target compounds in the zooplankton samples, OC and HMS are characterised by high lipophilicity and low water solubility (Table SM1). Their widespread use and global regulatory approval could contribute to their ubiquitous environmental presence (Al-Jamal et al., 2014; Holt et al., 2020; Fivenson et al., 2021). OC has been reported in a wide range of marine organisms and geographic locations, including molluscs and mussels, with concentrations reaching up to 256 ng g^{-1} d.w., along the French, Portuguese, and Hong Kong coasts (Bachelot et al., 2012; Cunha et al., 2015; Sang and Leung, 2016). OC, OD-PABA, and BP-3 have also been detected in crustaceans collected in Norway, with concentrations up to 68.9 ng g^{-1} d.w. (Langford et al., 2015). In polar regions, clams have been found to contain BP-3 concentrations as high as 112 ng g-1 d.w., while sea urchins have contained up to 8.6 ng g^{-1} d.w. (Emnet et al., 2015). Furthermore, fish, cephalopods, and crustaceans collected in China exhibited total oUVFs concentrations ranging from 35.566 to 596.31 ng g^{-1} d.w. (Peng et al., 2015).

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

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

BP-3 is one of the most frequently detected UVFs in marine waters globally, with concentrations ranging from a few ng L^{-1} to mg L^{-1} in regions such as Spain, China, and the United States (Downs et al., 2016; Tsui et al., 2014; Vila et al., 2016). Specifically, in the Macaronesia region (*e.g.*, Canary Islands), BP-3 has been reported in various marine species, including cetaceans (5.920 ng g^{-1} wet weight) (González-Bareiro et al., 2023; Íñiguez et al., 2025) and fish, with concentrations ranging from 0.07 to 0.29 μg g^{-1} d.w. (Gimeno-Monforte et al., 2020). It has also been detected in seawater, with peak values reaching 46.6 ng L^{-1} (Sánchez Rodríguez et al., 2015), suggesting its widespread distribution across different environmental compartments in this region. The detection of BP-3 in zooplankton may be due to their collection with a manta trawl near the sea surface, particularly within the sea surface microlayer (SML), a zone known to accumulate high concentrations of organic contaminants. As the SML is in direct contact with the atmosphere and contains elevated levels of organic matter, it can enhance the sorption and retention of organic compounds, even those with lower lipophilicity such as BP-3 (Pintado-Herrera and Lara-Martín, 2020). Moreover, the presence of BP-3 might be associated with co-formulated oUVFs such as HMS and EHS, which are commonly used together in PCPs to improve formulation stability and enhance UV protection (Nieddu et al., 2024).

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

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

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

4. Conclusion

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

An optimized method combining MAE with UHPLC-MS/MS was developed to detect and quantify eleven oUVFs in zooplankton matrices. Despite the challenges presented by these complex biological matrices, such as low lipid content and high taxonomic diversity, the method was validated and demonstrated reliability, but low efficiency due to the complexity of the matrix.

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

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

Glossary

4-MBC	4-methylbenzylidene camphor
ACN	Acetonitrile
BMDBM	Butyl methoxydibenzoylmethane
BP-3	Benzophenone-3
DS	Desertas
DTS	Drometrizole trisiloxane
EHS	Ethylhexyl salicylate
ESI	Electrospray ionization
EtOH	Ethanol
FQ	Frequency of Quantification
FX	Funchal
HEX	Hexane
HMS	Homosalate
ILOD	Instrumental Limit of Detection
ILOQ	Instrumental Limit of Quantification
IMC	Isoamyl p-methoxycinnamate
IS	Internal Standard
iUVFs	Inorganic Ultraviolet Filters
K_{ow}	n-octanol-water partition coefficient
LM	Lombada dos Marinheiros
MAE	Microwave Assisted Extraction
MeOH	Methanol
MLOD	Method Limit of Detection
MLOQ	Method Limit of Quantification
OC	Octocrylene
OD-PABA	Ethylhexyl dimethyl PABA
OMC	Ethylhexyl methoxycinnamate
oUVFs	Organic Ultraviolet Filters
PCPs	Personal Care Products
RSD	Relative Standard Deviation
REACH	Registration, Evaluation, Authorisation and Restriction of Chemicals
UHPLC-MS/MS	Ultra High Performance Liquid Chromatography tandem Mass Spectrometry
UV-360	Methylene bis-benzotriazolyl tetramethylbutylphenol
UVFs	Ultraviolet Filters

CRediT authorship contribution statement

Eva Íñiguez: Writing – original draft, Validation, Supervision, Methodology, Formal analysis, Conceptualization. **Margaux Gouazé:** Writing – original draft, Validation, Methodology, Investigation, Formal analysis. **Ana Dinis:** Writing – review & editing, Supervision, Funding acquisition, Conceptualization. **Zoraida Sosa-Ferrera:** Writing – review & editing, Supervision. **Nereida Cordeiro:** Writing – review & editing, Supervision, Project administration, Funding acquisition. **Manfred Kaufmann:** Writing – review & editing, Supervision. **Sarah Montesdeoca-Esponda:** Writing – review & editing, Writing – original draft, Validation, Supervision, Methodology, Formal analysis, Conceptualization.

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 data to this article can be found online at https://doi.org/10.1016/j.marpolbul.2025.119204.

Data availability

Data will be made available on request.

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