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Assessment of UV filter ethylhexyl methoxycinnamate photoisomerization in aquatic environments, cosmetics and *in vitro* skin by (micro)extraction GC–MS analysis

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ABSTRACT

This work examines the photoinduced isomerization of the UV filter ethylhexyl methoxycinnamate (EHMC) in different real samples, including environmental waters, cosmetic products, and human skin. Water samples (river, sea, and swimming pool water) spiked at environmentally relevant concentrations were irradiated with UV light and analyzed by solid-phase microextraction (SPME) followed by GC–MS. Natural waters showed minimal total degradation of EHMC, reaching an (*E/Z, trans/cis*)-photostationary state with slight predominance of the *Z* isomer. In contrast, swimming pool water exhibited rapid EHMC loss, likely due to disinfectants, reducing concentration below 20% within 10 min.

Cosmetic products (sunscreen cream, lip balm, and hair oil) were irradiated under the same UV conditions after application onto glass slides, and EHMC was extracted using vortex and ultrasound assisted extraction (UAE) followed by GC–MS. All samples exhibited formation of *Z*-EHMC, representing 30–50% of total EHMC at photostationary equilibrium, with minimal total degradation. Similar behavior was observed under natural sunlight, confirming that cosmetic products undergo photoinduced transformation under real conditions. To simulate human exposure, cosmetic products were applied to *in vitro* human skin and irradiated, again resulting in rapid formation of *Z*-EHMC. This isomer is known to be less effective as a sun protector and potentially more toxic.

These findings demonstrate that EHMC consistently converts into its *Z* isomer across environmental waters, cosmetic products, and human skin, highlighting potential implications for sunscreen efficacy as well as environmental and human health risks. Additionally, the applied extraction and analytical methods proved to be suitable for monitoring EHMC in complex matrices.

1. Introduction

2-Ethylhexyl-4-methoxycinnamate (EHMC), also known as octinoxate, is a widely used organic UV filter commonly incorporated in personal care products (PCPs), such as sun care products, facial treatment products, lipstick, hands, body, and hair products [1–4]. The maximum allowed concentration of EHMC in PCPs is 10% in Europe, according to Annex VI List of UV Filters Allowed in Cosmetic Products of the EU Cosmetic Regulation, and slightly smaller concentration 7.5% is valid in USA (European Chemicals Agency, 2024) [5].

A critical limitation of EHMC as a photoprotective agent stems from its photochemical instability, leading to a decrease in UV absorption efficiency [6], and other authors studied that EHMC undergoes degradation when exposed to light, but it remains stable when kept in the dark at various temperatures (up to 60 °C). This photoisomerization process significantly affects the photoprotective efficacy of sunscreen cream products. The *E* isomer (*trans* isomer) exhibits a maximum absorption wavelength at approximately 310 nm with a high molar extinction coefficient of 19,500 L mol^{-1} cm^{-1}, whereas the *Z* isomer (*cis* isomer) shows reduced UV absorption with a maximum at 312 nm and a substantially lower molar extinction coefficient of 10,000 L mol^{-1} cm^{-1} [7]. Studies have demonstrated that this isomerization can result in sun protection factor (SPF) reductions exceeding 30%, with the photoisomerization of EHMC potentially causing significant loss of UV

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filtering efficiency [8].

Previous investigations have primarily focused on photoisomerization kinetics under controlled laboratory conditions using simulated/natural light sources [2,9]. In brief, the light-induced transformation of EHMC is primarily driven by UV-induced excitation, followed by rotation around the C═C double bond in the excited state and subsequent relaxation to the ground state, leading to the formation of the *Z* isomer [10–12]. This transformation has raised significant concerns regarding its safety and environmental impact, particularly since the *Z* isomer has been shown to exhibit increased genotoxicity and potential endocrine disrupting effects compared to the parent *trans* isomer, raising concerns about its safety upon skin exposure and environmental release [13–15]. Endocrine disrupting potential of EHMC has been suggested in several *in vitro* and *in vivo* studies [16,17]. Its lipophilic nature facilitates bioaccumulation in aquatic biota of different trophic levels [18,19]. The effect of this compound on marine life and its potential for bioaccumulation require more detailed investigation, especially as it has been detected in water bodies worldwide, including the *cis* isomer although no quantitative data are available, highlighting the need for comprehensive studies on its environmental fate [20,21]. Recently, a previous study by the authors have identified and quantified the presence of both isomers in real Adriatic seawater samples, with *Z*-EHMC accounting for 18–64% of total (*E* + *Z*)-EHMC [22]. Based on these findings, the present work was conducted to investigate the isomerization of this UV filter under environmentally relevant conditions. Indeed, the UV filter EHMC (along with benzophenone-3) has shown to be harmful to coral reefs and other aquatic ecosystems even at very low concentrations (parts-per-trillion), prompting Hawaii to ban sunscreens containing these compounds [23]. In addition, the target compound was added to the EU's Watch list for monitoring substances in water [24], and subsequently seven candidates were proposed for the 4th Watch list, three of which are sunscreen agents, underscoring the importance of this group of water pollutants [25].

Studies have shown the presence of EHMC along with other UV filters in human breast milk [26], urine [27], and even in marine animals (shellfish) in the Mediterranean and Atlantic coast of France [28]. In light of recent Scientific Committee on Consumer Safety (SCCS) evaluations flagging *E*-EHMC for its potential endocrine-disrupting effects [29], investigating both the parent compound and its transformation product is essential for comprehensive environmental risk assessment. However, these evaluations do not account for the broader environmental exposure risk or the long-term ecological effects or behavior of EHMC photodegradation. Indeed, the potential persistence and the long-range transport of this compound have been demonstrated, as it has been found even in Antarctic snow samples [1,4].

Despite the extensive body of research detecting EHMC in many environmental waters, while others characterizing EHMC photoisomerization, critical knowledge gaps persist. Previous studies have predominantly employed artificial light sources, standardized solvents, and concentrations far from real-world exposure scenarios. The present study addresses these fundamental gaps by investigating EHMC photoisomerization under environmentally and dermally relevant conditions. This work examines photoisomerization in real water samples (seawater, river water, and swimming pool water) at low concentrations (parts per billion) using solid-phase microextraction (SPME) as the extraction technique followed by gas chromatography coupled to mass spectrometry (GC–MS). In addition, *E/Z* transformation is also monitored in authentic commercial cosmetic products containing much higher concentrations that those in the environmental waters (*E*-EHMC at percentage) under simulated UV light and natural sunlight, and on an artificial human skin model (VITRO-SKIN®) [30] to evaluate the EHMC degradation and formation of the *Z*-EHMC isomer during realistic exposure scenarios.

2. Experimental

2.1. Reagents and material

(*E*)-2-Ethylhexyl methoxycinnamate (*E*-EHMC, 98.5%) was purchased from Dr. Ehrenstorfer (Augsburg, Germany). Ethyl acetate (EtAc, 99.5%), and ultrapure water were provided by Scharlab (Barcelona, Spain). Methanol (MeOH, 99.9%) was purchased from Sigma-Aldrich. All solvents and reagents were of analytical grade. A stock solution of *E*-EHMC was prepared in MeOH at concentration of 1000 mg L^{-1} and further dilutions were made either in MeOH (for spiking water samples) or in EtAc (for direct injections). Stock and working solutions were stored in glass vials protected from light and kept in a freezer at −20 °C.

The manual SPME holder and the 65 μm polydimethylsiloxane/divinylbenzene (PDMS/ DVB) fiber were purchased from Supelco (Bellefonte, PA, USA). Prior the first use, the fiber was conditioned as recommended by the manufacturer, inserting them in the GC injector under helium flow at 250 °C (PDMS/DVB) for 30 min. Low-pressure mercury lamp (11 W, $\lambda = 254$ nm) was provided by OSRAM (Munich, Germany). Artificial skin (VITRO-SKIN®) was acquired from IMS testing group (ME, USA). VITRO-SKIN® (IMS USA) is an advanced testing material formulated to closely replicate the surface characteristics of human skin, including its topography, pH, critical surface tension, and ionic strength (Table S1). Glass slides and quartz cuvettes were provided by Labbox (Barcelona, Spain).

Three real water samples were obtained from three locations in Galicia (NW Spain): seawater, river water, and swimming pool water. All these samples were collected (30 mL - 1 L) in glass vials or bottles, transported and stored at −20 °C in the dark. EHMC was not detected in any of these water samples, confirming their suitability experiments with spiked samples. The river and seawater samples were collected in winter, when the probabilities of finding EHMC are low; whereas the swimming pool water was collected in June. This pool sample was obtained from an indoor swimming pool during the first hour in the morning to prevent EHMC contamination. This water was treated with chlorine species since the concentration of total chlorine was 0.1 mg L^{-1}. The total chlorine is displayed in Table S1 as well as pH, and conductivity values for all the water samples.

Cosmetic products explicitly labelled as containing EHMC were selected for this investigation. The three samples were acquired in local stores and included a sunscreen cream, a lip balm, and a hair oil (Table S1). The lip balm and hair oil samples had been previously used by consumers, whereas the sunscreen cream was acquired for this study. All products had been purchased 1–2 years prior to the analysis.

2.2. Photodegradation in water

100 mL of water samples (ultrapure water, seawater, river water, and swimming pool water) were spiked with *E*-EHMC at a concentration of 20 μg L^{-1}. Aliquots of 2.5 mL were placed in quartz cuvettes and irradiated with UV light (11 W, $\lambda = 254$ nm) at distance of 4 cm for the designated time (0, 10, 20, 40, 60 min). Dark tests (in the absence of UV irradiation) were also performed by placing the cuvettes at the same distance, maintaining the UV light lamp switched off for the correspondent time to assure that no isomerization occurred in the absence of light. Afterwards, the samples (non-irradiated and irradiated) were extracted using SPME and analyzed by GC–MS in full scan (FS) mode. The experimental process is shown in Fig. 1a, as well as the analysis of cosmetics and *in vitro* human skin.

The SPME experimental procedure was performed by using a method previously reported with minor modifications [31,32]. 2 mL of the sample were transferred into 10 mL glass vials sealed with aluminium caps furnished with PTFE-lined septa and placed in a water bath maintained at 100 °C, and allowed to equilibrate for 3 min. Subsequently, the PDMS/DVB was exposed to the vapor phase above the water sample (*i.e.*, in headspace mode) for 10 min. After extraction, the fiber was inserted

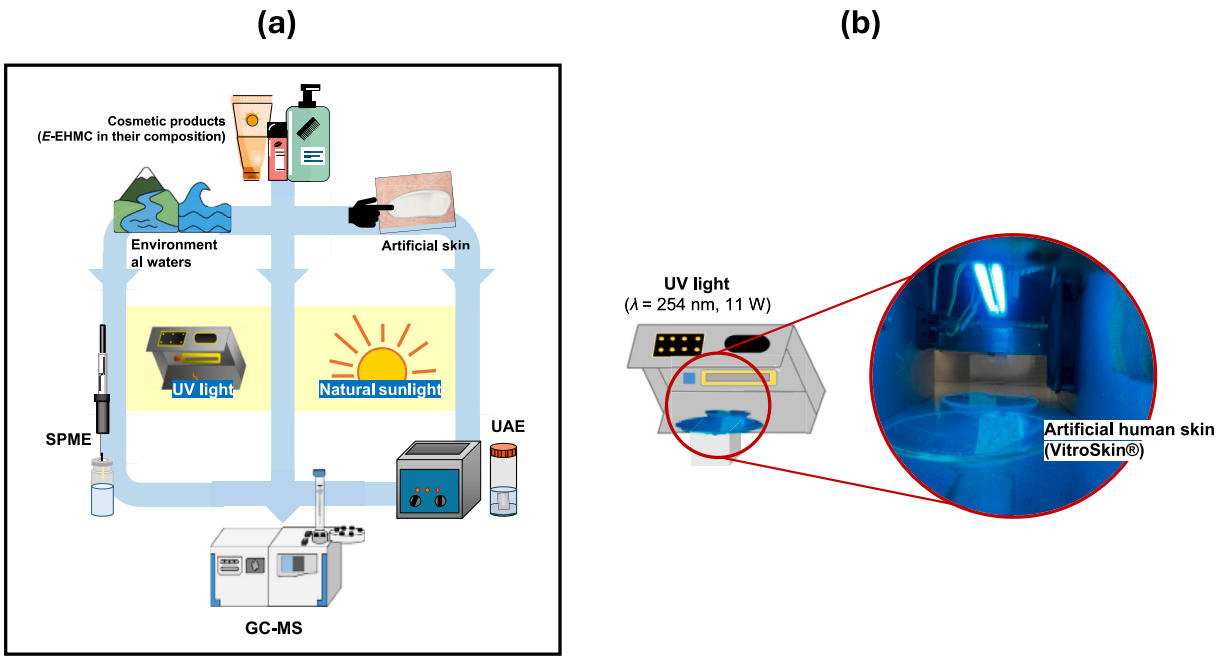

Fig. 1. (a) Scheme of the sample preparation and photoirradiation procedures by SPME and UAE (ultrasound assisted extraction) and analysis by gas chromatography–mass spectrometry; (b) representation of artificial skin exposure under UV light.

and immediately thermally desorbed in the GC injection port at 260 °C for 3 min, followed by GC–MS analysis. To prevent memory effects, blank samples were periodically performed using ultrapure water following the same SPME procedure.

2.3. Photodegradation of cosmetic products in different substrates: glass slides and in vitro human skin

About 0.02 g of each cosmetic product (sunscreen cream, lip balm, and hair oil) were applied either to a glass slide (2.5 × 3.7 cm) or to a 3 × 3 cm piece of *in vitro* human skin (VITRO-SKIN®) [30]. The product was carefully spread over the surface using circular motions with a finger to form a thin, uniform film. The samples were then subjected to irradiation under two different light conditions: a UV light lamp (11 W, λ = 254 nm) in a lab-made photoreactor (see Fig. 1b) and natural sunlight at the external laboratory terrace. The exposure times were 30 min to 4 h. The same samples were also prepared and maintained protected from the light to perform the corresponding dark tests. Both substrates were placed on a watch glass. For the *in vitro* skin, after the skin was conditioned (16–24 h chamber with 85/15 water/glycerin (*v/v*) solution), the cosmetic product was applied to the "skin topography" side, which was always facing the light.

To perform the analysis, irradiated and non-irradiated samples were place in falcon tubes and 10 mL of ethyl acetate were added. Then the tubes were immersed in an ultrasound bath at room temperature and sonicated for 15 min (50 kHz, 25 °C approximately). Afterwards, the solvent extract was diluted 1:2000 before GC–MS/MS analysis. The experiments were done per duplicate.

2.4. Gas chromatography-mass spectrometry analysis

Analyses were conducted on an Agilent 7890 A gas chromatography coupled to an Agilent 5975C mass selective detector featuring a triple-axis detector. A 30 m × 0.25 mm × 0.25 μm ZB-Semivolatiles column (Phenomenex, Torrance, CA, USA) was employed for chromatographic separation. High purity helium (99.999%) served as the carrier gas at a flow rate of 1.0 mL min^{-1}. The oven program was set as follows: initial temperature 100 °C (held 1 min), ramped to 290 °C at 25 °C min^{-1} (held 4 min), making a total run time less than 14 min. The transfer line, ion source, and quadrupole were maintained at temperatures of 290 °C, 150 °C, and 300 °C, respectively. The chromatographic GC–MS conditions were previously developed by the authors [33].

The mass spectrometer was run in positive electron ionization (EI) mode at +70 eV. The injection temperature was 260 °C. *Z*-EHMC and *E*-EHMC were analyzed in full scan (FS) mode. The retention times for *Z*-EHMC and *E*-EHMC were 8.2 and 8.7 min, respectively, and the quantification ion was *m/z* 178, while the identification ions were *m/z* 161 and *m/z* 133 (Table 1). The instrument was controlled with Agilent MSD ChemStation software (version E.02.00.493).

In the case of the cosmetic samples, most analyses were performed using a Thermo Scientific Trace 1310 GC system combined with a triple quadrupole mass spectrometer (TSQ 8000) and an IL 1310 autosampler (Thermo Scientific San Jose, CA, USA). Separation was achieved on a Zebron ZB-Semivolatiles column (30 m × 0.25 mm i.d., 0.25 μm film thickness, Phenomenex). Helium (purity 99.999%) was used as the carrier gas at constant flow rate of 1.0 mL min^{-1}. The oven program was set as follows: initial temperature 100 °C (held 1 min), ramped to 290 °C at 25 °C min^{-1} (held 4 min), making a total run time less than 14 min. Samples were introduced in surged splitless mode (200 kPa, 1.20 min), with the injector maintained at 260 °C. The MS was operated in positive EI mode at +70 eV, with transfer line and ion source temperatures held at 290 °C and 350 °C, respectively. The SRM transitions (*m/z*) and corresponding collision energies (eV) for both isomers were: 290.2 → 178.1 (10), 161.0 → 133.1 (10), and 177.9 → 133.1 (20) (25,26). The retention times for *Z*-EHMC and *E*-EHMC are 10.07 and 10.68 min, respectively (Table 1). Instrument control and data processing were carried out with Xcalibur 3.0 and Trace Finder™ 3.2 software.

3. Results and discussion

3.1. Method validation

Solid-phase microextraction (SPME) and ultrasound-assisted extraction (UAE) were selected as suitable techniques to extract the UV filter *E*-EHMC and its transformation product *Z*-EHMC from environmental waters and *in vitro* human skin, respectively. SPME conditions

Table 1
Retention times, quantification, and identification ions (*m/z*), and quantification and identification transitions for *E*-EHMC and *Z*-EHMC.

Compound	GC–MS			GC–MS/MS		
	Retention time (min)	Quantification ion (*m/z*)	Identification ion (m/z)	Retention time (min)	Quantification transition (collision energy, eV)	Identification transition (collision energy, eV)
Z-EHMC	8.2	178	161, 133	10.07	290 → 178 (10)	178 → 133 (20); 161 → 133 (10)
E-EHMC	8.7	178	161, 133	10.68	290 → 178 (10)	178 → 133 (20); 161 → 133 (10)

were based on previous studies from our research group [31,32]. The SPME conditions are described in Section 2.2., comprising a reduced extraction time of only 10 min providing satisfactory recoveries (91–95%, see Table S2). The precision was also satisfactory, with RSD values lower or equal to 11%. Recoveries were calculated by comparing the responses in the samples with the responses in ultrapure water spiked at the same level (the original samples were free of EHMC). Table S2 displays the performance of the SPME-GC–MS method. For the UAE procedure (experimental details in Section 2.3), this technique was selected over PLE (Pressurized Liquid Extraction) [30] because UAE is a more sustainable extraction approach. Unlike PLE, UAE does not require extreme conditions of high pressure and temperature to achieve quantitative recoveries. UAE operates at room temperature and atmospheric pressure, where cavitation favors the extraction of the target compound EHMC. As shown in Table S2, quantitative recoveries were obtained (91%, comparing the EHMC response in skin and in cosmetic) for the extraction of EHMC in cosmetics products applied to *in vitro* human skin, and satisfactory precision was achieved, with RSD values lower or equal to 11%. The chromatographic conditions including MS detection provided an unequivocal identification of both EHMC isomers (see Fig. S1).

3.2. Photoisomerization of EHMC in various water matrices

Four water samples, including ultrapure water and real environmental waters such as seawater, river water, and swimming pool water, were spiked with *E*-EHMC in duplicate to a final concentration of 20 μg L^{-1}. Photodegradation experiments were conducted in a lab-made photoreactor containing a UV light lamp (11 W, λ = 254 nm). Aliquots of 2 mL from these spiked samples were either analyzed directly or after photodegradation under UV light by SPME-GC–MS, following the procedure described in Section 2.2. The irradiated aliquots were exposed for different periods of time (10, 20, 40, and 60 min) before analysis and the results are presented in Fig. 2a. Fig. 2b shows the SPME-GC–MS ion chromatogram (ion *m/z* 178) of seawater and swimming

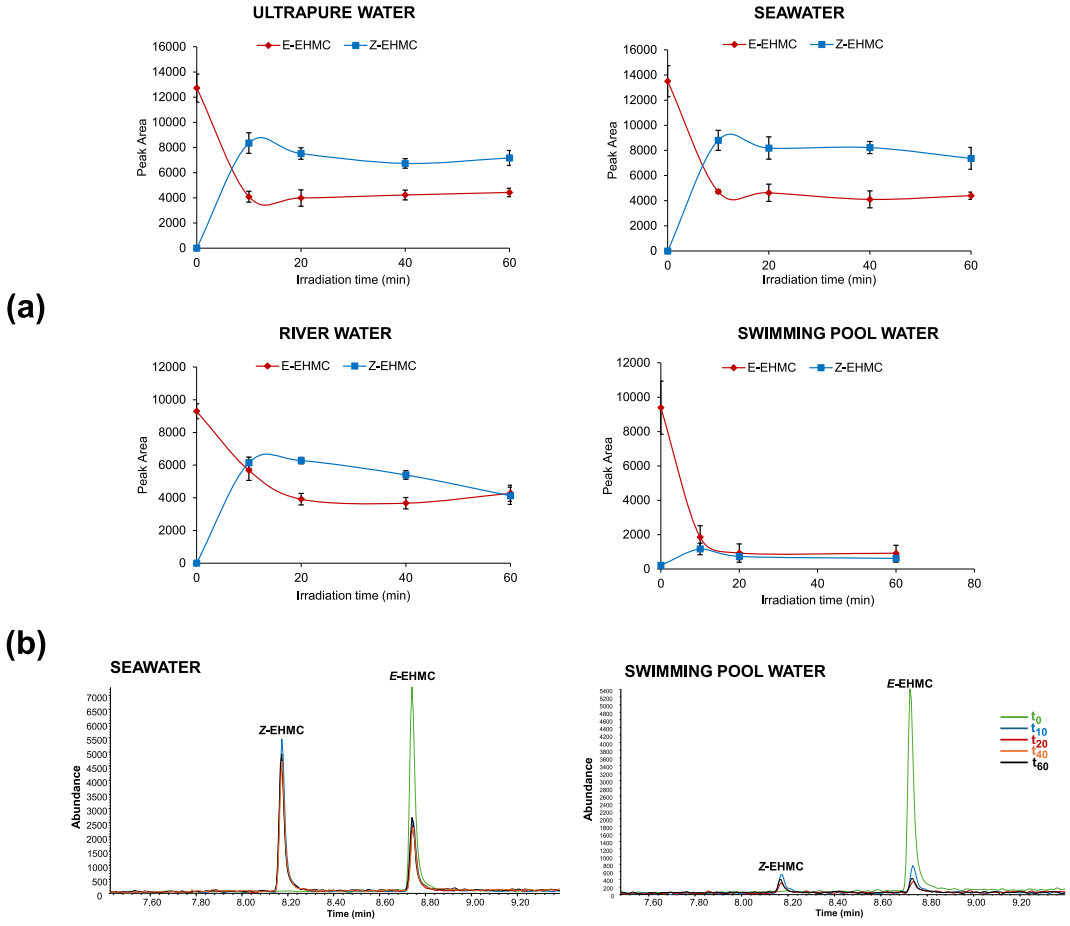

Fig. 2. (a) Graphics showing the peak area of undegraded *E*-EHMC and the peak area of generated *Z*-EHMC for the different water samples after different irradiation times: ultrapure water, seawater, river water, and swimming pool water; (b) SPME-GC–MS ion chromatograms (ion *m/z* 178) of seawater and swimming pool water samples showing the formation of Z-EHMC and the decay of E-EHMC for the different irradiation times.

pool water samples obtained for the different irradiation times.

The analysis of the non-irradiated samples (t_0) shows the single presence of the *E*-EHMC whereas the *cis* isomer (*Z*-EHMC) was not found (see Fig. 2a and b). However, all the other samples showed the presence of both isomers confirming the EHMC photoisomerization (*E/Z*). In all the irradiated samples, the *Z* isomer was predominant (irradiation time 10, 20, 40, 60 min). The chromatographic response for each one of the isomers was quite similar independently the exposure time showing such *E/Z* stationary state. Other authors have observed it in organic and aqueous media [2,34,35], in which the total amount of EHMC appears quite similar indicating a poor EHMC elimination.

The results are quite different for the swimming pool water (see Fig. 2a and b). In this case, a significant reduction in signal was already observed after 10 min of UV exposure, along with the formation of the *Z* isomer, although both isomers exhibited very weak signals. In this matrix, the presence of chlorine radicals, hypochlorous acid, and other reactive oxygen species may promote additional chemical reactions with organic compounds. These results were in consonance with the findings in literature [2,34–36] in which studied photodegradation of EHMC in the presence of reactive oxygen and chlorine species, using water medium. It reports that EHMC undergoes significant degradation when exposed to UV light in the presence of hydrogen peroxide (H_2O_2) and sodium hypochlorite (NaOCl), leading to oxidation and chlorination products [1].

3.3. Photoisomerization of EHMC in diverse cosmetic products

To investigate the environmental origin of *Z*-EHMC isomer, several real (non-spiked) cosmetic samples containing EHMC were analyzed. The selected samples represent different formulations and applications, including hair oil, lip balm, and sunscreen cream.

Quantitative analysis was performed to determine the concentration of EHMC in each sample. Given the typically high concentrations of EHMC in cosmetic formulations, a small amount of sample (5–8 mg) was weighed and homogenized in 4 mL of solvent using vortex mixing followed by ultrasonic agitation. An aliquot of the resulting solution was then diluted and analyzed by GC–MS/MS. As expected, in all cases, only the *E*-EHMC isomer was detected, with no observable presence of *Z*-EHMC, indicating that *Z*-EHMC is not inherently present in the original cosmetic formulations, even though two of the three samples had been previously used before this study and were acquired 1–2 years before. Regarding their concentrations, both the sunscreen cream and lip balm contained 57 mg g^{-1} of EHMC, while the hair oil contained 8.6 mg g^{-1}. These values are below the maximum concentration established by the SCCS Opinion on Ethylhexyl Methoxycinnamate, which considers EHMC safe for use in cosmetic products at levels up to 10% (100 mg g^{-1}) [29].

The three cosmetic products were applied to a glass slide (thin layer) to study the photodegradation of the cosmetic products itself and to an artificial skin model, in order to simulate real use conditions. The samples were then irradiated with UV light and natural sunlight. The detailed experimental procedure is described in Section 2.3.

3.3.1. Photoisomerization on glass slide

The cosmetic samples were irradiated for one hour under UV light in the photoreactor. To simulated even more environmental conditions, direct sun irradiation was performed by exposing the slides to natural sunlight for the same time (1 h). In parallel, a dark control test was performed to confirm that the possible formation of *Z*-EHMC was only due to UV and/or sun exposure. As expected, *Z*-EHMC was not detected in the samples kept in the dark and the t_0 assays. In the other cases, the *cis* isomer (*Z*-EHMC) was present in all samples after the exposure time for both UV light and sunlight (see Fig. 3). The predominant isomer was not the same for the three samples. In the case of the sunscreen cream, the transformation reaction occurs in a lesser extent, and the *trans* isomer is the predominant one, representing about 70% of the total. In the case of the lip balm, the *trans* is also in general more abundant, but the differences between isomers are minor, while the *cis* isomer predominated in the hair oil. This behavior could be partly explained by the different polarity of the media, as the fraction of the *trans* isomer has been reported to be higher in less polar oils [34]. As commented, the samples were quite diverse in both appearance and purpose. Regarding EHMC content, the oil has a lower concentration (about 7 times less). Considering that the oil is a fluid, and the concentration is minor could be logical to expect a faster EHMC transformation.

3.3.2. Photoisomerization on artificial skin treated with cosmetic products

To simulate even a more real scenario, the three cosmetic products were applied on *in vitro* human skin. After skin conditioning, the procedure was very similar to the one followed previously (see also Section 2.3.). After skin irradiation for 1 h and 2 h in the photoreactor, the *cis* isomer was again detected in all the samples. The results are shown in Table 2 and Fig. 4a. It can be seen that the results were quite parallel to

Table 2
Percentage of undegraded *E*-EHMC and generated *Z*-EHMC under controlled UV light exposure in human skin *(in vitro)* treated with the cosmetic formulation: sunscreen cream, lip balm, and hair oil.

Irradiation time (min)	Sunscreen cream		Lip balm		Hair oil	
	E-EHMC	*Z-EHMC*	*E-EHMC*	*Z-EHMC*	*E-EHMC*	*Z-EHMC*
0	100	0	100	0	100	0
30	88	12	78	22	47	53
60	78	22	63	37	48	52
120	70	30	58	42	46	54

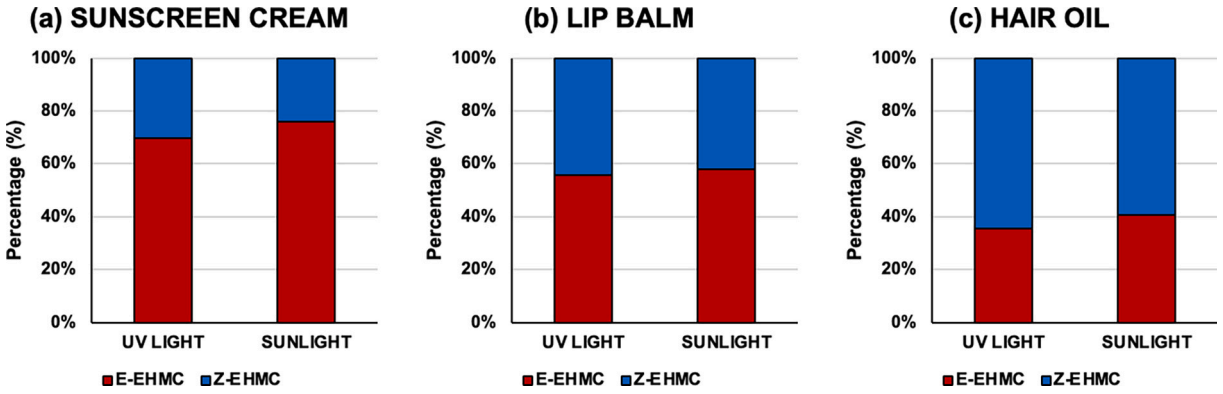

Fig. 3. Comparison of isomeric abundance results after UV light and real sunlight exposure in glass slide (1 h) for the (a) sunscreen cream, (b) lip balm, and (c) hair oil.

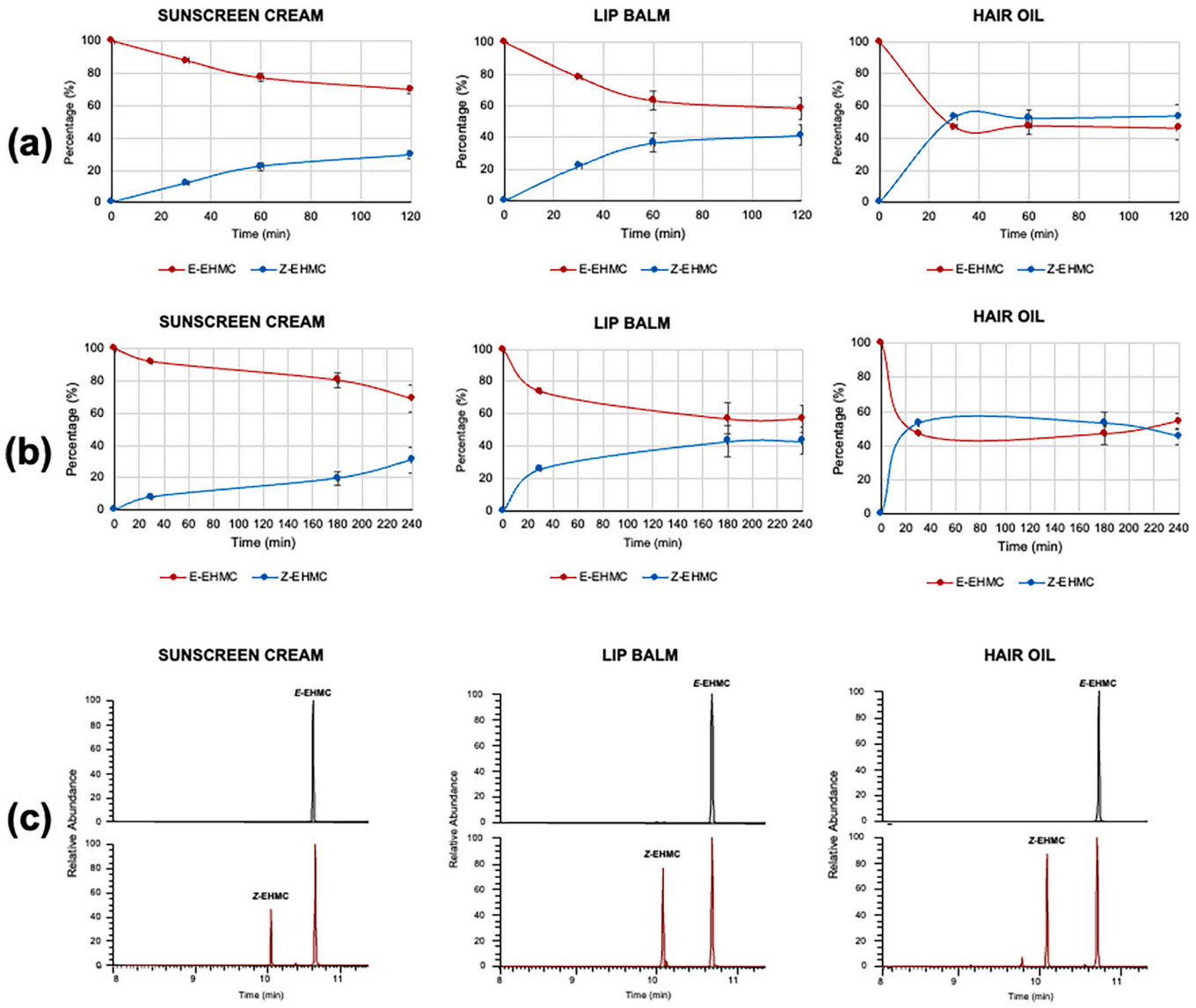

Fig. 4. (a) E/Z photoisomerization kinetics under controlled UV light exposure and (b) under controlled natural sunlight on artificial skin: sunscreen cream, lip balm, and hair oil; and (c) chromatograms obtained for each one of the cosmetic samples before (top part of the figure) and after UV light (1 h) irradiation (bottom part of the figure). The three real cosmetic samples are non-spiked since they contained the E-EHMC.

those observed on glass slide. For the sunscreen cream, the transformation occurs in a less extent with about 25% formation of *cis* isomer. The isomerization occurs more rapidly in the other matrices, especially in the hair oil where the response for both isomers were similar. The photoisomerization of EHMC in the hair oil is similar to that observed in the skin samples spiked with the EHMC standard (see Table S3 and Fig. S2), which is logical since this cosmetic formulation more closely resembles an organic solution. Regarding the exposure time, the results were also quite equivalent after 1 and 2 h confirming the photostationary state reached in other samples and commented in literature. This finding indicates that the dominant process was the *E/Z* photoisomerization as in diluted systems, other photoreactions leading to the formation of degradation products, like truxillate and truxinate dimers, that would imply the formation of aggregates could be excluded [12]. Fig. 4c shows the chromatograms obtained for each one of the samples before and after irradiation (irradiation time 1 h) where the chromatographic peaks for both isomers are clearly presented in the irradiated samples.

Photodegradation was also studied using real sunlight. The atmospheric conditions were a cloudy day, high humidity, an average temperature of 19 °C, and the UV index of 2–3 (see Table S4). The results shown in Table 3 and Fig. 4b were quite similar to the ones obtained by UV light exposure in the photoreactor and quite identical for all exposure times (30, 180, and 240 min). The facile formation of the *Z*-EHMC isomer in the *in vitro* human skin with all kinds of cosmetics is remarkable and of potential interest from both environmental and health perspectives, since the cosmetic formulation loses part of its effectiveness as a sun blocker and, additionally, a more toxic substance

Table 3
Percentage of undegraded *E*-EHMC and generated *Z*-EHMC under controlled sunlight exposure in human skin *(in vitro)* treated with the cosmetic formulation: sunscreen cream, lip balm, and hair oil.

Irradiation time (min)	Sunscreen cream		Lip balm		Hair oil	
	E-EHMC	*Z-EHMC*	*E-EHMC*	*Z-EHMC*	*E-EHMC*	*Z-EHMC*
0	100	0	100	0	100	0
30	92	8	74	26	47	53
180	81	19	57	43	47	53
240	69	31	57	43	54	46

is formed *in situ*.

4. Conclusion

This study demonstrates that EHMC undergoes rapid *E/Z* photoisomerization under realistic exposure conditions in both environmental and *in vitro* dermatological scenarios. Gas chromatography coupled to mass spectrometry was used to investigate photoisomerization behavior in ultrapure water, river water, seawater, and swimming pool water samples. In these aquatic environments, extraction performance at the μg L^{-1} level was monitored using rapid headspace solid-phase microextraction, allowing the isomerization process to be tracked efficiently across different water matrices. Photostationary state was achieved within minutes, and poor overall EHMC elimination was observed in all waters except swimming pool water, where both isomers degraded substantially due to reactions with reactive chlorine species and oxidants present in chlorinated water. These findings indicate that EHMC persists in natural aquatic environments, while chlorinated recreational waters facilitate more degradation. In cosmetic products only *E*-EHMC was initially detected in the commercial matrices (all within regulatory concentration limits 10% in the EU), and no *Z*-EHMC detected. After applying commercial formulations (sunscreen cream, lip balm, hair oil) to glass slide and to an *in vitro* human skin model and irradiating them, GC–MS/MS confirmed rapid formation of *Z*-EHMC and evolution toward an *E/Z* photostationary state. In sunscreen cream, the *E* isomer still represented around 70–80% of total EHMC, whereas in the hair oil, the *Z* isomer became comparable to the *E* isomer, showing more extensive transformation.

These results indicate that EHMC phototransformation is not an artefact laboratory irradiation but a systematic outcome of real-world exposure. This means consumers are directly and quickly exposed to *Z*-EHMC, implying both reduced photoprotection and increased biological risk on skin. Prior regulatory evaluation of EHMC focus largely on the parent compound concentration limits in cosmetics, but generally do not account for on-skin photochemistry, environmental persistence, or isomer-specific toxicity. *Z*-EHMC forms rapidly, persists in a near photostationary state, and can enter aquatic systems. Our results argue that of EHMC should no longer treat it as a single static molecule, but as a dynamic system of isomers and transformation products relevant to both environmental exposure and human health assessment.

CRediT authorship contribution statement

Hira Zulfiqar: Writing – review & editing, Writing – original draft, Visualization, Validation, Investigation, Formal analysis, Data curation. **Maria Llompart:** Writing – review & editing, Validation, Supervision, Resources, Project administration, Investigation, Funding acquisition, Conceptualization. **Ana Castiñeira-Landeira:** Writing – review & editing, Visualization, Validation, Investigation, Formal analysis, Data curation. **Andres Duque-Villaverde:** Writing – review & editing, Visualization, Validation, Investigation, Formal analysis, Data curation. **Daniele Fabbri:** Writing – review & editing, Resources, 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.microc.2026.117149.

Data availability

Data will be made available on request.

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