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Delphine Thallinger, Jerome Labille, Thomas Milinkovitch, Jean-luc Boudenne, Frédéric Loosli, et al.. UV filter occurrence in beach water of the Mediterranean coast – A field survey over 2 years in Palavas-les-Flots, France. *International Journal of Cosmetic Science*, 2023, 45 (S1), pp.67-83. 10.1111/ics.12904 . hal-04253200

HAL Id: hal-04253200

<https://hal.science/hal-04253200>

Submitted on 23 Oct 2023

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ORIGINAL ARTICLE

UV filter occurrence in beach water of the Mediterranean coast – A field survey over 2 years in Palavas-les-Flots, France

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Funding information

Agence Nationale de la Recherche, Grant/Award Number: ANR-18-CE34-0012; Agence Nationale de Sécurité Sanitaire de l'Alimentation, de l'Environnement et du Travail, Grant/Award Number: ANSES-21-EST-126

Abstract

Objective: A 2-year sampling campaign was realized on French Mediterranean beach (Palavas-les-Flots Hérault) in order to measure the concentration of UV filters released from the sunscreen used by bathers. Multiple factors suspected of playing determining roles in the UV filter pattern in water were explored, such as the seasonal and daily time evolutions, or the vertical and horizontal distributions, and they were regarded through the UV filter characteristics.

Methods: The beach was monitored during periods of high and low tourist attendance, typically before, during and after the summer peak. The beachgoers attendance was counted. Bathing water was sampled distinctly from the bulk column and from the top surface layer, testing different sampling tools. Sediments and mussels were also sampled and analysed as potential UV filter sinks. Three organic UV filters (octocrylene OCR, avobenzone BMDBM and octyl methoxycinnamate OMC) and one mineral (titanium dioxide TiO₂) were studied here as representatives of the current cosmetic market.

Results: Summer peak attendance on the beach was confirmed associated with peak levels of UV filter concentration in the bathing water, even more pronounced during a heat wave period. This relation was also observed at day scale with an afternoon peak, suggesting a rapid evolution of the UV filter pattern in water. Contrasted fates were measured between the four studied UV filters, that could be mainly explained by their respective characteristics, i.e. particulate or dissolved, hydrophilic or lipophilic, lifetime. Generally, this resulted in a concentration ranking TiO₂ > OCR > OMC > BMDBM, ranging from 0.5 to 500 µg/L. The most lipophilic and recalcitrant OCR was found most vertically differentiated and over concentrated in the top surface layer of water. Finally, a large horizontal

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heterogeneity was also observed in the UV filter concentration pattern, raising the need for sample replicates that cover a significant area.

Conclusion: This work fulfils some knowledge gaps on the issue of UV filter release in coastal environments, not only by providing original field data and methodological recommendations but also importantly in the comparison made of organic and mineral UV filters, which are often considered separately and rarely evaluated at the same time.

KEYWORDS

chemical analysis, environmental concentration, risk assessment, safety testing, spectroscopy, UV filter release

Résumé

Objectif: Une campagne d'échantillonnage de deux ans a eu lieu sur une plage de la Méditerranée en France (Palavas-les-Flots dans l'Hérault) afin de mesurer la concentration de filtres UV libérés par la protection solaire utilisé par les baigneurs. Plusieurs facteurs suspectés de jouer des rôles déterminants dans le modèle de filtre UV dans l'eau ont été étudiés, comme les évolutions saisonnières et quotidiennes, ou les distributions verticales et horizontales, et ils ont été examinés à travers les caractéristiques du filtre UV.

Méthodes: La plage a été surveillée pendant les périodes de fréquentation touristique élevée et faible, généralement avant, pendant et après le pic estival. La présence des baigneurs a été comptabilisée. L'eau de baignade a été prélevée distinctement de la colonne principale et de la couche superficielle supérieure, en testant différents outils de prélèvement d'échantillons. Des sédiments et des moules ont également été prélevés et analysés comme réservoirs de filtre UV potentiels. En l'occurrence, trois filtres UV organiques (octocrylène OCR, avobenzonzone BMDBM et octyl méthoxycinnamate OMC) et un minéral (dioxyde de titane TiO_2) ont été étudiés comme représentants du marché cosmétique actuel.

Résultats: Les pics estivaux de présence de baigneurs sur la plage ont été confirmés comme étant associés à des pics de concentration du filtre UV dans l'eau de baignade, encore plus prononcés pendant une période de vague de chaleur. Cette relation a également été observée à l'échelle d'une journée, avec un pic l'après-midi, suggérant une évolution rapide du profil de filtre UV dans l'eau. Les effets de contraste ont été mesurés entre les quatre filtres UV étudiés, ce qui pourrait s'expliquer principalement par leurs caractéristiques respectives, c'est-à-dire particuliers ou dissous, hydrophiles ou lipophiles, tout au long de la vie. En général, cela a donné lieu à un classement de la concentration: $\text{TiO}_2 > \text{OCR} > \text{OMC} > \text{BMDBM}$, comprise entre 0,5 et 500 $\mu\text{g/L}$. Il est apparu que c'est l'OCR le plus lipophile et le plus récalcitrant qui est le plus différencié verticalement et sur-concentré dans la couche supérieure de l'eau. Enfin, on a observé une grande hétérogénéité horizontale dans le profil de concentration du filtre UV, ce qui a nécessité des répliquats d'échantillons couvrant une zone significative.

Conclusion: Ce travail comble certaines lacunes en matière de connaissances sur la libération des filtres UV dans les environnements côtiers, non seulement en fournissant des données originales sur le terrain et des recommandations

méthodologiques, mais également en comparant des filtres UV organiques et minéraux, qui sont souvent pris en compte séparément et rarement évalués en même temps.

INTRODUCTION

With the increasing development of tourism, beaches and coastal areas are more and more solicited and are under strong anthropic pressure. The use of sunscreen products is widely encouraged by health professionals and governments to limit the risks induced by UV radiation such as sunburn, premature aging or skin cancer due to UVA, UVB and UVC radiations [1]. One example is the Australian “SunSmart” campaign, which has resulted in a 25% increase in the number of people using sunscreens over the past 30 years [2]. Sunscreen sales have also increased in France, with the market research company NPD group reporting a 91% and 58% increase in sales of body and facial sun products in 2022 compared to the same period in 2021. This growth was driven by the preference of high SPF sunscreen products, with body products SPF 50+ jumping of 117% for the same period ([Pharmacos-media.fr](https://www.pharmacos-media.fr)).

The key active ingredients of sunscreens are the UV filters. They can be of mineral and particulate nature, such as titanium dioxide (TiO_2) or zinc oxide (ZnO), or they can be synthetic organic molecules, such as octocrylene (OCR), avobenzene (BMDBM), octyl methoxycinnamate (OMC) ... [3]. In Europe, the list of UV filters authorized for sale on the cosmetic market is defined by the Cosmetics Regulation (EC) No 1223/2009 of the European Parliament and Council [4]. To obtain sufficient sun protection, manufacturers often combine different UV filters in the same sunscreen formulation, at varying concentrations according to their respective needs, and in respect of the regulations in place for each region of the world. For example, USA, Europe, Australia, Canada and South Korea have all approved the use of TiO_2 as a UV filter in sunscreens with a maximum concentration of 25% [5], while organic UV filters are approved in the USA up to a maximum of 6% for benzophenone-3, 15% for homosalate, 10% for octocrylene (OCR), 7.5% for octyl methoxycinnamate (OMC) and 5% for ethylhexyl salicylate. Same, or slightly different, authorized maximum concentrations take place in the European Union (i.e. 10%, for BP-3, HMS, OCR and OMC; 5% for OS) [4].

Upon sunscreen usage, UV filters can be released into the aquatic environment via different pathways. This includes indirect release via municipal wastewater effluent discharges, or waste disposal at the end of life of the product, and direct release via bathing in recreational waters

[6,7]. Among these multiple scenarios, a concern rises regarding the direct release taking place in recreational activities, as intense tourism in coastal areas often comes with fragile ecosystems, and more particularly in coral reef areas where the toxicological effects resulting from coral exposure to UV filters have been highlighted [8–10]. Some proactive governments have already decided to ban some organic filters from sunscreen formulations, based on recent studies on their risk to human and environmental health [11]. While the public and industry preferences could turn to mineral UV filters as a result of these bans, another concern arises as to how such a fine particulate material, often used in a nanometric form, may also present risks to consumer health or for the environment.

Most UV filter types, both organic and mineral, have already been reported to be detected in marine systems. Tsui et al. [12], found OCR in Hong Kong water at a concentration of 103–6812 ng/L and in New York at concentrations of 117–128 ng/L. In the marine environment, OMC was found at concentrations of 0.039–0.39 $\mu\text{g/L}$ in the summer on a Norwegian beach [13]. In recreational waters of the Mediterranean area, Tovar Sanchez et al. [14] and Labille et al. [7] measured TiO_2 concentration levelling at few tens of $\mu\text{g/L}$, and ZnO around 1 $\mu\text{g/L}$. These concentrations are in agreement with Boxall et al. [15] who predicted in water bodies some environmental concentration of TiO_2 associated with cosmetics origin, ranging from 24 to 245 $\mu\text{g/L}$.

The actual bioavailability of some UV filters to marine species has also been evidenced. Some studies reported that OCR can easily accumulate in aquatic organisms due to its high lipophilicity and can be found at a level of 2400 ng/g lipid weight (l.w.) in brown trout [16] or at 89–782 ng/g (l.w.) in Franciscan dolphins [17]. The environmental consequences of UV filters are still unclear and the studies addressing their impacts remain few. For example, Bordalo et al. [18] showed that exposure to BMDBM induced a decrease in mussel sperm viability at 1 and 10 $\mu\text{g/L}$ during in vitro exposures. For OMC, long-term toxicity to danio rerio zebrafish at larval or juvenile stage of life revealed a no-effect concentration (NOEC) above or equal to 30 $\mu\text{g/L}$ regarding survival rate and hatching, and a low effect concentration (LOEC) at 46.9 $\mu\text{g/L}$ regarding sexual development [19]. As for TiO_2 , it is a photo-catalyser capable of generating reactive oxygen species (ROS) that can induce oxidative stress on the skin or create DNA damage [20,21]. In order to reduce this catalytic effect, a mineral coating

of the particles is generally used [22]. However, some studies have shown a partial degradation of these coatings during exposure conditions [23–25]. The size and shape of the nanoparticles, and the different coatings will influence the ecotoxicological responses as well as the behaviour of the nanoparticles in the environment [26–28].

Nevertheless, while these studies provide insight as to UV filter toxicity and accumulation, only a handful of them investigated environmentally relevant exposure concentrations. This highlights the need for robust data characterizing the actual environmental occurrence of UV filters in marine systems. When summarizing the environmental concentrations of UV filters measured in seawater worldwide, a large variety of levels appears [29,30]. This can be due to the UV filter-specific fate in the marine environment, as these substances constitute a very diverse group. Their fate is the result of the combination of several parameters such as the hydrophobic/philic feature, biodegradability and water solubility of the chemical. While the octanol–water partition coefficient K_{ow} gives insight on the hydrophobic/philic feature, the solubility and lifetime of the UV filters in seawater remain mostly unknown. Moreover, contrasted fates appear even more in marine system when comparing organic and mineral UV filters. The reported concentration levels are rather diverging, as a ng/L range is usually reported for organic UV filters, while concentrations 1000× higher have been measured for TiO_2 both in seawater [7] and freshwater [31]. Of note, only a handful of studies analysed both organic and mineral UV filters together in a given field campaign, certainly due to the respective analytical procedures required, each presenting specific challenges in terms of analytical tools and optimization.

Meanwhile, a large variety of environmental concentrations have also been reported for the same UV filter. As an iconic example, the oxybenzone concentrations reported in near-reef water column from Hawaii or Virgin Islands ranged over 7 orders of magnitude from below 1 to above 10^6 ng/L [1,9,32]. Additional questions thus come into play in order to understand such variability. This includes the reliability of the results with regard to the analytical method and quality control. For example, the limit of quantification given by the analysis recovery depends strongly on the optimization of the extraction or digestion method employed before analysis of the organic or mineral UV filters, respectively. Additional considerations should also deal with the robustness of the sampling procedure on field. Temporal variation related to seasons, weather and beach attendance are likely key factors since they determine the extent of potential UV filter release at the sampling day and time. Spatial variability is also most

likely a determining factor as the UV filter concentration may vary from the local scale around the release point, i.e. the bather, to larger scale along with water streams and tide. Finally, the sampling depth should also be considered, as an over-concentration of UV filters has been reported in the top surface layer of water with regard to the deeper water column, in line with their hydrophobic feature and flotation tendency [7,14]. Among the existing field studies measuring the environmental concentrations of UV filters in coastal or beach areas, these additional considerations are rarely taken into account. Moreover, the analytical methods and the sampling methodologies vary a lot, and most of them consist in punctual measurements without estimation of the UV filter amount at the pollution source.

The aim of the present study was to develop and test a methodology adapted to address these lacks, from the field sampling to the laboratory analysis, to ultimately study the pattern of UV filter release into the bathing water and potentially relate it to these under-considered factors (UV filter intrinsic characteristics, time-, space-, and depth-dependent variability, sampling mode). A Mediterranean beach (Palavas-les-Flots, Southern France) was selected as a case study. It was monitored for two consecutive years during periods of high and low tourist attendance, including pre-summer, summer, during a heat wave and fall. At each sampling time, the beachgoers attendance was counted. Bathing water was sampled not only from the bulk column but also in the top surface layer, testing different sampling tools. Sediments were also sampled, as well as mussels near the bathing area, as potential UV filter sinks. Four representative UV filters were quantified in these compartments: titanium dioxide (TiO_2) as the mineral candidate, and octocrylene (OCR), avobenzone (BMDBM, for butyl methoxydibenzoylmethane) and octyl methoxycinnamate (OMC, also named ethylhexyl methoxycinnamate, or octinoxate, or EHMC) as organic UV filters. The results are discussed in terms of the various release and fate scenarios potentially taking place in the coastal environment.

MATERIALS AND METHODS

Study site: Palavas-les-Flots Beach

A 2-year sampling campaign was realized on the beach of Palavas-les-Flots, on the Mediterranean coast (Hérault, Southern France) in order to measure the concentration of UV filters potentially released from the sunscreen consumed by bathers. The region has a Mediterranean climate, which is characterized by hot, dry summers and mild, wet winters. This beach is covered with fine silica

sand, 7 km long, lined with restaurants, stores and jet-ski rental. It experiences the frequentation of the inhabitants of Montpellier metropolis located less than 20 km and a large tourist attendance during the summer season. In order to delimit the studied area, a 20 m width beach corridor (situated in front of the Ginies Mares street) has been virtually considered (see detail in Supporting Information), in which our sampling and analysis of the beach-goer attendance were realized.

The temporal evolution of UV filter concentrations in the beach water, sediment and mussels was studied at the scale of the season over two consecutive years. In 2020, three periods corresponding to pre-summer (May), summer (August) and post-summer (October) were compared, and in 2021, pre-summer (May) and summer (July, August) were compared, with further distinction of normal weather and a heat wave.

Sampling methods

In the bathing zone, three sampling points were practised through the studied beach corridor at a constant distance (15 m) from the shore, and 10 m distant from each other, constituting our replicates. In order to estimate the vertical distribution of the UV filters in water, three depths were sampled, namely the top surface layer, the water column and the sediment. The water column was sampled at 50 cm depth, using a 250 mL amber glass bottle. The top surface layer of water was sampled via two different protocols that could be compared afterwards. In the first protocol used in 2020, a 4 × 4 cm water-repellent polypropylene sorbent sheet was used, aiming at removing and collecting from the top layer any hydrophobic compound. The sheet was manually put in contact with the water surface and immediately returned upside down and put again in contact. In 2021, the second protocol was tested in which a 250 mL amber glass bottle was directly used to sample the top centimetres of water. Both waters from the top surface layer and column were collected at specific times, so as to study seasonal and hourly fluctuations in UV filter concentration with regard to beach attendance. The details of sampling times and types are summarized in Table 1. Briefly, 3 sampling times per day were realized, at 12:00, 16:00 and 18:00, so as to cover the beginning, full peak, and end of the beach affluence. In 2021, the time evolution was also explored at the scale of two consecutive days. The first day was sampled around 16:00 during peak attendance and the next day at 11:00, so that the possible overnight renewal of beach water could be explored. No sample preparation or filtration was made prior to analysis, so that the total content of the water sample could be analysed in the lab. Samples were stored in the dark at 3°C

from the time they were collected to the time they were analysed.

For sediment sampling, cores of 10 cm depth × 10 cm diameter were collected with a homemade cylindrical device, and decanted/reshaped in a glass flask. They were stored at 3°C and darkness until analysis. Sampling was realized in 2020 before the tourist period (June), during the tourist period (August) and off-season (October), and in 2021 at the pre-summer period (May) and during the summer (August). Moreover, in 2021, each sampling was doubled over two consecutive days so that the first point corresponded to the mid-afternoon during full peak attendance and the next point was taken on the next morning after possible overnight sedimentation.

For mussel sampling, a minimum of 10 individuals were collected from the surrounding rocks near the beach (coordinates 43°31'26.1" N 3°55'46.7" E). *Mytilus galloprovincialis* individuals of the same year class were selected (based on their size) so that lifetime exposure to UV filter was considered similar between individuals. Three collection times were practised, distributed in 2020 on pre-summer (June), summer (August) and off-season (October).

Geographical recordings

During the sampling campaigns, a follow-up of the beach attendance took place with a regular count of the people on the beach and the people in the water in the 20 m studied corridor. During the day, the temperature announced by Météo-France as well as the wind speed were recorded. The water temperature was measured with a Checktemp 1 from CIFEC (France), with an accuracy of ±0.2°C (range – 30 to 120°C), at the same time and 50 cm depth as the water sampling.

Water analysis

For inorganic UV filter quantification, the water samples from the bulk column and from the top surface layer were first digested prior to elemental analysis, so that the targeted particulate TiO₂ was first dissolved and the Ti element could be analysed. Digestion consisted as follows: 2 mL of water sample was added to a Teflon tube, where 1 mL of hydrogen peroxide (H₂O₂ 30%) was added to eliminate natural organic matter and let for reaction for 1 h minimum. Then, 1 mL of nitric acid (HNO₃ 67%–69%) was added, followed by 0.25 mL of hydrofluoric acid (HF 47%–51%). Finally, the mixture underwent a microwave acid digestion at 180°C (UltraWAVE Milestone Inc.). The digested solution was then adjusted to 25 mL in metal-free falcon tube with HNO₃ 2%, before

TABLE 1 Summary of sampling times, replicates and methods in 2020 and 2021.

Period	Date	Time	Water column	Top layer	Sediments	Mussels
2020						
Pre-Season	06/23/2020	13:30	Bottle x3	PP x3	–	–
		16:30	Bottle x3	PP x3	x3	10 to 15
		19:30	Bottle x3	PP x3	–	–
Summer	08/13/2020	13:30	Bottle x3	PP x3	–	–
		16:30	Bottle x3	PP x3	x3	10 to 15
		19:30	Bottle x3	PP x3	–	–
Post-Season	10/28/2020	13:30	Bottle x3	PP x3	–	–
		15:30	Bottle x3	PP x3	x3	10 to 15
		18:30	Bottle x3	PP x3	–	–
2021						
Pre-Season	05/20/2021	13:30	Bottle x3	Bottle x3	–	–
		16:30	Bottle x3	Bottle x3	x3	–
		19:00	Bottle x3	Bottle x3	–	–
Summer	05/21/2022	11:00	Bottle x3	Bottle x3	x3	–
	07/21/2021	13:30	Bottle x3	Bottle x3	–	–
		16:30	Bottle x3	Bottle x3	–	–
Heat wave	08/15/2021	19:00	Bottle x3	Bottle x3	–	–
		13:30	Bottle x3	Bottle x3	–	–
		16:30	Bottle x3	Bottle x3	–	–
Summer	08/23/2021	19:00	Bottle x3	Bottle x3	–	–
		13:30	Bottle x3	Bottle x3	–	–
		16:30	Bottle x3	Bottle x3	x3	–
	08/24/2021	19:00	Bottle x3	Bottle x3	–	–
		11:00	Bottle x3	Bottle x3	x3	–

Note: Blue: only organic UV filters analysed; black: both organic and mineral UV filters analysed; green: only TiO₂ analysed.

analysis by ICP-MS (PerkinElmer NexION 300X quadrupole ICP-MS). As high salt concentrations can be problematic for ICP-MS analysis, these acidification and dilution steps before analysis allowed to decrease the initial sample salinity from 30% to 2.4%, which permitted analysis without further sample preparation. The recovery of the procedure for Ti analysis was 94%–96% [27].

In order to distinguish the anthropogenic Ti contribution likely associated with UV filters from the natural Ti background, the latter was subtracted, based on the average Ti concentration measured during off-season in October 2020 ($Ti_{geo/wat} = 8.41 \pm 1.75 \mu\text{g/L}$). Finally, the Ti element concentration was converted to TiO₂ using a conversion factor x1.6683 based on the stoichiometry and respective molar masses of Ti and O in the mineral.

For organic UV filter quantification, 50 mL of water was adjusted to pH 3 using concentrated H₂SO₄. An internal standard (benzophenone-d10) was added, and a liquid–liquid extraction (LLE) of the samples was then

performed with 5 mL of MTBE with vigorous shaking for 2 minutes. Sodium sulfate (10g) was added to improve the separation of the organic and aqueous phases. The extracts (5 mL) were concentrated by exposing them to a gentle stream of nitrogen to a final volume of 0.5 mL at 50°C. The total concentration factor thus obtained was 100 (10 by LLE and 10 by volume reduction of MTBE).

Extracts of field samples were analysed using a UPLC system (Acquity, Waters) coupled to a quadrupole/time-of-flight mass spectrometry (Q/ToF-MS) with electrospray ion (ESI) source (Synapt G2 HDMS, Waters). Analyte separations were achieved using an Acquity UPLC BEH C18 column (Waters, 2.1 × 100 mm, 1.7 μm) at 40°C. The mobile phase consisted of water (A) and methanol (B). Both solvents A and B contained 5 mM ammonium formate (Fisher Chemical, Optima LC/MS). Elution was performed at a flow rate of 0.4 mL/min with a gradient starting at 20% of B and increasing to reach 90% within 4 min and held for 3 min. The sample injection volume was 7.5 μL. The ESI

source was optimized directly with the samples. Data were collected from 50 to 600 Da in positive ionization mode. Compounds were detected as their protonated molecules ($[M+H]^+$). During each chromatographic run, leucine enkephalin (2 mg/L, C28H37N5O7, MW 555.27, Waters Q-ToF product) was used for lockmass correction to obtain accurate masses for each organic component eluting from the column. A solution of sodium formate (HCOONa, Waters Q-ToF product) was infused daily in the ESI source to calibrate the instrument. Optimum ESI conditions were found using a 2.5 kV capillary voltage, 500°C desolvation temperature, 150°C source temperature, 10 L/h cone gas flow rate and 1000 L/h desolvation gas flow rate. Calibration curves were established for each UV filter by an external standard approach using the reference standard. Benzophenone-d10 (deuterated form of benzophenone) was used as a surrogate. Calibration standards were prepared by spiking reconstituted seawater with UV filters and then performing the same procedure used for sample analysis (LLE-UPLC-MS/MS). Quantification of UV filters was performed by following the same procedure used to establish the calibration curves and using the ion transition representing the highest abundance. Method accuracy was validated by calculating the per cent recovery using nine determinations over three concentration levels. Recovery ranged between 89% and 117%. Repeatability relative standard deviation (RSD) ranged between 8% and 16%. The range covered 70%–130% of the test concentrations. Within the studied concentration range, the calibration curves were linear ($r^2 > 0.99$). Limits of quantification (LOQ) were determined as a signal to noise ratio of 3:1 and ranged between 0.52 and 0.70 µg/L (see Table S2).

Polypropylene sorbent sheet analysis

Only the mineral UV filters were analysed from the polypropylene (PP) sorbent sheet after water top surface layer sampling, as there is no validated procedure for the organic UV filters extraction from this substrate to date. The 4 cm² PP sheet (200 mg) was introduced into a Teflon vial, and 10 mL HNO₃ was added. The reaction of sheet dissolution was left to reach completion over 2 weeks on hot plate, with degassing when necessary. Then, the mixture was transferred into a Teflon tube where 1 mL H₂O₂, and 2x1 + 5 mL HNO₃ were added.

Sediment analysis

Only the mineral UV filters were analysed from the sediment, due to limitations in the availability of the extraction methods required for the organic UV filters. The sediments were first freeze-dried and then crushed using

a RETSCH MM400 vibro-grinder, during 3 × 2 min at 30 Hz with ZrO beads of 1.5 cm diameter. Total digestion consisted of acid treatment followed by microwave treatment. Briefly, 0.1 g of sediment was introduced into Teflon tubes and acidified with successive addition of 2 mL nitric acid (HNO₃ 67%–69%), 1 mL hydrogen peroxide (H₂O₂ 30%), and 1 mL hydrochloric acid (HCl 34%–37%). The mixture was then homogenized by a first vortex, and successive additions of 2 mL HNO₃ and 2 mL HCl were completed, followed by second vortex and finally the addition of 0.5 mL hydrofluoric acid (HF 47%–51%). Small quantities were used successively so as to avoid any over-reaction leading to acid overflow. UltraWAVE microwave system (Milestone Inc.) treatment consisted of the following temperature sequence: 15 min increase to 170°C – 10 min delay – 10 min increase to 245°C – 10 min delay – 30 min cooling. The digested solutions were then adjusted at 25 mL with HNO₃ 2% in metal-free plastic tubes. This was followed by a 10-fold dilution with HNO₃ 2% so as to obtain an elemental concentration compatible with the ICP-MS analysis. The digestions were then analysed by ICP-MS (PerkinElmer NexION 300X quadrupole ICP-MS). The recovery of this method was evaluated at 114.8% using a reference soil (MESS-4). After analysis, the same treatment of raw data was processed as for water analysis. A natural background of Ti in the sediment was found at 626.36 µg/g ± 105.29 dry weight, which is in accordance with the geochemical data reported in the literature for marine sediment worldwide [33,34].

Mussel analysis

Only the organic part of the mussels was taken and analysed and not the shell. Five to six individuals harvested at the same time and place were pooled together to constitute a sample. The organic tissues were first freeze-dried and then crushed 3 × 2 min at 30 Hz with 1.5 cm ZrO ball using the RETSCH MM400 vibro-grinder. The mussels followed the same digestion and analysis protocol as for the sediments seen previously. After ICP MS analysis, the same treatment of raw data was processed as for water analysis, except that no natural background of Ti was subtracted here, as not applicable.

RESULTS AND DISCUSSION

Time evolution of UV filters in water through 2020–2021

Some key results of the UV filter monitoring over the 2-year campaign on the beach of Palavas-les-Flots are

presented in Figure 1. The concentrations of the 4 mineral and organic UV filters in the water column are given for seven different periods each sampled at 16:00. This sampling time was selected for presentation here as it corresponds to the peak attendance on the beach during summer periods, so that the most contrasted UV filter concentrations are expected through seasons. These values are put in parallel with the data of beach attendance, number of bathers, and air and water temperatures recorded at the same sampling times. A seasonality appears at the 2-year time scale shown here, where the summer periods were characterized by higher water and air temperatures coupled to a more intense tourist affluence. The air temperature evolved from 18°C in October 2020 to more than 28°C during summer time, reaching a maximum of 34°C at the heat wave recorded here on August 15th, 2021. At the same time, the water temperature evolved respectively from 16°C to more than 20°C and up to 28°C, while the beachgoer attendance ranged from 0 to 53 people on the beach and 0 to 30 in water. As a reminder, these values are given per 20 m width of the beach corridor studied. As for wind, no particular

episode was noted during the summer days studied here that could have altered the usual attendance (See all data in Table S1).

Generally, the large beach attendance co-occurred with high UV filter concentrations found in the water and the inverse. The four studied UV filters generally appear together in this pattern, but TiO₂ was always found in greater quantities than organics, and among the latter, OCR was found to be much more concentrated than BMDBM or OMC (2020 averages at 16:00 = 20.1 µg/L TiO₂, 1.5 µg/L OCR, 0.2 µg/L BMDBM). In 2020, this turned out to be TiO₂ = 13.3 × OCR and OCR = 9.4 × BMDBM. Moreover, this contrast was even more pronounced in 2021 where TiO₂ was found at higher concentrations, giving in average TiO₂ = 61.2 × OCR and OCR = 5.3 × BMDBM. During the heat wave, all the four UV filters reached their maximum measured concentration, i.e. 269.2, 5.0, 0.9 and 0.9 µg/L for TiO₂, OCR, BMDBM and OMC, respectively.

In addition to seasonality, we observed a trend toward an increase in the concentration of TiO₂ found in bathing waters between 2020 and 2021. This increase could be

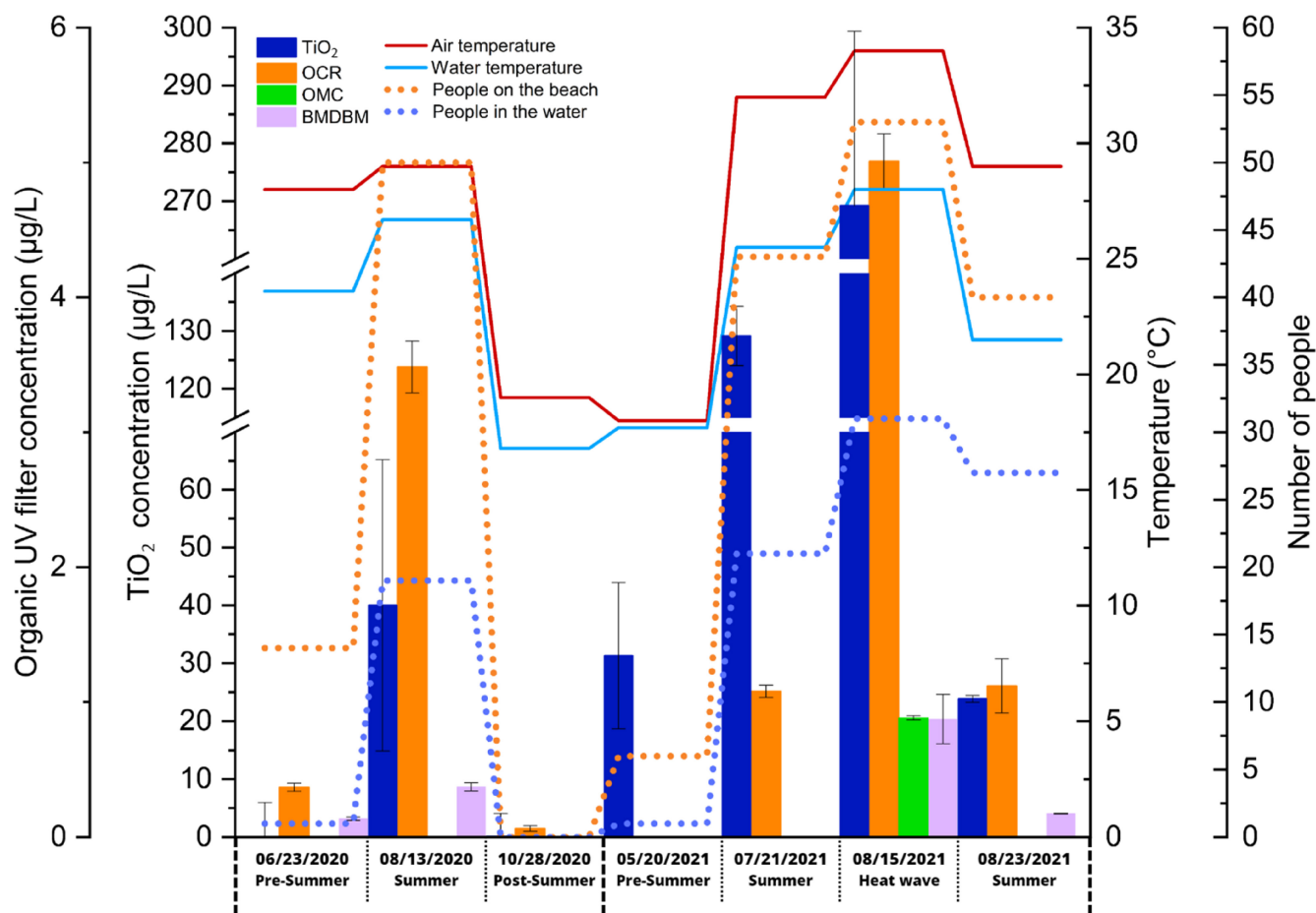


FIGURE 1 Concentrations of organic and mineral UV filters found in the bulk water column of Palavas-les-Flots at 16:00 of six different days through 2020–2021. OMC was not detected in 2020. Air and water temperatures and number of beachgoers in the studied beach corridor are superimposed.

linked to a growing interest of the consumers for products claimed to be safer for them and/or for the environment. For example, among other labels that could be preferred in this perspective, the BIO label benefits of a wide visibility and bans the organic (synthetic) UV filters, which in turn may result in the higher consumption on mineral products. There is also an overall trend of a higher UV filter concentration coverage in 2021 than in 2020, despite the fact that beachgoers attendance was similar over the two studied years. Finally, the occurrence of TiO_2 in water on May 20, 2021 could be explained by the relative higher presence of people on the beach, when compared with the 2020 pre-summer period.

Vertical distribution and persistence of the UV filters in the water column

Figure 2 presents all the concentrations of UV filters measured at every date and time sampled, in the top surface layer of water as a function of that in the bulk column found at the same place and time. The straight line ($y=x$) is plotted for easier reading, as the data appearing above this line correspond to the cases with over-concentration of the UV filter in the top surface layer with regard to bulk column, and the inverse. Regarding the top surface layer sampling mode, the organic UV filter data shown correspond only to the bottle sampling mode realized in 2021, while for TiO_2 , the results from the 2021 bottle sampling can be compared to those obtained with the PP sorbent

used in 2020, and to another sampling mode proposed in the literature, i.e. plastic plate connected to a funnel [7].

Concerning the organic UV filters, as seen in Figure 1, their overall concentrations in water range two orders of magnitude below those of TiO_2 , and following a ranking $\text{OCR} > \text{OMC} > \text{BMDBM}$. Meanwhile, in terms of quantities consumed, BMDBM usually predominates. Indeed, according to the application INCIBEAUTY that returns a list of ingredients when a given product is scanned with a smartphone, after a 30 days survey in 2021, the occurrence of UV filters in the products scanned by consumers was $\text{TiO}_2 = 33.5\%$, $\text{OCR} = 54.7\%$, $\text{BMDBM} = 67\%$ and $\text{OMC} = 20\%$. It is worthwhile noting that the concentration ranking found here in bathing water does not only reflect the proportions of usage in products but also the respective fate and persistence times of these chemicals in the marine system (Table 2). The photodegradation of OCR, OMC and BMDBM in seawater was reported by Celeiro et al. [35]. The authors measured half-life values of >60 min for OC and OMC and 5 min for BMDBM. This could explain why BMDBM was less detected here than OCR and OMC while it is much more present in the products used by the consumers.

Regarding the vertical distribution of the three organic UV filters between the top surface layer of water and the bulk column, three different trends can barely be distinguished in Figure 2. They become more evident when comparing the average slope of each series (Table 2), which reflects the tendency of the UV filter to over-concentrate in the top surface layer with regard to bulk column. This tendency is more pronounced for OCR, followed by OMC, while the slope for BMDBM < 1 rather suggests a slight under-concentration in the top surface layer. This comes in good agreement with the respective hydrophobic features of the three molecules, given through their log Kow values, 7.35 for OCR, 5.80 for OMC and 2.41 for BMDBM (Table 2). Nevertheless, in addition to the lowest Kow for BMDBM and its higher solubility, other elements must cause the molecule to under-concentrate in the top surface layer as seen here. Indeed, a molecule homogeneously dissolved in water would be expected to have a slope of 1, but the slope for BMDBM is 0.78. We hypothesize that such fractionation was actually due to the faster kinetics of degradation of BMDBM taking place in the top surface layer, where photolysis is likely stronger. On the opposite, such effect could not be seen with the two other organic UV filters because their higher hydrophobicity coupled to a higher half-life both tend to an over-concentration in the top surface layer. This hypothesis is comforted by the slopes > 1 obtained for both OCR and OMC. Of note, in addition to the top surface layer and bulk column compartments, the sediment was not studied here as a potential sink for organic UV filters. Nevertheless, it might also play

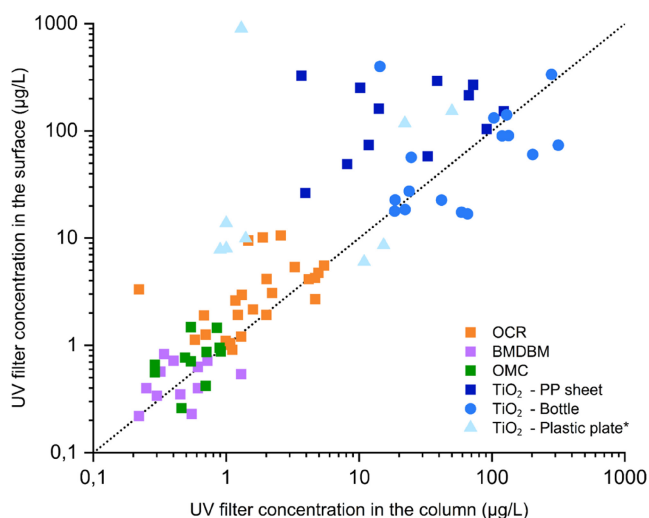


FIGURE 2 UV filters' concentrations measured in the top surface layer of water in relation to those in the bulk water column, and as a function of the sampling method used for top surface layer. These values are triplicate averages. All sampling times are represented. *Adapted from ref. [7].

TABLE 2 Linear slope of the UV filter series in Figure 2 and characteristics of the different UV filters.

	BMDBM	OMC	OCR	TiO₂ PP sheet	TiO₂ bottle	TiO₂ plastic plate
Linear slope	0.78 ± 0.15	1.28 ± 0.17	1.35 ± 0.23	2.26 ± 0.79	0.68 ± 0.22	3.48 ± 5.51
R ²	0.72	0.85	0.59	0.41	0.39	0.05
Solubility	2.2	Insoluble	Insoluble	Insoluble	Insoluble	Insoluble
Log Kow	2.41	5.80	7.35			
Half-life in seawater (min) [35]	5	>60	>60			

a role in their environmental fate, especially for the most lipophilic OCR for which a rapid dissipation from water to sediment was reported [36].

Concerning the mineral UV filter, the net overexpression measured with regard to the organic counterparts is confirmed again in Figure 2. It can be due to the higher persistence of TiO₂ in the environment, as this mineral has a very low solubility. In addition, this could also be due to the capability of the organic UV filters to pass the skin barrier, while particulate ones like TiO₂, even in the nano-size range, cannot pass more than in a very low degree [37] and are consequently more washed off in the bathing water. Indeed, this was already evidenced that most of the organic UV filters present in a sunscreen were found in the blood plasma of human volunteers soon after the product application on their skin [38,39], and this did not depend on the formulation type. Moreover, the mean maximum plasma concentrations of all 6 UV filters studied in this work were greater than 0.5 ng/mL, already on day 1 after a single application. It is worthwhile noting that such concentration is at a level comparable to that found in bathing water here. We can thus reasonably suspect that the retention factor of UV filters by the consumer body is higher for organic UV filters than for the larger mineral and particulate UV filters like TiO₂. This could thus likely contribute to the concentration ranking found in the bathing water, here and in former studies [7,14].

Despite the TiO₂ data are rather disparate in Figure 2, different trends appear according to the sampling mode of the top surface layer. The bottle mode led to data relatively distributed around the straight line, suggesting less vertical differentiation of the TiO₂, while the PP sorbent and the plastic plate modes both led to results showing an over-concentration in the top surface layer of the water. These differences can be discussed in terms of recommendation for the sampling mode most adapted to analyse the top surface layer of water. It is rather difficult to sample only the top surface part of the seawater with the bottle, because the 2 cm mouth implies a low accuracy in the sampling height, which added to the swell and the lapping of the water, makes it more likely to sample a water height deeper than wished, despite the care taken. Moreover, a

slope < 1 was obtained for TiO₂, indicating a lower average concentration in the layer sampled than in the deeper bulk column. We hypothesize that the particulate form of TiO₂, likely aggregated in seawater, favoured its sedimentation, which resulted in its faster removal from the top centimetres of the water column.

The sampling via sorbent PP appears more conclusive regarding the hypothesis that some hydrophobic UV filters are expected more concentrated, floating at the surface than dissolved in the bulk water column. But, as a limitation, it does not enable an accurate volume quantification of the hydrophobic substances sampled. Because the mode of action of this sampling tool is two-dimensional, it implies a bias in the estimation of the height of the water layer effectively covered. This layer thickness may not correspond strictly to that of the sheet (0.5 mm), but could also include a volume of water close below the sheet in which the UV filters are attracted and attached to the hydrophobic PP, being finally also quantified. This distance of action being unknown makes it difficult to convert to a distinct volume of water. Here we used 1 mm of water layer thickness as an approximation for the need of the conversion and comparison proposed in Figure 2.

Finally, the sampling by plastic plate used in the past confirmed clearly the hypothesis that hydrophobic UV filters are found more concentrated in the top surface layer. It is also easy to set up because the thin side of the tool and the connected funnel enable to really recover only the top 1 cm of water and rapidly pour the sample into an appropriate container. It appears, for the moment, as the most appropriate mode of surface layer sampling in seawater.

Horizontal heterogeneities of UV filters in water

Figure 3 represents the organic UV filter concentrations measured in top surface and in water column for all sample triplicates taken over 2021. They show not only the time of evolution at the seasonal scale already discussed

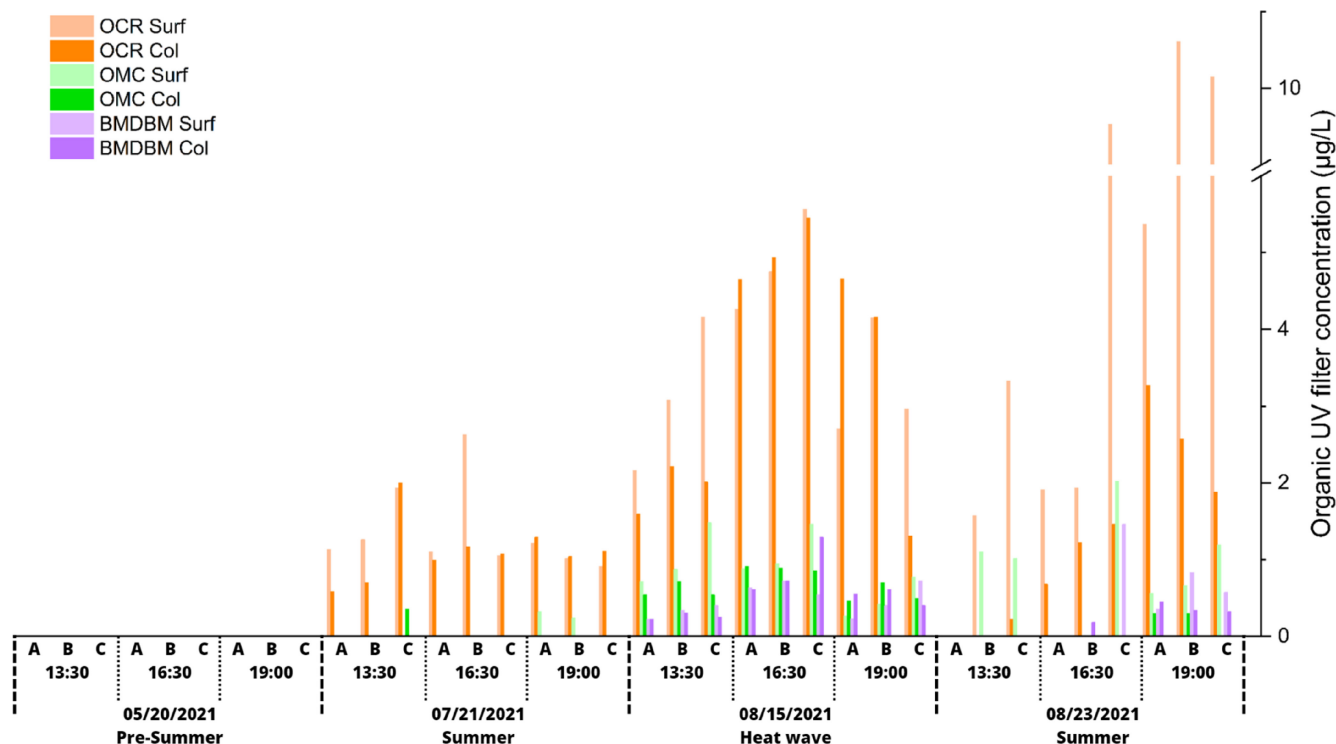


FIGURE 3 Concentrations of organic UV filters in water from the top surface layer, and from the bulk column. The triplicate samples A, B and C are presented distinctly as a function of the sampling period.

but also at the day scale. Water sampling achieved three times per day, at 13:30, 16:30 and 19:00 for organic UV filters enables us to observe a general trend of their concentration during summer days. It is characterized by a lower level at the beginning of the afternoon, certainly resulting from the night-time recovery, and a maximum value at 16:30 and 19:00 during peak attendance. This pattern is observed for the three studied organic UV filters, suggesting a relatively short remaining time of these molecules in the local environment studied. Data presented in Figure 3 also reveal a certain heterogeneity between the measurement triplicates taken at the same date and time. This is more pronounced when the concentrations measured are high. For example, the lower values measured on July 21st appear more reproducible than those taken on August 15th or August 23rd.

The triplicate heterogeneity is reported in Figure 4 in terms of the standard deviation of the triplicate samples as a function of the mean concentration value of the triplicate. A positive relation appears particularly for the BMDBM and OCR patterns, with standard deviation ranging from <0.01 to $1 \mu\text{g/L}$ for the lowest and the highest UV filter concentrations, respectively. The best reproducibility among triplicates was obtained at the lowest concentrations measured. This corresponds to values just above the respective LOD (Table S2), where the accuracy could be expected lower. Here, the counter-intuitive trend observed suggests that the large

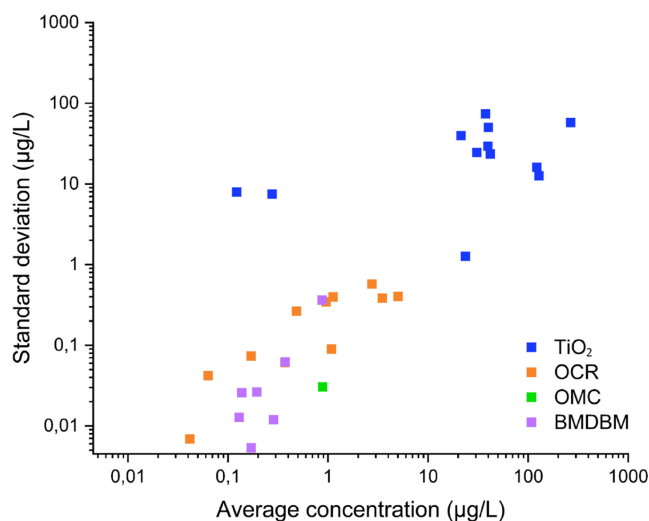


FIGURE 4 Standard deviations of the UV filter concentrations for the triplicate measurements in the water column, as a function of the mean value of the triplicate. Data from all sampling times, 2020–2021.

variation obtained for some replicates was not due to any analytical limit of quantification, but to some actual heterogeneity among the sample triplicates. As the triplicates were sampled at three different points of the studied beach area, taken at a constant distance from the shoreline and distant of 10 m from each other, it is

thus reasonable to conclude that the large variability obtained at high UV filter concentration is mainly due to the horizontal heterogeneity of the UV filter distribution in water, recently released from the bathers. This raises the need for sample replication on field, particularly in the bathing area in the context of UV filter analysis. As for the TiO₂ UV filters, the standard deviations obtained here are 1000× greater than the values for organic UV filters. This could likely be due to the particulate nature of the TiO₂ and the variability of its coating used, which together imply fate scenarios variable and different from that of the organic molecules, mainly driven by kinetics of dispersion, (hetero)aggregation or sedimentation.

UV filter accumulation in sediments and mussels

Table 3 summarizes the concentrations of TiO₂ equivalent found in the sediments in 2020 and 2021 and in the mussels in 2020. For sediment, there is no evident evolution with time neither at the seasonal scale, nor at the scale of two consecutive days. We hypothesize that the natural Ti background in the sediment is not constant, likely depending on submarine flow streams and continental inputs. For this reason as well, no geogenic proxy based on trace element ratio, like Ti/Nb or Ti/V, could successfully be used.

From the mussel analysis, no logical trend could be put in evidence here. Since the summer value is the lowest of the three periods studied, it seems that no accumulation linked with the tourist season could be highlighted. Such a result could be due to the fact that mussels were not efficiently exposed to the substances released from the recreational area or do not bioaccumulate TiO₂ from suncare

TABLE 3 TiO₂ concentrations found in sediments 2020–2021 and mussels 2020.

Compartments	Date	Time	TiO ₂ (µg/g) ^a
Sediments	06/23/2020	16:30	593.30
	08/19/2020	16:30	422.10
	10/28/2020	16:30	134.25
	05/20/2021	16:00	778.56
	05/21/2021	11:00	455.33
	08/23/2021	16:00	564.81
	08/24/2021	11:00	383.17
Mussels	06/23/2020	16:30	57.25
	08/19/2020	16:30	22.23
	10/23/2020	16:30	103.25

^aData refer to the sample dry weight.

product. In addition, a local Ti background in mussel tissues appears here levelling at few tens of µg/g dry weight, which could likely hide any lower contribution of the UV filters.

CONCLUDING REMARKS

In the present work, a field campaign was realized on the beach of Palavas-les-Flots (Mediterranean Sea, France), that was aimed at measuring the amounts of UV filters released from the beachgoers' skin to the bathing water. Multiple factors suspected of playing a determining role in such release were explored.

Parameters shaping the UV filter pattern in seawater

At the season time scale followed over two consecutive years, the summer periods, characterized by warm temperatures in the air and in water, were associated to peak attendance on the beach together with peak levels of UV filter concentration in the bathing water. The effect of a heat wave was also explored within this period. The extremely high water and air temperatures characterizing such short event appeared associated with the highest levels of beach attendance and of UV filter concentration ever recorded over the campaign. These results evidence the direct link between the UV filter pollution in coastal seawater and its recreational origin favoured during the warm season. Moreover, it suggests that such effect might become more and more pronounced in a close future with the expected multiplication of extreme meteorological events.

The time evolution of UV filter concentration in seawater was also studied at the day scale (for organic UV filters only), confirming that the maximum concentration measured generally coincides with the peak attendance on the beach, i.e. when sampled in the middle to end of the afternoon. This instantaneous relation between recreational attendance and UV filter pollution can be related to the fate of these substances in seawater. The main physical and chemical characteristics of the UV filters enabled us to explain the contrasted fates measured between the four candidates studied here. As a mineral UV filter, the fate of TiO₂ from the consumer's skin to the bathing water is driven by specific factors that include a particulate state with negligible solubility [40], a variable nature and lifetime of the surface coating, and a likely (hetero)aggregation. This resulted in the highest concentrations measured in seawater, as compared to its organic counterparts. The three organic UV filters studied here followed also some

specific fates. Of note, their possible vertical fate from the water phase to the sediment, that could be typically relevant for the most lipophilic molecules was not studied here. Nevertheless, their relative distribution between the top surface layer and the water column could be mainly explained by their hydrophilic or lipophilic features or by their molecule lifetime in the environment. OCR, characterized by the longest lifetime and the highest K_{ow}, was logically found at the highest concentrations in water, and more particularly concentrated floating in the top surface layer. To the opposite, BMDBM being most easily dissolved in water and degraded, was measured at the lowest concentrations and more distributed in depth. Finally, OMC displayed an insoluble feature coupled with a shorter lifetime than OCR, which likely resulted to some concentration levels in between OCR and BMDBM. It is worthwhile noting here that, despite its determining role in term of environmental exposure, a large lack of knowledge remains regarding the fate of synthetic organic UV filters in marine system. Indeed, very few data exist, to our knowledge, on the molecule degradation or transformation as a function of the environment characteristics encountered, such as water salinity, pH, temperature or light [19,36,41–43].

The non-homogeneous horizontal distribution of UV filters in the bathing water is an additional key parameter that came out of this work. The short distance, or the short time, covered between the point of release (bather) and the sampling point, makes it necessary to replicate the sampling at least in three different points, in order to average the pattern measured, because contrasted values are generally measured locally, especially during beach attendance.

Regarding the UV filter vertical distribution, our results confirmed the necessity of sampling the top surface layer of water as a distinct compartment from the water column, where the hydrophobic byproducts of the sunscreen are expected more concentrated, including some UV filters. Nevertheless, sampling such very thin layer can remain somehow challenging, particularly in the presence of waves. Neither the bottle sampling nor the polypropylene sorbent sheet used in this work appeared ideal for this purpose, and a plastic plate as used in Labille 2020 remains our first recommendation. Moreover, the sediment compartment was not analysed here in terms of the organic UV filter concentrations, but it may constitute a relevant sink for the most lipophilic substances. It is recommended that future works not only focus on the water phase but also on the sediment layer at the same place and time. This was studied here only for TiO₂. But no evident trend could however be recorded, certainly due to the major contribution of geogenic Ti element occurring in the marine sediment.

Mussels living on rocks close to the studied beach were also sampled in this work, for UV filter analysis, as they might have constituted relevant sentinels for UV filter bioaccumulation. Nevertheless, no logical trend could be evidenced following this approach, which questions on how to appropriately address this issue on the field. The mussels harvested here may not be exposed to the UV filter released in the bathing area, if water streamlines do not connect them to the bathers. An alternative approach for this purpose could consist in encaging mussels in a location directly facing the bathing zone, for example just beyond its limit.

Biological implications of UV filters in seawater

The environmental concentrations measured in this work can be discussed in terms of the implications that could be expected for the marine organisms living close to a bathing zone. Of note, the concentrations reported here are for the total water fractions sampled, as no filtration of the sample was processed prior to analyses. Thus, they do not reflect exactly the amounts of UV filter susceptible of being bioaccumulated by the local organisms, because a certain fraction of this total concentration may be associated with some particulate material that could alter the UV filter bioavailability.

Considering that exposure to contaminant is the first process leading to ecotoxicity, studies were already conducted in order to evaluate how marine mobiles and also sessile organisms can avoid UV filter exposure. These few studies [10,44,45], conducted in several taxa (Acoelomorph *Convolutriloba macropyga*, Actinopterygii *Sparus aurata*, Malacostraca *Palaemon varians*, respectively), showed that avoidance behaviour was not induced by minerals or organic UV filters – or was induced when concentrations were superior to 1 mg/L, which is higher than the environmental concentrations found in our study. These results suggest that marine organisms would not avoid UV filters at in situ concentrations and could therefore be exposed and subsequently incorporate these contaminants. Nevertheless, sedimentation or flotation tendency of some UV filter toward the sediment or top surface layer of water respectively, also constitutes a specific route of exposure, for which no or few data exist to our knowledge. Future ecotoxicological studies of UV filters should also take in consideration the habitat depth of the studied species as it determines the probability of exposure to the floating substance.

Regarding the incorporation process of organic UV filters, the most lipophilic molecules, such as OCR and OMC studied here and characterized by a log K_{ow} greater

than 4, are more likely bioavailable within a multitude of marine organisms: corals, [12], bivalves [46], fish [47], marine mammals [17]. Biomagnification, a cumulative increase as one progresses in the trophic chain [48], or maternal transfer processes has been evidenced on Franciscana dolphins with the detection of both UV filters in mother and foetus tissues [49]. However, environmental monitoring data provide only limited information on the bioaccumulation or magnification potential of the UV filters, as only few investigations were made in biota and water in parallel and the UV filters' concentrations vary by several orders of magnitude during seasons. Based on the determined fish bioconcentration factor data, obtained according to the criteria as laid down by ECHA 2017, OCR and OMC have been reported not bioaccumulative nor biomagnified through dietary exposure in fish [19,36]. Unlike lipophilic contaminants that accumulate in aquatic organisms, TiO_2 bioconcentration is controversial since differential bioaccumulation was reported between organs. For example, in crucian carp collected on field likely polluted with nano- TiO_2 , it was found more concentrated in fish muscle than in skin, gut and gills [50], suggesting a possible filtration effect of the particles or aggregates that limit their penetration in some tissues. However, it is our recommendation that not only the core nature of the mineral UV filter must be considered but also its surface coating, as this strongly influences the environmental fate and the likeliness of internalization of the particle [51].

Following incorporation, organic UV filters might have deleterious effects on organisms. Regarding most of the organic UV filters, authors reported LC_{50} in marine organisms (exposed during 48 or 96 h) close to 1 mg/L or higher, e.g. ref. [48,52,53]. These values are at least 100 times superior to the concentration values measured in situ in our study ($<10 \mu\text{g/L}$), and above the maximum water solubility for at least OCR and OMC [19,36]. This suggests that lethal acute toxicity would not occur in situ and that, consequently biological implications should consider the sub-lethal toxicity. Some biological markers of ecological significance (e.g. markers related to growth, reproduction, and energetic) are of interest since their modulation could reflect potential alteration at higher levels of biological organization such as the population or the community [54]. Among all biological functions, organic UV filters have been shown to particularly impact the reproduction – reviewed in ref. [55]. However, an overview of the literature on the topic showed that investigations were more particularly conducted in freshwater organisms and/or with high levels of concentrations [55]. Among the few studies conducted in marine organisms or with relevant environmental concentrations, concerns arise regarding

OMC and BMDBM that were measured at a maximum of $2.02 \mu\text{g/L}$ in our study. Indeed, at similar levels of concentration (1 and $10 \mu\text{g/L}$ during in vitro exposures) Bordalo et al. [18] showed that exposure to BMDBM induced a decrease in mussel sperm viability. As for OCR, it is certainly the most problematic of the UV filters studied here according to literature, as chronic exposure studies came to the conclusion that it is very toxic to aquatic organisms with long-lasting effects. Indeed, in a 28 days exposure study with the fish *Oryzias latipes*, a decrease of fertility was observed at $5 \mu\text{g/L}$ OCR [18], and in a 21 days exposure study of *Daphnia* (note: a freshwater species), a clear concentration response on daphnid reproduction revealed a no-effect concentration of $2.66 \mu\text{g/L}$ [36]. It is worthwhile noting that such OCR concentrations were surpassed several times during summer season in the bathing water studied here.

Regarding mineral UV filters, very few studies estimated, in marine organisms, the lethal concentration of these compounds; on the other hand, sub-lethal toxicity has already been evaluated in several taxa [56–58] and can consequently give an overview of mineral UV filters' biological impact. For example, at environmental concentrations, some effects of the TiO_2 UV filter were reported upon skeletal growth of sea urchin embryos [59]. Nevertheless, here again, the nature and lifetime of the surface coating generally used in mineral UV filters, play determining roles on the biological responses. In a worst-case scenario, the rapid coating degradation may switch the UV filter feature from a biocompatible surface chemistry to a generator of reactive oxygen species [60,61].

Finally, the adverse effects of sunscreens upon marine organisms could not be solely attributed to the UV filters but also to the combined action of multiple components used in the product and that may alter together its overall impact. For this reason, the entire sunscreen formulation must be considered in any approach to design a safer product that minimizes the environmental impacts along its lifecycle [29]. Furthermore, even as we do our best to reach it, zero risk does not exist, and the environmental footprint of sunscreen must be put in perspective with the many additional anthropogenic threats to the coastal environment. This includes notably the release of effluents from domestic, industrial, urban or agricultural origin, that may carry pollutants and nutrients, which altogether tend to alter the coastal ecosystem health.

ACKNOWLEDGEMENTS

The authors acknowledge the projects ANR-18-CE34-0012 CUTE and ANSES-21-EST-126 FILTRE-UV for funding this research.

CONFLICT OF INTEREST STATEMENT

The authors declare no conflict of interest.

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SUPPORTING INFORMATION

Additional supporting information can be found online in the Supporting Information section at the end of this article.

How to cite this article: Thallinger D, Labille J, Milinkovitch T, Boudenne J-L, Loosli F, Slomberg D, et al. UV filter occurrence in beach water of the Mediterranean coast – A field survey over 2 years in Palavas-les-Flots, France. *Int J Cosmet Sci.* 2023;45(Suppl. 1):67–83. <https://doi.org/10.1111/ics.12904>