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REPORT

Photochemical response of the scleractinian coral *Stylophora pistillata* to some sunscreen ingredients

Jean-Pierre Fel[1] · Catherine Lacherez[1] · Alaa Bensetra[1] · Sakina Mezzache[1] · Eric Béraud[2] · Marc Léonard[1] · Denis Allemand[2] · Christine Ferrier-Pagès[2]

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Abstract Ultraviolet (UV) filters and preservatives, which are common constituents of sunscreens and other cosmetics, are reported as a threat for coastal coral reef ecosystems; however, few studies have assessed the effects of these compounds on coral health. This study presents the chronic effects (of measured, long-term and low concentrations) of some preservatives (ethylparaben, butylparaben), mineral UV filter (zinc oxide, ZnO) and organic UV filters (terephthalylidene dicamphor sulfonic acid, drometrizole trisiloxane, ethylhexyltriazone, butylmethoxydibenzoylmethane and 2-ethylhexyl 2-cyano-3,3-diphenylacrylate) on the maximal photosynthetic efficiency (F_v/F_m) of the symbionts associated with the scleractinian coral *Stylophora pistillata*. It first shows that for many organic filters, measured concentrations were significantly lower than nominal concentrations, due to the lipophilic nature of the compounds. In addition, the F_v/F_m was more sensitive to ZnO than all other sunscreen ingredients, with exposure to 90 µg L^{-1} ZnO for 35 d, reducing F_v/F_m by 38% compared with controls. The other UV filters tested showed no adverse effect on coral symbionts or animal tissue up to the concentration corresponding to their water solubility limit (and even above). Similarly, no adverse effect was observed in our conditions with the preservative ethylparaben, but the preservative butylparaben decreased the F_v/F_m by 25% at the highest concentration of 100 µg L^{-1}. None of the sunscreen ingredients were as toxic to corals as the reference pollutants tributyltin, diuron and monuron, which significantly inhibited F_v/F_m at 10, 1 and 0.1 µg L^{-1}, respectively. Overall, this study highlights the need to improve our knowledge on the in situ concentrations of UV filters and preservatives as well as their individual and combined effects on corals.

Keywords UV filters · Preservatives · Herbicides · Coral · Photosynthetic efficiency

Introduction

Although they cover less than 0.1% of the earth's surface, coral reefs are the most biodiverse marine ecosystems in the world. This ecosystem is based on the symbiotic relationship between corals and dinoflagellates of the genus *Symbiodiniaceae*. Symbionts supply their hosts with photosynthetic products, which cover most of their energetic needs and enable them to thrive in oligotrophic environments. Today, coral reefs are facing severe threats that have already led to their degradation in many places, and to coral bleaching. Bleaching corresponds to the breakdown of the coral–dinoflagellate symbiosis, the subsequent loss of symbionts followed by nutrient starvation (Hoegh-Guldberg 1999). At the global scale, rising seawater temperature has now been recognized as one of the most serious causes of coral bleaching (Hoegh-Guldberg et al. 2017; Hughes et al. 2017). At the local scale, the top list of stressors includes overfishing, sedimentation from poor land-use practices and pollution from sewage and

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✉ Christine Ferrier-Pagès
ferrier@centrescientifique.mc

[1] L'Oréal Research and Innovation, Aulnay-sous-Bois, France

[2] Centre Scientifique de Monaco, 8 Quai Antoine Ier, 98000 Monaco, Monaco

agriculture, which introduces into the reefs huge amounts of nitrate, phosphate, herbicides and pesticides (Kroon et al. 2012; Duprey et al. 2016). On some coastal reefs, cosmetic products (mainly sunscreens containing both UV filters and preservatives) released in the water by swimmers have been reported to generate an additional stress to the benthic communities (Danovaro et al. 2008; Downs et al. 2014; McCoshum et al. 2016). Although it is likely that only a small percentage of reef corals, mainly those located in very shallow coastal environments subject to intense tourism and urbanization, are exposed to these products (see Wood report 2018), sunscreen contribution to coral bleaching has recently attracted attention from the media. Preservatives used in cosmetics (including sunscreens) such as parabens are continuously released at high levels (up to 30 μg L^{-1} and sometimes mg L^{-1}) into urban and hospital wastewaters (Aziza et al. 2011; Haman et al. 2015), while the reported concentrations of UV filters associated with sunscreens in marine waters are in the range of 1–100 ng L^{-1} (Langford and Thomas 2008; Tashiro and Kameda 2013; Bargar et al. 2015; Downs et al. 2016; Ma et al. 2016; Sang and Leung 2016; Sharifan et al. 2016) with maxima reaching concentrations of up to 10 μg L^{-1}. In addition, lipophilic organic UV filters may accumulate in marine sediments, where concentrations of hundreds to thousands ng g^{-1} dry weight have been measured in some locations (Amine et al. 2012; Kim and Choi 2014).

The impact of agriculture pollution, i.e., pesticides and herbicides, on corals has been well studied in laboratory experiments and is the subject of several reviews (i.e., Haynes and Johnson 2000; Cooper et al. 2009; Forbes et al. 2016; Lewis et al. 2016). However, with the exception of few studies (i.e., Cantin et al. 2007), most experiments were performed with relatively high concentrations of chemicals, during short-term exposure time (acute effect, Owen et al. 2002; Jones 2005; Negri et al. 2005; Markey et al. 2007); therefore, the chronic effects of these pollutants (in situ seawater concentrations, long-term exposure) remain unclear. Few studies have also been performed on UV filters used in sunscreens (Danovaro et al. 2008; Downs et al. 2014; 2016; Tsui et al. 2017; Corinaldesi et al. 2018) and one study only on preservatives such as butylparaben (Danovaro et al. 2008). They concluded that organic filters can induce coral bleaching and mortality via bacterial and viral contaminations of coral tissue (Danovaro et al. 2008; Downs et al. 2014). In contrast, there is a common public perception that mineral UV filters may be less harmful to corals, although a previous study has started to highlight the toxic effect of zinc oxide (Corinaldesi et al. 2018). Studies that test the chronic sublethal effects of a broad suite of sunscreen ingredients on coral are thus needed as this represents the scenario most likely to affect corals at the population level.

For this purpose, we tested the chronic effects of some UV filters and preservatives commonly found in sunscreens, on the photosynthetic efficiency of photosystem II (PSII) of symbionts of the scleractinian coral *Stylophora pistillata*, as an early marker for photosystem stress leading to bleaching (Jones et al. 1999). Herbicides monuron and diuron as well as the antifouling tributyltin are known to impact chlorophyll fluorescence (Jones 2005; Cantin et al. 2007) and were used as references. We studied both inorganic and organic UV filters, known to protect against UVB and UVA rays, including zinc oxide (ZnO), terephthalylidene dicamphor sulfonic acid (also called mexoryl SX), drometrizole trisiloxane (mexoryl XL), butylmethoxydibenzoylmethane (avobenzone), ethylhexyltriazone (uvinul T150) and 2-ethylhexyl 2-cyano-3, 3-diphenylacrylate (octocrylene). The first aim of the paper was to compare the chronic impacts of each of these common sunscreen ingredients on the coral's photosynthetic efficiency; the second aim was to confirm (Ralph et al. 2007, 2015) the utility of the Chl, a fluorescence technique as a rapid and effective tool for managers, regulators and industry to evaluate the numerous substances and mixtures released into sensitive coral reef environments.

Materials and methods

Biological material

Experiments were performed in the aquaria facilities of the CSM (Centre Scientifique de Monaco), using nubbins of the scleractinian coral *Stylophora pistillata* (Esper 1797; Scleractinia, Pocilloporidae) originating from the Gulf of Aqaba (Red Sea). A total of 240 nubbins (2–4 cm long) were prepared from ten genetically different mother colonies (identified with an electronic chip), by cutting their apical branches with a bone cutter (approximately 24 nubbins from each parent colony). Nubbins were attached to nylon wires and suspended in several open flow aquaria until tissue fully covered the skeleton, forming new colonies (ca. 3–4 weeks). Aquaria were continuously supplied with non-filtered seawater pumped from 50 m depth in front of the laboratory, at a flow rate of 20 L h^{-1}. Seawater temperature was kept constant at 25 °C ± 0.5 °C (in situ temperature in the Gulf of Eilat, Ezzat et al. 2017) using submersible resistance heaters connected to controllers (Visi-ThermH Deluxe, Aquarium Systems, France), and proper water mixing was ensured by submersible pumps. Light was provided by 400 W hydrargyrum quartz iodide (HQI) lamps (Philips, HPIT 400W, Distrilamp, Bossee,

France) at a photosynthetic photon flux density (PPFD) of 150 µmol photons m^{-2} s^{-1} (measured using a spherical quantum sensor; LiCor LI-193, Lincoln, NE, USA), with a 12:12 h light/dark cycle. Such irradiance, maintained during 12 h d^{-1}, corresponds to a daily dose of 18 mol photons m^{-2} d^{-1}, equivalent to the PPFD measured in reefs at 19 m depth (Edmunds et al. 2018), including Eilat reef (http://www.iuieilat.ac.il/Research/NMPMeteoData.aspx). It was chosen not to add further stress to the corals, as it would have been difficult to separate the effects of irradiance and toxicant on the coral response. Corals were fed once a week with *Artemia salina* (Linnaeus 1758) nauplii.

Toxicity tests

The preservatives, herbicides and UV filters, assessed in this experiment, are presented in Table 1, together with their chemical formula and water solubility. The maximal nominal concentration tested for each compound (Table 2) was chosen according to the lowest concentration for which an effect on the photosynthetic efficiency of the PSII was observed in preliminary assays performed over 1-week exposure. Corals were then exposed to these maximal nominal concentrations and lower ones over 5 weeks to assess a potential long-term effect. The preservatives and herbicides were tested at nominal concentrations ranging from 0.1 to 1000 µg L^{-1}, while the UV filters were tested at nominal concentrations, ranging from 10 to 5000 µg L^{-1}. In this study, water-soluble compounds were

Table 1 List of preservatives, herbicides and UV filters, tested in this experiment, together with their chemical formula and solubility in seawater. The values of water solubility are given according to the European Chemical Agency

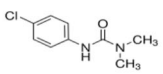
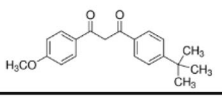
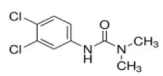
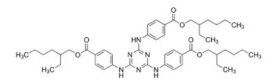
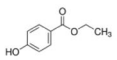
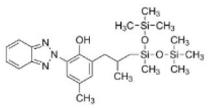
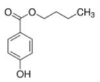
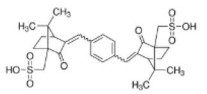
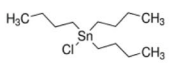
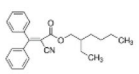
Name	Log Kow	Water solubility	CAS Number Formules	Name	Log Kow	Water solubility	CAS Number Formules
Monuron	1.79	240 mg L^{-1} 20°C	150-68-5 $ClC_6H_4NHCON(CH_3)_2$ 	Avobenzone	6.1	0.027 mg L^{1} 20°C	70356-09-1 $C_{20}H_{22}O_3$ 
Diuron	2.89	29 mg L^{-1} 20°C	330-54-1 $C_9H_{10}Cl_2N_2O$ 	Uvinul T150	7	0.006 mg L^{1} 25°C	88122-99-0  $C_{48}H_{66}N_6O_6$
Ethylparaben	1.81	885 mg L^{-1} 25°C	120-47-8  $C_9H_{10}O_3$	Mexoryl XL	> 6	<0.04 mg L^{-1} 20°C	155633-54-8  $C_{24}H_{39}N_3O_3Si_3$
Butylparaben	3.57	207 mg L^{-1} 20°C	94-26-8 $C_{11}H_{14}O_3$ 	Mexoryl SX	-1.8	6 x 10^5 mg L^{1}	92761-26-7  $C_{28}H_{34}O_8S_2$
TBT	2.2	0.076 mg L^{-1} 20°C	1461-22-9  $[CH_3(CH_2)_3]_3SnCl$	ZnO (Zn^{2+})	ND	2.9 mg L^{-1} 20°C	1314-13-2
				Octocrylene	6.1	0.1 mg L^{-1} 20°C	6197-30-4 $C_{24}H_{27}NO_2$ 

Table 2 Nominal and measured concentrations of the different compounds used in this study

Compounds	Nominal concentration (μg L^{-1})	Measured concentration (μg L^{-1})	Number of measurements
Monuron	0.1	< LOQ	–
	1.0	1.1 (± 0.2)	19
	10	11.1 (± 2)	12
Diuron	0.1	< LOQ	–
	1.0	1.1 (± 0.3)	19
	10	11.1 (± 2)	3
Octocrylene	100	74 (± 16)	12
	1000	519 (± 94)	12
	5000	1318 (± 212)	12
Avobenzone	100	< LOQ	–
	1000	87 (± 20)	9
	5000	516 (± 140)	8
Uvinul T150	100	< LOQ	–
	1000	< LOQ	–
	5000	177 (± 62)	8
Mexoryl XL	10	4.9 (± 0.4)	19
	100	54 (± 8)	19
	1000	480 (± 77)	16
	5000	305 (± 33)	16
Mexoryl SX	10	10 (± 0.5)	20
	100	99.5 (± 4.5)	16
	1000	678 (± 49)	20
	5000	5025 (± 777)	20
ZnO	10	24 (± 6)	12
	100	94 (± 4)	8
	1000	864 (± 70)	3

*Confidence interval level of 95%. Limit of quantification (LOQ). Ethylparaben and butylparaben are highly water soluble, and we assumed their actual concentrations would be similar to nominal

pre-diluted in seawater, while lipophilic compounds (log Kow > 6) were pre-diluted in methanol (MeOH) (67 μL L^{-1}), to facilitate the preparation of the solutions introduced in the aquaria and possibly increase the amount of compound solubilized in seawater (OCDE guidelines for aquatic toxicity tests).

Toxicity tests were conducted in several sets of six one-piece glass aquaria (15 L), filled with non-filtered seawater and containing each 3 nubbins (from 3 different colonies) of *S. pistillata*. Aquaria were maintained in the same conditions as the culture aquaria (25 °C, 150 μmol photons m^{-2} s^{-1} and a 12:12 h light/dark cycle), and water was continuously stirred with a pump (flow of 210 L h^{-1}, current speed of 4 mL min^{-1}). Three aquaria were dedicated to the analytical control of each compound concentration, while three aquaria were kept as controls (seawater or seawater amended with MeOH when compounds were diluted into MeOH). Nubbins were acclimated in the tanks for 30 min, until polyps were completely expanded. Tested compounds were dissolved in 100 mL seawater prior to addition (except for the control). This medium was renewed once a week for 5 weeks in total. Nubbins were fed once a week, with fresh artemia infusion, the night before the water renewal.

Dark-adapted maximum quantum yield of PSII (F_v/F_m) was then measured once a week, for 5 weeks, using a diving PAM fluorometer (Walz), according to Govindjee (1995) and Schreiber (2004). The basal level of fluorescence (F_0) was determined by applying a pulse of light after nubbins were kept for 10 min in the dark. The maximum fluorescence (F_m) was measured by applying a saturating pulse of actinic light (> 3500 μmol photon m^{-2} s^{-1}, peak wavelength 466 nm, full width half maximum 22 nm). The difference between F_m and F_0 is the variable fluorescence F_v. Chlorophyll fluorescence, especially the F_v/F_m, has been used to predict and monitor coral bleaching over short timescales (hours to days). Reduction in F_v/F_m is actually linked to damage in PSII and is thus a

precursor of bleaching (Hoegh-Guldberg and Jones 1999). In parallel, the apparent animal health was assessed by visual observation. When animals died (observed through tissue sloughing and/or total loss), no F_v/F_m measurement was possible and measurements were stopped.

Data analyses

Linear regressions were used to fit the photosynthetic efficiency (F_v/F_m) versus incubation time. In order to compare the final F_v/F_m values reached after five-week incubation in the aquaria and to use them as percent toxicity parameter (Ralph et al. 2007), we have taken into account (1) the decreasing tendency in some of the control F_v/F_m values and (2) the differences in the initial F_v/F_m values of the different treatments/samples. We have thus used the following formula:

$$\left[\left[\left(F_v/F_{m(\text{sample})}\right)/\left(F_v/F_{m(\text{control})}\right)\right]_T \times 100\right] / \left[\left(F_v/F_{m(\text{sample})}\right)/\left(F_v/F_{m(\text{control})}\right)\right]_{\text{Initial}}$$

Those values were used to compare the variation: (1) between coral nubbins maintained in the same treatment; (2) between nubbins maintained in control seawater and control seawater amended with 67 µL methanol; (3) between coral nubbins exposed to a toxic compound and maintained under the corresponding control conditions (with seawater or seawater + methanol). To that end, a *T* test was performed with the StatGraphics software (Dynacentrix, Neuilly-sur-Seine, France). In addition, the time needed to reach a yield equal to 50% of the initial F_v/F_m value (noted $T_{y=50\%}$) was calculated using the equation of the linear regressions, as an indication of significant damages on the PSII, when corals are submitted to an environmental stress. This low value of the quantum yield approximately corresponds to the minimal threshold, allowing the recovery of the PSII efficiency. Under this value, in vitro observations showed that colonies of *Stylophora pistillata* significantly decreased their calcification rate and then bleached and died (Moya et al. 2008).

Analytical measurements

Sample extraction

Water samples were taken 2 h after the introduction of the compounds in seawater and were not filtrated. Organic compounds were extracted and concentrated by 10–100 times from seawater before analysis. For monuron, diuron, mexoryl SX and mexoryl XL, a solid-phase extraction (SPE) cartridge (Oasis HLB, Waters) was used by adding ion pair (triethylamine, TEA) according to Balinova (1996). For each seawater sample, 1% of TEA was added. For mexoryl XL (MXL), during the SPE stage, the seawater was acidified with formic acid (pH = 2.5) in order to improve the extraction yields. The volume of percolation through the cartridge varied depending on the nominal concentration of the compounds (between 8 mL and 100 mL for the highest and lowest concentration tested). The cartridge compounds were eluted with 10 mL methanol. The eluate was then evaporated with nitrogen using a turbovap for 20 min, at 40 °C, and re-dissolved in a small volume of methanol (800 µL to 1 mL). For avobenzone, octocrylene and uvinul T150, the same SPE cartridge was used, but the ion pair mode was replaced by addition of 0.1% formic acid, to concentrate the compounds. The same protocol as described above was then used.

HPLC method

Except for the analysis of zinc oxide, which was done by ICP-MS (by subcontractor Intertek), the other compounds were analyzed with UPLC/UV (Waters Acquity system), using HPLC-grade reagents. Standard stock solutions of each compound (1000 µg mL^{-1}) were prepared in methanol or mix solvents (except for mexoryl SX soluble in water) and then diluted daily for the analysis. The vessel was washed with methanol and water before usage.

The separation was carried out on reverse-phase liquid chromatography with an Acquity BEH Phenyl column (2.1 × 30 mm 1.7 µm). The temperature from oven to column was thermostated to 50 °C, and the injection volume was 10 µL. The flow rate of the mobile phase was 0.6 mL min^{-1}. The mobile phase was composed of 500 mL water containing 3 mL of ammonium acetate at 7 M (A) and 500 mL methanol also containing 3 mL of 7 M ammonium acetate (B). The elution was carried out in gradient mode using an elution gradient, starting with 90% of A and 10% of B, and then B was increased to 100% in 2 min. Isocratic conditions were held for 3 min, and the system was set back to initial conditions within 2.5 min. The column was re-equilibrated for 2.5 min before the next injection. The detection was carried out by a diode array detector from 240 to 400 nm.

Results

The SPE-UPLC/UV analysis showed that measured concentrations of the water-soluble compounds, namely monuron, diuron, mexoryl SX and ZnO, were comparable to the nominal concentrations (Table 2). Ethylparaben and butylparaben are also highly water soluble (> 200 mg L^{-1}), and their actual concentrations were assumed to equal the nominal values. On the contrary, for mexoryl XL, octocrylene, avobenzone and uvinulT150,

measured concentrations were 2–22 times lower compared to the nominal concentrations, due to the lipophilic nature of the compounds (log Kow > 6). At the highest nominal concentrations tested (1000 and 5000 µg L^{-1}), the concentrations measured by SPE-UPLC/UV were sometimes higher than the water solubility limit values given in Table 1. This may be explained by the use of a solvent and the absence of filtration of the water samples to be analyzed. At these high nominal concentrations, a non-solubilized fraction of the compounds is likely to be present in the water samples and measured in addition to the solubilized fraction. This is in agreement with the large variation coefficients obtained at high nominal concentrations, leading to more heterogeneous samples. As a consequence, this method may overestimate the LOEC and NOEC values given in Table 4, when measured above the solubility limit. Nonetheless, from a practical standpoint, the presence of a non-solubilized fraction is likely to have contributed to maintain the solubilized fraction that was progressively adsorbing to the bottom and walls of the aquaria. In the following text for these compounds, the nominal and the measured concentrations (in brackets) will be both presented.

There was no significant difference in the F_v/F_m measured after 35 d between nubbins maintained in the same conditions (*T* tests, $p > 0.05$ for all conditions) or between nubbins maintained in control seawater and seawater amended with 67 µL L^{-1} methanol ($p > 0.05$). The coefficient of variation was less than 9% and 6%, respectively.

The evolution of the F_v/F_m during the 5-week incubation in control conditions (seawater or seawater + MeOH) and in the presence of chemicals is presented in Figs. 1a–f and 2a–e. All nubbins had F_v/F_m values around 0.6 at the beginning of the incubations, indicative of the good health of the PSII. F_v/F_m presented a maximal decrease of 15% in the control tanks after 5 weeks and never reached values below 0.5. These results suggest a tank effect (nutrient, water movement) on corals, but nevertheless, corals kept a maximal photosynthetic efficiency under our culture conditions for 35 d. Some compounds induced a significant drop in F_v/F_m below 0.2 followed by the death of the coral nubbins: avobenzone at the highest nominal concentration of 5000 µg L^{-1} (measured 520 µg L^{-1}) (Fig. 1a), ZnO at concentrations equal or above 1000 µg L^{-1} (Fig. 1e), diuron at 10 µg L^{-1} (Fig. 2a) and TBT at all concentrations (Fig. 2d). For these compounds, the F_v/F_m values measured after 5 weeks were thus significantly lower compared to the initial value or compared to the F_v/F_m of control corals (Table 3, Fig. 3a, b). In addition, we also observed a significant decrease in F_v/F_m for octocrylene at the highest concentration measured (1300 µg L^{-1}), avobenzone for measured concentrations above 87 µg L^{-1}, butylparaben at 100 µg L^{-1}, monuron at all concentrations and diuron at 1 µg L^{-1} (Table 3).

The time necessary to reach $T_{y=50\%}$ was considered as a good proxy for comparing the toxicity of each compound (Table 4, Fig. S1, S2), since this value indicates the loss of symbionts and/or their photosynthetic capacities and, hence, the onset of coral bleaching (Moya et al. 2008). This proxy is also in agreement with the LOEC and NOEC values (lowest and no observed effect concentration, respectively) determined in this study for each compound. Many treatments, in addition to controls, did not cause a decrease to $T_{y=50\%}$, even after linear extrapolation to 90 d (Table 4): ZnO at 24 µg L^{-1}, monuron at 0.1 and 1 µg L^{-1}, diuron at 0.1 µg L^{-1}, butylparaben at 10 µg L^{-1}, avobenzone at < 87 µg L^{-1} measured concentration, as well as all concentrations of mexoryl SX and XL, uvinul T150, octocrylene and ethylparaben. It should be noted, however, that some compounds like uvinul T150 and avobenzone showed very low measured concentrations compared to the nominal concentrations tested, suggesting that these products have been adsorbed on the aquaria glasses, or be transformed. This may partly explain their lack of effect. A decrease to $T_{y=50\%}$ after an estimated period of 50-d exposure to the toxic compound was observed for diuron at 1 µg L^{-1} and butylparaben at 100 µg L^{-1}. Finally, F_v/F_m reached $T_{y=50\%}$ in less than 35-d exposure for ZnO at 864 µg L^{-1} and all TBT concentrations tested. A similar effect was observed with diuron at 10 µg L^{-1} and avobenzone at the highest nominal concentration of 5000 µg L^{-1} (measured equal to 520 µg L^{-1}).

Discussion

The present study has tested the chronic effect of in situ-relevant concentrations of some organic and mineral UV filters, herbicides and paraben preservatives, on the photosynthetic efficiency of the PSII of coral symbionts. The lowest concentrations used in this study for UV filters and herbicides were in the same range as the maximal concentrations reported in seawater (Lewis et al. 2009; Tashiro and Kameda 2013; Du et al. 2014; Tsui et al. 2015). The main findings are that only the high concentrations of organic sunscreens affected F_v/F_m during chronic exposures and that they were less toxic than ZnO, herbicides and TBT.

The toxicological assays first show that the coral response to chemical exposure was concentration dependent, the highest decrease in the F_v/F_m corresponding to the highest concentration of chemicals. Among the UV filters explored in this study, ZnO induced the greatest damage on the symbiont's PSII photosynthetic activity at the lowest concentration tested. Exposure to 100 µg L^{-1} (90 µg L^{-1}

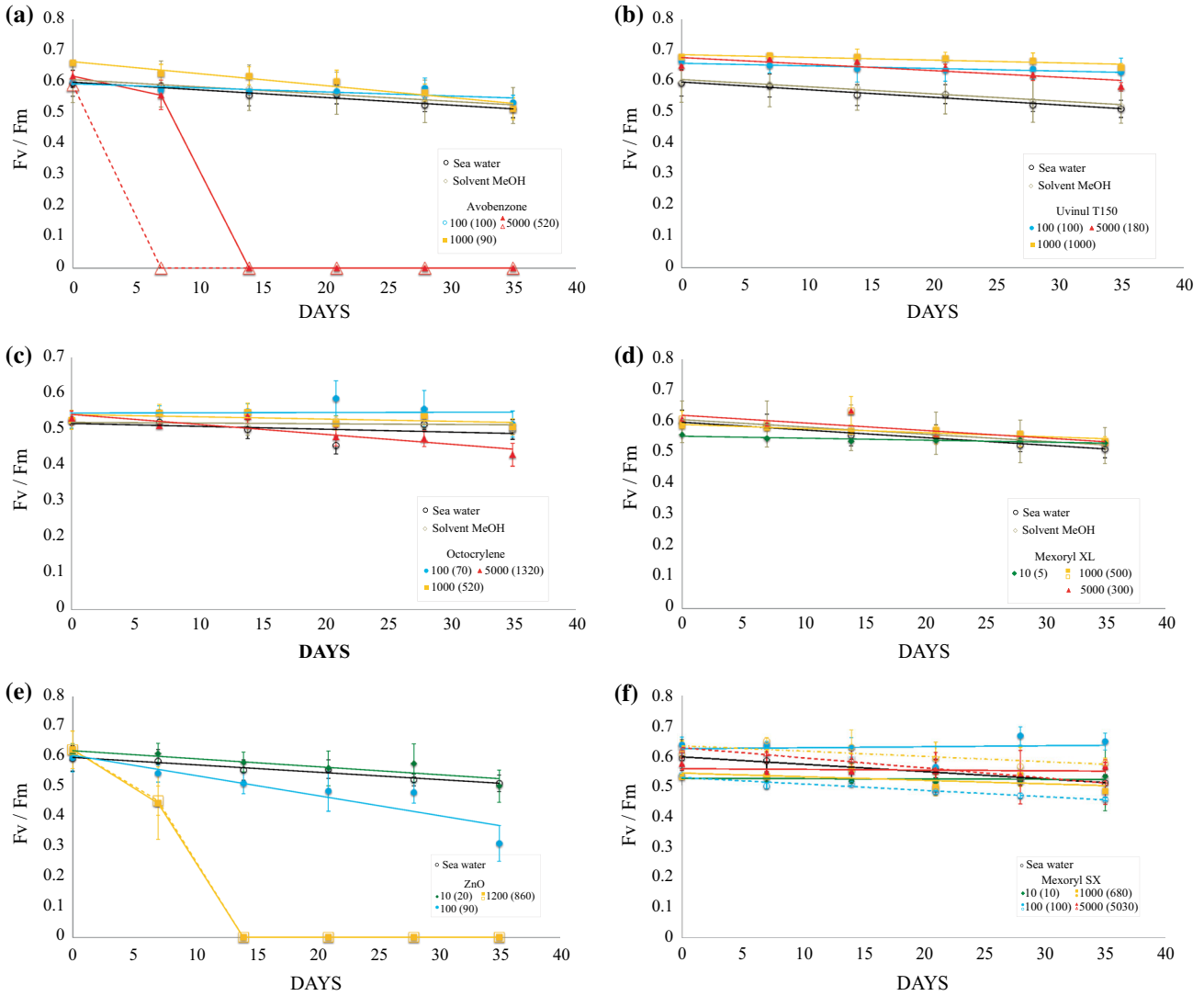


Fig. 1 Evolution of the maximal photosynthetic efficiency (F_v/F_m) of the corals maintained in the different concentrations of UV filters. Nominal and measured concentrations in the legend are in μg L^{-1}. Data represent mean and standard deviation of three nubbins. (–) means that no product can be measured in seawater

measured) ZnO for 35 d led to a significant decrease in the F_v/F_m down to a value of 0.30, which has been shown to induce coral bleaching and the loss of its photosynthetic capacities (Moya et al. 2008). The mechanisms by which ZnO nanoparticles can impact the health of living organisms can be mainly through the physical damage of direct contact, the effect of dissolved zinc ions and the oxidative stress induced by reactive oxygen species (ROS) (Hou et al. 2018). ZnO nanoparticles were indeed shown to induce oxidative stress in plants and algae (Suman et al. 2015). They can also attach to the coral's surface and mechanically disturb the physical state of the lipid membranes, as shown with acute stress on the coral *Seriatopora caliendrum* (Tang et al. 2017). Finally, they can release large quantities of zinc ions in seawater. Although zinc is an essential metal for living organisms at nanomolar concentrations, because it is a cofactor of more than 300 enzymes (Morel et al. 1994), it can rapidly become very toxic for aquatic organisms, from bacteria to vertebrates (Miao et al. 2005; Osmond and Mccall 2010; Wong et al. 2010; Manzo et al. 2013) including corals (Reichelt-Brushett and Harrison 1999; Corinaldesi et al. 2018). In particular, for photosynthetic organisms such as corals, it was shown that zinc impairs the flow of electrons in the photosynthetic chain, at the level of the secondary quinone electron acceptor (Mohanty et al. 1989). Zinc also enhances the growth of bacteria in seawater, leading to a disruption of the symbiosis in corals (Corinaldesi et al. 2018). The concentration at which dissolved zinc becomes toxic is species dependent. Fish are relatively resistant to zinc at all life stages (Mance 1987), while molluscs or bivalve larvae present a 2-d EC_{50} around 150 μg L^{-1} (Martin et al. 1981).

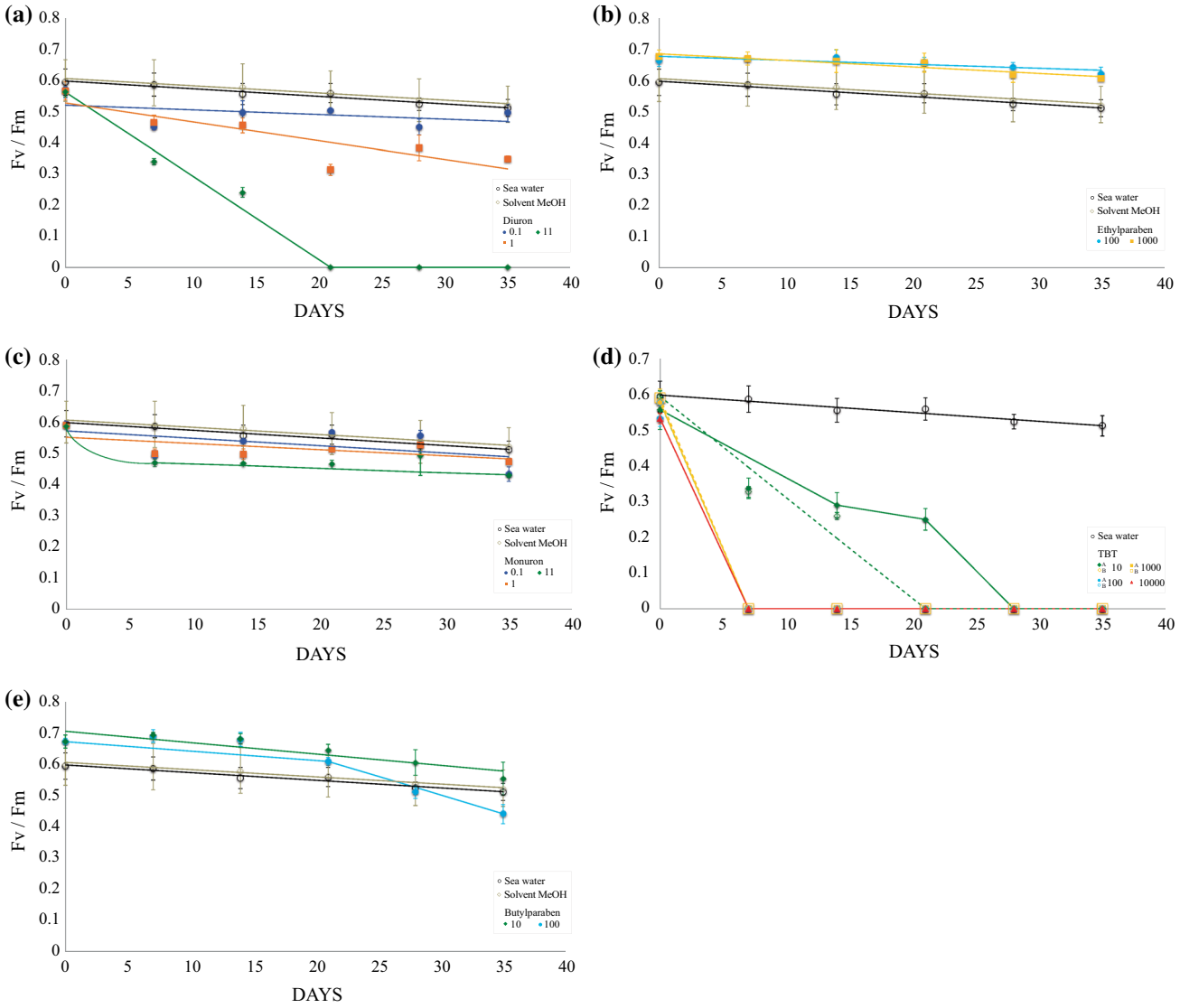


Fig. 2 Evolution of the maximal photosynthetic efficiency (F_v/F_m) of the corals maintained in the different concentrations of herbicides and TBT (tributyltin). Nominal and measured concentrations in the legend are in μg L^{-1}. Data represent mean and standard deviation of three nubbins

This study shows that ZnO has a similar toxicity for corals, with 38% inhibition at 100 μg L^{-1}.

Compared to ZnO, all organic UV filters tested in this study at low concentrations, relevant to in situ conditions, presented a much lower impact on the photosynthetic efficiency of the symbionts of *Stylophora pistillata*. The UV filters mexoryl XL, mexoryl SX and uvinul T150 showed no toxicity at all concentrations tested, even at nominal concentrations as high as 5000 μg L^{-1} (measured concentrations from 5025 to 177 μg L^{-1}, Table 2). The organic UV filter octocrylene did not impact the F_v/F_m after 5-week exposure to nominal concentrations below or equal to 5000 μg L^{-1} (measured 1318 μg L^{-1}) in agreement with previous measurements made with this chemical on the bleaching susceptibility of scleractinian corals (Danovaro et al. 2008). The reported measured concentrations of octocrylene in marine waters are several orders of magnitude below 5000 μg L^{-1} (Langford and Thomas 2008; Rodil et al. 2009; Tashiro and Kameda 2013) with maximal octocrylene concentration of 7.3 μg L^{-1} measured close to a crowded Norwegian beach (Langford and Thomas 2008). Avobenzone also induced a significant decrease in the F_v/F_m only at nominal concentrations above 1000 μg L^{-1} (measured 87 μg L^{-1}), which is well above in situ concentrations. The turbid solutions obtained at these high concentrations have likely generated physical effects from the non-solubilized fraction. Overall, the organic filters tested in this study have either no effect or have impacted *Symbiodinium* PSII at relatively high concentrations only.

Table 3 Results of the *t* tests used to compare the F_v/F_m measured after 5 weeks of exposure to the compounds

	Nominal concentration µg L^{-1}	Anova	
		F	*P* value
Octocrylene	100	1.60	> 0.05
	1000	0.38	> 0.05
	5000	24.30	0.008*
Avobenzone	100	0.23	> 0.05
	1000	10.08	0.025*
UvinulT150	100	2.52	> 0.05
	1000	153.52	> 0.05
	5000	1.60	> 0.05
Mexoryl XL	10	200.23	> 0.05
	1000	16.40	> 0.05
	1000	0.80	> 0.05
	5000	10.67	> 0.05
Mexoryl SX	10	319.23	> 0.05
	100	88.48	> 0.05
	100	1.95	> 0.05
	1000	2.80	> 0.05
	1000	2.32	> 0.05
	5000	18.55	> 0.05
	5000	2.08	> 0.05
Zn^{2+} (ZnO)	10	0.07	> 0.05
	100	29.36	0.003*
Monuron	0.1	51.33	0.002*
	1	33.92	0.004*
	10	138.87	0.001*
Diuron	0.1	0.01	> 0.05
	1	31,201	0.001*
Ethylparaben	100	5.69	> 0.05
	1000	1.50	> 0.05
Butylparaben	10	1.97	> 0.05
	100	49.66	0.001*

P values > 0.05 show that the F_v/F_m is not significantly lower than the F_v/F_m of the control (but can be superior to the control). *P* values < 0.05 show a significant impact of the compound tested compared to the control. For ZnO (1000 µg L^{-1}), diuron (10 µg L^{-1}), avobenzone (5000 µg L^{-1}) and all TBT concentrations, test could not be performed because corals died before the end of the experiment

The preservatives tested here, i.e., parabens (butyl and methylparaben), are extensively used in consumer goods such as sunscreens and are commonly contaminating surface water. We found that only butylparaben had an adverse impact on the PSII of coral symbionts at 100 µg L^{-1}, as previously observed during acute tests (Danovaro et al. 2008). Finally, and as expected, most concentrations of monuron, diuron and TBT induced a significant decrease in the F_v/F_m of the coral symbionts, as demonstrated in many previous studies on corals (Jones et al. 2003; Jones 2005; Negri et al. 2005). The effect of monuron and diuron on the F_v/F_m of coral symbionts was, however, milder than previously observed (Vandermeulen et al. 1972). However, the concentrations used in this study (0.1–10 µg L^{-1}) are well below the minimum inhibitory concentrations reported for algae and cyanobacteria (2–10 mg L^{-1}, Paterson and Wright 1988). These observations highlight the necessity to perform chronic experiments on the effect of chemicals on marine organisms.

Overall, results obtained in this study suggest that the organic UV filters tested are much less toxic for the PSII activity of coral symbionts than ZnO. These observations do not preclude any significant effect on other coral physiological parameters, in case contaminants are targeting for example the host rather than the symbionts. Therefore, mortality, which is an indicator of host stress, should be quantified in all experiments, in parallel with the PSII activity. In this experiment, we did not observe any host mortality following exposure to the chemicals, except for TBT, diuron, avobenzone and ZnO at the highest concentrations, which were, however, not relevant for in situ conditions. Two other acute stress studies, performed on the impact of the UV filters benzophenone-2 and benzophenone-3 on coral larvae (Downs et al. 2014, 2016), have shown structure alterations of the larvae when exposed less than 1 d at ca. 2.5 and 2.3 µg L^{-1}, respectively. Overall, these observations suggest that more studies should be performed at all developmental stages of corals, and on both host and symbionts, to have a broader view on the effect of UV filters and preservatives on coral health. The interactions between the different chemicals, which have not been investigated here, will also have to be taken into account in the future.

To date, there is also a lack of data detailing the fate and behavior of UV filters in seawater, to provide a realistic understanding of potential exposure levels and durations in the marine environment. Once released into the environment, these chemicals are subject to biotic and abiotic processes that contribute to their elimination and/or transformations. A large effort was made in this study to develop reliable analytical methods to determine the actual concentrations of each compound at different levels. These measurements are complex and time-consuming, and not all compounds at all concentrations could be determined in the frame of this study. Nevertheless, we observed that the measured concentrations of the hydrophilic compounds tested (ZnO, mexoryl SX) as well as the herbicides (monuron, diuron) were comparable to the nominal concentrations. On the contrary, only half, or less, of the hydrophobic/lipophilic compounds such as octocrylene and mexoryl XL were retrieved in seawater after 2 h. It is assumed that a fraction of these compounds may have

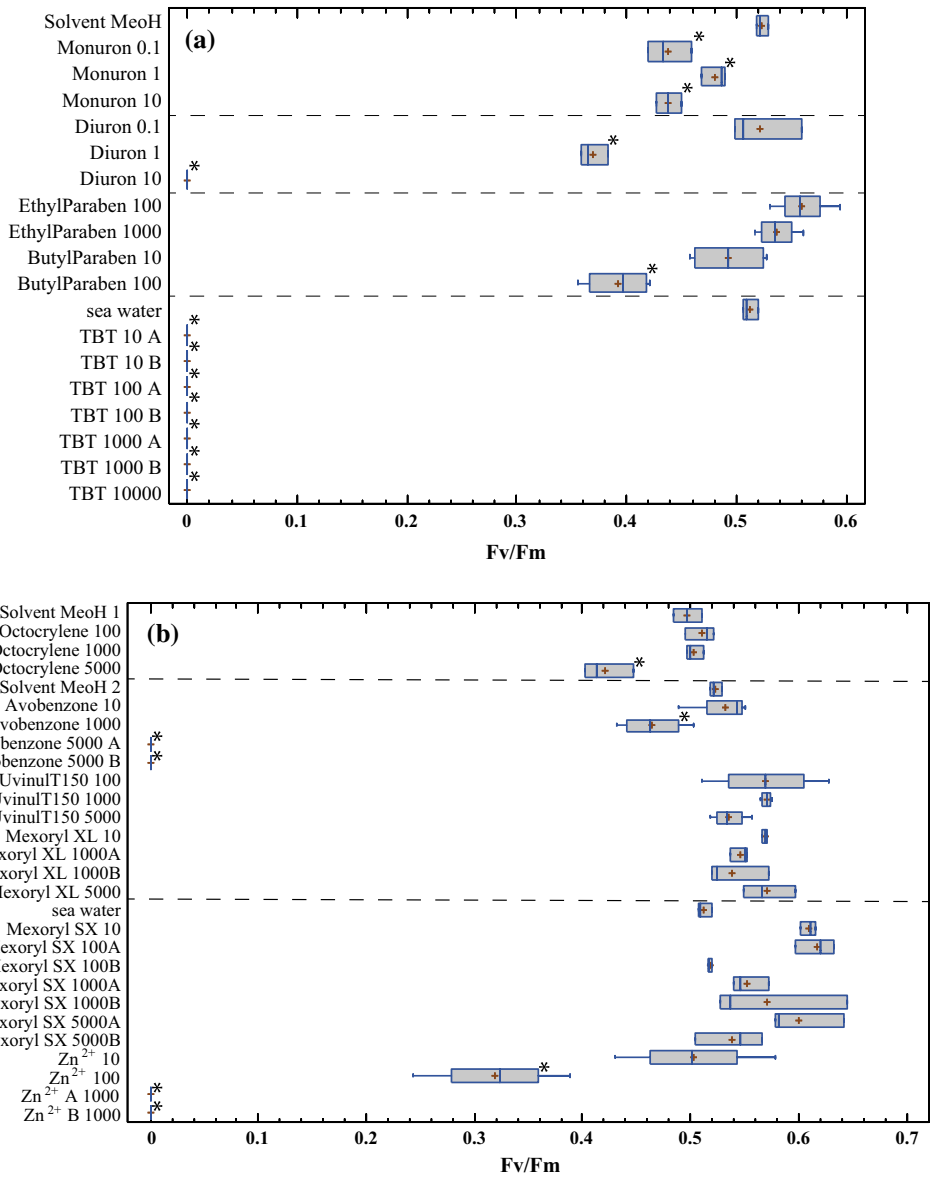


Fig. 3 Box plot of the effect of UV filters, herbicides and TBT on the corals. Data represent box plots, with median, lower and upper quartile of three nubbins

adsorbed on the aquaria walls or may have been taken up by the corals (Tsui et al. 2017), although this last hypothesis is unlikely considering that measurements were performed only 2 h after the introduction of the compounds in seawater. In the frame of this experiment, concentrations in the water remained high in comparison with commonly reported concentrations in natural marine waters. However, such adsorption of lipophilic compounds suggests that the determination of xenobiotic concentrations on reefs should be assessed both in the water column and in the sediment, where compounds can accumulate. Many organic UV filters are indeed generally hydrophobic, suggesting that they will associate with particulate organic matter in the environment. It would certainly be worth evaluating their fate and effect in sediments as for any lipophilic compounds released at significant amounts in the proximity of coral reefs.

In summary, our results indicate that several organic UV filters, at relevant seawater concentrations and taken individually, are not likely to cause a significant decrease in coral photosynthetic efficiency or coral bleaching. On the contrary, ZnO appeared as the most toxic compound. From a regulatory standpoint, ZnO is classified "Hazardous to the aquatic environment" according to the GHS criteria (United Nations Globally Harmonized System of Classification and Labelling of Chemicals 2011), the Hazard statements H400 (category acute 1: very toxic to aquatic life) and H410 (category chronic 1: very toxic to aquatic life with long lasting effects). ZnO is under complementary evaluation in the frame of the European Community rolling action plan (CoRAP), and since 2012, the Swedish

Table 4 Summary of the main results obtained

Treatment	Nominal (and measured) concentrations (μg L^{-1})	Changes in F_v/F_m after 35 d (% ± SD)	LOEC μg L^{-1}	NOEC μg L^{-1}	Time for $T_{y=50\%}$
Seawater		0		–	> 90
Seawater + solvent		0		–	> 90
Monuron	0.1 (–)	16 ± 4	0.1 (–)	< LOEC	> 90
	1 (1.1)	8 ± 2			> 90
	10 (11.1)	16 ± 2			89
Diuron	0.1 (–)	0.3 ± 6	1 (1.1)	0.1 (–)	> 90
	1 (1.1)	29 ± 2			41
	10 (11)	100			11
Ethylparaben	100	0	> 1000	1000	> 90
	1000	0			> 90
Butylparaben	10	6 ± 7	100	10	> 90
	100	25 ± 6			55
TBT	10	100	10	< LOEC	12.5
	100	100			3.5
	> 1000	100			4
Octocrylene	100 (74)	2 ± 3	5000 (1318)	1000 (519)	> 90
	1000 (519)	4 ± 2			> 90
	5000 (1318)	19 ± 5			> 90
Avobenzone	100 (–)	0	5000 (516)	1000 (87)	> 90
	1000 (87)	11 ± 6			> 90
	5000 (516)	100			6.5
Uvinul T150	100 (–)		–	5000 (177)	> 90
	1000 (–)		0		> 90
	5000 (177)		0		> 90
Mexoryl XL	10 (5)		–	5000 (305)	> 90
	100 (54)	6 ± 1			> 90
	1000 (480)	0			> 90
	5000 (305)	0			> 90
Mexoryl SX	10 (10)	0	–	5000 (5025)	> 90
	100 (100)	0			> 90
	1000 (678)	3 ± 3			> 90
	5000 (5025)	0			> 90
ZnO	10 (24)	2 ± 12	100 (94)	10 (24)	> 90
	100 (94)	38 ± 12			48
	1000 (864)	100			8

SD standard deviation, *LOEC* lowest observed effect concentration, *NOEC* no observed effect concentration, "–" no measurable concentration. Values under brackets are measured concentrations in seawater

authorities have banned the sale of paints containing ZnO (as antifouling agent) to protect marine life. Following recent studies, which reported that some organic UV filters were harmful for corals, inducing bleaching and viral development (Danovaro et al. 2008; Downs et al. 2014), it was suggested that mineral UV filters, such as ZnO, could replace these compounds. In fact, this mineral UV filter is frequently present at high concentration (> 20%) in certain sunscreens claimed to be "reef safe." This study, as well as two previous one (Tang et al. 2017; Corinaldesi et al. 2018), clearly shows that ZnO is not the most eco-friendly compound and the impact of both dissolved and nanoparticulate forms of ZnO should be thoroughly assessed on endangered coral reefs. Not surprisingly, other compounds already classified "Hazardous to the aquatic environment" according to GHS criteria (diuron, monuron oxybenzone

and tributyltin) had also severe impacts on coral nubbins and/or coral larvae (Danovaro et al. 2008; Downs et al. 2014, 2016). The GHS environmental hazard classification of chemicals is mostly based on aquatic toxicity data generated with standard soft water organisms such as microalgae, daphnids crustaceans and fish (see OECD technical guidelines N°201, 202, 203, 211, 210). Nonetheless, based on our preliminary data, we suggest that the most severe environmental hazard statements of these GHS classifications such as H400 (Category acute 1), H410 (Category chronic 1) and H411 (Category chronic 2) could provide a method to identify chemicals that should deserve a refined marine risk assessment if released in the proximity of coral reefs. The direct assessment of sunscreens formulations on coral health (instead of individual compounds), combined with studies on individual compounds, is recommended for a better evaluation of their potential impact on sessile benthic organisms. This applies also to all chemicals included in sunscreen formulae. Finally, this study highlights the needs for developing sensitive analytical methods that can detect very low but environmentally relevant concentrations of xenobiotics in seawater, to better assess the extent of marine contaminations. In addition, we also recommend performing analytical controls to determine the right concentration for poorly seawater-soluble and lipophilic substances (e.g., those with log Kow $>$ 3). Overall, this study suggests that actions are needed to stimulate the research and utilization of UV filters that do not threaten the survival of endangered tropical species.

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Compliance with ethical standards

Conflict of interest CFP, EB and DA have no conflict of interest.

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