

Occurrence and Ecological Risk of Sunscreen-Derived Metallic and Plastic Particles in Marine Environments

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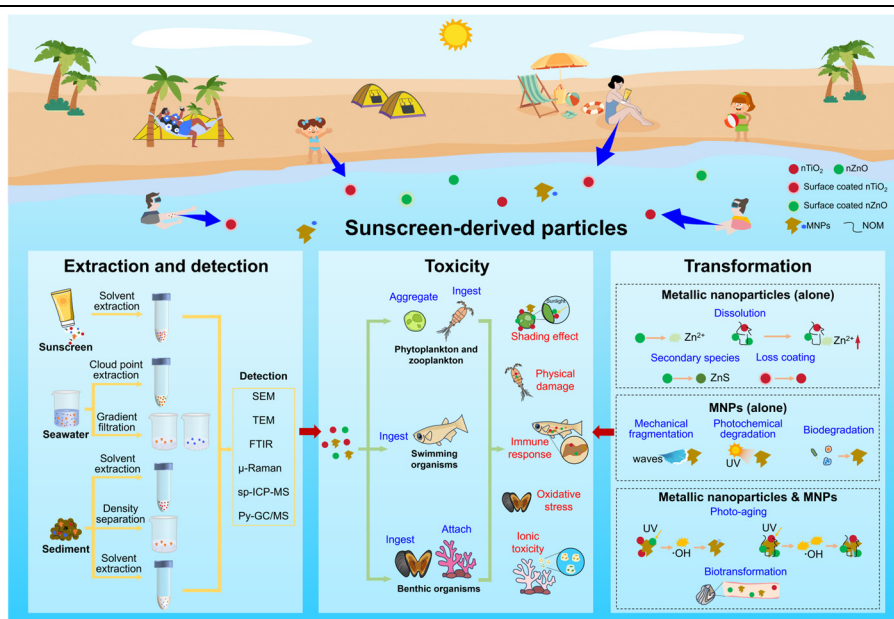
sunscreen;
metallic nanoparticles;
micro- and nano-plastics;
occurrence;
ecological risk;
transformation

Highlights

- Occurrences of sunscreen-derived nZnO and nTiO₂ in coastal waters were positively correlated with tourist activities.
- Sunscreen-derived metallic and plastic particles induced physical damage and oxidative stress toward marine organisms after attachment or ingestion.

Abstract: Sunscreens are extensively applied to protect human skin from ultraviolet radiation, leading to a substantial rise in the release of sunscreen-derived particles into marine environments. These particles, including metallic nanoparticles (e.g., nanosized zinc oxide, nZnO; nanosized titanium dioxide, nTiO₂) and plastic particles (e.g., micro- and nano-plastics, MNPs), are considered emerging contaminants after releasing into marine environment, raising growing concerns regarding their risk to both marine environment and human health. Therefore, this work focuses on these sunscreen-derived particles, and comprehensively reviews their extraction and detection approaches, occurrence, toxicity and ecological risk in marine environments. First, the extraction and detection approaches toward these particles from both original sunscreens and natural samples (e.g., seawater and sediment) are summarized. Based on these approaches, the occurrence of sunscreen-derived particles, primarily nZnO (11.2–14.8 µg/L) and nTiO₂ (6.0–903.1 µg/L), in coastal waters were summarized, which exhibit a significant correlation with tourist activities. Under environmentally relevant concentrations, these particles exhibit significant toxicity (e.g., physical damage and oxidative stress) after being attached or ingested by marine organisms. Based on the calculated risk characterization ratios, both nZnO and nTiO₂ exhibit medium/high risk in some coastal beaches. Additionally, the transformation of sunscreen-derived particles occurs in marine environment, and its role in the toxicity of these particles were further analyzed. Finally, research challenges toward these sunscreen-derived particles are pointed out. This review provides a better understanding of ecological risk of sunscreen-derived metallic and plastic particles in marine environments.

- Both nZnO and nTiO₂ exhibit medium to high ecological risks in some coastal beaches.
- Dissolution and photo-aging of sunscreen-derived particles occur in marine environments, thus leading to changes in their toxicity.



1. Introduction

Sunscreen is an important type of personal care product to against sunburn and skin cancer by protecting ultraviolet (UV) damage. The global market of sunscreens grows sharply, and is estimated to reach 20.34 billion USD by 2030 [1]. An estimated 6000–14,000 tons of sunscreens are annually released into marine environments during their frequent usage in coastal recreational activities (e.g., surfing and diving) and offshore working activities (e.g., fishing) [2–4]. Recently, ecological risk (especially for marine environments) and human health posed by sunscreen-derived liquid organic components have been widely reviewed [5,6]. Particulate component is also an important fraction (about 25 wt%) of sunscreens, which have attracted wide attention due to their actual concentrations, complex environmental behaviors and potential ecological risk after release into the oceans [7,8]. The particulate components in sunscreens can be divided into inorganic and organic polymeric particles based on their chemical composition (Table S1). However, a comprehensive review on the occurrence and ecological risk of these inorganic and polymeric particles is still lacking.

Inorganic particles in sunscreens mainly include titanium dioxide nanoparticles (nTiO₂) and zinc oxide nanoparticles (nZnO) as UV filters, silicon dioxide nanoparticles (nSiO₂) and aluminum oxide (Al₂O₃) as bulking agents, and iron oxide nanoparticles as coloring agents [9–11]. Among these inorganic particles, metallic nanoparticles are dominant in sunscreens [12,13]. Notably, the total content of nTiO₂ and/or nZnO in a single sunscreen product can reach up to 20 wt% [14]. Moreover, 72.4% of commercial sunscreens contain these two nanoparticle types, and this proportion is increasing as they are safer than conventional organic filters [15–17]. Therefore, nTiO₂ and nZnO were mainly focused in

this review as the representatives of inorganic particles. Various organic polymeric particles are also employed in commercial sunscreen products. Among them, particles such as acrylate copolymer and silicone-based cross-polymer, have been widely applied as viscosity regulators [18]. These polymeric particles are classified as the category of micro- and nano-plastics (MNPs).

These different types of sunscreen-derived particles are simultaneously released into marine environments during recreational activities [19–21]. For example, daily sunscreen input at a popular beach (3000 visitors) can introduce 633 g of nTiO₂ and 83 g of nZnO into coastal waters [19]. The substantial release of sunscreen-derived particles results in their accumulation in the marine environments. For example, the concentration of nTiO₂ in the seawater of bathing area (903 μg/L) of Prophète Beach (French) was much higher than that in the non-bathing area (7.8 μg/L) [19]. Additionally, the occurrence of sunscreen-derived particles in marine environments is strongly dependent on tourist activity and the frequency of sunscreen application [19–21]. It is therefore critical to assess their marine ecological risk based on their environmental concentrations.

The toxicity of sunscreen-derived particles toward specific marine organisms (e.g., barnacle larvae and button coral) has been confirmed, and nTiO₂ and nZnO were identified as the main particle components responsible for the observed toxicity [8,22]. nTiO₂ and nZnO are known to possess strong photocatalytic activity, which generates the production of reactive oxygen species (ROS) under UV irradiation [23]. The generated ROS can lead to adverse effect toward marine organisms. Similarly, MNPs have been demonstrated to induce cytotoxicity in marine organisms (e.g., seaworm), potentially via multiple biological mechanisms including oxidative stress, physical damage, and impaired cellular

function [24]. Additionally, these sunscreen-derived particles undergo transformation via environmental processes (e.g., light irradiation and mechanical fragmentation) in marine environments [25]. Such transformations (e.g., surface oxidation and enhanced hydrophilicity) may alter the toxicity of these particles towards marine organisms.

Notably, multiple types of sunscreen-derived particles (e.g., nZnO and MNPs) often coexist in the marine environments, thus leading to combined toxicity to marine organisms (e.g., barnacle larvae) [22]. For example, sunscreen-derived MNPs (i.e., acrylate copolymer) mitigated the toxicity of nZnO by reducing their dissolution to Zn²⁺ [22]. Moreover, abundant natural organic matter (NOM) exists in the marine environment, which can interact with sunscreen-derived particles [26]. This may further modulate the toxicity of these particles (e.g., nTiO₂, nZnO) toward marine organisms. It is thus necessary to summarize the interactions between environmental matrices and sunscreen-derived particles to better understand actual toxicity of these sunscreen-derived particles.

Therefore, this review systematically discusses the separation and detection approaches of typical sunscreen-derived particles (metallic nanoparticles and MNPs) in marine samples, and summarizes their occurrence in marine environments. Then, the toxicity and ecological risk of these particles in the marine environment are identified. Furthermore, the effect of transformation process on the toxicity of these particles is discussed. Finally, future research directions and challenges on detection, toxicity and risk assessment of sunscreen-derived particles are proposed.

2. Occurrence of Sunscreen-Derived Particles in Marine Environments

2.1. Extraction Approaches on Sunscreen-Derived Particles

To comprehensively obtain the key properties (e.g., particle size, morphology, and chemical composition) of sunscreen-derived particles, it is essential to directly extract these particles from original sunscreen products. Conventional procedures for the extraction of these particles from sunscreens include three key steps (Figure 1a): (1) dissolving the sunscreen matrices using compatible organic solvents (e.g., hexane, ethanol, and dichloromethane) [14,16]; (2) collecting solid particles from the solvent phase via centrifugation (typically at 3000–12,000 rpm for 5 min) or ultrafiltration (Table S2), as these two approaches show similar extraction efficiency [12]; and (3) washing the collected particles with deionized (DI) water or organic solvents, followed by repeated centrifugation to eliminate residual organic components and obtain purified sunscreen-derived particles [18].

Different solvents exhibit various efficiencies in dissolving sunscreen matrices. It is critical to select an

appropriate solvent for effective particle extraction. For example, hexane (a non-polar solvent) exhibits excellent solubility for esters (e.g., hexyl salicylate) and has been widely used for the extraction of inorganic nanoparticles (nTiO₂ and nZnO) from sunscreens [27,28]. However, single organic solvents are frequently limited in the capacity to remove multiple organic compounds (e.g., glycerol, polyethylene glycol) from sunscreens. Thus, solvent combinations based on different polarities are commonly required to improve extraction efficiency. For example, hexane alone cannot effectively dissolve polar compounds (e.g., glycerol) in sunscreens. To address this limitation, a sequential extraction strategy has been developed to extract metallic nanoparticles and MNPs from commercial sunscreens (Figure 1a). By using solvents of different polarities in steps, such as hexane followed by alcohol mixtures, the complex sunscreen matrices can be effectively removed to obtain the target particles [18].

For seawater samples, the extraction approaches toward sunscreen-derived particles depend on the particle types. Sunscreen-derived metallic nanoparticles (e.g., nTiO₂ and nZnO) can be efficiently extracted via the cloud point extraction (CPE) method (Figure 1b). This approach utilizes non-ionic surfactants (e.g., TX-114) to enrich nanoparticles via temperature-induced micellar aggregation and phase separation above the surfactant cloud point [29]. CPE method achieved recovery efficiencies exceeding 85% for metallic nanoparticles (e.g., nZnO) from aquatic environments [30]. For MNPs, three steps are involved (Figure 1c): (1) digestion of organic matter using appropriate reagents (e.g., Fenton reagent), (2) separation of microplastics (MPs) and nanoplastics (NPs) by filtration with filter membranes (1 μm in pore size), and (3) enrichment of the collected MNPs from the filters [31–33]. The selected digestion reagents need to completely remove organic matter without damaging the structure and properties of MNPs. Oxidative digestion using hydrogen peroxide (H₂O₂) and Fenton reagent is widely used due to the high removal efficiency toward organic matter [34]. In contrast, acid digestion is not recommended because it can dissolve MNPs. Enzymatic digestion cannot sufficiently remove organic matter either, which limits their application in this extraction process [35].

Due to complex composition of marine sediments, it is more challenging to extract sunscreen-derived particles from beach sediments than that from seawater (Figure 1d–g). Prior to extraction, sediment samples (e.g., the sediment from beach) are oven-dried and sieved (10–200 mesh) to remove large stones and biological materials (Figure 1d). For metallic nanoparticles, DI water extraction is widely used to disperse the sediment particles and metallic nanoparticles (Figure 1e). Extraction steps (e.g., static settling, centrifugation) are further conducted to separate the metallic nanoparticles from the sediment mixture. It is reported that

centrifugation exhibits a higher recovery than static settling [36]. For example, the recovery of metallic nanoparticles (e.g., Au) from marine sediment is significantly higher when using centrifugation ($76.27 \pm 4.27\%$) at $20\times$ g for 5 min compared to static settling ($66.28 \pm 1.98\%$) for 2 h [36]. For MPs, density separation is the primary approach with a recovery of 90% (Table S2). Four main steps are involved: flotation, digestion, filtration, and collection (Figure 1f) [37]. During flotation, MPs are separated from the sediment using saturated salt solutions and preliminarily extracted into the supernatant. It is important to select salt solution to ensure high extraction efficiency. For example, NaCl is effective for low-density MPs (e.g., polypropylene and

polyethylene), while ZnCl_2 is more suitable for high-density MPs (e.g., polyethylene terephthalate and polyvinyl chloride) [38,39]. For small-sized NPs ($<1 \mu\text{m}$), density separation is often ineffective because of their nanoscale size. Five extraction steps are recommended in Figure 1g. Among these steps, solvent extraction is a key step to improve extraction efficiency. Dichloromethane is an effective solvent for extracting NPs from sediment samples. This approach achieves the recovery rates higher than 75% for polystyrene and polymethyl methacrylate (PMMA) NPs [40,41]. However, dichloromethane may change the surface structure of MNPs, which may interfere with subsequent identification and characterization.

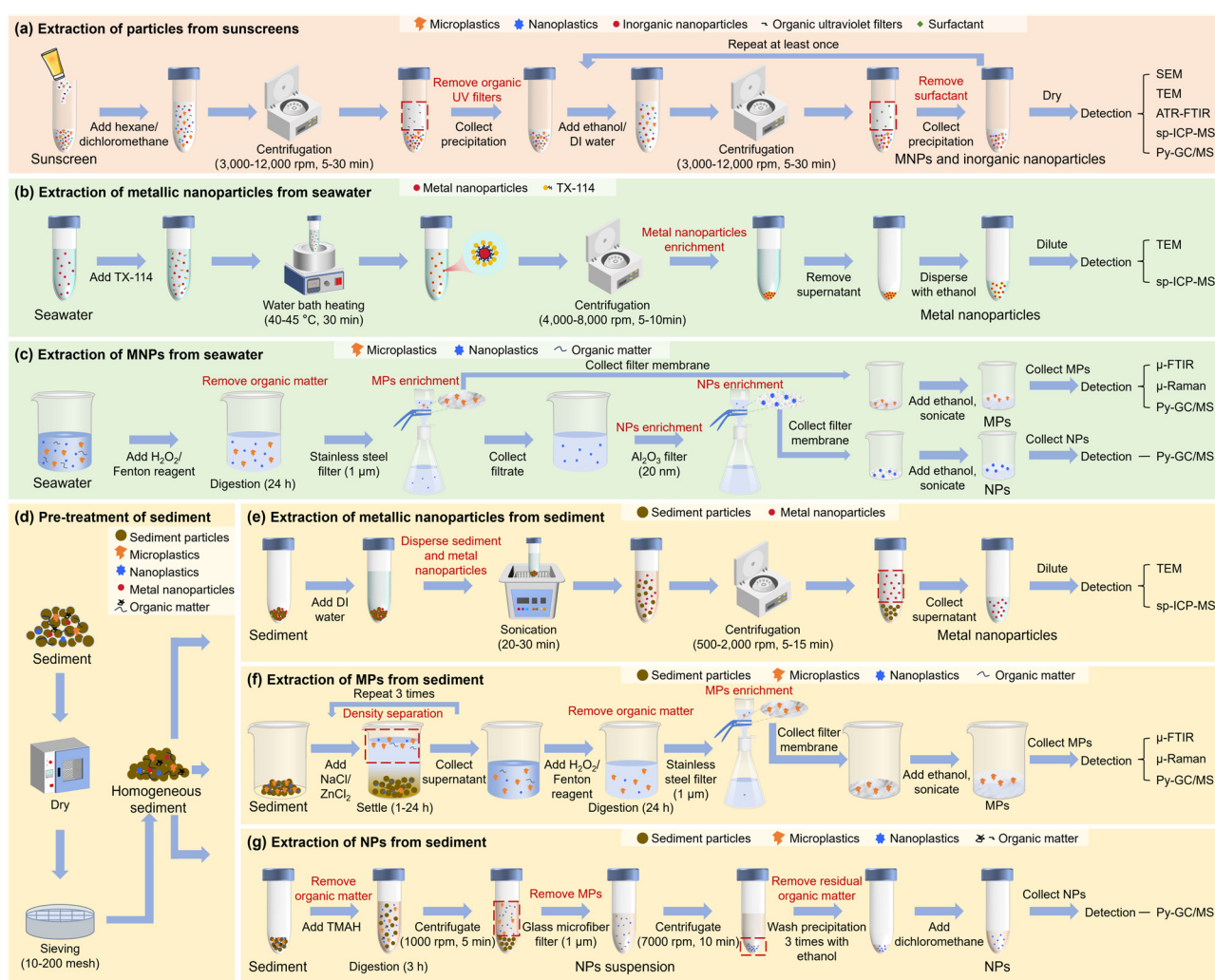


Figure 1. Schematic diagram on the extraction approaches and detection techniques of sunscreen-derived particles from sunscreens and environmental samples. (a): Solvent extraction of metallic nanoparticles and MNPs from sunscreens. (b,c): Extraction approaches and detection techniques of sunscreen-derived particles from seawater. Panel b represents extraction of metallic nanoparticles via cloud point extraction; Panel c represents extraction of MNPs via gradient filtration. (d–g): Extraction approaches and detection techniques of sunscreen-derived particles from sediments. Panel d represents the pre-treatment for metallic nanoparticle and MNP extraction from sediment; Panel e represents the extraction of metallic nanoparticles via aqueous dispersion and centrifugation; Panel f represents extraction of MPs via density separation; Panel g represents extraction of NPs via solvent extraction. SEM: Scanning electron microscopy; TEM: Transmission electron microscopy; ATR-FTIR: Attenuated total reflectance-Fourier transform infrared spectroscopy; sp-ICP-MS: Single-particle inductively coupled plasma mass spectrometry; Py-GC/MS: Pyrolysis coupled with gas chromatography and mass spectrometry; μ -FTIR: Micro-Fourier transform infrared spectroscopy; μ -Raman: Micro-Raman spectroscopy.

2.2. Detection Techniques on Sunscreen-Derived Particles

Qualitative identification is the first step after sunscreen-derived particle extraction. Attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR) and Raman spectroscopy can be used to identify the chemical composition of MPs based on characteristic spectral fingerprints. However, ATR-FTIR has limitations for metallic nanoparticles (e.g., nTiO₂ and nZnO) identification (Table S3), because inorganic materials lack the necessary chemical bond vibrations [42]. Conversely, Raman spectroscopy is effective for characterizing both organic (e.g., MPs) and inorganic nanoparticles (e.g., nTiO₂ and nZnO) [43,44], but not suitable for analyzing fluorescent samples because of strong signal interference [45]. Additionally, X-ray photoelectron spectroscopy (XPS) also provides information on the types of elements and their content proportions [18]. Furthermore, X-ray diffraction (XRD) is also used to identify crystal phases of sunscreen-derived metallic nanoparticles. For example, XRD can distinguish the rutile and anatase forms of nTiO₂, and the wurtzite structure of nZnO commonly found in sunscreens [46]. These analytical techniques can provide a comprehensive understanding of the chemical properties of sunscreen-derived particles.

For morphological characterization, electron microscopy techniques, such as scanning electron microscopy (SEM) and transmission electron microscopy (TEM) combined with energy dispersive spectrometer (EDS), are widely used to obtain information on particle size and elemental composition (Table S3). For example, nTiO₂ (44 ± 25 nm, sphere-shaped) and nZnO (128 ± 51 nm, rod-shaped) in commercial sunscreens have been successfully identified using these techniques [16,18,47]. High-resolution TEM (HRTEM) provides detailed information on the nano-scaled morphology. These techniques also enable the visualization of surface coatings, such as Al₂O₃ and SiO₂, which are applied to improve the dispersion and stability of inorganic nanoparticles [48,49].

Quantitative methods for sunscreen-derived particles vary depending on the particle type. Mass spectrometry has emerged as one of the most powerful analytical strategies to quantify sunscreen-derived particles. For sunscreen-derived metallic nanoparticles (e.g., nTiO₂ and nZnO), inductively coupled plasma mass spectrometry (ICP-MS) provides information on the metal types and their mass concentrations. Furthermore, the development of single-particle ICP-MS (sp-ICP-MS) allows the simultaneous determination of number concentration, particle size, and size distribution at the individual particle level. By using sp-ICP-MS, the number concentration of nTiO₂ (4.8 × 10⁵ particles/mL) and nZnO (1.0 × 10⁴ particles/mL) in commercial sunscreen products was successfully quantified, and the measured particle sizes were 107 nm and about 98 nm, respectively [50]. In addition, the ubiquitous presence of natural nTiO₂ in environmental

matrices can interfere with the accurate detection and characterization of sunscreen-derived nTiO₂. To address this concern, sp-ICP-MS coupled with time-of-flight mass spectrometry (sp-ICP-TOF-MS) has been developed [51]. This technique enables high-throughput analysis of multi-elements and multi-isotopes within single particles, providing a reliable way to distinguish sunscreen-derived nanoparticles and natural particulate matrices based on elemental ratio [51]. For sunscreen-derived MNPs, pyrolysis coupled with gas chromatography and mass spectrometry (Py-GC/MS) is used to determine the polymer types and their mass concentrations at the microgram level. This is achieved through the thermal decomposition of polymers followed by chromatographic separation and mass spectral identification. Based on the pyrolysis products (e.g., methyl methacrylate, ethylene glycol dimethacrylate), typical MPs in sunscreens were identified as acrylate copolymers [52]. However, the accurate quantification of sunscreen-derived MNPs in natural samples remains a major challenge, and more reliable analytical techniques need to be further developed.

2.3. Occurrence of Sunscreen-Derived Particles in Marine Environments

Sunscreen-derived nanoparticles (e.g., nTiO₂ and nZnO) are primarily released into the oceans through human recreational activities (e.g., surfing and diving) and offshore working activities (e.g., fishing). These particles are widely found in coastal waters (Table S4). It is reported that the concentrations of nTiO₂ in seawater (10–900 µg/L) are significantly higher than that of nZnO (max. 14.8 µg/L) [19]. This may be due to the amount of nTiO₂ added in sunscreen is higher than that of nZnO [12,46]. Meanwhile, nZnO is more likely to dissolve in the environment, resulting in a relatively low abundance. In addition, the abundance of nTiO₂ and nZnO in coastal waters shows a significant positive correlation with tourist numbers. For example, at Palavas-les-Flots Beach (France), the concentration of nTiO₂ in seawater increased from 31.3 to 269.2 µg/L with increasing tourist numbers (from 7 to 84 per 20 m length of shoreline) [21]. Another beach with greater tourist density (120 tourists per 20 m of shoreline) recorded a much higher nTiO₂ level at 903.1 µg/L [19,21]. Additionally, significantly different concentrations were observed between bathing zones and non-bathing areas [19,20]. For example, at Prophète Beach (France), the concentrations of sunscreen-derived nanoparticles outside the bathing zones (nTiO₂: 7.8 µg/L; nZnO: below limit of detection) were significantly lower than those in the bathing area (nTiO₂: 903.1 µg/L; nZnO: 11.2 µg/L) [19]. Moreover, the concentrations of these sunscreen-derived nanoparticles in coastal waters are also modulated by the amount of sunscreen applied. For instance, the higher sunscreen input at La Bajadilla Beach (109.3 mL/user) than at La Caleta Beach (76.3 mL/user) can be attributed to the

greater application volume per tourist (11.9 mL vs. 7.9 mL) [53]. Current data on the environmental concentrations of sunscreen-derived particles are mainly obtained through comparative analysis with control sites where sunscreen input is minimal [20]. Notably, metallic nanoparticles in beach water will also originate from other sources (e.g., shark nets and plastic debris), making it difficult to identify the sunscreen-derived particles. This may further result in the overestimation of environmental abundance of these particles. Additionally, the occurrence of these particles in sediment is poorly studied. Full characterization of the particles in original sunscreen products may be a good solution for accurate identification and tracking of sunscreen-derived particles in complex environmental matrices.

Laboratory simulations have emerged as an effective approach to estimate the concentration of sunscreen-derived particles in the environment. For example, a simulated washing experiment was conducted to evaluate the release of sunscreen-derived nanoparticles during recreational activities. In the experiment, volunteers applied sunscreens on their hands and then rinsed in water. The results showed that at least 25% of the applied sunscreen was washed off during swimming [54]. Further estimation indicates that 4000–6000 tons of sunscreen enter coral reef areas annually, this amount corresponds to 36–56 tons of nTiO₂ [54,55]. These findings highlight the heavy environmental burden of sunscreen-derived nanoparticles in marine ecosystems.

To our knowledge, there is no report currently on the occurrence of sunscreen-derived MNPs in marine environments. Various types of conventional MNPs (such as PE, PP, PET, and PMMA) have been detected in marine environments, including seawater (0.01–782,000 particles/m³) and sediment (0.03–49,600 particles/kg) [56–62], but specific sources (sunscreens or not) of these MNPs are unknown. This is because that source identification of sunscreen-derived MNPs in marine environments is difficult. For example, specific polymer components and their morphological features are largely unknown; the detection techniques toward these polymer components are lacking. These knowledge/technique gaps highlight the urgent need to fully characterize the sunscreen-derived MNPs in both sunscreen products and natural environments, and develop suitable qualitative and quantitative techniques.

3. Toxicity and Ecological Risk of Sunscreen-Derived Particles

3.1. Toxicity of Sunscreen-Derived Particles to Marine Phytoplankton and Zooplankton

Phytoplankton are the dominant marine primary producers, and zooplankton occupy critical trophic positions in marine food webs. After release into marine environments, sunscreen-derived particles can easily

interact with phytoplankton and zooplankton. It has been reported that sunscreen-derived metallic nanoparticles exhibit significant toxicity toward phytoplankton and zooplankton [63,64]. Specifically, these metallic nanoparticles mainly inhibit phytoplankton (e.g., marine microalgae) growth after forming nanoparticle-algae heteroaggregates [63]. For example, sunscreen-derived nTiO₂ could inhibit the growth of *Dunaliella tertiolecta* with a low median effective concentration (EC₅₀; 4.8 mg/L) after incubation for 24 h [63]. Two dominant toxicity mechanisms are involved (Figure 2a): (1) cell wall damage induced by physical penetration, and (2) photosynthesis reduced by shading effect [65,66]. Notably, it is reported that the 96-h EC₅₀ of nZnO (6 µg/L) to cyanobacteria was significantly lower than that of nTiO₂ (620 µg/L) [67], confirming that sunscreen-derived nZnO exhibited greater toxicity than nTiO₂. The release of Zn²⁺ from nZnO can cause oxidative stress, thereby facilitating the growth inhibition or even death [68]. For zooplankton, sunscreen-derived metallic nanoparticles mainly induce toxicity by oxidative stress and physical damage [64,68]. It is reported that the ingested plastic microbeads (2 µm) can block the digestive tract of zooplankton such as *Tigriopus japonicus*, causing developmental retardation and reduced fecundity [69]. Sunscreen-derived MNPs (e.g., acrylate copolymer and silicone-based cross-polymer) exhibit similar physical characteristic (e.g., size) with plastic microbeads [18,69]. Thus, these sunscreen-derived MNPs may also induce toxicity to zooplankton after ingestion, although there is no detailed report currently.

3.2. Toxicity of Sunscreen-Derived Particles to Swimming Organisms

Sunscreen-derived particles can easily be ingested by swimming organisms (e.g., marine fish), which may induce significant toxicity (Figure 2b). The gills are the primary tissues in marine fish for toxicant (e.g., sunscreen-derived metallic nanoparticles) uptake and accumulation through respiration [70]. ROS generated by metallic nanoparticles (e.g., nTiO₂ and nZnO) could induce severe oxidative stress, leading to cellular damage and further gill pathologies (e.g., edema of gill lamellae and gill filaments) [71–73]. However, the toxicity of sunscreen-derived MNPs (e.g., acrylate copolymers and silicone-based cross-polymer) toward fish gills is poorly understood, which needs further investigation.

Ingestion is also a dominant pathway for sunscreen-derived particles (e.g., metallic nanoparticles) entering swimming organisms, thereby accumulating in multiple tissues and organs (e.g., intestine and liver) and causing potential toxicity [74–76]. These particles can (1) activate the immune responses, thus leading to increased lipid peroxidation levels and liver damage (e.g., hemorrhage) [75,76], (2) cause a series of physical injuries, and

compromise intestinal integrity and nutrient absorption capacity [77], and (3) induce indirect oxidative stress by the released metal ions (Zn^{2+}), thereby aggravating the toxicity toward marine organisms (e.g., *Artemia franciscana*) [78]. Additionally, current studies mainly focus acute toxicity of sunscreen-derived particles toward marine organisms [8,22], future studies need to evaluate their chronic effect during long-term exposure (especially under environmentally relevant conditions).

3.3. Toxicity of Sunscreen-Derived Particles to Benthic Organisms

Ocean seafloor is considered the final sink for sunscreen-derived metallic and plastic particles. The

toxicity of these particles on benthic organisms has attracted increasing attention (Figure 2c). Benthic mollusks are highly sensitive to sunscreen-derived particles [79,80]. After ingestion by mussels (*Mytilus galloprovincialis*), metallic nanoparticles (e.g., $nTiO_2$) could primarily accumulate and induce physical damage in the gills [81]. Furthermore, these particles could reduce lysosomal membrane stability and trigger cellular apoptosis after entering other tissues (e.g., digestive gland), and ultimately impairing the immune functions [82]. Additionally, metal ions (Zn^{2+}) released from sunscreen-derived particles ($nZnO$) can reduce the activity of antioxidant enzymes (e.g., catalase) in mussels, thereby leading to oxidative damage [83].

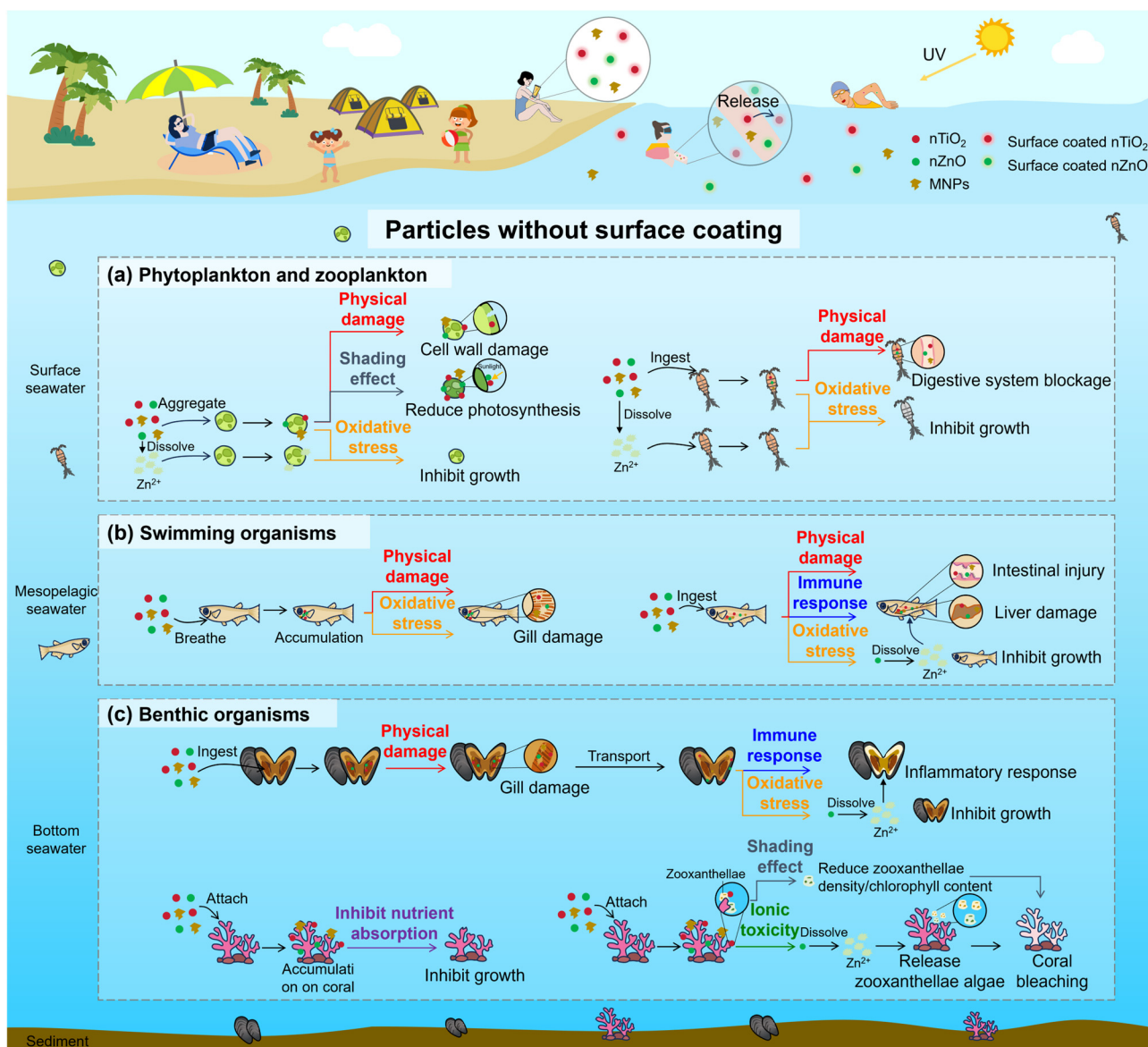


Figure 2. Toxicity of sunscreen-derived particles without surface coating and related mechanisms. (a): Toxicity to phytoplankton and zooplankton (for example, *Dunaliella tertiolecta* and *Tigriopus fulvus*). (b): Toxicity to swimming organisms (for example, *Oryzias melastigma*). (c): Toxicity to benthic organisms (for example, *Mytilus galloprovincialis* and *Zoanthus*).

Coral reefs are important benthic organisms in tropical marine ecosystems, and they are directly exposed to sunscreen-derived particles via recreational activities

(e.g., swimming, diving) [8,84]. After attachment to coral, these particles (e.g., metallic nanoparticles) can inhibit coral growth by interfering with prey capture and

nutrient uptake [8,85]. Additionally, these particles could reduce the density and chlorophyll content of zooxanthellae (the symbiont of coral), thus resulting in coral bleaching and death [8]. Notably, nZnO can undergo partial dissolution (24%) in the marine environment (high salinity, weak alkalinity), resulting in the release of Zn^{2+} [86,87]. Therefore, sunscreen-derived nZnO exhibits greater toxicity than nTiO₂ toward coral reefs due to the release of Zn^{2+} [8]. After incubation at the same concentration (400 µg/L) and exposure time (24 h), button coral (*Zoanthus* sp.) exhibited a growth inhibition rate of 16.7% under nTiO₂ treatment, much lower than that under nZnO exposure (up to 80%) [8]. This is because the released Zn^{2+} can decrease the density of zooxanthellae, and result in bleaching of corals [8]. However, the toxicity of sunscreen-derived MNPs toward benthic organisms (e.g., coral) remains largely unknown.

3.4. Factors Affecting the Toxicity of Sunscreen-Derived Particles

The toxicity of sunscreen-derived particles in marine environments is influenced by particle properties (e.g., surface coating, particle size). Coatings (e.g., SiO₂, Al₂O₃, stearic acid, and polydimethylsiloxane) are commonly found on the surface of sunscreen-derived metallic nanoparticles (e.g., nTiO₂ and nZnO), which could reduce the toxicity of these nanoparticles toward marine organisms (e.g., phytoplankton). For example, bare nZnO showed an obvious inhibition of *Dunaliella tertiolecta* growth (72 h EC₅₀: 2.0 mg Zn/L), which is much higher than that of the surface-coated nZnO extracted from sunscreens (72 h EC₅₀: 16.4 mg Zn/L) [63,88]. Surface coatings reduce the toxicity of sunscreen-derived metallic nanoparticles through two main pathways: (1) reduce ROS generation by suppressing the photocatalytic activity of these metallic nanoparticles (Figure S1a), and (2) inhibit the release of metal ions (e.g., Zn^{2+} released from nZnO) (Figure S1b) [89,90]. However, surface coatings can alter the hydrophobicity of these sunscreen-derived particles, thereby indirectly increasing their toxicity toward marine organisms [91,92]. Specifically, hydrophilic coating (e.g., SiO₂) could increase the toxicity of sunscreen-derived metallic nanoparticles by enhancing the dispersibility and uptake of these particles. For example, hydrophilic-coated metallic nanoparticles (e.g., SiO₂-coated nTiO₂) exhibit higher toxicity than bare ones toward sea urchin (*Paracentrotus lividus*) embryos. This is due to the higher uptake of hydrophilic-coated nanoparticles [93]. Hydrophobic-coated nanoparticles (e.g., Al₂O₃ and dimethicone/methicone copolymer-coated nTiO₂) increase the toxicity toward *Paracentrotus lividus* by damaging the hydrophobic membrane [93]. Moreover, both 1 mg/L of the hydrophilic-coated nanoparticles and 0.05 mg/L of the hydrophobic-coated nanoparticles can induce 20% of the embryonic

abnormality [93], suggesting that the hydrophobic-coated particles exhibit higher toxicity than hydrophilic-coated particles. Notably, these sunscreen-derived metallic nanoparticles with the hydrophobic surface coatings tend to aggregate in aqueous environments, thus leading to spatial separation from plankton (*Tigriopus japonicus*) and reducing bioavailability/toxicity [92].

Particle size is another factor to affect the toxicity of these sunscreen-derived particles (metallic nanoparticles and MNPs), which shows a negative correlation with toxicity (i.e., toxicity increases with decreasing particle size). For example, 10–30 nm nZnO showed higher toxicity (24 h LC₅₀: 7.77 mg/L) to *Dunaliella salina* than that of 80–200 nm nZnO (24 h LC₅₀: 9.63 mg/L) [94]. This is because that smaller nZnO releases more Zn^{2+} owing to its higher specific surface area [94,95]. For MNPs, NPs (80 nm) exhibit greater tissue penetration and higher bioaccumulation than MPs (1 µm and 20 µm), thereby NPs induced more severe oxidative damage and intestinal inflammation in sea cucumber *Apostichopus japonicus* [96].

NOM is widely distributed in marine environments, which could alter the toxicity of these sunscreen-derived particles by forming the aggregates with NOM. For example, the formation of aggregates between NOM and nTiO₂ enhances the ingestion of nTiO₂ by *Artemia salina*, resulting in more severe oxidative stress and higher mortality [97]. Similarly, the formation of aggregates between NOM and MPs could facilitate the ingestion of MPs by fishes, thereby enhancing the toxicity of MPs toward these fishes [98]. Additionally, the aggregation between NOM and MPs accelerates the settling of MPs. This sedimentation consequently decreases MP ingestion by organisms (e.g., plankton) [99,100].

3.5. Ecological Risk of Different Sunscreen-Derived Particles

The ecological risk was assessed based on the obtained toxicological data and environmental concentrations of sunscreen-derived particles in current literature. Species sensitivity distributions (SSD) curves of nTiO₂ and nZnO were constructed by a total of 75 toxicity endpoint values involving 58 marine organism species (Table S5), and the predicted no-effect concentrations (PNECs) for each particle type were calculated (Figure 3a, Table S6). Based on the SSD curves, the sensitivity to different sunscreen-derived particles shows significant interspecies variation. Clearly, for the sunscreen-derived nTiO₂ and nZnO, the most sensitive species were *Magallana gigas* and *Mytilus edulis*, respectively (Figure 3b,c). Notably, sunscreen-derived nZnO showed lower PNECs (3.90 µg/L) (Figure 3c) than nTiO₂ (54.53 µg/L) (Figure 3b), confirming that nZnO posed higher toxicity. Based on actual concentrations of sunscreen-derived particles (primarily nZnO and nTiO₂), the risk characterization ratios (RCRs) in coastal environments were calculated (Figure 3d), and both of

these particles exhibit medium/high risk in some specific marine areas. For example, at Santa Ponça Beach, the environmental concentrations of nTiO₂ and nZnO were 20.17 µg/L and 13.50 µg/L, respectively. “Medium risk” and “high risk” were found in this beach for nTiO₂ (RCR value: 0.37) and nZnO (RCR value: 3.46), respectively. It is reported that nZnO at environmentally relevant concentration (e.g., 10 µg/L) can activate hemocyte phagocytosis and upregulate inflammation-related genes expression in *Mytilus edulis* [101], which may explain the high toxicity (risk) of nZnO in beaches (e.g., Santa Ponça Beach). However, the risk assessment of nZnO is not available in some beaches (e.g., Palavas-les-Flots Beach) due to the lack of its actual concentration (Table S4).

However, the environmental concentrations of sunscreen-derived metallic nanoparticles could be overestimated because some of these nanoparticles may be

not originated from sunscreens and current approaches cannot make differentiation. This may result in an overestimation of the ecological risk of sunscreen-derived particles. Additionally, SSD curves of the sunscreen-derived MNPs (e.g., acrylate polymers) are difficult to obtain due to insufficient toxicological data. Available data on the environmental concentrations of sunscreen-derived MNPs remain scarce. Therefore, it is currently difficult to assess ecological risk of sunscreen-derived MNPs based on RCR approach. To address this issue, three aspects should be focused on: (1) establishing the characteristic chemical fingerprints of sunscreen-derived MNPs to support their accurate detection and source identification in marine environments; (2) obtaining accurate environmental concentration based on the advanced techniques and source identification; (3) conducting toxicological studies toward these sunscreen-derived MNPs.

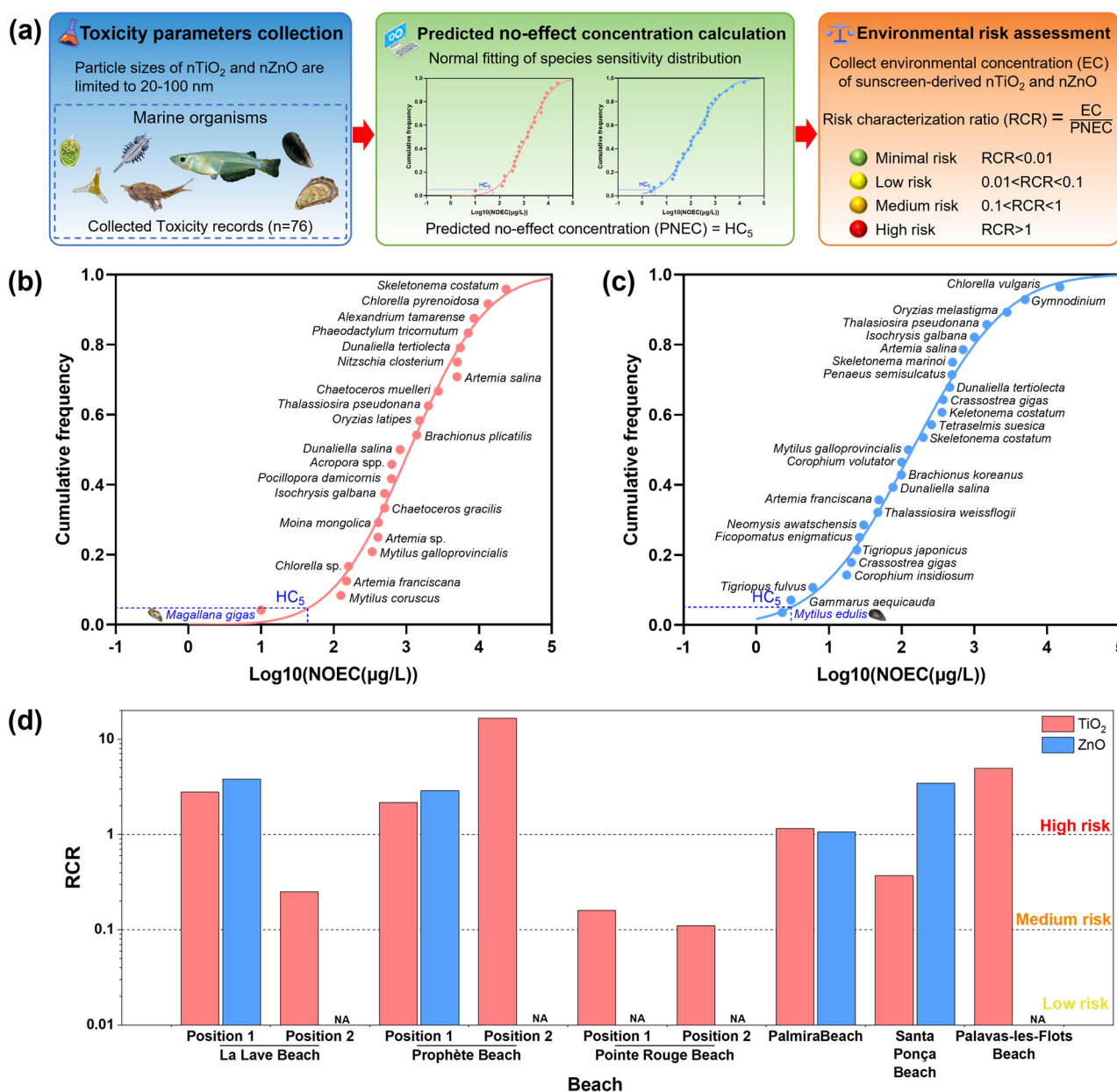


Figure 3. Ecological risk assessment of sunscreen-derived particles in marine environments based on risk quotient (RQ) method. (a): General framework of the RQ method for ecological risk assessment. (b): Species sensitivity distribution (SSD)

curve of marine organisms to nTiO₂ fitted with a normal distribution model. (c): SSD curve of marine organisms to nZnO fitted with a normal distribution model. In panels B and C, each point represents a toxicity endpoint derived from an individual marine species. The calculated PNECs based on these SSD curves for nTiO₂ and nZnO were 54.5 and 3.9 µg/L, respectively. The 5% hazardous concentration (HC₅) value indicates the concentration at which 5% of species are adversely affected. The most sensitive species are highlighted in blue. (d): Ecological risk (RCR) of nTiO₂ and nZnO in coastal beaches. In panel D, positions 1 and 2 represent the two different sampling sites within the same beach. The RCR values of nTiO₂ and nZnO in each beach were calculated based on the environmental concentrations and PNECs. The environmental concentrations of nTiO₂ and nZnO in the five beaches (listed in Table S2) was obtained from three previous studies [15–17]. RCR levels were classified as follows: 0.01 ≤ RCR < 0.1 (low risk), 0.1 ≤ RCR < 1 (medium risk), 1 ≤ RCR (high risk). NA represents the risk assessment of nZnO is not available due to the lack of its actual concentration.

4. Transformation of Sunscreen-Derived Particles and Implications for Toxicity

4.1. Transformation Pathways of Sunscreen-Derived Particles in Marine Environments

Sunscreen-derived particles inevitably undergo transformation in marine environments, which depends on the particle types (Figure 4a–c, Table S7). For sunscreen-derived metallic nanoparticles, two primary processes are involved (Figure 4a): (1) dissolution with the release of metal ions, and (2) formation of secondary chemical species. Specifically, sunscreen-derived nZnO tends to dissolve with the release of Zn²⁺, and this dissolution process could be facilitated by enhanced ocean acidification (pH ≈ 7.7) [102,103]. The released Zn²⁺ can subsequently react with sulfur and phosphate in marine environments to form secondary metallic particles (e.g., zinc sulfide, and zinc phosphate) [104]. For example, 11.8–17.1% of nZnO transformed into ZnS after 7 days of incubation in seawater [105]. In contrast, nTiO₂ is chemically stable and very difficult to transform or dissolve [106]. Moreover, nTiO₂ and nZnO are often coated (e.g., SiO₂-coated nTiO₂) to decrease the photocatalytic activity [107,108]. These surface coatings can inhibit the dissolution of sunscreen-derived metallic nanoparticles (Figure S2a). However, such protective coatings are susceptible to release in marine environments (Figure S2b). Previous study showed that 99% of the SiO₂ coating could be stripped off from nTiO₂ in seawater, as hydroxide ions cleave the Si-O bonds of the coating [91].

In addition, NOM widely exists in marine environments [109,110], which can inevitably interact with sunscreen-derived particles (e.g., metallic nanoparticles), thereby altering the transformation of these particles. The aromatic/carbonyl groups in NOM can form complexes with the dissolved Zn²⁺, further promoting the dissolution of nZnO [108,111]. Sunscreen-derived MNPs (e.g., PMMA) inevitably undergo transformation via mechanical fragmentation, sunlight irradiation, and biodegradation (Figure 4b). Wave action is a key force for the mechanical fragmentation of MNPs [112]. Specifically, the water molecules could be attracted by the hydrophilic groups, increasing the distance between polymer (e.g., PMMA) chains. This is because

water disrupts hydrogen bonds and van der Waals forces within the macromolecular network [113]. The mechanical forces generated by wave further accelerate the fragmentation of MNPs into smaller particles [112]. For example, ethyl methacrylate-methyl methacrylate (EMA-MMA) copolymer underwent fragmentation under mechanical stress (Table S7), resulting in a reduction (by 20%) in particle size after 84-h incubation [114]. Sunlight irradiation can also lead to the fragmentation of sunscreen-derived MNPs (e.g., EMA-MMA copolymer), with the formation of hydroxyl and carbonyl groups [114,115]. Microbial biodegradation can also induce the transformation of MNPs, leading to the mineralization of polymer and the formation of low-molecular weight products [116–118].

Sunscreen-derived particles (e.g., metallic nanoparticles and MNPs) coexist in marine environments and could undergo heteroaggregation through different interaction mechanisms (e.g., electrostatic interaction, hydrophobic interaction, and hydrogen bonds) [119]. These interactions between metallic nanoparticles and MNPs can further affect their transformation (Figures 4c and S2c). Specifically, sunscreen-derived metallic nanoparticles (e.g., nZnO) could generate abundant ROS (e.g., hydroxyl radical) under UV irradiation, accelerating the degradation of sunscreen-derived MNPs (acrylate copolymer and silicone-based cross-polymers) [18]. Notably, surface coatings of nTiO₂/nZnO can suppress ROS generation [90], thus reducing MNP photo-aging [120]. Conversely, MNPs are capable of altering the transformation of metallic nanoparticles [22]. For example, after ingestion by barnacle larvae, MNPs have been reported to lower the gut acidity of larvae by damaging their intestinal wall, thereby reducing the dissolution of nZnO into Zn²⁺ [22]. In marine environments, NOM affects the transformation of both MNPs and metallic nanoparticles. Currently, studies confirmed the NOM-mediated transformation of commercial MNPs [121,122]. As a photosensitizer, NOM is reported to accelerate the aging of MNPs by generating ROS (e.g., singlet oxygen, superoxide radicals) under UV irradiation [122]. In the presence of metallic nanoparticles, NOM can effectively quench ROS generated by nTiO₂ during UV irradiation [121], which may reduce the photo-aging of MNPs. Additionally, previous studies

have confirmed that pre-treated with NOM on MNPs or metallic nanoparticles can mitigate aggregation by weakening electrostatic interaction and enhancing steric interactions, thereby reducing the contact between these two particle types [123]. This process may weaken the

oxidative effect of ROS generated by metallic nanoparticles (e.g., nTiO₂) and further alleviate the aging of MNPs. However, the effect of NOM on the transformation of sunscreen-derived particles is poorly studied, which need further investigation.

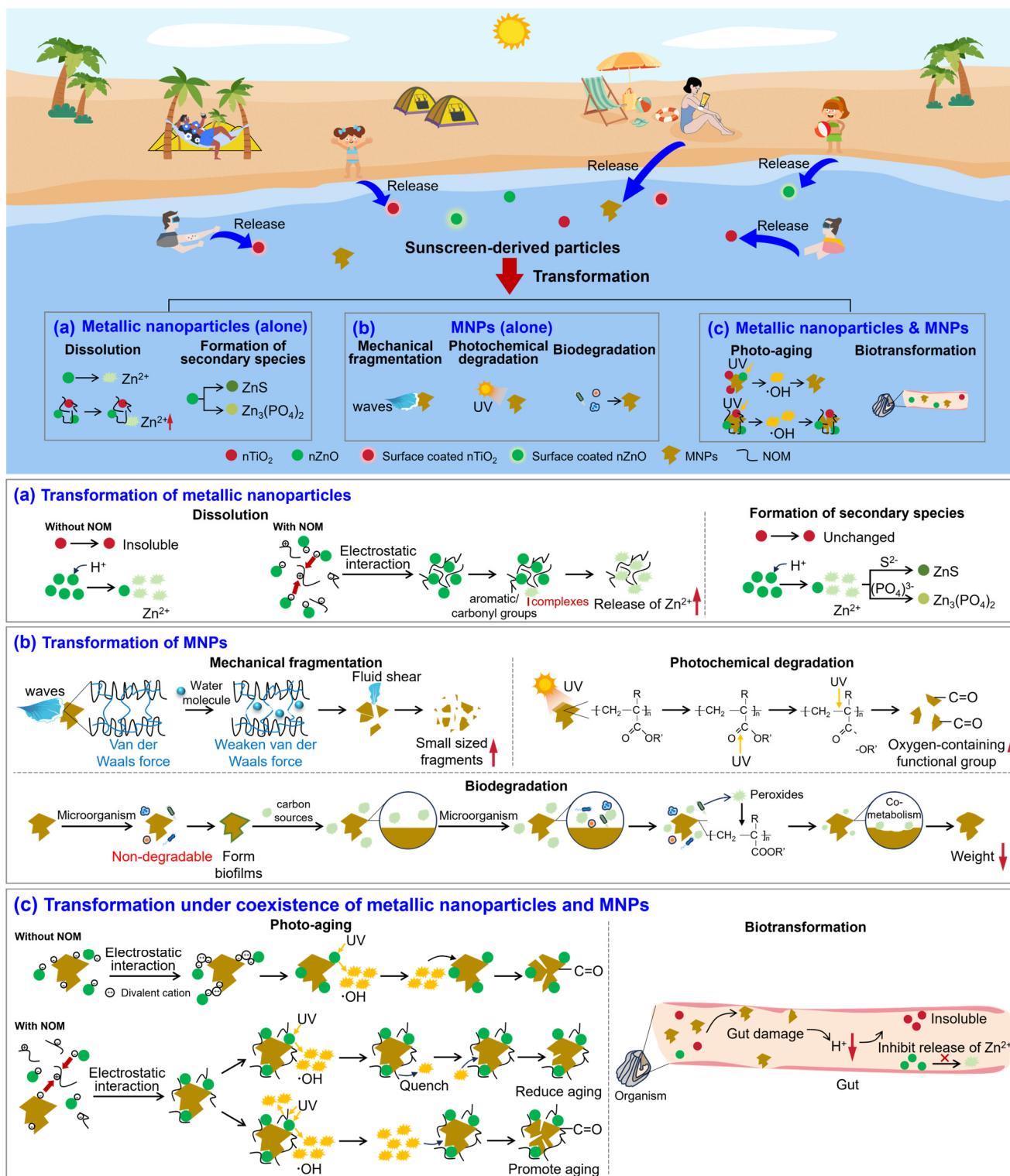


Figure 4. Transformation of sunscreen-derived particle and the effect of natural matter. (a): Transformation of metallic nanoparticles in seawater, including dissolution, and secondary species formation. (b): Transformation of MNPs in seawater, including mechanical fragmentation, photochemical degradation, and biodegradation. (c): Transformation of metallic nanoparticles and MNPs following their coexistence in seawater, including MNPs photo-aging, and metallic nanoparticle biotransformation.

4.2. Role of Transformation in the Toxicity of Individual Sunscreen-Derived Particle Type

The transformation of sunscreen-derived particles in marine environments alters their bioavailability and toxicity. For metallic nanoparticles, the release of metal ions can enhance their toxicity [22]. Previous study indicates that nZnO dissolution can enhance the bioavailability of Zn, thus promoting the bioaccumulation of Zn in marine organisms (e.g., sea anemones) [102]. Notably, Zn²⁺ may further transform into secondary products with low solubility (e.g., zinc sulfide, zinc phosphate), which typically exhibit lower toxicity than Zn²⁺ towards fish embryos due to the deposition of these secondary products [104]. It is known that NOM can promote the dissolution of nZnO, but not increase its toxicity. This is because that complexes of NOM with the dissolved Zn²⁺ can reduce the bioavailability of Zn²⁺ [124]. In addition, surface coating also plays an important role in altering the transformation and toxicity of sunscreen-derived metallic nanoparticles. For example, surface coating (e.g., SiO₂) could reduce the toxicity of nZnO by inhibiting the release of Zn²⁺ [89,125]. However, the loss of coating increases the potential exposure of bare nanoparticles, thereby potentially enhancing their toxicity toward marine organisms.

For MNPs, smaller secondary MNPs are formed by mechanical fragmentation [126]. Compared with the pristine sunscreen-derived MNPs, the secondary MNPs can increase the bioavailability and toxicity due to their smaller particle sizes [114]. Photochemical degradation can enhance the hydrophilicity of secondary MNPs through surface oxidation [22,114], improving the dispersion of these sunscreen-derived MNPs [114]. Previous research indicates that the increase of MNP suspension can directly enhance the cellular uptake, thereby increasing potential toxicity [114]. In addition, the degradation of MNPs also leads to the leaching of organics (e.g., cyclosiloxanes), causing the fragmentation of mitochondria and the reduction of cell vitality [114]. Notably, halogen ions (e.g., Cl⁻, Br⁻) in seawater can reduce the toxicity of photodegraded MNPs. This is because halogen ions decrease the leaching of toxicant (hydrogen peroxide) from MNPs [52].

4.3. Role of Transformation in Combined Toxicity of Different Sunscreen-Derived Particles

Sunscreen-derived particles (e.g., metallic nanoparticles and MNPs) coexist in marine environments, which can produce combined toxicity. Their combined toxicity (e.g., additive and antagonistic effects) toward marine organisms has been investigated [127–129]. For example, compared with nTiO₂ or MPs alone, co-exposure to MPs (polystyrene, 2.5 mg/L) and nTiO₂ (1 mg/L) induced additive effect on the marine algae (*Chlorella* sp.). This is because that MPs could form aggregates with nTiO₂

and promote the internalization of nTiO₂ by algae, thereby increasing the oxidative stress of algae cells [129]. Moreover, the combined toxicity of nTiO₂ and MPs to algae was concentration-dependent, and higher MP concentrations (e.g., 10 mg/L) caused stronger growth inhibition than low-concentration groups (e.g., 2.5 mg/L) [129]. Conversely, co-exposure to NPs and nZnO nanoparticles can induce the antagonistic effects on marine rotifer (e.g., *Brachionus koreanus*). NPs could adsorb nZnO and inhibit the release of Zn²⁺, thereby reducing the uptake and acute toxicity of nZnO [130]. In the coexistence of different metallic nanoparticles (e.g., nTiO₂ and nZnO), antagonistic toxicity on marine algae was observed. Specifically, the co-exposure of green algae to nTiO₂ (2 mg/L) and nZnO (1 mg/L) exhibited antagonistic toxicity. This is because that nTiO₂ and nZnO can form aggregates and thus decrease particle uptake by algae cells [131].

These sunscreen-derived particles undergo transformation in the marine environments, which further affects their combined toxicity toward marine organisms. It has been reported that sunscreen-derived nZnO can induce the oxidation of sunscreen-derived MNPs (acrylate copolymer and silicone-based cross-polymers) and fragment these MNPs into smaller particles [18]. The transformed MNPs possess higher adsorption capacity for nZnO [119], thereby may strengthen the antagonistic effects between the two particles. Moreover, in the gut of barnacle larvae, the toxicity of sunscreen-derived MNPs and metallic nanoparticles was reduced after co-exposure. This was because MNPs induced the decrease of gut acidity by damaging the intestinal wall, which reduced the dissolution of nZnO (500 µg/L) into Zn²⁺ by up to 40 % and alleviated nZnO-induced developmental inhibition [22].

5. Conclusions and Challenges

This review provides current knowledge on the occurrence and ecological risk of typical sunscreen-derived particles in marine systems. Notably, the concentrations of sunscreen-derived nanoparticles (e.g., nTiO₂ and nZnO) in coastal waters range from 14.8 to 903.1 µg/L, and are positively related to tourist activities. These particles could cause toxicity to different organism species, and the toxicity mechanisms include physical damage, oxidative stress, and metal-ion mediated toxicity. Moreover, nZnO exhibits higher toxicity than nTiO₂, which is primarily due to the dissolution and release of Zn²⁺. Species sensitivity distribution and risk assessments suggest that some coastal beaches are assessed as “high risk” for both sunscreen-derived nZnO and nTiO₂, thus highlighting more attention toward these sunscreen-derived particles. These particles undergo extensive transformation in marine environments, including mechanical fragmentation, photoaging, and biodegradation. These processes alter the toxicity of sunscreen-derived particles. However, current

investigation on the detection, environmental occurrence, toxicity, and transformation of sunscreen-derived particles is still at the early stage, and major challenges are outlined as follows:

- (1) The establishment of effective detection approaches to sunscreen-derived particles (primarily MNPs) is urgently needed. Although acrylate polymers and organosilicon compounds have been identified as typical polymer components, other polymer types in sunscreen remain largely unknown. Meanwhile, key morphological features (e.g., size, shape, and surface coating) and physicochemical properties (e.g., hydrophobicity and surface charge) of these sunscreen-derived MNPs are scarcely investigated, which limit the accurate investigation of their environmental occurrence and toxicity. Therefore, comprehensive chemical fingerprints of MNPs in sunscreens should be established using various advanced analytical techniques. Future studies should prioritize the creation of a spectral library using Py-GC/MS of common sunscreen polymer matrices (e.g., acrylates crosspolymer-6, vinylpyrrolidone (VP)/eicosene copolymer) to enable quantitative tracking of these specific MNPs in marine environment. Other advanced techniques (e.g., scanning electron microscopy-Raman spectroscopy, atomic force microscopy-based infrared spectroscopy) can also be used to obtain more morphological and chemical information of the sunscreen-derived MNPs.
- (2) Source identification of sunscreen-derived particles is important to accurately assess their environmental concentrations. Metallic nanoparticles and MNPs with high concentrations have been detected in the coastal beaches (e.g., seawater and sediment). The naturally metallic nanoparticles in the environment can interfere with the detection of sunscreen-derived metallic nanoparticles. Besides sunscreens, these particles could derive from other sources, such as shark nets and plastic debris. Source identification is important to clarify the environmental occurrence of sunscreen-derived particles (e.g., nTiO₂, nZnO, and MNPs). Current source identification mainly uses the indirect methods, such as correlation analysis with specific organic UV filters (e.g., oxybenzone). Future studies should develop the direct analytical approaches, such as the establishment of chemical fingerprint libraries of sunscreen-derived MNPs. Additionally, advanced detection techniques, such as sp-ICP-TOF-MS, could be employed to analyze the elemental composition of individual metallic nanoparticles and improve the accuracy of source tracking.
- (3) The studies on the toxicity of sunscreen-derived particles are still in their early stages. For the sunscreen-derived metallic nanoparticles, extensive studies have been conducted on the toxicity of bare

commercial metallic nanoparticles. However, sunscreen-derived metallic nanoparticles (e.g., nTiO₂) are commonly surface-coated (e.g., coated with SiO₂), which could significantly alter their chemical properties. To accurately assess their toxicity, future studies should use the surface-coated particles extracted directly from sunscreens. For the sunscreen-derived MNPs, acrylate polymers and organosilicon compounds are the main polymer types, which are significantly different from commonly used polymer types (e.g., polyethylene, polystyrene) in the reported studies. Thus, toxicological studies on the particles (metallic nanoparticles, MNPs, and other un-identified particles) directly originating from sunscreen products towards marine organisms (e.g., phytoplankton) need to be conducted.

- (4) The limitation in source identification may lead to the overestimation of environmental concentrations and the subsequent ecological risk of sunscreen-derived particles. Therefore, it is necessary to develop suitable approaches/techniques to better identify sunscreen-derived particles from other particles containing the same elements and/or from complex environmental matrices.
- (5) In addition to sunscreens, a wide range of personal care products (e.g., moisturizer, liquid foundation) also contain metallic and polymeric nanoparticles. It is unknown whether these released particles are the same as sunscreens or not. But it is ensured that these particles will enter the marine environments and pose potential threat toward marine organisms. Further identification, detection, and ecological risk assessment of particles from these personal care products are therefore strongly encouraged.

Supplementary Materials

The additional data and information can be downloaded at: <https://media.sciltp.com/articles/others/2606031420587833/GES-26030162-SM-FC-done.pdf>. Figure S1. Effects of surface coatings on the toxicity of sunscreen-derived particles. Figure S2. Transformation of sunscreen-derived particle with surface coating. Table S1. The type and function of particles in sunscreens. Table S2. Advantages and disadvantages of extraction approaches for metallic nanoparticles and MNPs from sunscreens, seawater and sediments Table S3. Advantages and disadvantages of detection techniques for sunscreen-derived metallic nanoparticles and MNPs Table S4. Occurrence of sunscreen-derived metallic nanoparticles in beach seawater. Table S5. Toxicity endpoints of marine species for TiO₂ and ZnO nanoparticles. Table S6. Fitting parameters of species sensitivity distribution (SSD) for deriving predicted no effect concentration (PNECs) of sunscreen-derived particles. Table S7. The transformation pathways of sunscreen-derived particles in marine environments. References [132–202] are cited in Supplementary Materials.

Author Contributions

J.W.: conceptualization, data collection and analysis, visualization, writing—original draft and review; R.L.: data collection and analysis, visualization, and draft review; P.W.: visualization, draft review, and funding acquisition; Z.L.: conceptualization, visualization, writing—original draft and review, and funding acquisition; Z.W.: data collection and analysis; M.T.: data collection and analysis; M.W.: draft review; J.Z.: conceptualization, visualization, writing—original draft and review, and funding acquisition. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest

The authors declare no conflict of interest.

Use of AI and AI-Assisted Technologies

No AI tools were utilized for this paper.

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