

Review

Cosmetic Ingredients as Emerging Pollutants of Environmental and Health Concern. A Mini-Review

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Abstract: Cosmetic and personal care products are used in huge quantities throughout the world; as a result of their regular use, they are continuously released into the environment in very large amounts. Many of these products are biologically active and are characterized by persistence and bioaccumulation potential, posing a threat to ecosystem and human health. On the basis of the most recent scientific literature available on this subject, this paper provides an overview of some cosmetic ingredients that are considered environmental emerging pollutants of particular concern such as UV filters, some preservatives (parabens, triclosan), and microplastics.

Keywords: cosmetics; UV filters; parabens; triclosan; microplastics; environmental pollutants

1. Introduction

According to EU Regulation 1223/2009 (article 2, 1.a), “cosmetic product means any substance or mixture intended to be placed in contact with the external parts of the human body (epidermis, hair system, nails, lips and external genital organs) or with the teeth and the mucous membranes of the oral cavity with a view exclusively or mainly to cleaning them, perfuming them, changing their appearance, protecting them, keeping them in good condition or correcting body odours” [1]. According to a widely accepted classification, cosmetics can be divided into leave-on and rinse-off products. A leave-on cosmetic is a product that for its functions is intended to stay on the skin for a rather extended period; examples are perfumes, decorative cosmetics, body and face creams, and antiperspirants. On the contrary, a rinse-off cosmetic is a product designed to be rinsed off after a short stay on the skin or mucous membranes, such as shampoos, soaps, shower gels, and toothpastes.

In the last few years, cosmetics, as well as pharmaceuticals and many other products for personal care that do not fall within cosmetic regulation (disinfectants, insect repellents, dietary supplements), have raised significant concerns as one of the most important classes of emerging pollutants because they are continually released into the aquatic environment; their ecological and environmental impact is associated with the large amounts used and with the fact that sometimes they are environmentally persistent, bioactive, and potentially able to bioaccumulate [2]. Moreover, sewage treatment plants are not always effective in removing chemicals used as cosmetic ingredients, as shown, for example, with synthetic musks [3,4], perfluoroalkyls compounds [5], some organic UV-filters [6] and microplastics [7]. Another object of concern is that some of these products can accumulate in sewage sludge during wastewater treatment and then enter the environment because of the common practice of using sludge as a fertilizer on crops [8]. Cosmetics pose the most pressing ecological problems compared to pharmaceuticals because they are used in much larger quantities and throughout the course of life and, being intended for external application, are not subjected to metabolic transformation; therefore they are introduced unaltered into the environment in large amounts during washing, showering, or bathing [9]. Since relatively little is known about the fate and the toxicity of personal care products

released into the environment, increasing attention is being placed on their occurrence, persistence, and potential threat to ecosystems and human health.

The role of some cosmetic ingredients in environmental pollution is well-known; this is the case, for example, with surfactants. As a result of their presence in a broad range of personal care products intended for cleaning purposes (body wash, shampoo, hand cleanser), huge amounts of surfactants are discharged every day into aquatic and terrestrial environments, with widely recognised ecological risk and toxic effects on plant and animal species and human health [10]. The objective of this review was instead to provide an overview of some commonly used cosmetic ingredients that have not historically been considered of ecological concern but are now being monitored because of their suspected adverse ecological effects; in particular, we focused our attention on UV filters, parabens, triclosan, and microplastics, which are being considered as emerging environmental contaminants. The stylized world map of Figure 1 shows the sampling sites cited in research papers used to compile this review and allows the reader to know at a glance where the research efforts are focused.



Figure 1. Graphic overview of the sampling locations for waters, sediments, and/or organisms cited in the References. ● = UV filters (References [5–31]); * = parabens (References [32–42]); ◆ = triclosan (References [34,42–51]); ✕ = plastic microbeads (References [52–57]).

2. UV Filters

UV-filters are chemicals that absorb or reflect ultraviolet radiation in sunlight; they are widely used in a variety of personal care products to protect the skin from UV-induced damage and sometimes to stabilize the colour and the fragrance of cosmetic formulations. In the European Union, the UV-filters approved for use in cosmetic products number 28 and are listed in Annex VI of the European Regulation on Cosmetic Products [1]. UV filters can provide protection against UV-A rays (400–320 nm), UV-B rays (320–280 nm), or both (so-called broad-spectrum filters). Currently, the active ingredients of sunscreens are classified as organic or inorganic chemical absorbers. Organic filters (formerly known as “chemical filters”) absorb radiation and then dissipate the absorbed energy through photophysical and photochemical pathways; inorganic mineral filters (once named “physical filters”) act partly by absorbing and partly reflecting and scattering UV radiation [11,12]. UV filters, which sometimes can account for up to 20% of sunscreen formulations [13], are being considered emerging pollutants due to their widespread presence in the environment. They can reach the aquatic environment directly, via wash-off from the skin surface during recreational activities (e.g., swimming, bathing) as well as indirectly through wastewater from the use of personal care products, washing clothes, and industrial

discharges; probably the most important sources of pollution are represented by the effluents from wastewater treatment plants and sewage sludge, often used as a fertilizer in agriculture [6,14].

The occurrence of UV filters is widely documented in different substrates and many different geographical locations. UV filters have been detected, for example, in surface waters such as seas, oceans and coastal waters [15–17], rivers [15,18], lakes [19,20,58], groundwater [59], and sediments [21]. Organic and inorganic UV filters will be discussed below separately because they raise distinct environmental and health issues.

2.1. Organic Filters

The distribution and the fate of organic UV filters entering the aquatic environment depend on their physico-chemical properties and their stability toward bio- and photodegradation. Some organic UV filters are characterized by stability in the aquatic environment and lipophilicity, with an organic partition coefficient in general greater than three [60]; therefore they can accumulate in sediment of body waters, a matrix with high organic carbon content, where they can act as a contaminant reserve posing high risk to benthic and sediment-dwelling organisms [22,60]. The presence of UV filters in riverine and marine sediment is widely documented in the literature. The filters most frequently identified in sediment are EHMC (ethylhexyl methoxycinnamate), OC (octocrylene), BMDM (butyl methoxydibenzoylmethane), OD-PABA (octyldimethyl-*p*-aminobenzoic acid), and benzophenone derivatives [21–23,60–63], with concentrations included in very broad ranges and, in some cases, amounting to hundreds or thousands of ng/g of dry weight. Other sun blockers (4-methylbenzylidene camphor, 4-MBC; isoamyl *p*-methoxycinnamate, IAMC; ethylhexyl salicylate, EHS; homosalate HMS), although detectable in surface waters, are not recovered in sediment, probably due to their reduced use in sunscreen formulations or to their degradation by microorganisms [64].

The occurrence of common organic UV filters has been documented in water samples collected in different countries, such as China, USA, Japan, Thailand and the North American Arctic region [15,60], Hong Kong [60], the Canary Islands [17], Switzerland [20], Korea [18], Taiwan [16], and Norway [24], to mention just the most recent investigations. Surprisingly, Tsui et al. [15] reported the occurrence of UV filters even in the Arctic region, where benzophenone-3 (BP-3), EHMC, and OC were detected at relatively low concentrations (median concentrations 16.6, 25.4, and 25.8 ng/L, respectively). The pathways by which organic UV filters arrive in the Arctic region are yet to be elucidated. Oceanic transport via ocean currents seems to be the most likely, especially for filters (e.g., BP-3 and OC) that are highly photostable towards UV irradiation, though atmospheric transport cannot be excluded. The concentrations of UV organic filters detected in these studies were comprised of a wide range of values, reaching in some cases hundreds or thousands of ng/L ([15], [25] and the literature therein). Variability in the composition profiles of UV filters was detected, and the concentrations reported depended on different factors; for example, the sampling location, differences in population densities, and the development level at each location, as well as differences in each national regulatory body for the cosmetic sector. UV filter concentrations were in general subjected to predictably large seasonal fluctuations (some filters exceeded 1000 ng/L in sea water samples collected at a popular beach in Hong Kong on hot summer days with strong UV radiation; [15]). An exception was constituted by Canary Island Gran Canaria, where no clear seasonal pattern was detected, probably due to an assiduous frequentation of its beaches during the year [17].

The Literature reports the occurrence of sunscreen organic compounds also in the water of swimming pools. The presence and concentration of UV filters in these facilities depends basically on their washing off from the skin of bathers during swimming and on the bather load. In swimming pools, UV filters occur at higher concentrations compared to other water bodies (rivers, lakes, seas), where chemical pollutants undergo high dilution, while in swimming pools the water is recycled [65]. Interestingly, [66] compared the sunscreen concentration in children's and adult's swimming pools and detected the highest concentrations of these compounds in baby pools, with amounts of sun blockers being ten times higher for the same number of users. Although the fate of UV filters in these closed

systems is not fully understood, it has been shown that they can undergo photodegradation and can react with the chlorine used to disinfect the water, with the formation of by-products being potentially harmful [67–70].

In aqueous environments, organic UV-filters can degrade by direct or indirect photolysis; the first process depends on the absorption of UV radiation by the organic compound, while the second one implies the participation of different photosensitizer agents (such as dissolved organic matter or reactive oxygen species (ROS)); the ecotoxicity of these by-products remains to be elucidated. Under UV radiation, some organic filters are also able to produce ROS [25]. Organic UV filters have been found in several aquatic organisms (marine invertebrates, fish, marine mammals, aquatic birds); often they were detected at significantly high concentrations (e.g., OC at up to 712 ng/g in the liver of the Brazilian dolphin *Pontoporia blainvillei*, [26]; octyl methoxycinnamate (OMC) at up to 256 ng/g dry weight, and OC at up to 7112 ng/g dry weight of *Mytilus* sp. collected along French coasts, [27]; EHMC at up to 701 ng/g lipids of the cormorant *Phalacrocorax* sp., [28]). Gago-Ferrero et al. [29] reported that several fish species from Iberian rivers contained detectable concentrations of lipophilic UV filters (BP-3, EHMC, 4-MBC, and OC) in the range of ng/g of dry weight. Overall these data show that some organic UV filters are able to bioaccumulate in the muscle and lipids of these organisms and are likely to enter marine food chains.

The toxicity of organic UV filters was evaluated in several aquatic organisms; some frequently used UV filters have proven to be toxic for phytoplankton species, microalgae, protozoa, and crustaceans ([25] and the literature therein). Danovaro et al. [71] demonstrated that some UV filters (EHMC, BP-3, and 4-MBC) can cause coral bleaching at very low concentrations; the results of their experiments, jointly with the estimated release of sunscreens in reef areas, strongly suggest that at least 10% of the reefs are likely to meet coral bleaching due to UV filters pollution. A number of studies also suggest that some organic UV filters possess, similarly to many other xenobiotics, endocrine-disruption capacities, in both in vitro and in vivo models. BP-3, for example, displayed a weak estrogenicity in vitro and strong anti-androgenic and weak estrogenic (but anti-estrogenic activity as well) activity in murine models [63]; moreover, adverse effects of this compound on reproduction of aquatic organisms were reported [63]. Kunz et al. [72] investigated the estrogenic activity of a panel of organic UV filters both in vitro, with a receptor-based assay, and in vivo on fish; the experiments demonstrated the potential endocrine-disrupting activity in vivo of 3-benzylidene camphor (3-BC), benzophenone-1 (BP-1), and benzophenone-2 (BP-2). In a rodent model of sexual brain differentiation, two UV filters with a known estrogenic-like activity, 4-MBC and 3-BC, were able to impair female sexual behaviour [73]. It is noteworthy that human milk samples analysed by Schlumpf et al. [74] contained UV filters in over 75% of the cases, indicating a possible exposure of the suckling neonate to these chemicals.

2.2. Inorganic Filters

The inorganic compounds approved by European Regulation as sunscreen are TiO₂ and ZnO. TiO₂ was authorized as a non-nano UV filter by the EU Cosmetic Regulation, Annex VI, while TiO₂ (nano) was introduced in this Annex by Commission Regulation (EU) 2016/1143 [75]. In May 2016, the European Commission recognized the use of ZnO as a UV filter in cosmetic products as safe, adding both in its nano and non-nano forms to Annex VI of the EU Cosmetic Regulation [76]. TiO₂ and ZnO are almost invariably present in sun blocker formulations as nanoparticles because the nanoscale improves skin retention, cosmetic acceptance for consumers, and the UV attenuation properties of these oxides when compared to their bulk counterparts [11]. The release of these compounds from cosmetics and personal care products applied on skin into the environment can occur due to immersion or abrasion with sand [77]. TiO₂ is also released into aquatic environments from sources other than sunscreens (anthropogenic input due to its use as a food ingredient, textile washing, leaching from facade coatings); wastewater treatment plants (WWTPs) remove the majority of TiO₂ present in the influent sewage, but a small amount is released into natural water bodies [30,77]. TiO₂ residues

released from sunscreen produce submicronic aggregates that remain in suspension in fresh water, while in seawater conditions (i.e., in presence of high salt concentrations) they aggregate and gradually settle, being confined to the sediment [77].

Nano TiO₂ and ZnO can undergo photocatalytic reactions when exposed to ultraviolet radiation, with the generation of ROS such as O₂⁻, ·OH, and H₂O₂ [78]; TiO₂ and ZnO extracted from commercial sunscreens can react with some chemicals and cause corrosion to paint surfaces when irradiated with UV rays [79,80]. This photoactivity can present the risk of cellular damage and environmental toxicity. To prevent the production of ROS, TiO₂ nanoparticles present in sunscreen are coated with silica and alumina and/or doped with manganese or vanadium, even though sometimes these coatings do not withstand contact with water [81].

To quantify the impact of inorganic UV filters release in coastal areas, Sánchez-Quiles and Tovar-Sánchez [31] performed laboratory experiments by suspending 1 g·L⁻¹ of a commercial sunscreen containing nano TiO₂ (77.6 mg·g⁻¹) in coastal seawater collected from Palmira Beach (Majorca Island, Spain); in 22 h, under controlled UV irradiation, 10,202 ± 606 nM of H₂O₂ was produced in seawater, i.e., 447 times the initial levels detected (22.8 ± 2.6 nM). The authors also investigated H₂O₂ and Ti⁴⁺ concentration in the water column at the same beach during 24 h of a summer day; the highest concentrations were measured at noon (278.0 ± 11.6 nM for H₂O₂ and 833.7 ± 50.1 for Ti⁴⁺). Finally, Sánchez-Quiles and Tovar-Sánchez [31] estimated the production of H₂O₂ ascribable to TiO₂ in the coastal waters of Palmira beach. Taking into account the average content of TiO₂ in commercial sunscreens (46 mg/g), the recommended amount of product that an adult should use for a typical application (36 g), the percentage of sunscreen that is removed by water during recreational activities (about 25%), and the average number of beachgoers per summer day at that location (approximately 10,000), the authors estimated a summer daily release of nano-TiO₂ of approximately 4 kg and an increment in the concentration of H₂O₂ of 270 nM/day, with the highest values at noon. These results suggest that the normal recreational activities in coastal resorts can result in the production of significant amount of H₂O₂ and consequent damage to or death of marine coastal phytoplankton; this could have reverberations on the marine food web, which relies on these microorganisms.

Studies on the toxic effects of nano-TiO₂ on algae, freshwater and marine invertebrates, and fish were reported in recent years in several papers ([82] and the literature therein, [83]). The partial information available on the physicochemical characteristics of the nanoparticles tested in different investigations and the different endpoints examined does not allow a reasonable comparison of the data obtained and thus does not permit firm conclusions to be drawn about the ecotoxicity of nano-TiO₂. Therefore, even though in some papers nano-TiO₂ has been reported to have negligible effects on various aquatic organisms [84–86], a dramatic increase of the toxicity of this compound occurs in the presence of exposition to strong sunlight or UV radiation due to the production of ROS [87–89]. As far as ZnO is concerned, its toxicity for aquatic organisms is well documented; for example, for zebrafish [90,91], marine algae [92,93], sea urchins [94], and other marine organisms [95,96], nano-ZnO was classified “extremely toxic” [95]. In contrast to TiO₂, the toxicity of nano-ZnO and the corresponding bulk particles is quite similar [83]; experimental data demonstrated that the toxic effect of ZnO is partly ascribable to the release of Zn⁺⁺ ions and partly to oxidative stress due to ROS generation [83,97].

Jeon et al. [98] evaluated the potential risk for human health of TiO₂ and ZnO nanoparticles release from commercial sunscreens into the water of an outdoor swimming pool in Seoul. The authors demonstrated that significant amounts nanoparticles were released from sunscreen-applied skin into the water during swimming activity, producing hydrogen peroxide; however, the estimated concentrations of H₂O₂ generated as a consequence of sunlight and UV irradiation in a typical day of pool activities (0.011–0.139 μM) were lower than those required to cause adverse effects on human health.

3. Parabens

Parabens are a class of preservatives that have been used for nearly a century for their antimicrobial properties in a wide range of products, such as cosmetics, foodstuffs, and pharmaceuticals; chemically they are esters of the *para*-hydroxybenzoic acid, with alkyl (methyl, ethyl, propyl, isopropyl, butyl, isobutyl, pentyl, heptyl) or aryl (benzyl, phenyl) substituents [99]. Although some of these compounds occur naturally since they are synthesized by bacteria or plants [100,101], all commercially available parabens are produced synthetically. In the European Union the use of parabens in cosmetics is regulated by the European Regulation on Cosmetic Products (2009) [1]; they are listed in Annex V and are allowed at a maximum concentration of 0.4% (w/w) for single ester and of 0.8% (w/w), expressed as *p*-hydroxybenzoic acid, for paraben mixtures. It is worth mentioning that the European Union has recently placed some restrictions on the parabens allowed in cosmetic formulations; in particular Regulation (EU) No 358/2014 recently amended Annex V of Regulation (EU) No 1223/2009 to prohibit the use of isopropylparaben, isobutylparaben, phenylparaben, benzylparaben, and pentylparaben in cosmetics [102]. Moreover, Regulation (EU) No 1004/2014 lowered the maximum concentration allowed for propylparaben and butylparaben, and prohibited their use in products for children [103].

In spite of these recent restrictions, parabens are still extensively employed in cosmetics and personal care products because of their broad spectrum of activity against yeasts, molds, and bacteria and their chemical stability, low toxicity, and low cost [99].

Parabens can be detected in air, dust, soil, and water [99]. They can be discharged in the environment from their production factories, but more importantly they are continuously released at relatively high levels into urban and hospital wastewaters, as a result of the wide use of personal care products, pharmaceuticals, and household chemicals containing them. In raw wastewaters, parabens can reach values up to 30,000 ng/L for methylparaben and 20,000 ng/L for propylparaben [104]. Parabens are present almost exclusively in the aqueous phase, due to their moderate water solubility (e.g., 2500 mg/L for methylparaben, 885 mg/L for ethylparaben; [104]); when the occurrence of five parabens was assessed in influent and effluent samples from three Tunisian wastewater treatment plants, they were detected in water at concentrations of mg/L, whereas their concentrations in suspended matter were some orders of magnitude lower ($\mu\text{g/L}$; [32]). Wastewater treatment plants effectively remove most parabens present in the aqueous phase, with an average removal rate of >90% [104,105]. In these plants, parabens, can adhere to the sewage sludge or can be degraded; in particular, they can undergo fast biodegradation, with the production of *p*-hydroxybenzoic acid as a main degradation product, or can react easily with free chlorine, forming several chlorinated by-products [106]. Halogenated parabens are removed as efficiently as their parent compounds in wastewater treatment plants, although they require more time to be degraded [105]. These halogenated derivatives can also be generated when paraben-containing cosmetics are mixed with chlorinated tap water at home; moreover, if traces of bromide are present in tap water, brominated parabens are preferentially formed [106]. Unfortunately, little is known about the potential risk of these halogenated derivatives for human health [104].

Despite their efficient removal in wastewater treatment plants, parabens are still detected in surface waters, especially rivers [33–36]. Methylparaben and propylparaben, the most common parabens present in cosmetics, are also the parabens most frequently detected in surface waters [99], with a wide range of concentrations that reach the highest values in Chinese rivers (1062 ng/L for methylparaben and 3142 ng/L for propylparaben) [33]). To the best of our knowledge there are no specific studies regarding the presence of parabens in marine and ocean waters; however, the occurrence of these preservatives and their metabolites (especially *para*-hydroxybenzoic acid) is well documented in several animals living in the sea or in coastal areas. Paraben occurrence was in fact reported in fish tissues [37–39], in marine mammals [40], and in the tissues of marine birds and their eggs [39]. The presence of parabens and their metabolite, *p*-hydroxybenzoic acid, even in animals from remote marine locations, such as polar bears from Alaska [40] and albatrosses from Midway

Atoll (Northwestern Pacific Ocean) [39], suggest that these compounds are ubiquitous in the oceanic environment. The occurrence of parabens in drinking water was investigated in a limited number of studies [104]. Generally parabens were not observed or were detected at very low concentrations in tap water; however, a recent investigation recorded the presence of parabens at concentrations of ng/L in bottled water [41].

Parabens have been detected in human urine, serum, adipose tissue, milk, amniotic fluid and placental tissue [107–113], and in human breast cancer tissues [114,115]. In humans, dermal exposure to paraben-containing products is important for their absorption because some parabens penetrate the human skin [116]; the systemic absorption of parabens after environmental exposure has also been confirmed, although it seems to be a less important paraben source [38]. Oral ingestion seems to be less important, as orally ingested parabens are metabolized by esterases to *p*-hydroxybenzoic acid [116].

For a long time, parabens were considered to have a very low toxicity and an excellent safety record; however, recently, concerns have been raised about their harmlessness, as parabens display endocrine-disrupting activity both in vitro and in vivo, and they have been associated with alterations of the reproductive system of male experimental animals [116]. In in vitro investigations, parabens exhibited a weak estrogenic activity, with a binding affinity for the estrogen receptors about five orders of magnitude lower than that of diethylstilboestrol [117]. Studies on the potential endocrine disruption of parabens on aquatic wildlife demonstrated that these compounds are able to interfere with the vitellogenin plasma concentration in some organisms, such as rainbow trout and Japanese medaka fish, although at concentrations largely exceeding the maximum concentrations detected in surface waters [99]. As far as the human species is concerned, several studies have been published claiming a link between the endocrine-disrupting activity of parabens and breast cancer [114,118]. These studies were subsequently rejected by a number of scientists and international health authorities, which concluded that there is no scientific evidence linking cosmetics or parabens with human breast cancer [119–122]. However, some recent studies seem to suggest a more cautious attitude. Pan et al. [123] described a potential synergy between parabens and epidermal growth factor, suggesting that parabens can be active at concentrations lower than those previously considered toxicologically relevant. Similarly, a recent paper reported that in immature Sprague-Dawley rats, after intragastric administration of paraben doses close to the acceptable daily intake, the in vivo estrogenicity of parabens is not as low as established by in vitro experiments [124].

Overall, current scientific knowledge is inadequate to demonstrate a clear correlation between parabens and human breast cancer risk, and further research would be necessary to definitively exclude this association; therefore, this controversy is still ongoing. In the light of current knowledge, it seems reasonable not to underestimate the possible consequences for human health of the continuous introduction of parabens into the environment.

4. Triclosan

Triclosan (TCS, 5-chloro-2-(2,4-dichlorophenoxy)phenol) is a lipid-soluble, broad-spectrum, antimicrobial agent, allowed as a preservative in personal care products such as hand soaps, shampoos, detergents, toothpastes, sunscreen, and deodorants, where it can be used at concentrations up to 0.3% (Annex V of European Regulation on Cosmetic Products) [1]. Due to its antibacterial and antifungal properties, TCS is also widely employed as an antiseptic, in medical devices, in household items, and as an additive in packaging, textiles, and functional clothing [125]. The most important pollution source of TCS is domestic sewage, where this compound is released with the rinsing of products containing it; the extensive use, the large amounts emitted and its incomplete removal in sewage treatment plants lead to the often considerable presence of this compound in the environment, with concentrations detected ranging from nanograms to micrograms per liter in sediments and waters [43,44]. TCS is found ubiquitously in the aquatic environment, where it partitions between sediment and water and can be thus detected in both phases [43,45], with a preferential accumulation in sediments, due to its lipophilicity. TCS is among the top 10 most commonly detected organic wastewater

compounds for frequency and concentration [2]. Its presence is ubiquitous; it has been found in surface water throughout the United States [46–48], the United Kingdom [34], South Korea [49], and China [126,127]. The occurrence and the concentration of TCS were recently examined in the Parisian sewer network [42], and high levels were found in wastewater (2140–5260 ng·L⁻¹). The results of this study were extrapolated at the national scale to give a national mass load of 18.8–22.2 tons·year⁻¹. In a study performed on 13 sites in Japanese rivers contaminated by domestic wastewater, sewage treatment plant effluent, or industrial wastewater, TCS was detected ubiquitously with concentrations up to 177 ng·L⁻¹ and little difference in concentration between sites with and without a sewerage service [36]. TCS presence has been also documented in terrestrial environments, due to the application of sewage sludge as fertilizer on farm land [128]. TCS persists in the environment but, during the wastewater treatment process, can also be converted into chlorinated derivatives, which are more toxic and more persistent than their parent compound [44]. Due to its stability and lipophilicity, TCS has a potential for bioaccumulation in algae [50], plants [129], and animals such as earthworms [130], marine mussels [51], snails [131], amphibian larvae [132], fish [133], and marine mammals [134]; moreover, methyl triclosan, an environmental transformation product of TCS, has been detected in fish from various lakes in Switzerland [135]. TCS present in the aquatic environment causes adverse ecological effects: it exhibits toxicity to algae species [136], alters benthic bacterial communities composition (fostering cyanobacteria over algae) [137], exhibits teratogenic responses and mortality in the embryos and larvae of zebrafish [138], and exhibits endocrine disruption in fish [139]. Epidemiological studies reported the presence of TCS in a wide range of concentrations in human body fluids such as urine, blood, and breast milk [44]. According to some researchers, the presence of TCS in human fluids is mostly correlated with the use of TCS-containing personal care products [140]; other authors believe that oral absorption can be significant, considering that TCS has been detected in drinking water [141,142]. Exposure to TCS can produce negative effects on human health, including thyroid function impairment, endocrine disruption, oxidative stress, and liver carcinogenesis ([44] and the literature therein). All data available on the environmental presence of TCS and its by-products and its health implications suggest that this compound should be considered a priority pollutant [143].

5. Plastic Microbeads

Plastic pollution of the marine environment represents a growing environmental concern, addressed at both macroplastic and microplastic debris; microplastic is classified as being material <5 mm, according to a scheme proposed by Moore [144]. The majority of small plastic particles in the seas come from the fragmentation of larger items; however, there is growing evidence that microplastic also enters the marine environment directly from a variety of sources, including cosmetics, clothing, and industrial processes. Plastic microbeads are present as abrasive scrubbers in a number of personal care and cosmetic products such as hand-cleansers, toothpaste, face scrubs, bubblebath, shampoos, and soaps [145,146], where they replace natural exfoliating materials previously utilized (pumice, oatmeal, apricot husks). In addition to the function of dead skin removal and deep cleansing, plastic microbeads can also play a decorative role in personal care products. Around 93% of the microbeads used in personal care products are made of polyethylene [147], but sometimes the material that they are made from is polypropylene, nylon, polyethylene terephthalate, or polymethyl methacrylate [148]. The microplastics present in cosmetics are too small to be trapped in sewage treatment plants, so they enter waterways via domestic drainage systems and are transported to seas and oceans [52,149], although some authors believe that the current treatment processes are effective for the removal of microplastic contaminants in wastewater treatment plants [53].

Although there is a large amount of literature that documents the presence of microplastics in the marine environment, organisms, and sediments [54,55,146,150], not as many works have been made to quantify the emission of microplastics from personal care products in different geographical areas. Gouin et al. [151] estimated that the per capita consumption of microplastics used in personal care products for the U.S. population is approximately 2.4 mg·person⁻¹·day⁻¹, so that the U.S. population

is emitting 263 tons·year⁻¹ of polyethylene microplastic. Quantification of cosmetic sources of plastic microbeads was attempted by Gouin et al. [147] on the basis of the results of a survey conducted in the European Union countries Norway and Switzerland by Cosmetics Europe, the European personal care association that represents more than 4000 personal care product manufacturers. All members of Cosmetics Europe were requested to complete a survey on the use of plastic microbeads in their cosmetic products for the year 2012. The survey results reported a total amount of 4360 tons of plastic microbeads used across the European Union market, including Norway and Switzerland. Polyethylene microbeads were reported to be the principal type of plastic material used as a scrubber in detergents (4073 tons), while the remaining 287 tons were made up of miscellaneous polymers. Some authors characterised the microbeads present in cosmetic products with respect to their shapes and size range [145,148]. In their recent study [148] didn't just characterize the plastic microbeads contained in six brands of facial scrubs present in supermarkets in the United Kingdom, but also investigated their capacity to accumulate and transport chemicals by using a mixture of phenanthrene (Phe) and dichlorodiphenyltrichloroethane (DDT) in seawater. The numbers of total particles in each product package varied greatly, ranging between 18,906 and 919 microparticles/mL; they also showed a wide size range (mean diameters between 327 and 164 µm). The authors of this study estimated that the quantity of microbeads released in a single use of these cosmetics could range between 4594 and 94,500. The results of adsorption experiments conducted with mixtures of ³H-Phe and ¹⁴C-DDT in seawater showed that PE microparticles extracted from facial scrubs were able to hold these contaminants onto their surface, with sorption capacity in all cases being significantly higher for DDT; "rough" microbeads were more efficient than "smooth" ones, probably due to the increased surface area. Other studies confirmed that microplastics can act as a transport medium for chemical pollutants in the marine environment [152,153].

Once in the environment, microbeads made of high-density plastics (polyester, polyvinyl chloride) settle out of the water column and accumulate in the sediment, while low-density microplastics (polyethylene, polystyrene) float on the sea surface [150]. Since there is no way of effectively removing microplastic contaminants from the marine environment, and they are highly resistant to degradation, microparticles can be ingested by aquatic organisms. Ingestion and accumulation of microplastics has been well documented in different marine organisms, including copepods [146], bivalves [52,54,154,155], fish [56], and seabirds [57].

Microplastics negatively impact upon marine biota. Many marine organisms may adsorb microplastics on their surfaces and may ingest small plastic fragments, mistaking them for their natural food source [156]; when exposed to polystyrene microparticles, some organisms, like copepods, are able to ingest them via filter-feeding and then egest them within hours in faecal pellets [157]. However, organisms can also be at risk from starvation or intestinal blockage, impairment of reproduction and feeding ability, and reduced growth rates consequent to microplastic ingestion [149,158]. A recent study [159] provided evidence that microplastics induce feeding modification and reproductive disruption in oysters; oyster experimentally exposed to polystyrene microspheres for two months during a reproductive cycle showed, in particular, significant decrease in oocyte number, diameter, and sperm velocity. Moreover, there is the potential for the microplastics to accumulate at higher levels of the food chain [156,160]. Another concern is the potential of microplastics to aid the delivery (after ingestion) of POPs (persistent organic pollutants); for example, polychlorinated biphenyls, polycyclic aromatic hydrocarbons, organochlorine pesticides, and alkylphenols, added during plastics manufacture or, more often, adsorbed and concentrated from the surrounding seawater [153,161,162], which can be transferred along the food chain and can harm fish and other aquatic organisms.

Considering the increasing concern expressed by the scientific community over microplastic pollution of the marine environment, several European countries (Belgium, Netherlands, Austria, and Sweden) have issued a joint call to outlaw microplastics in cosmetic formulations [163]; Cosmetics Europe [164] has recommended its membership to discontinue, in wash-off cosmetic products placed on the market as of 2020, the use of synthetic, solid, plastic particles used for exfoliating and cleansing

that are non-biodegradable in the marine environment. In December 2015, the U.S. President signed a bill that will phase out the manufacturing of cosmetics containing plastic microbeads by 1 July 2017 and their sale by 1 July 2019 [165]. In recent times, the major cosmetic companies have made commitments to phase out the use of microbeads in their products and are promoting natural alternatives such as pumice, walnut and coconut shells, ground palm nut, bamboo powder, apricot kernel shell, biodegradable hydrogenated oils waxes like jojoba beads, and diatomaceous earth.

6. Conclusions

The number of emerging contaminants released in the environment as a consequence of human activities is increasing day by day and reflects the growing consumption of a wide range of products, including cosmetics and personal care products. Chemical compounds that compose cosmetic formulations number in the several thousands, and the annual production and consumption of personal care products exceeds thousands of tons. The hazard of the continuous release of these huge amounts of chemicals into waters should not be underestimated. The environmental fate of these products is largely unknown, and, if in some cases they are removed in wastewater treatment plants, in other cases, they can escape conventional treatment processes, persist in the environment at unexpected levels, undergo bioaccumulation, and even react with other pollutants to originate new unpredictable contaminants.

Banning the products responsible for these problems is an impracticable option, except in particular circumstances (for instance, the use of sunscreen is banned in some marine ecoparks in Mexico [71]). Addressing this issue realistically requires different approaches and strategies. To some extent, our increased awareness of the pollution potential of these products is the result of the advanced technologies of analytical chemistry. Therefore, the development of improved extraction and analytical methods would allow a more comprehensive and accurate evaluation of environmental pollutants in complex matrices. On the other hand, further studies on the acute and chronic toxicity of these contaminants should be conducted to allow a more precise assessment of their actual ecological and health risk. Finally, information about the environmental impact of cosmetics on their packaging could encourage consumers to employ a more responsible and informed use of these products.

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