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An Insight into Ingredients of Toxicological Interest in Personal Care Products and A Small–Scale Sampling Survey of the Greek Market: Delineating a Potential Contamination Source for Water Resources

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Abstract: Wastewater is not a waste but a valuable resource that should be reused. Nevertheless, it should be devoid of physical, chemical, and microbiological parameters that can harm the consumer. Along with the multitude of possible pollutants found in wastewater treatment plants (WWTPs), emerging pollutants, such as Personal Care Products (PCPs), have arisen. The present research examines some of the main ingredients commonly found in PCPs, focusing on their toxicological profile on their occurrence in WWTPs influents and effluents worldwide and on their persistence and biodegradability. A small-scale market sampling of PCPs was performed in Athens, Greece, in June 2019, and their individual ingredients were recorded, coded according to their main activity, scanned for the presence of ingredients of important toxicological profile, and finally analyzed for the presence of other candidates of toxicological interest. Results show that some ingredients of concern (i.e., parabens and triclosan) are a decreasing trend. On the other hand, information on the presence of synthetic musks and perfume synthesis is scarce and encumbered by brand protection. Finally, UV filters are numerous, and they are used in various combinations, while other ingredients of toxicological interest are also present. Since the reclaimed water may well be used to cover irrigation needs in Greek areas with water deficiency or to enrich bodies of surface water, it is important to know what PCP ingredients are on the rise in the market, to monitor their presence in WWTPs influents and effluents and to extend research on their environmental fate and behavior.

Keywords: water quality; water pollutants; personal care products (PCPs); wastewater treatment plants (WWTPs); wastewater reuse; biodegradability; water reclamation

1. Introduction

Wastewater is not a waste. It is an essential part of the biosphere and a critical parameter of life. In the context of a circular economy and recharging of bodies of surface- or groundwater, wastewater is considered an essential resource after proper treatment. This task is accomplished in wastewater treatment plants (WWTPs) through a series of specialized treatments (primary, secondary, tertiary, etc.) [1]. The necessity of wastewater treatment is substantiated in [2], which is enforced in Greek law through [3] and its updates. Nowadays the majority of the population in Greece (9,643,700 people) has access to sanitation through 260 wastewater treatment plants (data of 2011).

The Directive [2] has been in force for 25 years; during these years, many changes have occurred: Depletion of natural resources, palpable manifestations of climate change, as well as novel environmental threats and pressures [4]. As such, the directive is now in the process of re-evaluation [4]. Throughout these 25 years, emerging pollutants such as personal care products (PCPs) have been added to the bulk of contaminants that should be treated in a WWTP. The short- and long-term effects of these pollutants on humans and other organisms are still mostly unknown. Their maximum concentration below effect level is in most cases still not defined. As such, their continuous emission and their presence in influents of WWTP, even in small quantities, cause concern [5]. Global water shortage and water quality deterioration are expected to increase in the following years, aided by climate change, thus amending policies and management plans of freshwater resources [6]. In this context, the present research focuses on PCPs, which comprise a vast number of market commodities that are used by millions of people for their personal hygiene needs and their beautification [7]. Most PCPs meet the definitions of cosmetics, while some are defined as both cosmetics and drugs (e.g., anti-dandruff shampoos). PCPs also comprise wet or dry hand tissues, sanitary towels, and baby-wipes [7]. Most PCPs are consumed through the dermal route, thus some part is washed off, they are used and misused extensively, and they may be disposed of improperly, contributing to pollution of water bodies [8]. Some studies have incriminated certain PCPs ingredients for negative effects on the health of humans and of other living organisms. Furthermore, due to their lipophilic nature, some of these ingredients adsorb particles and sediment and bioaccumulate along the trophic chain [5]. Much less is known for their fate and behavior in the environment and the degree of their catabolism in WWTPs. The aim of the present research is to show a comprehensive human hazard assessment of the most important ingredients of toxicological interest found in PCPs, focusing on their occurrence in WWTPs, since the recovered wastewater is commonly used to recharge water bodies. The identification of such substances in wastewater is very critical since typical WWTP processes usually do not remove them, and thus other solutions should be foreseen if they are present in order to reclaim and circulate the recovered water safely. An investigation of fundamentally distinct PCPs that are found in the Greek market (2019) was also performed in order to reveal present trends of these ingredients. Some useful conclusions are drawn regarding these polluting sources of WWTP influents, which may render effluents problematic for reuse.

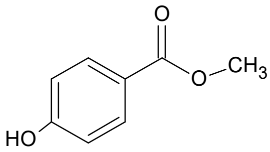
2. Materials and Methods

2.1. Ingredients of Toxicological Interest Commonly Found in PCPs

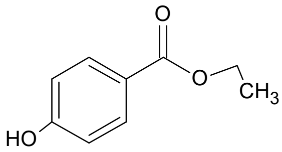
2.1.1. Parabens

Parabens (PBs) are esters of parahydroxybenzoic acid (Figure 1) and are widely used as preservatives due to their antimicrobial and antifungal activities. Despite their long and extensive use, concerns have arisen due to indications of endocrine disruption [9] in a number of in vitro and in vivo studies. More analytically, PBs tested positive in vitro for estrogenic activity [10], they induced the development of human MCF-7 breast cancer cells, and they altered the expression of estrogen-dependent genes [11–14]. Furthermore, in vivo studies in rodents showed an increase in uterine weight of immature female mice after exposure to isobutylparaben [12] and a testosterone decrease and/or other reproductive system alterations in male rats [15–17]. Epidemiological studies in humans revealed a statistically significant correlation between BuPB levels in urine and sperm DNA damage [18]. Furthermore, there was a statistically significant inverse correlation of PB levels in urine and thyroid hormones' levels in serum, which was more prominent in females [19].

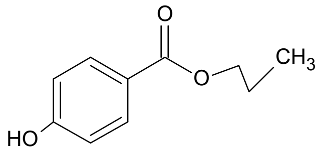
The environmental threats arising from the presence of PBs in WWTPs were noticed quite early (1996) [20]. Nevertheless, they are easily biodegradable in aerobic conditions and as such, can be effortlessly degraded in secondary biological treatment [21], reaching removal rates of up to 96.1% [22] at conventional WWTPs (Table 1). When advanced oxidation processes (AOPs) are applied to the effluents, removal rate may reach up to 99.9% [23].



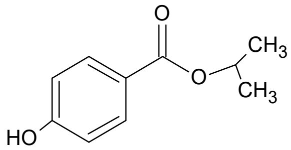
(**a**) methylparaben



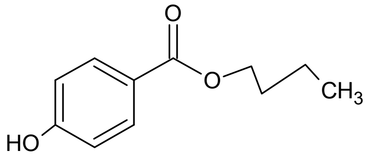
(**b**) ethylparaben



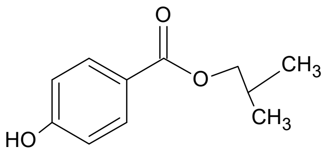
(**c**) propylparaben



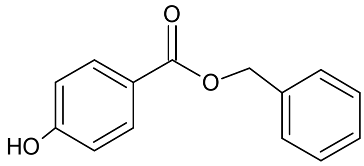
(**d**) isopropylparaben (banned in EU cosmetics)



(**e**) butylparaben



(**f**) isobutylparaben (banned in EU cosmetics)



(**g**) benzylparaben (banned in EU cosmetics)

Figure 1. Chemical structure of most common parabens (**a**–**g**) (PBs) used in cosmetics (drawn via ACD/Chemsketch).

Table 1. Occurrence of PBs in influents and effluents of wastewater treatment plants (WWTPs) worldwide.

Region	Substrate	MePB ng L^{-1}	EtPB ng L^{-1}	PrPB ng L^{-1}	BuPB ng L^{-1}	Reference
Sweden	Effluent	n.d.–300	<100–200	<100–300	-	[20]
Ontario, Canada	Influent Effluent	100–1470 20–30	20–270 <10	200–2430 <10–40	20–260 <10–10	[24]
Switzerland	Influent Effluent	65–9880 4.6–423	2.2–719 <0.3–17	43–1540 <0.5–28	9.7–864 <0.2–12	[22]
Wales, United Kingdom	Influent Effluent	661–30,688 <3–155	192–3312 <0.6–69	<2–8286 <1–95	<2–1595 <1–2	[25]
Galicia, Spain	Influent Effluent	1926–5138 <n.d.–1.5	452–549 <n.d.	1147–1302 <n.d.	150–181 <n.d.–3.6	[26]
Northwest Spain	Influent Effluent	290–10,000 6.1–50	250–1600 n.d–9.8	520–2800 n.d.–21	39–270 n.d.	[21]
Valencia, Spain	Influent Effluent	334 (av.) 11 (av.)	n.d. 72 (av.)	163 (av.) n.d.	15 (av.) n.d.	[27]
Pearl River Delta, China	Influent Effluent	1002–1140 5.1–7.6	156.2–166.2 0.9–1	499.7–579.8 7.2–10.6	14.9–26.8 0.3	[28]
Beijing, China	Influent Effluent	211–1002 2.14–15	32.9–220 0.08–0.70	287–605 0.04–0.99	16.6–35.5 0.02–0.12	[23]
New York, USA	Influent Effluent	18.3–320 0.14–1.73	0.50–66.80 0.14–1.47	8.19–113 0.14–490	3.15–112 0.14–3.55	[29]
Saidpur, Beur, Coimbatore, Udupi, Manipal, India	Influent Effluent	51–267 4.4–41	11.6–58.4 1.9–9.8	38.2–583 2.8–19.3	4.1–10.5 n.d.–2.9	[30]

n.d.: Not detected, av: Average. MePB: Methylparaben, EtPB: Ethylparaben, PrPB: Propylparaben, BuPB: Butylparaben.

2.1.2. Triclosan

Triclosan is a broad-spectrum antimicrobial agent (Figure 2) that can be found in numerous PCPs such as soaps, shampoos, deodorants, cosmetic creams, toothpaste, and mouthwash [31,32]. Its mode of action involves inhibition of lipid acids' biosynthesis and subsequent cellular membrane destabilization [33]. In 1998, triclosan worldwide annual production was approximately 1500 tn, out of which 350 tn were produced in the EU. Triclosan quantities used in the EU were approximately 450 tn in 2006 [34]. In the same countries, it has been estimated that 85% of triclosan quantities were incorporated in PCPs, while only 5% were used in fabrics and 10% in plastics [35].

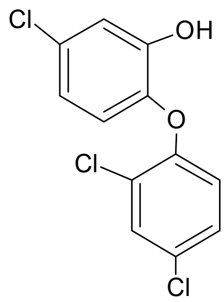


Figure 2. Chemical structure of triclosan (drawn via ACD/Chemsketch).

Triclosan is highly toxic to organisms such as algae and invertebrates [36], a characteristic which is not relevant for human toxicology, nevertheless it is highly relevant from an ecotoxicological point of view. Furthermore, in long-term exposure, algae have been proven to be the most susceptible trophic level, and their development was negatively affected even at concentrations as low as 1 μg L^{-1} [37].

Regarding mammalian toxicology, triclosan showed both anti-androgenic and anti-estrogenic action in MCF-7 cells in vitro [38]. In vivo experiments in higher vertebrates showed anti-androgenic effects on male Wistar rats [39], quicker sexual maturation in female rats [40], or increased uterine weight in immature rats [41]. Triclosan also reduced T4 (a thyroid hormone) levels in rat serum [42], and there was a concomitant negative effect both on thyroid hormones in dams and on sexual maturation of their progeny [43]. According to a recent epidemiological study [44], maternal urinary levels of triclosan concentrations during pregnancy were inversely correlated with infants' birth weight, length, head circumference, and gestational age. In addition, triclosan (and parabens) levels in urine of children aged 6–12 years old were positively associated with aeroallergen sensitization and manifestation of atopic asthma [45].

Triclosan is less readily biodegradable than PBs in WWTPs since it is hydrophobic, not particularly volatile, and hydrolytically stable [46]. There are high discrepancies between the removal success rates of triclosan in WWTPs, which are between approximately 17% and 98% (Table 2). According to [46] and [31], triclosan is firstly sorbed onto the suspended solids of activated sludge and afterward, it is directly biodegraded. An in situ experiment in Psitalleia WWTP in Athens showed that 45% of influent triclosan was adsorbed on sewage sludge, 46% was degraded, and the remaining 5% was detected in the effluent [47].

Table 2. Occurrence of triclosan in influents and effluents of wastewater treatment plants (WWTPs) worldwide.

Region	Substrate	Concentration ng L^{-1}	Reference
Agrinio, Greece	Influent Effluent	65.3–303 24.9–87	[48]
Ioannina, Ioannina hospital, Arta, Preveza, Agrinio, Grevena, Kozani, Veroia, Greece	Influent Effluent	n.d.–1742.5 n.d.–452.1	[49]
Athens, Chalkida, Mytilene, Herakleio, Nafplio, (also from an airport, a university and a hospital), Greece	Influent Effluent	170–23,900 <130–6880	[47]
Athens, Greece	Influent Effluent	328–1096 31–211	[50]
Dortmund Germany	Influent Effluent	1200 (av.) 51 (av.)	[31]
Colombus, Glendale, Loveland, West Union I, West Union II, USA (OH)	Influent Effluent	3830–16,600 240–2700	[51]
Tokyo (5 individual WWTPs), Japan	Influent Effluent	219–1020 26.6–330	[52]
California, USA	Influent Effluent	180–4400 n.d.–160	[53]
Jeonju, S. Korea	Influent Effluent	280–745 n.d.–29.6	[54]

n.d.: Not detected, av: Average.

2.1.3. Synthetic Musks

Ingredients used for perfume synthesis in PCPs are brand-protected, and they do not have to be explicitly written on the PCP container. The ingredients are simply stated as “parfum” and they usually contain synthetic musks. These musks add pleasant odor to perfumes, soaps, shampoos, and cosmetic creams and they are also used in other house commodities [55]. They belong to the categories of nitro-, polycyclic-, macrocyclic- or alicyclic musks (Table 3). Most nitro musks are outphased while alicyclic musks are supposed to be more environmentally friendly [56].

Musks are lipophilic, and they may accumulate in adipose tissue and breast milk in mammals [57]. A number of toxicological and ecotoxicological findings have been attributed to nitro-musks; according to the concise review of [57], tumorigenesis and cancer propagation may be facilitated via non-genotoxic mechanisms of nitro-musks. These compounds have also been found to be endocrine disruptors in in vitro models, however, there is still the question of whether the concentrations tested were environmentally relevant.

The polycyclic musk tonalide (AHTN) has shown estrogenic activity in MCF-7 cells [58], anti-estrogenic activity in 293HEK cells [59], and both tonalide and galaxolide have inhibited progesterone and cortisol production in H295R cells [60]. On the other hand, galaxolide did not show estrogenic activity in MCF-7 cells [58] but it did show anti-estrogenic activity in 293HEK cells [59]. According to [61], some compounds may act both as agonists and as antagonists and this depends on the cell line and the type of estrogen receptor tested; these compounds are named “selective estrogen receptor modulators” and tonalide may well be one of them. The “fourth generation of musks” [62] (cyclomusk, helvetolide, romandolide) are not as well studied but may be a promising alternative in the fragrance industry [56].

Table 3. Categories and chemical formulas of most commonly used synthetic musks (drawn via ACD/Chemsketch).

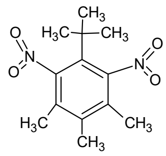
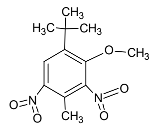
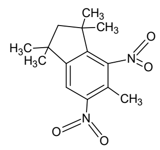
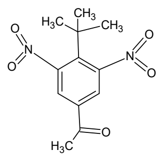
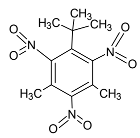
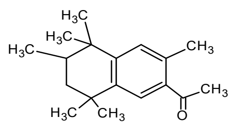
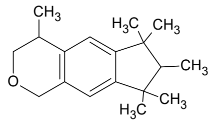
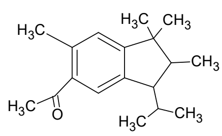
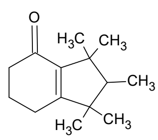
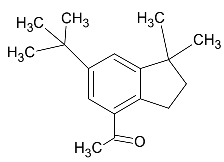
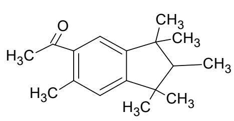
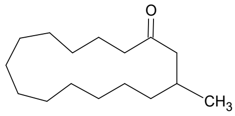
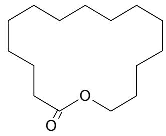
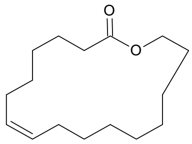
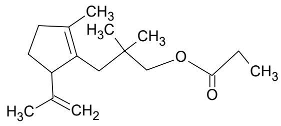
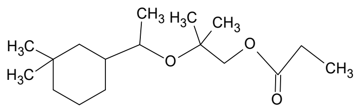
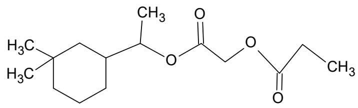
Category	Chemical Name	Chemical Formula
Nitro-musks	musk tibetene, MT	
	musk ambrette, MA	
	musk moskene, MM	
	musk ketone, MK	
	musk xylene, MX	
Polycyclic musks	tonalide, AHTN	
	galaxolide, HHCB	
	traseolide, ATII	
	cashmeran, DPMI	
	celestolide, ADBI	
	phantolide, AHMI	

Table 3. *Cont.*

Category	Chemical Name	Chemical Formula
Macrocyclic musks	muscone	
	exaltolide	
	ambrettolide	
Alicyclic musks	cyclomusk	
	helvetolide	
	romandolide	

Due to their lipophilic nature, synthetic musks are not easily biodegradable, and they tend to accumulate [61,63]. These characteristics enhance their persistence in WWTP (Table 4), which were not able to eliminate musks to a high extent [64]. To make matters worse, it has been estimated that 77% of skin applied HHCB [65], and 69.6% of skin applied AHTN [66] end up in sewage.

Table 4. Occurrence of synthetic musks in influents and effluents of WWTPs worldwide.

Region	Substrate	HHCB ng L^{-1}	AHTN ng L^{-1}	MX ng L^{-1}	MK ng L^{-1}	Reference
Catalonia, Spain	Influent Effluent	818–45,091 1.5–900	852–49,904 2–75,555	n.d.–632 n.d	n.d.–4110 n.d.–465	[64]
Texas, USA	Influent Effluent	4772–13,399 2989–10,525	509–2337 328–1754	n.d. n.d.	n.d.–812 n.d.–177	[67]
Beijing, China	Influent Effluent	30.9–3039 30.4–685.6	28.6–1486.1 14.26–195.3	<1.2–22.95 n.d.	52.25–165.8 22.77–91.6	[68]
Shanghai, China	Influent Effluent	1478–2214 181.1–242.2	553.5–1037.7 46.7–88.3	63–164 n.d.–6.5	74.5–161.3 6.7–18.5	[69]
Mittlere, Switzerland	Influent Effluent	2290–6810 570–1030	1130–2000 190–500	-	-	[70]
Ontario, Canada	Influent Effluent	246.7–567.5 138.8–234	47.2–136.7 24.7–62.8	10.8–16 4.3–7.6	12.5–15.5 8.3–8.5	[71]
Utrecht, Netherlands	Influent Effluent	1420–4300 1250–2220	540–1760 420–1200	-	-	[72]

n.d.: Not detected, av: Average, HHCB: Galaxolide, AHTN: Tonalide, MX: Musk xylene, MK: Musk ketone. *HHCB AHTN: Polycyclic musks, MX MK: Nitro-musks.

2.1.4. UV Filters

UV filters are extremely popular ingredients in PCPs since they protect from photo-induced skin damage and aging (Table 5). They belong to various chemical categories, and they can roughly be divided into organic and inorganic (ZnO and TiO_2) filters. In the EU, 25 organic and 2 inorganic filters are available in the market [73].

Table 5. Categories and chemical formulas of most commonly used UV filters (drawn via ACD/Chemsketch).

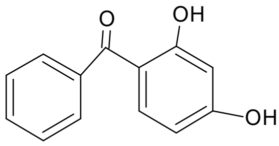
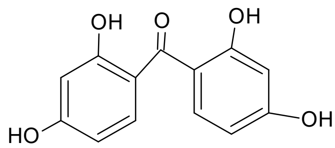
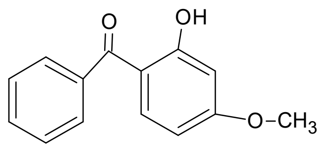
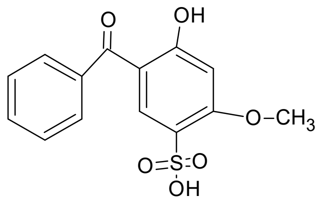
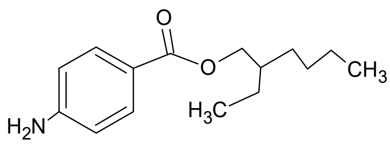
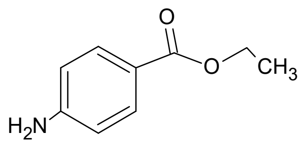
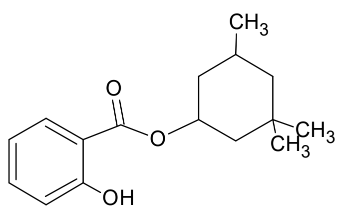
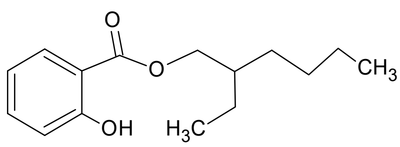
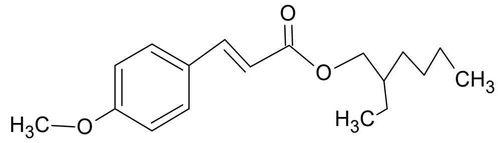
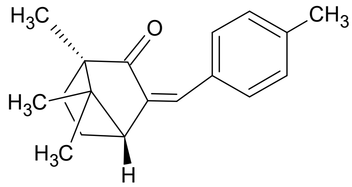
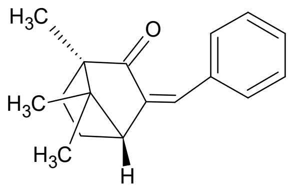
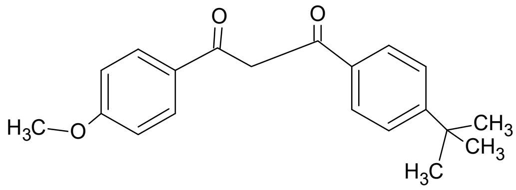
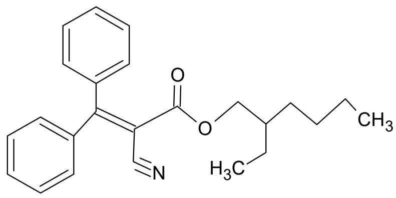
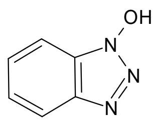
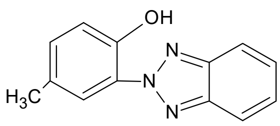
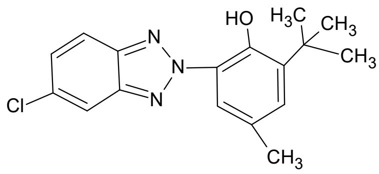
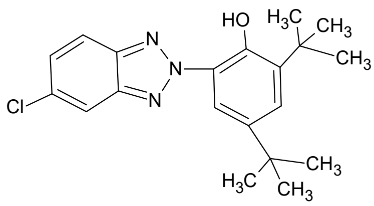
Category	Chemical Name	Chemical Formula
	benzophenone-1, BP1	
	benzophenone-2, BP2	
Benzophenones	benzophenone-3, BP3	
	benzophenone-4, BP4	
p-aminobenzoic acid derivatives	ethylhexyl dimethyl PABA, OD- PABA	
	ethyl ester PABA, Et-PABA	
salicylates	homosalate, HMS	
	octisalate, EHS, OS	

Table 5. *Cont.*

Category	Chemical Name	Chemical Formula
cinnamates	ethylhexyl methoxycinnamate, octinoxate, EHMC, OMC	
camphor derivatives	4-methylbenzylidene camphor, 4-MBC	
	3-benzylidene camphor, 3-BC (banned)	
dibenzoylmethane derivatives	avobenzone, BM-DBM	
Crylene derivatives	octocrylene, OC	
benzotriazoles	1-hydroxybenzotriazole, HBT	
	UVP	
	UV326	
	UV327	

A few studies have highlighted the significant ecotoxicological effect of UV filters on numerous aquatic organisms from invertebrates to fish [74,75]. Of high ecotoxicological importance is their ability (benzophenones, parabens, cinammates, camphor derivatives) to cause coral bleaching [74] with disastrous ecological effects. Regarding human toxicology, [76] concluded that most of them show multiple hormonal activities (estrogenic, anti-estrogenic, androgenic, anti-androgenic) in in vitro receptor-based assays. For example, non-cytotoxic concentrations of various UV-filters in recombinant yeast cells exhibiting human estrogen (hERα) or androgen (hAR) receptor produced multiple agonistic or antagonistic activities [77]. Furthermore, based on in vitro data on MCF-7 cell lines and on in vivo data on female rats, 4MBC and OMC were partial agonists for estrogenic receptors [78]. Finally, some UV filters (benzophenone-3 (BP3), 4-methylbenzylidene camphor (4-MBC), octinoxate (OMC)) have activated inflammatory cytokines in macrophages, and this is a mediator of allergic reactions [79], while epidemiological data have linked UV filters (benzophenones) with allergic dermatitis [80].

WWTPs are the main culprits for water pollution by UV filters since the latter were not successfully biodegraded [81]. According to [82], a conventional Modified Ludzack-Ettinger system of activated sludge showed the following removal efficiencies for UV filters: 99% for octisalate (EHS) and octocrylene (OC), >70% for benzophenone-1 (BP1), benzophenone-3 (BP3) and homosalate (HMS), 38%–77% for 4-methylbenzylidene camphor (4-MBC), 30%–55% for octinoxate (EHMC) and 10%–50% for avobenzone (BMDBM) and ethylhexyl-dimethyl PABA (OD-PABA). Different efficiencies were noted for a sequencing batch reactor secondary treatment, and important differences were also found for disinfection methods (chlorination vs UV irradiation) (Table 6).

Table 6. Occurrence of UV filters in influents and effluents of WWTPs worldwide.

Region	Substrate	BP3 ng L^{-1}	OD-PABA ng L^{-1}	EHMC ng L^{-1}	OC ng L^{-1}	BM-DBM ng L^{-1}	4MBC ng L^{-1}	HMS ng L^{-1}	Reference
15 WWTPs Portugal	Influent Effluent	5.4–323.3 <10–136	12.2–418 <10	33–689.5 35–483.4	<10–689 125–357	<50–2935 <50–168.1	45.8–155 <50	-	[83]
5 WWTPs Hong Kong China	Influent Effluent	114–450.7 18.4–541.1	<0.31–259 <11–224	50–1134 <0.85–505.2	<66–131 < 5.91	35–1290.2 <0.44–1018.3	<3.5–350 <4.58–207.2	<39–1650 <3.75–154.2	[82]
5 WWTPs Catalonia, Spain	Influent Effluent	75.6–306 7.71–34	-	-	-	-	<33–48.3 n.d.–23.8	-	[81]
2 WWTPs, Wales, United Kingdom	Influent Effluent	<104,000–3,975,000 <80,000–2,196,000	-	-	-	-	-	-	[25]
Adelaide, Australia	Influent Effluent	1059–3112 54–488	-	106–319 <0.7–53	88–89 <3.4–73	-	394–406 17–140	-	[84]
8 WWTPs Zurich, Switzerland	Influent Effluent	700–7800 <10–700	-	500–19,000 <10–100	100–12,000 <10–300	-	600–6500 60–2700	-	[85]

PB3: Benzophenone-3, OD-PABA: Ethylhexyl dimethyl PABA, EHMC: Ethylhexyl methoxycinnamate, OC: Octocrylene, BM-DBM: Avobenzone, 4MBC: 4-methylbenzylidene camphor, HMS: Homosalate.

2.2. Small Scale PCPs Market Sampling

A small-scale market sampling of PCPs was performed in a large chain supermarket in Athens, Greece, in April 2019. The PCPs collected are shown in the following Table 7.

The ingredients that were not supposed to be the active agent (e.g., retinol in face cream or chlorhexidine in a mouthwash) of the 52 individual items were further coded according to their action in the final product (e.g., whether it acted as an emulsifier, an antioxidant, etc.). According to this classification the categories “preservatives”, “antimicrobial agents”, “parfum” and “UV filters” were investigated further. Each ingredient was sought on the open-access database https://www.ewg.org/skindeep [86]. The database gives a rudimentary hazard assessment of PCPs ingredients, mainly on the toxicological topics of cancer, developmental and reproductive toxicity, sensitization potential and immunotoxicity, and less on ecotoxicity, endocrine disruption, bioaccumulation, etc.

Table 7. Categories of collected personal care products (PCPs).

No of Brands/PCP Category	No of Brand
Shampoo	6
Soap bar	1
Liquid bath soap	8
Liquid hand soap	3
Face cleansing gel	1
Face cleansing emulsion	1
Face cleansing balsam	1
Face cream	3
Eye cream	1
Body cream	2
Hair conditioner	2
Hand cream	2
Body lotion	1
Sunscreen	3
Sun protecting hair oil	1
Hair oil	1
Hair mousse	1
Hair gel	1
Hair styling mud	2
Stick deodorant	1
Eau de toilette	1
Eau de parfum	3
Nail enamel	1
Make-up removal wet tissues	1
Lipstick	1
Shaving mousse	1
Insect repellent lotion	1
Toothpaste	1

3. Results and Discussion

The 52 individual items contained in total 420 ingredients. Most PCPs contained 20–30 ingredients with a number of exceptions; a face cream contained 59 ingredients besides the active one, while a nail enamel contained 7 ingredients. These ingredients were grouped in the following categories: Softeners, hydrating agents, hygroscopic agents, surfactants, emulsifiers and emulsion stabilizers, cleansing agents, antioxidants, opacity regulators, absorbents, pH buffers, UV filters, parfum agents, solvents, preservatives, antimicrobial agents, antifoam agents, chelates, bulking agents, color additives, viscosity stabilizers, antistatic agents. It must be noted that some ingredients may act in more than one way; the substance benzyl salicylate, which was commonly found here, may act as a preservative as well as a parfum. The results for the categories in question (“preservatives”, “antimicrobial agents”, “parfum” and “UV filters”) are shown in Figure 3.

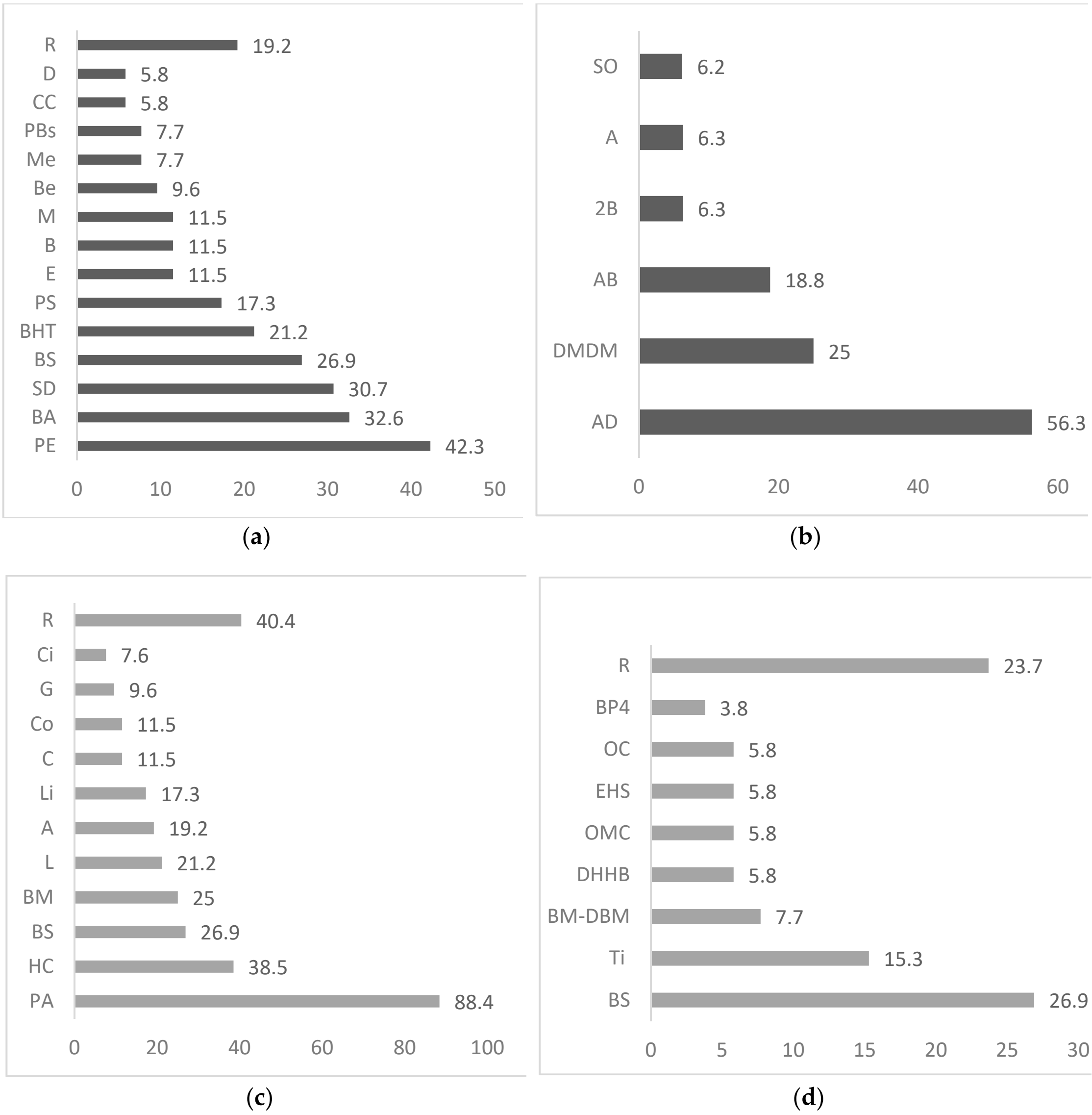


Figure 3. Percentage (%) of individual ingredients found in the 52 examined PCPs (**a**) preservatives in PCPs, Key: PE: Phenoxyethanol, BA: Benzyl alcohol, SD: Sodium benzoate, BS: Benzyl salicylate BHT: Butylated hydroxytoluene PS: Potassium sorbate E: Ethylhexylglycerin, B: Benzoic acid, M: Methylisothiazolinone, BE: Benzyl benzoate, ME: Methylchloroisothiazolinone, **PBS: Parabens**, CC: Cetrimonium chloride, D: Dehydroacetic acid, R: Rest, (**b**) antimicrobial agents in PCPs, Key: AD: Alcohol denatured, DMDM: DMDM hydantoin, AB: Alkyl benzoate, 2B: 2-bromo-2-nitropropane-1,3-diol A: Alcohol, SO: *Saponaria officinalis* extr, (**c**) perfum ingredients in PCPs, Key: **PA: parfum**, HC: Hexyl cinnamal, BS: Benzyl salicylate, BM: Lilial, L: Linalool A: Alpha-isomethyl ionone, LI: Limonene, C: Citronellol, CO: Coumarin, G: Geraniol, CI: Citral, R: Rest, (**d**) UV filters in PCPs, Key: BS: Benzyl salicylate, TI: Titanium dioxide, **BM-DBM: Avobenzone**, **OMC: Octinoxate, EHS: Octisalate**, **OC: Octocrylene**, **BP4: Benzophenone**, R: Rest. In bold are shown the ingredients analyzed in Sections 2.1.1–2.1.4.

Some useful qualitative and quantitative deductions can be made from this analysis; regarding preservatives in products commonly found in the Greek market, only 7.7% of the examined products contained PBs. This is somehow expected because parabens are slowly being phased out for marketing reasons, after the ban of [87] on isopropyl, isobutyl and benzyl-paraben, and the opinion of the European Scientific Committee on Consumer Safety on certain uses of propyl and butyl paraben [88]. As such, a lot of products now have a disclaimer "paraben-free" on their container. Thus, it can be safely assumed that their limited presence in WWTP effluents (they are easily biodegradable in most cases) will be further minimized. Nevertheless, another substance found was benzyl salicylate, which is also a parfum, UV filter, and it is supposed to be of moderate hazard (possible ecotoxicity, endocrine disruption) according to [86]. This substance was also present in the influents of two WWTPs in Spain, and it was somewhat successfully removed after secondary treatment [89]. It looks as if the trends in preservatives for PCPs are changing since consumers are clearly not fond of parabens (i.e., the safety of propyl and butyl paraben could not be unequivocally proven for certain uses, [88]). As such, the research should be targeted to the environmental fate and the biodegradability of these ingredients that will replace parabens. Triclosan was also conspicuously absent from our data set. Triclosan has also been phased out of a variety of products in EU, USA, Japan, and Canada; nowadays, in the EU it is not allowed in hygiene products and in detergent soaps [90]. Even though a recent evaluation [91] concluded that unless new data were presented, the current uses of triclosan in cosmetics did not pose a significant risk to humans, it can be assumed that triclosan was not popular and it will continue to decrease in WWTPs effluents. Furthermore, since different limitations exist in EU, USA, and Asian countries [91], multinational companies may not be willing to launch so many different products.

In total, in our products, only 16 out of 52 contained an antimicrobial agent. Out of these, DMDM hydantoin and 2-bromo-2-nitropropane-1,3-diol (bronopol) released formaldehyde locally. There were very little data (bronopol) on their presence in influents, which makes deductions on their removal efficiency problematic [92].

Much less can be deduced from the "Parfum ingredients" category; in 46 out of the 52 products the terms "parfum" or "aroma" were included in the ingredients, referring to aromatic compositions. Since they were industrial formulas not readily available to the public, information may be obtained by contacting the responsible physical or legal person and only on possible adverse effects, according to [73]. As such, it was almost impossible to quantify the hazard posed by the parfum ingredients and to backtrack the source of pollution in WWTPs. As stated before, these substances are lipophilic, not readily biodegradable, and of significant toxicological profile. They are also bioaccumulative, toxic to aquatic wildlife (even the polycyclic musks that are less toxic than the nitro-musks), and they have been detected in high concentrations in surface waters receiving WWTP effluents [36].

For UV filters, the variability noted in the products tested was quite high. Furthermore, these ingredients may be used in numerous combinations (one particular product contained 8 agents). Benzyl salicylate was again the most common ingredient, followed by TiO_2. Avobenzone (BM-DBM), which was insufficiently removed in WWTP [82] was also present to a modest extent (7.7%) followed by octinoxate (OMC, EHMC), octocrylene (OC), and others. Octinoxate is a partial agonist for estrogenic receptors [78] and linked to cytokine activation [79]. According to the data presented in Table 6, this substance was moderately removed from conventional WWTPs. The case of avobenzone was further complicated since it forms chloro-metabolites and chlorophenols under disinfection (chlorination, UV-irradiation) [93,94]. These products are generally toxic and little research has been carried out on their environmental fate, mainly on swimming pools and not on WWTP effluents. Furthermore, in the "rest" category, two products contained nanoforms of inorganic UV filters. Nanomaterials showed a completely different environmental fate and behavior than their bulk counterparts; as such, special attention should be paid to their increasing use.

Within this context, it is important not to forget that around 93% of the effluents produced by Greek WWTPs end up in lakes, rivers, and coastal water [95], while simultaneously, many parts of Greece suffer from water shortage, especially in the summer months, primarily in the agricultural sector. Reclamation and reuse of wastewater is a necessity for Greek society, and this situation may be aggravated due to climate change. Therefore, emphasis should be given on priority substances as laid out in [96], however, the possibility of PCPs ingredients in Greek WWTP effluents should be taken into account when reclamation and reuse are considered.

4. Conclusions

PCPs are an important category of emerging water pollutants due to their extensive use and the multitude of ingredients they contain. The ingredients examined in the present manuscript were parabens (preservatives), triclosan (antimicrobial agents), synthetic musks (parfums), and UV filters, which are of significant toxicological (and ecotoxicological) interest. These ingredients are degraded in WWTPs at various removal rates; some of them at unsatisfactory removal rates. A small-scale investigation for PCPs marketed in Greece revealed a decrease in the occurrence of parabens and triclosan. A few reasons are given for this apparent decrease. There was also a high diversity in UV filters, and it is known that some of them (i.e., avobenzone) are rendered more reactive after water disinfection. The occurrence of (possibly persistent) synthetic musks could not be evaluated due to non-disclosure of information. Other ingredients with unknown behaviors in WWTPs were also present. Based on this preliminary research, the following deductions can be made; (a) the multitude and the variability of ingredients found in PCPs (preservatives, emulsifiers, antimicrobial agents, bulking agents, parfums etc.) pose a threat to wastewater treatment and reclamation; (b) some classic ingredients of PCPs may be phased out and may be replaced by new ones, thus the monitoring of PCPs in WWTPs should be updated; (c) non-disclosure of information of the final PCP product makes it difficult to backtrack the pollution source. It is, therefore, important to extend and update research on fate and behavior of PCPs in the environment and especially on how well these substances can be degraded in WWTPs. It is also imperative to choose more environmental-friendly ingredients for PCPs thus that water reuse becomes a viable option that does not undermine public health and environmental quality.

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