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Personal Care Products in the Aquatic Environment

Springer

The Handbook of Environmental Chemistry

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Volume 36

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Personal Care Products in the Aquatic Environment

Volume Editors: M. Silvia Díaz-Cruz · Damià Barceló

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ISSN 1867-979X ISSN 1616-864X (electronic)
The Handbook of Environmental Chemistry
ISBN 978-3-319-18808-9 ISBN 978-3-319-18809-6 (eBook)
DOI 10.1007/978-3-319-18809-6

Library of Congress Control Number: 2015944206

Springer Cham Heidelberg New York Dordrecht London

Printed on acid-free paper

Springer International Publishing AG Switzerland is part of Springer Science+Business Media (www.springer.com)

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Aims and Scope

Since 1980, *The Handbook of Environmental Chemistry* has provided sound and solid knowledge about environmental topics from a chemical perspective. Presenting a wide spectrum of viewpoints and approaches, the series now covers topics such as local and global changes of natural environment and climate; anthropogenic impact on the environment; water, air and soil pollution; remediation and waste characterization; environmental contaminants; biogeochemistry; geoecology; chemical reactions and processes; chemical and biological transformations as well as physical transport of chemicals in the environment; or environmental modeling. A particular focus of the series lies on methodological advances in environmental analytical chemistry.

Series Preface

With remarkable vision, Prof. Otto Hutzinger initiated *The Handbook of Environmental Chemistry* in 1980 and became the founding Editor-in-Chief. At that time, environmental chemistry was an emerging field, aiming at a complete description of the Earth's environment, encompassing the physical, chemical, biological, and geological transformations of chemical substances occurring on a local as well as a global scale. Environmental chemistry was intended to provide an account of the impact of man's activities on the natural environment by describing observed changes.

While a considerable amount of knowledge has been accumulated over the last three decades, as reflected in the more than 70 volumes of *The Handbook of Environmental Chemistry,* there are still many scientific and policy challenges ahead due to the complexity and interdisciplinary nature of the field. The series will therefore continue to provide compilations of current knowledge. Contributions are written by leading experts with practical experience in their fields. *The Handbook of Environmental Chemistry* grows with the increases in our scientific understanding, and provides a valuable source not only for scientists but also for environmental managers and decision-makers. Today, the series covers a broad range of environmental topics from a chemical perspective, including methodological advances in environmental analytical chemistry.

In recent years, there has been a growing tendency to include subject matter of societal relevance in the broad view of environmental chemistry. Topics include life cycle analysis, environmental management, sustainable development, and socio-economic, legal and even political problems, among others. While these topics are of great importance for the development and acceptance of *The Handbook of Environmental Chemistry,* the publisher and Editors-in-Chief have decided to keep the handbook essentially a source of information on "hard sciences" with a particular emphasis on chemistry, but also covering biology, geology, hydrology and engineering as applied to environmental sciences.

The volumes of the series are written at an advanced level, addressing the needs of both researchers and graduate students, as well as of people outside the field of

"pure" chemistry, including those in industry, business, government, research establishments, and public interest groups. It would be very satisfying to see these volumes used as a basis for graduate courses in environmental chemistry. With its high standards of scientific quality and clarity, *The Handbook of Environmental Chemistry* provides a solid basis from which scientists can share their knowledge on the different aspects of environmental problems, presenting a wide spectrum of viewpoints and approaches.

The Handbook of Environmental Chemistry is available both in print and online via www.springerlink.com/content/110354/. Articles are published online as soon as they have been approved for publication. Authors, Volume Editors and Editors-in-Chief are rewarded by the broad acceptance of *The Handbook of Environmental Chemistry* by the scientific community, from whom suggestions for new topics to the Editors-in-Chief are always very welcome.

Damià Barceló
Andrey G. Kostianoy
Editors-in-Chief

Volume Preface

Nowadays major sources of water pollution are agricultural runoff and domestic and industrial effluent discharges. Organic pollutants present can accumulate in rivers and other water bodies and affect water quality and species survival. The active ingredients used in personal care products are increasingly detected in the environment and consist of a large group of chemicals with a wide range of physicochemical properties, which make them to be present in solution, adsorbed onto sediments and accumulated in biota. These substances are used in large quantities in everyday life, being added in cosmetics and personal hygiene products, such as deodorant, after shave, shampoo, perfume and makeup.

This book on *Personal Care Products in the Aquatic Environment* contains comprehensive information on the fate and removal strategies of the various ingredients used as personal care products and the aquatic environment as well as their impact on human health. Most of the published work so far deals with the stability of the commercial products and issues related to skin penetration. However, in the recent years, the general interests have shifted to know the risk of this large and diverse chemical group of anthropogenic contaminants in environment and humans. They can be considered part of the so-called emerging contaminants that are present worldwide in the aquatic environment, from groundwater to marine mussels. This book presents the latest developments as regards their determination, spatial distribution, degradation and risk categorization in the aquatic environment. This will be of great help to the reader to make a holistic picture of the current environmental problems connected with the widespread use of personal care products.

The book is structured in 14 chapters written by well-recognized experts in this field. The various chapters cover occurrence in water, solid samples and biota, advanced chemical analytical methods, non-conventional degradation technologies, (eco)toxicity and environmental and human risk assessment. The first chapter of the book is devoted to a general introduction to personal care products. It covers the key aspects of the diverse group of substances included in this category of chemicals (UV filters, preservatives, fragrances, etc.), which may be of especial

interest for newcomers and first-year Ph.D. students. The information provided includes physicochemical characterization, regulatory frameworks and health effects on biota and humans. In the final chapter, we discuss the major scientific achievements and future research trends. Knowledge gaps are identified too as regards the environmental and human issues associated to the daily use of personal care products.

We expect that *Personal Care Products in the Aquatic Environment* will become a useful book. The book is multidisciplinary, so it will attract experts from various fields of expertise like analytical and environmental chemistry, toxicology and environmental engineering. Since the book also covers not only continental but also marine waters, it should be of interest to the researchers working in marine pollution and related activities like aquaculture.

Finally, we would like to express our gratitude to all the contributing authors of this book for their willingness, effort and time devoted to the preparation of their respective piece of research.

Barcelona, Spain
March 2015

M. Silvia Díaz-Cruz
Damià Barceló

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Introduction: Personal Care Products in the Aquatic Environment

Daniel Molins-Delgado, M. Silvia Díaz-Cruz, and Damià Barceló

Abstract This chapter presents an overview of the main aspects relating to the occurrence and impact of ingredients in personal care products to the aquatic environment: methodologies of analysis, prevalence data, elimination processes, threats to the aquatic ecosystem, effects on biota and legislation with a special focus in European regulation. Water is a valuable resource for the environment as well as for human activities. Although it covers most of the Earth's surface, the amount of usable water is finite. Since ancient times until now, the use of water in human activities has been rapidly increasing along with the increase of the population, producing a continuous release of pollutants into the aquatic environment. Personal care products are a widely used group of substances that have been raising concerns during the last decades due to its continuous release into the environment and its proven effects (mostly on in vitro and in vivo assays) as a threat to all kinds of living organisms. Recent studies suggest that its continuous application on the skin or the intake of contaminated food may cause some concerning hazardous effects in human beings. In order to ensure the protection of this key ecosystem, a series of worldwide initiatives have been taking place during the last two decades, impelling monitoring programmes and governmental regulations worldwide. The common grounds of the European Union establish a series of regulations, such as the Water Framework Directive or the Regulation on Cosmetic Products, to protect both the

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M.S. Díaz-Cruz and D. Barceló (eds.), *Personal Care Products in the Aquatic Environment*, Hdb Env Chem (2015) 36: 1–34, DOI 10.1007/698_2014_302,

environment and the consumer with revisable lists of regulated hazardous compounds.

Keywords Aquatic environment, Environmental legislation, Health risk, Personal care products, Pollution sources

Contents

List of Abbreviations

4MBC	4-methylbenzylidiene camphor
AHTN	Tonalide
BP3	Benzophenone 3
BP4	Benzophenone 4
DEET	*N*,*N*-diethyl-meta-toluamide
EHMC	Ethylhexyl methoxycinnamate
EMEA	European medicine evaluation agency
EPA	Environmental protection agency
HHCB	Galaxolide
INCI	International nomenclature of cosmetic ingredients
Kow	Octanol-water partition coefficient
NP	Nonylphenol
NPEs	Nonylphenol ethoxylates
OC	Octocrylene
OTNE	Ethanone
PCPs	Personal care products

PVC	Polyvinyl chloride
REACH	Registration, evaluation, authorisation and restrictions of chemicals
UV234	2-(2*H*-benzotriazol-2-yl)-4,6-bis(1-methyl-1-phenylethyl)phenol
UV326	2-*tert*-buthyl-6-(5-chloro-2*H*-benzotriazol-2-yl)-4-methylphenol
UVP	2-(2*H*-benzotriazol-2-yl)-*p*-cresol
WFD	Water framework directive
WWF	World water forum
WWTPs	Wastewater treatment plant

1 Introduction

The aquatic environment as a system and resource. The quality of air, soil and water is of immediate concern because we interact with these natural resources in a daily basis, either personal, agricultural or industrial uses. Water is essential to sustain life, and it is a critical resource on which all social and economic activities, as well as the ecosystem functions, depend. Through history, the relation between human civilisation and water has been very tight: ancient Mesopotamia grew around the Tigris and Euphrates basins, ancient Egypt depended on the Nile, the Romans built an extensive network of aqueducts in order to supply enough water to their cities and commerce has been heavily carried out through navigable rivers, channels and seas. Mankind not only requires water for drinking purposes or for transportations of goods but for recreational activities, production of energy, agricultural purposes and to keep industrial activities going. Managing well this resource is critical and requires appropriate governance arrangements in order to protect it and to ensure the viability of both, the economic welfare of human activities and the sustainability of all the water-supported ecosystems, as water is not a commercial good, but a common heritage that we must protect, defend and acknowledge [1].

Water covers more than 70% of the Earth's surface. In land masses it appears under the form of rivers, streams, lakes and wetlands, while close to the continents, it takes the form of a few hundred deep shallow seas, estuaries, lagoons and bays, and the form of deep oceans when away from continental land masses. As life depends on water to survive, water bodies and water availability constitute the central factor of all habitats. If we are to consider the habitable places on Earth and the whole volume of water, it comprises nearly 99% of the Earth's habitat, being most of the vast water columns of the marine environment unobserved and mostly unknown to human beings.

There is now much concern about the extent of human actions, their capabilities to accelerate a climate change and what could be their possible outcomes. As climates on Earth are phenomena in constant change, only the magnitude of the rate at which it changes varies with time. For instance, temperature is the easiest and familiar magnitude to monitor. While land and air temperatures can vary dramatically, sea surface temperature changes are more subtle due to the high volume and high latent heat of water, conferring water bodies a great buffering

effect. When global temperatures rise, the melting of ice from the poles and the thermal expansion make the sea level to rise, producing other environmental changes. For instance, alterations on oceanic water bodies can induce important changes in climate; a weakening of the Gulf current could potentially change climate conditions and rainfall patterns.

Human population is mostly densely concentrated around water sources, particularly around rivers, mouths of estuaries and sheltered bays, being the focus of intensive human activities. Human activities are able to modify the aquatic environment through removal of biomass and habitats and via the addition of contaminants. Freshwater resources and population densities are unevenly distributed worldwide. As a result, demands already exceed supplies in regions with more than 40% of the world's population [2]. And 70% of the world's freshwater is currently used for irrigation, accounting for more than 95% of the developed water supply [3]. Sewage, agriculture and industrial pollution disrupt heavily the aquatic environment, and coming to understand the ecological responses of aquatic organisms is required in order to protect such an important source for life.

2 Anthropogenic Contamination as the Main Threat to the Aquatic Environment

The dawn of industrialisation and the quick growth of urbanisation brought a change into the social paradigm, transforming a predominantly rural planet into an urban one [4], bringing with it an increase on industrial and municipal waste in both garbage and sewage waste [5]. With it, new chemical compounds have been developed in order to improve our quality of life, increasing the productivity of activities of farms, ranches and forestry [5–7]. The quality of the aquatic environment depends deeply on both natural processes and anthropogenic activities [8]. Problems like eutrophication of the marine environment, anoxia of water bodies, loss of biodiversity, bioabsorption of pollutants and bioaccumulation processes in aquatic organisms have been reported worldwide [9, 10]. Also, the extreme changes in the weather due to climate change processes could be able to magnify them.

When talking about sources of contamination, we must define point source and nonpoint source of pollution. Point-source contaminants originate from a discrete source of contamination whose inputs into the aquatic environment can be defined through measurements of chemical residues in water, sediment or biota and/or because of a series of other factors like varying incidences of morbidity or mortality [11]. Examples of point source are municipal sewage treatment plants, industrial effluents, resource extractions and land disposal sites. Freshwater pollution has as a main source municipal wastewaters [12]. A huge volume of wastewater has been increasing along with urbanisation and economic development [13, 14] and those wastewaters are expected to grow [3]. There is a constant generation of new

contaminants with unknown short-, medium- or long-term effects in human health and biota whose maximum permissible concentrations have yet to be established. Their continual discharge into the environment, their persistence and presence, even at low concentrations, are causing major concern [15]. An increment in wastewater disposals increases the chance of pollutants reaching groundwater reservoirs [16–18]. Due to scarcity of freshwater resources, most small-scale farmers in urban and peripheral areas already depend on wastewaters to irrigate their crops [19, 20].

Nonpoint-source pollution is another source of pollution. Abuses in the use of chemical compounds together with the change in land use and management of the activities carried out in those lands can alter hydrological cycles and can lead to storm water urban and agricultural run-offs [21–27] and the degradation of the receiving waters [28]. It must be kept in mind that the distinction between a point and nonpoint source of contamination is difficult to establish. A discharge of metals to surface waters from mining operations may represent a point source of contamination, but the same metals could occur in the environment as a result of a natural process [29].

Polar contaminants will generally remain dissolved in water and are highly mobile in the environment. They have a little tendency to bioaccumulate in living organisms if there is not a chronic exposure to them, and they are rarely found in elevated concentrations in the environment. In areas where a polar compound occurs, it may be a common component of the influent wastewater at wastewater treatment plants (WWTPs). On the other hand, mid-polar and nonpolar compounds tend to be more likely associated with suspended particles or to accumulate on the sediment, which act as environmental repositories for organic compounds, and biota. Organic pollutants will then establish equilibrium between the sediment, the particulate, the biota and the water, and depending on the physical chemical properties of the medium, some contaminants could be mobilised and demobilised, determining the bioavailability of the pollutants [30]. Toxic contaminants may be deactivated due to the action of microbial, chemical and photolytic degradation in both water and sediment matrices, but these processes could also increase the hazardous potential of some of them, increasing their bioavailability [29]. The primary route for exposure to lipophilic compounds for biota and humans is through the diet.

Summarising, these pollutants follow two major pathways from human activities to the aquatic environment: a direct entry through recreational activities like direct bath in natural waters and an indirect entry through industrial discharges, run-offs and domestic uses. They may be released to the wastewaters and end up in a WWTP where they are relatively removed. Part of these compounds will be retained in the sludge whereas another fraction will be released into the natural waters through the effluent wastewater stream. Some contaminants may be retained in the sediments, whereas some others can be bioaccumulated in biota. Moreover, the sludge produced at the WWTPs may end in a landfill or be used for agricultural purposes, potentially polluting underground water reservoirs.

2.1 Behaviour of Organic Contaminants in Aquatic Biota

Emerging contaminants, including personal care products (PCPs), are mainly new substances that have been released into the environment during the last decades due to changes in the socio-economic structure of society. These compounds can be a potential risk to the aquatic environment due to the high quantities routinely released and their generally low biodegradability. Their monitoring is seldom included into the different environmental legislations around the world, and their fate is mostly unknown to most of them [31]. On the other side, food webs are, jointly with biogeochemical cycles, closely tied to metabolic processes involving the creation and use of organic matter, being able to quantify the individual anabolic and catabolic processes of each organism into the total of the whole ecosystem and representing the total organic matter production of an aquatic environment. Measurements on this subject contribute to widen the knowledge about changes in the biosphere. Nevertheless, the wide spread of mankind on Earth has produced a series of perturbations on aquatic ecosystems which consequences are hard to foresee [32]. One of these perturbations is the continuous release of pollutants into the aquatic environment. The presence of a xenobiotic compound in the aquatic environment does not immediately imply a risk to the environment by itself, as connections must be done before internal tissue concentrations of the pollutant and the early adverse effects may occur [33]. Some substances released from a source of contamination are not only hydrophilic but also lipophilic compounds, and they are able to suffer of a metabolic breakdown and rapid elimination, being those very difficult to study the fate or to determine the accumulation rate [34, 35]. Additionally, temperature variation may alter degradation processes and environmental partitioning of contaminants into different phases, increasing the availability of pollutants [36]. The term bioaccumulation is defined in many different ways. It is the total uptake of a substance from the environment, or the accumulation over time, or the retention of the substance [34]. Their factors can be calculated as the ratio of the studied compound in a biota sample compared with the one in the environment it lives in [37]. In order to assess this process, an accurate determination of the properties of the organic compounds is essential to predict and understand their hydrophobicity and thus their bioaccumulation potential, although there are some key problems to confront when calculating the octanol-water partition coefficient (Kow), such as poor and scarce data [38]. Therefore, bioaccumulation models are hard to craft, and they do not exist for all chemical compounds [31]. An associated process to bioaccumulation is biomagnification. Biomagnification is the process in which a substance present in the environment is transferred to the food web, from organism to organism, being the concentration of that substance in an organism is higher to that in their food source. Longevity and size of the organism are factors that could contribute to higher levels of chemicals in higher trophic levels [39]. This phenomenon has already been described in some hydrophobic and recalcitrant chemicals in fish [40, 41].

Since the early 1960s of the last century, mankind has been aware of the potential adverse effects that chemicals can generate for aquatic and terrestrial ecosystems [33]. When an effect finally becomes clear, the damage produced to the ecosystem may be beyond the point where remedial actions may not be enough to reverse the situation. There is a sequential order of responses triggered by a pollutant stress within a biological system; changes start from a molecular level, to a subcellular level, to higher orders such as tissues and organs, affecting the whole organism itself at last. This may produce changes in the population and the communities of organisms that may lead to a wide ecosystem disturbance, as some pollutants have been reported to affect the behaviour of organisms [42]. These scenarios have triggered the research for early warning signals reflecting the biological response towards aquatic pollutants. Biomarkers are any measurable piece of evidence that reflects the interaction between an ecosystem and a potential hazard, which may be chemical, physical or biological, which can be related to the toxic effects of environmental pollutants [43]. A bioindicator is the extracted information related from the interaction of an organism with its environment. A change of behaviour of an organism or even its absence in an ecosystem works as an indicator of quality of the environment the organism that acts as bioindicator lives in [33]. In order to assess these changes in an ecosystem, a widespread organism must be selected as control. Fishes can be found everywhere in the aquatic environment and play a major role in it as carriers of energy from low trophic levels to higher ones [44]. Because of that, fishes are considered the most feasible organisms for water pollution monitoring. Larger and long-living organisms tend to show higher pollutant concentrations in tissue than smaller or short-living species; nevertheless, the estimation of both processes, bioaccumulation and biomagnification, is really difficult as several parameters intervene, such as the compounds lipophilicity, its degradation or transformation kinetics and the large variability of a food web, which make difficult the prediction through mathematical models [45].

3 Main Ingredients in Personal Care Products

PCPs is a generic term that describes a group of organic chemicals included in different products widely used in daily human life (such as toothpaste, shampoo, cosmetics and even in food), being used in considerable quantities. After use, they may be absorbed by the body and excreted or washed after its application [46]. PCPs and their metabolites end up in WWTPs [47, 48]. There, they are partially eliminated and either retained in the sludge or released to the aquatic environment in the effluents [49]. In the last 20 years, the concern about the potential hazardous risk associated to them and their by-products, which can be more persistent and toxic [50], has been on the rise. According to their purpose, ingredients in PCPs can be ordered in the following main categories: UF filters (sunscreens), biocides (antimicrobials), preservatives, fragrances, insect repellents, siloxanes and detergents. The International Nomenclature of Cosmetic Ingredients

Table 1 List of some personal care products, their international nomenclature of cosmetic ingredient (INCI) name, abbreviation, their CAS number, their function in cosmetic products and their allowed levels in the European Union following the regulation 1223/2009/EC

Name	INCI	Abbreviation	CAS	Function	Max. concentration allowed according to regulation 1223/2009/EC
2-Hydroxy-4-methoxybenzophenone	Benzophenone 3	BP3	131-57-7	UV filter	10%
2-Hydroxy-4-methoxybenzophenone-5-sulphonic acid	Benzophenone 4	BP4	4065-45-6	UV filter	5%
3-(4-methylbenzylidene)-*d*1 camphor	4-Methylbenzylidene camphor	4MBC	36861-47-9	UV filter	4%
2-Ethylhexyl 4-methoxycinnamate	Ethylhexyl methoxycinnamate	EHMC	5466-77-3	UV filter	10%
2-Cyano-3,3-diphenyl acrylic acid, 2-Ethylhexyl ester/	Octocrylene	OC	6197-30-4	UV filter	10%
2-Ethylhexyl 4-(dimethylamino) benzoate	Ethylhexyl dimethyl PABA	OD-PABA	21245-02-3	UV filter	8%
Benzyl 2-hydroxybenzoate	Benzyl salicylate	BZS	118-58-1	UV filter	0.001% in leave-on products—0.01% in rinse-off products
2-Ethylhexyl salicylate/octisalate	Ethylhexyl salicylate	OS	118-60-5	UV filter	5%
Benzoic acid, 2-hydroxy-, 3,3,5-trimethylcyclohexyl ester	Homosalate	HMS	118-56-9	UV filter	10
2-(5-chloro-2H-benzotriazol-2-yl)-6-(1,1-dimethylethyl)-4-methyl-phenol	Bumetrizole	UV326	3896-11-5	UV filter	No data available
2-(2*H*-benzotriazol-2-yl)-*p*-cresol	Drometrizole	UVP	2440-22-4	UV filter	No data available
3,3′-(1,4-phenylenedimethylene) bis (7, 7-dimethyl-2-oxobicyclo-[2.2.1] hept-1-yl-methanesulphonic acid) and its salts/ecamsule	Terephthalylidene dicamphor sulphonic acid	TDSA	92761-26-7	Biocide	10%

Phenol,2-(2H-benzotriazol-2-yl)-4-methyl-6-(2-methyl-3-(1,3,3,3-tetramethyl-1-(trimethylsilyl)oxy)-disiloxanyl)propyl)	Drometrizole trisiloxane	DTS	155633-54-8	Biocide	15%
Benzoic acid, 4,4-((6-((4-(((1,1-dim ethylethyl)amino)carbonyl)phenyl) amino)-1,3,5-triazine-2,4-diyl)diimino) bis-, bis (2-ethylhexyl) ester	Diethylhexyl butamido triazone	DEBT	154702-15-5	Biocide	10%
2,2′-Methylene-bis (6-(2H-benzotriazol-2-yl)-4-(1,1,3,3-tetramethyl-butyl)phenol)	Methylene bis-benzotriazolyl tetramethylbutylphenol	MBBT	103597-45-1	Biocide	10%
2-Phenylbenzimidazole-5-sulphonic acid and its potassium, sodium and triethanolamine salts	Phenylbenzimidazole sulphonic acid	PBSA	27503-81-7	Biocide	8%
2,4,6-Trianilino-(p-carbo-2′-ethylhexyl-1′-oxy)-1,3,5-triazine	Ethylhexyl triazone	EHT	88122-99-0	Biocide	5%
2,2′-(6-(4-methoxyphenyl)-1,3,5-tri-azine-2,4-diyl)bis(5-((2-ethylhexyl) oxy)phenol)	Bis-ethylhexyloxyphenol methoxyphenyl triazine	BEMT	187393-00-6	Biocide	10%
1-(4-*tert*-butylphenyl)-3-(4-methoxyphenyl)propane-1,3-dione/ avobenzone	Butyl methoxydibenzoylmethane	BMBM	70356-09-1	Biocide	5%
1*H*-benzotriazole	Benzotriazole	BZT	95-14-7	Biocide	No data available
5-Chloro-2-(2,4-dichlorophenoxy) phenol	Triclosan	TCS	3380-34-5	Biocide	0%
1-(4-chlorophenyl)-3-(3,4-dichlorophenyl) urea	Triclocarban	TCC	101-20-2	Biocide	0.2%

(continued)

Table 1 (continued)

Name	INCI	Abbreviation	CAS	Function	Max. concentration allowed according to regulation 1223/2009/EC
1-(5,6,7,8-tetrahydro-3,5,5,6,8,8,-hexamethyl-2-naphthyl)ethan-1-one	Acetyl hexamethyl tetralin	AHTN	1506-02-1	Fragrance	Leave-on products: 0.1% Except: hydroalcoholic Products: 1% fine Fragrance: 2.5% fragrance Cream: 0.5% (b) rinse-off Products: 0.2%
1,1,2,3,3,6-Hexamethylindan-5-yl methyl ketone	Acetyl hexamethyl indan	AHDI	15323-35-0	Fragrance	2%
1, 3, 4, 6, 7, 8-Hexahydro-4, 6, 6, 7, 8, 8-hexamethylindeno[5, 6-c]pyran	Hexamethylindanopyran	HHCB	1222-05-5	Fragrance	No data available
1-(1,2,3,4,5,6,7,8-octahydro-2,3,8,8,-tetramethyl-2-naphthyl)ethan-1-one	Tetramethyl acetyloctahydronaphthalenes	OTNE	54464-57-2	Fragrance	No data available
5-*Tert*-butyl-2,4,6-trinitro-*m*-xylene	Musk xylene		81-15-2	Fragrance	(a) 1.0% in fine fragrance (b) 0.4% in eau de toilette (c) 0.03% in other products
4′-*Tert*-butyl-2′,6′-dimethyl-3′,5′-dinitroacetophenone	Musk ketone		81-14-1	Fragrance	(a) 1.4% in fine fragrance (b) 0.56% in eau de toilette (c) 0.042% in other products
2-Phenoxyethanol	Phenoxyethanol	2-PE	122-99-6	Preservative	1%
Methyl *p*-hydroxybenzoate	Methyl paraben	MeP	99-76-3	Preservative	0.4% (as acid) for single ester, 0.8% (as acid) for mixtures of esters
Ethyl *p*-hydroxybenzoate	Ethyl paraben	EtP	120-47-8	Preservative	0.4% (as acid) for single ester, 0.8% (as acid) for mixtures of esters
n-Propyl p-hydroxybenzoate	N-propyl paraben	n-PrP	94-13-3	Preservative	0.4 % (as acid) for single ester, 0.8 % (as acid) for mixtures of esters
Isopropyl *p*-hydroxybenzoate	I-propyl paraben	i-PrP	4191-73-5	Preservative	0.4% (as acid) for single ester, 0.8% (as acid) for mixtures of esters
n-Butyl *p*-hydroxybenzoate	N-butyl paraben	n-BuP	94-26-8	Preservative	0.4% (as acid) for single ester, 0.8% (as acid) for mixtures of esters

Isobutyl *p*-hydroxybenzoate	I-butyl paraben	i-BuP	4247-002-3	Preservative	0.4% (as acid) for single ester, 0.8% (as acid) for mixtures of esters
Nonylphenol	Nonylphenol	NP	25154-52-3	Surfactant	Prohibited
Dibutyl phthalate	Dibutyl phthalate	DBP	84-74-2	Surfactant	Prohibited
Diisopentyl phthalate	Diisopentyl phthalate	DIIP	605-50-5	Surfactant	Prohibited
N,*N*-diethyl-meta-toluamide	Diethyl toluamide	DEET	134-62-3	Insect Repellent	No data available
1-Piperidinecarboxilyc acid	Hydroxyethyl isobutyl piperidine carboxylate		119515-38-7	Insect Repellent	No data available
Octamethylcyclotetrasiloxane	Cyclotetrasiloxane	D4	556-67-2	Additives	No data available
Decamethylcyclopentasiloxane	Cyclopentasiloxane	D5	541-02-6	Additives	No data available
Dodecamethylcyclohexasiloxane	Cyclohexasiloxane	D6	540-97-6	Additives	No data available
Tetradecamethylcycloheptasiloxane	Cycloheptasiloxane	D7	107-50-6	Additives	No data available

(INCI) is the official dictionary for cosmetic ingredients adopted by many countries in the world since it was first established in the 1970s by the PCPs Council in the USA. Many countries require manufacturers of PCPs to use the INCI nomenclature and to submit all new ingredients for registration in the INCI.

In the following, the origin, use and fate of different hazardous compounds involved in the PCPs formulation are described. Many of the considered compounds have been used for decades worldwide, and there is not, in many cases, reliable data about their production rates. Emission inventories are mostly collected for scientific and administrative purposes, with great differences in their spatial and temporal coverage. Scientific studies often require data on other features, and many efforts have been undertaken to estimate source emission levels, environmental occurrence and fate [51–54]. Table 1 lists some of the most widely used PCPs, their INCI name, function and maximum allowed levels for cosmetic use in the European Union (EU). We have attempted to use both official and scientific sources when existing, but it has to be kept in mind that these figures are only a rough estimation.

3.1 Biocide Compounds

Antiseptic and disinfectant compounds are extensively used in many activities such as health care and hospitals for a variety of topical or hard-surface applications. A wide variety of chemicals with biocide properties are found in all kind of products, many of them known for hundreds of years, such as alcohols, iodine and chlorine, demonstrating a wide range of antimicrobial activity. However, the current knowledge about the processes that provide these active chemicals is really scarce. The exposure through diverse goods to these widespread chemical compounds has raised some speculation on the development of microbial resistance and on the possibility of these compounds of being able to induce antibiotic resistance. In this category, benzotriazole, triclosan and triclocarban are the most commonly used compounds.

3.1.1 Benzotriazole

Benzotriazole (1-*H*-benzotriazole) is a very versatile compound widely used by their anticorrosive, antifreeze, coolant, vapour phase inhibitor, photographic developer, drug precursor and biocide properties [55–57]. Its extensive use raises concerns about its presence in the environment. Benzotriazole is a very polar substance, and conventional wastewater treatment technologies are not efficient for its removal [58]. As a consequence, these compounds if not efficiently eliminated reach the aquatic environment and ultimately may reach the drinking water supply [59].

3.1.2 Triclosan and Triclocarban

Triclosan and triclocarban are antimicrobial agents found in a wide range of products, from soaps, deodorants, toothpastes and cosmetics to fabrics and plastics. They were originally developed to serve as a surgical scrub for medical professionals, but their use has been extended to a broad range of applications in consumer products in order to end all kinds of bacterial and fungal activity. Triclosan is more widely used globally in a broad range of application in consumer goods (0.3–1% of the total), whereas triclocarban is a high production volume chemical in the USA with a production of 250–500 t per year [60]. During common wastewater treatment, despite triclosan being found in effluent wastewaters [61], the removal rates for triclosan and triclocarban from the aqueous phase are relatively high due to their hydrophobic properties [62, 63] showing a small tendency to accumulate in sludge and sediments, where they can persist [64, 65].

3.2 Preservatives

Synthetic preservatives are a wide family of compounds used to prevent bacterial and fungal growth and oxidation and also inhibit natural ripening of fruits and vegetables. Some authors also include bactericide agents in this group. They are widely used in many goods (e.g. pharmaceuticals, soaps, gels, creams, food, etc.). The most commonly used are parabens which are a family of compounds derived from the parahydroxybenzoic acid. They are odourless and colourless and do not cause discoloration or hardening. Their effectiveness as being antibacterial and fungicidal jointly with its low production cost, their supposedly low toxicity and the lack of a suitable alternative make them really ubiquitous. To date, only a handful of studies have looked for paraben concentrations in WWTPs and surface water, finding generally lower concentrations in effluent water [66–68]. They have been also found in sediments, in sewage sludge [69] and in biota [70]. Amid their extensive use worldwide, there is growing evidence stating that they might be endocrine disruptors [71].

3.3 Fragrances

Fragrances are a group of compounds whose function is to offer a pleasant scent to any manufactured good, having a wide use especially in PCPs. Fragrances have been used since antiquity to improve attractiveness of people and items and consisted in mostly floral and animal extracts. Around 1950, synthetic fragrances became cheaper and their use increased considerably. These compounds are present in surface water and groundwater located near wastewater discharge areas, with

larger concentrations near effluent discharge points [72]. As fragrances are lipophilic, they have the tendency to get absorbed in sludge, sediments and biota [73]. On the other side, as humans are in close skin contact with perfumed products, their exposure is high.

3.3.1 Nitromusks

Nitromusks are a group of synthetic fragrances which rely heavily in the symmetry of the nitro groups in order to perform a wide range of scents. It has been reported that these compounds can be transformed into aniline transformation products both through wastewater treatments of biologic metabolism [74]. These transformation products, which could be more problematic than the actual compounds itself, are the main reason why nitromusks have been withdrawn from the European market; thus concentrations have been dropping significantly in the last years [50]. Nitromusks are water soluble, but they also have high octanol-water partition coefficients [72], having a great potential for bioaccumulation in aquatic biota [54, 74].

3.3.2 Polycyclic Musks

Developed as an alternative to nitromusks, several polycyclic musks have been introduced onto the market. However, HHCB and AHTN are the most used. HHCB and AHTN, the two most used, have been detected in surface water and sediments [75] and wastewater [61, 76]. Also, HHCB has shown to be highly sorptive to sludge [77]. Due to their high lipophilicity, polycyclic musks tend to bioaccumulate, affecting biota, especially at low trophic levels [73].

3.3.3 Macrocyclic Musks

Although not commonly used due to their synthesis process cost, macrocyclic musks are getting more and more available along with the advances in their synthesis methods over the last few years [78]. Compared to the polycyclic musks, their scent is more intense; thus less mass is needed to gain the same performance as the polycyclic ones and more easily degradable in the environment [50]. Although they have been detected in wastewaters [79] and sludge [78], the lack of available analytical methods to analyse them in other environmental matrices makes it really difficult to understand their fate in the environment.

3.4 Surfactants

Surfactants are a key group of chemicals in a large number of applications such as in the manufacture of detergents, the formulation of herbicides, in textile industry and as stabilising agent for fragrances in cosmetics. With a high production value estimated over 18 million tons [80], their wide use generates the disposal of large amounts of these compounds in WWTPs or improperly directly into the aquatic environment without any kind of treatment. Their amphoteric character allows them to be accumulated in sediments, sludge and biota, generating concern about the potential related hazard to the environment [81].

3.4.1 Phthalates

Phthalates are present in many consumer products because of their property as flexibiliser of rigid polymers such as PVC. They are used in the production of a wide range of products such as food wrappings, medical devices, children's toys, wood finishers, paints and plastic products. Besides that, in cosmetic products, phthalate esters are used as solvents or fragrances [82], suspension agents, antifoaming agents, skin emollients, plasticisers in nail polishes and fingernail elongators [83]. In 2002, a study found that 52 out of the 72 cosmetic products investigated contained phthalates at concentrations ranging from 50 μg/g to nearly 3% of the product. Of the 52 cosmetics, none had the phthalates listed in their product label [84]. Due to their extensive use and the wide range of applications, phthalates are distributed along the aquatic environmental compartments being reported in water [85], wastewater and sludge [86] and less commonly in sediment [87].

3.4.2 Nonylphenol and Nonylphenol Ethoxylates

Nonylphenol (NP) and nonylphenol ethoxylates (NPEs) are the most widely used compounds of the alkylphenol and alkylphenol ethoxylate family of nonionic surfactants. NP is primarily used as an intermediate in the manufacture of NPEs, whereas NPEs are surfactants that have been commercialised for over 50 years. The wide range of products that can contain NPEs include fabrics, paper processing, paints, resins and protective coatings. It is also widely used in loads of domestic uses as a component in cleaning products, degreasers, detergents and cosmetics. Despite being restricted in the EU as a hazard to human and environmental safety, its regulated use it is still allowed in countries worldwide. Nonylphenol and its ethoxylates have been detected on surface water [66], sediment [88], wastewater [89] and sludge [90].

3.5 Insect Repellents

Insect repellents are substances that discourage insects from approaching to an applied surface [91]. As some insects act as vector for some diseases, using insect repellents is critical when other forms of protection are not available. They are widely used in tropical regions, being able to heavily influence the infection rates of some pathogens [92]. There is little information about their long-term effects in the aquatic environment; however, they have been detected worldwide in wastewaters, groundwater, surface and drinking water [91, 93–95]. DEET (*N*,*N*-diethyl-meta-toluamide) is a commonly used broad-range spectrum insect repellent [94]. It was first formulated in 1946 and was registered for commercial use in 1957 [92]. It is estimated that only in the USA one third of the population has used DEET [96]. Although the actual repellent mechanism involved is not well understood, DEET shows a high repellent potential against mites, tsetse flies, *Aedes vigilax* and mosquitoes [97], being used in all kinds of insect repellent formulations worldwide. Residues of DEET have been detected in effluent wastewater [61, 98] and surface water [61, 91, 93, 99], being quite persistent in the aquatic environment [94].

3.6 UV Filters (Sunscreens)

UV filters, also known as sunscreen agents, have become very popular chemicals since they were shown to have a protective role against photoaging, photocarcinogenesis and photo immunosuppression promoted by UV sun radiation [100–102]. These compounds are not only extensively used in PCPs but also commonly used in a wide variety of industrial goods as textiles, paints or plastics to prevent photodegradation of polymers and pigments [103]. However, recent concern has risen due to their potential for endocrine disruption and development of toxicity [104–107]. UV filters enter the aquatic environment directly as a result of recreational activities when they are washed off from the skin or indirectly through wastewater resulting from the use of PCPs, washing clothes and industrial discharges. Residues of more polar organic UV filters have been found in all kinds of water matrices [108] including tap water [109]. Due to the high lipophilicity and poor biodegradability of many UV filters, they end up in sewage sludge during wastewater treatment [110] and accumulate in sediments [111, 112] and biota [113, 114].

3.7 Siloxanes

Siloxanes are a relatively new group of PCPs, consisting of a polymeric organic silicone that comprises a backbone of alternating silicon-oxygen units with an

organic chain attached to every silicon atom, conferring them a low surface tension, physiologic inertness, high thermal stability and a smooth texture [115]. Siloxanes are used in a broad range of consumer products (antiperspirants, skin-care creams, hair conditioners and colour cosmetics), as well as in industrial ones, such as automotive polishes, fuel additives and antifoaming agents. They are considered high production volume chemicals, having annual productions for some of them of 45–227 thousand tons worldwide; however, recent reports raise concern about the potential toxic effects of cyclic siloxanes [116]. Siloxanes are likely to be discharged into sewage systems through the use of "rinse-off" products and partially adsorbed onto sludge in WWTPs due to their high Kow and released to the aquatic environment through wastewater discharges [117–119], having also been found in sewage sludge [115, 119] and sediment [119, 120]. The siloxane family includes octamethylcyclotetrasiloxane (D4), decamethylcyclopentasiloxane (D5), dodecamethylcyclohexasiloxane (D6) and tetradecamethylcycloheptasiloxane (D7) [118].

4 Health Effects of PCPs on Biota and Humans

The general lipophilic nature of organic chemicals makes them to tend to accumulate in sediment, suspended particulate and in the adipose tissue of living organisms. Consumption of contaminated fish represents one of the pathways through which pollutants can reach the human body [121]. Even though they are commonly present at low concentration levels, the concern about the adverse effects of a chronic exposure to them is rising. The main concern relies on the capability of these contaminants to act as endocrine disruptors being able to interfere with the reproductive system and the normal development of living organisms. This topic will be deeply discussed in the next section.

There is limited data available about chronic and sub-chronic effects of PCPs in biota. For instance, UV filters such as benzophenone 3 (BP3), benzophenone 4 (BP4) and ethylhexyl methoxycinnamate (EHMC) are able to alter the transcription profile in fish, being able to alter genes related with the production of sexual hormones, whereas octocrylene (OC) may interfere with haematopoiesis, blood flow, blood vessel formation and organ development in adult and embryo zebrafish [122–125]. Studying the dietary impact of triclocarban in rats, for instance, concentrations higher than 25 mg/kg body weight per day had some effect on anaemia and body, liver and spleen weights in rats fed for 2 years [126]. Butyl and propyl paraben were able to influence the sperm quality of juvenile rats [127]. Spongiform myelinopathy has been reported in the brainstem of rats exposed to near-lethal doses of DEET [128].

Data about possible risks to human health on PCPs exposure is even scarce. Nevertheless, humans have a continuous and close contact to PCPs, and the effects of such an exposure are mostly difficult to predict. PCPs have been reported to be present in diverse human samples. For instance, fragrances have been reported to be

at ng/g lipids in human breast milk [129, 130] and human adipose tissue [73]; triclosan has been reported at the ng/mL level in urine [131, 132] and at ng/g lipids in adipose, liver and brain tissue [133]; parabens have been found at the same concentrations in urine [131], breast tissue [134] and human milk [129]. Similarly, UV filters have been determined in urine [131], human milk [129] and semen [135].

Triclosan is degraded to dioxins and is toxic to aquatic bacteria at levels found in the environment [136]. There is also a general concern about the capabilities of triclosan regarding the generation of antibiotic resistance. It is suggested that triclosan and other antimicrobial compounds could cause bacterial resistance against antibiotics [137] and may be related to allergic sensitisation in children [138]. Triclocarban may be able to induce the production of methemoglobin (an Fe^{+3}-based protein complex, similar to haemoglobin but unable to carry oxygen) through the transformation by heat into a primary amine in the bloodstream [139]. Exposure to fragrances has been associated with a wide range of health effects, such as allergic contact dermatitis, asthma, headaches and mucosal symptoms [140, 141]. Although humans metabolise phthalates, easily excreting them in 24–48 h through urine [142], the continuous exposure to it seems to be able to interact with a nuclear receptor (peroxisome proliferator-activated receptors) that has an important role in adipogenesis and lipid storage, disrupting homeostasis and increasing the risk for obesity and, thus, increasing diabetes risk [143] as well as immune and asthma responses [144]. Extensive topical application of DEET has resulted in poisonings (with symptoms like tremor, restlessness, slurred speech, seizures, impaired cognitive functions and coma) including deaths and being linked to possible neurotoxic effects [145]. Phthalates have been linked to asthma and allergies and behaviour changes [146, 147]. In addition, some compounds generate a significant concern due to their carcinogenic potential. One study has tried to correlate low levels of parabens with breast cancer tissue [134], and phthalates have been related to hepatic and pancreatic cancer in mice and rats [148], and a survey in Mexico reported a positive correlation between phthalate concentrations in urine and the risk of developing breast cancer [149]. It seems clear that there is growing concerns about the potential carcinogenicity of such widely used compounds.

4.1 PCPs as Endocrine Disruptors

There is not a general consensus about the correlation between human diseases and exposure to organic contaminants, especially for new emerging contaminants at low levels of concentration. Insufficient field studies, lack of data concerning occurrence in human samples, ecological background and dose relationship and contradictory results are listed as the main reasons about the lack of data on this specific issue. Frequently, the main effects associated with emerging contaminants and their transformation products is their potential to be able to act as endocrine-like molecules and to interfere in the normal functions of the endocrine system, that is, to be endocrine disruptors. The most common endocrine disrupting chemicals

reported to be found in the aquatic environment as well as in wastewaters and sludge include pesticides, steroids, surfactants and plasticisers [150, 151].

There is scarce data on the potential effects of biocides. Exposure to benzotriazole may occur through ingestion or dermal contact. This compound has been found to be able to interfere with the endocrine system through the expression and inhibition of some genes in fish [152]. Concerns about the possible effects of triclosan started due to the fact that triclosan has a similar structure to that of polychlorinated biphenyls and polybrominated diphenyl ethers, and thus, it could have a similar endocrine effect [153]. Although there are no extensive studies about the effects of triclosan in humans, it has been reported to have endocrine effects in rodents and in bullfrogs [153, 154]. It is involved in changes in fish length and sex ratios and decreased sperm count in some species of fish [155]. There is no information about the potential estrogenic effects of other related compounds such as triclocarban and methyl triclosan [54].

Moreover, fragrances show estrogenic effects [156, 157]. The nitromusk fragrances musk ketone and musk xylene possess estrogenic activity in vitro [156]. The same study reports that of the two polycyclic musks AHTN and HHCB; the first was shown to be estrogenically active [158], being a partial agonist of the oestrogen receptor and having threefolds more affinity to the oestrogen receptor than musk xylene; however, its activity compared with that of the 17β-estradiol is rather weak. The macrocyclic musks were found to be inactive [156].

Parabens are a group of PCPs that generate high concern about their potential endocrine effects due to their ubiquity in all kind of goods as well as in the environment. Therefore, the exposure to parabens occurs via ingestion, inhalation and mostly via direct skin contact. A great number of studies have reported agonistic androgen activity in both in vitro [134, 159–161] and in vivo [157, 162]. Thus, estrogenic activity seems to increase with the increase of the linear alkyl branch from methyl paraben to 2-etylhexyl paraben [163]. In addition, the most common transformation product of parabens, the p-hydroxybenzoic acid, also possesses estrogenic activity in both in vitro and in vivo assays [162, 164].

Exposure to phthalates can be produced through ingestion, dermal absorption and inhalation [144]. Among the estrogenically active compounds, phthalates are the only group of chemicals in PCPs with clear supporting evidence of endocrine effects in humans. Hormonal activity due to phthalates has been associated with some adverse reproductive system malfunctions, such as reduction on semen quality or alterations in the normal development of male genitals [142, 147, 165, 166].

Sunscreens enter the body mainly through skin penetration after dermal application. There are a few studies in both in vitro and in vivo, in which UV filters have been found to interfere in the normal reproductive process and the further development in fish and rodents [104, 105, 157, 167]. At least nine UV filters of the regulated compounds in the European cosmetic legislation have been found to possess estrogenic activity. 4MBC, for instance, can induce effects similar to those of the 17β-estradiol in mammal and amphibian cells, as well as EHMC, OC

and BP3 and their related compounds. Other sunscreens such as UVP, UV234 and UV326 have also been reported to display hormonal activity in vitro [106, 107].

As the group before, siloxanes enter the human body through dermal contact. Studies in the literature reported that the siloxane D4 has intrinsic weak estrogenic potential in both in vitro and in eutrophic in vivo models being able to interfere with the female reproductive system [168–170]. EPA received a study by Dow Corning Corporation about chronic and carcinogenic effects in rats reporting that siloxane D5 may increase uterine cancer probability [171].

5 Legislative Framework and Water Awareness Initiatives

Toxic cationic metals and hazardous organic compounds have been reported in natural waters worldwide. Due to this, increasing concern over the release of hazardous chemicals into the aquatic environment demands additional water quality standards. Nevertheless, legislation frameworks are constantly put up to date in order to assess the potential environmental and health risks of emerging contaminants. In this section we discuss some of the available legislative frameworks concerning the aquatic environment and water quality standards, with special focus on the European framework, as well as the diverse water awareness initiatives taken during the last decades.

5.1 European Framework

European water legislation dates to the second half of the 1970s, when the first laws concerning standards and targets for discharges of dangerous substances in drinking, fishing, and bathing waters and groundwater were developed in order to protect human health and the environment. A report done in 1988 reviewed and identified some gaps that could represent a potential risk to the environment, leading to further measures obliging Member States to control urban sewage (Urban Wastewater Treatment Directive, 1991 [172]), nitrogen fertilisers (Nitrates Directive, 1991 [173]) and pollution derived from industrial activities (Directive for Integrated Pollution and Prevention Control, 1996 [174]) and to set a quality standard for drinking water (Drinking Water Directive, 1998 [175]). Nonetheless it became clear that the EU needed a more specific approach about water policies. The commission started a huge and complex process of consults, gathering information and opinions from all levels of society, like the Member States, the European Parliament and local and regional authorities, industry, experts in the matter and non-governmental organisations. The Water Framework Directive 2000/60/EC (WFD) [176] is the main integrated policy in the EU to ensure and promote a sustainable use of water. The key strategy is to ensure long-term protection of water sources by progressively decreasing the amount of contaminants released to

the aquatic environment. The amended Decision 2455 of the WFD states water quality standards are based on a list of priority pollutants, a list which was started with a selection of candidate compounds based on previous official lists and monitoring programmes obtained from the Member States. So far, this list includes 33 priority compounds and 9 hazardous substances which have been subject to the emission control and included into the monitoring programmes. In addition, due to their potential associated risks, other compounds have been included into the review process for identification as priority or hazardous substances. This review process consists mostly in environmental risk assessment studies carried out by the European Research Area framework applied for new chemicals according to the Directive 67/548/EEC [177] and the guidelines of the European Medicine Evaluation Agency (EMEA), being both initiatives the basic pieces to assess the possible adverse effects of pharmaceuticals and PCPs.

The Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) regulation [178] is playing an important role globally with its intention to reform the policy for the EU policy of chemicals, setting a wide framework for regulating, allowing or restricting the use of chemicals in order to minimise the environmental impacts caused during their life cycle. The prioritisation of substances is based on the high production rates and on the possible hazards associated. REACH replaces other laws with the aim of achieving a sustainable development policy, in terms of economic growth and society and environmental protection. REACH also is intended to produce significant advances in the data availability and consistency for the risk assessment of the chemicals used in Europe.

Additionally, in order to ensure that PCPs are not a risk for human health, the EU adopted the regulation 1223/2009/EC [179] on cosmetic products in July 2013. This regulation aims to reduce the administrative burden and the ambiguities relating to cosmetic products as well as to strengthen some aspects of the regulatory framework for cosmetics. It also aims to ensure a high level of protection of human health. In addition, it establishes that a cosmetic product has to be traceable through all the manufacturing processes and claims for consumer protection. The Annex II of the regulation describes which compounds (more than 1,300) are prohibited in cosmetic products, whereas Annex III describes, from a list of 256 compounds, which ones must not be present in the final product or have restricted use, establishing a maximum concentration allowed (Table 1). This regulation has been continuously amended in order to update Annexes II and III as more information regarding PCPs' potential risks are known.

5.2 Other Frameworks

The main policy in the USA about water environment protection is the Clean Water Act of 1972 [180]. This law requires the US states to establish water quality standards for each specific use (such as bathing, fishing and industrial and municipal use) and to establish monitoring programmes to ensure the quality of water is

kept. Its initial focus was to mitigate and monitor point sources of pollution, originally with the objective of "zero discharge" of pollutants, an objective that was scaled down due to its unattainable and unrealistic objectives in a posterior amendment. During the 1990s, due to a series of lawsuits against the EPA, the focus of the law was forced to include nonpoint sources of pollution, introducing the total maximum daily load programme. This programme enters in action when water does not achieve proper quality standards and establishes the quantity of pollutants allowed in a water body based on the relationship between pollutant sources and quality standards, as well as limits for individual discharges. In addition, the Safe Drinking Water Act sets specific limits to the total amount of pollutants allowed in drinking waters as well as to establish monitoring programmes to ensure the overall quality of water to prevent potential risks for human health [181]. In total, the cumulative concentration of 123 compounds is settled as the basic criteria for water quality standards. For human use, PCPs are regulated under the Federal Food, Drug and Cosmetics Act and Title 21 of the Code of Federal Regulations (21 CFR). These regulations cover uses, labelling, public information and general warning statements and prohibitions [182].

In Asia, the Basic Environment law by the Japanese Ministry of Environment, jointly with the Water Pollution law, is the main framework to protect the aquatic environment. The Basic Environment law establishes two kinds of standards for protecting human health and the environment, establishing maximum levels of contamination for some common pollutants. Twenty-six substances relating to human health and 27 more are continuously reviewed due to their potential concerning risks. In addition, the Water Pollution Law establishes the legal framework to prevent pollution in natural waters due to human activities. Also, substances used in PCPs are regulated under the Pharmaceutical Affairs law and its successive amendments, regulated by the Ministry of Health, Labour and Welfare [183]. The South Korean government has settled its water quality standards through the Environmental Pollution Prevention Act of 1971, the Environmental Pollution Law of 1977 and the Water Quality Conservation law of 1990. These laws contemplate 17 substances that may pose risks for both human health and the environment [184]. For human use, allowed and prohibited PCPs are regulated under the Korean Cosmetic Products Act [185]. In China, water quality, pollutant discharges, monitoring and environmental studies are derived from the National Water Quality Standard (GB383-2006), based on quality standards of countries all over the world and without any specific protection objectives. Under this law, water quality is classified into five grades depending on the usage given to natural waters, but due to environmental pollution problems in wide areas of the country, the Sino-Environmental Protection Agency jointly with the Ministry of Science and Technology has started a series of projects to assess the environmental impact of pollution in China and to set a series of standards to ensure human health and environmental sustainability [186]. The Chinese Government's regulations for the Cosmetic Hygiene Supervision of 1990 and the Cosmetic Hygiene Standards of 2007 establish the list of allowed and prohibited PCPs, as well as their labelling and packaging [187].

5.3 Water Awareness Initiatives

The United Nations (UN) System organised during the 1970s a series of global conferences that aimed to discuss critical global issues at high decision-making level. These conferences were about the environment (Stockholm, 1972), population (Bucharest, 1974), food (Rome, 1974), women (Mexico City, 1975), human settlements (Vancouver, 1976), water (Mar del Plata, 1977), desertification (Nairobi, 1977) and new and renewable sources of energy (Nairobi, 1979). Since then, the only UN initiative referring to water has been the Mar del Plata conference. The objective of the Mar del Plata conference was to promote national and international levels of preparedness concerning water quality and responsible management in order to meet the socio-economic needs of the ever-expanding population and to avoid a global water crisis at the end of the twentieth century. The conference approved a plan consisting of two parts, the first one being a compendium of recommendations to ensure a minimum quality and sustainable management such as assessment, use and efficiency, environment, health and pollution control; policy, planning and management; natural hazards; public information, education, training and research; and regional and international cooperation; and the second one, 12 resolutions about a wide range of specific areas. The conference was considered a milestone in water development and had a non-questionable impact in diverse areas such as the generation of new knowledge and information, the settlement of regional analysis and monitoring programmes, and it was the starter for most water policies involving the management and conservation of the aquatic environment. The conferences of Rio de Janeiro and Dublin, both in 1992, treated to assess and debate the general world water situation and to revive the spirit and success of the Mar del Plata conference, but the general outcome of these two conferences resulted in not being as extensive as it was pretended [188]. In 1996, the World Water Council was established. It was created to increase the awareness on water problems and to promote initiatives to protect water and the environment. Their most notable initiative was the establishment of the so-called World Water Forums (WWF), a triennial non-governmental conference following the spirit of the Mar del Plata conference. The first WWF (Marrakesh, 1997) laid the basis for the development of a long-term "Vision for Water, Life and the Environment in the Twenty-First Century". In the year 2000, the report "A Water Secure World: Vision for Water, Life and Environment" done by the Water Commission on Water for the twenty-first century (established in partnership with the UN and the World Water Council) was the next institutional initiative carried out. This report reviewed the results of all previous consults, evaluating approaches in water management, participatory institutional mechanisms, price of water, innovation and the suggestion of creating new transparent regulatory frameworks for private uses of water, and was heavily discussed in the second WWF of Hague (2000). The second WWF focused on dealing with the state and ownership of water resources, their development, management, their financial impact and the environment. The third WWF (Japan, 2003) was focused in the debate of the goals at the Millennium Summit of

the UN, the International Freshwater Conference and the World Summit on Sustainable Development. The fourth WWF (Mexico City, 2006) gave a step onwards establishing the Water Integrity Network, a network that enlightens corruption around illicit water management. The fifth WWF (Istanbul, 2009) was the first one that had a Heads of State meeting. The forum produced a series of recommendations in order to adapt water infrastructures to emerging challenges such as pollution, to ensure a good water quality and to protect the aquatic environment. The last WWF to date was settled in Marseille (2012) and had its major focus on promoting solutions and triggering or strengthening commitments [189].

These initiatives have served as reminders of the problems relating to mismanagement of water and the aquatic environment and have served to launch all kinds of posterior initiatives in order to achieve a better understanding and control of such an important resource as water is. The diverse political initiatives, as well as the creation of governmental and intergovernmental over-watch organisations (e.g. EU Water Initiative and Water Environment Partnership in Asia) and private think tanks such as the World Water Council and the Global Water Partnership, are direct outcomes from these assessing processes. Despite the initiatives taken and as the growing concerns over new pollutants arise, the general concerns are focused on the presence of extensively studied pollutants. As the bulk of information regarding the potential harmful effects of emerging contaminants, as the PCPs, increases, it would be expected that new initiatives take place to include them between the already ongoing monitoring programmes to improve the quality of the aquatic environment worldwide.

6 Concluding Remarks

As world population increases, new technologies are needed to ensure a clean and healthy environment for living beings. The chemical industry worldwide creates tons of new and potentially hazardous chemical compounds every year in addition to those already existing, designed for specific purposes and often without a biological analogue. Nevertheless, the structure of some of the new synthetic compounds has some degree of resemblance to biologically produced molecules such as hormones. Water is a key resource for both the natural world and the socio-economical human activity. As the general concern about the quality state of water and to ensure the continuity and a good level of health of the aquatic environment, a series of initiatives and policies are being taken action during the last decades. PCPs are a wide group of chemicals with an extensive use in an even wider range of applications. Generally poorly removed during wastewater treatment processes, they tend to reach the aquatic environment. Data reported so far presented their ubiquity in the different environmental compartments, with mainly unknown effect in the living organisms. Further studies have to be conducted to assess the actual

magnitude of their presence and their potential risks to wildlife and human health. Besides that, improved and new wastewater treatment technologies have to be developed in order to ensure an efficient removal of these groups of emerging pollutants to avoid the persistence of such chemicals in the aquatic environment.

Acknowledgments This work has been financially supported by the Generalitat de Catalunya (Consolidated Research Groups "2014 SGR 418 - Water and Soil Quality Unit").

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Part I
Occurrence of Personal Care Products in the Aquatic Environment: Case Studies

Occurrence of PCPs in Natural Waters from Europe

Shivani Tanwar, Marina Di Carro, Carmela Ianni, and Emanuele Magi

Abstract In the framework of the study of emerging pollutants in the aquatic environment, personal care products (PCPs) play a relevant role as they are used in everyday life. They are continuously introduced into the natural water compartment, mainly through treated and untreated sewage but also via different pathways. This chapter describes the "state of the art" of the distribution and impact of PCPs on European natural waters (rivers, lakes, groundwater, drinking water, etc.). An extensive review of the recent literature has been carried out, gathering together the most relevant studies and presenting the results in five sections: fragrances, UV filters, detergents, preservatives, and repellents. In each section, data on the main molecules employed in PCP formulations are reported and compared. The physicochemical properties of many PCP compounds are summarized in the respective tables along with an additional table listing the measured concentrations of all PCPs detected in waters all over Europe.

Keywords Environmental analysis, European water monitoring, Natural water, Personal care products

Contents

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M.S. Díaz-Cruz and D. Barceló (eds.), *Personal Care Products in the Aquatic Environment*, Hdb Env Chem (2015) 36: 37–72, DOI 10.1007/698_2014_276,

1 Introduction

Environmental monitoring in water pollution control has been traditionally focused on conventional priority pollutants, especially on those considered as persistent, toxic, or bioaccumulative. In the past decade, there has been a growing interest in the occurrence of emerging pollutants in the terrestrial and aquatic environment and their environmental fate and potential toxicity. For this reason, the focus of research has been partly shifted to the analysis of these compounds that are now widely used in everyday urban activities. Many of these are not new chemicals, since they have been present in wastewaters for decades, but are only now being recognized as potentially significant water pollutants, even if largely unregulated. Their occurrence in the receiving waters is mainly due to the incomplete removal in sewage treatment plants, which are designed principally to control suspended solids emissions and oxygen demand of the final effluent [1–3].

Among these compounds, personal care products (PCPs) are a group of chemicals used in daily products such as hair and skin products, soaps, lotions, toothpaste, and perfumes. PCPs comprise fragrances, preservatives, detergents, sunscreens, and household chemicals used to improve the quality of daily life. While pharmaceuticals are intended for internal use, PCPs are for external use; thus, they are not subjected to metabolic alterations: the regular usage of large quantities led them to enter unchanged into the environment [4] mainly through the discharge of untreated and treated sewage and also bathing or swimming. Their presence is hence ubiquitous, and a regular monitoring of the environment is highly desirable.

The Global Beauty Market (GBM) is usually divided into five main business sectors: skin care, hair care, color (makeup), fragrances, and toiletries. The European market is the largest in the world for perfumery and cosmetics. Among them, Germany is the hub of the cosmetic market, followed by France, the UK, Italy, and Spain. These five countries are leaders in the number of new products launched, volume of production, exports, and imports [5]. The annual production of PCPs exceeded 550,000 metric tons for Germany alone in the early 1990s [2]. In the period 1998–2010, total cosmetics sales (beauty and personal care products) doubled, from 166.1 billion USD to 382.3 billion USD. Skin care was the most significant sector throughout 2010 with 23% of the market share, its growth propelled largely by the Asian market [6]. In the last decade, aging and sun-protecting agents played a vital role in the growth of skin care segment. According to Łopaciuk, GBM has grown by 4.5% a year on average in the past 20 years with annual growth rates ranging from around 3 to 5.5% [7]. The majority of global premium cosmetics sales is concentrated within the developed markets (mostly the USA, Japan, and France) [8].

Data reported on high production volume of PCPs highlights the need for the monitoring of these compounds in the aquatic environment, where they are discharged mainly through the sewage. Water is highly susceptible to pollutants, and its contamination can cause severe health problems in countries where it is the only source of drinking water. The potential sources of groundwater contamination

are storage tanks, septic systems, uncontrolled hazardous waste, landfills, chemicals, road salts and atmospheric contaminants that directly or indirectly end up in the groundwater. Therefore, high-quality, safe, and sufficient drinking water is vital for our everyday life, for drinking and food preparation, and also for cleaning, hygiene, washing, and watering plants.

Groundwater comprises the largest pool of freshwater in the world, accounting for over 97% of all freshwaters available on earth (excluding glaciers and ice caps), while the remaining 3% is covered mainly by surface water (lakes, rivers, wetlands) and soil moisture [9]. Groundwater is the main source of freshwater supplied as drinking water for 75% of European Union (EU) and 50% of US population; industries (e.g., cooling waters) and agriculture (irrigation) are also dependent on groundwater for resource. As per EU directive, groundwater should not only be considered as a water supply reservoir, but it should be protected for its own environmental value. Many rivers across Europe bring 50% of the annual flow from groundwater, reaching 90% in low-flow periods; therefore, deterioration of groundwater quality may directly affect related surface water and terrestrial ecosystems. Groundwater movement is very slow and the impact of anthropogenic activities may last for a long time: pollution that occurred either by industrial, agricultural, or human activities may still be menacing groundwater quality today and in future years.

In the past two decades, the detection of trace amounts (<1 μg L^{-1}) of organic compounds in water matrices has been possible, especially thanks to improvements in analytical instrumentation, which allowed very low limits of detection. Buchberger wrote a review highlighting the current approaches to trace analysis of personal care products in the environment [10].

Because of the elevated hydrophobicity of ingredients in PCPs, most of them significantly sorb onto sludge and sediments. In a case study, polycyclic musks were measured in streams of Hessen, Germany; data revealed 13,000 μg kg^{-1} total solids in suspended matter and 3,211 μg kg^{-1} dry weight in sediments; however, concentrations of few ng L^{-1} could be measured in water [11].

In a recent study, Brausch et al. reviewed the environmental concentration of personal care products in the aquatic environment and examined acute and chronic toxicity data available for personal care products, highlighting the areas of concern [12]. According to the toxicity studies reported so far, the authors concluded that only triclosan and triclocarban have the potential to cause chronic effects, while for other PCPs like paraben preservatives and UV filters there is evidence suggesting endocrine effects in aquatic organisms. The other main concern of PCPs regards their potential to bioaccumulate in aquatic organisms. UV filters, disinfectants, and fragrances have all been shown to bioaccumulate in biota; thus, the potential for biomagnification and for effects on higher-trophic-level organisms needs to be investigated.

In this chapter, personal care products have been divided into five main classes: fragrances, UV filters, phenolic compounds, preservatives, and repellents. A subsection has been dedicated to each class, where the literature related to the

occurrence of PCPs in groundwater, surface water, and drinking water across Europe has been reviewed and compared.

2 Fragrances

Fragrances are perhaps the most widely studied class of PCPs and are believed to be ubiquitous contaminants in the environment. The most commonly used fragrances are synthetic musks, which are present in a wide range of products including household chemicals, soaps, and detergents, with high concentration especially in perfumes, body lotions, and deodorants [13]. Synthetic musks comprise nitro musks, which were introduced in the late 1800s, and polycyclic musks, introduced in the 1950s. Nitro and polycyclic musks are water soluble, but high octanol/water coefficients (log $K_{ow} = 3.8$ for musk ketone and 5.4–5.9 for polycyclic musks) [14, 15] indicate high potential for bioaccumulation in aquatic species [16, 17]. Due to the bioaccumulation potential in the aquatic environment and the incomplete information about their chronic toxicity and degradation, musk xylene and musk ketone were included in 1997 in the EU third priority list (http://eur-lex.europa.eu/legal-content/EN/TXT/?uri=OJ:L:1997:025:TOC).

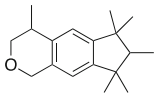
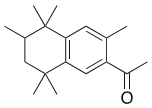
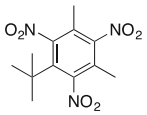
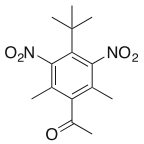
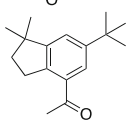
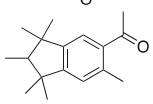
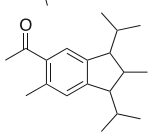
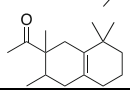
Among nitro musks, musk xylene, musk ketone, musk ambrette, musk moskene, and musk tibetene are the most common fragrances in PCPs. HHCB (1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexa-methylcyclopenta-(*g*)-2-benzopyran; trade name, Galaxolide®) and AHTN (7-acetyl-1,1,3,4,4,6-hexa-methyl-1,2,3,4-tetrahydronaphthalene; trade name, Tonalide®) are the two most important compounds in the group of polycyclic musks and essential ingredients of perfumery industries [18, 19]. In Europe, the usage amount of these two chemicals exceeds 2,000 tons per year [14]. OTNE ([1,2,3,4,5,6,7,8-octahydro-2,3,8,8-tetramethylnaphthalen-2yl] ethan-1-one) is the major constituent of one of the most popular fragrance mixtures in the last years, marketed as technical mixture Iso E Super® with 2,500–3,000 tons annually and a "woody" sensory impression rather than "musky" [20]. Table 1 shows abbreviations, structures, and analytically relevant data of most relevant fragrances dealt under this section.

Synthetic musks were identified in environmental samples nearly 30 years ago. Yamagishi et al. performed in Japan the first comprehensive monitoring for musk xylene and musk ketone in freshwater fish, marine shellfish, river water, and STW wastewater [22, 23].

In Europe, Gatermann et al. performed one of the first studies about synthetic fragrances, identifying nitroaromatic compounds such as musk xylene and musk ketone in 30 out of 33 North Sea water samples in concentrations up to 0.17 and 0.08 ng L^{-1}, respectively [18].

Polycyclic musks were studied for the first time in the 1990s by Eschke et al., who measured average concentrations of 370 ng $L^{-1}$of HHCB and 200 ng $L^{-1}$of AHTN in the Ruhr river [24, 25]. In the subsequent years, several data were published regarding the occurrence of these analytes, especially in water matrices.

Table 1 Analyte abbreviations, structures, and analytically relevant data of fragrances

Abbreviation	Trade name	Structure	Molecular formula	Log $K_{O/W}$
HHCB	Galaxolide		$C_{18}H_{26}O$	5.9[a]
AHTN	Tonalide		$C_{18}H_{26}O$	5.7[a]
MX	Musk xylene		$C_{14}H_{15}N_3O_6$	4.9[a]
MK	Musk ketone		$C_{14}H_{18}N_2O_5$	4.3[a]
ADBI	Celestolide		$C_{17}H_{24}O$	5.4[b]
AHMI	Phantolide		$C_{17}H_{24}O$	5.85[b]
AITI	Traseolide		$C_{18}H_{26}O$	6.3[b]
OTNE	Iso E Super®		$C_{16}H_{26}O$	5.18[c]

[a]Measured [15]
[b]Estimated (SRC [21])
[c]US EPA screening tool

HHCB, AHTN, and 4-acetyl-1,1-dimethyl-6-tert-butylindane (ADBI) were determined at concentrations up to 100 ng L^{-1} in the river Elbe, one of the major rivers of central Europe and a main carrier of contaminants, near Torgau [26].

Bester et al. determined HHCB (0.09–4.8 ng L^{-1} in the North Sea and 95 ng L^{-1} in the river Elbe estuary) and AHTN (0.08–2.6 ng L^{-1} in the North Sea and 67 ng L^{-1} in the river Elbe estuary) [27]. The values measured in water samples of the years 1990 and 1995 showed no statistically significant difference for AHTN, while HHCB showed a trend toward higher concentrations in 1995 at some stations. Musk ketone (2–10 ng L^{-1}), HHCB (36–152 ng L^{-1}), AHTN (24–88 ng L^{-1}), and low levels of ADBI (2–8 ng L^{-1}) were detected in water samples of river Elbe in Magdeburg, Germany [16].

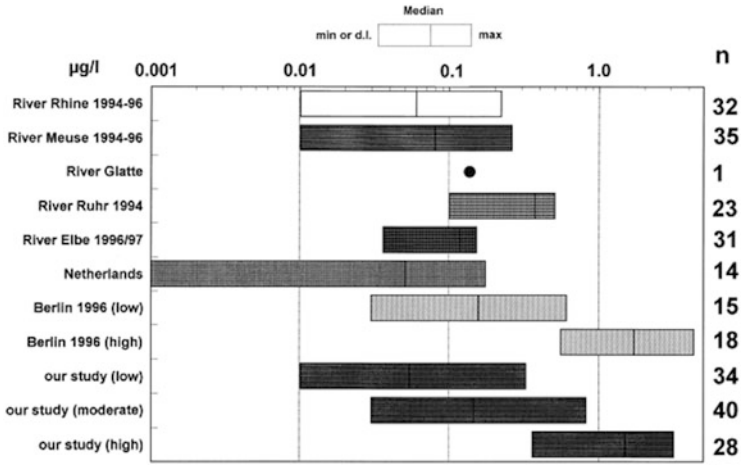


Fig. 1 Galaxolide (HHCB) in surface water samples from lakes and rivers. Low, moderate, and high relate to the proportion of sewage effluents in the aquatic system. Comparison with the results of another group, which examined representative sites in Berlin waters [28], showed good correlation with the contamination data presented, when considering only the results in identical areas of water, despite the different methodology (solid-phase microextraction) (Picture taken from [31] with permission)

Polycyclic musks and nitro musks were found as environmental pollutants in screening analyses of 30 representative surface water samples collected from rivers, lakes, and canals in Berlin [28]. In particular, HHCB, AHTN, and ADBI were detected in all the analyzed samples up to the µg L^{-1} level, with maximum values of 12.5, 6.8, and 0.52 µg L^{-1}, respectively. Musk ketone was the only nitro musk found in many water samples, even if in low concentration. On average, HHCB, AHTN, ADBI, and musk ketone were found with relative ratios of 20:10:1:1.

The occurrence of polycyclic musks [29] and musk xylene and musk ketone amino metabolites [30] was reviewed in 1999, considering all data regarding their monitoring in water, sediment and suspended particulate matter, sewage sludge, and biota. The highest concentrations of polycyclic musks (HHCB and AHTN) were found in water (max. concentration 6 µg $L^{-1}$of HHCB and 4.4 µg L^{-1} of AHTN).

Polycyclic musks (HHCB, AHTN, ADBI, AHMI, and ATII) within the framework of an exposure-monitoring program (1996 and 1997) were determined in 102 surface water samples collected from rivers Spree, Dahme, and Havel in Berlin [31]. HHCB was found at a mean concentration of 1.59 µg L^{-1}in surface water of areas strongly polluted with sewage, while a comparatively lower mean concentration of 0.07 µg $L^{-1}$was found in surface water hardly contaminated with sewage (Fig. 1). The median percentile proportion was 71% for HHCB and 22% for AHTN in samples where all five polycyclics could be measured.

AHTN has been detected in surface water at a concentration of 390 ng L^{-1} [28], in the range of 20–470 ng L^{-1} [31] in Berlin, Germany, and 73 ng L^{-1}in river Elbe, Germany [16].

Dsikowitzky et al. studied the occurrence and distribution of polycyclic musks in the Lippe river (a tributary of the Rhine river, Germany) in order to investigate their dynamic transport and partitioning between aqueous and particulate phases after their discharge into the river by sewage effluents [32]. Nineteen water samples, taken from a longitudinal section of the river, were analyzed to determine HHCB, AHTN, ADBI, and 6-acetyl-1,1,2,3,3,5-hexamethylindane (AHMI) concentrations. HHCB and AHTN were present in each water sample at concentrations ranging from <10 to 180 ng $L^{-1}$and <10 to 70 ng L^{-1}, respectively. The load of dissolved HHCB and AHTN (calculated on the basis of compound concentrations in water and the corresponding river runoff data) ranged from 3 to 293 g/day and from 1 to 108 g/day, respectively. Increasing loads of HHCB and AHTN along the river indicated a high input of sewage effluents to the densely populated areas along the central part of the river while decreasing loads at the lower reaches indicated that the rate of removal of musks was higher than the rate of input in the corresponding river sections.

Bester et al. measured concentrations of OTNE in the Ruhr river in the range 30–100 ng L^{-1} [33]. The authors employed the geo-referenced exposure model GREAT-ER (Geo-referenced Regional Exposure Assessment Tool for European Rivers) to simulate OTNE concentrations in the Ruhr river basin. According to this model, around half of the total OTNE emissions into the Ruhr river are transferred from surface water into the atmosphere and the sediment. Volatilization from lakes was identified as the major removal process for OTNE. Water samples from the Danube river (Hungary) were also analyzed. OTNE concentrations were present at concentration levels of the same order of magnitude (29–810 ng L^{-1}) of the Ruhr river basin but exhibited higher spatial variability (Fig. 2).

Nontarget screening analysis for the identification of organic contaminants in selected German and European rivers was carried out, and a number of PCPs (*N*,*N*,*N*′,*N*′-tetraacetylethylenediamine, methoxycinnamic acid, 2-ethylhexylester, drometrizole, HHCB, AHTN, ADBI, AHMI, oxoisophorone, lilial, viridine, dihydromethyljasmonate, cineol, DEET) were measured during this study [34]. Although no quantitative data were reported, this study demonstrated the usefulness of screening analyses to enlarge the number of substances that are detected during environmental monitoring. The synthetic musk fragrances HHCB and AHTN were detected with mean concentrations of 141 and 46 ng L^{-1}, respectively, in freshwater river systems in Hessen, Germany [35].

Gómez et al. carried out an extensive study regarding occurrence, fate, and temporal and seasonal distribution of PCPs in Henares River basin (central Spain), which is subjected to industrial, agricultural, and wastewater discharges [36]. Data showed that PCPs were the most commonly detected compounds in both treated wastewater and river waters. HHCB and AHTN were found in all the analyzed samples. The highest mean and maximum concentrations were measured for the fragrance HHCB in the WWTP effluents (above 10 μg L^{-1}) and in the river

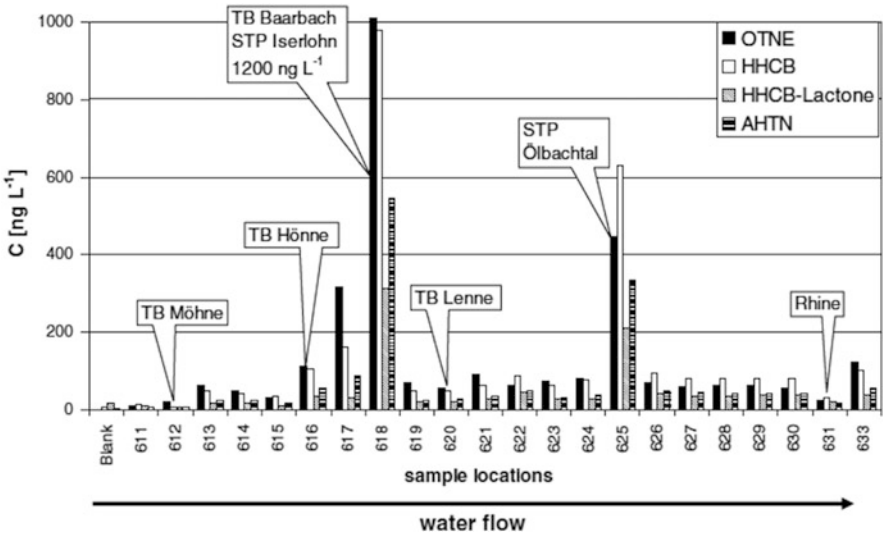


Fig. 2 Concentrations of synthetic fragrances (OTNE, HHCB, AHTN, and the metabolite HHCB-lactone) in surface waters from the Ruhr river basin (*TB* tributary). Picture taken from [33] with permission. The codes 611–633 represent location of sampling sites. OTNE concentrations in Ruhr river water showed an increasing trend from approximately 10 ng L^{-1} (upstream area) to 100 ng L^{-1} (mouth of Ruhr river), while concentrations in some of the tributaries were even higher (e.g., Ölbach, which is largely influenced by a major WWTP: 420 ng L^{-1}). OTNE concentrations in the Rhine river were lower (20 ng L^{-1}) due to dilution as the wastewater fraction in Rhine river is smaller than in Ruhr river

waters (above 100 ng L^{-1}in the less contaminated sample). AHTN was the second most concentrated compound after HHCB.

HHCB and AHTN were analyzed in remote and anthropogenically influenced Swiss surface waters and in Mediterranean seawater [37]. The measured concentrations of HHCB and AHTN in lakes were <2–47 and 1–18 ng L^{-1}, respectively, while in rivers and streams were 5–564 and 2.3–186 ng L^{-1}, respectively, with highest concentrations in small rivers downstream of WWTP effluents. In seawater samples collected in the south of Spain, both HHCB and AHTN were not detected.

A monitoring survey of wastewater and groundwater was undertaken at the Llobregat delta, south of Barcelona (Spain), where pharmaceuticals, personal care products, and heavy metals priority substances were investigated. In groundwater, HHCB was detected in 98% of the samples with concentration ranging from 2 to 359 ng $L^{-1}$and a mean value of 106.8 ng L^{-1} [38]. Jurado et al. reviewed in 2012 the presence of emerging organic contaminants in Spanish groundwaters, both in rural and urban areas, evaluating the potential sources of contamination and the occurrence and the fate of these compounds [39].

HHCB and AHTN were determined below 5 ng L^{-1} in Seine River sample, collected downstream of Paris in August 2003 [40].

In Italy, Villa et al. investigated the occurrence of selected polycyclic musks (HHCB, AHTN, and ADBI) in the Molgora River, Lombardia region, for the first time [41]. The authors reported spatial and temporal profiles of contamination. The results obtained were comparatively higher than monitoring data of other European regions, which indicated a significant higher level of analyte pollution of the Molgora River. Italy has the largest detergent consumption per capita in EU; nevertheless, few data about the occurrence of fragrances in Italian waters are available, urging the need to extend the monitoring to other Italian water frames, in order to achieve a better knowledge of the levels of polycyclic musks contamination in this country.

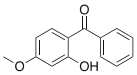
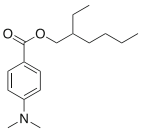
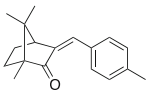
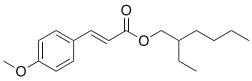
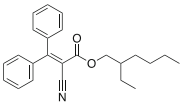
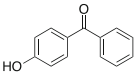
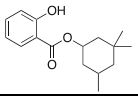
Terzic et al. determined fragrance compounds in municipal waters [42] of the region of Western Balkan (Bosnia and Herzegovina, Croatia, and Serbia). The concentrations measured ranged from 0.337 μg L^{-1} for traseolide (TRA) to 16.7 μg L^{-1} for amberonne (AMB). Among polycyclic musks, HHCB was the most abundant with average levels of 630 ng L^{-1}. Other common fragrances determined were AMB, acetyl cedrene (AC), and musk xylene (MX) with average concentrations of 2.8, 1.6, and 0.13 μg L^{-1}, respectively. A lactone metabolite of HHCB and AHTN was also detected in the samples.

The occurrence of seven synthetic musks (HHCB, AHTN, ADBI, AHMI, musk ketone, musk xylene, and Pentadecanolide®) was assessed in surface waters through an axial transect of the Tamar Estuary (UK) and the adjacent coastal environment. Concentrations of HHCB (6–28 ng L^{-1}) were higher than those of AHTN (3–10 ng L^{-1}); in general high concentrations reflect the inputs through WWTP outfalls into the receiving waters, with similar trends for both compounds along the estuary. Temporal variations in concentrations of HHCB and AHTN were found between June and July 2007: concentrations of HHCB and AHTN are approximately one order of magnitude lower at high tide than those at low tide in the considered area [1]. Similar studies were carried out in surface water of Denmark where five PCPs (cashmeran, methyl dihydrojasmonate, HHCB, and AHTN) were detected in the concentration range of 40–250 ng L^{-1} [43].

3 UV Filters

Organic UV filters are substances with the capability to absorb UV radiation in virtue of their large molar absorption coefficient in the UVA and UVB range and are often added to cosmetics, to shield human skin from the harmful effects of solar radiation [44]. These compounds are included in the formulation of many PCPs (e.g., sunscreen creams, beauty cosmetics, shampoos, lipsticks, hair sprays, etc.) in amounts between 0.1 and 10% [45]. UV filters can reach surface waters via release from the skin during swimming and bathing or through wastewater. Most UV filters are highly lipophilic (i.e., can bioaccumulate) and hardly degradable in sewage treatment plants; moreover, recent studies have shown estrogenic and other endocrine effects for several UV filters with a special emphasis to humans [46–49]. Due

Table 2 Analyte abbreviations, structures, and analytically relevant data of organic UV filters

Abbreviation	INCI name*	Structure	Molecular formula	Log $K_{O/W}$
BP-3	Benzophenone-3		$C_{14}H_{12}O_3$	3.8[a]
OD-PABA	Ethylhexyl dimethyl p-aminobenzoate		$C_{17}H_{27}NO_2$	6.15[b]
4-MBC	4-methylbenzylidene camphor		$C_{18}H_{22}O$	5.1[a]
EHMC/ OMC	2-ethylhexyl-*p*-methoxycinnamate		$C_{18}H_{26}O_3$	5.8[a]
OCR	Octocrylene		$C_{24}H_{27}NO_2$	6.9[c]
4-HB	4-hydroxybenzophenone		$C_{13}H_{10}O_2$	2.67[d]
HMS	Homosalate		$C_{16}H_{22}O_3$	6.16[c]

[a]EPIWIN v3.12 database
[b]Software calculated value, from SciFinder Scholar Database 2006: http://www.cas.org/products/sfacad/
[c]Syracuse Research Corporation (SRC) database
[d]KOWWIN v1.67 estimate
* INCI (international nomenclature for cosmetic ingredient) elaborated by CTFA and COLIPA

to their increased use and presence in the aquatic environment, UV filters have been included in the list of emerging contaminants [50], and various monitoring studies have been carried out in Europe and published in the literature. The most commonly studied compounds with their structures and acronyms are presented in Table 2.

One of the first reports on sunscreen residue measurement in water samples appeared in the literature in 2002, when Lambropoulou et al. developed an SPME-GC method for the determination of two UV-filter molecules BP-3 and OD-PABA, commonly employed in commercial products. Data for water samples collected in two swimming pools showed concentration values of 2.4–3.3 and 2.1 μg L^{-1} for BP-3 and OD-PABA, respectively, while shower water samples were in the range 8.2–9.9 and 5.3–6.2 μg L^{-1}, respectively [51]. Later on, Giokas et al. monitored different natural water samples across Greece; they reported for the first time trace levels of UV filters in coastal seawater, and, for example, they measured 1.8 ng L^{-1} of BP-3 in Ionian sea and 6.5–8.2 ng L^{-1} in other two touristic areas in Northwestern Greece [52, 53]. Similar levels of BP-3, 4-methylbenzylidene camphor (4-MBC), and hethylhexylmethoxycinnamate (OMC) were reported by these

authors in other water matrices: swimming pool (4.2–6.9 ng L^{-1}), game pool (3.0–5.7 ng L^{-1}), and shower wastewater (3.8–10.0 ng L^{-1}).

A new LC-MS method combined with stir bar sorptive extraction was developed by Nguyen et al. for the determination of UV-filter compounds in seawater [54]. The method was applied to investigate six UV filters in coastal seawater samples from Liguria, Italy. Only BP-3 and EHMC were measured in the analyzed samples (<LOQ–118 ng L^{-1}), although some of the remaining analytes were detected below the limit of quantitation. The authors reported also results from samples collected in a swimming pool where, not surprisingly, the analytes showed higher values than in seawater (up to 216 ng L^{-1} for BP-3).

Various authors considered the occurrence of these compounds in lakes and rivers. Poiger et al. determined five UV-filter compounds (EHMC, BP-3, 4-MBC, OC, and BM-DBM) in two Swiss lakes, Zürich Lake and Hüttnersee Lake, where a considerable direct input of UV filters was expected, due to recreational activities [55]. All the considered compounds were detected at low concentrations with a slightly higher contamination level revealed at Hüttnersee Lake, ranging between <2 and 125 ng L^{-1}, against <2–25 ng L^{-1} for Zürich Lake. Concentrations generally increased in summer, when direct input is expected due to bathing as shown in Fig. 3. Anyway, measured concentrations in both lakes were considerably lower than those predicted from estimates deriving from the number of visitors at the lakes' swimming areas and from a survey of the usage of sunscreens among these visitors.

Balmer et al. investigated the occurrence of four important UV-filter compounds (BP-3, 4-MBC, OMC, and OC) in wastewater and water and fish from various Swiss lakes, by GC-MS [57]. As expected all four UV filters were present in wastewater with a maximum concentration of 19 μg L^{-1} for EHMC; a general trend suggesting a seasonal variation was observed, with higher loads in the warmer season. UV filters were also detected in Swiss midland lakes and the river Limmat at low concentration levels (<2–35 ng L^{-1}); no UV filters (<2 ng L^{-1}) were detected in a remote mountain lake. By interpreting results from passive sampling (SPMDs), authors suggested some potential for accumulation of these compounds in biota.

Cuderman et al. determined six UV filters in different recreational waters of Slovenia, including rivers and lakes [58]. The most frequently detected compound was BP-3 (32–400 ng L^{-1}), although most of the remaining analytes were mostly below LOD probably because the employed method was not sensitive enough. BP-3 was also measured in the range of 6–28 ng L^{-1} in the Spanish rivers Ebro, Ter, and Llobregat [59].

PCPs and other chemicals (pharmaceuticals, endocrine disruptors, and illicit drugs) were monitored in River Taff and River Ely, South Wales, UK. Regarding UV filters, the authors stated that solely BP-4 was found at concentrations exceeding 100 ng L^{-1}, similarly to three other PCPs namely, methylparaben, 4-chloroxylenol, and 4-tert-octylphenol [60].

Magi et al. monitored the Sturla River in Genoa, Italy, from April to August 2011; three UV-filter compounds (BP-3, OC, and EHMC) were measured in the

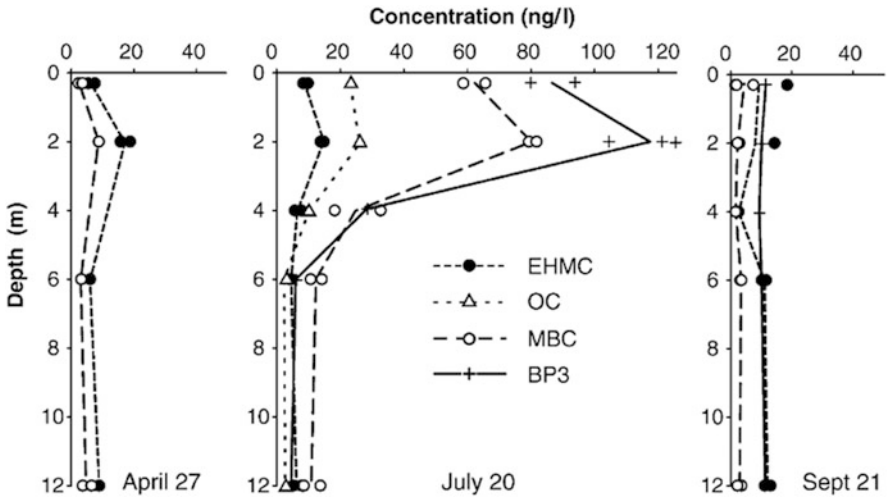


Fig. 3 Vertical concentration profiles of organic UV filters at Hüttnersee in 1998. Note the increased concentrations in July near the lake surface. Picture taken from [55] with permission. The first profile, measured in April 1998, shows low concentrations (≈3–20 ng L^{-1}) and rather uniform distribution over the whole water column. Concentrations of OC were not detected. The second profile, taken in July 1998, shows increased concentrations of BP-3, MBC, and OC in the surface layer of 80–125, 60–80, and 22–27 ng L^{-1}, respectively. The concentration increases correspond to total inputs of BP-3, MBC, and OC of approximately 45, 29, and 10 g, respectively, to the epilimnion of Hüttnersee (depth, 2.5 m; volume, 4.13×10^5 m^3) during the time between April and July, and probably higher, if some elimination of the UV filters occurred during this time. The third profile, measured in September 1998, again shows lower concentrations and uniform distribution over the water column, indicating rapid removal of all three compounds from the lake. While three compounds show significant seasonal variation of their concentrations at this lake, one (EHMC) does not. There are indications that EHMC is biodegradable under natural conditions in lakes [56] and degradation may well exceed input at lake Hüttnersee during summer

range 3–112 ng L^{-1} with the highest values detected in May, when an unusual hot and dry climate was observed [61].

Rodil et al. proposed a new method for the determination of nine UV-filter compounds in water by means of nonporous membrane-assisted liquid–liquid extraction and LC-MS/MS [62]. The method was then applied to real waters; the analysis of samples collected at the lake Cospuden (selected because of its inputs from recreational activities) revealed the presence UV filters at concentrations between 40 ng L^{-1} (BP-3) and 4,381 ng L^{-1} (OC). Later on, the same research group reported the results of a monitoring program on emerging pollutants, carried out on different water matrices from the Galicia region, Spain [63]. Within several PCPs, seven UV filter compounds were also measured in surface and tap water, typically below the 10 ng L^{-1} level. In particular, BP-4 was detected in 75% of surface waters and PBSA and 4-MBC in about 30%, showing the highest levels at the end of summer, probably due to recreational uses of water. These three

compounds were also detected in several tap water samples at a very low level, except BP-4, that was measured up to a maximum concentration of 62 ng L^{-1} (Fig. 6). Accordingly, BP-4 resulted to be one of the main UV filter in surface waters in the recent study of Gracia-Lor et al. on the determination of PCPs and pharmaceuticals in environmental samples [64]. In fact, BP-4 was measured in 82% of the surface water samples collected in the area of Valencia (Spain), with a maximum concentration level of 952 ng L^{-1} (the highest of all the considered benzophenones).

4 Phenolic Chemicals and Detergents

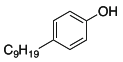
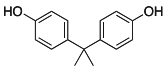
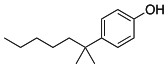
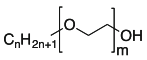
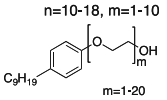
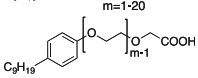
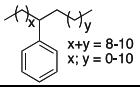
In the present section, phenolic compounds (mainly alkylphenols and their carboxylate and ethoxylate derivatives) and detergents are presented together; although phenols are released into the environment by different sources, they are widely used in the production of detergents. These are generally divided into four classes: anionic, cationic, amphoteric, and nonionic detergents. The nonionic surfactants are used extensively to produce detergents and cosmetics; some of these compounds, like alkylphenols and their carboxylate and ethoxylate derivatives, are known to exhibit endocrine-disrupting effects, similarly to many other nonsteroidal anthropogenic chemicals. Table 3 shows abbreviations, structures, and analytically relevant data of the most relevant phenolic compounds detected in Europe.

One of the first study on phenolic contaminants as a possible source of estrogenic effects in the aquatic environment was carried out in Germany by Bolz et al. [69]. They determined nine phenolic chemicals in various compartments, and data from 23 water samples (five streams and rivers) showed the predominance of 4-nonylphenol (4-NP), with concentration levels up to 458 ng L^{-1}.

In the same period, coastal waters and sediments of Spain were studied to obtain information on occurrence and distribution of nonionic surfactants and their degradation products [70]. Petrovic et al. collected 35 samples of coastal waters from the Spanish coast, including the harbors of Tarragona, Almeria, and Barcelona, the mouths of the Besos and Llobregat rivers, the Bay of Cadiz, and various yacht harbors in the Mediterranean coast.

The analysis indicated the presence of considerably high concentrations of nonylphenolethoxylates (NPEO) and NP near the points of wastewater discharges; NP was found in 47% of seawater samples, ranging from 0.15 to 4.1 μg L^{-1}. Distributions of the nonionic surfactants in water are shown in Fig. 4. The authors also measured linear alkylbenzenesulfonates (LAS), an important class of anionic detergents, employed even in PCP formulations; LAS were found in relatively high concentrations, with the highest values in water samples from the mouth of two rivers in Barcelona (up to 92 μg L^{-1}). Measured values were comparable with levels previously reported for densely populated zones, which discharge urban wastewaters directly into the sea. The same research group, during a study on sewage treatment plants and receiving river waters over a 7-month period in two

Table 3 Analyte abbreviations, structures, and analytically relevant data of phenols and detergents

Abbreviation	Compound	Structure	Molecular Formula	Log $K_{O/W}$
4-NP	4-nonylphenol		$C_{15}H_{24}O$	3.80–4.77[a]
BPA	Bisphenol A		$C_{15}H_{16}O_2$	3.4[b]
OP	4-tert-Octylphenol		$C_{14}H_{22}O$	4.12[c]
AEO	Alcohol ethoxylates			3.15–7.19
NPEO	Nonylphenolethoxylates			4.2[d]
NPEC	Nonylphenoxycarboxylates			
LAS	Linear alkylbenzenesulfonates			3.32 for C11.6

[a][65]
[b][66]
[c][67]
[d][68]

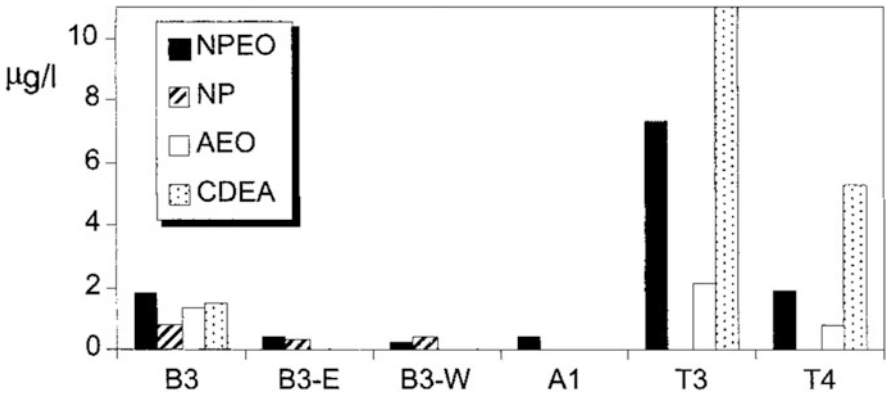


Fig. 4 Distributions of nonylphenolethoxylates (NPEO), nonylphenol (NP), alcohol ethoxylates (AEO), and coconut diethanol amides (CDEA) in seawater during different periods (Picture taken from [70] with permission)

tributaries of the Llobregat river, reported concentrations of up to 31 µg L^{-1} for NPEOs, 15 µg L^{-1} for NP, and 35 µg L^{-1} for nonylphenoxycarboxylate (NPE1C) in river water downstream of sewage treatment plants.

Results of a long-term survey from the Danish National Groundwater Monitoring Program, focused on the evaluation of levels and impacts of micropollutants on Denmark groundwater, were published in 2003 [71]. The comprehensive study (7,671 groundwater samples from 1,115 screens in the period 1993 to 2001) revealed the absence of nonylphenolethoxylates (NPEOs), while NPs were detected at the maximum concentration of 4.2 μg L^{-1} in eight of 705 screens.

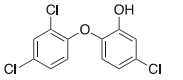
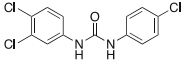
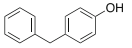
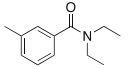
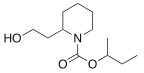
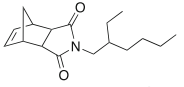
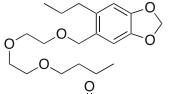
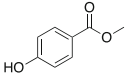
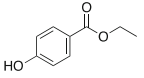
Another monitoring study was carried out in Austria; Hohenblum analyzed 400 ground and surface water samples and reported the concentration levels of various selected estrogenic compounds, including phenolic chemicals and their metabolites [72]. Results related to surface water showed that nonylphenoxycarboxylates occur more frequently and in higher concentrations than nonylphenolethoxylates; NP was measured in 138 out of 261 samples, with a maximum concentration of 890 ng L^{-1}. In groundwater NP was measured in about 50% of samples, with a maximum concentration of 1,500 ng L^{-1} and a median of 35 ng L^{-1}. It is worthy to mention here also the results on bisphenol A (BPA), although this chemical is mainly employed as a plastic softener; in fact, BPA is considered an endocrine disruptor and is often monitored with alkylphenols. In this study BPA presented a maximum concentration of 930 ng L^{-1} and a median of 24 ng L^{-1}.

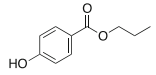
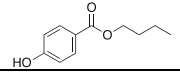
According to the recent pan-European survey on the occurrence of selected polar organic persistent pollutants in groundwater [73], BPA is one of the most relevant compounds detected in European groundwaters, either in terms of frequency of detection (40%) or maximum concentration level (2.3 μg L^{-1}).

An evaluation of the contamination of surface and drinking waters around Lake Maggiore, Italy, was reported by Loos et al. in 2007; together with other target analytes, various PCPs were considered in lake, river, tap, and rain water samples. In particular, nonylphenol was detected rarely at low very concentration, while its carboxylate and ethoxylate derivatives were present almost in all the collected samples with a maximum concentration in lakes of 307 ng L^{-1}. Levels of these compounds in drinking water produced from Lake Maggiore were similar to those found in the lake itself, indicating a poor removal efficiency of the local waterworks [74].

Further data on estrogenic phenols in Italy were obtained from surface and tap water of the Liguria region; Magi et al. estimated the time weighted average (TWA) concentration of contaminants in untreated drinking water, where BPA proved to be the most abundant ranging from 17.0 to 56.4 ng L^{-1}, while NP was in the range 2.4–9.9 ng L^{-1} [75]. The same research group employed the passive sampling approach to monitor three Ligurian rivers (BPA was the most abundant, in the range 185–459 ng/sampler) and the influent/effluent of a drinking water treatment plant in Liguria (in influent water, BPA was 453 ng/sampler after 2 weeks of exposure; NP was measured at 25 ng/sampler only after 4 weeks of exposure) [76, 77].

Table 4 Analyte abbreviations, structures, and analytically relevant data of disinfectants, repellents, and preservatives

PCP category	Abbreviation	Compound	Structure	Molecular formula	Log $K_{O/W}$
Disinfectants/antiseptics	TCS	Triclosan		$C_{12}H_7Cl_3O_3$	4.76[a]
	TCC	Triclocarban		$C_{13}H_9Cl_3N_2O$	4.8[a]
		Chloroxylenol		C_8H_9ClO	3.27[a]
		3,4,5,6-Tetrabromo-*o*-cresol		$C_7H_4Br_4O$	5.62[a]
		p-Benzylphenol		$C_{13}H_{12}O$	3.54[a]
Repellents	DEET	*N*,*N*-Diethyl-*meta*-toluamide		$C_{12}H_{17}NO$	2.18[a]
	Icaridin	Bayrepel		$C_{12}H_{23}NO_3$	2.57[a]
	MGK 264	*N*-Octylbicycloheptenedicarboximide		$C_{17}H_{25}NO_2$	3.76[a]
	PBO	Piperonylbutoxide		$C_{19}H_{30}O_5$	4.75[a]
Preservatives		Methylparaben		$C_8H_8O_3$	1.96[a]
		Ethylparaben		$C_9H_{10}O_3$	2.47[a]

Propylparaben		$C_{10}H_{12}O_3$	3.04[a]
Butylparaben		$C_{11}H_{14}O_3$	3.57[a]

[a]Syracuse Research Corporation (SRC) database

5 Preservatives

Preservatives are substances used in foods, pharmaceuticals, paints, wood, and PCPs to prevent deterioration of products whether from microbial growth or undesirable chemical changes. Depending on their origin, they are categorized into two classes: class I are naturally occurring, everyday substances, e.g., salt, honey, and woodsmoke; class II are synthetically manufactured. Table 4 shows abbreviations, structures, and physicochemical data of the most relevant preservatives determined in Europe.

Triclosan (TCS) and triclocarban (TCC) are biphenyl ethers widely used as antimicrobials in different types of PCPs (soaps, deodorants, skin creams, toothpaste) and in plastics [78]. TCS is an antimicrobial agent particularly used in many hand soaps (0.1–0.3%) [79], as a preservative and disinfectant in medical skin creams [80], and as a slow-release product in a wide variety of plastic products [81]. Methyltriclosan (MTCS) is a degradation product of the biocide TCS, which is formed in the wastewater in the treatment plant, and because of the incomplete elimination from the treatment plant, it enters in surface waters. The half-life of MTCS is longer than TCS as it degrades slowly, so it mainly exists in aquatic environments. The study of TCS and MTCS became a major point of concern in surface water because of their toxicity to certain algae species [80], and TCS is considered as a priority substance at EU scale for routine monitoring programs [82]. Bedoux et al. studied occurrence and toxicity of TCS and by-products in the environment all around the world [83]. The occurrence of TCS in water was verified in different European countries and often showed very low concentration levels: it was reported to be not detected and below LOQ in surface and wastewater samples collected from Germany [84] and Spain [59], below 10 ng L^{-1} in European groundwater samples [73] and surface water of Germany [85], and below 15 ng L^{-1} in lake and rivers in Italy [74]. Similarly, it was found below 60 ng L^{-1} in different rivers from South Wales [60], Spain [86], and Denmark [43]. Relatively higher concentration levels of TCS (26–140 ng L^{-1}) [87, 88] and of TCS and MTCS (21–300 ng L^{-1}) [89] were reported for other Spanish rivers. TCS was detected below 100 ng L^{-1} in lake and river water of Switzerland [80, 90] and in river water of the UK [91], Germany [92], and Slovenia [58]. Regarding the degradation product MTCS, quite low levels were detected in the river of Switzerland (<0.4–2 ng L^{-1}) [90] and in the surface water of Germany (0.3–10 ng L^{-1}); as shown in Fig. 5, taken from this latter study, MTCS concentrations were generally lower than those of TCS, with few exceptions [85]. Rodil et al. analyzed TCS in sewage, surface, and drinking water of Galicia (Spain); they found a median concentration of 57 ng L^{-1} in influent, 16 ng L^{-1} in effluent, and 10 ng L^{-1} in surface water samples, while TCS was never detected in drinking water [63] (Fig. 6).

Recently, Azzouz et al. studied the effect of seasonal climate variation on the removal efficiency of PCPs in a drinking water treatment plant of Spain. TCS was analyzed in water collected in different periods showing higher concentrations in

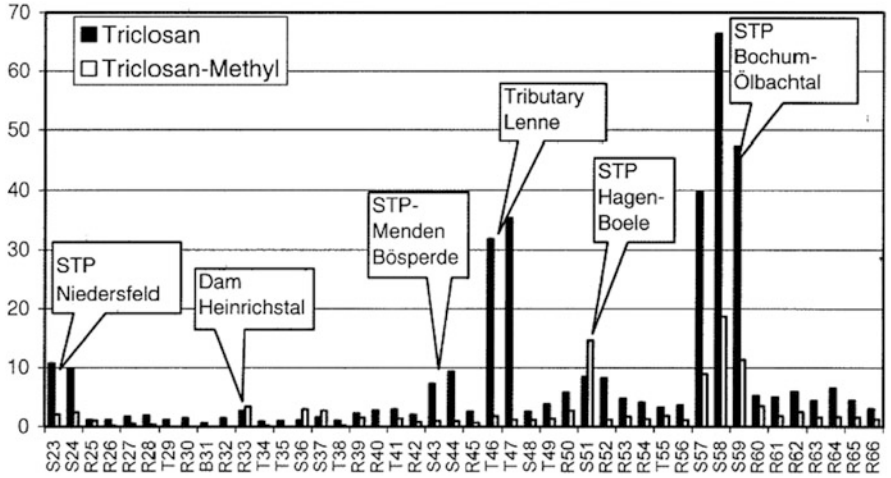


Fig. 5 Monitoring of TCS and MTCS in surface waters (concentrations in ng L^{-1}). *B* field blank, *R* riverine samples, *S* STP effluents, *STP* sewage treatment plant, *T* tributaries. Picture taken from [85] with permission. The concentrations of TCS ranged from <3 to 10 ng L^{-1} in surface water, whereas values up to 70 ng L^{-1} were found for STP effluents such as Bochum–Ölbachtal or Menden. High values were also detected for the tributary Lenne, which is heavily influenced by STP effluents. The concentrations of MTCS ranged from <0.3 to 5 ng L^{-1} in surface water samples, whereas they were up to 20 ng L^{-1} in effluent samples

winter (89 ng L^{-1}) than in autumn (56 ng L^{-1}) and the spring–summer period (35 ng L^{-1}) [93]. A similar trend was previously reported for Romanian river water, where the autumn and spring–summer concentrations were in the range 38–57 ng L^{-1} [94].

Another important class of preservatives is parabens, the alkyl esters of *p*-hydroxybenzoic acid, used since the 1930s as bactericidal and fungicidal properties in drugs, cosmetics, and foods. Nowadays, parabens can be found in makeup, soap, shampoos, shaving gels/creams, moisturizers, personal lubricants, deodorants, and toothpaste. Parabens have been found in samples of tissue from human breast tumors (an average of 20 ng g^{-1} of tissue) and displayed also estrogenic and other hormone-related activities [95]; nevertheless, no effective direct link between parabens and cancer has been established yet [96]. Regarding possible adverse effects of parabens on water aquatic organisms and their environmental toxicity, few data are available [97].

Villaverde et al. analyzed river water in Spain and quantified different parabens (methylparaben, ethylparaben, *i*-propylparaben, *n*-propylparaben (*n*-PrP), *i*-butylparaben, *n*-butylparaben, benzyl esters of 4-hydroxybenzoic acid); the concentration levels were in the range 0.8–105 ng L^{-1} [88] with the highest concentration obtained for *n*-PrP. Propylparaben and butylparaben were also detected in river water below 55 ng L^{-1} [98]. Methylparaben, ethylparaben, propylparaben, butylparaben, chloroxylenol, chlorophene, 3,4,5,6-tetrabromo-*o*-cresol, and *p*-benzylphenol were detected in Rivers Taff and Ely, UK, in a wide

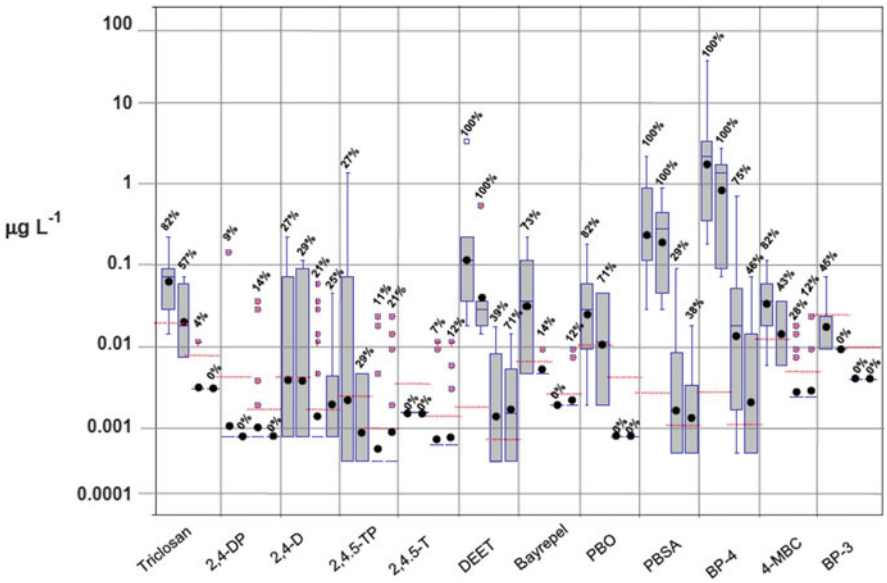


Fig. 6 Box-and-Whisker plots representing the concentrations of PCPs. From *left* to *right*: influent wastewater, effluent wastewater, surface water, and drinking water. Picture taken from [63] with permission. DEET was detected below 20 ng L^{-1} in both surface and tap water. The figure also shows the concentration range of other PCPs (one preservative TCS and three UV filters BP-3, BP-4, and 4-MBC)

concentration range (<0.3–400 ng L^{-1}) [60] with the highest concentration obtained for methylparaben in the River Ely. A relatively high concentration of methylparaben (208 ng L^{-1}) was detected in surface water of Spain [64]. During the British Geological Survey [99], massive high concentrations of parabens were frequently detected in UK groundwaters with a maximum concentration of 5,500 ng L^{-1} for propylparaben, which was potentially proposed as a marker of wastewater pollution in the freshwater environment. Very recently, during an innovative monitoring study for the fingerprinting of micropollutants in UK groundwater, Stuart et al. reported methylparaben and propylparaben below 100 ng L^{-1} concentration levels [100].

6 Repellents

Repellents are intended to be applied to the skin or clothing and provide protection against mosquito bites, tick bites, fleabites, chigger bites, and many other insect bites. Structures, abbreviations, and physicochemical data of most relevant repellents measured in Europe are presented in Table 4. *N*,*N*-diethyl-meta-toluamide (DEET) is probably the most common active ingredient in insect repellents, and it

acts by interfering with the orientation of insects. DEET has been associated with neurotoxic symptoms known as the Gulf War syndrome [113] and detected in many nontarget screenings in river water [114, 115] and in seawater [116]. DEET has been detected in the North Sea at a concentration of 1.1 ng L^{-1} [105] and in the concentration range of 0.4–13 ng L^{-1} in seawater from Tromsø–Sound, Norway [112]. In Germany, the concentrations of DEET have constantly decreased since 1999, when DEET was substituted by Bayrepel (1-piperidinecarboxylic acid, 2-(2-hydroxyethyl), 1-methylpropyl ester/Icaridin) in commercial insect repellent formulations [103]. DEET (6.7 μg L^{-1}) and Bayrepel (2.2 μg L^{-1}) were determined in the samples from the eastern part of Croatia (Osijek and Belišće), which is known to have problems with mosquitoes [42]. Later on, a major study on 164 individual groundwater samples from 23 European countries was carried out for 59 selected organic compounds; DEET was the most relevant compound in terms of frequency of detection (84%) and maximum concentration (454 ng L^{-1}) [73].

Rodil et al. measured several PCPs in wastewater, surface water, and tap water, including four insect repellents: DEET, Bayrepel, *N*-octylbicycloheptenedicarboximide (MGK264), and piperonylbutoxide (PBO) [63]. While MGK264 could not be detected in any sample, DEET, Bayrepel, and PBO were found in most influent wastewaters. DEET was detected in all samples, also showing rather high concentration, with a median value of 102 ng L^{-1}; its removal rate was close to 60%, and it was measured in all effluents, with a median value of 25 ng L^{-1}. Removal efficiency for Bayrepel and PBO was higher, and they were detected only in some effluents within the range LOQ-40 ng L^{-1}. In surface and tap water, DEET was found at comparatively lower levels (16 and 12 ng L^{-1}, respectively); PBO was not found, while Bayrepel was detected in some tap waters below 10 ng L^{-1}. A graphical summary of these results on PCPs levels in all the considered water matrices is shown in Fig. 6.

In the previous section on fragrances, we already discussed the nontarget screening approach proposed by Schwarzbauer et al. for the monitoring of organic contaminants in European rivers; in that study they also reported data on some insect repellents, and in particular, most of the considered water samples were positive to DEET [34]. Previously, during the qualitative characterization of organic compounds in river water, the same research group detected DEET in the two German rivers Rhine and Lippe [117, 118].

We also reported the monitoring study for the fingerprinting of micropollutants in UK groundwater, in the section on preservatives; in this study Stuart et al. measured concentration levels of DEET up to 300 ng L^{-1} during Oxford Observatory (2011 and 2012) and 60 ng L^{-1} during Boxford Observatory (2012) [100].

Table 5 Occurrence of PCPs in Europe

Country	PCP	Concentration	Water source	Reference
Europe	DEET	454 ng L^{-1}	Groundwater	[73]
	BPA	2.3 μg L^{-1}		
	Nonylphenoxy acetic acid (NPE1C)	11 μg L^{-1}		
UK	Methylparaben	0–0.08 μg L^{-1}	Groundwater	[100]
	Propylparaben	0–0.07 μg L^{-1}		
	4-*t*-Octylphenol	0–0.83 μg L^{-1}		
	Benzophenone	0–51 μg L^{-1}		
	BPA	5–12 μg L^{-1}		
	DEET	0.27–0.3 μg L^{-1}		
UK	HHCB, AHTN	3–28 ng L^{-1}	Tamar estuarine, surface water	[1]
UK	BP-1, BP-2, BP-3, BP-4, methylparaben, ethylparaben, propylparaben, butylparaben, TCS, 4-chloroxylenol, chlorophene, 3,4,5,6-tetrabromo-*o*-cresol, *p*-benzylphenol, BPA, 4-tert-octylphenol	<0.3–536 ng L^{-1} <0.3–1,293 ng L^{-1}	River Taff River Ely	[60]
UK	TCS	19–80 ng L^{-1}	River Aire	[91]
Germany	*N*,*N*,*N*′,*N*′-Tetraacetylethylenediamine, methoxycinnamic acid, 2-ethylhexylester, drometrizole, HHCB, AHTN, ADBI, AHMI, oxoisophorone, lilial, viridine, dihydromethyl-jasmonate, cineol, DEET	–	River water	[34]
Germany	BP-3, IAMC, 4-MBC, BM-DBM, OC, EHMC, EHS, HMS	40–4,381 ng L^{-1}	Lake water	[62]
Germany	OTNE (Iso E Super®)	30–100 ng L^{-1}	Surface water, Ruhr river	[33]
Germany	AHTN	0.10 μg L^{-1}	Wastewater effluent	[101]
	HHCB	0.73 μg L^{-1} <LOQ (groundwater)	Groundwater	
Germany	AHTN	311 ng L^{-1}	Surface water	[102]

Germany	TCS	<3–10 ng L^{-1}	Surface water	[85]
	MTCS	0.3–10 ng L^{-1}		
Germany	Bayrepel	0.3 μg L^{-1}	Anthropogenically influenced surface waters	[103]
Germany	TCS	11 ng L^{-1}	Surface water	[84]
		24 ng L^{-1}	Treated wastewater	
Germany	TCS	30–90 ng L^{-1}	River Itter	[92]
Germany	HHCB	60–330 ng L^{-1}	Naab rivers, surface water	[104]
Germany	HHCB	116 ng L^{-1}	Mulde–Saale river, surface water (1996–1997)	[104]
	AHTN	85 ng L^{-1}		
Germany	HHCB	275 ng L^{-1}	Ruhr river, surface water (1995/1996)	[104]
	AHTN	100 ng L^{-1}		
	ADBI	6 ng L^{-1}		
Germany	HHCB, AHTN	30–500 ng L^{-1}	Ruhr river, surface water (1994)	[104]
Germany	DEET	1.1 ng L^{-1}	Seawater	[105]
Germany	4-nonylphenol (4-NP), 4-*t*-octylphenol (4*t*OP), BPA, and hydroxybiphenyl (2OHBiP)	47–458 ng L^{-1}	Stream and river water	[69]
Germany	HHCB	850 ng L^{-1}	Berlin area, surface water (1996)	[28]
	AHTN	500 ng L^{-1}		
	ADBI	50 ng L^{-1}		
Germany	HHCB	118 ng L^{-1}	Elbe river, surface water	[16]
	AHTN	73 ng L^{-1}		
	ADBI	5 ng L^{-1}		
Germany	HHCB	0.09–4.8 ng L^{-1} in the North Sea and 95 ng L^{-1} in the river Elbe estuary	Water samples	[27]
	AHTN	0.08–2.6 ng L^{-1} in the North Sea and 67 ng L^{-1} in the river Elbe estuary		

(continued)

Table 5 (continued)

Country	PCP	Concentration	Water source	Reference
Spain	BP, BP-1, BP-3, BP-4, methylparaben, ethylparaben, propylparaben	3–221 ng L^{-1} (median)	Surface water	[64]
Spain	DEET, MGK264, PBO, 4-MBC, PBSA, BP-3, EHMC, OC, OD-PABA, BP-4, IAMC	<10 ng L^{-1}	Surface and drinking water	[63]
Spain	BP-3, BHT, EHMC, HHCB, octocrylene, TCPP, AHTN	7.23–134.78 ng L^{-1} (mean)	Groundwater 2008–2010	[106]
Spain	BHT	133.2 ng L^{-1}	Groundwater	[38]
	EHMC	38 ng L^{-1}		
	HHCB	106.8 ng L^{-1}		
	TCPP	29.38 ng L^{-1}		
Spain	BP-3	6–28 ng L^{-1}	River water	[59]
	TCS	<LOQ		
Spain	MeP	54 ng L^{-1}	River water 2009–2010	[88]
	EtP	30 ng L^{-1}		
	i-PrP	0.8 ng L^{-1}		
	n-PrP	105 ng L^{-1}		
	i-BuP	4.8 ng L^{-1}		
	n-BuP	6.4 ng L^{-1}		
	BzP	2.4 ng L^{-1}		
	TCS	58–138 ng L^{-1}		
Spain	PrP	13.3–23.8 ng L^{-1}	River water	[98]
	BuP	54.1 ng L^{-1}		
	TCS	107.1 ng L^{-1}		
Spain	TCS	26–105 ng L^{-1}	River water	[87]
Spain	TCS	21–300 ng L^{-1}	River water	[89]
	MTCS			
Spain	TCS	45 ng L^{-1}	River water	[86]
Spain	HHCB, AHTN	10–260 ng L^{-1}	Digterbach rivers, surface water	[104]

Spain	NPEO	31 μg L^{-1}	Freshwater aquatic systems	[107]
	NPEC	15 μg L^{-1}		
	NP	35 μg L^{-1}		
Spain	NPEO	<0.2–11 μg L^{-1}	Seawater	[70]
	NPEC	<0.1 μg L^{-1}		
	NP	<0.15–4.1 μg L^{-1}		
Spain	HHCB	136 ng L^{-1}	Glatt river, surface water (1994)	[108]
	AHTN	75 ng L^{-1}		
	ADBI	3.2 ng L^{-1}		
Netherlands	HHCB	60 ng L^{-1}	Rhein river, surface water (1994–1996)	[104]
	AHTN	50 ng L^{-1}		
Netherlands	HHCB	80 ng L^{-1}	Meuse river, surface water (1994–1996)	[104]
	AHTN	70 ng L^{-1}		
Netherlands	NPEO	0.04–2.7 ng L^{-1}		[109]
	NP	0.04–2.0 ng L^{-1}		
	NPEC	0.09–12 ng L^{-1}		
Greece	BP-3	6.5–8.2 ng L^{-1}	Bathing water	[53]
	4-MBC	13.1–19.7 ng L^{-1}		
	OMC	7.4–10.7 ng L^{-1}		
Greece	BP-3	1.8–5.7 ng L^{-1}	Ionian sea, swimming pool, and game pool	[52]
	4-MBC	5.4–6.9 ng L^{-1}		
	OMC	3–4.5 ng L^{-1}		
Greece	BP-3	2.4–3.3 μg L^{-1}	Swimming pool	[51]
	OD-PABA	2.1 μg L^{-1}		
	BP-3	8.2–9.9 μg L^{-1}	Shower water	
	OD-PABA	5.3–6.2 μg L^{-1}		
Italy	HHCB, AHTN, and ADBI	2.45–463 ng L^{-1}	Surface water, Molgora River	[41]
Italy	BP-3, OC, and EHMC	3–112 ng L^{-1}	River and seawater	[61]

(continued)

Table 5 (continued)

Country	PCP	Concentration	Water source	Reference
Italy	NP	15 ng L^{-1}	Lake water	[74]
	NPE1C	120 ng L^{-1}		
	NPE2C	7 ng L^{-1}		
	NPE3C	15 ng L^{-1}		
	NPEnOs, $n = 3$–17)	300 ng L^{-1}		
	TCS	0–4.1 ng L^{-1} (lake water)		
		0–15 ng L^{-1} (affected rivers)		
Italy	BP-3	25–216 ng L^{-1}	Swimming pool	[54]
	EHMC	53–86 ng L^{-1}		
	BP-3	<LOQ–118 ng L^{-1}	Seawater	
	EHMC	<LOQ–83 ng L^{-1}		
Switzerland	4-MBC	<2–28 ng L^{-1}	Lake water	[57]
	BP-3	<2–35 ng L^{-1}		
	EHMC	<2–7 ng L^{-1}		
	OC	<2–5 ng L^{-1}		
Switzerland	EHMC, BP-3, 4-MBC, OC, and BM-DBM	<2–125 ng L^{-1}	Hüttnersee Lake	[55]
		<2–25 ng L^{-1}	Zürich Lake	
Switzerland	HHCB, AHTN	<LOD	Sea	[37]
	HHCB	5–564 ng L^{-1}	Rivers and streams	
	AHTN	2.3–186 ng L^{-1}		
	HHCB	<2–47 ng L^{-1}	Swiss lakes	
	AHTN	<1–18 ng L^{-1}		
Switzerland	TCS	11–98 ng L^{-1}	River water	[80]
Switzerland	TCS	<0.4–74 ng L^{-1}	Lake and river water	[90]
	MTCS	<0.4–2 ng L^{-1}		
Denmark	HHCB, AHTN, BPA, TCS	5–59 ng L^{-1}	Surface waters	[43]
Denmark	Phenol	0.07–5.1 μg L^{-1}	Groundwater	[71]
	Nonylphenol	0.6–4.2 μg L^{-1}		

Romania	HHCB, AHTN	81–313 ng L^{-1}	Surface water	[94]
Romania	HHCB	237–299 ng L^{-1}	River water	[94]
	AHTN	80–106 ng L^{-1}		
	TCS	38–56 ng L^{-1}		
Croatia	NPnEO	1.1–6 μg L^{-1}	Brackish water layer	[110]
		0.1–0.7 μg L^{-1}	Saline water layers	
Croatia	NP	<20–1,200 ng L^{-1}	Estuarine waters	[111]
	NP1EO	<20–440 ng L^{-1}		
	NP2EO	<20–1,300 ng L^{-1}		
Slovenia	BP-3	114 ng L^{-1}	River water	[58]
	OD-PABA	47 ng L^{-1}		
	OMC	88 ng L^{-1}		
	OCR	35 ng L^{-1}		
	HMS	165–345 ng L^{-1}		
	TCS	68 ng L^{-1}		
France	HHCB, AHTN	<5–10 ng L^{-1}	Seine River waters	[40]
		4.4 μg L^{-1} (HHCB)	Drinking water	
Hungary	OTNE	29–810 ng L^{-1}	Danube river water	[33]
Norway	DEET	0.4–13 ng L^{-1}	Seawater	[112]

7 Concluding Remarks

The occurrence of personal care products in natural water across Europe has been presented in this chapter; for each of the considered classes (fragrances, UV filters, detergents, preservatives, and repellents), an extensive review of the recent literature has been considered, leading to a general picture of the European knowledge about the distribution and impact of PCPs on the aquatic compartment.

Data available on the concentration levels of these compounds in Europe, gathered and presented in Table 5, are not homogeneous, strongly depending on the country and on the type of chemical. To achieve a more precise knowledge of the situation, future monitoring studies should be carried out focusing on some key compounds and following previously defined protocols, as suggested by the integrated approach of the European Water Framework Directive to manage water resources and improve water quality.

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Personal Care Products in the Aquatic Environment in China

Qian Sun, Min Lv, Mingyue Li, and Chang-Ping Yu

Abstract Personal care products (PCPs) are a group of emerging contaminants which showed potential adverse effect on the environment and human health. In China, the production and consumption of PCPs continued a rapid growth because of the rapid economic growth and prosperity, which might lead to large ranges and quantities of PCPs releasing into the environment. Great concerns have been raised on the PCPs in the aquatic environment in China. So far, existing field studies have provided basic information on the occurrence and distribution of PCPs in the surface water, sewage water, sludge, and sediment. This chapter summarizes four major classes of PCPs in the aquatic environment in mainland China, including the antimicrobial agents, synthetic musks, UV filters, and preservatives. Generally, the PCP levels in China were comparable to the global levels. Seasonal and spatial variation of PCPs in the aquatic environment was observed. There are clear regional biases in the knowledge of PCPs in China. In the end, the limitations of the investigation are discussed, and the implications for future studies are proposed.

Keywords China, PCPs, Sediment, Sewage sludge, Surface water, Wastewater

Contents

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M.S. Díaz-Cruz and D. Barceló (eds.), *Personal Care Products in the Aquatic Environment*, Hdb Env Chem (2015) 36: 73–94, DOI 10.1007/698_2014_284,

1 Introduction

Personal care products (PCPs) are a class of emerging contaminants which include commonly used cosmetic, personal hygiene products, and household chemicals. PCPs have been widely detected in the aquatic environment all over the world [1, 2]. Great concerns have been raised about PCPs due to their potential adverse impacts on the ecological safety and human health [3].

2 Production and Usage of PCPs in China

In the past few decades, China underwent a rapid economic growth and prosperity. Because of the rising disposable incomes and the increased awareness of personal hygiene and outer appearance, the consumption of PCPs continued its rapid growth in China. For example, sales of shampoo products increased from 48,000 tons in 2000 to 387,000 tons in 2010 [4, 5]. In addition, the number of PCPs introduced into China continues to increase [6]. Euromonitor International estimated that the total sales of beauty and PCPs was US$24 billion in 2010, which was more than triple compared to 2000 [7]. Euromonitor International expected that the absolute value growth of beauty and PCPs reached over US$10 billion over 2010–2015 [7]. Due to the increased consumption and productions of PCPs in China, the range and quantities of PCPs released into the environment would inevitably increase. There is a great need to understand the occurrence and fate of PCPs in the aquatic environment in China.

3 Occurrence and Fate of PCPs in the Aquatic Environment in China

3.1 Antimicrobial Agents

Triclosan (TCS) and triclocarban (TCC) are the two common antimicrobial agents widely used in medical, household, and personal care products, such as soaps, shampoos, toothpaste, cosmetics, and sanitation goods [8]. Great concerns about TCS and TCC have been aroused in recent years, and the main reasons could be summarized as follows: (1) large consumption worldwide [9], (2) incomplete

removal in WWTPs [10, 11], (3) the endocrine-disrupting effect of TCS [12] and the potential endocrine-disrupting property of TCC [13], (4) the accumulation in organisms due to the high log*Kow* [14, 15], and the inadequately explored environmental impacts. So far, TCS and TCC have been widely detected in aquatic environment in China, reaching several to thousands of nanograms per liter (or gram). The removal efficiency for TCS and TCC in WWTPs showed big difference in different studies. With log*Kow* 4.7 and 4.9 for TCS and TCC, respectively, these antimicrobial agents tended to accumulate in the sludge and sediment [14], which may pose potential high risks to the environment. Therefore, more studies should be carried out to investigate the efficient removal of TCS and TCC in WWTPs and to comprehensively understand the behavior of TCS and TCC in aquatic environment.

3.1.1 Antimicrobial Agents in Sewage and Sludge

Studies on the occurrence of antimicrobial agents in WWTPs in China showed a strong regional bias, which were mainly conducted in Guangzhou in South China. Zhao et al. investigated TCS and TCC in four WWTPs in Guangzhou urban area during 2007 and 2008 [11]. TCS and TCC were detected in all effluents, with the concentration range of 10.9–241 and 23.9–342 ng/L, respectively. Chen et al. determined TCS and TCC in Zengcheng WWTP in Guangzhou City [16]. The concentrations of TCS and TCC were 113 and 267 ng/L in influent, 18.9 and 32.6 ng/L in effluent, and 189 and 887 ng/g (dry weight, dw) in dewatered sludge [16]. Yu et al. investigated TCS and TCC in the sewage from a WWTP in Guangzhou in 2008 [17]. The concentration ranges of TCS and TCC were 1,217.4–2,353.9 and 711.5–2,301.0 ng/L in the influent and 1,188 and 5,088 ng/g (dw) in the dewatered sludge. In addition, the occurrence of antimicrobial agents was studied in two WWTPs in Hangzhou City in East China in 2012 [18]. The concentrations of TCC in the sewage were in the range of 8.4–43.7 ng/L, while the concentrations of TCS were below the method detection limits (MDLs, 500 ng/L). High concentrations of TCS and TCC were observed in the sludge, with concentration in the range of below MDL (25 ng/g)–1,234 ng/g and 9,626–25,209 ng/g (dw) for TCS and TCC, respectively. In a recent study, Sun et al. investigated the occurrence of antimicrobial agents in a WWTP in Xiamen in Southeast China [2]. The concentrations of TCS and TCC were 35.1–108 and 5.04–67.4 ng/L in the influent and were 33.9–129 and 2.66–62.6 ng/L in the effluent, respectively. Results showed that there was big difference of the antimicrobial agent concentrations in the sewage and sludge among studies in China.

The antimicrobial agents could be partly removed from the sewage with removal efficiencies varied in different WWTPs in China. The removal rates of TCC in sewage could reach 80% in two WWTPs in Hangzhou [18]. The adsorption to sludge contributed to most of the reduction of TCC [18]. The removal efficiencies of TCS and TCC in the sewage in Guangzhou were 89.4–91.4 and 88.7–95.1%, respectively [17]. Through mass balance, about 13.2 and 48.4% of TCS and TCC

entering the WWTP finally adsorbed onto the dewatered sludge, indicating that sorption onto sludge was an important process for the removal [17]. The strong adsorption onto sludge for these antimicrobial agents was similar to the studies in the USA [15] and Sweden [10]. However, the removal efficiencies were quite low in the WWTP in Xiamen, with an average removal rate of 17.4% and −18.5% for TCS and TCC, respectively [2]. Results from this study suggested that biodegradation through activated sludge was not effective for the removal of the two antimicrobial agents in the investigated WWTP; however, the reduction of triclosan and triclocarban concentrations was observed during the disinfection process [2].

3.1.2 Antimicrobial Agents in Surface Water and Sediment

(1) Antimicrobial Agents in Surface Water The investigation of antimicrobial agents in surface water in China was not started until 2005, and most studies were focused on freshwater. The concentrations of TCS and TCC in surface waters in China are summarized in Table 1. The most frequently studied area was the Pearl River system in Southern China, including Pearl River [17, 22], Liuxi Reservoir [16], Liuxi River [11, 16], Zhujiang River [9, 11], Shijing River [11], Dongjiang River, [9] and the urban river of Guangzhou [19]. Other studied rivers included Liao River [9, 20], Yellow River [9, 21], Hai River [9] in North China, and Jiulong River [23] in Southeast China. In general, TCS and TCC were ubiquitous with the detection frequencies mostly up to 100%, except the Liuxi Reservoir where TCS and TCC had trace levels or even no detection [16]. The concentration ranges of TCS and TCC in freshwater were <LOQ (limits of quantity)-1,023 ng/L and <LOQ-338 ng/L, which were comparable to those in the USA [1, 24] but higher than those in Spain [25] and Germany [26]. So far, limited data was reported about TCS and TCC in the seawater. In a recent study, we investigated the occurrence of TCS and TCC in the estuary of Jiulong River [23]. TCS and TCC were both detected with 100% frequencies, and the levels were 2.56–34.3 and 0.298–5.76 ng/L, respectively, which were somewhat higher than the Hudson River Estuary in the USA [27] and estuary and seawater in Portugal [28].

Seasonal variations were observed in both the detection frequencies and the concentrations of the antimicrobial agents. The detection frequencies and the concentrations were relatively higher in the dry season than the wet season. For example, the detection frequencies and concentrations of TCS were 100% and 2.6–49.9 ng/L in the dry season (November 2008) and were 93% and <LOQ (0.5)–5.5 ng/L in the wet season (May 2008) in the Yellow River [21]. The concentrations of TCS and TCC Jiulong River were 8.65–53.5 and 1.84–13.7 ng/L in the dry season (January 2013) and were 0.918–14.1 and 1.21–6.50 ng/L in the wet season (June 2013), respectively [23]. The seasonal variations were mainly attributed to the dilution of rainwater in the wet season.

Spatial variations were also observed. TCS and TCC were below LOQ (1.2 ng/L for TCS and 3.9 ng/L for TCC) in Liuxi Reservoir due to little human activity, increased toward the downstream of the Liuxi River near Guangzhou, and increased

Table 1 Concentrations range, median concentration, and detection frequency of TCS and TCC in surface water (ng/L) and sediment (ng/g, dw) of WWTPs in China

Origin	Type	Sampling year	Season	TCS			TCC			Reference
				Range	Median	Freq (%)	Range	Median	Freq (%)	
Urban river of Guangzhou	W	2005–2006	Dry[a]	48–1,023	405	100				[19]
			Wet[a]	35–217	77	100				
Liuxi River	W	2007–2008		<LOQ (4.1)–26.2	11.9	75	<LOQ (3.9)–13.9	6.0	83	[11]
	S			<LOQ (1.9)–116	50.5	67	<LOQ (1.9)–426	134	75	
Zhujiang River	W			6.5–31.1	16.2	100	4.5–46.2	17.1	100	
	S			12.2–196	58.8	100	58.0–904	264	100	
Shijing River	W			90.2–478	238	100	68.8–338	145	100	
	S			345–1,329	693	100	748–2,633	1,039	100	
Liao River	W	2008	Dry[b]	6.7–81.4	24.6	100				[20]
			Wet[b]	6.5–70.5	33.2	100				
	S		Dry[b]	<LOQ (0.8)–23.7	2.6	62				
			Wet[b]	<LOQ (0.8)–33.9	1.7	52				
Yellow River	W	2008	Dry[c]	2.6–49.9	7.4	100				[21]
			Wet[c]	<LOQ (0.5)–5.5	2.3	93				
	S		Dry[c]	<LOQ (0.5)–14	<LOQ (0.5)	29				
			Wet[c]	<LOQ (0.5)–1.4	<LOQ (0.5)	7				

(continued)

Table 1 (continued)

Origin	Type	Sampling year	Season	TCS			TCC			Reference
				Range	Median	Freq (%)	Range	Median	Freq (%)	
Liao River	W	2008		2.40–404	18.0	100	<LOQ (0.7)–58.8	7.80	100	[9]
	S			N.D.(<0.47)–40.0	2.40	94.9	<LOQ (0.39)–896	30.4	100	
Hai River	W	2008		N.D.(<0.21)–34.4	4.55	95.5	2.60–117	26.5	100	
	S			<LOQ (1.58)–13.8	<LOQ (1.58)	100	0.80–136	8.90	100	
Yellow River	W	2008		N.D.(<0.21)–64.7	5.40	66.7	<LOQ (0.79)–36.8	2.20	100	
	S			N.D.(<0.47)–13.3	<LOQ (1.58)	72.4	N.D.(<0.12)–17.5	<LOQ (0.39)	93.1	
Zhujiang River	W	2007–2008		1.51–478	21.5	100	2.96–338	21.7	100	
	S			<LOQ (1.58)–1,329	86.0	100	0.36–2,633	394	100	
Dongjiang River	W	2008–2009		<LOQ (0.70)–170	6.43	100	3.32–269	18.1	100	
	S			<LOQ (1.58)–656	7.99	100	<LOQ (0.39)–2,723	67.3	100	
Liuxi Reservoir	W	Not available		N.D.(<0.02)	N.D. (<0.02)	0	7.5		100	[16]
	S			N.D.(<0.03)	N.D. (<0.03)	0	1.2		100	

Pearl River	W	2008		7.7–217.5	47.0	100	4.9–155.1	34.8	100	[17]
Pearl River	W	2007		0.6–347	14.7	100				[22]
Jiulong River	W	2012–2013	Dry[d]	8.65–53.5	17.9	100	0.918–14.1	3.59	100	[23]
			Normal[d]	4.94–64.5	22.2	100	0.270–2.18	0.628	100	
			Wet[d]	1.84–13.7	6.65	100	1.21–6.50	2.64	100	
Estuary of Jiulong River	W		Dry[d]	10.4–34.3	17.0	100	0.807–4.37	1.45	100	
			Normal[d]	2.56–27.3	15.3	100	0.298–1.18	0.593	100	
			Wet[d]	2.86–12.2	6.83	100	0.787–5.76	1.66	100	

[a]Dry: October, December 2005, and March 2006, wet: April, May, August 2006
[b]Wet: July 2008, dry: November 2008
[c]Dry: November 2008, wet: May 2008
[d]Dry: January 2013, normal: September 2013, wet: June 2013
W surface water, *S* sediment, *N.D.* not detected, *<LOQ* below limit of quantification

at the metropolitan sites in Zhujiang River and reached highest concentrations in Shijing River where it received large amount of raw domestic wastewater [11]. Zhao et al. (2013) investigated the occurrence of TCS and TCC in five rivers and found that TCS and TCC in riverine environments at the river basin scale were influenced by urban domestic sewage discharge and urban population [9]. The results showed that the spatial variation of antimicrobial agents was mainly caused by the anthropogenic activity.

(2) Antimicrobial Agents in Sediment As shown in Table 1, TCS concentrations were consistently higher than TCC in the surface water but were lower than TCC in the sediment. The detection frequencies of antimicrobial agents in the sediment were as high as those in surface water. The maximum concentrations of TCS and TCC were 1,329 ng/g (dw) [9, 11] and 2,723 ng/g (dw) [9], respectively. The high concentrations and detection frequencies might be because of the tendency to accumulate in the sediment due to the high log*Kow* of TCC and TCS [14, 15].

Spatial variations of antimicrobial agents were observed in the sediment. Higher levels of TCS and TCC were detected in the sediment of Pearl River [9, 11] than those in the sediment of Liao River [9, 20], Yellow River [9, 21], and Hai River [9]. The Yellow River showed the lowest levels of TCS and TCC in the sediment, with the majority of samples below LOQs (1.58 ng/g for TCS and 0.39 ng/g for TCC), which could be explained by the high sand contents and low total organic carbon contents in the sediment [9]. Minor variations were also observed for the sediment within a river. The concentrations of TCS and TCC in the sediment increased from Liuxi Reservoir to the downstream of the Liuxi River, to the metropolitan sites in Zhujiang River, and finally to the Shijing River [11]. Similar trend was also observed in the surface water, indicating that sediment is a sink for TCS and TCC and might further be a pollution source [11]. The mass inventories of TCS and TCC were strongly correlated with urban population and total and untreated urban sewage discharge amounts ($R^2 = 0.526–0.994$) [9].

3.2 Synthetic Musks

Synthetic musks have been widely used as fragrances in personal care and household products. With the dramatic increase in the industrial production and domestic use, the release of the synthetic musks to the aquatic environmental caused a great concern. The studies of the occurrence and distribution of synthetic musks in WWTPs, surface water, and sediments have been carried out in China. The galaxolide (HHCB) and tonalide (AHTN) were the predominant synthetic musks with higher concentrations and detection frequencies. The synthetic musk levels in WWTPs or the natural aquatic environment in China were in the same range or lower than those in other countries. Seasonal and spatial variation of synthetic musks in the aquatic environment was observed. High concentrations of synthetic musks, especially HHCB and AHTN, were observed in the sediments of the urban

area with a high population density. Thus, the synthetic musk level in the sediments was proposed as the chemical tracer to indicate the impact of anthropogenic activities and to assess the impact of domestic wastewater in the natural aquatic system. In addition, there are clear regional biases in the knowledge of synthetic musks in China. Therefore, more contamination information in different areas in China, especially the natural aquatic environment, is needed.

3.2.1 Synthetic Musks in Sewage and Sludge

The concentrations of the synthetic musks in the influent and effluent of WWTPs in China are summarized in Table 2. Eight targets, including HHCB, AHTN, cashmeran (DPMI), celestolide (ADBI), phantolide (AHMI), traseolide (ATII), musk ketone (MK), and musk xylene (MX), have been investigated. HHCB was detected in all of the domestic WWTPs, with concentrations of 30.9–6,665 ng/L in the influent and 22.6–3,065 ng/L in the effluent. AHTN also showed a relative high detection frequency in the domestic WWTPs. The concentrations of AHTN in the influent and effluent were 11.0–1,486 and 2.2–506 ng/L, respectively. In addition, the concentrations of MK and MX in the influents of the domestic WWTPs were in the range of 52–1,010 and 22–164 ng/L, respectively. However, ADBI, AHNI, DPMI, and ATII have not been detected in any samples from the domestic WWTPs [30, 32–37]. In terms of HHCB and AHTN, which were the most frequently detected targets, the highest level was observed in the WWTPs in Northeast China [37], followed by the WWTPs in Shanghai and Beijing [30, 32–34]. The HHCB and AHTN levels in Nanjing [36], Wuxi [36], and Xi'an [35] were relatively low. The synthetic musk levels in China were in the same range [38, 39] or lower [40, 41] than those in other countries. The synthetic musks could be partly removed in WWTPs. The removal efficiencies of HHCB and AHTN were $<$14.3–98.0 and $<$18.5–98.7%, respectively [32, 33, 35]. Most of the synthetic musks were adsorbed to the sludge, which indicated that the waste sludge from WWTPs might be a potential environmental pollution source [29]. The synthetic musks in the effluent would lead to a higher concentration in the surface water at the downstream of WWTPs.

The occurrence of synthetic musks in the sludge of WWTPs was investigated in Beijing and Shanghai and summarized in Table 2. Zhou et al. collected samples from three WWTPs in Beijing in 2007 and investigated HHCB and AHTN in the sludge [33]. The concentrations of HHCB and AHTN were in the ranges of 2.5–16.8 and 0.7–13.9 μg/g (dw), respectively. The results showed that HHCB and AHTN tend to accumulate in the return activated sludge [33]. Hu et al. collected samples from seven WWTPs in Beijing in 2008 and determined seven synthetic musks in the sludges [32]. HHCB, AHTN, and MK were detected in all the samples, with concentrations of 0.26–12.59, 0.01–2.56, and 0.13–0.53 μg/g (dw), respectively. ATII and MX showed low detection frequencies and relatively low concentrations. However, AHMI and ADBI were not detected in any samples [32]. Lv et al. investigated four synthetic musks in the WWTP in Shanghai in the four

Table 2 Concentrations of synthetic musks in the influent (ng/L), effluent (ng/L), and sludge (μg/g, dw) of WWTPs in China

Origin	Type	Sampling year	Synthetic musk concentration								Reference
			HHCB	AHTN	DPMI	ADBI	AHMI	ATII	MK	MX	
Cosmetic WWTP in Guangzhou	I	2004	549,680	64,600	24,940	6,540	4,700	N.D. (<60)			[29]
	E		32,060	5,410	1,970	620	N.D. (<60)	N.D. (<60)			
	S		479.73–601.27	49.69–107.61	40.75–52.38	1.46–4.01	1.38–3.63				
WWTPs in Shanghai[a]	I	2007	1,467–3,430	435–1,043	N.D. (<4)	N.D. (<2)	N.D. (<2)	N.D. (<4)	418–1,010		[30]
	E		233–336	74–94	N.D. (<4)	N.D. (<2)	N.D. (<2)	N.D. (<4)	43–101		
Domestic + industrial WWTP in Guangzhou[a,b]	I	2004	11,500–147,000	890–3,470	210–690	N.D. (<10)	N.D. (<10)	N.D. (<20)			[31]
	E		950–2,050	100–140	60–100	N.D. (<10)	N.D. (<10)	N.D. (<20)			
WWTP in Beijing	I	2008	30.9–3,039.0	28.6–1,486.1		N.D. (<1.2)	N.D. (<1.2)	N.D. (<1.2)	52.25–165	N.D. (<1.2)–23	[32]
	E		30.4–685.6	14.3–195.3		N.D. (<1.2)	N.D. (<1.2)	N.D. (<1.2)	22.77–91.6	N.D.(<1.2)	
	S		0.26–12.59	0.01–2.56		N.D. (<3.3)	N.D. (<3.3)	0.015–0.3	0.13–0.53	N.D.(<1.2)	
WWTP in Beijing	I	2007	1,251.4–3,003.8	111.9–286.3							[33]
	E		492.8–1,285.3	47.3–89.3							
	S		2.5–16.8	0.7–13.9							

WWTP in Shanghai	I	2007–2008	1,478–2,214	553–1,038					74–161	63–164	[34]
	E		181–242	47–88					7–18	N.D. (<0.2)–6.5	
	S		1.37–4.68	0.28–1.53					N.D.[c]–0.03	N.D. [c]–0.007	
WWTP in Xi'an[a]	I	2010–2011	82.8–182.5	11.0–19.3							[35]
	E		22.6–103.9	2.2–8.8							
WWTP in Nanjing[a]	I	2011	316	N.D. (<0.5)							[36]
	E		103	N.D. (<0.5)							
WWTP in Wuxi[a]	I	2011	306	N.D. (<0.5)							[36]
	E		88	N.D. (<0.5)							
WWTPs of 7 cities in Northeast China[a]	I	2004	1,699–6,665	278–1,486							[37]
	E		1,354–3,065	164–506							

[a]Sludge sample was not included
[b]30% domestic and 70% industrial wastewater (including two cosmetics plants) in Guangzhou
[c]The value of LOD was not available
I influent, *E* effluent, *N.D.* not detected

seasons during 2007 and 2008 [34]. HHCB and AHTN were the predominant compounds in the sludge, with concentrations of 1.37–4.68 and 0.28–1.53 μg/g (dw). The concentrations of MX and MK were in the range of N.D. (value was not available)-0.007 and N.D. (value was not available)-0.03 μg/g (dw), respectively.

The synthetic musks in the industrial WWTPs which contained wastewater from cosmetic plants were higher than those from domestic WWTPs. The concentrations of HHCB, AHTN, DPMI, ADBI, and AHMI in the influents were 11,500–549,680, 890–64,600, 210–24,940, 6,540, and 470 ng/L, respectively. The synthetic musks showed high concentrations even in the effluents. For example, the concentrations of HHCB and AHTN in the effluent of a cosmetic plant were 32,060 and 5,410 ng/L, respectively [31]. The results suggested that the wastewater from cosmetic plant caused significant high load of synthetic musks to the domestic WWTPs and the activated sludge treatment was insufficient to remove the synthetic musks [31]. In addition, the synthetic musks in the sludge samples of a typical cosmetic plant in Guangzhou were investigated [29]. The concentrations of DPMI, ADBI, AHMI, HHCB, and AHTN in the sludge were in the ranges of 40.75–52.38, 1.46–4.01, 1.38–3.65, 479.73–601.27, and 49.69–107.61 μg/g (dw). The concentrations of the synthetic musks increased from the primary sludge to the second sludge, indicating that the synthetic musks accumulated in the sludge, which was supported by their high log*Kow* values [29].

Seasonal variations were observed in the occurrence and removal efficiency of the synthetic musks [32, 34]. Significantly higher input loading of certain and total synthetic musks were observed in summer (June and July 2008) compared to the other seasons [34]. For example, the HHCB concentrations in a WWTP in Shanghai were 1,478, 2,214, 2,170, and 1,841 ng/L in spring (March and April, 2008), summer (June and July, 2008), autumn (October and November, 2007), and winter (December 2007 and January 2008), and the input loading of HHCB were 79.8, 132.9, 119.4, and 84.7 g/day, respectively [34]. However, lower levels of HHCB and AHTN in the influent and effluent of a WWTP in Beijing were observed in warm season (May 2008) than in cold season (January 2008) [32]. Therefore, further studies should be carried out to investigate the seasonal variation trend. In addition, higher removal efficiencies of synthetic musks were observed in the warm seasons (June and July 2008) compared to the other seasons in the anaerobic-anoxic-oxic wastewater treatment process [34]. The higher temperature, the stronger photodegradation, as well as the more abundant biomass and bioactivity in the warm seasons might lead to the high removal efficiencies of synthetic musks [34].

The input loading of synthetic musks to the WWTP was investigated in Shanghai [30]. The concentrations of HHCB and AHTN were 1,467–3,430 and 435–1,043 ng/L in the influent and 233–336 and 74–94 ng/L in the effluent, respectively. Based on the concentrations of HHCB and AHTN, the amount of sewage in Shanghai, and the average treatment rates of wastewater in Shanghai, 1.26 t HHCB and 0.38 t AHTN were discharged into the aquatic environment in 2007. In addition, based on the yearly input per inhabitant connected, the concentration of HHCB and AHTN in the influent, the inhabitants that WWTP serves, and the receiving capacity of WWTP, the yearly input per inhabitant into the WWTPs is

estimated to be 0.2 g/capita per year for HHCB and 0.06 g/capita per year for AHTN [30]. The yearly input per inhabitant was threefold lower than those in Switzerland [42], indicating the low consumption rate of synthetic musks per inhabitant in Shanghai compared to Switzerland.

3.2.2 Synthetic Musks in Surface Water and Sediment

(1) Synthetic Musks in Surface Water The occurrence and distribution of synthetic musks has been investigated in three surface water areas in China. In Haihe River in North China, the total concentrations of seven targets were in the range of 5.9–120.6 ng/L [43]. HHCB and AHTN showed high detected frequencies and were observed in all the surface water samples. The concentrations of HHCB and AHTN were in the range of 3.5–32.0 and 2.3–26.7 ng/L, respectively. MK, AHMI, and ATII showed low detected frequencies. However, MX and ADBI were not detectable in any water samples [43]. In Suzhou Creek in Shanghai, the concentrations of HHCB and AHTN were in the range of 20–93 and 8–20 ng/L, respectively [30]. However, DPMI, AGMI, ADBI, ATII, MK, and MX were not detected. In Songhua River in Northeast China, the concentrations of DPMI, ADBI, AHMI, ATII, HHCB, and AHTN were in the range of N.D. (0.66)–6.80, N.D. (0.90)–3.22, N.D. (0.15)–10.56, N.D. (1.29)–1.68, 28.55–195.38, and 9.99–87.53 ng/L, respectively [37]. The synthetic musk levels in the surface water in China were in the same range as those in the USA [44] and South Korea [45] but lower than those in Germany [46] and Switzerland [47].

Seasonal variation of synthetic musks was observed in Songhua River [37]. The concentrations of the total synthetic musks were higher in spring (April 2007 and 2009) and summer (August 2007 and 2009) compared to autumn (October 2006 and November 2008). The precipitation might affect the seasonal variation [37].

Spatial variations of the synthetic musks have been observed. The synthetic musks in the Haihe River showed higher concentrations in the urban area of Tianjin City [43]. Similarly, HHCB concentrations of the Suzhou Creek were higher in the urban areas in Shanghai [30]. In Songhua River, the synthetic musk levels were higher in the downstream of the city with high population density [37].

(2) Synthetic Musks in Sediment In the Liangtan River near Chongqing in West China, both HHCB and AHTN were frequently detected in the surface sediments with concentrations of <LOQ (10)–268.49 and <LOQ (10)–99.75 ng/g (dw), respectively [48]. MK was detected in 3 samples with concentrations of 15.80–21.95 ng/g (dw). However, MX was not detected in any samples [48]. The concentrations of HHCB and AHTN in the sediments of Suzhou Creek near Shanghai in East China were in the range of 3–78 and 2–31 ng/g (dw), respectively. However, DPMI, AHMI, ADBI, ATII, MK and MX were not detected [30]. In the Haihe River in North China, the concentrations of HHCB, AHTN, and total synthetic musks in the surface sediments were in the ranges of 1.5–32.3, 2.0–21.9, and 1.7–58.8 ng/g (dw), respectively [43]. In Songhua River in Northeast China, HHCB, AHTN,

ADBI, and AHMI were detected in all the sediment samples, with concentrations of 2.47–8.30, 0.50–4.18, 0.52–8.30, and 0.25–1.90 ng/g (dw), respectively. The concentrations of ATII and DPMI were in the range of N.D. (value was not available)-3.28 and N.D. (value was not available)-0.48 ng/g (dw) [37]. In addition, the total concentrations of synthetic musks were in the range of 7.27–167.35 ng/g (dw) in the sediment of Zhujiang River in South China [49]. Unlike in the surface water, the concentrations of the synthetic musks in the sediments showed slightly difference among different sampling seasons [37].

Spatial distribution was observed. High concentrations of synthetic musks, especially HHCB and AHTN, were observed from the urban area with a high population density [30, 37, 48, 49]. Therefore, the synthetic musk level in the sediments was suggested to be used as the chemical tracer to indicate the impact of anthropogenic activities and to assess the impact of domestic wastewater in the natural aquatic system [30, 48, 49].

3.3 UV Filters and UV Stabilizers

UV filters are widely used in sunscreens, skin creams, cosmetics, hair sprays, body lotions, and so on to protect from UV radiation. The usage of UV filters increased due to the concerns over the effects of UV radiation in humans. UV filters can be either organic (absorb UV radiation) or inorganic compounds (reflect UV radiation, e.g., TiO_2). In this section, the occurrence of organic UV filters will be discussed. In addition, the occurrence of UV stabilizers, which are used in the building materials, automobile polymeric component, waxes, films, and so on to prevent degradation reaction by UV radiation, will be included. The investigation of UV filters and UV stabilizers in the aquatic environment in China was few. So far, the occurrence of UV filters in the sewage of WWTPs in Tianjin and Xiamen was studied, in which the concentrations showed big difference. The UV stabilizers were well investigated among large scale in one study. In addition, the studies of UV filters in the surface water and sediment were scarce. Further studies should be carried out to understand the occurrence and environmental behavior of UV filters in the aquatic environment in China.

3.3.1 UV Filters and UV Stabilizers in Sewage and Sludge

Li et al. investigated UV filters in a wastewater reclamation plant (WWRP) in Tianjin, North China [50]. All the four UV filters, including benzophenone-3 (BP-3), 4-methylbenzylidene camphor (4-MBC), ethylhexyl methoxycinnamate (EHMC), and octocrylene (OC), were detected in the influent, and the concentrations were in the range of 34–2,128 ng/L. The occurrence and seasonal variations of 50 PPCPs, including two UV filters (BP-3 and OC), were investigated over four seasons in a WWTP in Xiamen, Southeast China [2]. The average concentrations of

BP-3 in the influent and effluent were 12.85 and 3.16 ng/L, respectively. However, OC were not detected in any samples. Generally, the UV filters concentrations in the wastewater in China were lower than those in Switzerland [51] and Australia [52].

UV filters in the wastewater were season dependent. The concentrations were higher in the hot season than those in the cool season in WWTPs in both Tianjin (July 2005) [50] and Xiamen (August 2012) [2]. The increased concentration was probably due to the more usage of sunscreens in summer. The total removal efficiencies of UV filters in the WWTP were 28–43% in Tianjin [50]. The results indicated that UV filters were incompletely removed and may be discharged to the environment through treated WWTP effluent.

Zhang et al. investigated five benzophenone UV filters, two benzotriazole corrosion inhibitors, and four benzotriazole UV stabilizers in the sludge samples of five WWTPs in Northeast China [53]. 2-hydroxy-4-methoxybenzophenone (2OH-4MeO-BP), 2,4-dihydroxybenzophenone (2,4OH-BP), 4-hydroxybenzophenone (4OH-BP), 1H-benzotriazole (1H-BT), 5-methyl-1H-benzotriazole (5Me-1H-BT), 2-(3-*t*-butyl-2-hydroxy-5-methylphenyl)-5-chlorobenzotriazole (UV-326), 2,4-di-*t*-butyl-6-(5-chloro-2H-benzotriazol-2-yl)-phenol (UV-327), 2-(2H-benzotriazol-2yl)-4,6-di-*t*-pentylphenol (UV-328), and 2-(5-*t*-butyl-2-hydroxyphenyl)benzotriazole (TBHPBT) were detected, with concentrations in the range of 2.05–13.3, 4.41–91.6, 2.66–10.1, 17.2–198, 30.0–104, 23.3–136, 1.80–8.40, 40.6–5,920, and 0.730–1.18 ng/g (dw). However, 2,2′,4,4′-tetrahydroxybenzophenone (2,2′,4,4′OH-BP) and 2,2′-dihydroxy-4-methoxybenzophenone (2,2′OH-4MeO-BP) were not detected in any sample [53]. Ruan et al. investigated the occurrence and distribution of nine benzotriazole UV stabilizers in the sludge samples from 60 WWTPs in 33 cities all over China [54]. 2-[3,5-bis(1-methyl-1-phenylethyl)-2-hydroxyphenyl]-benzotriazole (UV-234) was the most dominant analogue with a median concentration of 116 ng/g (dw), which averagely accounted for 27.2% of total UV stabilizers. 2-(2-hydroxy-5-*t*-octylphenyl)benzotriazole (UV-329), UV-326, UV-328, and 2-(2-hydroxy-5-methylphenyl)benzotriazole (UV-P) showed high abundance in the sludge with the median concentrations of 66.8, 67.8, 57.3, and 20.6 ng/g (dw), respectively. Significant correlations were found among the concentrations of benzotriazole UV stabilizers with daily treatment volume of WWTPs or the total organic carbon (TOC) of the sludge samples. There was no obvious geographic trend for the distribution pattern of UV stabilizers, indicating the universality of usage and contamination in China [54].

3.3.2 UV Filters and UV Stabilizers in Surface Water and Sediment

In a recent study, we investigated the seasonal and spatial variation of OC and BP-3 in Jiulong River and its estuary in Southeast China [23]. Both OC and BP-3 were widespread in the surface water, with more than 80% detection frequencies. The concentrations of OC and BP-3 were in the range of 0.12–1.94 and 0.25–37.2 ng/L in the Jiulong River and were 0.4–96.7 and 0.6–547 ng/L in the estuary,

respectively. The UV filters showed higher concentrations in the warm season (June 2012, and Sep 2012), since the consumption increased in the warm season. In addition, BP-3 and OC showed significantly higher concentrations near Gulangyu Island (a famous tourist resort) among the estuary samples in summer, which indicated that the UV filter contamination in the surface water was related to the tourists and high population density.

The occurrence of five benzophenones and six benzotriazoles was investigated in the sediments in Songhua River in Northeast China [53]. The average concentrations of 1H-BT, 2OH-4MeO-BP, UV-326, UV-327, and UV-328 were 0.385, 0.380, 1.86, 0.31, and 3.81 ng/g (dw), respectively. 5Me-1H-BT, 2,2′,4,4′-OH-BP, 4OH-BP, 2,4OH-BP, 2,2′OH-4MeO-BP, and TBHPBT were not detected in the sediments. Generally, the concentrations of UV filters or stabilizer in the sediments of Songhua River were lower than those in Saginaw and Detroit River in the USA [53].

3.4 Preservatives

Parabens are a class of chemicals widely used as preservatives in pharmaceuticals and cosmetics. The commonly used parabens are methylparaben (MeP), ethylparaben (EtP), propylparaben (PrP), butylparaben (BuP), and benzylparaben (BzP). The investigation of preservatives in the aquatic environment in China was mainly in South and Southeast China, including the surface water of Pearl River and Jiulong River and its estuary and wastewater from WWTPs in Guangzhou and Xiamen. However, to the best of our knowledge, the occurrence and distribution of the preservatives in the solid samples in China have not been reported. Further investigation should be carried out to understand the preservatives in the solid phase and in other areas in China.

Peng et al. investigated the preservatives in the major Pearl River and three urban streams at Guangzhou in 2005–2006 [19]. The concentrations of MeP and PrP were in the range of <LOQ (0.5 ng/L)–1,062 and 8–2,142 ng/L in the low-flow seasons (March, October, and December) and were <LOQ (0.5 ng/L)–213 and <LOQ (0.1 ng/L)–480 ng/L in the high-flow seasons (April, May, and August), respectively. However, BuP was not detected in any samples. Higher concentrations of preservative were observed in the low-flow season, which was probably attributed to the dilution effect caused by rainfall. Yu et al. investigated the occurrence of preservative in Pearl River at Guangzhou by collecting thirteen samples in March and May 2008 [17]. The concentrations of MeP, EtP, PrP, and BuP were in the range of 0.9–66.1, 0.2–23.1, 1.2–86.0, and <0.1–5.3 ng/L, respectively. In addition, four preservatives were detected in the WWTP in Guangzhou in 2008. The concentrations of MP, EP, PP, and BP were 1,194, 166, 500, and 27 ng/L in the influent, while the concentrations were 5.1, 1.0, 7.2, and 0.3 ng/L in the effluent, respectively [17]. Results showed that the preservatives could be well removed in the WWTP.

Sun et al. recently investigated the preservatives in a local WWTP in Xiamen, China [2]. The concentrations of PrP, MeP, and BzP were in the range of 129–392, 140–274, and <LOQ (0.1 ng/L)–0.2 ng/L in the influent, respectively. The concentrations of PrP and MeP in the effluent were 0.6–72 and 1.3–101 ng/L, respectively. However, the BzP was not detected in the effluent. PrP and MeP showed higher concentrations in March 2013 compared to August and December 2012 and May 2013. The lower dilution rate owing to the less water consumption might contribute to the higher preservative concentrations. In a recent study, we investigated the PrP and MeP in the Jiulong River and its estuary in Southeast China. The concentrations of PrP were in the range of 0.69–16.4 ng/L in Jiulong River and 1.4–128 ng/L in the estuary. The concentrations of MeP were in the range of 0.9–20.6 ng/L in Jiulong River and 1.1–229 ng/L in the estuary [23].

Generally, the preservative concentrations in the Pearl River were comparable to those in the Jiulong River. Higher concentrations of preservatives were observed in the influent in the WWTP in Guangzhou compared to Xiamen. Further investigations in the other areas of China should be carried out to understand the preservative occurrence and behavior in the aquatic environment.

4 Implication to Research

The production and consumption of PCPs continued to grow over the last few decades in China. It can be predicted that the presence and contamination of PCPs in the environment in China will arise. The occurrence and fate of PCPs in the aquatic environment in China has been investigated. However, there are still challenges in the future studies.

4.1 Improvement of the Monitoring Methods and Areas

So far, the investigation of the PCP occurrence only involved several PCP compounds in each study, which made it difficult to understand the contamination of a variety of PCPs. In addition, possible new PCPs and the transformation products of PCPs in the environment should be identified and included in the monitoring list because of their potential adverse effect. Therefore, the investigation involved in a variety of PCPs should be carried out in the future. Furthermore, since PCPs could show an environmental risk at the low levels, there is a need to develop more sensitive and selective analytical methods which could detect PCPs at trace levels.

There are clear regional biases in the knowledge of PCPs in China. Most of the investigation focused on the Beijing-Tianjin area, Yangtze River Delta, Pearl River Delta, Southeast China area, etc. There is a severe lack of PCP contamination status in China other than those hot spots [55], especially in the middle and west part of China. Among the PCP contamination data in the aquatic environment, most

studies investigated the PCPs in the WWTPs, including the wastewater and the sludge. A few studies focused on the river pollution, including the surface water and the sediment. However, the knowledge of PCPs in the groundwater, drinking water, coastal water, and sediment was scarce. In addition, the large-scale monitoring of PCPs in different regions of China in one study was lack, which made it difficult to compare the pollution status of target PCPs among studied areas. Therefore, more contamination information in different areas in China, especially the natural watershed, is needed.

Most studies were based on a single sampling or very short monitoring periods. It was difficult to understand the occurrence and pollution status of PCPs over an extended period. The occurrence and fate of PCPs in the WWTPs and natural watershed could change with seasons. Therefore, it is necessary to monitor the pollution status of PCPs over a long period.

4.2 Improvement of Control Strategies

The major source of PCPs to the environment is through the WWTPs [56]. The conventional wastewater treatment processes (flocculation, sedimentation, and activated sludge treatment) could partly remove the PCPs. However, the removal efficiencies were limited [55]. PCPs remained in the sewage or sludge would cause subsequent contamination to the receiving water bodies or soils. Considering the increase of PCP consumption in China, the increased loads in the WWTPs would lead to an environmental problem. Hence, the application of the innovative and advanced wastewater treatment processes to improve the removal of PCPs is necessary.

Due to the lack of financial support or incomplete sewer network, the conventional wastewater treatment facilities are not available in some rural areas of China [57]. The direct discharge of wastewater without any treatment might be the potential cause of nonpoint source pollution of PCPs. Therefore, more wastewater treatment facilities should be established to avoid the direct discharge of wastewater in the rural areas and to reduce PCP contamination. Finally, the regulations and legislation should be established for PCP management in China in the future.

Conclusions

Studies have investigated the occurrence of PCPs in the aquatic environment in China. The PCP levels were in the range of ng/L to μg/L in the surface water and sewage while ng/g to μg/g (dw) in the sediment and sludge, depending on the species of PCPs or the samples. Generally, the PCP levels, including antimicrobial agents, synthetic musks, UV filters, and preservatives in China, were comparable to the global levels. However, the concentrations

(continued)

of synthetic musks and UV filters in China were somewhat lower than those in the European countries. The investigation of PCPs in China showed strong regional biases, which mainly focused on the developed area with high population density. There is almost no information available for the areas other than the hot spots. In addition, studies with large scales and extended monitoring periods were still needed. Moreover, the environmental behavior, including the transport and transformation of PCPs, in aquatic environment was poorly understood. Considering the increasing consumption of PCP in China, the increased loads would lead to a severe environmental problem. Therefore, further studies are needed to get a better understanding of PCPs in the aquatic environment in China.

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Survey of Personal Care Products in the United States

Melody J. Bernot and James R. Justice

Abstract In 2013, the United States had a population of ~316 million people, increasing 2.4% from 2010, with 13.7% of the population 65 years or older. Coupled with population growth and an aging population is an increase in the development and use of personal care products (PCPs). With 4.7% of global freshwater resources in the United States, freshwater resources and services are influenced by increasing abundance of PCPs which have been detected in freshwaters throughout the United States. Though a majority of the studies on PCPs in freshwaters globally have been conducted in the United States, a predictive understanding of PCP abundance and fate remains lacking. Compounds commonly detected in US freshwaters at high detection frequencies (>50%) include antimicrobials, fragrances, insect repellants, and UV blockers.

Keywords Anthropogenic pollutants, Groundwater, Personal care products, Surface waters, Trace organic contaminants, Wastewater

Contents

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M.S. Díaz-Cruz and D. Barceló (eds.), *Personal Care Products in the Aquatic Environment*, Hdb Env Chem (2015) 36: 95–122, DOI 10.1007/698_2014_288,

1 Introduction

In 2013, the United States had a population of ~316 million people, increasing 2.4% from 2010 [1]. Population growth has increased the development and use of personal care products (PCPs), with the United States currently being the largest market for PCP sales [2]. PCPs are generally defined as personal hygienic products that are not prescribed or ingested. Rather, PCPs are commonly applied topically and include, though are not limited to, fragrances, antimicrobial agents, and cosmetics. Following use and disposal, PCPs with variable chemical and physical properties ultimately emerge in natural ecosystems where PCP movement and environmental fate are not well understood.

Because PCPs do not require a prescription and are generally used in larger volumes than pharmaceuticals, PCPs are likely more abundant in ecosystems relative to pharmaceutical contaminants. After topical application, PCPs can enter water systems through loss on washing. Thus, a primary entry point into natural ecosystems is through wastewater, and PCPs are more abundant in freshwater ecosystems relative to other environments. The United States has 4.7% of global freshwater resources housed in diverse lakes, streams, rivers, and wetlands (Fig. 1). All of these freshwater resources, and the services they provide, may be threatened by the increased PCP development and use. Some threats to freshwater ecosystems, such as nutrient enrichment and acidification, have been well studied, yielding predictive models that aid regulatory action. However, a predictive understanding of PCP abundance and fate remains lacking with limited research to guide assessments of regulatory need. Unlike some European countries, no PCP compounds are currently federally regulated in the United States. Limited understanding of PCP abundance is confounded by both the diversity of PCP compounds and the diversity of freshwater ecosystems in the United States. Freshwater ecosystems in the United States have variable geology, geography, surrounding vegetation, and land use in the sub-watersheds (Fig. 1), all of which may influence PCP movement and degradation within aquatic ecosystems.

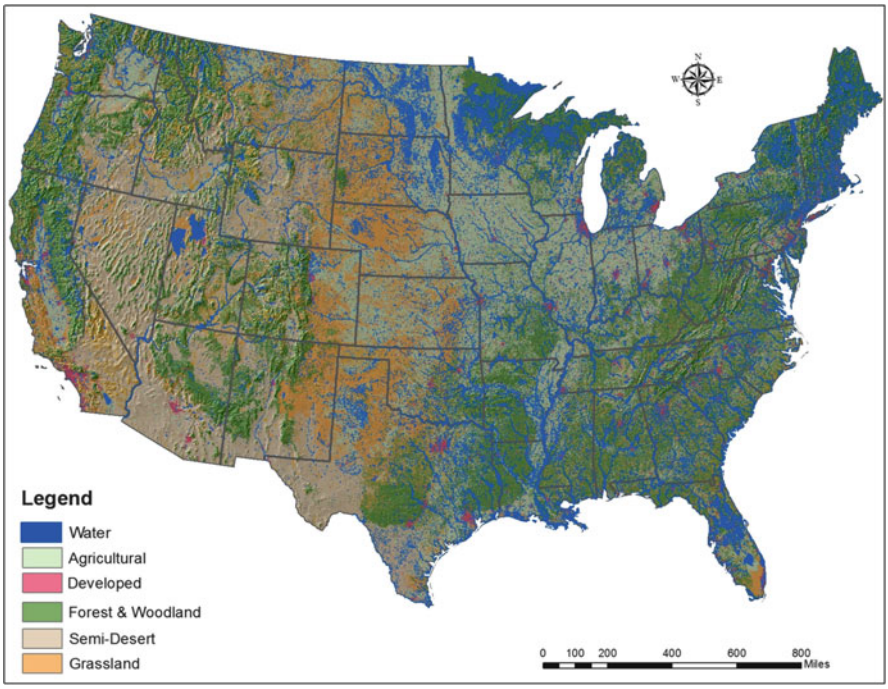

Fig. 1 Freshwater in the United States is influenced by variable vegetation and surrounding land use

Though data on the environmental abundance and fate of PCPs in the United States are limited relative to other contaminants (e.g., pharmaceuticals, nutrients, pesticides), a majority of the studies on PCPs in freshwaters globally have been conducted in the United States [3]. This limited research has focused on determining PCP abundance predominantly in urban watersheds, and data are further skewed by geographic location. In 2011, only 22 US states (44%) had multiple assessments of PCP abundance in aquatic ecosystems inclusive of both national reconnaissance and regional studies [3]. Despite limited PCP research in the United States, some general patterns have emerged. Specifically, PCP compound classes commonly detected in surface water at high detection frequencies (>55%) include antimicrobials, fragrances, ultraviolet (UV) light blockers, and insect repellents with additional anthropogenic inputs of novel PCPs such as microplastics and nanomaterials. Further, PCPs are consistently measured above detection limits across the country in both urban and agriculturally influenced areas. However, the specific compounds detected and the range in concentrations measured varies both within and among previous studies (Table 1). Beyond commonly detected compounds, few published syntheses or multidisciplinary studies are available to elucidate predictive patterns.

Most research documenting abundance of PCPs in the United States has focused on surface waters inclusive of streams and rivers with fewer studies in lakes. One of

Table 1 Select published studies of dissolved PCP concentrations (ng/L) and detection frequencies (%) in the United States

Location	Water source	Sites (#)	Samples (#)	Data type	DEET		Triclosan		References
					ng/L	%	ng/L	%	
Indiana	Streams	2	24	Range	8–290	64	9.1–22	12	Veach and Bernot [4]
Indiana	Streams	1	180	Maximum	180	70	230	57	Bernot et al. [5]
National	Streams	139		Maximum	1,100	74.1	230	57.6	Kolpin et al. [6]
Georgia	Streams	26		Maximum	120	23.9	400	56	Frick and Zaugg [7]
Wisconsin	Lake Michigan; effluent	7		Maximum			41		Blair et al. [8]
Nevada	Lake Mead	1	8	Mean	37		27		Vanderford et al. [9]
Minnesota	Varied	65		Range	27–47,000	23.9	88–4,300	8.2	Lee et al. [10]
Iowa	Surface water	23	76	Maximum	130	3.7	140	3.33	Kolpin et al. [11]
National	Surface water; effluent	40		Maximum	2,100	70	1,600	62.5	Glassmeyer et al. [12]
South Dakota	Surface water; wastewater	12		Maximum	80		<100		Sando et al. [13]
California	Drinking, reclaimed; wastewater	5		Mean	300		627		Loraine and Pettigrove [14]
National	Surface; groundwater	74		Maximum		14		8.1	Focazio et al. [15]
National	Groundwater	47		Maximum	13,500	34.8		14.9	Barnes et al. [16]
California	San Francisco Estuary	13		Mean	80				Oros et al. [17]
Massachusetts	Groundwater	20		Maximum	6	5			Schaider et al. [18]

the first surface water reconnaissance efforts by the United States Geological Survey (USGS) [6] at the national scale provided a broadscale baseline for which subsequent regional scale studies have been able to compare PCP detection frequencies and concentrations. In the 2002 national reconnaissance of 139 streams across 30 states, Kolpin et al. [6] detected organic waste contaminants in 80% of streams sampled. Of the PCPs analyzed, *N*,*N*-diethyltoluamide (DEET; insect repellant), triclosan, and 4-nonylphenol (nonionic detergent metabolite) were the most frequently detected with significant variation among sites. PCP compound abundance on the national scale is variable by both PCP compound type and the concentrations at which they occur. At local and regional scales, the range of concentrations and compounds detected are muted relative to the national scale, though can still vary by more than two orders of magnitude.

Nationally, groundwater provides drinking water for 40% of US residents as well as natural baseflow to surface waters [19, 20]. However, groundwater may also transport environmental contaminants, including PCP compounds, that can threaten organismal and ecosystem health. It is unclear whether groundwater is serving as a source of PCPs to surface waters or surface waters are serving as a source of PCPs to groundwater though it is likely system and condition specific [16, 21]. A nationwide assessment of PCP concentrations in groundwater detected at least one organic wastewater contaminant in 81% of groundwater sites surveyed in the Unites States (susceptible sites selected for measurements) [16]. Across use categories, plasticizers (39%) had the highest frequency of detection followed by insect repellants (38%) and fire retardants (35%) [16]. Per unit concentration, plasticizers, insect repellants, and detergent metabolites contributed 66% of the total PCP concentration in groundwater (sum of all compound concentration) [16]. Despite relatively high detection frequencies and concentrations, at the national scale groundwater PCP detection frequencies and concentrations are lower relative to surface waters, suggesting surface waters may generally serve as a source of PCPs to groundwater [6, 16].

2 Antimicrobials and Disinfectants

Widely used and commonly detected antimicrobial agents in US freshwaters include triclosan, triclocarban, and phenol with most studies focused on triclosan. Triclosan has been used extensively for nearly 40 years in toothpastes, soaps, and lotions resulting in triclosan (and its methyl derivative, methyl-triclosan) consistently present in US surface waters (Table 1). A recent meta-analysis [22] of triclosan in freshwater from data spanning 1999–2012 found 83% of effluent samples had measurable concentrations of triclosan (mean concentration = 775 ng/L).

2.1 Streams and Rivers

The first reconnaissance effort by the USGS [6] on the national scale detected triclosan (median concentration = 140 ng/L, maximum = 2,300 ng/L) in 57.6% of stream water samples. In a nationwide survey of streams receiving wastewater effluent, triclosan was detected at a frequency of 62.5%, with median and maximum concentrations of 120 and 1,600 ng/L, respectively [23]. Similarly, river water samples collected near a wastewater outfall in Tennessee contained 171 ng/L triclosan [24]. Under low flow conditions, triclosan was found in 10% of water samples from Iowa streams, with a maximum concentration of 140 ng/L [11]. Similar to streams across Iowa, Veach and Bernot [4] detected triclosan in 12% of stream samples collected in Indiana (mean concentration = 22 ng/L).

Outside of Europe, few studies have quantified methyl-triclosan in streams, with more studies in the United States needed. In Texas streams, Coogan and La Point [25] detected a maximum methyl-triclosan concentration of 40 ng/L, with greater detection frequency (100%, $n = 5$) than previously reported triclosan parent-compound detection frequencies.

Similar to triclosan, triclocarban has relatively high detection frequencies. For example, 68% of Maryland streams sampled had triclocarban concentrations above detection limits [26]. Across regions, triclocarban concentrations in US aquatic ecosystems can vary by orders of magnitude. The maximum detected triclocarban concentration from New York environmental samples was 6,750 ng/L [26], while Kumar et al. [27] detected a maximum triclocarban concentration of just 49 ng/L in water from the Vernon River in Georgia.

Phenol and 4-methyl phenol are disinfectants also found in US freshwaters, typically at lower detection frequencies than triclosan and triclocarban as evidenced by nationwide studies. Across 85 sites in the continental United States, phenol was detected in 8.2% of samples (median concentration = 700 ng/L) [6]. Further, 4-methyl phenol was detected in 24.7% of samples nationwide though with a median concentration 14× lower than phenol (mean 4-methyl phenol = 50 ng/L) [6]. Glassmeyer et al. [23] detected phenol in 40% of stream waters receiving effluent from ten locations across the United States. In contrast, phenol was detected in 30% of Iowa streams with a maximum concentration of 1,200 ng/L under low flow conditions, while 4-methyl phenol was not detected in any samples [11].

2.2 Lakes

Recent attention has been placed on PCPs in the Laurentian Great Lakes, where greater water volume relative to streams was previously thought to minimize PCP concentrations. However, recent studies suggest antimicrobial agents have become increasingly ubiquitous in the Great Lakes. Several studies have assessed PCPs in

the Great Lakes in both the United States and Canada [8, 28–32] with sampling efforts primarily conducted near shore. Triclosan was detected in 74% of water samples collected from seven Lake Michigan sites [8]. Near Milwaukee (Wisconsin), mean triclosan concentrations were 2.7 ng/L (max = 7.4 ng/L; 71.4% detection) at sites >3 km from effluent inputs [8]. In a Lake Ontario harbor, triclosan concentrations were 20 ng/L. However, triclosan concentrations in Lake Ontario open water were only 1 ng/L [33]. Ferguson et al. [3] detected triclocarban in 98% of water samples collected in eight southern Lake Michigan sites ($n = 64$) with concentrations ranging from 2.5 to 14 ng/L. Overall, antimicrobial agents are measured at higher concentrations in streams relative to large lakes where PCPs are further diluted. Nevertheless, reported concentrations of antimicrobial agents in the Great Lakes still indicate a potential threat to lake ecosystems and aquatic organisms.

2.3 Marine Environments

Particularly in marine environments, abundance and ecological consequences of PCPs are poorly understood. In the United States, few studies have quantified estuarine and marine PCP abundance; further, confounding factors such as salinity and tidal cycles likely influence PCPs differentially relative to inland freshwaters. In Greenwich Bay (Rhode Island) [34], dissolved triclosan concentrations ranged from 0.5 to 7.4 ng/L, an order of magnitude lower than measurements in land-based surface waters (Table 1) but comparable to dissolved triclosan concentrations from Charleston Harbor (South Carolina; max = 1 ng/L) [35]. Greenwich Bay (Rhode Island) sediment triclosan concentrations ranged from <1 to 32 ng/g [34]. Interestingly, Katz et al. [34] found wastewater discharges in close proximity to sampling sites did not predict spatial distribution of triclosan in estuaries. Therefore, sources other than effluent discharge of PCPs to estuarine habitats should also be considered, such as atmospheric deposition and groundwater runoff of solid wastes.

2.4 Groundwater

Few studies have quantified PCPs from groundwater samples, with future research needed. In a nationwide study, triclosan and phenol were measured from 47 groundwater sites across 18 states [16]. Phenol was not detected at any site; however, triclosan was detected in 14.9% of groundwater samples using a non-quantitative detection method [16]. Detectable triclosan concentrations from groundwater wells in west Texas ranged from 53 to 120 ng/L [36]. Interestingly, the overlying land in west Texas from which these groundwater samples were collected had a history of receiving biosolid application [36].

2.5 Sediment and Biosolids

In contrast to studies measuring dissolved PCP concentrations, few national scale assessments of sediment-bound PCP concentrations have been conducted to provide broad comparisons among studies. However, multiple regional studies have measured dissolved and sediment-bound PCPs in concert. In general, dissolved PCP concentrations tend to be higher relative to sediment concentrations though this is compound specific. Triclosan has been detected in Mississippi River sediment (max = 14 ng/L) cores as far back as 1960 when triclosan was initially produced [37]. In Lake Michigan, PCPs detected in water samples differed from compounds measured in sediment samples though triclosan was measureable in both matrices [8].

Miller et al. [38] examined the historic presence of triclosan and triclocarban in estuarine sediment cores from Jamaica Bay (New York) and the Chesapeake Bay (Maryland). Across both sample locations, triclocarban was detected at higher concentrations than triclosan. Jamaica Bay sediment contained more triclocarban (max = 24,000 ng/g) and triclosan (max = 800 ng/g) than Chesapeake Bay sediment, which yielded a maximum triclocarban concentration of 3,600 ng/g with triclosan below detection limits [38]. In the Puget Sound (Washington), more than a third of the estuary sediment samples collected contained triclocarban, with a maximum concentration of 16 ng/g [39].

Kumer et al. [27] detected a mean triclocarban concentration of 37 ng/g from Vernon River (Georgia) sediment. Interestingly, triclocarban was not detected in water samples from seven Lake Michigan sites near Milwaukee (Wisconsin) [8]. However, underlying benthic sediment in Lake Michigan contained a mean triclocarban concentration of 33 ng/g and a mean triclosan concentration of 26 ng/g [8].

Digested municipal sludge, produced in the United States at ~7 million dry tons annually, is frequently applied to land, thereby providing a potential source of PCPs to US freshwaters [40]. With over 3,000 wastewater application sites in the United States, research has focused on the potential use of reclaimed wastewater to serve increasing water demands [41, 42]. A nationwide mass balance modeled 5–15 tons of PCPs annually are applied to US soils via biosolid application [43].

In a survey of biosolids across the United States, triclosan (mean = 12,600 ng/g) and triclocarban (mean = 36,000 ng/g) were the most abundant analytes accounting for 65% of the total PCP mass [40]. A 3-year mesocosm study of biosolids in Maryland quantified the degradation of common PCPs. Interestingly, triclosan (half-life = 187 ± 6 days) was degraded over time, while triclocarban showed no measurable degradation [44]. The results of the mesocosm study by Walters et al. [44] may explain why agricultural soils in Michigan that had previously received biosolid applications contained higher concentrations of triclocarban (range = 1.2–6.5 ng/g) relative to triclosan (range = 0.16–1 ng/g). Further, direct analysis of the biosolid prior to agricultural application revealed the biosolid contained much greater amounts of triclocarban (9.28 μg/g) and triclosan (7.06 μg/g) relative to biosolid

amended agricultural soils [45]. Given the nearly 3.5 million dry tons of biosolids annually applied to land, antimicrobial agents are likely to be abundant downstream of biosolid application sites.

2.6 Biota

In terrestrial ecosystems, triclosan has been measured in soybean root tissue (16,900 ng/g) [41], presumably associated with biosolid application. Specifically from biosolid application sites, triclosan and phenol have also been detected in earthworms at concentrations of 1,830 and 2,610 ng/g, respectively [46].

In aquatic ecosystems, few studies have quantified PCPs in higher-trophic-level species. However, blood plasma in wild bottlenose dolphins from South Carolina and Florida had measureable triclosan ranging from 0.12 to 0.27 ng/g wet weight with 23% of samples having detectable concentrations (detection limit = 0.005 ng/g) [47]. Triclocarban was consistently measured at higher concentrations relative to triclosan and methyl-triclosan in algae and snail tissue collected from an effluent-receiving stream, Pecan Creek (Texas) [48]. Algal triclocarban ranged from 200 to 400 ng/g, while mean triclosan and methyl-triclosan concentrations were 125 and 70 ng/g, respectively [48]. Mean triclocarban concentration in snail tissue (caged snails placed in Pecan Creek for 14 days) was 299 ng/g, while triclosan and methyl-triclosan concentrations were 58.7 and 49.8 ng/g, respectively [48]. Leiker et al. [49] detected methyl-triclosan in every carp sample ($n = 29$) collected from Lake Mead (Nevada), with a mean body concentration of 596 ng/g.

3 Fragrances

Fragrances have become ubiquitous within the environment, with the potential to be toxic to organisms as well as bioaccumulate in tissues [50]. Fragrances were first identified in environmental samples >30 years ago in Japanese rivers [51]. More recently, fragrances have been detected in many European environmental samples though less anthropogenic fragrance research has been conducted in the United States. Synthetic musk fragrances, which are subclassified as either nitro musks or polycyclic musks, are commonly used fragrances in many cosmetics, lotions, and perfumes. Common nitro musks include musk xylene and musk ketone, while common polycylic musks include celestolide, traseloide, toxalide, tonalide, and galaxolide. Overall, polycyclic musks are used in greater quantities than nitro musks [50, 52]. Additional fragrances of concern include acetophenone, ethyl citrate, indole, isoborneol, and skatol. However, most of these compounds, except acetophenone and ethyl citrate, are not typically detected in environmental samples.

3.1 Streams and Rivers

Nationally, fragrances are likely to occur in lotic freshwaters throughout the United States; however, national contaminant sampling efforts have focused minimally on fragrances. Acetophenone was the only fragrance of 95 total organic contaminants to be sampled by Koplin et al. [6] in a national trace organic reconnaissance effort. Acetophenone occurred in 9.4% of stream water samples at a maximum concentration of 410 ng/L [6]. In effluent-receiving streams across the United States, the maximum acetophenone concentration was 780 ng/L (detection frequency = 7.5%) [23]. Additional detected fragrances included ethyl citrate (detection frequency = 72.5%, max = 520 ng/L), galaxolide (detection frequency = 57.5%, max = 530 ng/L), and tonalide (detection frequency = 80%, max = 2,600 ng/L) [23]. Future national reconnaissance efforts specifically focused on fragrances are required to understand the distribution and abundance of these potentially toxic compounds. Given the high detection frequencies and environmental concentrations of certain fragrances identified in studies outside of the United States, fragrances may have adverse ecosystem-level effects on streams and rivers.

Regionally, in Iowa streams, commonly detected fragrances were comparable to the national scale [11]. Tonalide was detected at the highest frequency and concentration (36.7%, max = 1,200 ng/L, respectively) with galaxolide occurring in 20.0% of stream samples (max = 260 ng/L) [11]. Similar to the national scale, acetophenone was the least detected fragrance in Iowa streams (detection frequency = 3.3%, max = 220 ng/L) [11]. In contrast, fragrance concentrations in the upper Hudson River (New York) were lower than measurements in Iowa streams, though tonalide was consistently detected at higher concentrations than galaxolide across most Hudson River sites [53]. Dissolved tonalide and galaxolide concentration ranges in Hudson River were 5.09–22.8 and 3.95–25.8 ng/L, respectively, with the highest fragrance concentrations occurring near Albany (New York) [53]. Tonalide has also been detected in 60% of samples ($n = 5$) and galaxolide in 57% of samples ($n = 7$) within samples from the Potomac River basin (Washington, D.C.), with a maximum galaxolide concentration of 27.0 ng/L [54]. In US lotic ecosystems, few studies have documented abundance, behavior, and fate of widely used fragrances, such as musk xylene, musk ketone, and celestolide, leaving little knowledge available to aid regulations and policies.

3.2 Lakes

Similar to antimicrobials and disinfectants, most US research documenting fragrances in lentic ecosystems has been conducted in the Laurentian Great Lakes, with lake research targeting more fragrance types relative to stream and river research. The Great Lakes Water Institute has classified synthetic musk compounds as an emerging contaminant threat to the Great Lakes, reporting musk compound

concentrations in open lake water as high as 4.7 ng/L and higher concentrations in main tributaries (41 ng/L) [55]. Maximum musk xylene (0.04 ng/L), musk ketone (0.04 ng/L), galaxolide (2.0 ng/L), and tonalide (0.2 ng/L) concentrations in Lake Ontario open water were between zero and four times less than fragrance concentrations in an adjacent harbor location [33]. Of eight fragrance compounds analyzed in Lake Michigan, cashmeran was the only compound not detected, and musk xylene was detected in 100% of Lake Michigan water samples ($n = 14$) [56]. In Lake Michigan, other frequently detected fragrance compounds were galaxolide (92%), toxalide (92%), tonalide (85%), and traseloide (69%) [56]. Similar to streams and rivers, galaxolide (mean = 4.7 ng/L) and tonalide (mean = 1.0 ng/L) in the Great Lakes are generally detected at higher concentrations than other measured fragrances [56].

Contrary to Lake Michigan, musk xylene was not detected in any Lake Mead (Nevada) water samples ($n = 14$), with Osemwengie and Gerstenberger [57] speculating that nitro musks may be absorbed to benthic sediment rather than remaining in the water column. Galaxolide (Lake Mead mean = 0.36 ng/L) was over an order of magnitude lower in Lake Mead water relative to Lake Michigan [56, 57]. However, Lake Michigan tonalide concentration was over five times greater than tonalide dissolved in Lake Mead (Lake Mead mean = 0.19 ng/L). Similar to the Great Lakes, Lake Mead water samples generally contained galaxolide and tonalide at higher concentrations than all other fragrances [56, 57].

3.3 Marine Environments

The majority of research assessing fragrance compounds in marine environments has been performed outside of the United States, with some trends emerging. Generally, galaxolide and tonalide are dominant fragrance compounds in foreign marine environments [58–60]. The abundance, distribution, and environmental fate of fragrances in US marine environments remain largely unknown. Oros et al. [17] analyzed a host of organic contaminates in the San Francisco Bay estuary (California), with galaxolide and tonalide both occurring in 100% of water samples across 13 sites. Galaxolide (range = 3–131 ng/L) had a mean concentration of 43 ng/L, while tonalide (range = 1–8 ng/L) had a mean concentration of 3 ng/L [17]. Maximum concentrations of galaxolide and tonalide were both detected at the South Bay site of San Francisco Bay, suggesting anthropogenic inputs of wastewater effluent [17]. Future research should examine the abundance and distribution of increasingly ubiquitous fragrances in historically contaminated US estuaries such as the Chesapeake Bay ecosystem and Mississippi River delta.

3.4 Groundwater

National reconnaissance efforts comparing abundance of contaminants in groundwater relative to surface water suggests fragrances have lower detection frequencies and concentrations in groundwater than in surface water [15]. Focazio et al. [15] sampled 12 fragrance compounds from 25 groundwater sites across the United States, detecting at least one fragrance compound in 15% of groundwater samples. Conversely, no fragrances were detected from 20 groundwater sites in Massachusetts [18]. In Texas, tonalide was detected at maximum concentrations of 72 and 56 ng/L from two groundwater sites underlying a biosolid-land application site [61]. Galaxolide and celestolide were also detected at trace concentrations from the same two groundwater sites, however at much lower concentrations (<5.0 ng/L) than tonalide [61].

3.5 Sediments and Biosolids

Similar to surface waters, common fragrances in environmental sediments include galaxolide and tonalide. Across three Hudson River sites, galaxolide and tonalide were consistently detected between one and two orders of magnitude higher in sediments than in water (388 and 113 ng/g, respectively) near Troy (New York) [53]. Further downriver, tonalide sediment concentration was 544 ng/g near Catskill (New York) [53]. Conversely, Koplin et al. [54] did not detect common fragrances in Potomac River (Washington, D.C.) basin sediment even though fragrances were detected in neighboring water samples.

Lake Ontario surface sediments had measurable concentrations of six fragrance compounds with a mean galaxolide concentration (16 ng/g) at least ten times greater than any other detected fragrance [62]. Other fragrances detected in Lake Ontario sediments included tonalide (0.96 ng/g), traseloide (0.27 ng/g), and celestolide (0.10 ng/g). Galaxolide was the only fragrance detected in Lake Erie surface sediments, having a mean concentration of 3.2 ng/g [62]. Lake Mead (Nevada) sediment contained more galaxolide (max = 27 ng/L) than tonalide (max = 4.2 ng/L) [63]. A less commonly detected fragrance, acetophenone, was also found in Lake Mead sediment at a maximum concentration of 25 ng/L [63].

Mean musk xylene concentrations in San Francisco Bay (California) sediments were 0.034 ng/g with a similar mean musk ketone concentration of 0.038 ng/g [64]. The highest nitro musk concentrations in San Francisco Bay sediment were detected at the southernmost sampling site where Oros et al. [17] observed the highest concentration of dissolved fragrances. Fragrance contamination in South San Francisco Bay is likely the result of effluent but could also result from rainwater runoff of biosolid applications or more directly from biosolid applications aimed at combating erosion.

Galaxolide concentrations in biosolids ranged between 1,100 and 1,790 ng/g, and tonalide concentrations ranged between 400 and 900 ng/g across six biosolid sources collected from five states in the United States [65]. Another biosolid survey from nine sites across seven states also detected galaxolide (median = 3,900 ng/g of organic carbon) and tonalide (median = 116,000 ng/g organic carbon) [66]. Kinney et al. [66] detected galaxolide (mean = 427,000 ng/g) at higher concentrations than tonalide (mean = 177,000 ng/g) in biosolid used for land applications in the Midwestern United States. Acetophenone has also been detected in Midwestern US biosolids with a mean concentration of 3,450 ng/g [66]. Soil from a Midwest site receiving biosolid applications contained comparatively less fragrance concentrations than the biosolid source. However, fragrance compounds were still detected at concentrations higher than natural sediment, with galaxolide, tonalide, and acetophenone having mean concentrations of 3,340, 279, and 110 ng/g, respectively [66].

3.6 Biota

Käfferlein et al. [67] described in detail how musk fragrances have the potential to be bioaccumulative. Musk fragrances have recently been detected in higher-trophic-level organisms, including humans [68]. Specifically, fragrance body content was quantified from 49 humans living in New York City (New York). Females generally contained higher fragrance body content than human males. Overall mean galaxolide concentrations in human tissue was 96.9 ng/g, and mean tonalide concentration was ~4× less at 22.8 ng/g. Human fragrance body content was generally reported higher than any other large vertebrate species [68] as would be expected based on human fragrance use.

Galaxolide is typically detected at greater concentrations than tonalide in higher-trophic-level species [68]. Almost 40% of sea otter tissue samples off the California coast contained galaxolide (range = <1–32 ng/g) and tonalide (mean = 1.1 ng/g) [68]. Galaxolide and tonalide concentrations in waterfowl collected from New York were comparable across four waterfowl species (common merganser, greater scaup, lesser scaup, mallard) [68]. Both compounds were detected in 100% of waterfowl with galaxolide ranging between 1.9 and 4.2 ng/g and tonalide ranging between 1 and 1.7 ng/g. The highest reported galaxolide concentrations in US mammals were detected in striped dolphin tissue collected off the Florida coast (mean = 14 ng/g; $n = 4$). Interestingly, no fragrances were detected in the tissue of Alaskan polar bears ($n = 5$), suggesting organisms inhabiting undeveloped regions of the United States are less exposed to fragrance compounds [68].

Galaxolide and tonalide have also been reported in carp ($n = 84$) tissue collected from Lake Mead (Nevada) at mean concentrations of 3.0 and 2.4 ng/g, respectively [57]. Many other fragrance compounds were also detected in Lake Mead carp tissue, including toxalide (mean = 1.1 ng/g), traseloide (mean = 2.5 ng/g), celestolide (mean = 1.0 ng/g), musk xylene (mean = 0.6 ng/g), and musk ketone

(mean = 2.7 ng/g) [57]. In contrast, fragrance body composition in Hudson River fishes was highly variable, dependent on both fish species and sample location [53]. For example, channel catfish collected near Troy (New York) had a mean body galaxolide concentration of 21.3 ng/g, while tissue from channel catfish collected near Catskill (New York) had no detectable galaxolide. However, white catfish collected near Catskill had a galaxolide body concentration of 5.79 ng/g [53].

Musk fragrances had up to 100% detection frequencies in oysters collected from the San Francisco Bay estuary [69]. Galaxolide (median = 246 ng/g) and tonalide (median = 157 ng/g) were detected at concentrations higher than any other fragrances in oyster tissue. Celestolide, musk xylene, and musk ketone were also reported in San Francisco Bay oysters at median concentrations between 2.1 and 16.7 ng/g with 60–80% detection frequencies [69]. Zebra mussels from the Hudson River [53] contained less galaxolide (mean = 13.1 ng/g) and tonalide (mean = 55.6 ng/g) than San Francisco Bay oysters. Reducing future fragrance inputs into the environment may be imperative, given the bioaccumulative nature and current abundance of fragrance compounds in biota.

4 Insect Repellants

Of the many PCP compounds found in the environment, insect repellants can be particularly toxic to organisms due to their modes of action. *N*,*N*-Diethyl-*meta*-toluamide (DEET) has been identified specifically as a compound of concern due to both the potential for toxicity as well as its recalcitrance in the environment [70, 71]. Further, DEET concentrations are highly variable. For example, variable water sources across Minnesota ($n = 65$) yielded DEET concentrations ranging from 27 to 47,000 ng/L DEET (24% detection frequency; Table 1) [10]. 1,4-Dichlorobenzene and naphthalene, both commonly used pesticides, have also been identified as having potential for adverse environmental effects though have been less studied in the United States.

4.1 Surface and Groundwaters

In a national reconnaissance of streams and rivers, DEET was measured in 74.1% of streams with a maximum concentration 1,100 ng/L [6]. In contrast, a national reconnaissance of streams receiving wastewater effluent measured DEET concentrations ~2-fold higher (maximum = 2,100 ng/L) [23] but with similar detection frequency (70%).

Regional studies have measured DEET concentrations in surface waters ranging across several orders of magnitude. For example, in central Indiana streams, DEET ranges from 8 to 290 ng/L (64–70% detection frequency) [4, 5]. In contrast, Georgia

streams had lower detection frequency of DEET (24%) across streams sampled ($n = 26$) as well as lower concentrations (maximum = 120 ng/L) [7]. Iowa and South Dakota surface waters had even lower detection of DEET (3.7% samples; $n = 76$) but comparable concentrations (Iowa maximum = 130 ng/L, South Dakota maximum = 80 ng/L) [11] relative to samples measured in Georgia streams. In Colorado stream and groundwater, maximum DEET concentrations measured in urban streams (maximum = ~500 ng/L) were an order of magnitude higher relative to forested streams (maximum = ~90 ng/L) [72].

Using passive samples to develop semiquantitative estimates in surface water and wastewater effluent in Nebraska, DEET concentrations ranged from 7.3 to 1,616.5 ng/L across eight sites [73]. However, wastewater effluent discharges in Iowa and Colorado metropolitan areas had DEET concentrations <100 ng/L, though this was higher relative to the other >200 organic compounds measured [74]. In Puget Sound (Washington), a west-coast estuarine community without effluent point sources of pharmaceuticals but having ~10,000 septic systems, *N*, *N*-diethyl-*meta*-toluamide (mean = 2.7 ng/L) was detected in multiple samples [75].

In the Mississippi River basin, DEET was found at trace concentrations across 26 main stem and tributary sites (range = 5–201 ng/L, 84.6% detection frequency) [76]. In contrast, in the lower Clackamas River basin (Oregon) in the western United States, pesticides were measured in 30 sites from 2000 to 2005 with only 7% detection frequency and a higher maximum concentration of 790 ng/L [77]. In Massachusetts, DEET was measured in only 5% of groundwater samples with a maximum concentration of 6 ng/L [18], lower than measurements in surface water.

In groundwater, DEET was measured at concentrations an order of magnitude higher (maximum = 13,500 ng/L) but with lower detection frequency (34.8%) relative to national reconnaissance efforts in surface water (Table 1) [6, 23]. Similarly, in nationwide reconnaissance studies, 1,4-dichlorobenzene has been detected in 25.9% of US surface waters (maximum = 90 ng/L) [6] and 6.4% groundwaters (maximum = 1,170 ng/L) [16]. In the same studies, naphthalene was detected in 16.5% of surface waters (maximum = 80 ng/L) [6] and 8.5% of groundwaters (maximum = 1,510 ng/L) [16]. Few studies have quantified 1,4-dichlorobenzene and naphthalene in regional assessments of US surface and groundwaters. Further, studies quantifying insect repellants in sediments and biota in the United States are limited. However, in West Virginia, naphthalene was detected in smallmouth bass blood-plasma samples (maximum = 50.9 ng/g).

5 Organic Sunscreen Agents

The United States Food and Drug Administration (US FDA) approves the use of 17 different ultraviolet filters as active ingredients in over-the-counter sunscreen products. Commonly used organic ultraviolet filters include avobenzone, oxybenzone, and octinoxate. Commonly used inorganic ultraviolet blockers,

which are further discussed as novel threats, include zinc oxide and titanium dioxide [78]. No comprehensive surveillance efforts aimed at understanding the environmental abundance and distribution of sunscreen agents have been conducted in the United States. Further concern regarding environmental distribution of sunscreen agents should be raised with concentrations of sunscreen (octinoxate) exceeding 450 ng/L in finished drinking water [14]. Research quantifying environmental sunscreen in the United States has focused on saltwater systems, with no baseline data in US rivers and lakes to aid in predicting and regulating sunscreen agents.

5.1 Marine Environments

Oros et al. [17] quantified octinoxate at five locations throughout the San Francisco Bay ecosystem. Of the 20 contaminants analyzed, octinoxate was detected at a higher concentration than any other analyte, more than doubling the concentration of the second highest detected analyte. With a concentration range of 3–963 ng/L, octinoxate was the only PCP to be detected at every sampling site. The higher concentration of sunscreen in San Francisco Bay, relative to more widely studied contaminants, including galaxolide, tonalide, and atrazine, highlights the need for further sunscreen surveillance efforts in US ecosystems.

Bratkovics and Wirth [79] analyzed organic sunscreen compounds off the coasts of the US Virgin Islands, Florida Keys, and South Carolina. Mean oxybenzone and avobenzone surface water concentrations in samples collected from a remote water reef system (US Virgin Islands) were 292 and 69 ng/L, respectively. From reef sites in the Florida Keys, oxybenzone (mean = 5 ng/L) was detected in 18% of surface water samples, while the oxybenzone detection frequency near the US Virgin Islands was 100%. In the Florida Keys, surface water concentrations of avobenzone, octinoxate, and octocrylene were 60, 66, and 125 ng/L, respectively [79]. Seawater samples from South Carolina beaches generally contained higher concentrations of sunscreen agents than surface water samples from the Florida Keys or US Virgin Islands. Oxybenzone (range = 10–1,221 ng/L), avobenzone (range = 62–321 ng/L), octocrylene (range = <25–1,409 ng/L), and octinoxate (range = <25–1,409 ng/L) were all sunscreen agents frequently detected in South Carolina seawater. South Carolina and San Francisco Bay seawater contained comparable amounts of octinoxate [17, 79]. Sulisobenzone and dioxybenzone are also commonly used sunscreen agents; however they were not detected in any South Carolina seawater samples. Oxybenzone and octocrylene detection frequencies were both influenced by seasonal changes in South Carolina with detection frequencies highest during summer sampling events, suggesting beach activity (i.e., sun-bathing, swimming) and concurrent sunscreen use increases sunscreen concentrations in waters adjacent to recreational beaches [79].

6 Novel Threats

Though numerous PCP compounds have been described in US freshwaters, many novel contaminants have yet to be assessed. Further, new PCPs are continuously being developed with limited evaluation of environmental fate and potential for adverse effects. Thus, novel threats may alter ecosystem processes, compounding adverse effects of historic and well-documented contaminants. Recently characterized novel PCP contaminants include, but are not limited to, microbeads, nanomaterials, and siloxanes. However, public concern over these compounds persisting in the environment has rapidly grown in the United States over the last decade. For example, in May 2014, Minnesota banned triclosan-containing products in the state with the law to go in effect January 2017. Additionally, in June 2014, Illinois became the first US state to ban microbeads in PCPs, with three other states considering similar legislation.

Microbeads are primarily used in face and body soaps for skin exfoliation. Made of polyethylene or polypropylene, microbeads are expected to float on the surface of natural waterways following discharge through sewage effluent [80]. Microbeads deposited in sewage sludge may be released into the environment following biosolid applications [81]. Eriksen et al. [80] surveyed microplastics, including microbeads, across three Great Lakes (Lake Superior, Lake Huron, Lake Erie). Of all collected microplastics less than 1.0 mm in size ($n = 736{,}749.6$), over 58% were considered to be pellet shaped and originating from PCPs. Mean microplastic abundance (count/km^2) in Lake Superior, Lake Huron, and Lake Erie were 5,390.8, 2,779.4, and 105,502.6, respectively [80]. Mircoplastic abundance in a river system near Chicago (Illinois) was found to be influenced by a local wastewater treatment plant. Specifically, microplastics upstream of effluent were found at ~2 particles/m^3; in contrast, microplastics increased by nearly an order of magnitude downstream of effluent [82]. Future research should assess degradation, organismal ingestion, and microbial colonization of microplastics and microbeads.

Nanotechnology is a rapidly expanding field that produces engineered nanomaterials with dimensions <100 nm for use in industrial and commercial applications [83]. Nanomaterials may present future challenges to freshwater ecosystems [84]. Zinc oxide nanoparticles (antimicrobial, UV blocker), titanium dioxide nanoparticles (UV blocker, pigment), and silver nanoparticles (antimicrobial) are commonly used in PCPs and hypothesized to be discharged into aquatic ecosystems, where their adverse effects remain unknown [85, 86]. Methods for quantifying nanomaterials in situ remain difficult or unavailable to a majority of researchers. Gottschalk et al. [87] modeled zinc oxide nanoparticle concentration in US waters at 1 ng/L with much greater concentrations in sewage effluent (300 ng/L). Modeled global concentration of titanium dioxide nanoparticles in aquatic ecosystems is 700 ng/L, with high emission scenarios resulting in concentrations as high as 16,000 ng/L [87]. Global silver nanoparticle concentrations are modeled to approach 30 ng/L [88]. Further modeling efforts expect silver nanoparticle concentrations to be greater in Europe than North America [87] suggesting environmental concentration

of nanomaterials is dependent on human population density. Trace nanomaterial concentrations in aquatic ecosystems may result in sublethal effects on microbes and organisms. For example, environmentally relevant concentrations of silver nanoparticles interfere with the ability of freshwater snails (*Physa acuta*) to sense predation risk [89].

Siloxane compounds, used in a wide array of commercial applications, consist of altering silicone-oxygen bonds. Siloxanes are used in PCPs, such as lotions, to provide a smooth texture. Commonly used cyclic siloxanes in PCPs are octamethylcyclotetrasiloxane (D_4), decamethylcyclopentasiloxane (D_5), and dodecamethylcyclohexasiloxane (D_6) [90], while octamethyltrisiloxane (L_3), decamethyltetrasiloxane (L_4), and dodecamethylpentasiloxane (L_5) are commonly used linear siloxanes [91]. Despite their widespread use, environmental fate and occurrence of siloxanes are not well understood [92]. Recent research has assessed siloxane abundance in water, air, and biota in China and Scandinavia [93–96]. Similar research focusing on the United States remains limited. Contrary to many emerging PCP contaminants, siloxanes generally have high volatility and are expected to persist in the atmosphere [97]. Genualdi et al. [91] measured air concentration of linear and cyclic siloxanes across five US sites, producing some general distribution and abundance trends. Sites near populated areas had higher siloxane concentrations than a remote site in Borrow (Alaska). Further, cyclic siloxanes were detected at higher concentrations than liner siloxanes across all sites. No linear siloxanes were detected in Alaska, while cyclic siloxane concentrations in air ranged between 0.13 and 0.66 ng/m^3. Hilo (Hawaii) is as geographically remote as Borrow, but more densely populated. Near Hilo, L_3 and L_4 were both detected at a concentration of 0.19 ng/m^3, while L_5 was not detected [91]. Concentrations of cyclic siloxanes at the same site ranged from 4.5 to 32 ng/m^3. Air samples near Point Reyes (California) contained linear siloxanes (range = 0.011–0.046 ng/m^3) and cyclic siloxanes (range = 0.57–6.5 ng/m^3) at concentrations comparative to Hilo, Hawaii. Overall, D5 was generally detected at the highest concentration of any siloxane compound, with the highest concentration (96 ng/m^3) occurring in Groton (Connecticut) [91]. A separate study detected D_5 in air samples near Chicago at concentrations (mean = 210 ng/m^3) [98] much higher than those reported by Genualdi et al. [91]. Given the environmental abundance of siloxanes near urban areas, future regulation of siloxanes may be necessary to maintain air quality and public respiratory health in populated areas.

7 Factors Controlling PCP Abundance

Some of the spatial variation in PCP concentrations among studies has been attributed to site proximity to wastewater (i.e., effluent), though clear relationships between wastewater and PCP abundance have not consistently been identified across studies [4–6, 32, 99]. Thus, wastewater influences PCP concentrations though direct relationships are confounded by other factors including water

treatment methods, population density, and wastewater reuse strategies. For example, in arid regions of California, where treated wastewater is regularly used for irrigation, turfgrass has been shown to attenuate PCPs though there is variable susceptibility among compounds [100].

Across the United States, research has highlighted that PCPs do not enter the environment solely from point source wastewater effluent but also from diffuse sources originating from septic systems and industrial activities. Thus, PCPs are consistently above detection limits in rural as well as urbanized areas, and nonpoint sources of PCPs, such as septic systems and industrial activities, are likely as significant as point source wastewater input to PCP abundance in the environment. In Massachusetts, groundwater PCP concentrations were correlated with the extent of unsewered development [18]. In Indiana, agricultural streams had comparable PCP concentrations relative to streams receiving combined sewer overflow (CSO) and wastewater effluent [4, 5, 99]. In a Rhode Island estuary, wastewater treatment plant proximity did not predict spatial distributions of triclosan [34]. Nevertheless, PCP abundance has been correlated with wastewater effluent and urbanization in some regional studies. For example, in the Pacific Northwest, PCP concentrations were highest in industrial harbors and near major cities (Seattle) relative to more remote areas [39]. Consistent with relationships between PCP concentrations and wastewater, concentrations of compounds have also been related to usage rate with more commonly used compounds more frequently detected and measured at higher concentrations.

Studies have consistently demonstrated temporal trends, though predictive ability of peak PCP temporal abundance is still lacking as some studies highlight higher PCP abundance in summer and others have found higher abundance of PCPs in winter. In a Los Angeles (California) metropolitan wastewater facility, some compounds (e.g., triclosan) also had distinct diurnal variability in effluent, while others (e.g., triclocarban) remained consistent over a 24 h cycle [101].

In Lake Mead (Nevada), PCP concentrations were negatively related to water volume [102] suggesting that drought and reduced flow may intensify PCP abundance which has implications for how climate change may influence PCP abundance. Discharge has also been related to PCP abundance in lotic ecosystems in nationwide assessments [6], though regional-scale studies suggest discharge is not a dominant control [4, 99].

8 Lessons Learned and Research Needs

The question is no longer whether PCPs are present in US ecosystems. Rather, the questions that need to be addressed are how we can predict when and where PCPs will be abundant and whether this affects water quality as resource use and ecosystem function. Some studies suggest that PCPs are a minor concern to public health supplies (resource use) but may be a more significant concern to ecosystem function. A recent meta-analysis [22] of triclosan in freshwater from data spanning

Table 2 Regional or local-scale studies on PCP abundance in freshwaters of the United States listed by state. Nationwide reconnaissance studies excluded from counts

State	Studies (#)	References
Alabama		
Alaska		
Arizona		
Arkansas	1	Haggard et al. [105]
California	4	Bondarenko et al. [100]; Fram and Belitz [106]; Oros et al. [17]; Loraine and Pettigrove [14]
Colorado	3	Schultz et al. [107]; Yang and Carson [108]; Sprague and Battaglin [72]
Connecticut		
Delaware		
Florida		
Georgia	1	Frick and Zaugg [7]
Hawaii	1	Knee et al. [109]
Idaho		
Illinois	1	Barber et al. [74]
Indiana	4	Bunch and Bernot [99]; Veach and Bernot [4]; Bernot et al. [5]; Ferguson et al. [32]
Iowa	1	Schultz et al. [107]; Kolpin et al. [11]
Kansas		
Kentucky	1	Loganathan et al. [110]
Louisiana		
Maine		
Maryland		
Massachusetts	3	Schaider et al. [18]; Rudel et al. [111]; Zimmerman et al. [112]
Michigan		
Minnesota	1	Lee et al. [10]
Mississippi		
Missouri	1	Wang et al. [113]
Montana		
Nebraska		
Nevada	1	Vanderford et al. [9]
New Hampshire		
New Jersey		
New Mexico		
New York	2	Reiner and Kannan [53]; Benotti et al. [102]
North Carolina	2	Giorgino et al. [114]; Ye et al. [115]
North Dakota		
Ohio	1	Wu et al. [29]
Oklahoma		

(continued)

Table 2 (continued)

State	Studies (#)	References
Oregon	1	Rounds et al. [116]
Pennsylvania		
Rhode Island	1	Katz et al. [34]
South Carolina	1	Hedgespeth et al. [117]
South Dakota	1	Sando et al. [13]
Tennessee	1	Yu and Chu [24]
Texas		
Utah		
Vermont		
Virginia		
Washington	1	Dougherty et al. [75]
West Virginia		
Wisconsin	1	Blair et al. [8]
Wyoming		

1999–2012 found effluent waters had 83% detection of triclosan across studies (mean = 775 ng/L), though in finished drinking water triclosan was largely undetected (1% detection frequency; mean = 4 ng/L). PCP concentrations measured in the environment are generally below the US cutoff value for Tier II Environmental Risk Assessment (ERA) at 1 μg/L. Thus, drinking water standards do not exist for most organic compounds in the United States to put into the context of human health. However, Gallagher et al. [103] suggested wastewater-impacted drinking water was a risk factor for breast cancer in one region of Cape Cod (Massachusetts).

Studies in the United States have consistently demonstrated that compounds with the highest detection frequency are not necessarily among those with the highest concentrations. Thus, it is critical that compounds are prioritized based on the detection frequency as well as their concentration and toxicity. Some studies have compared across continents to identify compounds of concern and research needs [71, 104]. Kumar and Xagoraraki [104] developed a priority list of 100 pharmaceuticals and PCPs in US stream water and finished drinking water. Notably, priority lists for the two water types were statistically different indicating management of finished drinking water and source waters must be independent. Regional studies, where predictive variables are likely to be identified, have been conducted in 23 out of 50 states (Table 2). However, nationwide reconnaissance efforts have quantified PCPs from at least one sample in 47 states. National or regional studies have predominantly focused on susceptible sites with more research needed in rural areas. Further, research in the United States has focused on a limited number of PCP compounds with additional research needed on both existing (e.g., UV blockers) and emerging (e.g., siloxanes, nanomaterials) PCP compounds.

Acknowledgements We thank Randy Bernot for helpful comments and Allison Veach, Aubrey Bunch, Patrick Ferguson, Amanda Jarvis, Jee Hwan Lee, and the Bernot Laboratory for discussions on PCPs that aided in development of this synthesis.

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Occurrence of Personal Care Products and Transformation Processes in Chlorinated Waters

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Abstract Personal care products (PCPs) have been found in surface water, wastewater, tap water, and swimming pool water. The chlorine used in the disinfection process of water reacts with these compounds generating chlorinated byproducts that may possess enhanced toxicity.

In the case of swimming pool water chlorine also reacts with organic material released by swimmers such as amino acids and other nitrogen compounds yielding chlorinated compounds. Besides this organic material, sunscreen cosmetics used by swimmers are also released into pool water and react with chlorine. UV-Filters 2-ethylhexyl-*p*-dimethylaminobenzoate (EHDPABA), benzophenone-3 (BP-3), benzophenone-4 (BP-4), 2-ethylhexyl-4-methoxycinnamate (EHMC), and 4-*tert*-butyl-4′-methoxy-dibenzoylmethane (BDM) are known to suffer an electrophilic aromatic substitution of one or two atoms of hydrogen per one or two chlorine atoms leading to mono- and di-chlorinated byproducts. It has also been observed the presence of halobenzoquinones (HBQs) in pool water that results from the chlorination of UV-filters such as BDM, octocrylene, and terephthalilidene dicamphor sulfonic acid. The chlorination of some parabens has also been studied. It is known that some of the formed chlorinated byproducts are genotoxic. In this chapter we present a review on the work done so far to determine the stability of PCPs in chlorinated water and to identify the chlorinated byproducts.

Keywords Chlorinated byproducts, Chlorination, Personal care products, UV-filters

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M.S. Díaz-Cruz and D. Barceló (eds.), *Personal Care Products in the Aquatic Environment*, Hdb Env Chem (2015) 36: 123–136, DOI 10.1007/698_2014_263,

Contents

1 Introduction

Personal care products (PCPs) have been found in surface water such as lakes, rivers, and sea, wastewater, and tap water [1–4]. The main reason for this is that during the wastewater treatment, the parental compounds are not totally removed and, in several cases, they also suffer biodegradation and biotransformation [5]. Then, the release of these effluents in the environment leads to the occurrence of PCPs and derivatives in the locations above mentioned. PCPs have been also found in bathing waters and swimming pool water due to their use by swimmers [6] by washing bath effect during bathing and swimming activities [7]. The problem is that, as in drinking water, the chlorine used in the disinfection process reacts with these compounds generating chlorinated byproducts that may possess enhanced toxicity [6, 8, 9]. Also body fluids such as urine and sweat mainly constituted by organic compounds can act as disinfection byproducts (DBPs) precursors [10]. Urea, amino acids, uric acid, gluconic acid, and sodium chloride are the major components of urine and sweat released by swimmers [11, 12]. However, waters disinfection is essential to kill microbial pathogens [13] that are mostly introduced into the water by humans [6].

In this chapter we present a review of reports on the chlorination of PCPs.

2 Reaction with Chlorine

2.1 Chlorination of Organic Matter Present in Body Fluids

In 2007, Li and Blatchley III [14] conducted a study to identify DBPs that result from chlorination of organic-nitrogen compounds present in pool waters due to urine and sweat released from human body. For instance, they verified that urea, creatinine, L-histidine, and L-arginine are trichloramine precursors. A few years later, Kanan and Karanfil [15] observed that some amino acids in urine, such as histidine and aspartic acid, are responsible for high formation rates of haloacetic acids (HAA), and that citric acid present both in urine and sweat is a chloroform precursor, just like albumin. All these information is compiled in Table 1.

Table 1 Disinfectant byproducts (DBPs) and corresponding precursors present in body fluids

DBP	Precursor	Body fluid
Haloacetic acids	Aspartic acid	Urine
	Histidine	Urine
Chloroform	Albumin	Urine, sweat
	Citric acid	Urine, sweat
	Creatinine	Urine, sweat
	Urea	Urine
	Glucuronic acid	Urine
	Hippuric acid	Urine
	Lactic acid	Urine
	Uric acid	Urine
Trichloramine	Creatinine	Urine, sweat
	L-histidine	Sweat
	L-arginine	Sweat
	Urea	Urine, sweat
Dichloromethylamine	Creatinine	Urine, sweat
Dichloroacetonitrile	L-histidine	Sweat

Based on [14, 15]

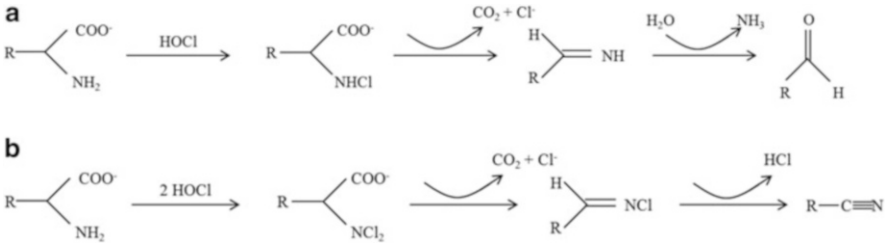

Fig. 1 Amino acid chlorination depending on chlorine dose: (**a**) formation of monochloramines due to the reaction with one HOCl molecule and (**b**) formation of dichloroamines due to the reaction with two HOCl molecules. Adapted from [13, 16]

Concerning amino acids chlorination, it begins with organic mono- or dichloramines formation which depends on chlorine dose and is followed by carbonyl or nitrile compounds production through decarboxylation and deamination (Fig. 1).

The chlorination of body fluids and other compounds is regulated by several factors. The presence of ion bromide (Br^-) influences the levels of halogenated DBPs increasing them, because it is more reactive than chlorine in HAA formation. Although its contribution for DBPs formation is complicated and without a defined pattern, the pH also interferes in this reaction. In some situations, such as nitrile formation, low pH acts favoring the DBPs formation [16] but, in another cases, it does exactly the opposite [13]. Water temperature, total organic content, and number of people in the water [6], dose and residual disinfectant available in the water and contact time between reactants [7] also impact DBPs formation.

2.2 Chlorination of Personal Care Products

On the other hand, pool water also contains PCPs. Inside this category are cosmetic ingredients, food supplements and other products like shampoos, lotions, and sunscreens cosmetics [17]. Sunscreens cosmetics are any cosmetic which contains a UV filter in its formulation to protect human skin from the solar UV radiation since they absorb, reflect and/or scatter UV radiation with a wavelength between 320 and 400 nm for UVA and between 290 and 320 for UVB [7, 18, 19]. There are two types of UV-filters: the organic (or chemical) and the inorganic (or physical) [19]. Inorganic UV-filters category only contains titanium dioxide (TiO_2) and zinc oxide (ZnO), which are known to reflect and scatter UV radiation. Regarding organic UV-filters, there are several classes such as *para*-amino-benzoates, cinnamates, benzophenones, dibenzoylmethanes, camphor derivates, and benz-imidazoles and these compounds absorb the UV radiation [7]. There are many UV-filters allowed for use but their maximum concentration depends on legislation. Although European legislation differs from other countries legislation, like the USA and Japan, the usual concentration of UV-filters in cosmetics is between 0.1 and 10% [19].

Most of the organic UV-filters are relatively lipophilic and their structures contain aromatic rings, conjugated with carbon–carbon double bonds [18] and one benzenic moiety (or more) which has an efficient electronic delocalization due to the conjugation with electron releasing and electron acceptors groups located in either *ortho* or *para* positions. It is this feature that provides a specific maximum absorbance wavelength to the UV-filters [7].

UV-filters are known to react with chlorine leading to halomethanes, such as chloroform, haloacids, halonitriles, haloaldeydes, haloketones, halonitromethanes, haloamines, haloamides, and haloalcohols [17, 20] and also chlorinated UV-filter structures [18].

2.2.1 UV-Filters Chlorination

Few papers have been published in order to study both the UV-filters stability in chlorinated waters and to identify the resulting DBPs. In Fig. 2 we represent the UV-filters whose chlorination reaction was already studied.

In 2008, Negreira and co-workers [18] performed a study to assess the reactivity of three UV-filters containing hydroxy or amino groups in chlorinated waters: 2-ethylhexyl salicylate (ES), 2-ethylhexyl-*p*-dimethylaminobenzoate (EHDPABA), and benzophenone-3 (BP3). They found that the stability of these UV-filters is related with the pH: EHDPABA is more stable at basic water and for BP3 it happens exactly the opposite. ES showed a high stability independent of pH whereby ES halogenated reactions were considered negligible in real-life situations, since in this case there are several organic species competing for available chlorine. The following order of stability for these UV-filters was observed to be: BP3<EHDPABA<ES. However,

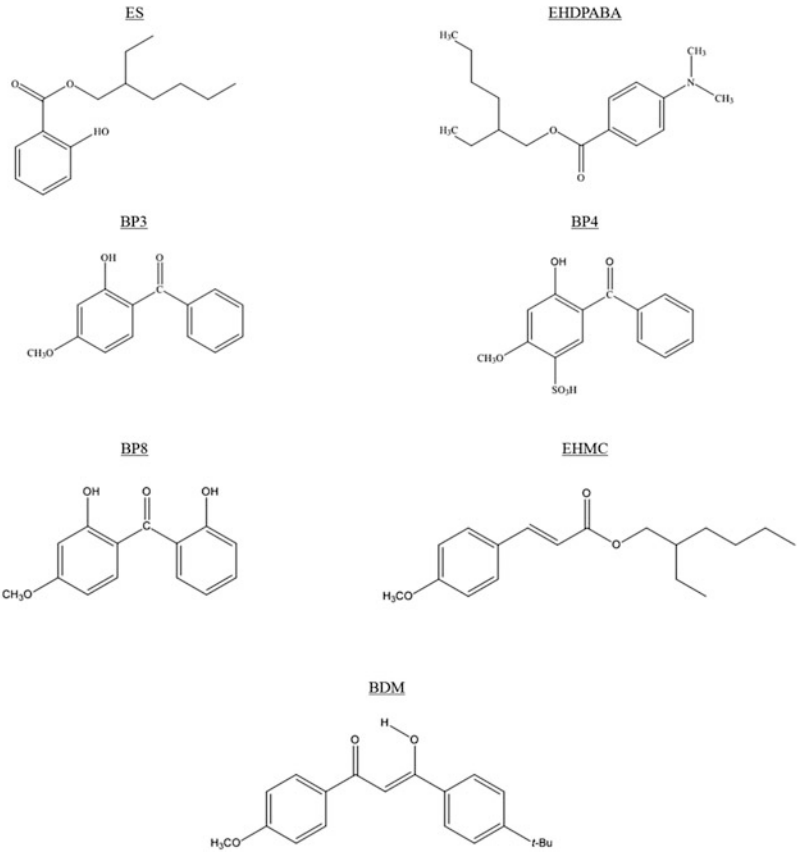

Fig. 2 Chemical structure of 2-ethylhexyl salicylate (ES), 2-ethylhexyl-*p*-dimethylamino-benzoate (EHDPABA), benzophenone-3 (BP3), benzophenone-4 (BP4), benzophenone-8 (BP8), 2-ethylhexyl-4-methoxycinnamate (EHMC) and 4-*tert*-butyl-4′-methoxydibenzoylmethane (BDM)

it was verified that bromide addition, even at low concentrations, reduces the UV-filters stability, especially for EHDPABA. This occurs due to bromide formation which largely reacts with aromatic compounds. Thus, differences among stabilities show the effect of different organic groups on the activation or deactivation of the phenolic ring towards electrophilic substitution reactions [7].

About DBPs, Negreira et al. [18] observed the formation of mono-halogenated species resulting from EHDPABA chlorination and the formation of mono- and di-substituted byproducts from BP3. These DBPs are formed by hydrogen replacement per chlorine in the aromatic rings. Although it is not demonstrated, looking at the parent species structure and considering the activation effects of the hydroxyl and amino groups towards electrophilic substitution reactions, it can be assumed

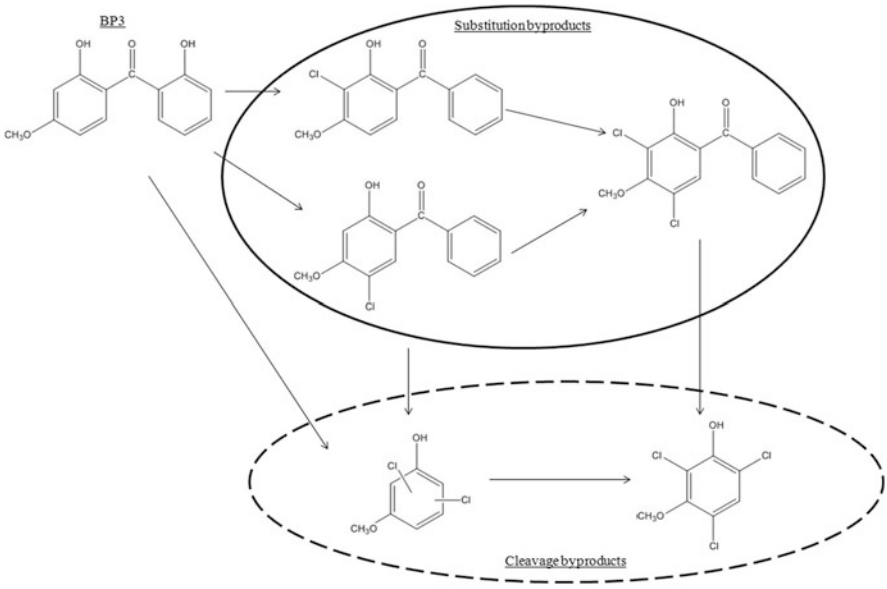

Fig. 3 Degradation pathway for BP3 proposed by Negreira et al. [18]

that these replacements occurred at the carbons in *ortho-* to the amino moiety (EHDPABA) and in *ortho-* and *para-* to the hydroxyl group (BP3).

Summarizing, EHDPABA has a relatively simple degradation pathway and the same pattern was also verified for BP3 which resulted in mono- and dihalogenated byproducts: Cl-BP3 (2 isomers) and Cl_2-BP3 (1 isomer). However, in the case of BP3, another group of byproducts was detected. Negreira et al. [18] identified halogenated forms of 3-methoxyphenol generated from cleavage of the carbonyl bond between the two aromatic rings in the BP3 molecule followed by methoxyphenol fragment halogenation. Moreover, mono- and dihalogenated BP3 substitution byproducts might also break down rendering different halogenated methoxyphenols. Figure 3 represents the reaction pathway for BP3 proposed by Negreira et al. [18]. All the DBPs of EHDPABA and BP3 showed a considerable stability.

The degradation of EHDPABA was previously studied by Sakkas et al. [21] in distilled, sea, and swimming pool water and the authors found one dichlorinated byproduct of the UV-filter and also mono- and dichlorinated degradation products of EHDPABA.

BP3 belongs to the benzophenones class of UV-filters approved by European legislation, which contains only another filter: benzophenone-4 (BP4) (Fig. 2). The stability of BP4 and its chlorination as well as its DBPs were also determined by Negreira et al. [22]. BP4 shows a low stability which decreases even more with pH increasing. As it happens with BP3, bromide addition decreases BP4 stability for the same reason of the first one.

The reaction between BP4 ($C_{14}H_{12}O_6S$) and chlorine yields three DBPs designated as B1 ($C_{14}H_{11}O_6SCl$), B2 ($C_{14}H_{11}O_7SCl$), and B3 ($C_{14}H_{10}O_7SCl_2$) by Negreira et al. [22]. B1 results from an electrophilic substitution of hydrogen per chlorine and this reaction is similar to the BP3 chlorination described above. The difference between B1 and B2 is one atom of oxygen which occurs due to the oxidation of the carbonyl group to an ester moiety (known as the Baeyer–Villiger reaction) with loss of a benzoyl moiety and ester bond established between the carbonyl group and the BP4 phenolic ring. Regarding B3, a dichlorinated byproduct, it is formed when B2 suffers electrophilic substitution of hydrogen per chlorine in carbon number 6 of the phenolic ring. Although the presence of hydroxyl- and methoxyl-functionalities in carbons located in meta-position deactivates this type of reaction, there exists an atom of oxygen in *ortho*- to carbon number 6 due to the Baeyer–Villiger reaction, which increases the probability of a electrophilic attack by chlorine [22].

Re-evaluating the BP3 chlorination with the methodology used in BP4 studies, Negreira [22] observed two other BP3 byproducts which had empirical formula $C_{14}H_{10}Cl_2O_4$ and $C_{14}H_9Cl_3O_4$. The first one is formed when the UV-filter undergoes its most important reaction pathway: two successive electrophilic substitutions of hydrogen per chlorine in carbons located at positions number 3 and 5 in the phenolic ring [18] but only when chlorine level is 0.03 μg/mL and at long reactions [22]. However, this byproduct is also compatible with oxidation of the carbonyl bridge in the molecule of BP3 to an ester group but only after the first reaction. The second byproduct ($C_{14}H_9Cl_3O_4$) appears due to further electrophilic substitution of hydrogen per chlorine in carbon number 6 of the $C_{14}H_{10}Cl_2O_4$ at chlorine concentrations above 2 μg/mL [22].

So, it can be said that the most favorable reaction pathway of both BP3 and BP4 with free chlorine consists of electrophilic substitutions of hydrogen per chlorine in carbon numbers 3 and 5 (*ortho*- and *para*- to the 2-hydroxyl moiety). Only after this reaction or when these carbons are already attached to other functionalities, the carbonyl group is converted into an ester moiety which links the two aromatic rings of these UV-filters. Finally, the aromatic ring bonded to the atom of oxygen in the ester group might undergo a further electrophilic substitution reaction [22]. Figure 4 represents the reaction pathway of this BP4 with free chlorine proposed by Negreira et al. [22].

Chloroform was also found as stable byproduct in the chlorination of BP3 and another benzophenone: benzophenone-8 (BP8) (Fig. 2) [20]. Chloroform formation is a function of pH and occurs in the presence of excess chlorine. However, BP3 and BP8 exhibited different chloroform formation behavior depending on pH: for the first one, chloroform formation decreases when pH increases from 6 to 10. This behavior is generally not only due to the speciation of aqueous chlorine (HOCl to Cl^-) but also due to the speciation of BP3 to the phenolate form, since chloroform/phenol molar yields have pH 8 as average for phenols and substituted phenols. Therefore, there is less HOCl to react with BP3. Concerning BP8, chloroform formation increases as pH increases from 6 to 10, probably due to 3-methoxy and the *ortho*- substituted phenolic moieties in BP8 molecular structure being less

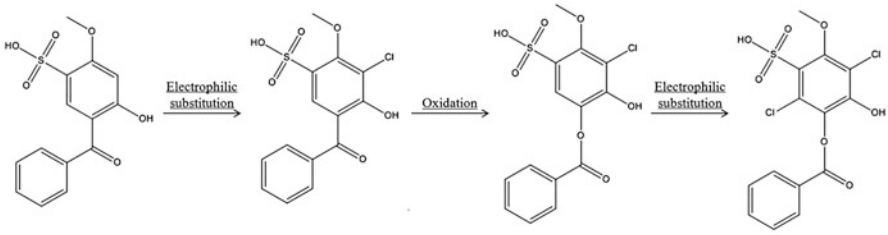

Fig. 4 Chlorination reaction for BP4 proposed by Negreira et al. [22]

reactive with aqueous chlorine than BP3. Despite all of this, 3-methoxyphenol moiety appears to be the primary function group responsible for chloroform formation for both UV-filters [20].

There are two other UV-filters which are typically together in many commercial sunscreens: 2-ethylhexyl-4-methoxycinnamate (EHMC) and 4-*tert*-butyl-4′-methoxydibenzoylmethane (BDM). The first one has absorption capacity in the UVB range and the second one in UVA. Therefore, these two UV-filters combined offer UV protection over a wider range of wavelengths. Although EHMC and BDM are present in sunscreens as the isomer *E* for the first one and as enol form for the second one, under irradiation EHMC suffers isomerization from *E* to *Z* form (Fig. 5a) and BDM tautomerizes from enol to keto form (Fig. 5b) [7].

Santos et al. [23] observed six byproducts resulted from EHMC chlorination: two of them are dichlorinated products ($C_{18}H_{24}O_3Cl_2$) and the rest of them are monochlorinated byproducts ($C_{18}H_{25}O_3Cl$). Both types of byproducts are probably the result of hydrogen replacement by chlorine in the benzene ring of EHMC in the same way already described above. Regarding BDM byproducts it was observed one monochlorinated byproduct ($C_{20}H_{21}O_3Cl$) and one dichlorinated ($C_{20}H_{20}O_3Cl_2$). However, a similar reaction pattern is observed for these two UV-filters because the substitution of hydrogen atoms by chlorine can only occur in the benzene ring containing methoxy group, since chlorination in the benzene ring containing the *t*-Bu group is highly prohibitive due to the large volume of this group.

The reaction between chlorine and each of these UV-filters is regulated by some factors, such as pH, chlorine concentration, temperature, dissolved organic matter (DOM), and irradiation time. The principal factor affecting the EHMC chemical transformation is pH since the lower is the pH, the higher is the transformation percentages of EHMC. The explanation for this fact is that the main chlorine species present at low pH is HOCl (in contrast with at higher pH, where the hypochlorite anion (OCl^-) is prevalent) which is more reactive towards EHMC, resulting in higher degradation. Nevertheless, higher temperature values also lead to higher transformation percentages and this is almost independent of the pH. Concerning BDM, chlorine concentration is the principal factor affecting its transformation percentage, since higher concentrations of chlorine will favor chlorine attack and the incorporation of chlorine in the UV filter structure even at high

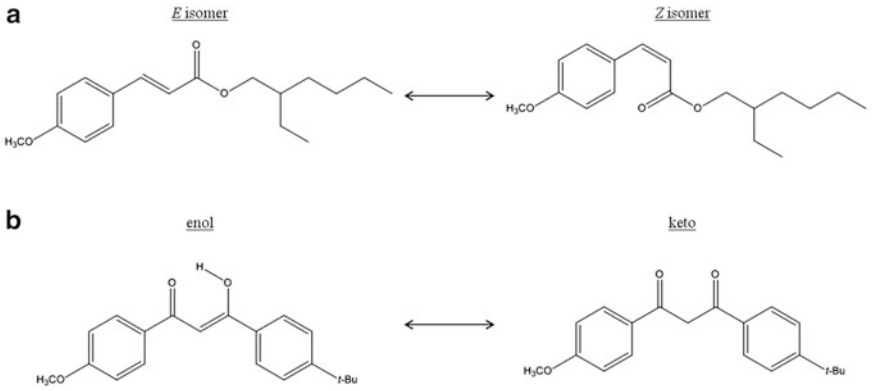

Fig. 5 (**a**) Photoisomerization of the UV-filter 2-ethylhexyl-4-methoxycinnamate (EHMC); (**b**) tautomerism of the UV-filter 4-*tert*-butyl-4′-methoxydibenzoylmethane (BDM)

pH values. However, in presence of DOM, transformation percentages of BDM are low probably due a competition process between the UV-filter and DOM for the available chlorine [23].

Halobenzoquinones Formation

It was also observed the presence of halobenzoquinones (HBQs) in pool water that resulted from sunscreens chlorination. Aromatic structures in these PCPs such as phenols and quinones are likely to be the precursors of HBQs as well as some common ingredients of lotions, like benzyl alcohol, lecithin, parabens, and fragrances. UV-filters such as avobenzone, octocrylene (2-ethylhexyl-2-cyano-3,3-diphenyl-2-propenoate, OCT), and terephthalilidene dicamphor sulfonic acid may also be HBQ precursors [24]. Wang et al. [24] observed the formation of 2,6-dichloro-1,4-benzoquinone from the reaction between chlorine and four sunscreens containing organic and inorganic UV-filters. Although warm water provides a comfortable environment for swimmers, this fact may accelerate the chlorination reaction to produce more HBQs [24].

Besides 2,6-dichloro-1,4-benzoquinone, 2,6-dichloro-3-methyl-1,4-benzoquinone, 2,3,6-trichloro-1,4-benzoquinone, and 2,6-di-bromo-1,4-benzoquinone also are common DBPs in chlorinated water [25].

2.2.2 Parabens Chlorination

Besides sunscreens, other PCPs such as parabens may also be present in pool water. Parabens belong to a group of bactericides and preservative agents in PCPs and they are continuously released in aquatic media through domestic wastewater and, although they are almost completely removed during sewage water treatments,

they have been detected in rivers at low ng L^{-1} level. Considering the extensive employment of the compounds in PCPs, activities like showering and bathing constitute a source of dermal exposition to parabens DBPs [26]. The potential degradation of four alkylated parabens (methyl, ethyl, propyl, and butyl paraben) and the formation of DBPs were investigated by Canosa et al. [26]. Five transformation species were detected for each parent paraben corresponding to mono- and dichlorinated compound. Similar to some UV-filters, they are formed by a substitution of one or two atoms of hydrogen per chlorine in the aromatic ring and this chlorination occurs in both carbons in *ortho*- to the phenolic group, since the *para*-position is blocked with the ester moiety. In tap water, the chlorine content is usually enough to produce significant amounts of these DBPs in few minutes. However, the dichlorinated byproducts are rather resistant to undergo further chlorine substitution reactions or cleavage of the aromatic ring, even in presence of relatively high concentrations of chlorine. So, if they are generated in real-life situation, their presence in the aquatic environment is feasible [26].

3 Toxic Effects of UV-Filters and Its Chlorination Byproducts

It is known that byproducts formed from reaction between chlorine and natural organic matter of water, such as chloroform as well other trihalomethanes, nitrosamines, haloacetic acids, etc., have toxic effects like carcinogenic effects in animals and human beings [27]. Now, it is mandatory to assess the toxicity of DBPs formed from PCPs chlorination. The knowledge of this subject is still poor but there are already a few papers published in order to study the toxicity of some of these compounds.

Bladder cancer has been associated with exposure to chlorination byproducts in drinking water, and experimental evidence suggests that exposure also occurs through inhalation and dermal absorption during swimming in pools because certain DBPs have high volatility and dermal permeability. Villanueva et al. [28] observed that subjects who had ever swum in a pool showed an increased risk of bladder cancer compared with those who had never swum in pools and former and current smokers present an excess risk of bladder cancer. This study also revealed a duration-response relation for cumulative time spent in swimming pools. To evaluate the genotoxicity of swimming pool water in swimmers, Kogevinas and co-workers [29] examined some biomarkers of genotoxicity in an experimental study in which adults swam for 40 min in a chlorinated, indoor swimming pool, comparing the biomarker results with the concentrations of four THMs (bromoform, bromodichloromethane, chloroform, and chlorodibromomethane) in exhaled breath. It was observed increases in two biomarkers of genotoxicity (micronuclei in peripheral blood lymphocytes and urinary mutagenicity). Although only brominated THMs showed genotoxicity, all four are carcinogenic in rodents.

It was also verified that recreational pool waters are more genotoxic [30] and cytotoxic than tap water and this elevated genotoxicity and cytotoxicity are associated with many classes of nitrogenous-DBPs (N-DBPs) [10]. The higher genotoxicity of the recreational pools compared to the tap water source could reflect prolonged disinfectant contact times [30].

Furniture conditions, such as illuminations condition, also affect the cytotoxicity of pool water [10, 30]: The pool water under indoor conditions was more cytotoxic ($LC_{50} = 24.2\times$) than when it was operated as an outdoor pool ($LC_{50} = 181.4\times$). The outdoor pool exposed to sunlight featured lower cytotoxicity than the same pool under indoor conditions which indicate that either the compounds responsible for the cytotoxicity, or their precursors, may be photolabile [10] or have increased volatilization [30]. Physical activity appears to enhance the absorption of DBPs [31].

UV-filters have high lipophilicity (mostly with $\log K_{ow}$ 4–8) whereby they have been shown to accumulate in the food chain and in human milk fat. However, at present, there is a scarcity of data on environmental concentrations of UV-filters [32, 33]. Moreover, concentrations reported fluctuate significantly as a function of sample location, size of the system under study (e.g., lakes and swimming pools), frequency and type of recreational activities, season of the year, and hour of the day. Still, maximum concentrations reported have corresponded to mid-day on warm summer days, as expected [33]. Among UV-filters, octocrylene is of great concern since it has a high lipophilicity (K_{ow} 6.88). Actually, this UV-filter has already detected in liver tissues of dolphins (*Pontoporia blainvillei*) with concentrations in the range 89–782 ng/g lw and there is evidence that maternal transfer may occur trough placenta and likely also through breast milk [34].

4 Conclusions and Further Researches

Disinfection of drinking water is important for public health but many people are exposed to chlorination byproducts not only through ingestion but also through other activities such as showering, bathing, and swimming [35]. So, future studies should evaluate more completely the uptake and potential effects of a range of DBPs present in pool water [29]. Although the mixture of the byproducts may differ by geographic area and time, studies are needed to examine the potential effects of these mixtures [35]. Furthermore, it is important to examine the various exposure pathways and routes other than ingestion in more detail.

Reports on the occurrence of sunscreen agents in natural waters have so far been scarce and have mainly focused on bathing waters in closed systems (e.g., swimming pools or small lakes). A great deal of additional data is needed to understand the significance of UV-filters in the aquatic environment. It is also necessary to increase knowledge of their bioaccumulation in humans and wildlife [33]. It is also important that further researches take into account pool operation/maintenance. Pool disinfection is essential to preventing exposure to pathogens; still, DBP

formation can be reduced with proper disinfectant use along with known engineering solutions. Unhygienic practices enhance the amount of organic matter released by swimmers through urine and other body fluids. So, substantial investments into education and outreach will be necessary to affect these behaviors and practices. By improving disinfection practices and reducing the input of contaminants both chemical and biological, the goal of healthier pools and healthier people can be achieved [6]. For example, showering and using toilet facilities, washing off sunscreen lotions, and applying water-tight diapers can reduce the bather load and help to reduce the potential for DBP formation [36]. If swimmers take showers frequently, DBPs will be removed on skin preventing them from deeper penetration [37].

Environmental chemistry studies should also focus on strategies to minimize the formation of chlorinated byproducts of UV-filters by the development of new sunscreen formulations that prevent the release of UV-filters into chlorinated water [23].

Haloquinones have been proving to be more toxic than the regulated halomethanes [25]. The potential toxic effects of these compounds warrant further investigations into the occurrence, human exposure, and management of haloquinones in chlorinated water [25].

Regarding other cosmetics ingredients further studies are needed to evaluate potential human health risks and ecotoxicological effects of halogenated byproducts and to know their fate in the environment [26, 27].

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Part II
Toxicological Effects and Risk Assessment

Environmental Risk Assessment of Personal Care Products

Babu Rajendran Ramaswamy

Abstract Extensive usage and continuous release of personal care products (PCPs) lead to ubiquitous contamination of aquatic environment. As PCPs are mainly intended for external use on the human body, they are not subjected to metabolic alterations; therefore, large quantities enter the environment as such. Being biologically active and persistent, they are expected to pose a wide range of risks to aquatic habitat. Although studies on environmental concentration and toxicity endpoints are available for many PCPs, environmental risk assessment (ERA) was scantily reported. It was observed that most of the ERAs were based on hazard/risk quotient approach and not following three-tier approach due to lack of sufficient toxicological data (i.e., long-term toxicity at environmentally relevant (ppt–ppb) concentrations). From the ERA reports, it was understood that disinfectants, triclosan and triclocarban, cause high risk to aquatic organisms. In case of preservatives (parabens), the risk was low. Some fragrances (synthetic musks) and UV filters were also shown to be toxic in the aquatic habitat; however, majority of them are categorized as less risky. Other than the risk to macro forms, the antibacterial PCPs are likely to affect the community structure of nontarget (nonpathogenic) bacteria and may aid in developing (multidrug) resistance among pathogenic and nonpathogenic species. Therefore, for better risk assessment, environmentally relevant studies on nontarget organisms are to be given due importance, and it may include interactions of chemical mixture, degradation products, and bioavailability criterion as well.

Keywords Antimicrobials, Bacterial resistance, Environmental risk assessment, Hazard quotient, Personal care products

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M.S. Díaz-Cruz and D. Barceló (eds.), *Personal Care Products in the Aquatic Environment*, Hdb Env Chem (2015) 36: 139–164, DOI 10.1007/698_2014_297,

Contents

1 Introduction

Chemical pollution by pesticides, biocides, pharmaceuticals and personal care products, industrial chemicals, etc., poses a greater (cumulative) threat to environment. Personal care products are a varied group of compounds comprising preservatives (e.g., parabens), disinfectants (e.g., triclosan), fragrances (e.g., musks), UV filters/stabilizers (e.g., methylbenzylidene camphor, benzotriazoles), and insect repellants (e.g., DEET). Millions of consumers use cosmetic/personal care products and their ingredients on a daily basis to improve the quality of life. The unavoidable growth in the use of cosmetics/PCPs burdens the environment with their residues. The global production of personal care products is expected to reach 333 billion dollars by 2015 [1].

Although PCPs provide various benefits to the quality of life of the consumer, viz., soap, shower gels, toothpaste are to maintain hygiene and dental care, deodorants prevent body odor, and sunscreens protect human skin against adverse effects of UV light, they are generally excreted and emitted through the sewerage/wastewater system after use and ultimately released into nearby terrestrial or aquatic systems (Fig. 1).

Chemicals used in personal care products are biologically active compounds that are designed to interact with specific pathways and processes in humans and animals. A number of personal care products have been identified in environmental matrices and drinking waters [3–7], and their concentrations in environmental matrices are mostly in the range of ng–μg level. Many PCPs are environmentally persistent and bioactive and have the bioaccumulation potential. Thus, humans and terrestrial/aquatic ecosystems are greatly exposed to unknown cocktail of chemicals of parent as well as transformed products. Environmental (chemical) risk assessments of transformed products are rather complex than parent

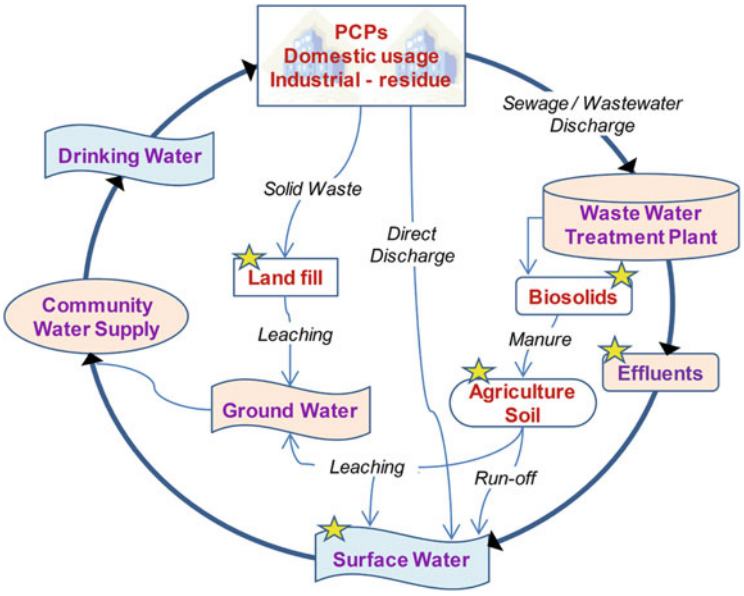

Fig. 1 Life cycle of PCPs in the environment with *star (mark)* showing the risk assessment (Adapted with modification from [2])

compounds due to scarce or nonavailability of toxicity data. The safety of a chemical in use is obviously based on a hypothetical zero-risk situation; however, that does not exist/or possible in a real-world situation. This peculiar, albeit unrealistic, aspect poses a major challenge for the risk assessment of chemicals and their ingredients/metabolites.

There have been a number of publications since the past few decades reporting on toxicity, fate, and transport of endocrine disrupting chemicals; nevertheless, information on residue levels and environmental risk assessment (ERA) of PCPs is scarce or nil until the end of the last century, and researchers started showing interest on analytical methods, bioaccumulation, and risk evaluation of PCPs only in the recent past.

Apart from the health risk to macroorganisms, the impact of PCPs on microbial community is still a question with few key outcomes. As we are aware, the prevalence of antibiotic-resistant bacteria in hospital, industrial [8], as well as domestic wastewater [9] environment is not uncommon; nevertheless, increasing use of antimicrobial compounds leads to similar problem of resistance in bacteria from sewage and surface water, drinking water, etc. [10–12]. Bacterial resistance for PCPs such as parabens in aquatic system is a growing environmental problem [11]. Moreover, a number of pollutants (i.e., pesticides, pharmaceuticals, illicit drugs, etc.) are continuously released into the environment, and their long-term effects on the receiving ecosystems are relatively unknown. Furthermore, interactions (synergistic/antagonistic) among the co-occurring compounds can also take

place, complicating environmental assessment [13]. Considering the importance of PCPs' emerging threat, this paper summarizes their risk assessment in the environment.

2 Pathways of Exposure and Uptake

The entry of PCPs into the aquatic environment includes direct disposal of domestic sewage and wastewater from hospitals and manufacturing industries, also they enter through wastewater treatment plant (WWTPs) effluents, leakage from septic tanks or leaching of landfill sites, and surface water runoff. The effluent and sludge from WWTPs and biosolids as manure shall be the prime source of PCPs in agriculture soil. The exposure of PCPs by organisms in the environment varies depending on the usage and resulting residual concentration/dilution in receiving waters, WWTP efficacy, and other possible exposure pathways.

The uptake of PCPs in aquatic ecosystem is mainly via contaminated water and secondarily by sediment. Some of the PCPs (e.g., triclosan) are ionizable substances, and the uptake of such ionizable substances depends on environmental conditions such as pH and soil/sediment characteristics. Mostly, the studies consider the bioavailability and uptake based on the properties such as octanol–water partition coefficient, bioconcentration/biomagnification factor, etc. [14]. However, no clear data on PCP uptake through food chain exists, so much research needs to be imparted to understand the real scale of PCPs bioavailability ([5, 14, 15] and references therein).

3 Methods of Risk Assessment

According to European commission [16], ERA is defined as an attempt to address the concern for the potential impact of individual substances on the environment by examining both exposures resulting from discharges and/or releases of chemicals and the effects of such emissions on the structure and function of the ecosystem.

Risk assessment identifies potential hazardous consequences of anthropogenic chemicals and determines the probability to occur in a specific environment (i.e., exposure assessment) and their severity (i.e., toxicity) [16]. Methods for assessing the ecological risks of anthropogenic pollutants are ample, and the most followed is the hazard quotient (HQ) approach [6, 16–18]. The quantitative approach to ERA includes three main components, viz., exposure assessment (predicted environmental concentration in different compartments such as water, soil/sediment, etc.), effect assessment (predicted no-effect concentration from dose–response relationship), and the risk characterization (calculating HQ). The hazard quotient or risk quotient (RQ) is calculated as the ratio between the predicted environmental concentration (PEC) or measured environmental concentration (MEC) and the

predicted no-effect concentration (PNEC) in organisms [17]. The HQ/RQ values <0.1, 0.1–1, and >1 indicate low, medium, and high risks, respectively, of the individual compound [4].

The PEC for PCPs can be calculated based on multiple factors like type of substance, sales, population density, and usage statistics, and it may vary for each country and/or region. Nowadays, developed countries like the USA started using computational models (e.g., E-FAST) to predict the flux of PCPs in waterways [19]; nevertheless, it is quite difficult to calculate for developing countries where substantial statistics on production, sale, exact population, effluent load, etc., are hard to collect. In such condition, the relative MEC of specific compound is used instead of PEC. For calculating PNEC, most of the studies rely on either short-term acute toxicity (e.g., LC50, EC50, etc.) or long-term (sub-)chronic toxicity outcomes (e.g., no observed effective concentration (NOEC), lowest observed effective concentration (LOEC), etc.). Often, NOEC is calculated for individual organisms based on their toxicity endpoints; however, single NOEC representing multiple organisms (based on acute/chronic toxicity results) can be calculated by software such as ecological structure activity relationships (ECOSAR) of United States Environmental Protection Agency (USEPA). Indeed, for proper assessment, cumulative effect (chronic toxicity: growth rate, fecundity, abnormalities, etc.) is always preferred over one-time acute toxicity assay, because chronic data provides much better idea for the "true" risk of chemicals or chemical group and significantly lowers the use of uncertainty in risk assessment [20].

In risk calculation, an uncertainty/safety assessment factor (e.g., 10, 100, 1,000, etc.) is applied to acute or chronic toxicity endpoints to arrive at the PNEC. This application of uncertainty factor is based on the nature/form of toxicological data for different classes of organisms in each level of hierarchy/food chain. Usually, a safety factor of 1,000 is applied for acute toxicity endpoints, whereas safety factor of 10 is applied for chronic toxicity [17]. In general, among PNECs the lowest value for a specific taxonomic group was used to estimate the maximum risk posed by the chemical of concern [20].

The conventional PNEC calculated for a compound or stressor may not represent wider species assemblage or population (natural community). Therefore, to determine PNEC which is protective for most species/population/community, species sensitivity distribution (SSD) approach is followed, which represents the cumulative probability distributions of toxicity values from multiple species. Therefore, SSD is used in many instances [15, 21, 22], rather than conventional (single species) approach ([23] and references therein).

Jjemba [24] proposed an ecotoxicity potential (EP) to assess the extent of the risk of pharmaceutical and personal care products (PPCPs) based on fate (i.e., degradability), exposure factor (i.e., bioavailability), and effect factor (i.e., susceptibility) of the substance of concern.

$$\mathrm{EP} = T/V(\mathrm{NOEC})$$

where T and V are the overall residence time and concentration of a substance in the environment, respectively. It is obvious that the lower the degradability (or the

higher the persistence) and/or the higher the bioavailability of a chemical to nontarget organisms, the higher the magnitude of ecotoxicity potential.

Conventional HQ predicts risk based on MEC or PEC obtained from limited area and may not necessarily reflect a risk for larger ecosystem (e.g., entire river stretch). To fill the gap, environmental exposure models are developed to more precisely determine (weigh) the nominal exposure, for large area, over a period of time. Apart from PEC and MEC, exposure assessment models use variables such as the pathways of contaminant, form of the chemical(s) released, and its fate in different environmental compartments. Models like P*h*ATE™ (Pharmaceutical Assessment and Transport Evaluation) and GREAT-ER (Geo-referenced Regional Exposure Assessment Tool for European Rivers) can be adopted for exposure assessments [25].

Apart from toxicity studies, computational approaches are gaining importance to replace/append the present risk prediction techniques (e.g., HQ), and one such approach is QSAR (quantitative structure activity relationship). Garcia et al. [26] performed the QSAR study using EPI Suite™ interface, to understand the possible adverse effects of 96 PPCPs and metabolites with negligible experimental data and established a ranking of concern based on persistence (P), bioaccumulation (B), and toxicity (T) (extensive) of those PPCPs in Spanish aquatic environments. Their findings revealed that higher number of metabolites has got ranking equal to or greater than their parent compounds. Further, P, B, and T indexes are recommended recently by the Registration, Evaluation, Authorization and Restriction of Chemicals (REACH) regulation to estimate the potential negative impact of chemicals on the environment [26].

Regarding PCPs, most of the studies either report the environmental concentration or its toxicological profile; however, only few studies were performed for risk assessment. In the present review, literature-based risk assessments of PCPs pertaining to HQ were primarily collected and grouped in Tables 1 and 2. The worst-case scenario reported for organisms in each of the study was taken for discussion. Further, the main purpose of the review was to collectively present the available ERAs of PCPs.

4 Classification and Risk of PCPs

Regarding classification, each country adopts their own way of classification, e.g., sunscreens are cosmetics in the EU, whereas in the USA they are OTC drugs. Hair dyes are cosmetics in the EU but quasi-drugs in Japan, and their safety would be subjected to drug regulations necessitating drug-like safety dossiers [38]. Moreover, the PCPs can be grouped into categories based on their application (Fig. 2) such as antimicrobials (disinfecting agents and preservatives), insect repellants, fragrances (musks), UV filters/stabilizers, and siloxanes.

Table 1 Aquatic risk assessment of disinfectants and preservatives based on PNEC and MEC

Compound	Matrix	Country	Organism	Toxicity endpoint	PNEC (μg/L)	MEC/PEC (μg/L)	Maximum HQ/RQ/RCR	Risk	Reference
Disinfectants									
Triclosan	River water	Eight countries	*Pseudokirchneriella subcapitata*	NOEC[a]	0.053	1.023	>10	High	Tamura et al. [27]
			Danio rerio, *Ceriodaphnia dubia*		2.6–3	1.023	>0.1	Medium	
	River water	India	*D. magna*, *P. promelas*, *Lepomis macrochirus*, *O. mykiss*, *Oryzias latipes*, *D. rerio*	EC50[b]/LC50[b]/NOEC[b]	0.22–3.4	5.16	1.51–23.4	High	Ramaswamy et al. [6]
	River water/sediment	China	Aquatic organism	NOEC[a]	0.05	0.478	9.55–28.47	High	Zhao et al. [28]
	Lake water, WWTP effluent	USA	Aquatic organism	ECOSAR[a]	NA	0.041–0.85	1.2–11.8	High	Blair et al. [7]
	WWTP effluent	Greece	Invertebrates, fishes, algae	NOEC[a]/LC50[b]/EC50	NA	0.452	>0.1 to >100	Medium–high	Kosma et al. [29]
Triclocarban	River water	USA, China	*P. subcapitata*, *C. dubia*, *D. rerio*	NOEC[a]	0.19–2.4	5.6	>1 to >10	High	Tamura et al. [27]
	River water, sediment	China	Aquatic organism	NOEC[a]	0.058	0.338	5.83–24.54	High	Zhao et al. [28]
	Lake water, WWTP effluent	USA	Aquatic organism	ECOSAR[c]	NA	0.015–0.98	0.5 to >10	Medium–high	Blair et al. [7]

(continued)

Table 1 (continued)

Compound	Matrix	Country	Organism	Toxicity endpoint	PNEC (μg/L)	MEC/ PEC (μg/L)	Maximum HQ/RQ/ RCR	Risk	Reference
Resorcinol	River water	China	*P. subcapitata*, *C. dubia*	NOEC[a]	17–6,700	0.0531	>0.001 to >0.1	Low–medium	Tamura et al. [27]
p-Thymol	River Water	Japan	*P. subcapitata*, *C. dubia*, *D. rerio*	NOEC[a]	107–250	0.715	>0.01	Low	
Phenoxyethanol	River Water	Japan	*P. subcapitata*, *C. dubia*, *D. rerio*	NOEC[a]	580–13,000	14	>0.01	Low	
Preservatives									
Methyl, Ethyl, Isopropyl, Propyl, isobutyl, Butyl, Benzyl parabens	Surface water/ WWTP	Belgium, Canada, UK	*D. magna*/*P. promelas*	NOEC	NA	NA	0.00023–0.0000078	Unlikely	Dobbins et al. [30]
Methyl, *i*-butyl, benzylbutyl parabens	River Water	Japan	*O. latipes*	NOEC[a]/ LC50[b]/ EC50	NA	0.002–0.676	0.00032–0.0042	Low	Yamamoto et al. [31]
Ethyl, *n*-propyl, *i*-propyl, *n*-butyl parabens			*D. magna*	LC50[b]/ EC50	NA	0.046–0.207	0.017–0.00087	Low	
Methyl, Ethyl, Propyl, Butyl parabens	River water	India	*P. promelas*, *D. magna*	LOEC[a]	20–2,500	0.0432–11.3	0.000008–0.001	Low	Ramaswamy et al. [6]

ERA environmental risk assessment, *RQ* risk quotient, *RCR* risk characterization ratio, *HQ* hazard quotient, *PNEC* predicted no-effect concentration, *MEC* measured environmental concentration, *PEC* predicted environmental concentration

[a]Chronic

[b]Acute

[c]Predicted

Table 2 Aquatic risk assessment of synthetic musks and UV filters based on PNEC and MEC

Compound	Matrix	Country	Organism	Toxicity Endpoint	PNEC (μg/L)	MEC/PEC (μg/L)	Maximum HQ/RQ/RCR	Risk	Reference
Synthetic musks									
Toxalide	River Water	South Korea	Fish	NOEC	43.45	NA	>0.01	Low	Lee et al. [32]
Galaxolide, Musk ketone					0.646–6.8	NA	≥0.1	Medium	
Total musks					NA	NA	≥1	High	
Toxalide	NA	NA	Aquatic organisms	NOEC	3.5	0.3	0.086	Low	Balk and Ford [33]
			Fish-eating predators		10[a]	0.12[a]	0.012	Low	
			Sediment organisms		11[b]	0.48[b]	0.44	Medium	
			Soil organisms		0.32[b]	0.029[b]	0.091	Low	
			Worm-eating predators		10[a]	0.065[a]	0.007	No	
Galaxolide	NA	NA	Aquatic organisms	NOEC	6.8	0.5	0.074	Low	Balk and Ford [33]
			Fish-eating predators		100[a]	0.12[a]	0.001	No	
			Sediment organisms		25[b]	0.16[b]	0.064	Low	
			Soil organisms		0.32[b]	0.032[b]	0.1	Medium	
			Worm-eating predators		100[a]	0.099[a]	0.001	No	

(continued)

Table 2 (continued)

Compound	Matrix	Country	Organism	Toxicity Endpoint	PNEC (μg/L)	MEC/PEC (μg/L)	Maximum HQ/RQ/RCR	Risk	Reference
UV filters									
BP1	Surface water	Hong Kong	*P. promelas*	Vitellogenin induction[c]	4,919/2,668	15.5	>0.01	Low	Tsui et al. [34]
BP3			*O. latipes*	Egg production[c]	16	54.1	≥1	High	
			D. rerio	Transcriptional activity[c]	84	54.1	≥0.1	Medium	
			D. magna	EC50[c]/LC50	1,670/1,900	54.1	>0.01	Low	
			D. subspicatus	IC10[c]	560	54.1	≥0.1	Medium	
			Acropora sp.	Bleaching rate[c]	2,376	54.1	>0.01	Low	
BP4			*D. rerio*, *D. magna*	Transcriptional activity[c] LC50[c]	3,000–0,000	49.7	>0.01	Low	
EHMC			*O. latipes*, *P. promelas*, *D. rerio*	Transcriptional activity[c]	2.2–9,873	50.5	>0.01 to ≥1	Low–high	
			D. magna, *Desmodesmus subspicatus*	EC50[c]/LC50/IC10[c]	570/290/240	50.5	≥0.1	Medium	
			Acropora sp.	Bleaching rate[c]	1,999	54.1	>0.01	Low	
4MBC			*O. latipes*	Transcriptional activity[c]	9,922	20.7	>0.01	Low	
			D. magna, *D. subspicatus*	EC50[c]/LC50/IC10[c]	800/560/210	20.7	>0.01 to ≥0.1	Low–medium	
			Acropora sp.	Bleaching rate[c]	1,053	20.7	>0.01	Low	

BP1	NA	NA	*O. mykiss*	LOEC[c]	49.2	0.125	0.003	No	Fent et al. [35]
BP2			*O. mykiss*	LOEC[c]	12	0.125	0.01	Low	
BP3, BP4	NA	NA	*D. magna*	LOEC[c]/EC50[d]	6–50	0.44–0.849	0.02–0.07	Low	Fent et al. [36]
EHMC			*D. magna*, *O. latipes*	EC50[d]/LOEC[c]	0.29–9.9	0.39	0.04–1.35	Low–high	
E-PABA	NA	NA	*O. mykiss*	LOEC[c]	43.9	0.125	0.003	No	Fent et al. [35]
3BC	NA	NA	*D. magna*, *O. mykiss*	LOEC[c]	0.03	0.009–0.082	0.3–2.73	Medium–high	Fent et al. [35, 36]
4MBC	NA	NA	*D. magna*, *O. latipes*	EC50[d]/LOEC[c]	0.56–9.9	0.799	0.08–1.43	Low–high	Fent et al. [36]
EHMC	NA	NA	*Paracentrotus lividus*	EC10[d]	0.488	0.052	0.11	Medium	Paredes et al. [37]
BP3			*Isochrysis galbana*		0.037	0.068	1.86	High	
4MBC			*I. galbana*		0.054	0.084	1.57	High	

ERA environmental risk assessment, *RQ* risk quotient, *RCR* risk characterization ratio, *HQ* hazard quotient, *PNEC* predicted no-effect concentration, *MEC* measured environmental concentration, *PEC* predicted environmental concentration

[a]μg/g fw

[b]μg/g dw

[c]Chronic

[d]Acute

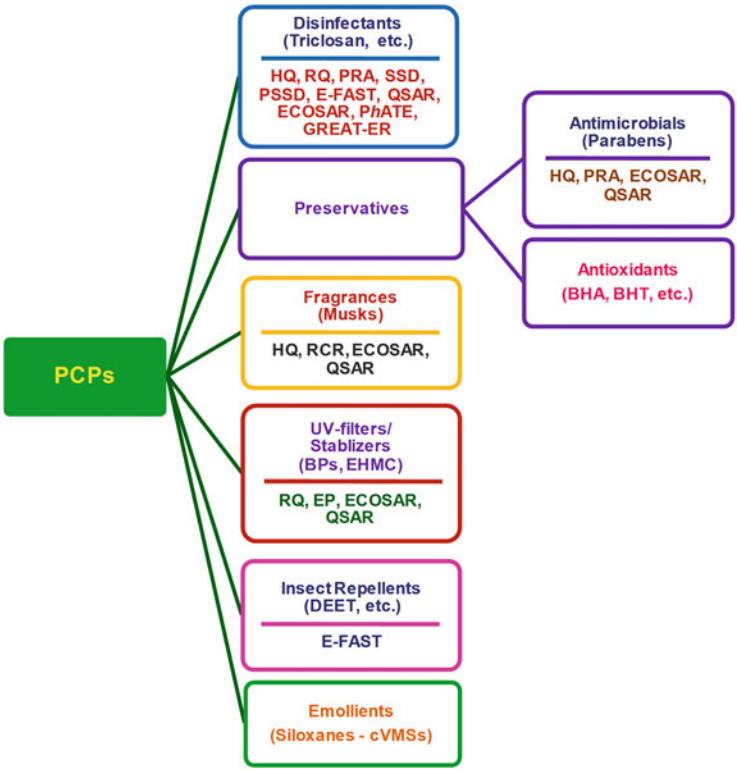

Fig. 2 Major classes of PCPs with examples in *parentheses* and available ERA

4.1 Disinfecting Agents

Disinfecting agents are antimicrobial compounds that are added as ingredients in sanitizers, disinfectants, and sterilants to control, prevent, or destroy harmful microorganisms (i.e., bacteria, viruses, or fungi). Since no single disinfectant is adequate for all situations, multiple disinfecting compounds are added in the formulations of PCPs [39].

Triclosan (TCS) (5-chloro-2-(2,4-dichlorophenoxy)phenol) and triclocarban (TCC) (3,4,4′-trichlorocarbanilide) are broadly used as antimicrobial and antifungal agents in household products of daily use (e.g., soaps, deodorants, skin creams, toothpaste and plastics, antimicrobial sprays, etc.). Due to extensive and inadvertent usage, residues of triclosan are ubiquitously found in surface water and sediment, WWTP influent/effluent, and fish ([6, 40] and references therein). Occasionally, fraction of TCS can occur as negative phenolate ion in environment due to its pKa (~8) and pH of the environment, which is considered to cause lesser toxicity than neutral (parent) form [41]. Further, Price et al. [41] opined that the risks of TCS

calculated based on PEC/PNEC ratio will be an overestimate, so aquatic toxicity evaluation based on speciation is warranted.

Both TCC and TCS, having a log Kow of 4.2–4.76, are highly expected to get adsorbed onto solids and sediments and thus available for bioaccumulation [42–44]. Bioaccumulation studies showed that higher pH in environment can favor TCS bioaccumulation whereas lower pH could favor methyl-TCS to accumulate more [5].

Ecological risk assessment based on acute and (sub-)chronic toxicity tests was mostly available only for five antimicrobial agents in which TCS in river water from various countries (Switzerland, Japan, the USA, Slovenia, Spain, the UK, China, and India) showed high risk based on HQ for algae and most of the fishes and medium risk for crustacean (*C. dubia*) [6, 27]. Zhao et al. [28] reported high risk of TCS in Pearl River (Liuxi, Shijing, and Zhujiang rivers) water and sediment from China with maximum HQ observed as 23.4 and 28.7, respectively. Aside from rivers, Michigan lake and STP effluent in the USA were also found to contain the TCS at high risk level based on ECOSAR PNEC [7]. In addition to surface water samples, Kosma et al. [29] reported that TCS in WWTP effluents discharged into the rivers in Greece (Kalamas, Arachthos, Acheloos, Grevenitis, and Aliakmonas) may pose high risk to algae (HQ >100), fish (HQ >1), and invertebrates (HQ >1) in outfall locations.

Similar to TCS, TCC was also found at alarming level in river water (the USA and China), showing HQ >10 [27]. Zhao et al. [28] also indicated higher risk of TCC in water (HQ = 5.8) and sediment (HQ = 24.54) from the tributaries of Pearl River in China. In Michigan lake water (in the USA), medium risk was reported for TCC; however, effluent entering into the lake showed high risk (HQ >10) [7]. From Table 1, it is prominent that most of the HQs obtained for TCS (15 results out of 18) and TCC (6 results out of 7) were >1, pointing their risk in the aquatic environment is more likely. Among other disinfectants, resorcinol showed low (algae, *P. subcapitata*) and medium risk (*C. dubia*) for river water in Japan, whereas *p*-thymol and phenoxyethanol were found with low risk for daphnia, algae, and fish. This indicates that the risk from *p*-thymol and phenoxyethanol in Japanese rivers is minimal, unlike TCS and TCC [27].

Apart from risk assessment based on individual MEC, Reiss et al. [45] performed probabilistic exposure estimation based on transport and fate of TCS in wastewater effluents in the USA by using a model. The study compared the estimated exposure concentration with PNEC of most sensitive species of algae, plant, fish, and invertebrates and reported that some sensitive algae and plants may be at risk at effluent outfall with meager dilution. Further, the risk at downstream of the river is considered less because of dissipation of triclosan. While HQ is mostly derived from individual PNEC, some of the studies have generated common PNEC by SSD. Capdevielle et al. [15] constructed SSD based on chronic toxicity values for 14 aquatic species including fish, invertebrates, macrophytes, and algae and predicted lower risk of TCS to pelagic species immediately downstream of wastewater treatment plant discharge points in rivers of Europe (GREAT-ER model based on Calder river) and the USA (P*h*ATE™ model based on 11 catchment

areas) by using a common PNEC of 1,550 ng/l. Further, Lyndall et al. [22] reported that 95th percentiles of measured and predicted TCS levels for water, sediment, and biota are consistently below the fifth percentile of the respective SSD, indicating no adverse effect of TCS.

The application of biosolids and wastewater containing TCC, TCS, and drugs to plant (soybean) showed higher accumulation of antimicrobials (at root tissue and beans) rather than drugs [46]; further it was reported that antimicrobials are not metabolized and thus accumulated whereas drugs can be eliminated/transformed by plants' metabolism. So similar bioconcentration condition may favor the bioaccumulation of antimicrobials in aquatic food chain also. While there are ample reports on fate and risks of parental compounds, investigation on risk assessment of their derivatives/metabolites is scantily found. For instance, methyltriclosan, having greater hydrophobicity and bioaccumulation potential than triclosan, is less studied for its toxicity. Therefore, the environmental risk assessment may not be complete unless data on major derivatives/metabolites are also available.

4.2 Antimicrobial Preservatives

Among preservatives, parabens (alkyl esters of *p*-hydroxybenzoic acid) are widely used as bacteriostatic and fungistatic agents in cosmetic (creams, skin lotions, shampoos, soaps, toothpaste, etc.), pharmaceutical, and food industries [3, 31]. There are seven different types of parabens currently in use (benzyl, butyl, ethyl, isobutyl, isopropyl, methyl, and propyl). Although reports on environmental occurrence of parabens are ample ([3] and references therein), environmental risk assessment was scantily carried out [6, 30, 31].

Probabilistic risk assessment (PRA) of parabens in *D. magna* and fathead minnow was performed by Dobbins et al. [30] based on acute and chronic toxicity data. The observed HQs based on NOEC were much lower ($7.8 \times 10^{-6} - 2.3 \times 10^{-4}$) than 1 (Table 1), which indicates no/little risk of parabens to fathead minnow and *D. magna* in surface waters of developed countries such as Belgium, Canada, and the UK [30]. Further, Yamamoto et al. [31] carried out an elaborate risk assessment for seven parabens in Tokushima and Osaka rivers in Japan. Unlike other studies, the NOEC values obtained from vitellogenin expression of fish were used, and the HQ showed no risk to aquatic organisms (algae, daphnia, and medaka) with the highest HQ obtained for *n*-propylparaben (0.01). Nevertheless, the sum of HQs of individual parabens showed low risk (HQ = 0.017) to those riverine organisms, and the PNEC based on *n*-butylparaben equivalence-based approach also showed low risk, with a maximum HQ of 0.018. They suggested that chronic tests at early life stages of fish are important for less erroneous risk assessment. Among developing countries, Ramaswamy et al. [6] evaluated the risk of four parabens in major rivers (Kaveri, Vellar, and Tamiraparani) of southern India. The lowest and highest HQs were observed for ethylparaben (8×10^{-6}) and butylparaben (0.001) to fish, respectively.

However, the calculated HQs for crustacean (*D. magna*) and fish (*P. promelas*) in all the rivers for all the parabens were below low risk criteria of 0.01.

4.3 Antioxidant Preservatives

Antioxidants are chemical substances used to prolong the shelf life of food items. Due to less stability of natural antioxidants, synthetic phenolic antioxidants (SPAs) like butylated hydroxytoluene (BHT) and butylated hydroxyanisole (BHA) are often preferred for their fat-soluble nature. The level of BHT was higher than triclosan and parabens in the rinse-off and leave-on cosmetics, respectively [47]. Their undisputed usage has resulted in trace quantities in food and environmental samples [26, 47]. Although BHA and BHT were classified as noncarcinogenic by the USEPA and safe food additives by the FDA and the EU, they possess estrogenic properties [48, 49]. Further, there are no environmental risk assessments available due to lack of toxicity data.

4.4 Insect Repellents

DEET (*N*,*N*-diethyl-meta-toluamide or *N*,*N*-diethyl-3-methylbenzamide), a broad-spectrum repellent and the most common active ingredient in insect repellents, is efficacious against mosquitoes and other insects of medical and veterinary importance. Till date, only few studies have reported acute toxicity in invertebrates, fish, and algae with EC50/LC50 in the range of 71.3–388 mg/l [5, 50]. Costanzo et al. [50] measured DEET residues in surface waters from Australia, Germany, the Netherlands, and the USA at safer level (75,000 times lower than EC50/LC50) for aquatic organisms such as algae (*Chlorella prothecoides*), water flea (*D. magna*), scud (*Gammarus fasciatus*), and fishes (*Pimephales promelas*, *Gambusia affinis*, *Oncorhynchus mykiss*). Further, Aronson et al. [19] estimated the flux of DEET in US rivers by iSTREEM (in-STREam Exposure Model) and E-FAST (Exposure and Fate Assessment Screening Tool) and predicted that DEET level was not expected to reach the lowest NOEC (521 mg/l) observed for algae, crustaceans, and fishes, indicating no risk of DEET in riverine habitat. Another insect repellent, 4-dichlorobenzene showed short-term exposure toxicity among invertebrates, fishes, and algae at lower concentration (1–60 mg/l) than DEET ([5] and references therein). Although newer repellents such as icaridin (1-piperidinecarboxylic acid 2-(2-hydroxyethyl) 1-methylpropyl ester) [51] and *m*-toluamide (*N*,*N*-diethyl-m-methylbenzamide) [52] are reported in the environment, their toxicity and risk assessment studies are not yet available.

4.5 Fragrances

Fragrances, the most widely used PCPs, seem to be omnipresent in the environment [3, 5]. Synthetic musks (SMs), being the most commonly used fragrances, are present in a wide range of products comprising deodorants, soaps, and detergents. Commonly used nitro musks are musk xylene (MX) and musk ketone (MK), whereas musk ambrette (MA), musk moskene (MM), and musk tibetene (MT) are used less frequently. In the case of polycyclic musks, celestolide (ABDI), galaxolide (HHCB), and toxalide (AHTN) are used most frequently, and traseolide (ATII), phantolide (AHMI), and cashmeran (DPMI) are used less often [3].

Although they are water-soluble compounds, due to high octanol–water partition coefficient of MK (log Kow = 3.8) and polycyclic musks (log Kow of 5.4–5.9), potential accumulation is expected in aquatic organisms. Rather than biomagnifications, direct impact on organisms is often understood by deriving HQ. In Nakdong River, South Korea, Lee et al. [32] reported low risk of toxalide and medium risk of galaxolide and musk ketone to fish. Combined risk of total SMs (Table 2) clearly indicates higher risk than individual, with higher contribution from MK. Apart from species-specific PNEC, Balk and Ford [33] used common PNEC to determine the risk of musks (AHTN and HHCB) in various environmental matrices, and the obtained HQ was always <1 (either no or low or medium risk). The risk characterized for AHTN based on NOEC for aquatic organism and fish-eating predators showed low risk (0.01–0.08), whereas medium risk (HQ = 0.44) was ascertained for sediment-dwelling organisms. For, HHCB, aquatic and sediment-bound organisms showed low risk, whereas no risk was determined for fish-eating predators. Interestingly, no risk was observed for worm-eating predators from HHCB (HQ = 0.001), even though medium risk (HQ = 0.1) was anticipated for soil organisms. Earlier, Tas et al. [53] also performed environmental risk assessment to understand the safety level of MK and MX in the Netherlands and found HQ ≤0.1 for both aquatic and sediment-dwelling organisms, while much lower HQ (0.01) was observed for fish-eating predators. Nevertheless, higher HQs were predicted for soil organisms with 0.5 for MK and 1.3 for MX, indicating medium to high risk, respectively and elevated HQ obtained for soil organisms implies the need for consideration of sludge being applied as fertilizer. Based on collective toxicity data and MECs, Brausch and Rand [5] suggested that probable risk for aquatic wildlife is more certain due to AHTN than other musks. However, chronic toxicity data on algae and benthic invertebrates are still lacking for effective aquatic risk assessment [5]. Apart from SMs, fragrances such as acetophenone, camphor, D-limonene, ethyl citrate, indole, isoborneol, isoquinolone, and skatole were also reported in surface waters. However, no acute/chronic toxicity data is available to evaluate their environmental risk [5].

4.6 UV Filters and Stabilizers

UV filters and stabilizers are found mainly in cosmetics and to some extent included in other personal care products, pharmaceuticals, food packaging, plastics, textiles, and vehicle maintenance products. Among organic and inorganic (ZnO, TiO_2) variants, the organic forms are mainly used. Currently, 27 UV filters were designated for use in cosmetics, plastics, etc., and they are used in combinations (up to eight compounds) ([5] and references therein). The common feature of organic UV filters is the presence of an aromatic moiety with a side chain having different degrees of unsaturation and forming benzophenones (BPs), 4-methyl-benzylidine-camphor (4MBC), 3-benzylidine-camphor (3BC), homosalate (HMS), 2-ethyl-hexyl-4-trimethoxycinnamate (EHMC), ethyl-PABA (E-PABA), etc. After usage (showering, wash-off, laundering, automobile servicing, etc.), these chemicals enter the aquatic system indirectly (major input) from wastewater treatment plants and directly due to recreational activities such as bathing and swimming in lakes, rivers, and coastal waters (beaches).

In the environment, they may stay for longer duration because of high lipophilicity (log Kow 4–8) and poor biodegradability and eventually accumulate in sediments and biota as well [5, 54]. Like many xenobiotics, sunscreens do cause effects on aquatic animals [3, 55]. Danovaro et al. [56] reported that UV filters (commercial sunscreens, MBC, ethylhexylmethoxycinnamate, octocrylene, BP3, etc.) at very low concentrations cause rapid and complete bleaching of corals. The BCF for 4-MBC in roach, *Rutilus rutilus*, was calculated (9,700–23,000) ten times lower than methyltriclosan having similar log Kow (5) [55]. Due to potential bioaccumulation and toxicity, use of sunscreen products is now banned in some of the famous tourist destinations including marine ecoparks in Mexico ([56] and references therein).

Several studies have reported degradation of UV filters by photolysis ([57] and references therein), and the ecotoxicological data on parental compounds and their degradation products is scarce. Even though little information is available on their toxicity, environmental concentrations suggest low potential risk [58]. However, Gago-Ferrero et al. [58] presumed long-term risk associated with its pseudo-persistency in the environment. According to Diaz-Cruz and Barcelo [59], most of the UV filters and their metabolites are found to elicit hormonal (estrogenic and androgenic) activities based on bioassays (Fig. 3). Five compounds (including four BPs) showed high estrogenic activity, whereas only two showed high androgenic activity, and this indicates that UV filters possess endocrine disrupting potential.

Based on risk assessment of UV filters (Table 1), among benzophenones, BP1 and BP4 were found at levels to cause low risk (HQ >0.01) to fish and daphnia, respectively. Another benzophenone (BP3) showed medium, low, medium, ow risks to fishes, crustaceans, algae, and corals, respectively, indicating the variable toxicity expected in aquatic community. For the same organisms, 4-methyl-benzylidine-camphor showed low risk (HQ >0.01), except for algae with medium risk (HQ ≥ 0.1). Similarly, EHMC also pose low to high risks over a range of organisms; particularly, high risk was assumed for fishes. As reported by Fent

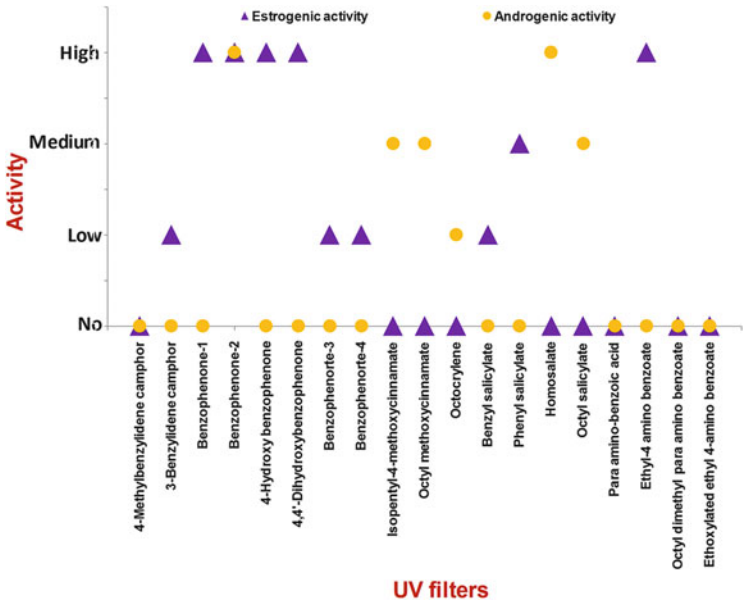

Fig. 3 Endocrine disrupting potentials of UV filters based on hormonal bioassays (*no*: activity not detected; *low*: submaximal dose–response curves with <30% efficacy; *medium*: submaximal dose–response curves with ≥30% efficacy; *max*: response curves with ≥80% efficacy) (From [59])

et al. [35, 36], 3BC can cause serious risk to *O. mykiss* (HQ = 2.73) and *D. magna* (HQ = 1.43), and EHMC too pose a risk to *D. magna* (HQ = 1.35). Among other compounds, BP1 and E-PABA showed no risk, and BP2-4 showed low risk to aquatic species. Fent et al. [36] suggested the consideration of additive interaction of UV filters in mixtures for risk assessment; they investigated the acute (48 h) and chronic (21 day) toxicities on *D. magna* and found that acute toxicity increased with lipophilicity. In case of sea urchin (*Paracentrotus lividus*) and microalgae (*Isochrysis galbana*), medium (EHMC) to high risk (BP3 and 4MCB) was observed by Paredes et al. [37], and they opined that RQ is dependent on the selection of assessment factor which is still a debatable topic indeed.

Apart from the above compounds, 2-hydroxyphenyl derivatives of benzotriazoles (BTZs) are also one of the major groups of UV stabilizers reported in surface waters and biota ([60, 61] and references therein). Regarding the toxicological status, few studies are available based on acute studies which suggested BTZs and their derivatives are nontoxic with NOEC at few μg/l level for freshwater and marine organisms [60] and suggested for more chronic toxicity data for the organisms in different food chain for deriving any conclusion relevant to environmental risk assessments.

4.7 Siloxanes

Siloxanes used in many PCPs and industrial coatings are now ubiquitously reported in freshwater and marine environment [62–64]. Mostly, cyclic volatile methylsiloxanes (cVMSs), commonly called as cyclosiloxanes, are widely added as carrier solvents and emollients in cosmetics and other PCP formulations. Therefore, now the concern is about their potential toxicity, transport, and fate in the environment [65]. So far, cVMSs have received very little attention in ecotoxicological research, i.e., hazards and risks to aquatic biota. Wang et al. [63] reviewed the toxicological properties of octamethylcyclotetrasiloxane (D4), decamethylcyclopentasiloxane (D5), and dodecamethylcyclohexasiloxane (D6) with their respective log Kow (4.45, 5.20, and 5.86) and suggested strong tendency of cVMSs to bind organic matter in soil and sediment. Further, the BCF for D4, D5, and D6 were reported in the range of 1,875–10,000, 3,362–13,300, and 1,600, respectively, with most of the studies confirming the bioaccumulative (>2,000) and very bioaccumulative (>5,000) criterion ([63] and references therein). Further, Wang et al. [63] observed the most sensitive fish toxicity (acute/chronic) values for cVMSs in the range of 4.4–69 μg/l; however, to our knowledge, no ERA has been performed.

4.8 Antibacterial Resistance

Apart from the toxicity of antimicrobials to macro life forms, the more affected are the nontargeted microbes in the environment. It may hamper the bacterial diversity in environment, thereby affecting the community structure. Ricart et al. [66] demonstrated that environmental concentration of TCS can eliminate 85% of bacterial population at 500 μg/l level. Moreover, the biocidal effect [67] can trigger antibacterial resistance among the bacterial community. Evidences are growing on the prevalence of multidrug-resistant bacteria in the environment, drinking water, and patients, especially in developing countries such as India [68, 69], and the antibiotic-resistant genes (ARGs) have been isolated from the surface water, sewage, and in hospital environment [10]. Such conditions lead to the emergence/transmission of antibiotic resistance among bacteria in the environment [68]. Although the contribution of antibacterials in antibiotic resistance or multidrug resistance is largely unknown, the scientific committee on emerging and newly identified health risks by the EU [70] pointed that antibacterial resistance may develop rapidly when exposed to preservative(s). Therefore, uncontrolled and continuous use of antimicrobial/preservative compounds (triclosan, triclocarban, parabens, etc.) may lead to resistance in bacteria. Recent studies confirmed antibacterial resistance of PCPs (parabens, triclosan) from wastewater and surface water [11, 71]. Selvaraj et al. [11] reported bacterial resistance in common pathogens in effluents of sewage treatment plants in India for parabens and suggested the

possible transfer of resistant genes to other pathogenic bacteria in natural waters because of the release of untreated wastewaters directly into the environment. Moreover, the resistant strains have the potency to modify PCPs into toxic compounds [72] which may further affect the organisms.

5 Present Risk and Future Prospective of PCPs in the Environment

On comparing the risk levels of major PCPs (Fig. 4), it is understood that most of the antimicrobials and UV filters showed medium to high risk whereas synthetic musks pose high risk only on total concentrations. Further, it clearly demonstrates that all the compounds within a group do not elicit similar toxicity but elicit cumulative risk. Apart from these three classes as shown in Fig. 4, reports on ERAs for antioxidants, fragrances, and siloxanes are lacking to be represented.

In most of the studies, ERAs were performed based on individual compound and not for mixtures present in the environment; therefore, it is critical to assess and to understand their activity in mixture (combinations). Further, for more appropriate environmental risk assessment of PCPs, it appears essential to consider not only mixtures of parent compounds but also degradation products (metabolites, photodegradates, and chlorination by-products). This may pose an undefined

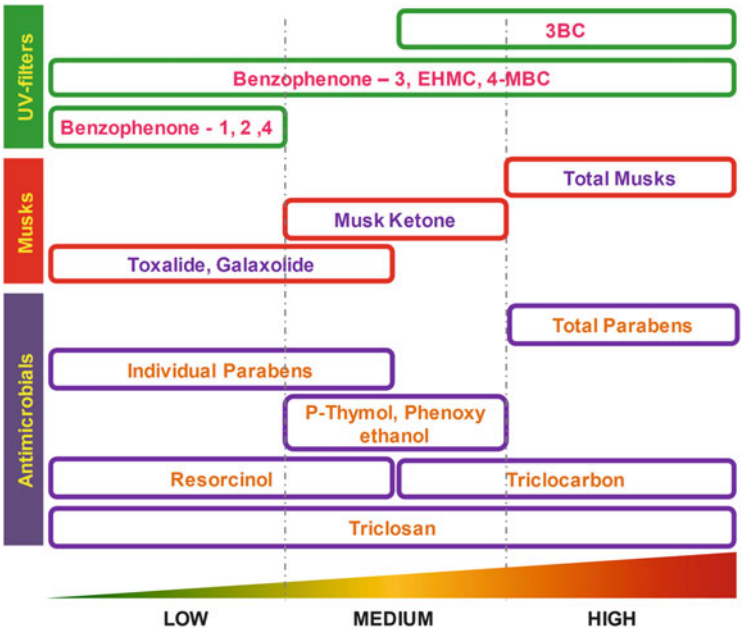

Fig. 4 Aquatic health risk of PCPs based on literature data [6, 7, 27–37]

ecotoxicological risk to resident organisms as well as a great challenge to ecotoxicologists. Moreover, testing chemical mixtures for toxicity is not an easy task due to the possible presence of thousands of organic and inorganic compounds (pollutants) in the environment; however, integrated dose–response relationships may be promising. In addition, the effect of individual components in the mixture can be extrapolated to understand/predict the cumulative effect via in silico approach, which can be further validated selectively through bioassays.

6 Conclusive Remarks

The impact of anthropogenic pollutants on the environment is severe and being given priority to understand well in this century. Despite their occurrence at submicrogram level in environment, the risk ascertained is quite high in many parts of the world. Developed countries are reporting high removal efficacy of WWTPs for few PCPs; however, higher risk is anticipated in developing countries where no proper treatment facilities are available. The exponential growth of population depletes freshwater resources and results in water shortage in this twenty-first century and in future. To combat water scarcity, reuse of wastewater is often advocated; such reuse has raised many questions with the occurrence of PCPs and other emerging chemicals residues.

Current environmental risk assessment procedures are limited in their proven ability to evaluate the combined effects of multiple xenoestrogens. Hence, ERA for mixtures (various forms of chemicals and their environmental derivatives) based on potential synergistic and/or antagonistic effects should be considered. As of the present situation, wider chronic toxicity studies should be imparted for many PCPs. Further, the effect of PCPs in the base of food chain may lead to adverse consequences through food chain magnification and ultimately on ecosystem. However, at present such scenario is entirely speculative and more appropriate studies to probe for this outcome have not yet been conducted holistically. Apart from the risk to aquatic organisms, some PCPs such as triclosan, parabens, etc., entering the aquatic environment may reduce the bacterial diversity and also act as buffers for the emergence of multidrug-resistant bacteria such as “superbug.” These concerns also need to be addressed for the safety of future generation.

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Human Exposure to Chemicals in Personal Care Products and Health Implications

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Abstract Human exposure to major classes of personal care products (PCPs) that include disinfectants (e.g. triclosan), fragrances (e.g. musks), insect repellents (e.g. DEET), preservatives (e.g. parabens), and UV filters (e.g. benzophenones) has been reviewed. Concentrations of these toxicants in human matrices (blood, urine, or tissues) have been compiled, alongside with relevant health implications.

Keywords Disinfectants · Fragrances · Humans · Insect repellents · Personal care products · Preservatives · UV filters

Contents

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M.S. Díaz-Cruz and D. Barceló (eds.), *Personal Care Products in the Aquatic Environment*, Hdb Env Chem (2015) 36: 165–188, DOI 10.1007/698_2014_301,

1 Introduction

Personal care products (PCPs) contain a wide range of chemicals that are under increasing scrutiny. Current knowledge about these contaminants in PCPs has significant gaps with regard to their toxicity (towards humans), bioaccumulation, exposure, doses in humans, and biotransformation products (metabolites). Some of the contaminants in PCPs belong to chemical groups which have raised concerns regarding endocrine disruption.

An average person is exposed to numerous chemicals from cosmetics, soaps, moisturizing skin creams, lipsticks, makeup formulations, nail polishes, after-shave lotions, or hair-care products in addition to a variety of other PCPs. PCPs are widely used in our everyday life for personal hygiene and beautification purposes. Even though consumers may assume that these products are safe, some of the ingredients are untested for their safety and some are unregulated. Furthermore, ingredient labels can be misleading about the safety of the products.

Human exposure doses and sequestration of these chemicals in human bodies are key concerns for these chemicals due to their broad applications. Several ingredients of PCPs may be characterized as persistent, bioaccumulative, and toxic, while others are associated with endocrine disruption. Human exposure to these chemicals was not studied until recently. As the analytical methodologies advance, sensitive methods have been applied in the detection of these chemicals in human specimens. In this chapter, we systematically investigate the levels of selected PCPs and their metabolites in human matrices and suggest health implications from such exposures.

2 Xenobiotics: Biotransformation and Adjustment of Urinary Concentrations

Once a xenobiotic compound enters the human body, it is transformed into its metabolites by cytochrome P450 enzymes. The impact of each xenobiotic on humans differs depending on its toxicity and route of elimination from the body. Biotransformations occur mainly in the liver, lungs, intestines, and skin, and xenobiotics are subject to phase I and phase II metabolism. In general, xenobiotics are excreted as the parent compound and metabolites, and as free or conjugated species (i.e. glucuronides and sulphates). Thus, the total concentration of a xenobiotic refers to its total sum concentration of free and conjugated species.

In recent years, biomonitoring techniques have been used in the assessment of human exposure to environmental chemicals. In most biomonitoring studies, total concentrations of xenobiotics are determined in human specimens such as blood or urine. However, in the absence of analytical standards for conjugated species, a back calculation method involving analysis of concentrations of free species and "total" forms can provide information regarding the concentrations of conjugated

fraction. For the determination of total concentrations, the samples are hydrolyzed to free the conjugated fraction of the xenobiotic from the bound chemical groups (i.e. glucuronic acid). Hydrolysis is performed through the addition of a strong acid such as hydrochloric acid or through enzymatic methods. Without the hydrolysis step, only the free fraction of the chemical can be determined. When enzymatic hydrolysis is applied, the enzyme β-glucuronidase (mainly from *Helix pomatia*, since it has also sulphatase activity) is mainly used.

Urine is a most commonly used human specimen in biomonitoring studies. However, concentrations of xenobiotics in urine can vary depending on the volume of urine excreted at the time of sampling. The effect of urinary dilution/volume can be accounted for by determining the amount of the environmental chemical per amount of urinary creatinine in a given volume of urine. In addition, there are a number of normalization procedures, and the two most common ones are specific gravity and creatinine correction. Nevertheless, there are some controversies with regard to the correction of urinary concentrations of environmental chemicals to creatinine levels. Urine's specific gravity determines the content of various water-soluble molecules excreted through the kidneys into urine. On the other hand, creatinine is a by-product of skeletal muscle metabolism of creatine and is cleared from the blood plasma into the kidney at an approximately constant rate. In this chapter, unless mentioned otherwise, we report concentrations of PCPs on an unadjusted basis.

3 Exposure to Disinfectants

Triclosan (TCS) and triclocarban (TCC) are known for their extensive use as antimicrobials in PCPs [1]. They are used in PCPs, such as toothpaste, soap, shampoo, deodorant, mouthwash, and cosmetics. They can also be found in kitchen utensils, toys, and textiles. Thus, human exposure can occur through oral and dermal contact [2, 3].

TCS and TCC have been determined in urine, serum, plasma, and human breast milk. All levels are expressed in total concentrations (unconjugated and conjugated species). Urine is the most common biological media for monitoring TCS and TCC since urinary excretion is the major route of elimination [2–5] (Table 1).

Urinary TCS levels have revealed great differences in concentrations of up to three orders of magnitude (Table 1). Moreover, the detection rate is high, with most studies reporting a detection rate of >70 %. On the contrary, TCC levels, in most cases, were less frequently detected and at lower concentrations than TCS.

A study from China demonstrated that females had statistically higher geometric mean concentrations of TCS than males [13]. In contrast, Allmyr et al. [14] reported higher levels of TCS in serum from males than in females, and 31–45-year-old individuals had higher levels of TCS in comparison with the other age groups. TCS was also found in human breast milk but at lower levels than in plasma [15]. Milk samples from women who used TCS-containing PCPs had statistically significantly

Table 1 Reported total concentrations (or mentioned otherwise; ng mL^{-1}) and frequency of detection of triclosan (TCS) and triclocarban (TCC) in human urine

Human matrix	Population (*N*)	Origin of samples (country)	Target chemicals	Concentration ranges (and max., median, average or geometric mean if available)	Detection rates (%)	References
Urine	506 (pregnant women)	USA	TCS	19–44 ng mL^{-1} (mean: 29 ng mL^{-1})	100	[6]
Urine	46 (26 males and 20 females; average age: 34.5 years old)	Canada	Free TCS	Not detected–20 ng mL^{-1} (median: 0.07 ng mL^{-1})	95.7	[7]
			TCS-glucuronide	Not detected–702 dg mL^{-1} (median: 15 ng mL^{-1})	97.8	
			TCS-sulphate	Not detected–0.09 ng mL^{-1} (median: below detection limit)	21.7	
			TCS	Not detected–703 ng mL^{-1} (median: 15 ng mL^{-1})	100	
Urine	3,728	USA	TCS	105–127 ng mL^{-1} (mean: 116 ng mL^{-1})	100	[8]
Urine	1,870	Korea	TCS	1.5–1.9 ng mL^{-1} (mean: 1.7 ng mL^{-1})	92.6	[9]
Urine	131	Belgium	TCS	Not detected–599 ng mL^{-1} (geometric mean: 3 ng mL^{-1})	74.6	[10]
Urine	4,037	USA	TCS	Not detected–3,620 ng mL^{-1} (median: 12 ng mL^{-1})	77.3	[11]

(continued)

Table 1 (continued)

Human matrix	Population (*N*)	Origin of samples (country)	Target chemicals	Concentration ranges (and max., median, average or geometric mean if available)	Detection rates (%)	References
Urine	100	Greece	TCS	Not detected–2,583 ng mL^{-1} (geometric mean: 8 ng mL^{-1})	71	[3]
			TCC	Not detected–2 ng mL^{-1} (geometric mean: 0.6 ng mL^{-1})	4	
Urine	105 (pregnant women)	Puerto Rico	TCS	25th percentile–max: 4–2,780 ng mL^{-1}	79.0–88.9	[12]

Table 2 Estimated daily intake of TCS on the basis of biomonitoring data

Target chemicals	Origin of samples (country)	Estimated daily intake (EDI) (μg/kg BW/day)	Equation used	References
TCS	Greece	0.1–1,059 (median: 2.4)	Estimated daily intake (EDI; μg/kg BW/day) = 15.8 × [Σ_6Parabens] (μg/L) × 1.7 (L/day)/65.5 kg	[3]

higher levels of TCS compared to those women who did not use TCS-containing PCPs [15]. Pycke et al. [16] measured total TCS, TCC, and the metabolites of TCC, namely, 2′-OH-TCC, 3′-OH-TCC, and 3′-Cl-TCC in human urine. 2′-OH-TCC was present at higher detection rate amongst all three metabolites (27.1%), followed by 3′-OH-TCC (16.6%) and 3′-Cl-TCC (12.7%) [16]. The concentration ranges of 2′-OH-TCC, 3′-OH-TCC, and 3′-Cl-TCC were 0.02–0.5, 0.01–0.08, and "not detected" −0.02 ng mL^{-1}, respectively, while the precursor compound, TCC, was found at a concentration range of 37–151 ng mL^{-1} [16].

Based on the measured urinary concentrations of TCS and simple steady-state toxicokinetic model, exposure dose to TCS was estimated by Asimakopoulos et al. [3] (Table 2). It was reported that only 6.3% of TCS penetrates the human skin after dermal application. Since the major exposure route of TCS is dermal application of PCPs, a factor of 15.8 was applied in the estimation of the total intake (6.3 × 15.8–100 %) of TCS (Table 2) [3].

In 2010, TCS was removed from the EU list of provisional additives for use in plastic food-contact materials, since TCS is considered more toxic than many other disinfectants [3]. TCS is potentially genotoxic in certain types of organisms and/or

cell types [3]. Exposure to TCC was associated with methemoglobinemia in humans [3].

4 Exposure to Fragrances

Synthetic musk fragrances are widely used in PCPs, such as laundry detergents, softeners, soaps, antiperspirants, deodorants, and other cosmetics. Synthetic musks are divided into two main groups, nitro and polycyclic musks. Amongst the nitro musks, musk xylene (MX) and musk ketone (MK) are the most commonly used chemicals, followed by ambrette (MA), musk moskene (MM), and musk tibetene (MT). Amongst the polycyclic musks, celestolide (ADBI), galaxolide (HHCB), and tonalide (AHTN) are the most commonly used followed by traseolide (ATII), phantolide (AHMI), and cashmeran (DPMI). In recent years, polycyclic musks are used in higher quantities than nitro musks. In addition, the polycyclic musks are studied widely since they are suspected to act as endocrine disruptors [17]. Even though it was thought that the most likely exposure pathway is dermal exposure and absorption through the skin, research now focuses towards indoor air inhalation and indoor dust ingestion as important sources for musk exposure due to their use in diverse household products (e.g. air fresheners) and their high particle-binding affinities. Even though the overall impact of synthetic musks on human health is currently unknown, this is an active area of research [18].

Synthetic musks maintain a lipophilic nature and low biodegradability and have been detected in human biological media (Table 3). HHCB is found at the highest median concentration in human milk, followed by AHTN and MX. Concentrations of MK were very low and often not detectable or not quantifiable (Table 3).

A downward trend in exposure to MX was observed by Covaci et al. [18], since the industry voluntarily replaced the nitro- with polycyclic musks (Table 3). Moreover, HHCB is by far the most common polycyclic musk, as its production and use increased at the same time as production and use of nitro musks decreased [18]. Women with a high use of perfume during pregnancy had elevated concentrations of HHCB in their breast milk [25, 26]. In addition, elevated concentrations of AHTN in women were observed when they reported using perfumed laundry detergent [25, 26]. Hutter et al. [25] reported higher plasma concentrations of HHCB in older individuals, and the finding was correlated to the higher use of lotions and crèmes for their skin. Polycyclic musk compounds are bioaccumulative since they are found in human fat tissues and they are very stable chemicals. However, even though humans are constantly exposed to musks, routine toxicology screens have not shown any toxicity at low-dose exposures [27].

Table 3 Reported total concentrations (ng mL^{-1} or ng g^{-1}) and frequency of detection of musk fragrances (free-form plus conjugates) in human media

Human matrix	Population (*N*)	Origin of samples (country)	Target chemicals	Concentration ranges (and max., median, average or geometric mean if available)	Detection rates (%)	References
Human milk	10	China	HHCB	12–68 ng g^{-1} lw	100	[19]
			AHTN	23–118 ng g^{-1} lw	100	
			MK	Not quantifiable	60	
Human milk	100	China	HHCB	Median: 63 ng g^{-1} lw	99	[20]
			AHTN	Median: 5 ng g^{-1} lw	75	
			MK	Median: 4 ng g^{-1} lw	60	
			MX	Median: 17 ng g^{-1} lw	83	
Human milk	54	Switzerland	HHCB	6–310 ng g^{-1} lw (median: 36 ng g^{-1} lw)	83	[21]
			AHTN	5–29 ng g^{-1} lw (median: 10 ng g^{-1} lw)	13	
			MK	0.25–12 ng g^{-1} lw (median: 0.6 ng g^{-1} lw)	63	
			MX	0.25–32 ng g^{-1} lw (median: 1 ng g^{-1} lw)	87	
Human milk	20	South Korea	HHCB	0.06–0.5 ng g^{-1} lw	100	[22]
			AHTN	0.02–0.09 ng g^{-1} lw	65	
			MK	0.02–0.2 ng g^{-1} lw	53	
			MX	0.02–0.2 ng g^{-1} lw	65	
Human milk	31	USA	HHCB	Median: 136 ng g^{-1} lw	97	[23]
			AHTN	Median: 53 ng g^{-1} lw	56	
			MK	Median: 58 ng g^{-1} lw	85	
			MX	Median: 17 ng g^{-1} lw	36	
Plasma	204	China	HHCB	Median: 0.9 ng mL^{-1}	98	[24]
			AHTN	Median: 0.5 ng mL^{-1}	85	
Plasma	53	Austria	HHCB	Max.: 7 ng mL^{-1}	89	[25]
			AHTN	Max.: 0.3 ng mL^{-1}	19	
			MK	Max.: 0.2 ng mL^{-1}	43	
			MX	Max.: 0.3 ng mL^{-1}	62	

(continued)

Table 3 (continued)

Human matrix	Population (*N*)	Origin of samples (country)	Target chemicals	Concentration ranges (and max., median, average or geometric mean if available)	Detection rates (%)	References
Serum	114	Austria	HHCB	Median: 0.4 ng mL^{-1}	91	[26]
			AHTN	Median: not detected	17	
Maternal serum	20	South Korea	HHCB	0.2–1 ng g^{-1} lw	90	[22]
			AHTN	<0.2–1 ng g^{-1} lw	35	
			MK	Not quantifiable	0	
			MX	0.2–0.5 ng g^{-1} lw	5	
Cord serum	20	South Korea	HHCB	0.7–3 ng g^{-1} lw	70	[22]
			AHTN	<0.7–3 ng g^{-1} lw	15	
			MK	Not quantifiable	0	
			MX	Not quantifiable	0	

lw lipid weight

5 Exposure to Preservatives

Parabens are the most commonly used preservatives found in PCPs, and in fact, they are regarded as the most common ingredients in cosmetics. They are present in approximately 80% of PCPs surveyed [28]. In a study conducted by Rastogi et al. [29], parabens were found in approximately 80% of rinse-off and 100% of leave-on cosmetics. Although commercially used parabens are of synthetic origin, it is known that some organisms are able to produce them naturally [30]. An acceptable daily intake (ADI) of <10 mg/kg-body weight (bw)/day was suggested for methylparaben (MeP), ethylparaben (EtP), and propylparaben (PrP) by the Joint Food and Agriculture Organization (FAO) and World Health Organization (WHO) Expert Committee on Food Additives (JECFA) [2, 3]. Estrogenic activities have been reported in numerous bioassays for MeP, EtP, PrP, and butyl paraben (BuP) [2, 3]. Recently, epidemiological studies showed an association between human exposure to parabens and adverse health effects [31, 32]. In 2007, the ADI set for PrP was withdrawn by JECFA, and in 2011, Denmark banned the use of PrP and BuP in children's cosmetic products [2, 3]. Other parabens that are applied in PCPs, but less extensively, are benzylparaben (BzP) and heptylparaben (HeptP). Recently, methyl-protocatechuate (OH-MeP) and ethyl-protocatechuate (OH-EtP) were documented as novel metabolites of exposure to methyl- and ethyl-paraben, respectively [33]. Following oral or dermal administration, parabens are rapidly hydrolyzed by non-specific esterases and widely distributed in the body (i.e. skin, subcutaneous fat tissue, and digestive system). Several parabens end up in two common metabolites, p-hydroxybenzoic acid (4-HB) and protocatechuic acid (3,4-dihydroxybenzoic acid; 3,4-DHB) [33].

Parabens, once they enter into the bloodstream through oral or dermal application, are excreted through urine, as free-form or glycine, glucuronide, or sulphate conjugates [30]. Therefore, parabens are mainly determined in human urine and blood serum [30] (Table 4). In a biomonitoring study in Greece, Asimakopoulos et al. [3] measured the total concentrations of parabens (Σ_6Parabens: [MeP] + [EtP] + [PrP] + [BuP] + [BzP] + [HeptP]) in urine from 100 individuals. Considerable differences in concentrations were revealed, ranging from 2 to 1012 ng mL^{-1}, with a geometrical mean value of 24 ng mL^{-1}. All parabens were found in urine, and the rank order of detection rate (DR) was MeP (100%) > EtP (87%) > PrP (72%) > BuP (46 %) > BzP (6%) > HeptP (4%). This pattern of detection rate of parabens is in accordance to previous studies on human biologic media [3]. The distribution profiles of paraben concentrations in urine followed the order of MeP >> PrP > EtP, which was also similar to those reported in previous studies on human biologic media [3]. Moreover, MeP and PrP are used in combination in many PCPs, and therefore, a significant correlation was found between these two parabens in urine samples across a number of studies [45].

For the first time, alkyl protocatechuates were determined and quantified by Wang and Kannan [33]. They found that in the urine of children, the concentrations of OH-MeP were an order of magnitude lower than the concentrations of MeP,

Table 4 Reported total concentrations (ng mL^{-1} or ng g^{-1}) and frequency of detection of parabens and metabolites (free-form plus conjugates) in human specimens

Human matrix	Population (N)	Origin of samples (country)	Target chemicals	Concentration ranges (and max., median, average or geometric mean if available)	Detection rates (%)	References
Urine	506	USA	MeP	Mean: 104 ng mL^{-1}	100	[6]
			PrP	Mean: 19 ng mL^{-1}	98.4	
Urine	100	USA	MeP	5–95th percentiles: 4–680 ng mL^{-1}	99	[34]
			EtP	5–95th percentiles: not detected–48 ng mL^{-1}	58	
			PrP	5–95th percentiles: 0.2–279 ng mL^{-1}	96	
			BuP	5–95th percentiles: not detected–30 ng mL^{-1}	69	
			BzP	5–95th percentiles: not detected–0.5 ng mL^{-1}	39	
Urine	2,548	USA	MeP	10–95th percentiles: 6–974 ng mL^{-1}	99	[35]
			EtP	10–95th percentiles: not detected–57 ng mL^{-1}	42	
			PrP	10–95th percentiles: 0.3–299 ng mL^{-1}	93	
			BuP	10–95th percentiles: not detected–20 ng mL^{-1}	47	
Urine	60 (males)	Denmark	MeP	Not detected–2,002 ng mL^{-1}	98	[36]
			EtP	Not detected–564 ng mL^{-1}	80	
			PrP	Not detected–256 ng mL^{-1}	98	
			BuP	Not detected–68 ng mL^{-1}	83	
			BzP	Not detected–2 ng mL^{-1}	7	
Urine	120 (pregnant women)	Spain	MeP	Median: 191 ng mL^{-1}	100	[37]
			EtP	Median: 9 ng mL^{-1}	98	
			PrP	Median: 30 ng mL^{-1}	88	
			BuP	Median: 2 ng mL^{-1}	90	
Urine	30 (children)	Spain	MeP	Median: 150 ng mL^{-1}	100	[37]
			EtP	Median: 8 ng mL^{-1}	100	
			PrP	Median: 22 ng mL^{-1}	80	
			BuP	Median: 1 ng mL^{-1}	83	

Urine	194 (males)	USA	MeP	10th percentile-maximum: 5–1.080 ng mL^{-1}	100	[31]
			PrP	10th percentile-maximum: 0.4–294 ng mL^{-1}	92	
			BuP	10th percentile-maximum: not detected–65 ng mL^{-1}	32	
Urine	860	USA	MeP	0.5–14.900 ng mL^{-1}	NA	[32]
			EtP	0.5–1,110 ng mL^{-1}	NA	
			PrP	0.1–7,210 ng mL^{-1}	NA	
			BuP	0.1–1,240 ng mL^{-1}	NA	
Urine	653	USA	MeP	Not detected–23.200 ng mL^{-1}	99.7	[38]
			PrP	Not detected–2,870 ng mL^{-1}	96.5	
			BuP	Not detected–998 ng mL^{-1}	65.4	
Urine	30 (adults)	USA	MeP	0.8–240 ng mL^{-1}	100	[33]
			OH-MeP	Not quantified–40 ng mL^{-1}	98	
			EtP	0.1–24 ng mL^{-1}	100	
			OH-EtP	Not quantified–6 ng mL^{-1}	60	
			4-HB	81–6,220 ng mL^{-1}	100	
			3,4-DHB	8–2,960 ng mL^{-1}	100	
	40 (children)		MeP	2–5,240 ng mL^{-1}	100	
			OH-MeP	2–94 ng mL^{-1}	100	
			EtP	Not quantified–8 ng mL^{-1}	60	
			OH-EtP	0.6–107 ng mL^{-1}	100	
			4-HB	134–2,900 ng mL^{-1}	100	
			3,4-DHB	9–6,780 ng mL^{-1}	100	
Urine	879 (females)	USA	MeP	Not detected–4,282 ng mL^{-1}	99.9	[39]
			EtP	Not detected–3,010 ng mL^{-1}	60	
			PrP	Not detected–1,002 ng mL^{-1}	98	
			BuP	Not detected–309 ng mL^{-1}	65	

(continued)

Table 4 (continued)

Human matrix	Population (N)	Origin of samples (country)	Target chemicals	Concentration ranges (and max., median, average or geometric mean if available)	Detection rates (%)	References
	970 (males)		MeP	Not detected–7,909 ng mL^{-1}	99.5	
			EtP	Not detected–771 ng mL^{-1}	38	
			PrP	Not detected–1,486 ng mL^{-1}	91	
			BuP	Not detected–723 ng mL^{-1}	28	
Urine	108 (pregnant women)	Japan	MeP	Not detected–1,238 ng mL^{-1}	94	[40]
			EtP	Not detected–2,022 ng mL^{-1}	81	
			PrP	Not detected–5,380 ng mL^{-1}	89	
			BuP	Not detected–82 ng mL^{-1}	54	
Urine	46 (pregnant women)	Korea	MeP	25–75th percentiles (specific gravity adjusted concentrations): 61–452 ng mL^{-1}	98	[41]
			EtP	25–75th percentiles (specific gravity adjusted concentrations): 17–203 ng mL^{-1}	100	
			PrP	25–75th percentiles (specific gravity adjusted concentrations): 0.9–65 ng mL^{-1}	98	
			BuP	25–75th percentiles (specific gravity adjusted concentrations): not detected–0.5 ng mL^{-1}	28	
	46 (newborn infants)		MeP	25–75th percentiles (specific gravity adjusted concentrations): 40–272 ng mL^{-1}	100	
			EtP	25–75th percentiles (specific gravity adjusted concentrations): 1–8 ng mL^{-1}	98	
			PrP	25–75th percentiles (specific gravity adjusted concentrations): 0.8–15 ng mL^{-1}	100	
			BuP	25–75th percentiles (specific gravity adjusted concentrations): not detected–2 ng mL^{-1}	41	

Urine	100 (50 males and 50 females)	Greece	MeP	1–803 ng mL^{-1}	100	[3]
			EtP	<0.5–61 ng mL^{-1}	87	
			PrP	<0.5–575 ng mL^{-1}	72	
			BuP	<0.5–113 ng mL^{-1}	46	
			BzP	<0.2–0.8 ng mL^{-1}	6	
			HeptP	<0.2 ng mL^{-1}	4	
			OH-EtP	<2–71 ng mL^{-1}	87	
Serum	15	–	MeP	0.4–301 ng mL^{-1}	100	[42]
			EtP	Not detected–5 ng mL^{-1}	53	
			PrP	Not detected–67 ng mL^{-1}	80	
			BuP	Not detected	–	
			BzP	Not detected	–	
Urine	60 (males)	Denmark	MeP	Not detected–60 ng mL^{-1}	95	[36]
			EtP	Not detected–21 ng mL^{-1}	30	
			PrP	Not detected–6 ng mL^{-1}	93	
			BuP	Not detected–0.9 ng mL^{-1}	3	
			BzP	Not detected–3 ng mL^{-1}	3	
Urine	261 (123 males and 138 females)	Belgium	MeP	0.3–7,576 ng mL^{-1} (geometric mean: 19 ng mL^{-1})	100	[43]
			EtP	Not detected–887 ng mL^{-1} (geometric mean: 2 ng mL^{-1})	96.6	
			PrP	Not detected–692 ng mL^{-1} (geometric mean: 2 ng mL^{-1})	83.1	
			BuP	Not detected–81 ng mL^{-1} (geometric mean: NA)	41	
Urine	71	USA	MeP	5–95th percentiles: 10–1,830 ng mL^{-1}	100	[44]
			EtP	5–95th percentiles: not detected–347 ng mL^{-1}	59	
			PrP	5–95th percentiles: 0.5–589 ng mL^{-1}	100	
			BuP	5–95th percentiles: not detected–58 ng mL^{-1}	70	

(continued)

Table 4 (continued)

Human matrix	Population (N)	Origin of samples (country)	Target chemicals	Concentration ranges (and max., median, average or geometric mean if available)	Detection rates (%)	References
Amniotic fluid	69		MeP	5–95th percentiles: not detected–3 ng mL^{-1}	42	
			EtP	Not detected	–	
			PrP	5–95th percentiles: not detected–1 ng mL^{-1}	58	
			BuP	5–95th percentiles: not detected–0.3 ng mL^{-1}	6	
Urine	109	China	MeP	0.4–608 ng mL^{-1} (geometric mean: 7 ng mL^{-1})	100	[45]
			EtP	0.1–439 ng mL^{-1} (geometric mean: 2 ng mL^{-1})	100	
			PrP	0.1–202 ng mL^{-1} (geometric mean: 4 ng mL^{-1})	100	
			BuP	0.01–129 ng mL^{-1} (geometric mean: 0.1 ng mL^{-1})	60	
			BzP	0.01–0.1 ng mL^{-1} (geometric mean: 0.01 ng mL^{-1})	19	
Urine	105 (pregnant women)	Puerto Rico	MeP	25th percentile–maximum: 39–7,550 ng mL^{-1}	99.5–100	[12]
			PrP	25th percentile–maximum: 5–3,490 ng mL^{-1}	98.1–99.3	
			BuP	25th percentile–maximum: <0.2–188 ng mL^{-1}	58.4–74.8	
Breast tumours	20	UK	MeP	Mean: 13 ng g^{-1}	NA	[46]
			EtP	Mean: 2 ng g^{-1}	NA	
			PrP	Mean: 3 ng g^{-1}	NA	
			BuP	Mean: 3 ng g^{-1}	NA	
			BzP	Not detected	NA	

Table 5 Estimated daily intake of parabens through human biomonitoring studies

Target chemicals	Origin of samples (Country)	Estimated daily intake (EDI) (μg/kg BW/day)	Equation used	References
Σ_6Parabens ([MeP] + [EtP] + [PrP] + [BuP] + [BzP] + [HeptP])	Greece	2.1–1,313 (median: 23.8)	Estimated daily intake (EDI; μg/kg BW/day) = 50 × [Σ_6Parabens] (μg/L) × 1.7 (L/day)/65.5 kg	[3]
MeP, EtP, PrP, ΣParabens ([MeP] + [EtP] + [PrP])	China	MeP: geometric mean: 6.69 for males	Estimated daily intake (EDI; μg/kg BW/day) = 50 × Ci (μg/L) × 1.7 L (L/day) / BW	[45]
		Geometric mean: 15.9 for females	(C_i : measured urinary concentration of individual parent parabens; BW: 62.7 kg for males and 54.8 kg for females)	
		EtP: geometric mean: 2.50 for males		
		Geometric mean: 3.06 for females		
		PrP: geometric mean: 3.63 for males		
		Geometric mean: 8.94 for females		
		Σparabens: geometric mean: 18.4 for males		
		Geometric mean: 40.8 for females		

whereas in the urine of adults, the total concentrations of OH-MeP were higher than those of MeP, suggesting a potential difference in metabolism between these two age groups [33]. Moreover, 4-HB and 3,4-DHB, two established endocrine-disrupting compounds, were found to be predominant in the urine of children and adults [33].

Based on the measured urinary concentrations of parabens and simple steady-state toxicokinetic models, exposure to parabens was estimated by Asimakopoulos et al. [3] and Ma et al. [45]. Higher concentrations of parabens in females than in males have been associated with high use rates of PCPs by the former group (Table 5) [45].

6 Exposure to UV Filters

UV filters are used as sunscreen agents in PCPs for the protection of skin and hair from UV irradiation [47]. Even though UV filters are designed for external application on the skin or hair, some of them can be absorbed in the human body, further metabolized, and eventually bioaccumulated and/or excreted. Thus, for adequate consumers' protection, the maximum allowed concentrations of UV filters have been regulated worldwide by legislation. The absorption of these chemicals by the human body is linked to various adverse health effects, such as allergic contact dermatitis and endometriosis [47, 48]. Chisvert et al. [47] categorized the UV filters into 9 classes:

1. *p*-Aminobenzoic acid (PABA) and derivatives (i.e. ethylhexyl dimethyl *p*-aminobenzoic acid (EDP) and PEG-25 *p*-aminobenzoic acid (P25))
2. Benzimidazole derivatives (i.e. phenylbenzimidazole sulphonic acid (PBS) and disodium phenyl dibenzimidazole tetrasulfonate (PDT))
3. Benzophenone derivatives (i.e. benzophenone-3 (BZ-3) and diethylamino hydroxybenzoyl hexyl benzoate (DHHB))
4. Benzotriazole derivatives (drometrizole trisiloxane (DTR) and methylene bis-benzotriazolyl tetramethylbutylphenol (MBT))
5. Camphor derivatives (3-benzyliden camphor (3BC), 4-methylbenzylidene camphor (MBC), benzylidene camphor sulphonic acid (BCS) polyacrylamidomethyl benzylidene camphor (PBC), camphor benzalkonium methosulfate (CBM), and terephthalylidene dicamphor sulphonic acid (TDS))
6. Methoxycinnamates (ethylhexyl *p*-methoxycinnamate (EMC) and isoamyl *p*-methoxycinnamate (IMC))
7. Salicylates (ethylhexyl salicylate (ES) and homosalate (HS))
8. Triazine derivatives (diethylhexyl butamido triazone (DBT), ethylhexyl triazone (ET), and bis-ethylhexyloxyphenol methoxyphenyl triazine (EMT))
9. Other filters (butyl methoxydibenzoylmethane (BDM), octocrylene (OCR), and polysilicone-15, P15)

For very few UV filters, BZ-3, MBC, EDP, and PABA, their metabolic pathways are elucidated in vivo and/or in vitro studies [47]. BZ-3 is biotransformed amongst others into 2,4-dihydroxybenzophenone (2,4-OH-BP; or BP-1), 2,2′,4,4′-tetrahydroxybenzophenone (2,2′,4,4′-OH-BP or BP-2), 2,2′-dihydroxy-4-methoxybenzophenone (2,2′-OH-4MeO-BP; or BP-8), 4-hydroxybenzophenone (4-OH-BP), and 2,3,4-trihydroxybenzophenone (2,3,4-OH-BP) [2, 3]. MBC is mainly biotransformed to 3-(4-carboxybenzylidene)camphor (CBC) and four isomers of 3-(4-carboxybenzylidene)hydroxycamphor (CBC-OH) (3-(4-carboxybenzylidene)-6-hydroxycamphor (CBC-6OH) is the major one) [47]. EDP is mainly biotransformed to *N*,*N*-dimethyl-p-aminobenzoic acid (DMP) and *N*-monomethyl-p-aminobenzoic acid (MMP) [47], while PABA is mainly biotransformed to *p*-aminohippuric acid (PAH), *p*-acetamidobenzoic acid (PAcB), and *p*-acetamidohippuric acid (PAcH) [47].

Table 6 Reported total concentrations (ng mL^{-1} or μg g^{-1}) and frequency of detection of BP-UV filters and metabolites (free-form plus conjugates) in human urine and other bodily fluids

Human matrix	Population (*N*)	Origin of samples (country)	Target chemicals	Concentration ranges (and max., median, average, or geometric mean if available)	Detection rates (%)	References
Urine	440 (females)	USA	BP-3	Geometric mean (creatinine-corrected weighted): 27 μg g^{-1}	NA	[49]
Urine	100 (50 males and 50 females)	Greece	BP-1	<1–1,117 ng mL^{-1}	78	[3]
			BP-2	<1–54 ng mL^{-1}	40	
			2,3,4-OH-BP	<1–41 ng mL^{-1}	33	
			BP-8	<2–25 ng mL^{-1}	24	
			4OH-BP	<0.7–47 ng mL^{-1}	23	
Urine	US children (38)	USA and China	BP-3	0.2–713 ng mL^{-1} (geometric mean: 10 ng mL^{-1})	97	[50]
			4-OH-BP	0.1–61 ng mL^{-1} (geometric mean: 0.9 ng mL^{-1})	100	
			BP-1	<0.08–738 ng mL^{-1} (geometric mean: 4 ng mL^{-1})	87	
			BP-2	0.1–18 ng mL^{-1} (geometric mean: 0.2 ng mL^{-1})	29	
			BP-8	<0.2–8 ng mL^{-1} (geometric mean: 0.3 ng mL^{-1})	68	
	US adults (30)		BP-3	0.5–413 ng mL^{-1} (geometric mean: 16 ng mL^{-1})	100	
			4-OH-BP	0.07–6 ng mL^{-1} (geometric mean: 0.3 ng mL^{-1})	93	
			BP-1	0.08–67 ng mL^{-1} (geometric mean: 4 ng mL^{-1})	100	
			BP-2	<0.2–2 ng mL^{-1} (geometric mean: 0.3 ng mL^{-1})	60	
			BP-8	<0.1–1 (geometric mean: 0.2 ng mL^{-1})	53	
	Chinese children (70)		BP-3	0.3–6 ng mL^{-1} (geometric mean: 0.6 ng mL^{-1})	100	
			4-OH-BP	<0.07–0.7 ng mL^{-1} (geometric mean: 0.08 ng mL^{-1})	83	
			BP-1	<0.08–2 ng mL^{-1} (geometric mean: 0.1 ng mL^{-1})	81	
			BP-2		39	

(continued)

Table 6 (continued)

Human matrix	Population (*N*)	Origin of samples (country)	Target chemicals	Concentration ranges (and max., median, average, or geometric mean if available)	Detection rates (%)	References
				<0.2–1.3 ng mL^{-1} (geometric mean: 0.2 ng mL^{-1})		
			BP-8	<0.1–1.4 ng mL^{-1} (geometric mean: 0.09 ng mL^{-1})	20	
	Chinese adults (26)		BP-3	<0.2–9 ng mL^{-1} (geometric mean: 1 ng mL^{-1})	96	
			4-OH-BP	<0.07–6 ng mL^{-1} (geometric mean: 0.08 ng mL^{-1})	77	
			BP-1	0.3–14 ng mL^{-1} (geometric mean: 0.9 ng mL^{-1})	100	
			BP-2	<0.2–23 ng mL^{-1} (geometric mean: 0.9 ng mL^{-1})	77	
			BP-8	<0.1–2 (geometric mean: 0.2 ng mL^{-1})	65	
Urine	506	USA	BP-3	Mean: 60 ng mL^{-1}	100	[6]
Whole blood	101 (children, fetuses, pregnant women, adults)	China	BP-3	<0.4–3 ng mL^{-1}	30–83	[51]
			4OH-BP	0.2–2 ng mL^{-1}	100	
			BP-1	<0.06–0.2 ng mL^{-1}	0–10	
Urine			BP-3	<0.1–45 ng mL^{-1}	25	
			4OH-BP	<0.06–8 ng mL^{-1}	61	
			BP-1	<0.07–20 ng mL^{-1}	57	
Urine	71	USA	BP-3	5–95th percentiles: 4–6,740 ng mL^{-1}	100	[44]
Amniotic fluid	69			5–95th percentiles: not detected–16 ng mL^{-1}	61	
Urine	261 (123 males and 138 females)	Belgium	BP-3	Not detected–663 ng mL^{-1} (geometric mean: 1 ng mL^{-1})	82.8	[43]
Urine	105 (pregnant women)	Puerto Rico	BP-3	25th percentile–maximum: 8–39,700 ng mL^{-1}	99.5–10	[12]
Urine	625 (females)	USA	BP-3	<0.3–5,900 ng mL^{-1}	99	[48]
			BP-1	<0.08–3,200 ng mL^{-1}	93.3	
			4OH-BP	<0.08–22 ng mL^{-1}	83.8	

Table 7 Estimated daily intake of BP-UV filters through biomonitoring data

Target chemicals	Origin of samples (country)	Estimated daily intake (EDI) (μg/kg BW/day)	Equation used	References
Σ_5 BP-UV filters ([BP-1] + [BP-8] + [BP-2] + [2,3,4-OH-BP] + [4OH-BP])	Greece	0.6–1,458 (median: 5.8)	Estimated daily intake (EDI; μg/kg BW/day) = 50 × [Σ_6Parabens] (μg/L) × 1.7 (L/day)/65.5 kg	[3]

The rank order of the studied human biological media for BP-UV filters in descending order is urine > blood plasma or serum > faeces, breast milk, and semen > tissues (liver, kidney, intestine, spleen, brain, heart, testes, placental, skin, and adipose tissue). The most studied class of UV filters is the "benzophenone derivatives" class, and the majority of studies by far are focused on BP-3 (and metabolites) (Table 6).

Calafat et al. [52] determined the total concentrations of BP-3 in 2,517 urine samples (between 2000 and 2004). The concentrations ranged from 0.4 to 21,700 ng mL^{-1}, with a mean value of 23 ng mL^{-1}. Kunisue et al. [48] determined the total concentrations of BP-3 in urine samples from 625 women in ranges from <0.3 to 5,900 ng mL^{-1}. In a biomonitoring study in Greece, Asimakopoulos et al. [3] measured the total concentrations of BP-UV filters (Σ_5BP-UV filters: [BP-1] + [BP-2] + [2,3,4-OH-BP] + [BP-8] + [4OH-BP]) in urine from 100 individuals and also revealed great differences in concentrations, ranging from 0.5 to 1,120 ng mL^{-1}, with a geometrical mean value of 4 ng mL^{-1}. Moreover to our knowledge, the study of Asimakopoulos et al. [3] is the first in which the concentrations of BP-UV filters are expressed on three different bases (volume-, specific gravity-, and creatinine-adjusted bases).

The daily intake assessment of BP-UV filters is more complicated than the other PCPs because of the lack of clear knowledge on metabolic pathways; for example, BP-1 and BP-8 can be found in urine as parent compounds, as they are used directly in sunscreens, but they can also be formed as metabolic products of BP-3 [3]. Thus, taking into consideration that a maximum of 2 % of BP-3 applied on human skin could reach the bloodstream, a factor of 50 was applied to estimate the total exposure amount (50 × 2 = 100 %) [3] (Table 7).

7 Exposure to Insect Repellents

N,*N*-diethyl-m-toluamide (DEET) is the most common active ingredient in insect repellents, and is routinely detected in the environment. Because these insect repellents are sprayed directly on the skin, human exposure is inevitable. DEET is currently registered for use in 225 products in the USA, and it is estimated that the annual usage exceeds 1.8 million kg [53]. DEET is metabolized in the human body

and excreted in urine [54, 55]. Although DEET metabolism is not fully understood, some dealkylated and oxidized metabolites have been reported [1]. The studies on human biomonitoring of DEET are a few compared to the other PCPs. In a study on the general population of the USA (2001–2002), urine samples from 2,535 individuals were analyzed and demonstrated a 95th percentile value of 0.18 ng mL^{-1} [1].

8 Concluding Remarks and Future Perspectives

On the basis of the information presented in this chapter, humans are exposed to a range of chemicals present in PCPs. Toxicological significance of exposure to complex mixture of these chemicals on human health is not known. More information is needed, mostly regarding the importance of the exposure pathways and the factors that affect these exposures. Linking adverse health effects to various PCPs is a very difficult and complicated, and more epidemiological studies are deemed necessary.

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Part III
Determination of Personal Care Productions in the Aquatic Environment

Analytical Methodologies for the Determination of Personal Care Products in Water Samples

Alberto Chisvert and Amparo Salvador

Abstract Personal-care products (PCPs) could reach the aquatic environment and cause a great impact in the aquatic ecosystem. In this sense, the monitoring of these emerging pollutants in the environment yields valuable information. For this reason, analytical methods to determine PCPs in environmental waters are needed. Due to the low concentration of the PCPs, i.e. ng L^{-1}, sensitive methods are needed. This required sensitivity can be achieved by using sensitive analytical techniques during the measurement step, or by employing enrichment techniques during the sample treatment step. Obviously, the combination of both sensitive analytical techniques and extraction techniques considerably improves the quality of the determination.

In this way, in the last years, different analytical methods have been developed to determine PCPs in environmental waters from different origin, i.e., water from sea, lake, river, influent and/or effluent wastewater treatment plant, swimming pool, tap, and groundwater. The aim of this chapter is to compile and discuss the analytical literature dealing with the development and validation of analytical methods for determining PCPs in environmental water samples, emphasizing both the employed sample treatment and the subsequent analytical technique.

Keywords Analytical methods, Insect repellents, Musk fragrances, Preservatives, UV filters

Contents

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M.S. Díaz-Cruz and D. Barceló (eds.), *Personal Care Products in the Aquatic Environment*, Hdb Env Chem (2015) 36: 191–230, DOI 10.1007/698_2014_265,

Abbreviations

ADBI	Celestolide
AHMI	Phantolide
AHTN	Tonalide
APCI	Atmospheric pressure chemical ionization
APPI	Atmospheric pressure photoionization
ATII	Traseolide
BAμE	Bar adsorptive microextraction
BDM	Butyl methoxydibenzoylmethane
BP	Butylparaben
BZ	Benzophenone
BZ1	Benzophenone-1
BZ10	Benzophenone-10
BZ2	Benzophenone-2
BZ3	Benzophenone-3
BZ4	Benzophenone-4
BZ6	benzophenone-6
BZ8	Benzophenone-8
BzP	Benzylparaben
BzPh	Benzylphenol
C18	Octadecyl functionalized silica
C8	Octyl functionalized silica
CAR	Carboxen
CLP	Chlorophene
CMI	Chloromethylisothiazolinone
CPE	Cloud-point extraction
CXL	Chloroxylenol
DART	Direct analysis in real time
DCMI	Dichloromethylisothiazolinone
DEET	*N*,*N*-diethyl-*m*-toluamide
DI	Direct immersion
DLLME	Dispersive liquid–liquid microextraction
DPMI	Cashmeran
dSPE	Dispersive solid phase extraction

dμSPE	Dispersive microsolid phase extraction
ECD	Electronic capture detector
EDP	Ethylhexyl dimethyl PABA
EGS	Ethyleneglycol silicone
EI	Electronic ionization
EMC	Ethylhexyl methoxycinnamate
EP	Ethylparaben
ES	Ethylhexyl salicylate
ESI	Electrospray ionization
EW	Effluent wastewater
FID	Flame ionization detector
GC	Gas chromatography
GCxGC	Two-dimensional gas chromatography
GW	Groundwater
HFLPME	Hollow-fiber liquid-phase microextraction
HHCB	Galaxolide
HMS	Homosalate
HS	Head-space
ICA	Icaridin
IL	Ionic liquid
IMC	Isoamyl methoxycinnamate
IPBC	Iodopropynyl butylcarbamate
IW	Influent wastewater
KWLPME	Knitting wool liquid phase microextraction
LC	Liquid chromatography
LDPE	Low-density polyethylene
LK	Lake
LLE	Liquid–liquid extraction
LVI	Large volume injection
MA	Musk ambrette
MALLE	Membrane-assisted liquid–liquid extraction
MBC	4-Methylbenzylidene camphor
MCNPME	Magnetically confined nanoparticle microextraction
MEPS	Microextraction by packed sorbent
MI	Methylisothiazolinone
MK	Musk ketone
MLOD	Method limit of detection
MM	Musk moskene
MNPs	Magnetic nanoparticles
MP	Methylparaben
MS	Mass spectrometry
MS/MS	Tandem mass spectrometry
MSA	Magnetically stirring assisted
MT	Musk tibetene
MX	Musk xylene

NPCPs	Non-personal care products
OCR	Octocrylene
PA	Polyacrylate
PBO	Piperonyl butoxide
PBS	Phenylbenzimidazole sulphonic acid
PCPs	Personal care products
PDMS	Polydimethylsiloxane
PER	Permethrin
PID	Photoionization detector
PMA	Polymethylmethacrylate
PP	Propylparaben
PS-DVB	Polystyrene divinylbenzene copolymer
PS-DVB/MH	Polystyrene divinylbenzene copolymer modified with hydroxyl groups
PS-DVB/MP	Polystyrene divinylbenzene copolymer modified with pyrrolidone groups
PVP-DVB	Polyvinylpyrrolidone divinylbenzene copolymer
PVP-DVB/MCX	Polyvinylpyrrolidone divinylbenzene copolymer modified with cationic exchange groups
RV	River
SBE	Solvent back extraction
SBSE	Stir-bar sorptive extraction
SDME	Single-drop microextraction
SP	Swimming pool
SPE	Solid-phase extraction
SPME	Solid-phase microextraction
SW	Seawater
TBC	Tetrabromocresol
TC	Temperature-controlled
TCC	Triclocarban
TCS	Triclosan
TD	Thermal desorption
TW	Tap water
UDSA	Up-and-down shaker assisted
USA	Ultrasounds assisted
USAEME	Ultrasounds-assisted emulsification microextraction
UV	Ultraviolet spectrometry
VA	Vortex assisted

1 Introduction

Personal-care products (PCPs) could reach the aquatic environment through direct and indirect sources [1]. Moreover, different studies evidence that some of them present a great impact in the aquatic ecosystem, since some of them can alter the

flora growth [2–4] or present endocrine-disrupting activity in the aquatic fauna [2, 5–9]. This topic was deeply described in a previous chapter.

For these reasons, there has been a growing concern about the quality of environmental waters in the last years. In this sense, the monitoring of these emerging pollutants in the environment yields valuable information. However, there are no official analytical methods to cover this social demand, and then, the development of reliable analytical methods to monitor the presence of these emerging pollutants in the environment is needed. Fortunately, the analytical chemistry community is aware of this situation and in the last two decades, especially in the last five years, different analytical methods focused in the determination of different groups of PCPs (i.e., organic UV filters, musk fragrances, preservatives, and insect repellents) in environmental waters have been published [10–15]. This is an unequivocally reflection of the social concern about the need of preserving the aquatic ecosystem.

Due to the different groups of PCPs and the high number of compounds under each group, the published analytical methods usually focus on the determination of a relatively high number of compounds belonging to a specific group. Moreover, in some cases there are significant differences in the chemical nature of compounds of the same group. Nevertheless, some authors have proposed multi-residue analytical methods where different PCPs belonging to different families are jointly determined with the aim to cover the impact of these different families. However, they do not cover a high number of compounds from the same group but they chose a short representation of compounds from the different groups.

It should be emphasized that the determination of PCPs in environmental waters entails an added drawback, since they appear at a very low concentration. Consequently, sensitive analytical methods are needed. This can be achieved using sensitive analytical techniques during the measurement step or employing enrichment techniques during the sample treatment step. Obviously, the combination of both sensitive analytical techniques and extraction techniques improves considerably the quality of the determination.

Regarding sensitive analytical techniques, mass spectrometry (MS), or even MS in tandem (MS/MS), coupled with either liquid chromatography (LC) or gas chromatography (GC), depending on the physico-chemical properties of the target compounds, shows higher sensitivity than other classical detectors like ultraviolet-visible spectrometry (UV–Vis) for LC or flame ionization detection (FID) for GC.

Regarding enrichment techniques, extraction techniques play a crucial role, since they can be used not only for enrichment purposes but also for separating the target compounds from potentially interfering compounds. In this sense, classical extraction techniques like liquid–liquid extraction (LLE) or solid-phase extraction (SPE) have been used. Nevertheless, other more modern techniques based on the 'microextraction' concept have been employed, either in solid or in liquid phase. These techniques try to minimize the high volumes of the hazardous organic solvents employed in both LLE and SPE, besides reducing the extraction time and improving the enrichment factors.

In this way, different analytical methods have been developed to determine PCPs in environmental waters from different origin, i.e., water from sea, lake, river, influent and/or effluent wastewater treatment plant, swimming pool, tap, and groundwater. In general terms, water is sampled and collected in pre-rinsed glass bottles, transferred to the laboratory and analyzed. However, in some cases, passive samplers, such as semipermeable membrane devices (SPMD) that trap non-polar compounds [16–19] are left during large periods of time (i.e., days, weeks or even months) in the desired aquatic ecosystem (lake, river, etc.) to monitor the amounts of UV filters. These devices mimic the natural bioaccumulation in the fatty tissues of aquatic organisms, allowing to estimate the exposure of these aquatic organisms to the PCPs. Similarly, polar organic chemical integrative samplers (POCIS) that trap hydrophilic compounds [20, 21] have also been used. These devices mimic the respiratory exposure of aquatic organisms.

The aim of this chapter is to compile and discuss the analytical literature dealing with the development and validation of analytical methods for determining PCPs in environmental water samples, emphasizing both the employed sample treatment and the subsequent analytical technique. Table 1 lists, in a chronological order, those published papers dealing with UV filters. In the same way, Table 2 is devoted to musk fragrances, Table 3 to preservatives, and finally Table 4 to insect repellents. Those papers focused on the application of an analytical method to measure the removal rate of PCPs in wastewater treatment plants or the occurrence of the PCPs in waters are not considered here, but they are dealt in depth in [138–140], respectively.

2 Extraction Techniques

Due to the complexity of the matrix, e.g., high organic matter in case of influent and effluent wastewater, high salt content in case of seawater or high chlorine content in case of water from swimming pool, it is usual to employ extraction techniques in order to isolate the target compounds from the rest of the matrix, thus avoiding interferences in the subsequent measurement including suppression or enhancement in MS. Nevertheless, as mentioned previously, extraction techniques are also employed to concentrate the target compounds and thus achieve the determination at lower concentration levels.

In case of traditional extraction techniques, high enrichment factors are usually obtained in both LLE and SPE. This is the result of employing high amounts of sample (up to 1,000 mL). Although high amounts of extracting or eluting solvents, respectively, are used, the obtained extracts are evaporated and the residues reconstituted in less than 1 mL of a solvent compatible with the subsequent analytical instrument. This means that if the extraction efficiency (i.e., the amount extracted) was around 100%, an enrichment factor up to 1,000 would be achieved. To increase the extraction efficiency and thus the enrichment factor, the nature of the solvent (in both LLE and SPE) or the nature of the sorbent (in case of SPE) plays

Table 1 Published papers on UV filters determination in environmental water samples (chronological order)[a]

Target compounds	Water origin	Extraction technique	Analytical technique	MLOD (ng L^{-1})	Recoveries (%)	References
BZ3, EDP	Seawater Swimming pool	*(DI)SPME* (5 mL sample; PDMS fiber; 45 min; thermal desorption)	(TD)GC-MS(EI^+)	360–750	85–97 (SW) 94–95 (SP)	[22]
		(HS)SPME (5 mL sample; PDMS fiber; 45 min; thermal desorption)		220–1,340	91–98 (SW) 89–97 (SP)	
BDM, BZ3, EMC, MBC	Seawater Swimming pool	*SPE* (500 mL sample; C18 disks; 50 µL (LC) or 10 µL (GC) final volume)	LC-UV (for BDM)	7.3	87 (SW) 88 (SP)	[23]
			GC-MS(EI^+) (for the rest)	0.21–0.42	93–96 (SW) 96–99 (SP)	
BDM, BZ3, EMC, MBC, PBS	Seawater	*CPE-SBE* (50–100 mL sample; Triton X-114 + methanol (LC) or hexane (GC); 50–100 µL final volume)	LC-UV (for BDM and PBS)	300–1,270	95–99	[24]
			GC-MS(EI^+) (for the rest)	2.2–30.0	97–102	
BZ, BZ3, BZ10	River	*SBSE* (10 mL sample; PDMS stir bar; 120 min; thermal desorption)	(TD)GC-MS(EI^+)	0.5–1	98–115	[25]
BZ, BZ1, BZ3, BZ8 and others	River Lake	*LLE* (100 mL sample ; 50 µL final volume)	GC-MS(EI^+)	5–10	62–114	[26]
BDM, BZ3, EMC, HS, MBC, OCR (and other PCPs and NPCPs)	Seawater Swimming pool Lake River	*SPE* (500 mL sample; PS-DVB/MP cartridges; 500 µL final volume)	GC-MS(EI^+)	13–129 (SW) 27–266 (SP) 17–194 (LK) 26–181 (RV)	75–93 (SW) 60–95 (SP) 50–93 (LK) 65–97 (RV)	[27]
BZ1, BZ2, BZ3, BZ4 (and other PCPs and NPCPs)	River Influent/effluent wastewater	*SPE* (250–1,000 mL sample; PVP-DVB/MCX cartridges; 0.5 mL final volume)	LC-MS/MS(ESI^-)	0.1–5 (RV) 1–30 (IW) 0.5–25 (EW)	67–117 (RV) 17–50 (IW) 24–118 (EW)	[28]
BZ, BZ3, BZ10	River	*(DI)SDME* (2 mL sample; 15 min ; 2 µL final volume)	GC-MS(EI^+)	10	93–101	[29]
BZ1, BZ3, BZ10 and others	River	*SBSE* (10 mL sample; PDMS stir bar; 120 min; thermal desorption)	(TD)GC-MS(EI^+)	0.5–2	102–128	[30]
BDM, BZ3, EDP, EMC, ES, HS, IMC, MBC, OCR	Lake River Effluent wastewater	*SBSE* (20 mL sample; PDMS stir bar; thermal desorption)	(TD)GC-MS(EI^+)	0.2–63	78–109 (LK) 77–116 (RV) 75–115 (EW)	[31]

(continued)

Table 1 (continued)

Target compounds	Water origin	Extraction technique	Analytical technique	MLOD (ng L^{-1})	Recoveries (%)	References
BDM, BZ3, BZ4, EDP, IMC, MBC, OCR, PBS, PDT	River Seawater Influent/effluent wastewater	*SPE* (200 mL sample; PVP-DVB cartridges; 1 mL final volume)	LC-MS/MS($ESI^{+/-}$)	7–46	74–102 (RV) 66–91 (SW) 29–93 (IW) 55–108 (EW)	[32]
BZ3, BZ4, EDP, EMC, IMC MBC, OCR, PBS (and other PCPs and NPCPs)	Tap water Seawater Influent/effluent wastewater	*SPE* (200–500 mL sample; PVP-DVB cartridges; 1 mL final volume)	LC-MS/MS($ESI^{+/-}$)	0.6–30	66–115 (TW) 77–128 (SW) 69–104 (IW) 56–132 (EW)	[33]
BDM, BZ3, BZ4, EDP, EMC, ES, HS, IMC, MBC, OCR, PBS	Influent/effluent wastewater	*SPE* (200 mL sample; PVP-DVB cartridges; 30 mL methanol; 1 mL final volume)	LC-MS/MS($ESI^{+/-}$)	500–5,950	15–70 (IW) 29–106 (EW)	[34]
			LC-MS/MS($APPI^{+/-}$)	700–8,340	18–85 (IW) 45–113 (EW)	
BZ1, BZ3, BZ8, ES, HS	River Influent/effluent wastewater	*(DI)SPME* (10 mL sample; PDMS-DVB fibres; 30 min; thermal desorption)	(TD)GC-MS(EI^+)/MS	0.15–3	97–106 (RV) 48–93 (IW) 89–115 (EW)	[35]
BDM, BZ3, EDP, EMC, ES, HS, IMC, MBC, OCR	Lake Influent/effluent wastewater	*MALLE* (15 mL sample; LDPE bags with 100 µL propanol; 120 min; 100 µL final volume)	LC-MS/MS($APPI^{+/-}$)	0.4–16	66–106 (LK) 35–86 (IW) 52–114 (EW)	[36]
BZ1, BZ8, BZ3, OCR, EDP (and other PCPs)	River Influent/effluent wastewater	*SPE* (100–500 mL sample; PS-DVB/MH cartridge; 5 mL final volume)	LC-MS/MS($ESI^{+/-}$)	1–4 (RV) 3–10 (IW, EW)	46–101 (RV) 27–89 (IW) 20–92 (EW)	[37]
BZ1, BZ2, BZ3, BZ4, BZ6, BZ8	River Influent/effluent wastewater	*SPE* (200–500 mL; PVP-DVB cartridges; 3 mL methanol; 1 mL final volume)	LC-MS/MS($ESI^{+/-}$)	0.1–2.4 (RV) 0.3–9.7 (IW) 0.2–4.2 (EW)	84–105 (RV) 83–101 (IW) 91–104 (EW)	[38]
BZ3, EMC, MBC, OCR (and other PCPs and NPCPs)	River Effluent wastewater	*LLE* (500 mL sample; 1.2–3 mL final volume)	(LVI)GC-MS(EI^+)	4–12 (RV) 10–30 (EW)		[39]
BZ, OCR (and other PCPs and NPCPs)	Tap water Effluent wastewater	*SPE* (200 mL sample; PS-DVB/MP cartridges; 0.2 mL final volume)	GC-MS(EI^+)	5–10	90–96	[40]
BZ3, EDP, ES, HS, MBC, OCR	Lake	*SBSE* (250 mL; PDMS stir bar, 20 h; DART)	MS($DART^+$)	0.28–4.3		[41]

BZ3, EDP, EMC IMC, MBC, OCR	Seawater River	*IL-(DI)SDME* (20 mL sample; 37 min; ~10 μL final volume)	LC-UV	60–3,000	92–107 (SW) 96–115 (RV)	[42]
BZ1, BZ2, BZ3, BZ4, PBS (and other PCPs and NPCPs)	River Influent/effluent wastewater	*SPE* (100–1,000 mL sample; PVP-DVB cartridges; 500 μL final volume)	LC-MS/MS($ESI^{+/-}$) LC-MS/MS($APCI^{+/-}$)	0.15–1.5 (RV) 1.5–15 (IW) 0.75–7.5 (EW)	53–130 (RV) 96–180 (IW) 66–105 (EW) 82–135 (RV) 59–107 (IW) 62–117 (EW)	[43]
BZ3, MBC, OCR, EMC (and other PCPs)	Lake Effluent wastewater	*MEPS* (800 μL sample; C8 sorbent; 50 μL final volume)	(LVI)GC-MS(EI^+)	35–87	61–109	[44]
BZ3, BZ8, EDP, OCR (and other PCPs)	River Influent/effluent wastewater	*SBSE* (50 mL sample; PDMS stir bar; 180 min; 200 μL final volume)	LC-MS/MS($ESI^{+/-}$)	2.5 (RV) 5–10 (IW, EW)	31–87 (RV) 25–84 (IW) 28–89 (EW)	[45]
BDM, BZ3, EMC, HS	Seawater Swimming pool	*(on-line)SPE* (9 mL sample; PVP-DVB cartridges; 0.9 mL final volume)	LC-UV	450–3,200		[46]
BZ1, BZ3, BZ8 + other	Seawater	*DLLME* (5 mL sample; 60 μL final volume)	GC-MS(EI^+)	32–50	65–222	[47]
BZ3, EDP, EMC, ES, HS, IMC, MBC, OCR	River Swimming pool Influent/effluent wastewater	*DLLME* (10 mL sample; 45 μL drop volume)	GC-MS(EI^+)	0.6–4.2	87–109 (RV, SP, EW) 80–117 (IW)	[48]
BZ3, ES, MBC, OCR (and other PCPs)	River	*(DI)SPME* (3 mL sample; PDMS fiber, 90 min; thermal desorption)	(TD)GC-MS(EI^+)	0.2–2.0	64–117	[49]
BZ3 (and other PCPs and NPCPs)	River	*SPE* (200 mL sample; PS-DVB/MP cartridges; 100 μL final volume)	GCxGC-MS(EI^+)	40	94	[50]
BZ1, BZ3 + others	Lake	*MSA-DLLME* (20 mL sample; 80 μL drop volume)	LC-UV	200–800	91–97	[51]
BZ3, EDP, EMC, ES, HS, IMC, MBC, OCR	River Swimming pool Influent/effluent wastewater	*(DI)SPME* (100 mL sample; silicone discs; 14 h; 0.2 mL final volume)	(LVI)GC-MS(EI^+)	1–12	90–104 (RV) 76–93 (SP) 49–108 (IW) 75–93 (EW)	[52]
BZ3, EDP, EMC, ES, HS, IMC, MBC, OCR	Seawater Tap water River	*dSPE* (75 mL sample; $CoFe_2O_4$@olceic acid MNPs sorbent; 4 min; 50 μL final volume)	GC-MS(EI^+)	0.2–6.0	73–125 (SW) 63–110 (TW) 74–119 (RV)	[53]
BDM, BZ3, EMC, ES, HS, MBC, OCR	Effluent wastewater	*SPE* (500 mL sample; PS-DVB cartridges; 1 mL final volume)	LC-UV		76–130	[54]

(continued)

Table 1 (continued)

Target compounds	Water origin	Extraction technique	Analytical technique	MLOD (ng L^{-1})	Recoveries (%)	References
BZ3, EDP, EMC, ES, HS, OCR	Seawater	*SBSE* (10 mL sample; PDMS stir bars; 180 min; 1 mL final volume)	LC-MS/MS(APCI$^{+/-}$)	8–1,200	71–100	[55]
BZ3, EMC, MBC (and other PCPs and NPCPs)	River Effluent wastewater	*SBSE* (100 mL sample; PDMS stir bars; 14 h; thermal desorption)	(TD)GCxGC-MS(EI^{+})	0.02–0.18 (RV) 0.04–0.07 (WE)	109–146 (RV) 81–141 (EW)	[56]
BDM, BZ3, BZ4, BZ8, EDP, EMC, OCR	Tap water Seawater	*SPE* (200 mL sample; PVP-DVB cartridges; 0.5 mL final volume)	LC-MS/MS(ESI^{+})	0.5–25	74–109 (TW) 71–111 (SW)	[57]
BZ3, EDP, EMC, MBC, OCR	Tap water	*SPE* (200 mL sample; C18 cartridges; 0.5 mL final volume)	GC-MS(EI^{+})	0.14–7.4	74–111	[58]
BZ, BZ1, BZ3, MBC	River Tap water	*IL-(DI)HFLPME* (10 mL sample; 50 min; ~7 µL final volume)	LC-UV	300–500	83–106 (TW) 95–105 (RV)	[59]
BZ, BZ3 (and other PCPs and NPCPs)	Tap water	*(DI)SPME* (40 mL sample; PA fibers; 125 min; thermal desorption)	(TD)GC-MS(EI^{+})	2–9	75–110	[60]
BZ, BZ3, ES, HS, MBC	River	*(DI)SPME* (7 mL sample; graphene sorbent; 40 min; thermal desorption)	(TD)GC-MS(EI^{+})	0.5–6.8	99–114	[61]
BZ, BZ3, ES, HS	Swimming pool River Tap water	*IL-USA-DLLME* (10 mL sample; ~17 µL drop volume)	LC-UV	200–5,000	81–117 (TW) 81–118 (RV) 71–117 (SP)	[62]
BZ, BZ1, BZ3, ES, HS + other	River	*VA-DLLME* (10 mL sample; 50 µL drop volume)	GC-MS(EI^{+})	8–45	76–120	[63]
BZ3, MBC + others	River Tap water	*IL-USAEME* (1.5 mL sample; 60 µL drop volume)	LC-UV	500–1,000	96–107 (RV) 96–105 (TW)	[64]
BZ3, EDP, EMC, ES, HS, OCR	Seawater River Wastewater	*SBSE* (50 mL sample; PDMS stir bars; 5 h; 1 mL final volume)	LC-MS/MS(APCI^{+})	0.6–114	64–85	[65, 66]
BZ, BZ1, BZ2, BZ3, BZ4 (and other PCPs and NPCPs)	River Seawater Lake Effluent wastewater	*SPE* (100 mL sample; PVP-DVB cartridges; 1 mL final volume)	LC-MS/MS(ESI$^{+/-}$)	0.1–1 (RV, SW, LK) 2–12 (EW)	70–120	[67]

BZ3, OCR (and other PCPs and NPCPs)	Seawater Influent/effluent wastewater	*SBSE* (100 mL sample, PDMS stir bars, 8 h; 200 μL final volume)	GC-MS(EI^+)	0.6–2	28–60	[68]
BZ, BZ3, ES, HS	Swimming pool Tap water	*IL-TC-DLLME* (10 mL sample; ~18 μL final volume)	LC-UV	200–5,000	88–116 (SP) 91–104 (TW)	[69]
BZ1, BZ3, BZ8, PBS	River	*(in-line)SPE* (1,000 mL sample; PVP-DVB/MCX cartridges; 0.5 mL final volume)	CE-MS(ESI^-)	10–50		[70]
BZ, BZ1, BZ3	Swimming pool	*KWLPME* (20 mL sample; polyester wool; 30 μL final volume)	LC-UV	20–30	77–103	[71]
BZ, BZ3, BZ8	Swimming pool Lake Effluent wastewater	*IL-UDSA-DLLME* (5 mL sample; 40 μL final volume)	LC-UV	200–1,300	92–112 (SP) 93–109 (LK) 96–120 (EW)	[72]
BZ1, BZ2, BZ3, BZ4, BZ8, MBC + other	River Groundwater Influent/effluent wastewater	*(on-line)SPE* (5 mL sample; PS-DVB cartridges)	LC-MS/MS($ESI^{+/-}$)	0.3–3 (GW) 0.5–3.5 (RV) 5–10 (IW) 1–4 (EW)	86–101 (GW) 65–89 (RV) 18–40 (IW) 37–63 (EW)	[73]
BZ, BZ3 and other	River	*(DI)SPME* (10 mL sample; C12-Ag wire; 0.2 mL final volume)	LC-UV	580–1,860	70–102	[74]
BZ1, BZ3, BZ8, ES, HS	River Effluent wastewater	*USA-DLLME* (10 mL sample; 5 μL final volume)	GC-MS(EI^+)	1–2	70–93 (RV) 73–91 (EW)	[75]
BZ3, EDP, EMC, ES	River Effluent wastewater	*IL-USA-DLLME* (10 mL sample; ~30 μL final volume)	LC-UV	60–160	93–114	[76]
BZ, BZ1, BZ3 + other	Seawater Effluent wastewater	*BAμE* (25 mL sample; pyrrolidone or activated carbon sorbents; 4 or 16 h; 1.5 mL final volume)	LC-UV	300–500		[77]
BZ3, EMC, ES, OCR + other	Influent/effluent wastewater	*SPE* (500 mL sample; PS-DVB/MP cartridges; 1 mL final volume)	GC-MS/MS(EI^+)	2	62–107	[78]
BDM, BZ, MBC, (and other PCPs and NPCPs)	River	*SPE* (1,000 mL sample; C18 cartridges; 2 mL final volume)	LC-MS/MS($ESI^{+/-}$)	12	59–93	[79]

(continued)

Table 1 (continued)

Target compounds	Water origin	Extraction technique	Analytical technique	MLOD (ng L^{-1})	Recoveries (%)	References
BZ1, BZ3, BZ8 (and other PCPs and NPCPs)	Influent/effluent wastewater	*SBSE* (50 mL sample; EGS stir bars; 4 h; 2 mL final volume)	LC-MS/MS($ESI^{+/-}$)	5–10		[80]
BZ3, EDP, EMC, ES, HS, IMC, MBC, OCR	Seawater	*DLLME* (5 mL sample; ~50 µL final volume)	GC-MS(EI^{+})	10–30	82–117	[81]
BZ, BZ1, BZ3, BZ8 + others) (and other NPCPs)	Lake River Seawater Tap water	*SPE* (800 mL sample; PVP-DVB cartridges; 600 µL final volume)	GC-MS(EI^{+})	0.1–1.6 (LK) 0.2–1.9 (RV) 0.2–1.7 (SW) 0.4–1.3 (TW)	98–110	[82]

[a]See list for key abbreviations

Table 2 Published papers on musk fragrances determination in environmental water samples (chronological order)[a]

Target compounds	Water origin	Extraction technique	Analytical technique	MLOD (ng L^{-1})	Recoveries (%)	References
HHCB, ADBI, AHTN MK	River	*(DI)SPME* (3.5 mL sample; PDMS-DVB, 45 min; thermal desorption)	GC-MS(EI^+)	14–22		[83]
MX, MK, MA, MT, MM HHCB, AHTN, ATII, ADBI, DPMI, AHMI, AETT	Effluent wastewater	*(on-site)SPE* (60 L sample; PMA-DVB cartridges; 1 mL final volume)	GC-MS(EI^+)	0.02–0.30		[84]
DPMI, ADBI, AHMI, ATII, HHCB, AHTN	Influent/effluent wastewater	*(HS)SPME* (10 mL sample; CAR-DVB or PDMS-DVB fibers; 25 min; thermal desorption)	GC-MS(EI^+)	0.1–9		[85]
MX, MM, MT, MK	Tap water Influent/effluent wastewater	*(HS)SPME* (10 mL sample; CAR-DVB or PDMS-DVB fibers; 25 min; thermal desorption)	GC-ECD	0.25–3.60	84–106 (TW) 92–102 (IW) 96–108 (EW)	[86]
MX, MM, MK DPMI, ADBI, HHCB, AHTN, AHMI, ATII (and other NPCPs)	Tap water Swimming pool Seawater Influent/effluent wastewater	*USAEME* (10 mL sample; <100 µL final volume)	GC-MS(EI^+)	6–29	80–91 (SW) 86–103 (SP) 85–113 (IW) 88–114 (EW)	[87]
HHCB, AHTN, ADBI, ATII, DPMI, AHMI	Effluent wastewater	*(HS)SPME* (20 mL sample; PDMS-DVB fiber; 4 min; thermal desorption)	GC-MS(EI^+)	0.05–0.1	64–89	[88]
ADBI, AHMI, ATII, HHCB, AHTN (and other NPCPs)	Seawater River Lake	*DLLME* (5 mL sample; 20 µL final volume)	GC-MS(EI^+)	7–60 (SW) 7–64 (RV) 7–69 (LK)	65–92 (SW) 61–89 (RV) 60–84 (LK)	[89]
MK, MX ADBI, AHMI, ATII, HHCB, AHTN (and other PCPs and NPCPs)	River Effluent wastewater	*LLE* (500 mL sample; 1.2–3 mL final volume)	(LVI)GC-MS(EI^+)	0.4–11 (RV) 1–21 (EW)		[39]
HHCB, AHTN MX, MK	Lake Groundwater Influent/effluent wastewater	*SPE* (1 L sample; C18 cartridges; 1 mL final volume)	GC-MS(EI^+)	0.09–0.18	86–107	[90]
ADBI, HHCB, AHTN MK	Tap River	*SBSE* (30 mL sample; PDMS sorbert; 4 h; 200 µL final volume)	(LVI)GC-MS(EI^+)	12–19	84–108	[91]

(continued)

Table 2 (continued)

Target compounds	Water origin	Extraction technique	Analytical technique	MLOD (ng L^{-1})	Recoveries (%)	References
	Seawater Influent/effluent wastewater					
HHCB, AHTN (and other NPCPs)	Lake Effluent wastewater	*MEPS* (800 µL sample; C8 sorbent; 50 µL final volume)	GC-MS(EI^+)	37–54	57–109	[44]
ADBI, AHMI, ATII, HHCB, AHTN (and other PCPs)	River	*(DI)SPME* (3 mL sample; PDMS fiber, 90 min; thermal desorption)	(TD)GC-MS(EI^+)	0.4–9.6	64–117	[49]
DPMI, ADBI, HHCB, AHTN ambrettolide (and other NPCPs)	River	*SPE* (200 mL sample; PS-DVB cartridges; 100 µL final volume)	GCxGC-MS(EI^+)	2–51	41–96	[50]
DPMI, ADBI, AHMI, ATII, HHCB, AHTN MX, MM, MK	River Influent/effluent wastewater	*SBSE* (100 mL sample; PDMS stir bar; 4 h; thermal desorption)	(TD)GC-MS(EI^+)	0.02–0.3	82–95	[92]
MA, MX, MK, MM HHCB, AHTN, DPMI, ADBI, AHMI, ATII Muscone, ethylene brassilate, globalide, thibetolide	River Influent/effluent wastewater Groundwater	*SBSE* (30 mL sample; PDMS stir bar; 240 min; thermal desorption)	(TD)GC-MS(EI^+)	2–24		[93]
MA, MX, MT, MM, MK	Seawater River Irrigation channel Influent/effluent wastewater	*DLLME* (5 mL sample; ~10 µL final volume)	GC-MS(EI^+)	4–33	87–93 (SW) 92–105 (RV) 99–106 (IC) 98–109 (IW) 93–116 (EW)	[94]
MK, MX HHCB, AHMI, AHTN, ATII	River Effluent wastewater	*SBSE* (100 mL sample; PDMS sorbent; 14 h; thermal desorption)	(TD)GCxGC-MS(EI^+)	0.04–1.86 (RV) 0.02–2.54 (WE)	123–153 (RV) 101–161 (EW)	[56]
HHCB, AHTN, DPMI, ADBI, AHMI, ATII	River Effluent wastewater	*USA-DLLME* (10 mL sample; 5 µL final volume)	GC-MS(EI^+)	0.2	70–98 (RV) 75–90 (EW)	[95]
HHCB MK (and other PCPs and NPCPs)	Tap water	*(DI)SPME* (40 mL sample; PA fibers; 125 min; thermal desorption)	(TD)GC-MS(EI^+)	2–9	75–110	[60]
DPMI, ADBI, AHMI, ATII, HHCB, AHTN	River Influent/effluent wastewater	*SBSE* (100 mL sample; PDMS stir bars; 4 h; thermal desorption)	GC-MS(EI^+)	0.02–0.3		[96]

MX, MM, MK (and other PCPs)						
DPMI, ADBI, AHMI, ATII, HHCB, AHTN	Influent/effluent wastewater	*IL-(HS)SDME* (10 mL sample (1:2); 45 min; 1 μL final volume)	GC-MS/MS(EI^+)	10–30		[97]
MA, MX, MK; MM						
DPMI, ADBI, AHMI, ATII, HHCB, AHTN	Influent/effluent wastewater	*MALLE* (150 mL; 240 min; LDPE bags with 200 μL hexane; 200 μL final volume)	(LVI)GC-MS(EI^+)	4–25	47–124 (IW) 50–126 (EW)	[98]
MX, MK; MM	Estuary				69–138 (ES)	
MA, MX, MT, MM, MK	Seawater River Effluent wastewater	*SPE* (200 mL sample; MIS sorbent; 200 μL final volume)	GC-MS(EI^+)	1.5–2.7		[99]
DPMI, ADBI, AHMI, ATII, HHCB, AHTN	Influent/effluent wastewater Estuary	*MEPS* (5.5 mL sample; C18 sorbent; 50 μL final volume)	(LVI)GC-MS(EI^+)	5–25 (IW) 7–39 (EW)	76–135 (IW) 75–133 (EW)	[100]
MA, MK, MM				8–84 (ES)	81–102 (ES)	
HHCB, AHTN, AHDI, ATII, DPMI	Tap water Lake Effluent wastewater	*SPE* (1,000 mL sample; PVP-DVB cartridges; 1 mL final volume)	GC-MS/MS(EI^+)	1.04–1.56 (TW) 1.01–2.04 (LK) 1.01–2.01 (EW)	87–112 (TW) 93–116 (LK) 96–113 (EW)	[101]
ADBI, AHMI, ATII, HHCB, AHTN	River	*dμSPE* (10 mL sample; C18 sorbent; 1 min; thermal desorption)	(TD)GC-MS(EI^+)	0.5–1	80–93	[102]

[a]See list for key abbreviations

Table 3 Published papers on preservatives determination in environmental water samples (chronological order)[a]

Target compounds	Water origin	Extraction technique	Analytical technique	MLOD (ng L^{-1})	Recoveries (%)	References
TCS and others	River Influent/effluent wastewater	*(DI)SPME* (22 mL sample; PA fibers; 30 min; thermal desorption)	GC-MS(EI^+)	2–7 (RV) 4–14 (IW, EW)	95–105	[103]
MP, EP, PP, BP, BzP	River Influent/effluent wastewater	*(DI)SPME* (10 mL sample; PA fiber; 40 min; thermal desorption)	GC-MS/MS(EI^+)	0.3–8	98–114 (RV) 92–104 (IW) 87–96 (EW)	[104]
TCS	Seawater River Influent/effluent wastewater	*SPE* (1,000 mL sample; C18 cartridges; 0.2 mL final volume)	GC-MS/MS(EI^+)	0.25	83–110	[105]
TCS	Tap water	*(DI)HFLPME* (10 mL sample; 20 min; ~5 μL final volume)	GC-MS(EI^+)	20	84–114	[106]
CLP, TCS (and other PCPs)	Seawater Swimming pool Lake River	*SPE* (500 mL sample; PS-DVB/MP cartridges; 500 μL final volume)	GC-MS(EI^+)	143–163 (SW) 113–178 (SP) 10–28 (LK) 17–18 (RV)	88–95 (SW) 87–98 (SP) 79–96 (LK) 81–97 (RV)	[27]
MI, CMI and others	Tap water River Influent/effluent wastewater	*SPE* (500 mL sample; C18/PS-DVB/MP cartridges; 200 μL final volume)	GC-MS(EI^+)	8–21 (TW) 80–210 (IW) 40–104 (EW)	10–103	[107]
MP, EP, PP, BP CLP, TCS, CXL, TBC, BzPh (and other PCPs and NPCPs)	River Influent/effluent wastewater	*SPE* (250–1,000 mL sample; PVP-DVB/MCX cartridges; 0.5 mL final volume)	LC-MS/MS(ESI^-)	0.05–5 (RV) 0.6–31 (IW) 1–26 (EW)	40–140 (RV) 6–139 (IW) 8–186 (EW)	[28]
TCS	Influent/effluent wastewater	*SBSE* (25 mL sample; PDMS stir bars; 1 h; 200 μL final volume)	LC-UV	100		[108]
TCS	River	*SBSE* (10 mL sample; PDMS stir bars; 120 min; thermal desorption)	(TD)GC-MS(EI^+)	5	92–108	[109]
MP, EP, PP, BP, BzP	Tap water River Influent/effluent wastewater	*SPE* (500 mL sample; PVP-DVB cartridges; 2 mL final volume)	(LVSS)CE-UV	25–31	97–104 (TW) 99–106 (RV) 62–94 (IW) 90–111 (EW)	[110] [111]
MP, EP, PP, BP	River	*(DI)SDME* (3 mL sample; 20 min; ~3 μL final volume)	GC-MS(EI^+)	1–15	72–99	[112]

TCS (and other PCPs and NPCPs)	Tap water Seawater Influent/effluent wastewater	*SPE* (200–500 mL sample; PVP-DVB cartridges; 1 mL final volume)	LC-MS/MS($ESI^{+/-}$)	6	82 (TW) 79 (SW) 57 (IW) 105 (EW)	[33]
TCS	Tap water River Influent/effluent wastewater	*DLLME* (10 mL sample; 39 μL final volume)	GC-MS/MS(EI^{+})	0.6–1.5	103 (TW) 103 (RV) 93 (IW) 96 (EW)	[113]
TCS, TCC	Tap water River Effluent wastewater Irrigation channel	*DLLME* (5 mL sample; 35 μL final volume)	LC-UV	42–134	81–106 (TW) 71–96 (RV) 77–81 (EW) 64–85 (IC)	[114]
MP, EP, PP, BP, BzP TCS, TCC	River Influent/effluent wastewater Lake	*SPE* (200–500 mL sample; PVP-DVB cartridges; 1 mL final volume)	LC-MS/MS(ESI^{-})	0.008–20 (RV) 0.02–50 (IW)	69–118 (RV) 62–137 (IW) 69–123 (EW)	[115]
MP, EP, PP, BP TCS (and other NPCPs)	River Swimming pool Influent/effluent wastewater	*(HS)SPME* (10 mL sample; DVB-CAR-PDMS fibers; 15 min, thermal desorption)	GC-MS/MS(EI^{+})	4–17	85–102	[116]
MP, EP, PP, BP TCS (and other NPCPs)	River Swimming pool Influent/effluent wastewater	*USAEME* (10 mL sample; 5 min; ~100 μL final volume)	GC-MS/MS(EI^{+})	4–16	85–94	[117]
MP, EP, PP, BzP TCS, TCC (and other PCPs)	River Influent/effluent wastewater	*SPE* (100–500 mL sample; PS-SDV/MH cartridge; 5 mL methanol/5 mL dichloromethane; 5 mL final volume)	LC-MS/MS(ESI^{-})	1–3 (RV) 3–10 (IW, EW)	69–101 (RV) 27–85 (IW) 20–92 (EW)	[37]
TCS (and other PCPs and NPCPs)	River Effluent wastewater	*LLE* (500 mL sample; 1.2–3 mL final volume)	(LVI)GC-MS(EI^{+})	18 (RV) 44 (EW)		[39]
CLP, TCC, TCS, IPBC (and other PCPs and NPCPs)	River Influent/effluent wastewater	*SPE* (100–1,000 mL; PVP-DVB cartridges; 500 μL final volume)	LC-MS/MS($ESI^{+/-}$) LC-MS/MS($APCI^{+/-}$)	0.15–0.6 (RV) 1.5–15 (IW) 0.75–7.5 (EW)	97–120 (RV) 95–108 (IW) 90–100 (EW) 106–128 (RV) 93–110 (IW) 99–112 (EW)	[43]
TCC, TCS (and other PCPs)	River Influent/effluent wastewater	*SBSE* (50 mL sample; PDMS stir bar; 180 min; 200 μL final volume)	LC-MS/MS($ESI^{+/-}$)	2.5 (RV) 5 (IW, EW)	50–87 (RV) 46–89 (IW) 44–84 (EW)	[45]

(continued)

Table 3 (continued)

Target compounds	Water origin	Extraction technique	Analytical technique	MLOD (ng L^{-1})	Recoveries (%)	References
TCC	Effluent wastewater	*SBSE* (10 mL sample; PDMS stir bars; 22 h; 1.5 mL final volume)	LC-MS/MS(ESI^-)	1	92–96	[118]
TCC, TCS	Tap water Effluent wastewater	*IL-DLLME* (5 mL sample; ~100 μL final volume)	LC-MS/MS(ESI^-)	40–580	72–103 (TW) 70–98 (EW)	[119]
MP, EP, PP, BP, BzP TCS	River Influent/effluent wastewater	*MALLE* (18 mL sample; LDPE bags with 400 μL chloroform; 90 min; 400 μL final volume)	(LVI)GC-MS/MS(EI^+)	0.1–1.4	83–104	[120]
MI, CMI, DCMI	Tap water River Effluent wastewater	*Direct injection*	(LVI)LC-MS/MS ($APCI^+$)	30–110	82–109 (TW) 21–99 (RV) 10–95 (EW)	[121]
TCS (and other PCPs and NPCPs)	River	*SPE* (200 mL sample; PS-DVB/MP cartridges; 100 μL final volume)	GCxGC-MS(EI^+)	3	93	[50]
TCS (and other PCPs and NPCPs)	River Effluent wastewater	*SBSE* (100 mL sample; PDMS sorbent; 14 h; thermal desorption)	(TD)GCxGC-MS(EI^+)	0.06 (RV) 0.12 (WE)	144 (RV) 147 (EW)	[56]
TCS	River Influent/effluent wastewater	*SPE* (100 mL sample; C18 cartridges; 100 μL final volume)	(LVI)GC-MS(EI^+)	0.4	78–110 (RV) 60–71 (IW) 73–99 (EW)	[122]
MP, PP, BP, BzP TCS	Tap water Influent/effluent wastewater	*SBSE* (5 mL sample; PDMS stir bars; 60 min; thermal desorption)	(TD)GC-MS(EI^+)	0.54–4.12		[123]
MP, EP, PP, BP TCS	Influent/effluent wastewater	*MEPS* (2 mL sample; C18 sorbent; 50 μL final volume)	(LVI)GC-MS(EI^+)	10–590	86–120	[124]
TCS	Tap water River Lake	*DLLME* (5 mL sample; 50 μL final volume)	LC-MS/MS(ESI^-)	2	87–105 (TW) 93–111 (RV) 84–116 (LK)	[125]
MP, EP, PP, BP	Tap water River	*DLLME* (8 mL sample; ~20 μL final volume)	GC-FID	2,500–22,000	~100	[126]
TCS, CLP, CLX (and other PCPs and NPCPs)	Tap water	*(DI)SPME* (40 mL sample; PA fibers; 125 min; thermal desorption)	(TD)GC-MS(EI^+)	2.5–7	85–103	[60]
MP, EP, PP, BP (and other PCPs and NPCPs)	River Seawater Lake Effluent wastewater	*SPE* (100 mL sample; PVP-DVB cartridges; 1 mL final volume)	LC-MS/MS($ESI^{+/-}$)	0.3–1 (RV, SW, LK) 4–10 (EW)	70–120	[67]

MP, EP, PP, BP (and other PCPs)	River Influent/effluent wastewater	*SBSE* (100 mL sample; PDMS stir bars; 4 h; thermal desorption)	GC-MS(EI^+)	0.03–0.3		[96]
MP, EP, PP, BP	Tap water	*DLLME* (5 mL sample; ~50 μL final volume)	LC-UV	21–46	61–108	[127]
MP, EP, PP, BP TCC, TCS (and other PCPs and NPCPs)	Tap water Influent/effluent wastewater	*SPE* (PVP-DVB cartridges; 1 mL final volume)	LC-MS/MS($ESI^{+/-}$)	0.01–0.09 (TW) 0.02–1.50 (IW) 0.01–1.17 (EW)	59–148 (TW) 20–156 (IW) 39–149 (EW)	[128]
TCS (and other PCPs and NPCPs)	Seawater Influent/effluent wastewater	*SBSE* (100 mL sample, PDMS stir bars, 8 h; 200 μL final volume)	GC-MS(EI^+)	0.2	24	[68]
TCC, TCS (and other PCPs and NPCPs)	River	*SPE* (1,000 mL sample; C18 cartridges; 2 mL final volume)	LC-MS/MS(ESI^-)	0.2–2	76–97	[79]
TCC, TCS (and other PCPs and NPCPs)	Influent/effluent wastewater	*SBSE* (50 mL sample; EGS stir bars; 4 h; 2 mL final volume)	LC-MS/MS($ESI^{+/-}$)	5–10		[80]
MP, EP, PP, BP	River	*dμSPE* (10 mL sample; Fe_3O_4@aminopropyl MNPs sorbent; 5 min; 5 μL final volume)	GC-PID	50–300	95–103	[129]
TCS	River Lake	*USAEME* (8 mL sample; 0.5 min; ~20 μL final volume)	GC-ECD	4	91–97	[130]
MP, EP, PP, BzP TCC, TCS (and other NPCPs)	River Influent/effluent wastewater	*(on-line)SPE* (2–5 mL sample; C18 column)	LC-MS/MS(ESI^-)	0.021–0.27(RI) 0.18–2.1(IW) 0.12–1.5(EW)	62–116 (RI) 59–126 (IW) 59–125 (EW)	[131]
MP, EP, PP, BP	Seawater Swimming pool	*MCNPME* (30 mL sample; Fe_3O_4@SiO_2@C18 MNPs sorbent; 20 min; 100 μL final volume)	GC-MS(EI^+)	23–86	99–106 (SW) 96–102 (SP)	[132]
MP, EP, PP, BP (and other PCPs and NPCPs)	Influent/effluent wastewater	*USA-DLLME* (5 mL sample; 1.5 min; 50 μL final volume)	GC-MS/MS(EI^+)	8–230	86–95 (IW) 94–98 (EW)	[133]

[a]See list for key abbreviations

Table 4 Published papers on insect repellents determination in environmental water samples (chronological order)[a]

Target compounds	Water origin	Extraction technique	Analytical technique	MLOD (ng L^{-1})	Recoveries (%)	References
ICA	River Influent wastewater	*SPE* (500–1,000 mL sample; PS-DVB/C18 cartridges; 200 µL final volume)	GC-MS(EI^+)	10 (RV) 50 (IW)	98 (RV)	[134]
ICA	Lake	*SPE* (500 mL sample; C8 cartridges; 300 µL final volume) *SBSE* (250 mL sample; PDMS stir bars; 14 h; thermal desorption)	GC-MS(EI^+)	25 25	105	[135]
DEET, ICA, PBO, PER and others	Lake River Influent/effluent wastewater	*SBSE* (20 mL sample; PDMS stir bars; 180 min; thermal desorption)	(TD)GC-MS(EI^+)	0.5–150	82–102 (RV, LK) 3–94 (IW) 12–99 (EW)	[136]
DEET, ICA, PBO and others (and other PCPs and NPCPs)	Tap water Seawater Influent/effluent wastewater	*SPE* (200–500 mL sample; DVB-NVP cartridges; 1 mL final volume)	LC-MS/MS($ESI^{+/-}$)	0.6–3.7	72–117 (TW) 64–124 (SW) 72–109 (IW) 64–107 (EW)	[33]
DEET, ICA (and other PCPs and NPCPs)	Tap water Influent/effluent wastewater	*SPE* (DVB-NVP cartridges; 1 mL final volume)	LC-MS/MS($ESI^{+/-}$)	0.01 (TW) 0.02 (IW) 0.01 (EW)	80–137 (TW) 65–108 (IW) 60–106 (EW)	[128]
DEET (and other PCPs and NPCPs)	Seawater Influent/effluent wastewater	*SBSE* (100 mL sample, PDMS stir bars, 8 h; 200 µL final volume)	GC-MS(EI^+)	74	12	[68]
DEET, PER	Tap water Groundwater River Swimming pool Seawater	*BAµE* (25 mL sample; activated carbon sorbents; 16 h; 200 µL final volume)	(LVI)GC-MS(EI^+)	8–20		[137]

[a]See list for key abbreviations

a key role depending on the nature of the target compounds. Different organic solvents with different polarities such as methanol, dichloromethane, hexane, ethyl acetate, acetone, etc. have been used. Regarding SPE sorbents, different types, usually packed into cartridges, have been used. Some examples are: classical octadecyl functionalized silica (C18) or polystyrene-divinylbenzene copolymer (PS-DVB) based on non-polar interactions; polyvinylpyrrolidone-divinylbenzene copolymer (PVP-DVB) based on both polar and non-polar interactions due to its hydrophilic-lipophilic balance (HLB); polymethacrylate-divinylbenzene copolymer (PMA-DVB) also based on both polar and non-polar interactions; polystyrene divinylbenzene copolymer modified with either pyrrolidone groups (PS-DVB/MP) or hydroxyl groups (PS-DVB/MH) exhibiting more polar interactions than PVP-DVB; and polyvinylpyrrolidone-divinylbenzene copolymer modified with cation-exchanger (PVP-DVB/MCX) or anion-exchanger (PVP-DVB/MAX) groups.

On the contrary, when microextraction techniques are used, it is not usual to achieve a high extraction efficiency. However the microextraction volume where the analytes are collected is extremely low (just a few microliters). Therefore, although the amount extracted is low, a high enrichment factor could be achieved. Moreover, unlike LLE or SPE, the whole extract (and hence the entire amount extracted) can be totally transferred to the analytical instrument, thus improving the analytical signal. Regarding solid phase-based microextraction techniques, solid phase microextraction (SPME), and stir bar sorptive extraction (SBSE) have been extensively used to determine PCPs in environmental waters. Different available commercial sorbents of different polarity, such as polydimethylsiloxane (PDMS), polydimethylsiloxane-divinylbenzene (PDMS-DVB), polyacrylate (PA), carbowax-divinylbenzene (CW-DVB) or carboxen-divinylbenze (CAR-DVB) have been used in SPME, depending on the target compounds. With regard to SBSE, PDMS is used in most of the cases, since no other coatings were available up to a few years ago. Regarding liquid phase-based microextraction techniques, single drop microextraction (SDME), hollow-fiber liquid-phase microextraction (HFLPME), cloud-point extraction (CPE), and membrane-assisted liquid–liquid extraction (MALLE) have been occasionally used for PCPs determination. However, it was not until the appearance of dispersive liquid–liquid microextraction (DLLME), and its successive modifications, when liquid phase-based microextraction techniques achieved to be competitive with solid phase-based microextraction techniques. In general terms, solid phase-based microextraction techniques are more time consuming than the liquid phase-based ones, since phases contact, and thus mass transfer, is more hindered. Thus, as can be seen in Tables 1, 2, 3, and 4, SPME, SBSE, and related techniques need extraction times of about one hour or more and sometimes it is even necessary to leave than overnight (10–14 h). High extraction times are also required in liquid phase-based microextraction techniques when the extracting solvent remains static, such as SDME, HFLPME or MALLE. However, very short extraction times are needed by means of DLLME due to the contact between the donor and acceptor phases is infinitely large and the equilibrium state is instantaneously achieved.

Before describing the different extraction techniques employed for the determination of PCPs in water samples, it should be mentioned that no quantitative extraction efficiencies are often obtained. This is especially relevant in those microextraction techniques where the equilibrium state is not usually achieved, such as SPME, SBSE, and SDME. In these cases, it is advisable to prepare the standard solutions in water and subject them to the same extraction procedure than samples, and then refer to the relative extraction efficiency instead of the absolute extraction efficiency.

2.1 UV Filters

As can be seen in Table 1, traditional LLE has been used only few times for determining UV filters [26, 39], whereas SPE has been extensively used. Different sorbents have been used in SPE for UV filters determination in environmental waters. Classical C18 [23, 58, 79] and polymeric PS-DVB [54, 73] sorbents based on non-polar interactions have been scarcely used. However, PS-DVB/MP [27, 40, 50, 78], PS-DVB/MH [37] or PVP-DVB [32–34, 38, 43, 46, 57, 67, 82] are preferred in some cases as there are some UV filters with more polar properties (e.g., benzophenones). Pietrogrande et al. compared C18 with PS-DVB/MP obtaining a better performance with the second one [40]. When compounds with acidic properties (e.g., benzophenone-4 (BZ4) and phenylbenzymidazole sulfonic acid (PBS)) are also pursued, PVP-DVB/MCX shows better performance compared to PVP-DVB [28, 70], since the non-acidic compounds are well retained in the PVP-DVB skeleton, whereas the acidic ones prefer the modified moieties.

On-line SPE has also been used in some cases [46, 73] in order to not only reduce the amounts of organic solvents employed but also reduce the high handling of the sample. Oliveira et al. used a multisyringe-lab-on-valve approach [46] and Gago-Ferrero et al. employed a commercial on-line SPE device [73], in both cases coupled to LC. Maijó et al. performed SPE in-line coupled to capillary electrophoresis (CE) by inserting the SPE sorbent between two pieces of the capillary [70].

Another proposed approach is that proposed by Román et al., who used dispersive SPE (dSPE) with oleic acid-coated cobalt ferrite magnetic nanoparticles ($CoFe_2O_4$@oleic acid) [53].

In addition, microextraction techniques, either in the solid or liquid phase, have also been employed. SPME usually in the direct immersion (DI) mode due to the relatively low volatility of the UV filters has been used [22, 35, 49, 52, 60, 61, 74]. Nevertheless, Lambropoulou et al. compared both DI and head-space (HS) strategies obtaining comparable results for the tested compounds [22]. However, Negreira et al. found a clear improvement when using DI compared to HS in case of benzophenone-type UV filters [35]. Regarding the sorbents employed, PDMS has been used in some cases [22, 49], providing the best extraction efficiency for poorly polar compounds, but a low extraction efficiency for relatively polar compounds such as hydroxylated benzophenones, which were better

extracted with more polar sorbents like PDMS-DVB or PA [35, 60]. Nevertheless, new home-made sorbents have been proposed as an alternative to commercial ones, such as a graphene-based sol-gel coating [61] and a silver wire coated with a dodecyl chain (C_{12}-Ag) [74], and even disposable silicone disks [52], obtaining good analytical performances. With regard to the desorption step, thermal desorption (TD) is preferred [22, 35, 49, 60, 61] when GC is used, since all the retained amount is transferred to the injection port. Consequently, sensitivity is higher than if liquid desorption (LD) was used, since in this last approach an important part is usually lost (i.e., not all the solution is injected). However, LD is mandatory [74] if LC is going to be used. Microextraction by packed sorbent (MEPS) was also used by Moeder et al. [44], followed by LD in 50 μL of ethyl acetate, which were all injected into the GC system employing the large volume injection (LVI) approach using a programmed temperature vaporizer (PTV) injector. SBSE constitutes another solid phase-based microextraction technique commonly employed for UV filters determination in environmental water samples [25, 30, 31, 41, 45, 55, 56, 65, 66, 68, 80]. In most of the cases non-polar PDMS stir bars are used since no other coatings were available. This could jeopardize the extraction of relatively polar compounds. Kawaguchi et al. proposed an in situ derivatization with anhydride acetic to form the less polar acetylated derivatives [30]. Recently, Gilart et al. compared the classical PDMS with two new commercially available sorbents (i.e., polyacrylate-polyethyleneglycol (PA-PEG) and ethyleneglycol modified silicone (EGS)) concluding that the new EGS enables better extraction of some polar compounds as well as improves the extraction of apolar compounds [80]. More recently, this lack of coatings encouraged Almeida et al. to employ an alternative microextraction that had named bar adsorptive microextraction (BAμE) a few years before, based on a polyethylene cylindrical tube covered by an adhesive tape where a solid sorbent is pasted, affording the use of more sorbents. The extraction principles are the same than in SBSE. They compared a PS-DVB, a modified pyrrolidone, a ciano derivative, and five activated carbons of different surface area, as sorbents [77], thus boasting that this novel microextraction technique presents higher versatility than SBSE since allows to taylor-make the sorbent manifold.

Regarding liquid phase-based microextraction techniques, Giokas et al. used for the first time this type of microextraction techniques for the determination of UV filters in water samples. These authors employed CPE with the non-ionic surfactant Triton X-114 to extract the target UV filters from water samples, which were back-extracted into an appropriate solvent thus avoiding the entrance of the surfactant rich phase into the further analytical system [24]. Later, both, Okanouchi et al. [29] and Vidal et al. [42] employed SDME in the DI mode, by using conventional solvents as extracting solvents in the first case and with ionic liquids (IL) in the second case. Later, Ge and Lee used the (DI)HFLPME approach, where a drop of the IL 1-hexyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate was supported inside and in the pores of a tubular and porous piece of polypropylene [59]. The use of supporting membranes was also used by Rodil et al. in MALLE, who employed a low density polyethylene (LDPE) membrane containing 100 μL of

propanol [36]. More recently, Zhang and Lee used a polyester knitting wool as holder of the extracting solvent [71]. However, as said before, it was not until the appearance of dispersive DLLME when liquid phase-based microextraction techniques competed with solid phase-based microextraction techniques. Thus, Tarazona et al. [47], Negreira et al. [48] and later Benedé et al. [81], proposed classical DLLME with organochlorine solvents and acetone as extracting and disperser solvents, respectively. In order to increase the dispersion of the extracting solvent into the aqueous samples, Wu et al. [75] proposed the use of ultrasounds to produce finer extracting droplets in the so-called ultrasound-assisted DLLME (USA-DLLME) approach. However, in order to avoid the presence of the disperser solvent, which usually decreases the partition coefficient of the target compounds into the extracting solvent, new approaches have been used. Thus, Zhang et al. [51] and Zhang and Lee [63] proposed magnetic stirring and vortex mixing, respectively, as disperser forces of the extracting solvent (i.e., magnetic-stirring-assisted DLLME (MSA-DLLME) and vortex-assisted DLLME (VA-DLLME), respectively). The use of IL as extracting solvents in DLLME has been also used obtaining good analytical characteristics. However, due to the high viscosity of the IL, different strategies have been used to disperse the IL into the water sample. IL-based USA-DLLME (i.e., IL-USA-DLLME) was first proposed by Zhang and Lee [62] and later by Xue et al. [76]. Ku et al. [72] proposed to use an up-and-down shaker instead of ultrasounds in their approach, that was termed IL-based up-and-down shaker-assisted DLLME (IL-UDSA-DLLME). Ge and Lee [64] preferred to avoid the disperser solvent without sacrificing the advantages of ultrasounds in the so-called IL ultrasound-assisted emulsification microextraction (IL-USAEME). Finally, it is worthy to mention the paper published by Zhang et al. [69], where temperature is changed to solve and to disperse the IL and to form the cloudy solution. This approach is known as IL-based temperature-controlled DLLME (IL-TC-DLLME).

2.2 Musk Fragrances

In case of musk fragrances, the published methods are summarized in Table 2. As it was described for UV filters, traditional LLE [39] and SPE [50, 84, 90, 99, 101] have been used for the enrichment of musk fragrances. Non-polar sorbents like C18 [90] or PS-DVB [50] have been used. However, Osemwengie and Steinberg [84] found that PMA-DVB with polar and non-polar properties showed better performance than the non-polar PS-DVB for on-site SPE extraction of different nitro and polycyclic musks. In the same way, Wang et al. [101] found better extraction yields with PVP-DVB than with C18. Finally, it should be said that López-Nogueroles et al. [99] synthesized a molecularly imprinted sorbent based on silica, which showed better extraction efficiency and selectivity compared with the conventional PVP-DVB.

Microextraction techniques, both in the solid and in the liquid phase have been also employed. In this sense, SPME, in both DI and HS modes, has been employed.

Winkler et al. [83] observed the following tendency in the extraction efficiency for DI(SPME) depending on different fibers tested: PDMS-DVB > PA ~ CAR > PDMS. Liu et al. [49] did not test the influence of the fiber nature, but selected the PDMS based on the non-polar properties of the target compounds. However, Basaglia and Pietrogrande [60] preferred to use a PA fiber, justifying their choice in that PA has better resistance than PDMS for on-fiber derivatization with BSTFA. However, García-Jares et al. observed better performance with (HS)SPME than with (DI)SPME for the extraction of polycyclic [85] and nitro musks [86], respectively, by using either CAR-PDMS or PDMS-DVB fibers. Wang et al. [88] used (HS)SPME for extracting polycyclic musk, using a PDMS-DVB fiber based on the findings of García-Jares et al. [85], and studied the influence of heating the sample by microwave radiation during the extraction, which resulted in a substantial decrease of the extraction time. MEPS was also used in the determination of musk fragrances. It was used first by Moeder et al. [44], and later by Cavalheiro et al. [100], in both cases injecting LVI into the GC system by means of a PTV injector. It can be seen from Table 2 that SBSE with PDMS has been also employed for the extraction of different nitro and polycyclic musks with extremely high extraction times [56, 91–93, 96]. Finally, another solid phase-based microextraction approach termed dispersive micro solid phase extraction (dμSPE) was proposed by Chung et al. [102] for polycyclic musks determination, in which 3.2 mg of a C18 sorbent was dispersed into an aliquot of the aqueous sample, achieving the equilibrium in just 1 min.

Regarding liquid phase-based microextraction techniques, the most employed liquid phase-based microextraction technique for the determination of musk compounds has been DLLME, either in its classical mode [89, 94] or assisted by ultrasounds (i.e., USA-DLLME) [95]. Similarly Regueriro et al. [87] used USAEME by dispersing the extracting solvent by ultrasounds but avoiding the use of a disperser solvent. Posada-ureta et al. [98] used MALLE with LDPE bags filled with hexane; and Vallecillos et al. [97] used a fully automated manifold for IL-based (HS)SDME.

2.3 Preservatives

The published analytical methods for the determination of preservatives are summarized in Table 3. Just in one case no sample extraction was carried out and the sample was directly injected into an LC system [121]. This is not the current trend since concentration of the target compounds and removing of potentially interfering compounds are needed.

Thus, traditional LLE have just been used once to determine different PCPs including triclosan [39]. With regard to traditional SPE, different SPE sorbents have been employed depending on the nature of the target compounds, due to the different polarity when comparing triclosan, parabens or isothiazolinones. Thus, non-polar C18 [79, 105, 122] is used in few cases for triclosan, while PS-DVB

modified sorbents [27, 37, 50, 107] or PVP-DVB-based sorbents [28, 33, 43, 67, 110, 111, 115, 128] that promote polar and non-polar interactions are preferred when more polar compounds like parabens, isothiazolinones or other PCPs are determined, trying to cover a wide range of retention capacity. It should be mentioned the paper published by Gorga et al. [131] who proposed on-line SPE for the determination of different PCPs including some preservatives.

Regarding microextraction techniques, both solid phase-based and liquid phase-based have been proposed. SPME, usually in DI injection mode, has been used for the determination of triclosan [60, 103], parabens [104] and other preservatives [60], using PA fibers in all the cases, since more non-polar sorbents like PDMS did not exhibit good extraction efficiencies. However, Regueiro et al. [116] proposed the HS mode instead of DI for the extraction of parabens and triclosan. They performed in situ acetylation, converting the parent compounds into the more volatile acetylated derivatives. Moreover, they found better results when using PDMS-DVB or DVB-CAR-PDMS fibers compared to PA fibers, but it should be taken into account that they extracted the acetylated derivatives instead of the more polar underivatized ones as in the other papers. As can be seen in Table 3, SBSE has been also extensively used in the determination of preservatives, exclusively [108, 109, 118, 123] or together with other PCPs [45, 56, 68, 80, 96] in environmental waters. Due to the lack of commercially available sorbents, PDMS has been the most used one, but recently Gilart et al. found that EGS exhibits better extraction efficiency than PDMS for triclosan and triclocarban [80]. Another solid phase-based microextraction techniques, such as MEPS was proposed by González-Mariño et al. [124] for the extraction of triclosan and parabens. Abbasghorbani et al. [129] used dμSPE to determine different parabens by dispersing 5 mg of Fe_3O_4@aminopropyl MNPs into the water sample. Alcudia-León et al. [132] also used MNPs as sorbent to extract different parabens. In this case they used Fe_3O_4@SiO_2@C18, but these MNPs were not dispersed but magnetically confined in a holder, and therefore these authors termed this approach as magnetically confined nanoparticle microextraction (i.e., MCNPME).

Regarding liquid phase-based microextraction techniques, as mentioned in the case of UV filters and musk fragrances, DLLME has been the most commonly used. In this sense, classical DLLME has been employed for triclosan and triclocarban [113, 114, 119, 125] and parabens [126, 127, 133]. In just one case, the parabens were previously derivatized, with anhydride acetic, to increase the extraction efficiency [126]. Its variant USAEME was also applied [130] for extraction of triclosan, or for the simultaneous acetylation and extraction of parabens [117]. Other liquid phase-based microextraction techniques, such as SDME [112], HFLPME [106], and MALLE [120] have been used in a much lesser extent.

2.4 Insect Repellents

Analytical methods for the determination of this group of compounds are relatively scarce compared to the other ones. There are very few articles devoted to the determination of insect repellents themselves. They are sometimes included in

some methods focused in the determination of different families of PCPs. All of them are listed in Table 4. Moreover, some of these compounds can be used as pesticides, and appear in some publications devoted to the determination of pesticides in water samples, but they have not been considered here since they are out of the scope of this chapter.

The articles listed in Table 4, mainly dealing with the determination of *N*,*N*-diethyl-*m*-toluamide (DEET) and icaridin (ICA), employ different extraction and microextraction techniques, but it is noteworthy that all of them are based in the solid phase approach. Thus, classical SPE [33, 128, 134, 135] and more modern SBSE [68, 135, 136] techniques have been employed. Very recently, Almeida et al. [137] have used BAμE as an alternative to SBSE, allowing the use of more sorbents.

3 Analytical Techniques

Separation techniques are generally needed in order to determine a mixture of the target compounds. Moreover, it should be pointed out that despite an exhaustive sample treatment is performed to remove potential interfering compounds from the matrix, some of them could still be present in the extract and could interfere in the subsequent measurement. In this sense, LC and GC have been, by far, the most employed analytical techniques for PCPs determination in water samples. Besides, CE has been occasionally used.

Highly sensitivity detectors are necessary to achieve the determination at the low levels they are found in the environmental waters. Regarding LC, and despite the performed enrichment step, method limits of detection (MLOD) of the order of μg L^{-1} are generally obtained if a UV spectrometry detector is used, whereas MLOD of the order of ng L^{-1} are generally obtained when an MS/MS detector is used.

However, LC-MS/MS is a sophisticated and expensive analytical instrumentation, often not available in many laboratories. In this sense, GC, instead of LC, coupled to an MS detector is used, providing MLOD of the order of ng L^{-1} if an enrichment technique is carried out. Higher MLOD are obtained when other less sensitive detectors, such as flame ionization detector (FID) are used.

3.1 UV Filters

Due to the physico-chemical properties of UV filters, LC is the most suitable analytical technique, although GC has been also employed. As can be seen in Table 1, UV spectrometry detectors are only used for LC in some cases [23, 24, 46, 54, 74, 77] especially when low volatility solvents are used as extracting solvents, such as octanol [51, 71] or IL [42, 59, 62, 64, 69, 72, 76]. On the contrary, MS detectors are preferred. Therefore, LC-MS/MS is usually performed by a triple quadrupole (QqQ) mass analyzer. Just in one case, a hybrid triple quadrupole linear ion trap mass spectrometry (QqLIT-MS) was employed [73] showing very good analytical performance. As can be seen in Table 1, electrospray ionization (ESI), either in positive or

negative mode depending on the target compound, is preferred rather than atmospheric pressure chemical ionization (APCI) as ionization mode. In fact Wick et al. performed a comparison of both strategies obtaining better results in the former [43], on the contrary than Nguyen et al. [55] who obtained better results with APCI. Nevertheless, Rodil et al. [34] compared ESI with APPI and concluded that this last ionization mode was subjected to lesser matrix effects, causing suppression or enhancement of the signal, than ESI, although the MLOD obtained were higher.

Regarding GC-MS, simple quadrupole analyzers (Q) are used in most of the cases, whereas ionic tramps (IT) [75] and time-of-flight (TOF) analyzers [50, 56] have been also used but in scarce occasions. In the case of TOF, it was coupled to two-dimensional GC (i.e., GCxGC) [50, 56]. It should be emphasized that the use of the more sophisticated GC-MS/MS has been used in just two cases [35, 78] by means of IT in both cases. Nevertheless, in all the cases electronic ionization (EI) in positive mode was used. The use of chemical ionization (CI) has never been used for the UV filters determination in water samples. As can be seen in Table 1, LOD in the low ng L^{-1} level are achieved in most of the cases. However, it should be pointed out that some UV filters do not present enough volatility to be efficiently determined by GC. In order to increase their volatility, they are sometimes derivatized. Silylation, either with *N*-methyl-*N*-(trimethylsilyl)trifluoroacetamide (MSTFA) [26, 27, 35, 82], *N*,*O*-bis(trimethylsilyl)trifluoroacetamide (BSTFA) [47, 53, 60, 61, 63, 75] or *N*-(*tert*-butyldimethylsilyl)-*N*-methyltrifluoroacetamide (MTBSTFA) [68], is preferred in most of the cases in case of target compounds presenting labile hydrogens, although acetylation with anhydride acetic has been also used [30]. Oxime formation by means of reaction of carbonyl groups with *O*-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine (PFBHA) has been proposed in the case of target compounds without labile hydrogens [82]. The derivatization is usually carried out after the extraction, by adding the derivatizing agent to the extract. Nevertheless, on-fiber silylation has been proposed after SPME by exposing the fiber to the vapors of the derivatizing agent [35, 60, 61]. Recently, Wu et al. [75] performed an in situ silylation by adding the derivatizing agent at the same time than the disperser and the extractant solvents in the DLLME, which increases the reaction yield. As was said before, Kawaguchi et al. [30] performed an in situ acetylation at the same time than SBSE, increasing the extraction yield since the acetylated derivatives are more extractable than their parent compounds.

Capillary electrophoresis (CE) has been only used in one occasion [70]. Finally, it should be commented the paper published by Haunschmidt et al. [41], who used the direct analysis without using a separation technique. In this case, MS was measured directly on a stir bar after SBSE by direct analysis in real-time (DART).

3.2 Musks Fragrances

Either nitro, polycyclic, or macrocyclic musks have enough volatility and stability to be determined by GC, and therefore this has been the technique of choice, as can

be seen in Table 2. No other analytical technique has been used for the determination of musks in environmental water samples. GC is coupled to a single quadrupole MS in most of the cases. Other MS analyzers, such as IT [83, 102] or TOF [50, 56] analyzers have been used in a few occasions. Besides, when MS/MS is performed, it has been done by means of an IT [97] or a triple quadrupole (QqQ) [101]. In all cases, EI in positive mode is used.

In addition, GC with an electronic capture detector (ECD) [86] was used once for the determination of nitro musks taking advantage of the sensitivity and selectivity that this detector presents to compounds with nitro moieties.

3.3 Preservatives

As can be seen in Table 3, both LC and GC have been used in most of the cases. CE has been only used a couple of times [110, 111]. Nevertheless, due to the low volatility of these compounds, the usual analytical technique for their determination should be LC, preferably with MS/MS detection in order to increase the sensitivity and the selectivity. However, UV detection has been used in some cases [108, 114, 127]. Regarding LC-MS/MS, it is used by means of QqQ analyzers and in the ESI mode. Nevertheless, APCI was used in a few cases [43, 121]. In fact, Wick et al. [43] compared both ionization modes and found that ESI provided a better analytical performance than APCI when comparing sensitivity and it was less affected by matrix effects.

Despite its low volatility, GC has been extensively used in the determination of preservatives in waters, but in most of the cases a derivatization step was carried out in order to increase their volatility. Thus, it is common to perform a silylation [27, 60, 103, 104, 112, 122, 133], generally after the extraction is accomplished, or acetylation [96, 106, 116, 117, 120, 123, 129, 132], generally during the extraction in order to increase both the extraction efficiency and volatility.

GC is mainly coupled to single quadrupole MS analyzers. In some cases IT is used [103, 122], especially if MS/MS is performed [104, 105, 113, 116, 117, 119]. In all cases, the ionization is achieved in EI mode. Regarding the employment of other detectors, FID and photoionization detector (PID) were used by Prichodko et al. [126] and Abbasghorbani et al. [129], respectively, obtaining poor sensitivity in the determination of parabens. However, Shih et al. [130] employed an ECD for triclosan determination taking advantage of the good instrumental sensitivity that the chlorine atoms of this compound have in this detector.

3.4 Insect Repellents

The few analytical methods used for the determination of insect repellents are based on LC and GC, coupled in all the cases with MS detectors.

Knepper [134] used GC-MS for quantitative determination of ICA in river and influent wastewater. Moreover, LC-MS with a single quadrupole and also with a TOF

analyzer were used to characterize and to calculate the mass of this compound. Later, Standler et al. [135] developed a GC-MS method for the determination of this same compound in lake water samples. Rodil et al. proposed a GC-MS method to exclusively determine eight insect repellents, including ICA and the highly used DEET [136]. Later, the same research group proposed a multi-residue analytical method based on LC-MS/MS for the determination of different PCPs including some insect repellents [33], in the same way that Chen et al. [128] did a few years later. Recently, both Pintado-Herrera et al. [68] and Almeida et al. [137] presented the determination of different insect repellents by analytical methods based on GC-MS.

4 Matrix Effects

It is worth mentioning that despite the exhaustive sample treatment and the use of selective analytical techniques, results are sometimes affected by the presence of the so-called matrix effect. This effect causes no quantitative recoveries in samples although standards were subjected to the same procedure than samples. This could be due to a difference in the behavior of the target compound in the presence of the sample matrix that can not only enhance or mitigate the signal in the analytical instrument but also affect the extraction efficiency in the extraction step. This phenomenon has been observed and reported by different authors in the determination of PCPs in water samples, especially in wastewater influents and effluents that contain high contents of organic matter, or even in waters from rivers receiving wastewater effluents. In addition, it has also been observed in seawaters, due to the high saline content, or in swimming pool waters, due to the high chlorine content. Different approaches have been used to correct this deleterious effect: (1) matrix-matched calibration, i.e., the use of the same matrix (but free of analytes) to prepare the standard calibration solutions; (2) standard addition calibration, i.e., to prepare the standard solutions calibration into the sample itself; or (3) the use of surrogates, i.e., internal standards included at the beginning of the process in order to correct extraction and measurement differences.

Matrix-matched calibration is often nonvalid because the matrix effect is sample-dependent, i.e., it has a different extent depending on the sample and thus differences are observed for different samples. In this case, standard addition calibration could be a useful approach, but it is time consuming. The use of surrogates seems to be a good alternative, but however, it is difficult to find compounds that have the same behavior than the target analytes. Isotopic labelled standards of the target compounds represent a good choice, since they are expected to have the same extraction and instrumental behavior than the non-labelled ones. However, on the one hand there are not always isotopic labelled compounds for all the target compounds, and on the other hand they are extremely expensive. Anyway, all this should be taken into account in order to achieve reliable analytical methods. The obtained recoveries for the described methods have also been included in Tables 1, 2, 3, and 4 for information purposes.

5 Conclusions and Further Research

After reviewing the analytical literature concerning the determination of PCPs in environmental water samples, it should be pointed out that a large number of analytical methods to control different families of PCPs in this type of samples are nowadays available. These methods have been developed in the last two decades as a consequence of the society's demand to control the quality of the aquatic ecosystem, given that different studies have shown that PCPs are causing a negative impact in the environment.

These developed methods need, not only to be sensitive, in order to determine the PCP in the ng L^{-1} range in which they appear in the environment, but also to be selective in order to avoid interferences caused from the matrix. In this sense, the developed methods tend to be based on separation techniques, especially in both liquid and gas chromatography, coupled to mass spectrometry detectors, and moreover, samples are subjected to an extraction treatment, thereby providing the required sensitivity and selectivity. Moreover, in the last years, different multi-residue methods have emerged trying to cover a wide range of PCPs.

The developed methods have been applied to water samples of different origin, covering a wide range of the aquatic ecosystem (such as sea, rivers, lakes, tap, influents and effluents of wastewater treatment plants, etc.), and they have been appropriately validated.

To conclude, the analytical community is encouraged on working in the development of highly sensitive and selective multi-residue analytical methods to monitor present and future PCPs that could cause a negative impact in the environment.

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Analysis of Personal Care Products in Sediments and Soils

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Abstract Sample extraction and preparation methods are described for the most relevant groups of personal care products (PCPs) (disinfectants, fragrances, preservatives, UV filters and stabilisers) in solid samples from aquatic environments. The extraction methodologies have been separated into two groups, conventional and novel procedures, to compare the improvements and advantages implemented in recent years to produce more efficient and simple methods. The difficulties related to the treatment of solid samples and to complex matrices are discussed in depth. The analytical methods employed after the extraction procedures, all of which are based on mass spectrometry detection, are also covered. Finally, an overview of the measured concentration of these families of PCPs in the environment is provided, which can be useful in the establishment of future trends.

Keywords Extraction techniques, Gas chromatography, Liquid chromatography, Personal care products, Solid samples

Contents

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M.S. Díaz-Cruz and D. Barceló (eds.), *Personal Care Products in the Aquatic Environment*, Hdb Env Chem (2015) 36: 231–262, DOI 10.1007/698_2014_264,

Abbreviations

1H-BT	1H benzotriazole
2,2′,4,4′OH-BP	2,2′,4,4′-Tetrahydroxybenzophenone
2,2′OH-4MeO-BP	2,2′-Dihydroxy-4-methoxybenzophenone
2,4,6-TCP	2,4,6-Trichlorophenol
2,4-DCP	2,4-Dichlorophenol
2,4OH-BP	2,4-Dihydroxybenzophenone
2OH-4MeO-BP	2-Hydroxy-4-methoxy-benzophenone
4-MBC	4-Methylbenzylidene camphor
4OH-BP	4-Hydroxybenzophenone
5Me-1H-BT	5-Methyl-1H-benzotriazole
ABDI	Celestolide or 4-acetyl-1,1-dimethyl-6-*tert*-butylindan
AHMI	Phantolide or 6-acetyl-1,1,2,3,3,5-hexamethylindan
AHTN	Tonalide or 7-acetyl-1,1,3,4,4,6–hexamethyl-1,2,3,4-tetrahydronaphthalene
Allyl-bzt	2-(2H-Benzotriazol-2-yl)-4-methyl-6-(2-propen-1-yl)-phenol
ATII	Traseolide or 5-acetyl-1,1,2,6-tetramethyl-3-isopropylindan
BH	Benzhydrol
BP	Benzophenone
BP-3	Benzophenone-3
BSTFA	*N*,*O*-bis(trimethylsilyl)trifluoroacetamide
BuP	Butylparaben
BZP	Benzophenone
BzP	Benzylparaben
BZS	2-Hydroxy-phenylmethyl ester benzoic acid
DHB	2,4-Dihydroxybenzophenone
DHMB	2,2′-Dihydroxy-4-methoxybenzophenone
DPMI	Cashmeran or 1,2,3,5,6,7-Hexahydro-1,1,2,3,3-pentamethyl-4H-inden-4-one
EHMC	Ethylhexyl methoxycinnamate
EHS	Ethylhexyl salicylate
etocrylene; EC	Ethyl2-cyano-3,3-diphenylacrylate
EtP	Ethylparaben
HBP	4-Hydroxybenzophenone
HepP	Heptylparaben
HHCB	Galaxolid or 1,3,4,6,7,8-Hexahydro-4,6,6,7,8,8-hexamethylcyclopenta(g)-2-benzopyran
HMB	2-Hydroxy-4-methoxybenzophenone
HMS	Homosalate
IAMC	*Iso*amyl methoxycinnamate
*i*PrP	*Iso*propylparaben)

MeP	Methylparaben
MK	Musk ketone or 4-*tert*-butyl-3,5-dinitro-2,6-dimethylacetophenone
MTBSTFA	*N*-(*t*-butyldimethylsilyl)-*N*-methyltrifluoroacetamide
MX	Musk xylene or 1-*tert*-butyl-3,5-di-methyl-2,4,6-trinitrobenzene
n-PrP	*n*-Propylparaben
Octocrylene; OC	2′-Ehylhexyl2-cyano-3,3-diphenylacrylate
Octyl Salicylate; OS	2-Ethylhexyl-2-hydroxybenzoate
ODPABA	Ethylhexyldimethyl *p*-aminobenzoate
PrP	Propylparaben
TBHPBT	2-(5-*t*-butyl-2-hydroxyphenyl) benzotriazole
THB	2,3,4-Trihydroxylbenzophenone
UV-120	2,4-Di-*t*-butylphenyl-3,5-Di-*t*-butyl-4-hydroxybenzoate
UV-1577	2-(4,6-Diphenyl-1,3,5-triazine-2-yl)-5-[(hexyl) oxy]-phenol
UV-234	2-(2H-Benzotriazol-2-yl)-4,6-bis(1-methyl-1-phenyl-ethyl) phenol
UV-320	2-(2H-benzotriazol-2-yl)-4,6-bis(1,1-dimethylethyl)-phenol
UV-326	2-(5-Chloro-2-benzotriazolyl)-6-*tert*-butyl-*p*-cresol
UV-327	2,4-Di-*t*-butyl-6-(5-chloro-2H-benzotriazol-2-yl)phenol
UV-328	2-(2′-Hydroxy-3′,5′-di-*tert*-amylphenyl) benzotriazole
UV-329	2-(2H-benzotriazol-2-yl)-4-(1,1,3,3-tetramethylbutyl) phenol
UV-360	2-(Benzotriazol-2-yl)-6-[[3-(benzotriazol-2-yl)-2-hydroxy-5-(2,4,4-trimethylpentan-2-yl)phenyl]methyl]-4-(2,4,4-trimethylpentan-2-yl)phenol
UV-571	2-(Benzotriazol-2-yl)-6-dodecyl-4-methylphenol
UV-P	2-(2-Hydroxy-5-methylphenyl)-benzotriazole

1 Introduction

Personal care products (PCPs) are a group of emerging contaminants that can be persistent due to their continuous introduction in the environment. Unlike pharmaceuticals, which are intended for internal use, PCPs are used in an external way on the human body and thus are not subjected to metabolic alterations; therefore, large quantities of PCPs enter the environment unaltered [1].

Several PCPs (e.g., triclosan, triclocarban and most UV-filtering compounds) show affinity to solid matrices due to their hydrophobicity. As a consequence, to allow correct evaluation of the ecological impact of these substances, evaluation of their prevalence in solid matrices is important [2].

For the determination of the most relevant PCPs in solid samples related to aquatic environments, the biggest problem was the extraction and purification of the complex environmental solid matrices, which is frequently tedious due to the large

number of interferences and the strong interactions between the analytes and the sample. Moreover, their analysis represents a difficult task because of the usually low concentration at which the target compounds are present in such samples. Therefore, one of the major trends in analytical chemistry is the development of fast and efficient procedures for the extraction and preconcentration of trace analytes in environmental matrices [3].

The most studied PCPs in the current literature are disinfectants, preservatives (parabens), synthetic fragrances, UV filters and stabilisers (presented in Table 1).

Disinfectants or antimicrobials are mostly represented by triclosan (TCS) and triclocarban (TCC), which are biphenyl ethers used in soaps, deodorants, skin creams and toothpastes. TCS is known to undergo phototransformation in aqueous solution to form 2,8-dichlorodibenzo-*p*-dioxin (2,8-DCDD) [17]. Further, degradation products, such as methyl derivative methyl triclosan (M-TCS), are relatively stable and lipophilic [18].

Synthetic fragrances are added to deodorants, shampoos, detergents, etc. and can be classified into two groups. The first one includes the nitro musks: musk xylene (MX), musk ketone (MK), musk ambrette (MA), musk moskene (MM) and musk tibetene (MT). In the environment, their nitro substituents can be reduced to form amino metabolites. The second one consists of the polycyclic musks, which were developed after the nitro musks but currently are used in higher quantities [7]. Celestolide (ABDI), galaxolide (HHCB) and tonalide (AHTN) are used most commonly, whereas traseolide (ATII), phantolide (AHMI) and cashmeran (DPMI) are used less often [18].

Although nitro and polycyclic musks are water soluble, they present high octanol–water coefficients (log Kow = 3.8 for MK and 5.4–5.9 for polycyclic musks) [19, 20]. Because they may be quite hydrophobic, they tend to adsorb to suspended particles in wastewater samples [21]. Other type of synthetic musks are the macrocyclic musks, which present some advantages; for example, they seem to have more intensive smells; thus, less mass is needed to gain the same performance in perfumery, and they are more easily degradable in the environment, but they are also more expensive [22]. Although they are being used more, to the best of our knowledge, there are no reports on their presence in the environment.

Parabens (esters of the phydroxybenzoic acid) are the most common preservatives and bactericides used in PCPs. Methylparaben (MeP) and propylparaben (PrP) are the most widely used and are normally used together due to their synergistic effects [23]. Benzyl, butyl, ethyl, isobutyl and isopropyl (BzP, BuP, EtP, *i*BuP and *i*PrP, respectively) complete the list of the parabens that we can found in the environment.

UV filters (UVF) and UV light stabilisers (UVLS) are used in sunscreens, skin creams, lipsticks, and several personal care products. Twenty-seven organic compounds have been approved in the European Union as UV filters, including benzophenones, *p*-aminobenzoic acid and derivatives, salicylates, cinnamates, camphor derivatives, triazines, benzotriazoles, benzimidazole derivatives, dibenzoyl methane derivatives and compounds, such as octocrylene and benzylidene malonate polysiloxane [21]. Most of these compounds are lipophilic (log Kow 4–8) with

Table 1 Analysis of PCPs in solid aquatic samples using conventional extraction techniques

Compound	Matrix	Extraction technique	Mesured concentrations (ng g^{-1})	References
Methyl Triclosan	River sediments	Sequential dispersion extraction (acetone: hexane) + silica purification	<0.5–450	[4]
Triclosan Tricarban	River sediments	USE (ethylacetate) + silica purification	12.2–2,633	[5]
Triclosan Triclocarban	River sediments	USE (MeOH: 0.1 formic acid in milli Q water, 1:1) + SPE	1.2	[6]
HHCB, AHTN, ABDI, ATII, AHMI, DPMI, MK and MX	Lake sediments	Soxhlet (DCM)	0.049–16	[7]
HHCB, AHTN, ABDI, ATII, AHMI and DPMI	River and coastal sediments	Soxhlet (DCM)	<0.3–121	[8]
MeP, EtP, *i*PrP, PrP, BzP and BuP	River sediments	SAESC (ACN)	0.18–6.35	[9]
MeP, EtP, *i*PrP, PrP, BzP and BuP	River sediments	SAESC (ACN) + MISPE	0.63–11.5	[10]
MeP, EtP, PrP and BuP	River sediments	USE (MeOH:0.1% formic acid in Milli-Q water, 1:1) + SPE	nd	[6]
MeP, EtP, PrP, BzP, BuP and HepP	River and lake sediments	Shaking (MeOH:water, 5:3) + SPE	0.072–64.5	[11]
BP, BH, HMB, DHB, DHMB, THB	River and lake sediments	Shaking (MeOH + ethylacetate)	0.53–18.4	[12]
HBP, DHB, HMB, DHMB, DHDMB, EHS, HMS	Sediments	USE (ethylacetate:MeOH, 90:10)	1.2–20	[13]
UV-P, BZP, BP3, EC, BZS, 4MBC, UV 326, ODPABA, EHMC, OS, HMS, UV 329, OC, UV 327, UV 1577, UV 328, UV 234, UV 120, HHCB	River and lake sediments	USE (DCM + acetone) + Secuencial SPE (hexane:acetone, 100:0, 95:5, 0:100)	0.1–3,026	[14]
2OH-4MeO-BP, 2,4OH-BP, 2,2′ OH-4MeO-BP, 2,2′,4,4′OH-BP, 4OH-BP, 1H-BT,5Me-1H-BT, UV 326, UV 327, UV 328, TBHPBT	River sediments	Shaking (ethylacetate:DCM, 1:1) + SPE	0.13–224	[15]
UV 320, UV 326, UV 327, UV 328	Coastal and river sediments	Soxhlet (DCM:hexane, 8:1)	0.3–320	[16]

conjugated aromatic rings and are relatively stable against biotic degradation [24]. These compounds have been found in marine organisms, and it has been suggested that they appear to be persistent and bioaccumulative in the aquatic food chain [14].

2 Extraction Procedure

The analysis of PCPs in environmental samples is characterised by the difficulty in the determination of low concentrations in complex matrices [25]. The extraction of analytes from solid samples in environmental applications presents added complications because the solute–matrix interactions are very difficult to predict and overcome [26].

Isolation and purification are necessary for three main reasons: to remove interferences that would otherwise affect the determination of the analytes, to enrich the target compounds to detectable concentrations and to perform solvent switching to the desired solvent conditions used for instrumental detection [3]. All of these steps are necessary to obtain high recoveries and minimise interference. Therefore, sample preparation often represents the most tedious and time-consuming part of the analytical process.

Ultrasonic extraction (USE) and Soxhlet extraction have been common methods for the extraction of emerging contaminants from solid samples, although the use of microwave-assisted extraction (MAE) or more advanced techniques, such as pressurised liquid extraction (PLE) and supercritical fluid extraction (SFE), are becoming important extraction methods for environmental samples [7]. Other modern, but less used, sample-preparation techniques will also be discussed in the following sections, including microextraction techniques designed originally for liquid samples.

Usually the extraction step is not selective and a clean-up step is necessary; solid phase extraction (SPE) is the most commonly used. In the case of PLE and Matrix Solid Phase Dispersion (MSPD), the clean-up can be performed during the extraction, and thus, the laboriousness and time consumption of the methods are reduced. However, this extraction plus clean-up combination is not always selective enough, and a final clean-up is also necessary for some applications [27].

During the last decade, the most recent tendencies have been towards automation through the coupling of sample preparation units and detection systems [3], such as On-line SPE coupled to chromatographic systems, which minimise the sample loss and contamination during handling and improve repeatability [28].

2.1 Conventional Techniques

Classical methods have been widely employed for the extraction of PCPs from solid samples and offer good results in terms of repeatability and recovery, but these

traditional techniques are characterised by long analytical times, manual manipulation of the extracts, large consumption of sample and reagents and generation of large amounts of waste [27]. It should be highlighted that in most of the works that use conventional extracted procedures two or three consecutive extractions were performed. Table 1 shows some examples of PCPs extracted using conventional methods.

2.1.1 Shaking

Extraction via shaking a sample in an organic solvent is the most simple and basic preparation method and provides acceptable analytical parameters but requires considerable time and large solvent volumes. Zhang et al. used 50 mL of ethylacetate:dichloromethane (DCM) (1:1, v/v) for the analysis of sediment samples from the Songhua (China) and Detroit (USA) Rivers. They employed a simple procedure based on shaking, centrifugation, evaporation, reconstitution and purification by SPE. Recoveries over 70% were obtained for 13 different UV filters and UV light stabilisers and several benzophenones and benzotriazoles were detected at concentrations of several hundreds of nanograms-per-gram [15].

Another example of UV filter extraction using shaking was published by Jeon et al. Sediments were collected in Korea and extracted using 20 mL of MeOH. Then, 5 mL of ethylacetate was added, and the sample was placed in a freezer (−30°C) for the separation of the organic layer. The high recoveries (60–125%) and low RSD values (less than 17.2%) allowed for the quantification of four of the seven target analytes at concentrations between 0.53 and 18.38 ng g^{-1} [12].

This technique was also recently employed in the analysis of six parabens in surface sediment (0–12 cm) and sediment core samples (up to 285 cm) collected from several locations in the USA, Japan and Korea, including rivers and lakes. The extraction was carried out three times using 5 mL of a solvent mixture of MeOH and water (5:3, v/v) in an orbital shaker at 250 oscillations min^{-1} for 60 min. The sample was purified by passing through an Oasis MCX cartridge. All analysed samples contained at least one of the six target parabens analysed, and the concentrations of parabens increased gradually from the bottom to the surface layers of the sediment cores from the USA, suggesting a recent increase in the influx of these compounds [11].

2.1.2 Ultrasonic Extraction (USE)

In this technique, the diffusion of analytes from the solid sample to the solvent is facilitated by ultrasonic energy. Generally, USE requires less volume of organic solvents than shaking, although sometimes high volumes are employed. For example, Kameda et al. used 20 mL of DCM and 20 mL of acetone for the extraction of UV filters and UV light stabilisers from Japanese rivers and lakes [14]. Their main disadvantage is the poor reproducibility because of the lack of uniformity in the distribution of ultrasound energy, as well as low selectivity and limited sample-

enrichment capabilities. Moreover, USE is not easily automated and is not suitable for volatile analytes. A risk in the application of USE is the potential degradation of the organic analytes [3], as occurred in the shaking procedure, usually the extracts from USE require sequential steps of centrifugation and concentration before injection.

The presence of two commonly used antimicrobial agents, triclosan and triclocarban was investigated in the Pearl River system in China (Zhujiang River, Liuxi River and Shijing River) employing USE as the extraction technique [5]. Surface sediment samples (0–10 cm) were collected from two positions (less polluted sediments and heavily polluted sediments), which were 10–20 m away from river bank. The samples were extracted (repeated twice) using ethyl acetate and then purified by passing through a silica gel column (1 g), and eluted with n-hexane, ethyl acetate and MeOH in sequence. The final extracts were redissolved in 1 mL of MeOH. TCS and TCC were found to be almost ubiquitous in sediments of the Pearl River system, where municipal sewage was the original source of contamination. The highest concentrations were found in the Shijing River, and relatively lower concentrations were detected in the Zhujiang River and Liuxi River. No significant temporal differences were observed. The accumulation of these analytes in the sediments of the three rivers could be a sink but also a source for release back into the surface water.

A complementary study was carried out in 2012 by the same authors in the Liuxi Reservoir for a multiresidue screening, including four paraben preservatives (methylparaben, ethylparaben, propylparaben and butylparaben) and the two disinfectants triclosan and triclocarban. In this case, the compounds were extracted from the sediments using MeOH and then MeOH–0.1% (v/v) formic acid in Milli-Q water (5:5, v/v). The supernatants were combined and diluted with Milli-Q water to reduce the MeOH content to below 10%, which contributed to the retention of the target compounds by the packing of the Oasis HLB SPE cartridge [6]. In this case, only triclocarban was measured in sediment samples at a concentration of 1.2 ng g^{-1}.

A modification of this technique is the *Sonication-Assisted Extraction in Small Columns* (*SAESC*). Nuñez et al. published two papers in 2008 and 2010 to determine parabens in sediments obtained from the Manzanares River (Madrid, Spain), Ria Arousa and Ria Pontevedra (Galicia, Spain) and from the Mediterranean Sea (Piles, Valencia, Spain) using SAESC. In the first paper [9], polyethylene frits were placed at the end of the glass column (10×2 cm i.d.), and 10 g of the sample was added. Subsequently, 7 mL of ACN was added, the columns were immersed in an ultrasonic water bath, and two consecutive, 15-min extraction steps were carried out. After the extraction, the columns were placed in a vacuum manifold, and the extracts were collected in graduated tubes. Satisfactory recoveries were obtained ranging from 83% to 110%, and some target analytes were measured between 0.18 and 6.35 ng g^{-1}. In the second work [10], a molecularly imprinted solid-phase extraction procedure (MISPE) was incorporated into the analytical method. The extraction of the parabens was performed as in the previous case but using 15 g of sample and 8 mL of ACN every time. Then, MISPE was applied as clean-up step. Four different polymers were tested combining the use of ACN or toluene as porogen, and 4-vinylpyridine (VP) or

methacrylic acid (MAA) as monomer, using benzylparaben (BzP) as a template molecule. Although all of the polymers were able to recognise the template in the rebinding experiments, the molecularly imprinted polymer (MIP) prepared in toluene using MAA showed better performance. This polymer was also able to recognise other parabens (methyl, ethyl, isopropyl, propyl, isobutyl, butyl and benzyl paraben) allowing for the development of an appropriate MISPE procedure for this family of compounds. Despite the clean-up procedure, significantly better recoveries were not achieved in comparison with the previous paper (from 86% to 89%). Higher levels, up to 11.5 ng g^{-1} in sea sediments, were found, and better sensitivity was obtained (0.04–0.14 ng g^{-1} without MISPE procedure and 0.16–0.27 ng g^{-1} employing MISPE).

In another study published by the same research group, eight different UV filters were extracted from river sediments (Manzanares, Jarama, Henares, Guadarrama and Lozoya) and on the Mediterranean coast (Spain), the samples were extracted with ethylacetate–MeOH (90:10, v/v) assisted by sonication, performing a simultaneous clean-up step [13]. These sediment sampling sites were selected because of their location in areas of bathing or recreational activities. C_{18} was mixed with anhydrous sodium sulphate and, to carry out the simultaneous extraction-clean-up procedure, this mixture was transferred to a glass column (20 mL) containing two filter paper circles with 2-cm diameters at the end. The sediment was placed in the column, and the analytes were extracted twice using ethyl acetate–MeOH (90:10, v/v). This combination of extraction and clean-up in a single step provided recoveries greater than 90%. The most frequently detected analytes in the studied marine and fluvial sediments were EHS (3.5–20.0 ng g^{-1}) and DHDMB (1.2–6.1 ng g^{-1}).

2.1.3 Soxhlet Extraction

In a Soxhlet system, the sample is repeatedly placed in contact with new portions of organic solvent at an elevated temperature. Although Soxhlet is time consuming, labour intensive and requires the use of large volumes of organic solvents, it has been applied for organic compound extraction from solid matrices due to its high extraction efficiency [27].

Sediments from the Dongjiang River and Xijiang River and from the coast of Macao (China) were Soxhlet-extracted for 72 h using DCM to analyse polycyclic musk. After a concentration procedure, the solvent extracts were exchanged into *n*-hexane and cleaned on a silica/alumina column in three fractions: the first were eluted with hexane, the second with hexane:DCM (3:1) and the third with DCM. The last fraction contained the target analytes and was concentrated using a rotary evaporator. The sample was further reduced to a volume of 0.5 mL under a gentle stream of nitrogen. Two polycyclic musks, HHCB and AHTN, were the dominant components in the sediment, and the concentrations of total polycyclic musks ranged from 5.76 to 167 ng g^{-1} [8].

A shorter extraction time (24 h) was employed by Peck et al. for the extraction of polycyclic and nitro musk fragrances from sediments collected in Lake Ontario and Lake Erie (U.S). DCM was employed for the extraction, and the samples were

exchanged into hexane. The sulphur was removed from the resulting 4-mL hexane extract via the addition of copper filings activated by concentrated hydrochloric acid. Column chromatography was used to remove interferences, and three 50-mL eluent fractions were collected in series: hexane, dichloromethane and MeOH. HHCB was detected in Lake Erie, whereas six compounds were detected in Lake Ontario. The authors concluded that the influx of these compounds into the lakes is increasing [29].

A similar study using Soxhlet extraction with DCM/hexane (8:1, v/v) was carried out in sediments collected from the Ariake Sea, Japan for the analysis of UV stabilisers. Some of them (UV 320, UV 326, UV 327 and UV-328) were detected in all of the analysed samples at concentrations up to 320 ng g^{-1} [16].

2.1.4 Sequential Dispersion Extraction

Another technique that can be considered conventional is the extraction carried out by dispersing the samples in the solvent using a high-speed dispersion tool [30].

Methyl triclosan and different fragrances were extracted from river sediments by sequential dispersion extraction with acetone and n-hexane [7]. Each extraction was followed by centrifugation and decantation of the solvent and separated into six fractions using liquid chromatography on silica gel using mixtures of pentane, DCM and MeOH. Methyl triclosan and fragrances were measured at concentration up to 450 and 90 ng g^{-1}, respectively [4].

2.2 Novel Techniques

During the last decade, alternative sample preparation methods have been developed to be more selective, faster and miniaturised, requiring less extraction solvent and smaller samples. In addition, the automation of these techniques allows on-line extraction, which increases the number of samples that can be processed and reduces human errors by minimising operator intervention [31]. Table 2 shows examples of extraction using novel techniques, which will be described below.

2.2.1 Pressurised Liquid Extraction (PLE)

In Pressurised Liquid Extraction the sample is in contact with a relatively small amount of solvent inside a chamber with high pressure (1,500–2,000 psi) and temperature (50–200°C), which facilitate the disruption of analyte–matrix interactions. PLE allows for a reduction in the extraction time and solvent consumption (15–30 mL) with a high level of automation and result in better recoveries than those achieved using classical extraction techniques [44]. PLE provides cleaner extracts than Soxhlet and ultrasonic extraction, which results in reduced background noise during the subsequent analyte determination, which is especially important in LC-MS analysis due to ion-suppression/enhancement effects

Table 2 Analysis of PCPs in solid aquatic samples using novel extraction techniques

Compound	Matrix	Extraction technique	Measured concentrations (ng g^{-1})	References
Triclosan 2,4-DCP and 2,4,6-TCP	Marine sediments	PLE (DCM) + SPE	0.27–130.7	[32]
Triclosan 2,4-DCP and 2,4,6-TCP	River and marine sediments	MAE (Acetone:MeOH, 1:1) + SPE	4.4–35.7	[33]
Triclosan	Marine sediments	FMASE (DCM and water)	9.5 (using DCM) 5.9 (using water)	[34]
Triclosan	Marine sediments	SHLE (DCM:water) + LLE of water extract with Hex	15.2	[35]
Triclosan	Sediments	MAE (methylene chloride:MeOH, 2:1)	nd	[36]
Triclosan	Sediments	PLE (water:isopropanol, 1:1) + SPE	–	[37]
Triclosan Methyl Triclosan	River sediments	SBSE	–	[38]
Triclosan Methyl Triclosan	River and marine sediments	MSPD	8.6–201	[39]
HHCB and AHTN	River sediments	Sequential dispersion extraction (acetone: hexane)	<0.5–90	[4]
HHCB, AHTN, ABDI, ATII, AHMI and DPMI	Sediments	MA-HS-SPME	0.1–5.9	[40]
HHCB, AHTN, MK, Skatol Acetophenone, and Isophorona	Sediments	PLE (water:isopropanol, 1:1) + SPE	–	[37]
MK	Sediments	MAE (methylene chloride:MeOH, 2:1)	nd	[36]
BuP	Marine sediments	MAE (ionic-liquid based surfactants)	370	[41]
MeP, *i*PrP, BzP, BuP and *n*-PrP	River sediments	SBSE	–	[38]
Methylsilicate	Sediments	PLE (water:isopropanol, 1:1) + SPE	–	[37]
EHS, HMS, IAMC, 4MBC, BP3, EHCM, ODPBA, OC	Lake sediments	PLE (ethylacetate:n-hexane, 80:20)	14–93	[42]
UV P, UV 326, UV 327, UV 328, UV 329, UV 360, UV 571	Marine sediments	MAE (ACN) + On-line SPE	0.18–24	[28]
UV P, Allyl-bzt , UV 320, UV 326, UV 327, UV 328	Coastal and river sediments	MSPD (DCM)	5.6–56	[43]

[3]. The main limitations of PLE are that the selectivity towards the analytes during extraction is not as high as might be desired and many interferences may be coextracted, depending on the type of sample. Other disadvantages include dilution of the analytes, especially when a large number of cycles are used [45] and, of course, the high initial cost of the extraction system.

Burkhardt et al. have employed PLE coupled with solid-phase extraction (SPE) as a clean-up process for the determination of a disinfectant (TCS), two fragrances (AHTN, HHCB) and a UV filter (methyl salicylate) in a multiresidue study of 61 compounds, reducing the sample preparation time and the solvent consumption to one-fifth of that required using Soxhlet extraction and minimising the background interferences in the subsequent detection technique. The analytes were extracted first with water:isopropanol (IPA) (1:1, v/v) at 1,240°C to obtain the majority of the polar and heat susceptible compounds, and then with water/isopropanol (1:4, v/v) to obtain the more hydrophobic compounds, which are generally more thermally stable. The extracts were collected in vials containing 3 mL of pentane to provide a cooling effect and an upper organic barrier to help prevent sample compound volatilisation losses and provide a solvent for the hydrophobic compounds to determine their mixing into the coextracted matrix material. Finally, a purification using Oasis HLB and Florisil cartridges was carried out [37].

Another PLE procedure followed by SPE was developed for the extraction of triclosan from marine sediment samples collected at the outflow of WWTPs to the Almería Sea (Spain). Before loading the samples in a PLE cell, a cellulose filter was placed in the outlet, followed by a 1-g layer of hydromatrix to obtain cleaner extracts. One cycle of extraction using DCM was carried out and then the extracts were concentrated to a final volume of 5 mL. An additional clean-up was applied using extraction cartridges packed with 1 g of silica. All of the analysed samples were found to contain triclosan up to 130.7 ng g^{-1} in marine sediments, offering a seasonal dependence [32].

Rodil et al. also developed a method for the determination of UV filter compounds by employing PLE in combination with the use of non-porous polymeric membranes in sediment from lakes surrounding the city of Leipzig to cover inputs from recreational activities (swimming/bathing). The authors claim that this combination of PLE and clean-up into a single-step is efficient and easy, resulting in recoveries higher than 73% and precisions with RSD < 19% [42].

2.2.2 Superheated Liquid Extraction (SHLE)

Similar to PLE, Superheated Liquid Extraction is a technique developed to reduce the solvent consumption of classical extractions [46]. SHLE uses aqueous or organic solvents at high temperature without reaching the critical point and pressures high enough to maintain the liquid state of the target extractants. In addition to reducing solvent usage, it is also able to reduce manipulation, improve selectivity and increase automation [47]. In both techniques, PLE and SHLE, the high temperatures enhance the solubility of analytes, the speed of diffusion rates, and the

disruptive power of the strong solute–matrix interactions, thus improving the penetration of the solvent into the matrix [46].

An example of SHLE applied to PCPs is the extraction of triclosan from marine sediments [35], in which a sequential superheated fluid extraction with DCM where water is removed. The sample was mixed with 3 g of sand as a dispersing agent and placed in the extraction chamber for a dynamic extraction with DCM and water. The organic and aqueous extracts are independently collected and treated by evaporation and liquid–liquid extraction, respectively. This sequential extraction with polar and low-polarity superheated liquids was necessary due to the wide polarity range of the target analytes (the paper describes a multiresidue analysis for pesticides, pharmaceuticals and personal care products). Using DCM as an extractant, triclosan was found at 15.2 ng g^{-1} in sediment samples collected at the outflow of a WWTP to the sea.

2.2.3 Microwave-Assisted Extraction (MAE)

Microwave-assisted extraction is based on the application of microwave energy to a ceramic vessel containing the sample, resulting in heating of only the sample. This technique offers substantial improvements over other sample-preparation techniques, such as short extraction times, use of small amounts of solvent and the possibility of extracting multiple analytes simultaneously, without as high of an initial investment as PLE or SHLE. However, additional clean-up of the extract of the samples is generally necessary prior to analysis, and MAE is not amenable to automation.

This procedure, followed by a clean-up step and based on on-line SPE, was satisfactorily applied to seven UV benzotriazole stabilisers in two types of marine sediments (beach sediments and sediments near an outfall of sewage waters) using 2 mL of a weak organic solvent, such as ACN, and applying 300 W of power for 5 min. The MAE extract was diluted with Milli-Q water to 20 mL and passed through an on-line SPE system. Recoveries between 50.1 and 87.1% were obtained, and concentrations in the range 0.18–24.0 ng g^{-1} were measured in the sediments near the outfall. These values were higher closer to the outfall, as expected [28].

Triclosan and musk ketone were analysed but not detected by an MAE procedure in the surface sediment samples collected along the shore of Lake Erie adjacent to the effluent pipe of a WWTP serving a town in upstate New York. A preliminary study was completed to determine which extraction solvent resulted in the greatest recovery; methylene chloride, MeOH, acetone and hexane were tested. Finally, a mixture of methylene chloride and MeOH was selected. The temperature was ramped from room temperature to 115°C over 8 min, and the final temperature was held for 15 min [36].

Another procedure developed for the determination of triclosan allows for its determination in river sediments in the North West of Spain at concentrations between 4.4 and 35.7 ng g^{-1} [33]. In this case, the extraction was made using 30 mL of acetone: MeOH (1:1, v/v) at 130°C for 20 min followed by an SPE procedure.

A process using surfactants as extractants was employed by Delgado et al. The procedure was developed for the determination of, among other compounds, one paraben (butylparaben) from marine sediments. The sediments were extracted using two ionic-liquid (IL)-based surfactants, 1-hexadecyl-3-methyl imidazolium bromide (C_{16}MIm–Br) and 1-hexadecyl-3-butyl imidazolium bromide ($C_{16}C_4$Im–Br). The water-soluble IL that contained the extracted analytes from the sediments was transferred to a water-insoluble IL ($C_{16}C_4$Im–NTf_2 or C_{16}MIm–NTf_2) via a simple metathesis reaction, and the extracted analytes experience an important preconcentration in the water-insoluble IL, forming a microdroplet of a few mL. Using this procedure, butylparabene was detected at 370 ng g^{-1} in the marine sediments [41].

A modification of the MAE procedure, the *Focused Microwave-Assisted Soxhlet Extraction* (*FMASE*), was employed by Morales Muñoz et al. for the determination of triclosan in marine sediments collected in Almería (Spain). FMASE maintains the advantages of conventional Soxhlet extraction and overcomes certain problems, such as the long extraction time and non-quantitative extraction of strongly retained analytes due to the easier cleavage of analyte–matrix bonds by interactions with focused microwave energy power. Moreover, it is viable for automation and avoids wasting large volumes of organic solvents [34]. The focused microwave-assisted Soxhlet extractor operates similarly to conventional Soxhlet extraction, but the sample receives microwave irradiation over a preset period when it is in contact with the extractant. The total extraction time of this procedure was 75 min (which corresponds with 25 min of DCM extraction and 50 min of water extraction), which is a short time compared with conventional Soxhlet extractions. Mean recoveries of 96% for triclosan were obtained, and the measured concentrations were 9.5 and 5.9 ng g^{-1} using DCM and water as extractants, respectively [34].

2.2.4 Matrix Solid Phase Dispersion (MSPD)

In MSPD, the samples are dispersed with a suitable sorbent and then packed into a polypropylene syringe that contains a clean-up sorbent to retain co-extracted interfering species. Matrix solid-phase dispersion is a low-cost technique that combines the limited consumption of organic solvents, the use of mild extraction conditions and the potential for integrated extraction and purification [25].

This technique has been satisfactorily employed for the extraction of six benzotriazole UV stabiliser compounds in coastal and river sediments with recoveries of 78–110% [43]. Diatomaceous earth and silica, deactivated to 10%, were used as inert dispersant and clean-up co-sorbents, respectively. Satisfactory recoveries were obtained for all of the compounds (between 78% and 110%), and the levels of concentration reach a maximum of 56 ng g^{-1} for UV 328.

Two disinfectants, triclosan and methyl triclosan, were also extracted using this technique from river and marine sediment samples. As in the previous paper, the samples were dispersed with diatomaceous earth. The obtained recoveries were even better, ranging from 100% to 111%. Methyl triclosan was not detected in any

analysed sediments, while triclosan was found in 50% of these samples in the range 8.6–201 ng g^{-1} [39].

2.2.5 Microextraction Techniques

The demand to reduce the sample volumes and avoid the use of toxic organic solvents has given rise to many microextraction methods in the last several decades, which have led to simplifications in the extraction procedures. Some of these procedures, originally developed for liquid samples, have been applied to the extraction of PCPs from solid samples.

An example is the extraction carried out by Casas Ferreira et al. of several parabens (methylparaben, isopropylparaben, n-propylparaben, butylparaben and benzylparaben), and two disinfectants (triclosan and methyltriclosan) from river sediment samples in Germany using *Stir Bar Sorption Extraction* (*SBSE*). SBSE involves the extraction of the analytes from the matrix using a magnetic stir bar with a coating of polydimethylsiloxane (PDMS), a nonpolar polymeric phase. Usually, their use for solid samples requires a previous extraction step using another technique, such as USE or PLE, and then, the extract, previously diluted in water, is subjected to the SBSE procedure [38]. These authors have published one of the few references available concerning the extraction of pollutants using the twister directly in the soil sample, where the sample was placed in a headspace vial, and then, 5 mL of a 0.4-M aqueous solution of $NaHCO_3$ was added, and the stir bar was inserted into the mixture. The resulting recoveries were between 91% and 110%, and although differences were observed in the behaviour between the parabens and the triclosan and methyl triclosan, it was possible to determine all of these compounds in real samples, choosing appropriate working conditions for a multicomponent protocol. This approach provides important advantages, such as minimising the sampling handling, completely eliminating the use of organic solvents and simplifying the analytical procedure with reduced time consumption [38].

Solid-phase microextraction has also been applied as a solvent-free technique, in this case for the determination of synthetic polycyclic musks in sediment samples. The procedure is based on a one-step in situ *Microwave-Assisted Headspace Solid-Phase Microextraction* (*MA-HS-SPME*). The dehydrated solid sample mixed with 20 mL of deionised water was extracted using a polydimethylsiloxane-divinylbenzene (PDMS-DVB) fibre placed in the headspace when the extraction slurry was microwave irradiated at 80 W for 5 min. The rapid microwave-assisted heating provides better extraction efficiency and sample throughput than using water-bath heating. Overall, the one-step in situ MA-HS-SPME appears to be a good alternative extraction method for the determination of organic compounds in environmental samples; it is a simple, effective, low-matrix-effect and eco-friendly sample pretreatment method [40].

3 Analysis

As previously stated, PCPs cover a large range of polarities and physico-chemical properties. Obviously, this fact compromises not only the selection of a proper extraction/pre-concentration technique (as discussed previously) but also the choice of using a proper chromatographic and detection system. Moreover, PCPs are usually found in highly complex environmental samples at low-ppt levels, which means that both sensitive and selective analytical methods are required.

Currently, both gas chromatography (GC) and liquid chromatography (LC) techniques, in conjunction with the sample preparation methodologies described above, meet the analytical requirements for trace and ultra-trace determination over the entire range of PCPs in solid environmental matrices. The choice of using GC or LC depends, once again, on the physico-chemical properties of the target analytes.

As an example, highly volatile synthetic polycyclic musks can be easily determined in complex samples (e.g., sewage sludges/sediments [40] or river sediments [8]) by GC without any further derivatisation steps, whereas other PCPs, such as some organic UVFs [48] or parabens [38], need an initial derivatisation step if GC is to be successfully employed; they are much more amenable to analysis using LC-related techniques (e.g., [6, 11, 28]).

Within this field of environmental chemistry, we have observed some prominent trends. The common use of GC allows for the separation of PCPs and has to a large extent been replaced by LC [31]. This fact has been attributed to two main causes: (1) the low volatility and/or thermal stability of many of the PCPS found in solid environmental samples, and (2) the inclusion of some tedious sample preparation steps (mainly sample derivatisation by methylation, sylation or pentafluorobenzylation) that increase the analysis time and the uncertainty in the analytical measurements. Despite these limitations, GC has not been completely ruled out because it is still the method of choice for separating some highly volatile and/or hydrophobic PCPs that show poor ionisation in LC-MS analysis (e.g., fragrances and benzotriazoles). However, alternative LC applications have also been reported for most of these groups.

There is an important trend towards multiresidue and multi-class methods. Current advances in instrumentation have allowed the simultaneous determination of a large number of PCPs (including different families) within a single analytical run [15, 31, 49]. The recent emergence of higher resolution LC equipments enabling the use of sub-2-μm particle sizes and high backpressures (UHPLC), the development of new column packages and the on-line coupling/automation of the sample preparation steps and detection systems have also contributed to this trend, allowing PCPs to be resolved more easily and in shorter analytical run times.

In the following sections, the intricacies of most of the analytical methodologies employed for the determination of PCPs in solid environmental samples (sediments and soils) are reviewed in detail. All of the reviewed techniques are based on LC and GC separation systems using MS detection.

3.1 Liquid Chromatography

While high-performance liquid chromatography (LC or HPLC) is a mature and widely used analytical technique for the analysis of PCPs, the advent of ultra-high performance liquid chromatography (UHPLC) has energised disciplines that employ this technique extensively. In UHPLC, columns packed with sub-2-μm particles are used, and when combined with elevated backpressures, result in a significant reduction of the retention times and solvent consumption, which reduces length of the chromatograms and the total times required for the determination of the analytes.

In current UHPLC systems, the analysis times can be decreased by a factor of 9 when compared to LC analysis. This fact clearly enhances the throughput for high-volume analyses and accelerates method development time cycles, which is advantageous for experiments using various methods. Other advantages of UHPLC include greater sensitivity because of the sharper peak profiles and better reproducibility.

LC and UHPLC separation of PCPs presents some properties that complicate the choice of an appropriate analytical column, the mode of separation, and the best chromatographic conditions, especially when dealing with multiresidue analysis [50].

Given the hydrophobic nature of most of the PCPs found in solid environmental samples, the stationary phases employed in the literature mainly consist of reversed-phase (RP) packing materials with C_{18} as the most commonly employed by a wide margin (e.g., [5, 6, 15]).

Almost as an exception to C_{18} columns, Nuñez and co-workers [9, 10] opted for an XDB-C_8 HPLC column (150 × 4.6 mm, 5 μm) for the chromatographic separation of several parabens (methyl, ethyl, isopropyl, propyl, benzyl and butylparaben) in solid environmental samples. The less hydrophobic nature of C_8 with respect to C_{18} columns seems to not affect the retention of the selected parabens, and even the use of high percentages of organic solvent was required to elute the analytes from the stationary phase. Nevertheless, most of the authors still opt for classical C_{18} RP columns for this family of preservatives: Delgado et al. [41] employed C_{18} HPLC Column (150 × 4.6 mm, 5 μm); Liao et al. [11] selected a C_{18} column (100 × 2.1 mm, 5 μm); whereas Chen et al. [6] opted for SB-C_{18} (100 × 3 mm, 1.8 μm). MeOH, ACN and Milli-Q water are the preferred solvents used for the gradient elution of parabens. Some additives, such as formic acid and ammonium acetate, have been used to promote the ionisation of the analytes into the MS interfaces.

In the particular case of parabens ($\log K_{ow}$ from 1.96 to 3.57 and pK_a between 8.79 and 8.9), Angelov et al. [51] observed that the neutral forms of these analytes occur at pH in the range of 3–6.5. At highly acid mobile phases compositions (pH < 3), the protonated forms will exist, whereas at pH above 6.5 the de-protonated ions will be formed. Thus, considering that the ionic forms are usually poorly or even not retained when RP chromatography is employed, the mobile phases should be prepared to favour the neutral forms of the selected

preservatives ($6.5 > pH > 3$). However, this condition is not often taken into consideration in the reviewed literature.

Disinfectants are another family of PCPs that have been traditionally determined in solid samples using GC-related techniques (e.g., [33, 37]) but that have also been gradually replaced by LC-based techniques. This fact could be attributed to the ease with which the main disinfectants, triclosan, triclocarban and their derivatives, are ionised at the current LC-MS interfaces. Once again, the hydrophobic nature of both TCS and TCC ($\log K_{ow}$ of 4.7 and 4.9, respectively [5]), has led to the use of RP columns as the primary stationary phase in their determination in solid matrices.

Zhao et al. [5] recently developed an analytical method based on the rapid resolution of liquid chromatography-tandem mass spectrometry (RRLC-MS/MS) with electrospray ionisation (ESI) to determine the levels of TCS and TCC in river surface waters and sediments. The column employed was a SB C_{18} column (100×3.0 mm, 1.8 μm), while the elution of the analytes was carried out using a binary mixture of water and ACN as the mobile phase without any further additives. The authors employed isotopically labelled internal standards ($^{13}C_{12}$-TCS for TCS and TCC-d_7 for TCC) for quantification purposes and reported very low LODs (0.6 ng g^{-1} for both TCS and TCC) that allowed them to determine the presence of both antimicrobial agents in real river sediment samples.

Agüera et al. [32] reported a comparison of two chromatographic techniques for the determination of TCS in marine sediments and urban wastewaters. The first one was based on GC-negative chemical ionisation (NCI)-MS, whereas the second was based on LC-ESI-MS/MS. These authors reported that, despite the higher LODs for TCS using the LC-MS/MS technique, it allowed for the proper identification and quantification of biphenylol, which was not possible to determine using GC-NCI-MS. The LC separation of the analytes was achieved using an MS C_8 column (100×2.1 mm, 3.5 μm). A gradient elution was performed using ACN and 0.02% ammonium hydroxide in water (pH 10.5) as mobile phase solvents.

The last family of PCPs for which the LC-MS related techniques have been gaining importance are the benzotriazole UV light stabilisers (BUVs). The highly lipophilic behaviour of these compounds (K_{ow} between 3.0 and 10) [16] usually requires the use of high percentages of organic solvents in the mobile phases when working with reversed phase (RP) columns, which is the most widespread mode of separation [25]. Among UVF and UVLS, BUVSs also show remarkably basic behaviour ($pK_a > 7$), which can also have an influence on the chromatographic separation parameters (retention times, peak shape, tailing, etc.), especially for the less lipophilic benzotriazoles.

Montesdeoca-Esponda et al. have developed and applied some analytical methodologies based on octadecilsilica-based RP-UHPLC (100×2.1 mm, 1.7 μm) coupled to an MS/MS detector [28, 52, 53] for the determination of benzotriazoles in environmental samples. In all of their work, an isocratic elution based on 100% MeOH for 1 min was sufficient to determine seven BUVSs; however, the co-elution of three of them (UV 326, UV 327 and UV 328) was unavoidable. Ruan et al. [54] reported the development and application of an analytical methodology based on LC-MS/MS for the determination of 12 BUVSs in solid environmental samples.

They employed a C_{18} column for chromatographic separation (150 × 4.6 mm, 5 μm). The gradient employed was MeOH:water (80:20, v/v) with a flow rate of 1 mL min^{-1} and a linear increase to 100% MeOH over 20 min. The authors did not report the retention times of the analytes or any related chromatograms. Nevertheless, considering the analytical conditions employed, co-elution of some of the analytes is highly probable.

As stated before, multi-residual analysis of PCPs using LC-MS techniques has gained importance during the recent years. As an example, Blair and colleagues [55] developed a multiresidue LC-MS/MS methodology based upon US EPA [56], for the trace determination of 54 PCPs (including some parabens, fungicides, sex hormones, antibiotics, etc.) in water and sediment samples from Lake Michigan (USA). They employed a MAX-RP (250 × 4.6 mm, 4 μm) column and a binary gradient elution for the determination of the selected analytes. Similarly, Chen et al. [6] optimised and applied a sensitive and robust method using SPE and USE extraction followed by UHPLC-MS/MS for the determination of 19 biocides, including four paraben preservatives (methylparaben, ethylparaben, propylparaben and butylparaben) and two disinfectants (TCS and TCC), in surface water, wastewater, sediment, sludge and soil samples. The employment of an SB-C_{18} (100 × 3 mm, 1.8 μm) provides high retention, good reproducibility and excellent resolution of the target compounds. To achieve this goal, they tested different mobile phase compositions (MeOH, ACN, Milli-Q water, acetic acid, formic acid, oxalic acid, and aqueous ammonia and ammonium acetate in different ratios and different combinations). The authors also assessed the matrix effects by comparing extracts of the matrix spiked with standard solutions with the corresponding standard solution in the mobile phase solvent. They reported that the target compounds in surface waters, sediments and soils were not significantly affected by the matrix interferences (matrix effect within 70–120%), whereas significant matrix effects were observed for wastewater and sludge samples for almost all the analytes.

Generally, the co-elution of some of the PCPs reviewed here have been observed, especially within the groups or families presenting very high lipophilicity, such as BUVSs [25], which, in conjunction with the high complexity of the solid environmental samples, could severely compromise the quantification of these analytes because the response factors of each analyte can vary significantly (Fig. 1). In addition, both facts also lead to competitive ionisation during the electrospray processes [57], resulting in signal suppression/enhancement and impairing the proper quantification of the analytes when MS detection systems are employed [58]. Therefore, the appropriate separation and quantification of these pollutants continues to be an exceptional chromatographic challenge considering the matrix effects associated with complex materials, such as sediment and soil samples.

Based on these facts, we suggest that further investigation of different types of column packages, sizes, or even combined separation mechanisms, such as mixed-modes columns, e.g., based on both size exclusion and polarity retention [59], is required to overcome the main drawbacks observed in current publications,

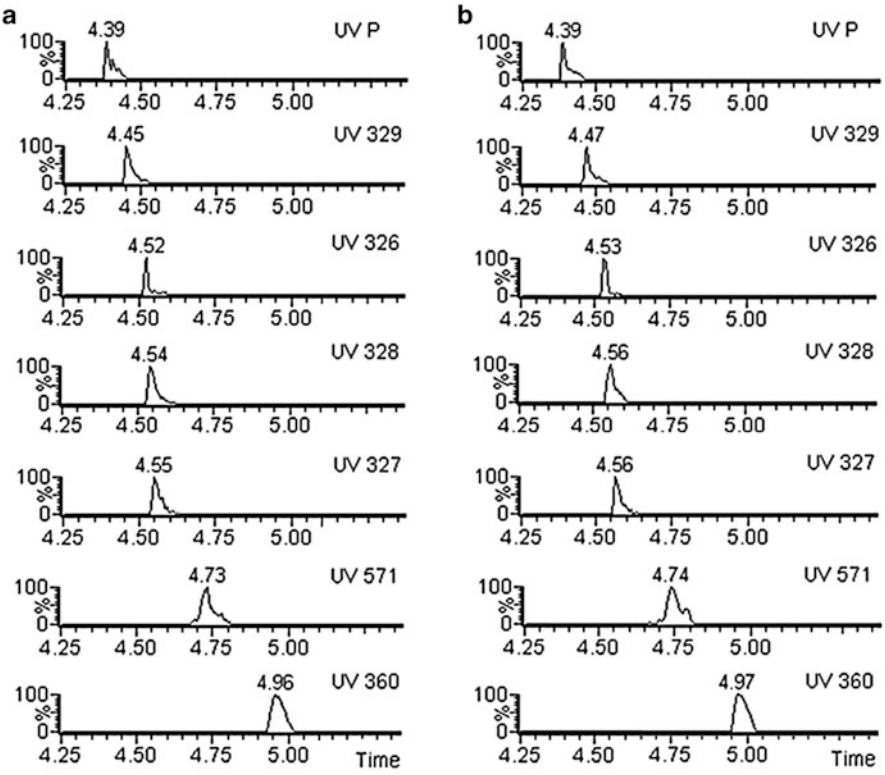

Fig. 1 Total ion current chromatogram of (**a**) sediment sample and (**b**) sludge sample spiked with BUVSs mixture (From [28])

including the use of high volumes of organic solvents and the co-elution of various compounds during chromatographic separation.

3.1.1 Detection Systems

The application of advanced LC-MS technologies has become an important tool for the identification and quantification of PCPs over the last decade. Particle beam (PB) and thermospray (TSP) were the first interfaces employed in this combined technique in the early 1990s (e.g., [60]). However, the recent interest of the scientific community in these pollutants has led to the exclusive use of atmospheric pressure interfaces (API) in the determination of PCPs. These types of interfaces allow the successful elimination of the mobile phase from the column and provide the proper ionisation of the analytes at the high vacuum conditions required for their determination by MS.

Today, electrospray (ESI) and atmospheric pressure chemical ionisation (APCI) interfaces are the most widely used interfaces for LC-MS and LC-MS/MS analyses

of these emerging pollutants. Theoretically, both ESI and APCI interfaces offer a soft ionisation mode compared to the previously mentioned PB, TSP or even MALDI (Matrix-Assisted Laser Desorption Ionisation); thus, they are more appropriate for quantitative analysis in both single ion monitoring (SIM) and multiple reaction monitoring (MRM) detection modes. It has been reported on countless occasions that ESI provides better sensitivity for compounds over a wide range of molecular weights and medium to high polarity, whereas APCI provides an optimum interface for the ionisation of chemicals over a wide range of molecular weights but primarily with medium to low polarity, which is the case of several PCPs associated with solid environmental samples.

Regardless of ionisation technology employed, parabens and disinfectants are usually determined in negative ion (NI) mode as $(M\text{-}H)^-$. In most studies, ESI has been the unique interface employed for the LC-MS analysis of parabens and disinfectants in sediment and soil samples to date [5, 6, 9–11, 32]. Ammonium formate, ammonium acetate, ammonium hydroxide and formic acid have been employed as mobile phase additives to promote the ionisation of these analytes in the API chambers. These substances are amenable to fragmentation in the collision cells of triple quadrupole mass spectrometers (TQDs), forming stable and reproducible product ions. In this sense, their determination using MS/MS in MRM mode is highly recommended. This acquisition mode allows more selective and sensitive detection, resulting in limits of quantification (LOQs) that are far lower than those reported using single-quadrupole detectors (QD) working in SIM mode, regardless of whether LC, UHPLC or even GC is employed as the separation technique (Table 3).

Among all of the UVFs and UVLs compounds, only BUVs and benzophenone UVFs have been determined using LC-MS-related techniques in sediment and soil. In contrast to parabens and disinfectants, these substances are mainly determined in positive ion (PI) mode as $(M\text{-}H)^+$ and using both ESI and APCI interfaces.

Montesdeoca-Esponda et al. have developed an UHPLC-ESI-MS/MS method to detect and quantify BUVSs in different types of samples, including marine sediments and sludges from WWTP Montesdeoca-Esponda et al. [28]. Ruan et al. [54] employed an LC-MS/MS system for the determination of 12 BUVSs in sludge samples using an APCI interface for the ionisation of the analytes. They also determined BUVS under PI using nitrogen as the nebuliser and drying gas and argon as the collision gas. Zhang and co-workers [15] developed another LC-ESI-MS/MS method for the determination of two benzotriazole and five benzophenone derivatives in sediment and sludge samples in which the negative ion $(M\text{-}H)^-$ was successfully employed, reporting LODs below 0.1 and 0.5 ng g^{-1} for sediment and sludge samples, respectively.

The main negative aspect of LC-MS analysis of PCPs in these types of environmental samples has been clearly attributed to the occurrence of matrix effects. Due to the co-extracted matrix constituents, the MS analysis may suffer from ionisation suppression or enhancement in the API interfaces, thereby hindering the adequate quantification [57]. In particular, it has been reported that ESI is much more susceptible to this signal suppression/enhancement phenomena than APCI sources,

Table 3 Analysis of PCPs in solid aquatic samples using LC

Compound	Matrix	Mobile phase composition	Chromatographic column	Instrumental analysis (LODs)	References
MeP, EtP, *i*PrP, PrP, BzP and BuP	River sediments	5 mM ammonium formate in MeOH(A) 5 mM ammonium formate in water (B)	C_8 (150 × 4.6 mm, 5 μm)	LC-MS/MS (0.06–0.14 ng g^{-1})	[9]
MeP, EtP, *i*PrP, PrP, BzP and BuP	River sediments	5 mM ammonium formate in MeOH(A) 5 mM ammonium formate in water (B)	XDB-C_8 (150 × 4.6 mm, 5 μm)	LC-MS/MS (0.16–852 ng g^{-1})	[10]
MeP, EtP, PrP and BuP	River sediments	5 mM ammonium acetate and 0.05% formic acid in water (A) and MeOH (B)	SB-C_{18} (100 × 3 mm, 1.8 μm)	UHPLC-MS/MS (0.01–6.37 ng g^{-1})	[6]
MeP, EtP, PrP, BzP, BuP and heptyl	River and lake sediments	MeOH (A) and water (B)	C_{18} (100 × 2.1 mm, 5 μm)	LC-MS/MS (0.015–0.03 ng g^{-1})	[11]
UV P, UV 326, UV 327, UV 328, UV 329, UV 360, UV 571	Marine sediments	0.1% formic acid in MeOH (v/v) (isocratic)	C_{18} (50 × 2.1 mm, 1.7 μm)	UHPLC-MS/MS (53.3–146 ng kg^{-1})	[28]
Triclosan 2,4-DCP and 2,4,6-TCP	Marine sediments	Acetonitrile (A) and 0.02% ammonium hydroxide in water (B)	MS C_8 (100 × 2.1 mm, 3.5 μm)	LC- MS/MS (3.5–4 ng g^{-1})	[32]
Triclosan Tricarban	Lake sediments	0.1% Ammonium acetate and 0.1% Acetic Acid in water (A) 1:1 MeOH: ACN (B)	MAX-RP (250 × 4.6 mm, 4 μm)	LC-MS/MS (2.7–56 ng g^{-1})	[50, 55]
Triclosan Tricarban	River sediments	Water (A) and ACN (B)	SB C_{18} (100 × 3 mm, 1.8 μm)	RRLC-MS (0.6–1.9 ng g^{-1})	[5]
Triclosan Triclocarban	River sediments	5 mM ammonium acetate and 0.05% formic acid in water (A) and MeOH (B)	SB-C_{18} (100 × 3mm, 1.8 μm)	UHPLC-MS/MS (0.01–6.37 ng g^{-1})	[6]

LODs limits of detection

which as mentioned before, have been used less often for PCPs because the sensitivity is lower than ESI [61].

These matrix effects can be reduced by applying extensive and selective clean-up procedures prior to LC-MS analysis, by improving the chromatographic separation, and by diluting the final extract [48]. However, the most common and effective technique consists of the use of isotope-labelled compounds or surrogate standards, which allow us to compensate for the matrix effects of the analogous native analytes throughout the entire analytical procedure. Although this approach is a better solution than standard addition or matrix match calibration, which are more time consuming and laborious, these isotopically isotope-labelled standards can often be expensive or not commercially available.

Taking into consideration the physico-chemical properties and fragmentation behaviour of the PCPs mentioned in this section, the use of other MS techniques, such as ion trap (IT), time of flight (TOF), and even hybrid-MS systems like quadrupole-time of flight (Q-TOF), quadrupole-ion trap (Q-IT) and Orbitrap-MS, is also plausible. These detectors could offer additional and more versatile recognition of degradation products and metabolites due to their highly accurate mass measurements, low LODs, speed and sophisticated MS-scanning techniques.

Table 3 summarises the main characteristics of the LC-MS methods that have been developed for the determination of PCPs in sediment and soil samples. This table includes the type of column employed in each work, the mobile phase compositions, MS-interfaces, detection mode and detector type.

3.2 Gas Chromatography

Gas chromatography (GC) coupled to mass spectrometry detectors (MS and MS/MS) has been the major instrumental technique used for the environmental analysis of PCPs in sediment and soil during the last decade, especially for those with boiling points lower than 450°C (volatile and semi-volatile PCPs). However, its application can be extended to "non-volatile" and polar compounds if a proper derivatisation step is included during the analytical protocol. This procedure enhances the volatility and thermal stability of the analysed species, which is still the main drawback of GC analysis [23]. In this sense, derivatisation reactions must allow the detection of the compounds containing polar functional groups with adequate signal-to-noise (S/N) ratio, provide complete derivatisation (>90%) and be time efficient [23].

Some of the PCPs included in this work (e.g., parabens and some UV filters) are highly polar and/or thermally fragile compounds that require transformation into more volatile compounds to make them suitable for GC analysis [7]. Silyl reagents are the most commonly employed for PCP analysis by GC. They provide rapid and quantitative reactions that yield stable products that can be easily separated on GC columns. A large variety of silyl reagents, and also combinations of them, have been used to produce different ether derivatives: *N*-*t*-butyldimethylsilyl-*N*-

methyltrifluoroacetamide (MTBSTFA), *N*,*O*-bis(trimethylsilyl)trifluoroacetamide (BSTFA), *t*-butyldimethylchlorosilane (TBDMSCl), *N*-Methyl-*N*-(trimethylsilyl) trifluoroacetamide (MSTFA) or trimethylchlorosilane (TMCS) are among the most employed (see Table 4).

Some pentafluoro reagents, such as pentafluoropropionic acid anhydride (PFPA) and pentafluorobenzyl bromide (PFBBr), have also been employed for derivatisation purposes in the GC analysis of several PCPs in environmental samples. The most important advantage of pentafluoro reagents with respect to silyl reagents is that they convert the analytes into highly electrophilic derivatives due to the introduction of 5 or 10 fluorine atoms, which lead to a significant improvement of the final sensitivity and selectivity of the MS detection [23]. Methylation is another derivatisation technique that has been employed to a lesser extent to transform polar PCPs into methyl derivatives. Diazomethane has been employed to reach this goal, however, it has been reported that this substance is poisonous, carcinogenic and explosive, so its use is not recommended [23]. Casas-Ferreira et al. [38] optimised an in situ derivatisation step based on the acetylation of parabens, triclosan and methyl triclosan from soil, sediment and sludge samples followed by the determination of the selected analytes via GC-MS. These authors stated that a noticeable increase in the signals of the compounds was observed when derivatisation took place, reporting LODs below ng g^{-1}.

It is important to address the fact that derivatisation requires the optimisation of several variables to perform correctly, including the derivatising agent, derivatisation solvent, reaction temperature, duration of reaction, etc., which could explain why many of the authors opt to determine some of the reviewed PCPs without any derivatisation of the analytes, even in some cases where the addition of a derivatisation reagent could improve the LODs of the analytical method.

However, from the perspective of analytical chemistry, several PCPs are amenable to gas GC-MS or even GC-MS/MS determination without any further derivatisation. For example, to the best of our knowledge, BUVSs have exclusively been determined using GC-MS related methodologies in solid environmental samples without the derivatisation of the analytes (e.g., [14–16, 43]). Synthetic musk fragrances (e.g., [4, 7, 8, 40]) and disinfectants (e.g., [32, 37]) are also usually determined without any further derivatisation step.

Currently, there are many different types of GC columns commercially available. However, only a few of them, mainly based on fused silica-(5%-phenyl)-methylpolysiloxane, have been used for PCPs. Helium is usually employed as the carrier gas at constant flow rates between 1 and 1.5 mL/min. With respect to the injection mode, the split-less mode is preferred by most researchers for the determination of these substances in soil and sediment samples.

Table 4 Analysis of PCPs in solid aquatic samples using GC

Compound	Matrix	Chromatographic column	Instrumental analysis (LODs)	References
BP, HBP, HMB, DHB, DHMB, THB	River and lake sediments	Fused-silica capillary column coated with a 0.33 μm bonded film of 5%-diphenyl-95% dimethylsiloxane (30 m × 0.2 mm)	GC-MS (0.005–0.10 ng g^{-1})	[12]
EHS, HMS, LAMS, 4MBC, BP3, EHCM, ODPBA	Lake sediments	HP-5MS capillary column coated with a 0.25 μm bonded film (30 m × 0.25 mm)	GC-MS (BSTFA) (1–30 ng g^{-1})	[42]
HBP, DHB, HMB, DHMB, DHDMB, EHS, HMS	Sediments	ZB-5MS capillary column coated with a 0.25 μm bonded film of 5% phenyl polysiloxane (30 m × 0.25 mm)	GC-MS (BSTFA) (0.07–0.10 ng g^{-1})	[13]
UV-P, BZP, BP-3, EC, BZS, 4-MBC, UV 326 ODPABA, EHMC, OS, HMS, UV 329, OC, UV-327, UV 1577, UV 328, UV 234, UV 120, HHCB	River and lake sediments	Fused silica capillary column (VF-35 ms), (30 m × 0.25 mm)	GC-MS (0.05–1.0 ng g^{-1})	[14]
2OH-4MeO-BP, 2,4OH-BP, 2,2′ OH-4MeO-BP, 2,2 ,4,4 OHBP, 4OH-BP, 1H-BT,5Me-1H-BT, UV 326, UV 327, UV 328, TBHPBT	River sediments	ZB-5MS capillary column coated with a 0.25 μm bonded film of 5% phenyl polysiloxane (30 m × 0.25 mm)	GC-MS (0.06–0.33 ng g^{-1})	[15]
UV P, UV 9, UV 320, UV 326, UV 327, UV 328	Coastal and river sediments	HP-5MS capillary column coated with a 0.25 μm bonded film (30 m × 0.25 mm)	GC-MS/MS (0.9–4.5 ng g^{-1})	[43]
UV 320, UV 326, UV 327, UV 328	Coastal and river sediments	HP-5MS capillary column coated with a 0.25 μm bonded film (30 m × 0.25 mm)	GC-MS (not reported)	[16]
TCS, 2,4-DCP, 2,4,6-TCP	Sediments	HP-5MS capillary column coated with a 0.25 μm bonded film (30 m × 0.25 mm)	GC-MS/MS (MTBSTFA) (0.12 ng g^{-1})	[33]
TCS	Marine sediments	HP DB-17MS capillary column coated with a 0.15 μm 50% phenyl/50% methylpoly-siloxane bonded film (30 m × 0.25 mm)	GC-MS/MS (<0.004 ng g^{-1})	[35]

(continued)

Table 4 (continued)

Compound	Matrix	Chromatographic column	Instrumental analysis (LODs)	References
*i*PrP, MeP, *n*PrP, BuP, BzP, MeTCS	Soil and sediments	HP-5MS capillary column coated with a 0.25 μm bonded film (30 m × 0.25 mm)	GC-MS (Acetic acid anhydride) (0.08–1.06 ng g^{-1})	[38]
HHCB, AHTN, ADBI, ATII, DPMI, AHMI	Sediments	DB-5MS capillary column coated with a 0.25 μm bonded film (30 m × 0.25 mm)	GC-MS (0.04–0.1 ng g^{-1})	[40]
HHCB, AHTN, ADBI, ATII, DPMI, AHMI	Sediments	HP-5MS capillary column coated with a 0.25 μm bonded film (30 m × 0.25 mm)	GC-MS (0.3–0.67 ng g^{-1})	[8]
HHCB, AHTN, ADBI, AHMI, ATII	Sediments	HP-5MS capillary column coated with a 0.25 μm bonded film (30 m × 0.25 mm)	GC-MS (0.025–0.15 ng g^{-1})	[7]

3.2.1 Detection Systems

Most of the published methods for PCP analysis in sediments and soils report GC with single-quadrupole MS as the preferred detection system (Table 4). Full-scan mode is usually employed for identification, whereas SIM mode is used for quantification. However, GC-MS/MS has increasingly been applied in the determination of these contaminants due to the extremely high selectivity and sensitivity of its MRM detection mode, as well as reduced matrix effects and interferences [23]. Among all the ionisation sources employed in these hybrid techniques (e.g., electron-impact ionisation (EI), cold electron-impact ionisation (cold-EI), or chemical ionisation (CI)), EI has been the most commonly employed [33, 38, 40]. With respect to MS detectors, QD [12, 13, 36, 40], TQD [34, 35, 43] and ITs [33] have been the only ones used to date.

More specifically, synthetic musk fragrances are commonly analysed using GC-EI-MS, a technique that has been routinely used for detection of these substances, due to their high volatility [22]. However, GC-NCI-MS is more sensitive to the nitro musk fragrances [31]. As isotopically labelled standards are not commercially available, a variety of internal standards have been used instead for the analysis of these substances, including deuterated PAHs and various labelled and unlabelled PCBs [31]. High-resolution or tandem mass spectrometric techniques are rarely used because the sensitivity of the low resolution mass spectrometers is usually enough for the analysis of these substances [31]. Table 4 summarises the main characteristics of some of the GC-MS-related techniques that have been employed for the determination of synthetic musk fragrances in solid environmental samples.

Disinfectants have also been traditionally determined using GC-EI-MS with SIM as the monitoring mode for the qualitative and quantitative analysis of the target analytes. All the authors employed electron-impact ionisation mode, usually at 70 eV [32, 33, 37, 38]. Lower LODs can be achieved if a proper derivatisation step is included during the analytical protocol (Table 4). Labelled ^{13}C12 TCS and ^{13}C12 methyl-TCS are currently available for use as recovery standards [31].

In the particular case of disinfectants, some authors opted for IT detectors for the determination of both TCS and TCS and their derivatives instead of classical linear quadrupole detectors [33–35]. IT detection offers some advantages over QD and TQD detection. For example, it allows the possibility of working in MS^n mode without any additional cost. To achieve this goal, the selected precursor ion is isolated in the trap, and once there, it can be fragmented several times (n) by colliding it with helium molecules. Subsequently, the product ions obtained are registered during each fragmentation stage (n), and therefore, more precise and complete information regarding the chemical structures of the analysed compounds can be obtained. However, ITs allow an instrumental technique that generally results in a less linear response and higher limits of detection and quantification compared with those obtained using TQD in MRM mode [25].

Due to the high polarity observed in some UV filters, such as benzophenone-type compounds, the complete derivatisation of these analytes is required to increase

their GC sensitivity. *N*-methyl-*N*-(trimethylsilyl)trifluoroethyl acetamide (MSTFA) [12] and BSTFA with 1% TMCS [13] have been used to transform UV filters into their trimethylsilylethers and improve the detection limits of the final methodologies. Classical GC stationary phases, such as 5% phenylpolysiloxane, are frequently used for the separation of these compounds [12, 13, 42]. Once again, all the mentioned authors opted for the split-less mode for sample injection, EI at 70 eV for ionisation, and GC-MS working in SIM mode for the detection and quantification of the analytes.

The analysis of BUVSs in complex environmental samples using GC-MS and LC-MS/MS often reveals matrix effects mainly due to their hydrophobic nature [25]. However, GC-MS/MS has increasingly been applied instead of GC-MS for the determination of trace organic contaminants due to the extremely high selectivity and sensitivity of its MRM mode and it has several advantages, such as reduced matrix effects and interferences [25].

As an example, [43] [43] developed a novel and highly sensitive GC-MS/MS method for benzotriazole UV absorbers in sediments. They used a GC-MS/MS system with an IT mass spectrometer that was equipped with an EI ionisation source to assess these compounds in river and marine sediments. In this work, they reached LOQs between 3 and 15 ng g^{-1} by combining the matrix solid-phase dispersion technique developed for the extraction of the analytes and the GC-MS/MS employed for the detection.

More details and examples regarding GC-MS and GC-MS/MS methodologies for PCP analysis have been highlighted in Table 4.

4 Conclusions and Future Trends

We thoroughly reviewed the literature from the past decade on the determination of the most relevant PCPs in solid matrices derived from aquatic environments.

Conventional methodologies, such as shaking, ultrasounds and Soxhlet, are still used due to their simplicity and low cost. They provide acceptable extraction yields. However, many disadvantages, such as long times and high consumption rates of the sample and reagents, have led the increased use of novel techniques based on increased automation (PLE, SHLE) or miniaturisation (SBSE, MA-HS-SPME). The methodologies employed for the extraction, preconcentration and purification of solid samples for the analysis of PCPs include both conventional and novel procedures. Several examples have been found for the determination of the most important groups (disinfectants, fragrances, preservatives and UV filters) in aquatic environments. The measured concentrations were very low (between low ng kg^{-1} to high ng g^{-1}) and require further development of the methodologies to preconcentrate and purify the analytes from complex matrices.

The current instrumental techniques employed for the determination of PCPs that have been reported in the literature are based on LC, UHPLC and GC separation techniques coupled with different mass spectrometry detectors (single quadrupole,

triple quadrupole, and ion trap) for the chemical analysis of these pollutants in solid environmental samples. Further investigation into liquid chromatography is required to avoid the co-elution of other analytes and matrix interferences when the reversed-phase separation mode is employed because co-elution clearly impairs the proper quantification of PCPs in complex matrices when MS detection is used. Moreover, the use of other MS techniques, such as ion trap, time of flight, or even novel hybrid-MS systems, could offer additional and more versatile recognition of degradation products and metabolites.

Given these facts, GC-MS and GC-MS/MS are still suitable techniques for the determination of several volatile and semi-volatile PCPs in complex matrices because they still offer reasonably good analytical performance and, for many samples, derivatisation is not required. Moreover, gas chromatography-tandem mass spectrometry has increasingly been applied to the determination of trace organic contaminants, including UV filters and light stabilisers, due to its extremely high selectivity and sensitivity in multiple reaction monitoring mode; GC–MS/MS also has several advantages, such as reduced matrix effects and interferences, compared to GC-MS and LC-MS/MS.

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Analysis and Occurrence of Personal Care Products in Biota Samples

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Abstract Personal care products (PCPs) constitute a large group of emerging environmental pollutants, potentially hazardous compounds that have been receiving steadily growing attention over the last decade. Because of the lipophilic properties of these substances, it is expected that they can reach and accumulate in tissues of aquatic organisms in different trophic levels. Their continuous environmental input may lead to a high long-term concentration and promote continual but unnoticed adverse effects on aquatic and terrestrial organisms.

This chapter summarizes the developed analytical procedures for the analysis of four important different families of PCPs: UV filters, synthetic musk fragrances, antimicrobials, and parabens. Sampling extraction and preparation, instrumental analysis, and method performance have been considered and discussed. The present work also summarizes the available data on the presence of these substances in

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M.S. Díaz-Cruz and D. Barceló (eds.), *Personal Care Products in the Aquatic Environment*, Hdb Env Chem (2015) 36: 263–292, DOI 10.1007/698_2014_313,

biota samples, providing ranges of concentration for the different compounds in the species that have been evaluated in each study.

Keywords Analysis, Antimicrobials, Biota, Fragrances, Occurrence, Parabens, Personal care products, UV filters

Contents

Abbreviations

2AMK	2-Amino musk ketone
2AMX	2-Amino musk xylene
3BC	3-Benzylidene camphor
4AMX	4-Amino musk xylene
4DHB	4-Dihydroxybenzophenone
4MBC	4-Methylbenzylidene camphor
ACN	Acetonitrile
ADBI	Celestolide
AHMI	Phantolide
AHTN	Tonalide
APCI	Atmospheric pressure chemical ionization
APPI	Atmospheric pressure photoionization
ATII	Traseolide
BCF	Bioaccumulation factor
BeP	Benzyl paraben
BM-DBM	Butyl methoxydibenzoylmethane
BP1	Benzophenone-1
BP2	Benzophenone-2
BP3	Benzophenone-3
BP4	Benzophenone-4
BuP	Butyl paraben
CI	Chemical ionization
d.w.	Dry weight
DCM	Dichloromethane

dSPE	Dispersive solid-phase extraction
ECD	Electron capture detector
EHMC	Ethylhexyl methoxycinnamate
EI	Electron impact
ESI	Electrospray ionization
EtAc	Ethyl acetate
EtP	Ethyl paraben
Et-PABA	Ethylhexyl PABA
f.w.	Fresh weight
GC	Gas chromatography
GC-FID	Gas chromatography with a flame ionization detector
GC–MS	Gas chromatography coupled to mass spectrometry
GC–MS/MS	Gas chromatography coupled to tandem mass spectrometry
GC–NCI-MS	Gas chromatography coupled to negative chemical ionization mass spectrometry
GPC	Gel permeation chromatography
HHCB	Galaxolide
HMS	Homosalate
IAMC	Isoamyl *p*-methoxycinnamate
IDM	Isopropyl dibenzoylmethane
l.w.	Lipid weight
LC	Liquid chromatography
LC–MS	Liquid chromatography coupled to mass spectrometry
LC–MS/MS	Liquid chromatography coupled to tandem mass spectrometry
MA	Musk ambrette
MAE	Microwave-assisted extraction
MeOH	Methanol
MeP	Methyl paraben
MK	Musk ketone
MLOD	Method limit of detection
MM	Musk moskene
MSPD	Matrix solid-phase dispersion
MSTFA	N-methyl-*N*-(trimethylsilyl)trifluoroacetamide
MT	Musk tibetene
MTBE	Methyl *tert*-butyl ether
MTCS	Methyl-triclosan
MX	Musk xylene
OC	Octocrylene
OD-PABA	Ethylhexyl dimethyl PABA
OT	Octyl triazone
PCP	Personal care products
PLE	Pressurized liquid extraction

PrP	Propyl paraben
QuEChERS	Quick, easy, cheap, effective, rugged, and safe
RP-HPLC	Reversed-phase high-performance liquid chromatography
SIM	Selected ion monitoring
SRM	Selected reaction monitoring
TCC	Triclocarban
TCS	Triclosan
UHPLC	Ultrahigh performance liquid chromatography
UV-F	UV filters
WWTP	Wastewater treatment plant

1 Introduction

Personal care products (PCPs) constitute a large group of emerging environmental pollutants, potentially hazardous compounds that have been receiving steadily growing attention over the last decade. Several personal care product ingredients are among the most commonly detected organic compounds in many relevant studies, including in the seminal report on organic contaminants in US streams [1]. These substances are extensively used and enter the aquatic environment mainly via wastewater treatment plants (WWTPs). Many PCPs and metabolites have become pseudo-persistent in the environment. Because of the lipophilic properties of these substances, it is expected that they can reach and accumulate in tissues of aquatic organisms in different trophic levels. Their continuous environmental input may lead to a high long-term concentration and promote continual but unnoticed adverse effects on aquatic and terrestrial organisms. Therefore, effects can accumulate so slowly that changes remain undetected until they become irreversible. However, there are scarce data about, and limited understanding of, the environmental occurrence, fate, distribution, and effects of many PCPs and related metabolites and other transformation products, despite their extensive use. The lack of data is especially pronounced regarding on biota, since just few studies focus on determining these compounds in such complex matrices.

One of the main reasons for the scarcity of data was the lack of suitable analytical methods capable of detecting PCPs at trace level in biological tissues. Due to the advances in analytical instruments, particularly by the use of gas and liquid chromatography coupled to mass spectrometry (LC–MS), some sensitive and selective analytical methodologies have been developed for the environmental determination of PCPs in biota samples, and data on this topic is rapidly growing.

This chapter aims to summarize the existing information about the developed analytical methods for the determination of four important families of PCPs including UV filters (UV-F), synthetic musk fragrances, antimicrobials, and parabens in biota samples. The chapter focuses on sample extraction and preparation, instrumental determination, and method performance. Other objective of the present work is to summarize the existing data about the occurrence of the

mentioned families of PCPs in organisms, providing concentration ranges for the compounds detected in the diverse species studied belonging to different levels of the trophic web.

2 Analysis and Occurrence

2.1 General Comments on Analytical Methodologies

2.1.1 Sampling

PCPs have been analyzed in several organisms present in the aquatic environment. Sampling procedures used for the analysis of PCP residues in aquatic biota mainly involve traditional fishing, either by native fishers or by electric fishing (special permissions are usually needed).

Biota sampling is generally more difficult than other kinds of matrices due to the added difficulty of the availability of samples of the desired species, often depending on external factors which are difficult to control. Other additional problem may be the variability between individuals of the same species (size and living cycle), which hinders comparison of results.

Most studies have focused on fish, a representative matrix of the aquatic environment assumed to be able to retain and bioaccumulate PCPs due to the lipophilic character of most of these substances. Studies have also been conducted on algae, macrozoobenthos, bivalves, and birds. Collecting samples of marine mammals is significantly more difficult. These samples were obtained in most cases under the permission of appropriate agencies and normally from animals that have been found dead, stranded along coasts or incidentally caught in fishing nets. There are other particular ways of obtaining samples from exotic species. One example can be found in the study carried out by Kannan et al. [2], where livers from polar bears, originating from the coastal waters of Alaska, were collected from native subsistence hunters.

The most usual type of tissue analyzed is muscle. This fact can probably be explained by its low lipid content in comparison with other tissues and also because it is part of the human diet. Other tissues, such as hepatic and hepatopancreatic tissues, have also been used. It is also common to analyze the whole organism in the case of small organisms (fish, mussels, or macrozoobenthos). Selected tissues are homogenized by blending and often freeze-dried before extraction.

2.1.2 Sample Contamination Remarks

Due to the extended use of PCPs, background contamination was revealed as a common problem in the determination of these compounds in biota at environmentally relevant concentrations. In order to prevent this problem, basic precautions

include avoiding the use of target PCPs and the use of gloves for sample handling. All glassware used must be previously washed and heated overnight at 400°C and, after this, sequentially rinsed with different organic solvents, such as acetone, methanol (MeOH), dichloromethane (DCM), and HPLC grade water. High-purity solvents should be used. In addition, a set of operational blanks should be processed to monitor for contamination from the laboratory environment and any other sources.

2.1.3 Instrumental Analysis/Extraction and Preparation Methods

The low concentration of PCPs in biota samples requires high sensitivity and selectivity. Therefore, mass spectrometric (MS) detection is the most suitable technique for the determination of these compounds in such complex matrices.

Determination of PCPs in the aqueous environment has been mainly performed by gas chromatography coupled to mass spectrometry (GC–MS). Matrix effects are not critical for the ionization modes typically used, and good method limits of detection (MLODs) are achieved. However, these methods have some limitations. They solely can be applied to substances that are volatile and of low polarity or can be derivatized (where differences in matrix components may result in quite different derivatization efficiencies which compromise precision and accuracy of the analysis). If the objective is to perform the simultaneous determination of several PCPs, with a wide range of physicochemical properties, liquid chromatography (LC) offers better features than GC. LC allows the analysis of a wide range of compounds and significantly increases the potential or the analysis of transformation products and metabolites, which are usually more hydrophilic than the parent compounds, without the need of derivatization. Thus, LC coupled to tandem mass spectrometry (LC–MS/MS) is the technique of choice for a multiclass PCP determination in environmental samples. For the ionization of the PCPs, three different techniques have been applied, i.e., electrospray ionization (ESI) (which is by far the most commonly used for trace analysis of these pollutants in environmental samples), atmospheric pressure chemical ionization (APCI), and atmospheric pressure photoionization (APPI). ESI is the most used technique and offers good results for the ionization of the analytes even though it is presumed to be susceptible to signal suppression or signal enhancement due to the influence of sample matrix, as shown by previous PCP studies carried out in complex matrices [3, 4].

2.2 UV Filters

2.2.1 Sample Extraction and Preparation

Different procedures have been used in the analysis of UV-F in biota samples. Several of the sample preparation methods described here have been previously

reviewed in detail [5]. The developed methodologies are summarized in Table 1. Extraction of the target compounds has been achieved using several techniques including conventional Soxhlet extraction (which has been a common method for the extraction of environmental pollutants, but it has become less attractive because of the time and solvent consumed) [6, 7], pressurized liquid extraction (PLE) [8, 9], solid–liquid extraction [8, 10–13], microwave-assisted extraction (MAE) [14], and matrix solid-phase dispersion (MSPD) [15]. These techniques lead to the co-extraction of a lipid fraction that must be removed before determination of the UV-Fs.

The cleanup of biota sample extracts is usually a two-stage process. Sample extracts can first be subjected primarily to gel permeation chromatography (GPC) to remove lipids followed by adsorption chromatography on silica or Florisil® columns. Quite often, reversed-phase chromatography (RP-HPLC) has also been used for extraction and purification. GPC or column purification with silica or Florisil is useful whenever compounds of similar physicochemical properties are separated from matrix interfering substances which are present in the sample. When these methods are applied to a mixture of compounds with different physicochemical properties, they become less effective. RP-HPLC proved to be a suitable alternative when UV-Fs with a large range of physicochemical properties have to be analyzed [5].

The first methodology on UV-F analysis in biota was presented by Nagtegaal et al. [7]. Target analytes included benzophenone-3 (BP3), 4-methylbenzylidene camphor (4MBC), homosalate (HMS), ethylhexyl methoxycinnamate (EHMC), ethylhexyl dimethyl PABA (OD-PABA), Isopropyl dibenzoylmethane (IDM), and Butyl methoxydibenzoylmethane (BM-DBM). UV-Fs were extracted from fish tissue (homogenized and dried with sodium sulfate) using Soxhlet extraction, with a mixture of petroleum ether/ethyl acetate (2:1, *v*/*v*). Lipids and other potential matrix interferences were removed by GPC (BioBeads S-X3) with cyclohexane/acetone (3:1, *v*/*v*) as mobile phase. In order to perform the analysis through GC–MS, some compounds (IDM and BM-DBM) were derivatized by adding CH_3I/NaOH to half of the extract. Then, the two parts of the extract were purified with a silica column separately, using hexane/ethyl acetate in different proportions. Meinerling and Daniels [6] analyzed the UV-Fs 4MBC, BP3, EHMC, and OC in fish muscle using a similar procedure based on Soxhlet extraction (using n-hexane/acetone (9:1, *v*/*v*)) and followed by GPC (BioBeads S-X3) using cyclohexane/ethyl acetate (1:1, *v*/*v*) as eluent. In a further cleanup step, a Florisil® column was used to remove more polar compounds. Balmer et al. [8] presented an interesting method for the analysis of 4MBC, BP3, EHMC, and OC, where the fish samples were extracted with PLE using DCM/cyclohexane (1:1, *v*/*v*) and further purified by GPC, using a BioBeads S-X3 column and DCM/cyclohexane (35:65, *v*/*v*) as eluent, followed by silica purification. Buser et al. [10] extracted 4MBC and OC by successive extractions using potassium oxalate, ethanol, diethyl ether, and n-pentane and then a purification method similar to the one described by Balmer et al. [8]. Zenker et al. [11] developed for the first time a methodology suitable for the simultaneous determination of nine UV-Fs with different physicochemical

Table 1 Analytical methodology and occurrence data for UV filters in biota

Matrix	Species	Tissue	UV filter	Sample amount	Extraction	Purification	Technique	Chromatographic column	Recovery (%)	MLOD	Concentration ranges	References
Fish	Bluegill (*Lepomis macrochirus*)	Muscle	4MBC, OC	1 g	Rotary extraction with acetone	Silica purification	GC–EI-MS	XTI-5 (30 m × 0.25 mm; 0.25 μm)	98–99	5.3–17 ng g^{-1} f.w.	n.d.	[12]
	Sonora sucker (*Catostomus insignis*)	Muscle, belly flap, and skin	4MBC, OC	1 g	Sonication with acetone	GPC and silica purification	GC–MS/MS	VF-5 MS (30 m × 0.25 mm; 0.25 μm)	57–79	36–120 ng g^{-1} f.w.	n.d.	
Fish	White fish (*Coregonus* sp.)	Muscle	4MBC, BP3, EHMC, OC	5 g	PLE: homogenized with diatomaceous earth 3 cycles DCM/cyclohexane (1:1, *v*/*v*) at room temperature	GPC (EnviroSep-ABC or BioBeads S-X3) and silica purification	GC–EI-MS	BGB-5 (30 m × 0.25 mm; 0.25 μm) or SE54 (25 m × 0.32 mm; 0.25 μm)	93–115	7–380 ng g^{-1} l.w.	72 (OC) ng g^{-1} l.w.	[8]
	Roach (*Rutilus rutilus*)			20 g	Homogenized with sodium sulfate Column extracted with DCM/cyclohexane (1:1, *v*/*v*)					3–37 ng g^{-1} l.w.	44–94 (4MBC), 66–118 (BP3), 64 (EHMC) ng g^{-1} l.w.	
	Perch (*Perca fluviatilis*)									10–56 ng g-1 l.w.	166(4MBC), 123 (BP3), 25 (OC) ng g^{-1} l.w.	
Fish	Brown trout (*S. trutta fario*)	Muscle plus adipose tissue under the skin	4MBC, OC	10–25 g	Solvent extraction using potassium oxalate (2 ml, 35 %), ethanol (100 ml), diethyl ether (50 ml), and *n*-pentane (70 ml)	GPC (EnviroSep-ABC or BioBeads S-X3) and silica purification	GC–EI-MS	BGB-5 (30 m × 0.25 mm; 0.25 μm) or SE54 (25 m × 0.32 mm; 0.25 μm)	n.r.	5–20 ng g^{-1} l.w.	50–1,800 (4MBC) 40–2,400 (OC) ng g^{-1} l.w.	[10]
Fish	Rainbow trout (*Oncorhynchus mykiss*)	Muscle	4MBC, BP3, EHMC, OC	10 g	Homogenized with sodium sulfate Soxhlet extracted with n-hexane/acetone (9:1, v/v)	GPC (BioBeads S-X3) and Florisil purification	LC–ESI-MS/MS	PerfectSil 120 ODS-2 (125 × 3 mm; 3.5 μm)	86–108	2.4 ng g^{-1} f.w.	214(4MBC), 193–525(BP3), 414 (EHMC), 300 (OC) ng g^{-1} f.w.	[6]

Fish	Barb (*Barbus barbus*), chub (*Leuciscus cephalus*)	Muscle plus adipose tissue under the skin	4MBC, 3BC, BP1, BP2, 4DHB, BP3, BP4, EHMC, Et-PABA	4 g	Solvent extraction using EtAc, n-heptane, and HPLC water (1:1:1, *v*/*v*/*v*) or solvent extraction with MeOH/ACN (1:1, *v*/*v*)	RP-HPLC (RP Spherisorb ODS2 column) (4.6 × 150 mm; 5.0 µm)	LC–ESI-MS/MS and GC–EI-MS	Zorbax SB-C18 (150 × 3.0 mm; 3.5 µm) and OPTIMA-5-MS (50 m × 0.2 mm; 3.5 µm)	76–99 (BP4 not extracted)	8–205 ng g^{-1} l.w.	45–700 (EHMC) ng g^{-1} l.w.	[11]
	Barb (*Barbus barbus*) and chub (*Leuciscus cephalus*)	Muscle plus adipose tissue under the skin	BP4, 4DHB, BP1, BP2, Et-PABA	1 g	Solvent extraction with MeOH/ACN (1:1, *v*/*v*)	Syringe filtration	LC–ESI-MS/MS	Zorbax SB-C18 (150 × 3.0 mm; 3.5 µm)	80–99	1.8–10.7 ng kg^{-1} f.w.		
Fish	Roach (*Rutilus rutilus*)	Muscle, offal, rest and whole fish	IDM, BM-DBM, 4MBC, OD-PABA, HMS, EHMC, BP3	n.r.	Homogenized with sodium sulfate Soxhlet extraction with petroleum ether/EtAc (1:1, *v*/*v*)	GPC (BioBeads S-X3)	GC–EI-MS	SE-54-CB (50 m × 0.55 mm; 0.25 µm)	89–106	50–90 ng kg^{-1} f.w.	*Muscle*: 810 (4MBC), 310 (EHMC), 298 (BP3), 3,100 (HMS); *offal*: 880 (4MBC), 283 (BP3), 185 (HMS); *rest*: 990 (4MBC), 50 (EHMC), 40 (BP3), 79 (HMS) *whole fish*: 930 (4MBC), 120 (EHMC), 150 (BP3), 791 (HMS) ng g^{-1} l.w.	[7]
	Perch (*Perca fluviatilis*)			n.r.							*Muscle*: 161 (4MBC), 41 (EHMC), 230 (BP3), 720 (HMS), 150 (IDM); *offal*: 106 (4MBC), 270 (BP3), 970 (HMS), 210 (BM-DBM); *rest*: 60 (4MBC), 16 (EHMC), 22 (BP3), 41 (HMS), 9 (IDM),	

(continued)

Table 1 (continued)

Matrix	Species	Tissue	UV filter	Sample amount	Extraction	Purification	Technique	Chromatographic column	Recovery (%)	MLOD	Concentration ranges	References
											18 (TDM); *whole fish*: 78 (4MBC), 20 (EHMC), 78 (BP3), 237 (HMS), 29 (IDM), 44 (BM-DBM) ng g^{-1} l.w.	
Macrozoobenthos	Mussels (*Dreissena polymorpha*)	Whole macroinvertebrate	BP1, BP2, BP3, BP4, 4DHB, Et-PABA, EHMC, 4MBC, 3BC	4 g (fraction 1) and 1 g (fraction 2)	Fraction 1: solvent extraction with EtAc, *n*-heptane, and HPLC water (1:1:1, *v.v:v*) or solvent extraction with MeOH/ACN (1:1, *v*/*v*) Fraction 2: solvent extraction with MeOH/ACN (1:1, *v*/*v*)	Fraction 1: RP-HPLC (RP Spherisorb ODS2 column) (4.6 × 150 mm, 5.0 µm) Fraction 2: syringe filtration	LC–ESI-MS/MS and GC–EI-MS	Zorbax SB-C18 (150 +3.0 mm; 3.5 µm) and OPTIMA-5-MS (50 m × 0.2 mm; 0.35 µm)	70–105	6–50 ng g^{-1} l.w.	22–150 (EHMC) ng g^{-1} l.w.	[13]
	Gammarus sp.										91–133 (EHMC) ng g^{-1} l.w.	
Fish	Chub (*Leuciscus cephalus*)	Muscle plus adipose tissue under the skin									23–79 (EHMC) ng g^{-1} l.w.	
	Brown trout (*Salmo trutta*)										91–151 (BP3), 11–173(EHMC) ng g^{-1} l.w.	
	Barb (*Barbus barbus*)										9–337 (EHMC) ng g^{-1} l.w.	
	Eel (*Anguilla anguilla*)										<LOQ (BP3), 30 (EHMC) ng g^{-1} l.w.	
Bird	Cormorants (*Phalacrocorax* sp.)	Muscle									16–701 (EHMC) ng g^{-1} l.w.	
Bivalves[a]	Mussels (*Mytilus edulis and Mytilus galloprovincialis*)	Soft tissue	EHMC, OC, OD-PABA	3 g	MAE with acetone/heptane (1:1, *v*/*v*)	Filtered (0.2 µm) through 10 g anhydrous sodium sulfate RP-HPLC (RP Spherisorb ODS2 column) (4.6 × 150 mm, 5.0 µm)	GC–MS/MS	SGE-BPX5 (30 m × 0.25 mm; 0.25 µm)	89–116	2 ng g^{-1} d.w.	3–256 ng g^{-1} (EHMC) 2–7,112 ng g^{-1} (OC) d.w.	[14]

Fish	Barb (*Luciobarbus sclateri*), carp (*Cyprinus carpio*)	Whole fish	BP1, BP3, 4HB, 4DHB, EHMC, 4MBC, OC, OD-PABA	1 g	PLE (AcEt, DCM) (1:1, *v*/*v*) with Florisil in the extraction cell	SPE with Isolute C18 (500 mg, 3 ml)	LC–ESI-MS/MS	Hibar Purospher STAR HR R-18 (50 × 2.0 mm; 2 µm)	42.110	0.1–6.0 ng g^{-1} d.w.	11–24 (BP3), 19–241(EHMC), 30.4 (OC) ng g^{-1} d.w.	[9]
Bivalves	Mussel (*Mytilus galloprovincialis*), cockle (*Cerastoderma edule*)	Muscle	4MBC, BP3, IAMC, EHMC, Et-PABA, OC, EHS, HMS,	0.5 g	MSPD extraction with Florisil and ACN	Polypropylene syringe containing C18 as cleanup sorbent for lipid retention	GC–EI-MS	HP-5 (30 × 0.25 mm; 0.25 µm)	80–101	1–9 ng g^{-1} d.w.	211–281 (OC) ng g^{-1} d.w.	[15]
Marine mammals	Dolphin (*Pontoporia blainvillei*)	Liver	OC	1 g	PLE with DCM/hexane (1:1, *v*/*v*)	Acid attack (H_2SO_4) and SPE with alumina	LC–ESI-MS/MS	Hibar Purospher STAR HR R-18 (50 × 2.0 mm; 2 µm)	n.r.	23 ng g^{-1} l.w.	79–782 l.w. (OC) ng g^{-1} l.w.	[17]

[a]*n.r.* not reported, *n.d.* not detected

properties. Mid-polar and lipophilic compounds were obtained from homogenized tissue by solvent extraction using a mixture of ethyl acetate, n-heptane, and water (1:1:1, *v*/*v*). The extracts were purified by RP-HPLC and further analyzed by GC–MS. Polar and mid-polar UV-Fs were analyzed by HPLC–MS after the extraction using a mixture of MeOH and acetonitrile (ACN). The same method proved to be also suitable for the analysis of macrozoobenthos and bird samples. A methodology based on the extraction by MAE, using a mixture of acetone/heptane (1:1, *v*/*v*), was developed by Bachelot et al. [14] for the determination of EHMC, OC, and OD-PABA in marine mussels. After the extraction, further purification was carried out by RP-HPLC following a procedure adapted from a previous study [11]. A low solvent consumption method for the determination of eight UV-Fs (with low and medium polarities) in bivalve and fish samples was recently developed by Negreira et al. [15]. Target compounds were extracted using MSPD. Extractions were performed with 0.5 g of freeze-dried samples blended with 2 g of Florisil. After thorough homogenization, the blend was transferred to a polypropylene syringe containing C18 as cleanup sorbent for lipid retention. Recently, Gago-Ferrero et al. [9] developed a new methodology for the simultaneous determination of eight UV-Fs, including two transformation products with a wide range of physicochemical properties in fish based on PLE, using a mixture of AcEt/DCM (1:1, *v*/*v*) with Florisil in-cell purification and further SPE extra purification using C18 cartridges, obtaining good results.

2.2.2 Instrumental Analysis and Method Performance

LC is the technique of choice for the analysis of UV-Fs in cosmetic products. In contrast, GC is generally preferred for their environmental analysis. Nevertheless, both techniques have been applied to the analysis of biological samples.

UV-Fs are amenable to GC with very few exceptions (e.g., octyl triazone (OT), BM-DBM). Matrix effects are not critical for the ionization modes such as electron impact (EI) or chemical ionization (CI) typically used in GC–MS. As a consequence, method limits of detection (MLODs) are usually quite low [16]. On the other hand, this technique can only be successfully applied to a limited number of nonpolar and volatile compounds. LC–MS allows the analysis of a wider range of compounds and significantly increases the potential of analyzing metabolites, as it was previously mentioned. Some studies analyzing UV-Fs with a large range of physicochemical properties used GC–EI-MS for the analysis of the most lipophilic ones, while the more polar ones were detected by LC–MS. [11, 13]. Determination of UV-F using GC–MS has been carried out in all cases using GC–EI-MS. Quantification is achieved by operating in selected ion monitoring mode (SIM) (Table 1) or selected reaction monitoring (SRM), which improves the selectivity and sensitivity (Table 1). Substances used as surrogate standard in GC–MS UV-F analysis include $^{13}C_{12}$-PCB 77 [8], $^{15}N_3$-musk xylene [10], benzophenone-d_{10} [11–13], $^{13}C_6$p-n-nonylphenol [12], and chrysene-d_{12} [14].

Moreover, the different chiral forms of 4MBC were separated and determined by Buser et al. [10] using GC–MS-based enantioselective techniques.

Methods based on LC–MS normally deal with a higher range of physicochemical properties and/or include metabolites. All the approaches for the LC–MS determination of UV-Fs in biota employed ESI, which offers good results for the ionization of the analytes even though this ionization mode is presumed to be susceptible to strong matrix effects due to the influence of sample matrix. Benzoic-d_5 was used by Zenker et al. [11], and recently Gago-Ferrero et al. used deuterated BP3 (BP3d_5) and 4MBC*d4* [9].

High recovery rates were achieved in all the methods reported, especially when the lipid content of the biological sample analyzed was low. Most studies analyzing lipophilic UV-Fs used solvent extraction and further cleanup by GPC and usually achieved good recoveries. Approaches using PLE and further SPE purification or MSPD also showed good method performances.

For biota samples, MLODs are in the sub ng g^{-1} range, although authors normalize to different parameters depending on the matrix and express the results in ng g^{-1} lipid weight (l.w.), ng g^{-1} dry weight (d.w.), or ng g^{-1} fresh weight (f.w.). Presence of UV-Fs in blanks is eventually reflected by higher MLODs. MLODs are highly dependent on the analyzed matrix. Biological matrices may be quite different depending on the selected organism, the species, and the chosen tissue, and even so, still there exists great variability. As an example, Balmer et al. [8] obtained three significantly different MLOD ranges for the analysis of four lipophilic UV-Fs as a function of the fish species analyzed. Generally, MLODs are lower when analyzed with GC–MS as the matrix effect has usually less effect, but the ones obtained in the LC–MS/MS methodologies allow a reliable quantification of these compounds in the studied matrices. Table 1 summarizes the recoveries and MLODs ranges obtained in each study.

2.2.3 Occurrence in Biota

Bioaccumulation of UV-Fs in aquatic organisms of different trophic levels has been studied, although data on this topic is still scarce. Several fish species, which are important bioindicators of the occurrence of persistent lipophilic contaminants, have been investigated together with mollusks, crustaceans, aquatic birds, and, recently, marine mammals. Table 1 summarizes UV-F occurrence data in biota.

OC and EHMC were by far the most ubiquitous compounds and the ones detected at higher concentrations, reflecting its high use in cosmetic products and their low biodegradability. BP3, 4MBC, and HMS were also detected in an appreciable amount of samples at relevant concentrations. Values from 9 to 2400 ng g^{-1} l.w. have been reported for UV-F in fish samples in a few studies [6–11, 13], and concentrations over 7,000 ng g^{-1} were detected in mussels [14, 15].

Fent et al. [13] detected EHMC in crustacean and mollusks in the range 22–50 ng g^{-1} l.w. and in fish at values up to 337 ng g^{-1} l.w. The higher concentration, above 700 ng g^{-1} l.w., was reported for fish-eating birds (*Phalacrocorax* sp.),

which suggests that biomagnification occurs through the food web. High values of OC (79–782 ng g^{-1} l.w.) have been determined in Franciscana dolphins from different areas of the Brazilian coast [17], which also suggest biomagnification due to the fact that these organisms are in the top of the food web.

2.3 Synthetic Musk Fragrances

2.3.1 Sample Extraction and Preparation

Extraction procedures for synthetic musk fragrances from biota samples are similar to those described previously for UV-F, being the most used Soxhlet extraction [2, 18–23] and PLE [24–29]. Other approaches employed include matrix dispersion-extraction [30] and solid–liquid extraction [12, 31]. The main parameters of the developed methodologies are summarized in Table 2. The different studies focused on the analysis of polycyclic musk fragrances, including galaxolide (HHCB), tonalide (AHTN), traseolide (ATII), celestolide (ADBI), and phantolide (AHMI), and nitro musk fragrances and metabolites, mainly musk xylene (MX), musk ketone (MK), musk ambrette (MA), musk moskene (MM), musk tibetene (MT), 2-amino musk xylene (2AMX), 4-amino musk xylene (4AMX), and 2-amino musk ketone (2AMK).

Rimkus and Wolf [31] analyzed for the first time nitro musk fragrances in biota samples, including fish, mussels, and shrimps. Target analytes were extracted from the different tissues by solid–liquid extraction using the mixture water/acetone/petroleum ether. After removal of the extractant, the lipid extracts were cleaned up by GPC followed by silica gel adsorption chromatography for purification. Several methodologies perform the extraction of both polycyclic musk fragrances and nitro musk fragrances by mixing the tissues (fresh tissue or freeze-dried) with sodium sulfate or other agents (alumina, diatomaceous earths) and then using Soxhlet or PLE with a variety of solvent mixtures including hexane/EtAc [24–26], hexane/acetone [18, 19, 23], EtAc/cyclohexane [19, 20], DCM/hexane [2, 21, 22], hexane [27, 28], or cyclohexane/AcEt [29]. In general, methodologies including nitro musk fragrances and metabolites used solvent mixtures with higher polarities due to the higher polarity of these compounds in comparison to polycyclic musk fragrances. Generally, after the extraction steps, additional removal of lipids is necessary. In most cases, lipids are removed from extracts using GPC. Lipids cannot be removed destructively with sulfuric acid for the determination of these substances due to the simultaneous destruction of the target compounds [32]. GPC phases used in the developed methodologies for the analysis of synthetic musk fragrances in biota samples include BioBeads S-X3 with different solvent mixtures (e.g., hexane/DCM or cyclohexane/AcEt) and Envirogel and Phenogel guard column with DCM [12, 22, 23, 25–31]. Final extract purification was carried out using silica (mainly), Florisil, Strata NH_2, or alumina with a variety of eluents.

Table 2 Analytical methodology and occurrence data for synthetic musk fragrances in biota

Matrix	Species	Tissue	Compound	Sample amount	Extraction	Purification	Technique	Chromatographic column	Recovery (%)	MLOD	Concentration ranges	References
Fish	Rainbow trout (*Oncorhynchus mykiss*), carp (*Cyprinus carpio* L.)	Muscle	MX, MK, MA, MM, MT	n.r.	Solid–liquid extraction with water/acetone/ petroleum ether	GPC and silica purification	GC-ECD	DB-5 (60 m × 0.25 mm; 0.25 µm), DB-1701 (60 m × 0.25 mm; 0.25 µm)	n.r.	10 ng g^{-1} l.w.	10–1,060 (MX), 10–380 (MK) ng g^{-1} l.w.	[31]
Mussel	Blue mussels (*Mytilus edulis*)	Whole tissue									10–40 (MX), 10–40 (MK) ng g^{-1} l.w.	
Shrimp	Sea shrimps (*Crangon crangon*)	Whole tissue									10 (MX), 30–50 (MK) ng g^{-1} l.w.	
Fish	Trout (*Salmo trutta fario L.* and *Salmo trutta lacustris L.*), sheatfish (*Silurus glanis*), crucian carp (*Carassius carassius*), Italian nose (*Chondrostoma soetta*), chub (*Leuciscus cephalus*)	Muscle	HHCB, AHTN, ATII, ADBI, AHMI	3 g	PLE with hexane/EtAc (5:1, *v/v*)	Alumina purification	GC–EI-MS	Supelcowax 10 (30 m × 0.20 mm; 0.20 µm)	105	0.5–2 ng g^{-1} f.w.	4–5 (AHMI), 4–47 (HHCB), 4–105 (AHTN) ng g^{-1} f.w.	[24]
Crustaceans	Lobsters (*Homarus americanus*)	Digestive gland or hepatopancreas	HHCB, AHTN, MX, MK, 2AMX, 4AMX, 2AMK	5 g	Soxhlet extraction with hexane/acetone (9:1, *v/v*)	Silica purification	GC–EI-MS	DB-5 (20 m × 0.25 mm; 0.25 µm)	66–85	2–8 ng g^{-1} l.w.	2–3 (MX), 110–190 (MK), 10–120 (HHCB), 7–12 (AHTN) ng g^{-1} l.w.	[18]
Fish	Striped bass (*Morone saxatilis*), winter flounder (*Pseudopleuronectes americanus*), American eel (*Anguilla rostrata*), Pollock (*Pollachius virens*), Atlantic menhaden (*Brevoortia tyrannus*), spiny dogfish (*Squalus acanthias*), lake trout (*Salvelinus namaycush*), herring (*Clupea harengus*)	Liver, muscle, or whole fish									2–49 (MX), 76–2,700 (MK), 29–100 (HHCB), 17–70 (AHTN) ng g^{-1} l.w.	
Bivalves	Clam (*Mya arenaria*), mussel (*Mytilus edulis*)	Whole tissue									110 (MX), 2,200–17,700 (MK), 1,650–3,000 (HHCB), 1,100 (AHTN) ng g^{-1} l.w.	

(continued)

Table 2 (continued)

Matrix	Species	Tissue	Compound	Sample amount	Extraction	Purification	Technique	Chromatographic column	Recovery (%)	MLOD	Concentration ranges	References
Fish	Eels (*A. anguilla*)	Muscle	MX, MK	10 g	Soxhlet extraction with hexane/acetone (9:1, *v*/*v*)	Silica purification	GC-ECD	HP-1 and HP-5 (50 m × 0.20 mm; 0.50 μm)	n.r.	n.r.	1–170 (MX), 1–380 (MK) ng g^{-1} f.w.	[20]
Fish	Eels (*A. anguilla*)	Muscle	HHCB, AHTN, ATII, ADBI, AHMI	10 g	Soxhlet extraction with EtAc/cyclohexane (50.4:49.6, *v*/*v*)	Silica purification	GC–EI-MS	DB-XLB (30 m × 0.25 mm; 0.25 μm)	78–95	4–30 ng g^{-1} f.w.	50–4,800 (HHCB), 32–2,300 (AHTN), 8–190 (ATII), 2–17 (ADBI), 2–210 (AHMI) ng g^{-1} f.w.	[19, 20]
Fish	Carp (*Cyprinus carpio*)	Whole fish	HHCB, AHTN, ATII, ADBI, AHMI, MX, MK, MA, MM, MT, 2-AMX, 4-AMX, 2-AMK	2.3 g	PLE with hexane/EtAc (1:5, *v*/*v*)	GPC (Envirogel) and alumina/Strata NH_2 purification	GC–EI-MS	HP-5MS (30 m × 0.25 mm; 0.25 μm)	88–110	0.05–2 ng kg^{-1} f.w.	0.5–52.4 ng g^{-1} f.w.	[25, 26]
Fish	Trout	Whole fish (except guts and fins)	HHCB, AHTN, ATII, ADBI, AHMI, MX, MK, MA, MM, MT	10 g	Homogenization with acetone/pentane (1:3, *v*/*v*)	GPC (BioBeads S-X3) and Florisil purification	GC–EI-HRMS, GC–EI-MS, GC-ECD	DB-5MS (30 m × 0.25 mm; 0.20 μm) HP-5 (30 m × 0.25 mm) DB-17 (60 m) and Sil-5CB (50 m)	70–97	0.03–0.6 ng g^{-1} f.w.	0.03–55.6 ng g^{-1} f.w.	[30]
Marine mammals	Polar bears (*Ursus maritimus*), sea otters (*Enhydra lutris nereis*), harbor seals (*Phoca vitulina*), California sea lions (*Zalophus californianus*), bottlenose dolphins (*Tursiops truncatus*), spinner dolphins (*Stenella clymene*), pygmy sperm whales	Liver and blubber	HHCB, AHTN	1–5 g	Soxhlet extraction with DCM/hexane (3:1, *v*/*v*)	Silica purification	GC–EI-MS	DB-5 (30 m × 0.25 mm)	85–98	1 ng g^{-1} f.w.	1–25 (HHCB), 1.9–2.3 (AHTN) ng g^{-1} f.w.	[2]

	(*Kogia breviceps*), river otters (*Lontra canadensis*), mink (*Mustela vison*)											
Fish	Atlantic sharpnose sharks (*Rhizoprionodon terraenovae*), Atlantic salmon (*Salmo salar*), smallmouth bass (*Micropterus dolomieu*)	Liver and muscle									1–5.4 (HHCB), 1.4–1.9 (AHTN) ng g^{-1} f.w.	
Bird	Merganser (*Mergus merganser*), lesser scaup (*Aythya affinis*), greater scaup (*Aythya marila*), mallard (*Anas platyrhynchos*)	Liver									1.9–4.2 (HHCB), 1–2.7 (AHTN) ng g^{-1} f.w.	
Marine mammals	finless porpoise (*Neophocaena phocaenoides*)	Blubber	HHCB, AHTN, MX, MK, MA	1–4 g	Soxhlet extraction with DCM/hexane (8:1, *v*/*v*)	Silica purification	GC–EI-MS	DB-1 (30 m × 0.25 mm; 0.25 µm)	92–108	2.5–9.1 ng g^{-1} f.w.	13–149 (HHCB), 9.6 (AHTN) ng g^{-1} f.w.	[21]
Fish	Hammerhead sharks	Liver									16–48 (HHCB) ng g^{-1} f.w.	
Algae	Bladderwrack (*Fucus vesiculosus*)	Whole tissue	HHCB, AHTN, ATII, ADBI, AHMI, MX, MK	1–5 g	PLE with *n*-hexane	GPC (BioBeads S-X3) and silica purification	GC–EI-MS	Rtxs-50 column (30 m × 0.25 mm, 0.1 µm)	83–135	0.1–0.5 ng g^{-1} f.w.	0.29 (HHCB), 0.28 (AHTN) ng g^{-1} f.w.	[27]
Bivalves	Blue mussels (*Mytilus edulis*), zebra mussels (*Dreissena polymorpha*)	Whole tissue									0.28–29 (HHCB), 0.23–25 (AHTN), 0.11–1.1 (ATII), 0.2–1 (ADBI), 0.1–1.3 (AHMI), 0.1–0.3 (MX), 0.21 (MK) ng g^{-1} f.w.	
Fish	Eelpout (*Zoarces viviparus*), bream (*Abramis brama*)	Muscle									10–18,400 (HHCB), 8–4,790 (AHTN), 14–600 (ADBI), 6–643 (AHMI), 14–1,230 (ATII), 3–273 (MX), 5–295 (MK) ng g^{-1} l.w.	
Bird	Herring gulls (*Larus argentatus*)	Eggs									20–30 (HHCB), 15–25 (AHTN), 5–6 (MX) ng g^{-1} l.w.	

(continued)

Table 2 (continued)

Matrix	Species	Tissue	Compound	Sample amount	Extraction	Purification	Technique	Chromatographic column	Recovery (%)	MLOD	Concentration ranges	References
Tidal flat water organisms	Several species	Whole body, soft tissue, hepatopancreas, liver, or blubber	HHCB, AHTN, MX, MK, MA	1–4 g	Soxhlet extraction with DCM/hexane (8:1, *v*/*v*)	GPC and silica purification	GC–EI-MS	BPX-5 column (30 m × 0.25 mm, 0.25 µm)	99–113	0.12–0.4 ng g^{-1} f.w	0.55–9.1 (HHCB), 0.62–2.1 (AHTN) ng g^{-1} f.w.	[22]
Shallow water organisms	Several species										0.57–51 (HHCB), 0.27–5.9 (AHTN) ng g^{-1} f.w	
Marine mammals	Finless porpoise (*Neophocaena phocaenoides*), striped dolphins (*Stenella coeruleoalba*)										1–135 (HHCB) ng g^{-1} f.w.	
Fish	Bluegill (*Lepomis macrochirus*)	Muscle	HHCB, AHTN, ADBI, MX, MK	1 g	Rotary extraction with acetone	Silica purification	GC–EI-MS	XTI-5 capillary column (30 m × 0.25 mm; 0.25 µm)	87–105	4–17 ng g^{-1} f.w.	234–970 (HHCB), 33–97 (AHTN) ng g^{-1} f.w	[12]
	Sonora sucker (*Catostomus insignis*)	Muscle, belly flap, and skin			Sonication with acetone	GPC and silica purification	GC–MS/MS	VF-5 MS capillary column (30 m × 0.25 mm; 0.25 µm)	67–107	12–397 ng g^{-1} f.w.	n.r.	
Fish	Crucian carp, silver carp (*Hypophthalmichthys molitrix*), common carp (*Cyprinus carpio*)	Muscle	HHCB, AHTN, ATII, ADBI, AHMI, MX, MK	1 g	PLE with *n*-hexane	GPC (BioBeads S-X3) and alumina purification	GC–EI-MS	HP-5MS (0.25 mm; 0.25 µm)	89–110	1–1.2 ng g^{-1} d.w.	2.2–5.3 (HHCB), 2.9–6.8 (AHTN), 2.2–2.7 (AHMI), 3.1–3.2 (ATII), 4.1–7.9 (MK) ng g^{-1} d.w	[28]
Fish	Herbivorous, omnivorous, and carnivorous fish (several species)	n.r.	HHCB, AHTN, ATII, ADBI, AHMI, MX, MK	4 g	Soxhlet extraction with hexane/acetone (1:1, *v*/*v*)	GPC and silica–alumina purification	GC–EI-MS	HP-5 MS fused silica capillary column (30 m × 0.25 mm; 0.25 µm)	72 (*average value*)	0.4–1 ng g^{-1} l.w.	1–52.9 (HHCB), 1–7.5 (AHTN), 1–50.8 (MX), 1–469.7 (MK) ng g^{-1} l.w	[23]
Fish	French and Russian carp, pike, eel, barb	Muscle, liver, and whole fish	HHCB, OTNE, lilial, hexylcinnamaldehyde, acetyl cedrene	1 g	PLE with cyclohexane/AcEt (1:1, *v*/*v*)	GPC (BioBeads S-X3)	GC–MS/MS	DB-XLB (30 m × 25 mm; 0.5 µm)	83–110	10 ng g^{-1} f.w.	13–1,700 (HHCB), 10–510 (OTNE), 10 (lilial), 10 (hexylcinnamaldehyde), 14–93 (acetyl cedrene) ng g^{-1} f.w	[29]

n.r. not reported

2.3.2 Instrumental Analysis and Method Performance

Synthetic musk fragrances are semi-volatile organic compounds and highly lipophilic. Thus, the technique of choice for its analysis is GC–MS. Synthetic musk fragrances are commonly analyzed by GC–EI-MS, but gas chromatography coupled to negative chemical ionization mass spectrometry (GC–NCI-MS) is more sensitive for nitro musk fragrances. Other techniques such as gas chromatography with a flame ionization detector (GC-FID) or an electron capture detector (GC-ECD) have been also used in the analysis of these substances. This information is summarized in detail in Table 2. Detection is achieved operating mainly in SIM mode and in some cases in SRM mode, for improved selectivity and sensitivity (Table 2).

Due to the lack of isotopically labeled standards commercially available, a variety of internal standards have been used instead for the analysis of musk fragrances, including deuterated PAHs and various labeled and unlabeled PCBs, among others. In the most recent studies deuterated AHTN (d_3-AHTN) has been used as surrogate standard [23, 28, 29].

The GC–MS-based methodologies described herein show good selectivity and sensitivity. Recoveries obtained are mainly above 70% for all the studied compounds. The obtained MLODs for biota samples were in the very low ng g^{-1} f.w. range. These values are often expressed in ng g^{-1} l.w. Table 2 summarizes the recoveries and MLODs ranges obtained in the cited studies.

2.3.3 Occurrence in Biota

Musk fragrances have low vapor pressure and relatively high octanol/water partition coefficients. Nitro and polycyclic musk compounds are assumed to be nonbiodegradable [32], although a larger fraction is eliminated during wastewater treatment. These facts make them compounds with high potential for bioaccumulation in aquatic species, as revealed by the bioconcentration and bioaccumulation factors (BCF) determined in various studies [32, 33].

Bioaccumulation of these substances in aquatic organisms both from fresh- and saltwater has been investigated in few studies. The high number of species analyzed draws attention. The list includes several species of fish, bivalves, and birds but also a great number of marine mammals, including dolphins, whales, and even polar bears, among others. Relevant levels of synthetic musk fragrances were determined in almost all the studied species, including dolphins and whales. An exception would be the polar bears from the Alaskan Arctic, with no positive results [2].

Data obtained in the different studies revealed that significant concentrations were determined for this family of substances. Concentration ranges for each compound are summarized in detail in Table 2. HHCB and AHTN (the ones with the highest BCF [32]) were by far the major musk fragrances in biota samples among the polycyclic ones, whereas MK and MX were the most ubiquitous and

concentrated substances among the nitro musk fragrances. These substances reached in many cases concentrations above 1,000 ng g^{-1} l.w.

Some authors claim that there are remarkable different patterns of concentration of these substances depending on the continent (America, Europe, Asia (Japan)) [18, 21] due to differences in the consumption patterns of these products. In the case of Europe, it can be observed that the highest levels for these compounds were detected in the 1990s. In recent years, concentrations have decreased [27].

Fromme et al. [19] observed a clear relationship between the content of polycyclic musk fragrances in eel samples and the proportion of sewage water in the area concerned, demonstrating the good indicator function of this substance class as evidence of the degree of contamination of flowing waters by organic substances entering from sewage works.

Regarding biomagnification, the available data is still scarce and somewhat ambiguous. In general, no significant differences in the concentration levels were observed between species of different trophic levels. Nakata et al. [22] demonstrated biodilution for HHCB, whereas Zhang et al. [23] suggested biomagnification for this compound and biodilution for AHTN taking place along the freshwater food chain. Differences in this issue are probably due to differing retention and metabolism of these compounds in different organisms [22].

2.4 Antimicrobials

2.4.1 Sample Extraction and Preparation

Methods for the extraction of triclosan (TCS), triclocarban (TCC), and the TCS metabolite methyl-triclosan (MTCS) from biota samples are summarized in Table 3.

Okumura and Nishikawa [34] developed a method for the analysis of TCS and the compounds tetra(II)closan, tetra(III)closan, and pentaclosan. In this method, the extraction was carried out by centrifuging the homogenized sample with 50 ml of ACN. The ACN phase was combined with 500 ml of water, 6 g of NaOH, and 25 g of NaCl in a separation funnel and washed with 50 ml of *n*-hexane. The solution was acidified with HCl and extracted twice with 50 ml of *n*-hexane and then the methylation was performed. Finally, the extracts were purified with Florisil. In a study carried out by Balmer et al. [35], MTCS was extracted from homogenized fish mixed with sodium sulfate by mixing with cyclohexane/DCM or from homogenized fish mixed with diatomaceous earth by PLE with cyclohexane/DCM. Extracts from both methods were purified by GPC with an EnviroSep-ABC column and DCM/hexane mobile phase or BioBeads S-X3 and DCM/cyclohexane mobile phase. Extracts were then purified with deactivated silica. In the studies performed by Coogan et al. [36, 37], different tissues including algae and snails were mixed with anhydrous sodium sulfate and Soxhlet extracted with DCM. High molecular weight lipids were removed by GPC with an ABC Laboratories (Columbia, MO,

Table 3 Analytical methodology and occurrence data for antimicrobials in biota

Matrix	Species	Tissue	Compound	Sample amount (g)	Extraction	Purification	Technique	Chromatographic column	Recovery (%)	MLOD	Concentrations ranges	References
Fish	n.r.	n.r.	TCS, tetra (II)closan, tetra(III) closan, pentaclosan	10	Homogenization with ACN; centrifugation; dissolution in water and LLE with hexane	Saponification with KOH EtOH; extraction with hexane; Florisil purification	GC–EI-MS (diazomethane)	Ultra-2 (30 m × 0.25 mm; 0.25 μm)	85–119	0.9–2.5 ng g^{-1} f.w.	n.r.	[34]
Fish	White fish (*Coregonus* sp.), roach (*Rutilus rutilus*), trout (*Salmo trutta*)	Muscle	MTCS	5	PLE: homogenized with diatomaceous earth 3 cycles DCM/cyclohexane (1:1, *v*/*v*) at room temperature	GPC (EnviroSep-ABC or BioBeads S-X3) and silica purification	GC–EI-MS	DB-5 (25 m × 0.32 mm; 0.25 μm)	76–108	1–5 ng g^{-1} l.w.	4–365 ng g^{-1} l.w.	[8, 35]
				25	Homogenized with sodium sulfate Column extracted with DCM/cyclohexane (1:1, *v*/*v*)							
Algae	*Cladophora* spp.	Whole algae	TCS, TCC, MTCS	2	Soxhlet extraction with DCM	GPC (EnviroSep-ABC)	GC–EI-MS and LC–MS	Econo-Cap phase 5 (30 m × 0.25 mm; 0.25 μm); Zorbax C18 (150 × 2.1 mm; 5 μm)	80–115	5–10 ng g^{-1} f.w.	100–150 (TCS), 200–400 (TCC), 50–90 (MTC) ng g^{-1} f.w. (mean concentrations)	[36, 37]
Gastropods	Snail (*Helisoma trivolvis*)	Whole tissue without shell							93–127	5–10 ng g^{-1} f.w.	5.9–58.7 (TCS), 9.8–299 (TCC), 0.8–49.8 (MTC) ng g^{-1} f.w.	

(continued)

Table 3 (continued)

Matrix	Species	Tissue	Compound	Sample amount (g)	Extraction	Purification	Technique	Chromatographic column	Recovery (%)	MLOD	Concentrations ranges	References
Fish	Bluegill (*Lepomis macrochirus*)	Muscle	TCS	1	Rotary extraction with acetone	Silica purification	GC–EI-MS (MSTFA)	XTI-5 (30 m × 0.25 mm; 0.25 μm)	98	5.5 ng g^{-1} f.w.	17–31 ng g^{-1} f.w.	[12]
	Sonora sucker (*Catostomus insignis*)	Muscle, belly flap, and skin			Sonication with acetone	GPC and silica purification	GC–MS/MS (MSTFA)	VF-5 MS (30 m × 0.25 mm; 0.25 μm)	93	38 ng g^{-1} f.w.	n.r.	
Marine mammals	Dolphin (*Tursiops truncatus*)	Plasma	TCS, MTCS	2–4	Acidification and denaturation with isopropanol LLE with methyl-tert-butyl ether/hexane	Silica purification	GC–EI-HRMS (diazomethane)	DB-5 (60 m × 0.25 mm; 0.25 μm)	51	0.005 ng g^{-1} f.w.	0.025–0.27 ng g^{-1} f.w.	[38]
Fish	Several species	Muscle	TCS, TCC	5	Solid–liquid extraction using acetone/hexane (1:1, *v*/*v*)	Silica purification	UHPLC–MS/MS	Ascentis Express C18 (100 × 2.7 mm; 2.1 μm)	79–86	1–6 pg g^{-1} f.w.	0.021–507 (triclosan), 0.004–157 (triclocarban) ng g^{-1} f.w.	[39, 40]
Fish	Several species	Whole fish	TCS	1	Based on QuEChERS; solid–liquid extraction with ACN and application of specific salt (4 g $MgSO_4$, 1 g NaCl)	Dispersive SPE with $MgSO_4$, PSA (primary and secondary amine exchange material), and C18	UHPLC–MS/MS	Acquity BEH C18 column (50 × 2.1 mm; 1.7 μm)	44–90	0.3–0.9 ng g^{-1} d.w.	0.62–17.4 ng g^{-1} d.w.	[41]

n.r. not reported

USA) Model SP-1000 GPC processor according to manufacturer's recommended procedures. TCS has also been extracted from fish through solid–liquid extraction using acetone and, further, GPC and silica purification [12]. This compound was extracted from the plasma of Atlantic bottlenose dolphins [38]. In this methodology the plasma samples were acidified with HCl and denatured using isopropanol. After extraction with methyl *tert*-butyl ether (MTBE)/hexane, the volume was reduced and potassium hydroxide solution was used to partition the contaminants into two fractions: neutral and phenolic. The neutral fraction containing MTCS was cleaned on acidified silica. The phenolic fraction containing TCS was acidified with sulfuric acid, re-extracted with MTBE/hexane, and dried over sodium sulfate. TCS and TCC were extracted from freeze-dried fish muscle tissues by homogenizing with anhydrous sodium sulfate and extracting with a mixture of hexane and acetone using a high-speed solvent extractor [39, 40]. The extracts were further purified with silica. Jakimska et al. [41] carried out a very interesting work where different sample preparation methods were tested in order to select and optimize the most suitable one for the determination of 19 endocrine disruptor compounds including TCS in fish samples. The first extraction protocol was based on Huerta et al.'s [42] method and consisted of PLE followed by GPC cleanup. The second extraction method was a modification of a previous one, but in this case, PLE was followed by Florisil cleanup. The third approach and the one which showed the better performance was based on QuEChERS (quick, easy, cheap, effective, rugged, and safe; QuEChERS Kits, Agilent Technologies) and involved two steps: extraction with ACN in aqueous conditions followed by the application of specific salt (4 g $MgSO_4$, 1 g NaCl) used for salting out of water from the sample and to induce liquid–liquid partitioning and purification with dispersive solid-phase extraction (dSPE) using sorbent mixture (900 mg $MgSO_4$, 150 mg PSA (primary and secondary amine exchange material), 150 mg C18).

2.4.2 Instrumental Analysis and Method Performance

Direct determination of the compounds TCS and TCC by GC is complex, so they should be derivatized to more volatile analytes. The use of diazomethane to derivatize this class of compounds in the extracts of biota samples has been reported [34, 38]. However, due to its toxicity, its use in routine analysis is not recommended [43]. The silylating reagent N-methyl-*N*-(trimethylsilyl)trifluoroacetamide (MSTFA) has also been used with this purpose [12]. The concentration of TCS can be overestimated with this method due to the fact that MTCS, which is also one compound of interest, is the main transformation product of TCS. MTCS concentration can be determined prior to methylation or in a different aliquot of the extract.

TCS, MTCS, and TCC have been analyzed by LC–MS/MS [39–42], LC–MS (TCC) [36, 37], and GC–MS with or without derivatization [35–37]. TCC is best analyzed by LC-based methods. SIM is the monitoring mode used for the qualitative and quantitative analysis of the target analytes in single quadrupole MS. Analysis by LC–MS/MS was carried out in SRM mode. The isotopically

labeled compounds $^{13}C_{12}$ TCS and $^{13}C_{12}$ methyl-TCS and the deuterated TCC (d_7 TCC) are currently available and are widely used for recovery evaluation and as surrogate standards.

All the assessed methodologies provided good recovery rates for all compounds and low MLODs (usually in the very low ng g^{-1} range), which allow an accurate quantification of the target analytes in the studied matrices. Lower detection limits are achieved with derivatization using GC–MS. As expected, LC–MS/MS provided higher sensitivity than LC–MS.

2.4.3 Occurrence in Biota

The presence of antimicrobials in biota samples has been assessed in a few studies. These studies have been carried out mainly in fish samples. However, the bioaccumulation of these substances in other organisms including algae [36], gastropods [37], and even dolphin plasma [38] has also been reported.

In Sweden, high levels of TCS (240–4,400 ng g^{-1} f.w.) were determined in the bile of fish living downstream of a WWTP discharge site [44]. Generally, TCS degrades into MTCS, a primary degradation product in the environment. According to Balmer et al. [35], MTCS is more persistent in the environment than the parent compound (TCS) and has a higher potential to bioaccumulate due to its higher lipophilicity. Concentrations of MTCS in the range 4–365 ng g^{-1} l.w. were determined in the muscle tissue of different fish species in Germany [8, 35]. Coogan et al. [36] determined TCS, TCC, and MTCS in algae samples in a WWTP receiving stream (values up to 400 ng g^{-1} l.w.), and Coogan and La Point [37] reported higher concentrations for TCC (299 ng g^{-1} l.w) than TCS (59 ng g^{-1} l.w) in snails from the same WWTP, located in Texas (USA). TCS was also determined in the range 17–31 ng g^{-1} f.w. by Mottaleb et al. [12] in bluegill fish samples from Texas (USA).

TCS was detected in the blood plasma of wild Atlantic bottlenose dolphin (*Tursiops truncatus*) from Florida (USA) (0.025–0.27 ng g^{-1} f.w.) by Fair et al. [38]. This study indicates the possible accumulation of this compound in biota inhabiting coastal ecosystems. No detectable levels of MTCS were found. Ramaswamy et al. [40] performed a deep study analyzing samples of twenty fish species from Manila Bay in the Philippines. In this study, concentrations of TCS (0.021–507 ng g^{-1} f.w.) were generally higher than TCC (0.004–157 ng g^{-1} f.w.); however, the median values of the two compounds were comparable. TCS exhibited significantly lower values compared with the fish from Manila Bay, in the range 0.62–17.4 ng g^{-1} d.w., in samples corresponding to twelve different fish species from four Spanish Mediterranean river basins [41].

2.5 Parabens

2.5.1 Analysis of Parabens in Biota

Analysis of parabens in biota samples has not received much attention. There are just a few methods published dealing with the analysis of these compounds in these matrices which are summarized in Table 4. In all cases the described methodologies were not developed exclusively for the analysis of parabens but were developed for a wide range of contaminants including antimicrobials, stimulants, or flame retardants, among others. The analysis of parabens is dominated by LC–MS/MS due to the physicochemical properties of these compounds and the low levels of concentration in the analyzed tissues.

Kimet et al. [39] developed a multi-residue methodology including four paraben compounds: methyl paraben (MeP), ethyl paraben (EtP), propyl paraben (PrP), and butyl paraben (BuP). This method is based on high-speed solvent extraction followed by silica gel cleanup, and the instrumental analysis is performed by UHPLC–MS/MS. The method yielded good recovery rates (85–89%) and MLODs below 15 pg g^{-1} f.w. for all compounds. Renz et al. [45] developed another methodology for analyzing the same compounds in fish brain tissue based on solid–liquid extraction using first EtAc and then hexane. Derivatization by dansyl chloride was required, and the extracts were analyzed by HPLC–MS. No method performance parameters were reported.

Finally, Jakimska et al. [41] developed a sensitive and rapid method based on QuEChERS approach followed by UHPLC–MS/MS analysis (explained in the Sect. 2.4.1). The method was applied to the determination of nineteen endocrine disruptors including four parabens: MeP, EtP, PrP, and for the first time benzyl paraben (BeP). The procedure provided recoveries ranging from 40% to 113% and low MLODs in the range 0.002–0.14 ng g^{-1} d.w.

2.5.2 Occurrence in Biota

Data concerning parabens bioaccumulation is scarce. Kim et al. and Ramaswamy et al. conducted studies and determined the compounds MeP, EtP, PrP, and BuP with high frequency in samples of several fish species [39, 40]. Target compounds were found in over 90 % of the analyzed samples, with the exception of EtP, which was determined only in 70 % of the samples. MeP was the most ubiquitous compound and also the one which showed the highest levels (up to 3,600 ng g^{-1} f.w.). EtPB, PrPB, and BuPB concentrations reached values of 840 ng g^{-1} f.w., 1,100 ng g^{-1} f.w., and 70 ng g^{-1} f.w., respectively. The study carried out by Ramaswamy et al. showed total parabens concentrations more than two times higher in adult fish compared to juvenile fish, which may indicate growth-dependent compound accumulation [40]. Recently, Jakimska et al. [41] determined lower concentrations for four parabens (MeP, EtP, PrP, BeP). In this work, MeP

Table 4 Analytical methodology and occurrence data for preservatives (parabens) in biota

Matrix	Species	Tissue	Compound	Sample amount	Extraction	Purification	Technique	Chromatographic column	Recovery (%)	MLOD	Concentration ranges	References
Fish	Several species	Muscle	MeP, EtP, PrP, BuP	5 g	Solid–liquid extraction using acetone/hexane (1:1, *v*/*v*)	Silica purification	UHPLC–MS/MS	Ascentis Express C18 (100 × 2.7 mm; 2.1 μm)	85–89	1–15 pg g^{-1} l.w.	0.05–3,600 (MeP), 0.011–840 (EtP), 0.024–1,100 (PrP), 0.003–70 (BuP) ng g^{-1} l.w.	[39, 40]
Fish	Alewife (*Alosa pseudoharengus*), smallmouth bass (*Micropterus dolomieu*), shad (*Alosa fallax*)	Brain	MeP, EtP, PrP, BuP	n.r.	Solid–liquid extraction with EtAc and hexane	n.r.	HPLC–MS (derivatization with dansyl chloride)	C8 Hypersil GOLD column (100 × 4.6 mm; 5 μm)	n.r.	n.r.	n.d.	[45]
Fish	Several species	Whole fish	MeP, EtP, PrP, BeP	1 g	Based on QuEChERS; solid–liquid extraction with ACN and application of specific salt (4 g $MgSO_4$, 1 g NaCl)	Dispersive SPE with $MgSO_4$, PSA (primary and secondary amine exchange material), and C18	UHPLC–MS/MS	Acquity BEH C18 column (50 × 2.1 mm; 1.7 μm)	40–113	0.002–0.14 ng g^{-1} d.w.	0.8–84.9 (MeP), 0.8 (EtP), 0.6–7.4 (PrP), 0.3–0.5 (BeP) ng g^{-1} d.w.	[41]

n.r. not reported, *n.d.* not detected

was again the most ubiquitous and more concentrated preservative, with maximum values of 84.9 ng g^{-1} f.w. Levels for the other compounds were always below 7.4 ng g^{-1} f.w.

Renz et al. conducted a study analyzing parabens in fish tissue with no positive results in any sample [45].

3 Conclusions and Future Trends

Advances in the analytical instrumentation, particularly the widespread use of triple quadrupole analyzers, have led to the appearance of an increasing number of methods for the analysis of PCPs in biota samples. These methods also include a greater number of target compounds and reach lower MLODs, more suitable for the expected levels in real samples. Regarding the sample treatment, the heterogeneity of the studied matrices and the wide spectra of physicochemical properties of the analytes hinder the development of standardized methods. However, the reliability of the most usual procedures used for trace analysis of PCPs has been critically checked and showed to be effective. All these developments have enabled the emergence of the first data on the occurrence of PCPs in biota samples.

The studies reviewed in this chapter provide valuable data on the presence of various types of PCPs in aquatic biota. However, data are sparse and too scarce to draw solid conclusions about the distribution and behavior of these compounds in the environment. More high-quality data are needed to obtain a realistic view of the presence of PCPs in organisms and in the environment. In this regard, it seems also necessary to improve the monitoring strategies, since many studies do not allow conclusions beyond the occasional presence of certain substances in certain specific organisms. However, other better-focused studies from this point of view showed interesting trends in the distribution of some contaminants through the food chain, allowing even the calculation of biomagnification factors. Therefore, a good monitoring strategy is crucial to improve the quality of the obtained data.

An increase in collaboration between analytical chemists and toxicologists is also necessary. In many cases we are facing the problem of having abundant data about traces of PCPs and other pollutants in the environment without reaching final conclusions about their (eco)toxicological relevance.

In the future, increased attention will have to be paid to transformation products. Organisms can accumulate transformation products such as metabolites or biodegradation by-products generated during wastewater treatment, among others. Moreover, these organisms can also accumulate and metabolize the parent PCPs. The analysis of these substances may provide important clues about the behavior of these pollutants and valuable ecotoxicological data. Identification and determination of transformation products is normally a hard process and requires more advanced analytical instrumentation. Currently, recent advances in high-resolution mass spectrometry (HRMS) have opened up new windows of opportunity in the field of complex sample analysis. The use of these techniques allows the

identification of suspect and even non-preselected pollutants, very useful for the identification of metabolites. This approach allowed for the evaluation of the presence of high amounts of substances without purchasing the standards for all of them but only for which there was solid evidence that indeed they were present in the samples, leading to considerable economic savings. A significant increase in the development and use of methodologies using HRMS for the analysis of PCPs and derivatives in biota can be expected.

Acknowledgments Authors acknowledge the Spanish Ministry of Economy and Competitiveness, project SCARCE (Consolider Ingenio 2010 CSD2009-00065), and the Generalitat de Catalunya (Water and Soil Quality Research Group 2014 SGR 418).

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Part IV
Removal of Personal Care Products Under Non-conventional Treatments

Fungal-Mediated Biodegradation of Ingredients in Personal Care Products

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Abstract Many efforts have been devoted in developing technologies to remove emerging organic pollutants from freshwater systems. This chapter examined the applications of the environmental friendly technology based on fungal-mediated treatment for the degradation of ingredients in personal care products (PCPs), which are frequently detected at relevant concentrations in the aquatic environment. PCPs are daily-use products used in large quantity that includes several groups of substances (UV filters, preservatives, fragrances, etc.). Removal efficiencies

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M.S. Díaz-Cruz and D. Barceló (eds.), *Personal Care Products in the Aquatic Environment*, Hdb Env Chem (2015) 36: 295–318, DOI 10.1007/698_2014_329,

reported varied significantly among different experimental set-up, organic substance, and type of fungi. The mechanisms and factors governing the degradation of PCPs by fungi, mainly white-rot fungi and their specific lignin-modifying enzymes, are reviewed and discussed. Beyond, the identification of the intermediate products and metabolites produced as well as the degradation pathways available for some PCPs are presented.

Keywords Biocides, Biodegradation, Enzymes, Fragrances, Insect repellents, Metabolites, Parabens, Personal care products, Redox mediators, Sewage sludge, Triclosan, UV filters, Wastewater, White-rot fungi

Contents

Abbreviations

1-HBT	1-Hydroxybenzotriazole
4DHB	4-Dihydroxybenzophenone
4-MBC	4-Methylbenzylidene camphor
ABTS	2,2′-Azino-bis(3-ethylbenzothiazoline-6-sulfonic acid
AOPs	Advanced oxidation processes
BP1	Benzophenone 1
BP3	Benzophenone 3
CAS	Conventional activated sludge
CLEAs	Cross-linking of enzyme aggregates
dw	Dry weight
DEET	*N*,*N*-Diethyl-meta-toluamide
DMP	2,6-Dimethoxyphenol
EDC	Endocrine-disrupting chemicals
FBR	Fluidized bed reactor
GOD	Glucose oxidase
K_m	Michaelis–Menten constant
K_{ow}	Octanol–water partition coefficient
l.w.	Lipid weight

LIPs	Lignin peroxidases
LMEs	Lignin-modifying enzymes
MBR	Membrane bioreactor
MnPs	Manganese-dependent peroxidases
MS	Mass spectrometry
MS/MS	Tandem mass spectrometry
NCPA	*N*-(4-Cyanophenyl)acetohydroxamic acid
NHA	*N*-Hydroxyacetanilide
OC	Octocrylene
PAHs	Polycyclic aromatic hydrocarbons
PBR	Packed bed reactor
PCBs	Polychlorinated biphenyls
PCPs	Personal care products
PEG	Poly-(ethylene glycol)
POPs	Persistent organic pollutants
TCS	Triclosan
TNT	Trinitrotoluene
TrOC	Trace organic contaminant
UV-F	UV filters
VP	Versatile peroxidases
WRF	White-rot fungi

1 Introduction

Anthropogenic trace organic contaminants (TrOCs) found in aquatic environments have increasingly raised concern with regard to their uncertain environmental fate and potentially adverse ecological and human effects. Emerging organic contaminants are a diverse and relatively new group of unregulated compounds of different origin, mainly domestic and industrial, which include pharmaceuticals, personal care products, pesticides, and industrial chemicals, among others. Many of these pollutants have been identified as endocrine-disrupting chemicals (EDCs), mimicking hormones or interfering with the action of endogenous hormones by binding to the estrogen receptor or suppressing a normal biological response [1–3]. These emerging organic pollutants have been frequently detected in sewage-impacted water resources worldwide at concentration levels from a few nanograms per liter (ng/L) to several micrograms per liter (μg/L) [4]. Risk for chronic and acute environmental toxicity has not been extensively investigated so far. However, adverse toxicological effects of a number of TrOCs have been reported, such as inhibition of growth in embryonic kidney cells cultured with a mixture of 13 pharmaceuticals [5]. Regarding human health, reduction in mean birth weight and neurotoxicity has been related with disinfection by-products [6].

Due to the limitations observed in the removal of many of these compounds by current bacterial-driven conventional activated sludge (CAS) wastewater treatment

processes [7–9], numerous efforts have been made to explore alternative treatments for their improved removal. In the last decade, the development and implementation of advanced oxidation processes (AOPs), nitrifying-denitrifying treatments, membrane technology, and adsorption on activated carbon have been applied to improve the removal of recalcitrant emerging contaminants. For instance, Ternes et al. showed that the ozone was efficient at removing pharmaceuticals, musk fragrances, and estrogens [10]. Gago-Ferrero et al. also demonstrated that ozonation and peroxone oxidation improved removal of benzophenone UV filters [11]. However, advanced treatment processes are still rather expensive to build and maintain and require a high level of energy leading to economical limitation for the feasibility of this technology. Besides that, the chemical quality of the water obtained from these treatments is lower than that provided by the conventional biological technologies currently applied. Membrane filtration and activated carbon demonstrated improved removal efficiencies for compounds including some pharmaceuticals (sulfonamide antibiotics, ibuprofen, and naproxen) and industrial chemicals (bisphenol A); however, degradation was still poor for other drugs and personal care products, such as carbamazepine, diclofenac, and a number of fragrances [12–16].

A scarcely explored biotechnology for the effective degradation of TrOCs involves the application of fungi, particularly white-rot fungi (WRF) and their ligninolytic enzymes. The concept of using WRF for the degradation of xenobiotics appeared in the 1980s, as reviewed by Gao et al. [17]. Since then, the development of biotechnologies using WRF has been developed to degrade a wide variety of xenobiotics, mainly persistent organic pollutants (POPs), such as synthetic dyes, PAHs, and PCBs [18–20]. More recently, research moved towards the application of WRF to remove emerging pollutants. From these organic contaminants, EDCs comprise the most studied group [21–27], followed by pharmaceutical compounds [28–39]. In contrast, the degradation by WRF of personal care products has been less studied. In this chapter, we will examine the capability of WRF and their lignin-modifying enzymes (LMEs) to degrade personal care products as well as the mechanisms involved and the metabolism products formed in the process.

2 White-Rot Fungi

WRF are a diverse group of fungi capable of extensive aerobic depolymerization and mineralization of lignin, the natural polymer which forms the hard cover protecting soft wood. WRF present an extracellular oxidative system employed in the primary attack of lignin and its posterior mineralization in a nonspecific and nonselective mechanism [40]. This enzymatic system includes one or more LMEs, especially peroxidases and laccases, which are extracellular and metal-containing oxidoreductases. The reactions they catalyze include lignin depolymerization through demethoxylation, decarboxylation, hydroxylation, and breakdown of aromatic rings.

Several features make WRF interesting agents for use in fungal remediation applications: (1) the nonspecificity of their enzymatic system, providing them with the ability to oxidize a wide range of pollutants and reducing the need to adaptation at polluted sites or matrices; (2) most oxidative enzymes are extracellular, which permits the degradation of low-solubility contaminants; (3) the wide distribution and hyphae growth, facilitating the colonization and the access to pollutants; (4) lignocellulosic wastes can be employed as substrate/carrier for growth/inoculation of WRF, as they are also necessary as nutrient source during co-metabolic removal of TrOC. Moreover, some of those enzymes are expressed under nutrient-deficient conditions (mostly C or N) and can operate over wide ranges of pH and temperature [41].

2.1 Enzymatic Systems

2.1.1 Lignin-Modifying Enzymes (LMEs)

The production of LMEs is responsible for the decomposition of lignin. WRF secrete mainly three different classes of LMEs: lignin peroxidases (LIPs), manganese-dependent peroxidases (MnPs), and laccase [42]. The main difference is the electron acceptor, O_2 for laccases and H_2O_2 for peroxidases. Besides the fungal oxidative enzymes, the reactions of lignin breakdown also involve secreted fungal mediators (phenolic and other aromatic compounds, peptides, organic acids, lignocellulosic-derived compounds, and metal ions) which expand the range of compounds they are able to degrade [41, 43].

The secretion pattern is species dependent; different WRF species produce various combinations of the main lignin-degrading enzymes (LiP, MnP, and laccase). A particular strain may not secrete all three of them. For instance, although *Trametes versicolor* has been associated with all three enzymes [44, 45], the strain ATCC 7731 secretes mostly laccase [46]. The secretion of specific enzymes may also depend on culture conditions. According to their enzyme production, WRF can be classified in three categories [47]: LiP–MnP group, like *Phanerochaete chrysosporium*; MnP–laccase group, including *T. versicolor*, *Dichomitus squalens*, *Ceriporiopsis subvermispora*, *Pleurotus ostreatus*, *Lentinus edodes*, and *Panus tigrinus*; and LiP–laccase group, like *Phlebia ochraceofulva*.

Peroxidases

Peroxidases include LiP, MnP, and, a hybrid of both, the versatile peroxidases (VP) [48]. All of these enzymes are extracellular and contain protoporphyrin IX (heme) as prosthetic group. They use H_2O_2 or organic hydroperoxides as electron-accepting co-substrates during the oxidation of diverse TrOCs. LiP and MnP were first isolated from the WRF *P. chrysosporium* [49].

LiP also known as ligninase or diarylpropane oxygenase (E.C. 1.11.1.14) is the most powerful fungal peroxidase. In the presence of H_2O_2, LiP catalyzes oxidation of the endogenously generated redox mediator veratryl alcohol, which subsequently generates aryl cation radicals through one-electron oxidations of non-phenolic aromatic nuclei in lignin. These are then degraded to aromatic and aliphatic products, which are mineralized intracellularly. The produced radicals can participate in diverse reactions, including phenols oxidation, carbon–carbon bond cleavage, hydroxylation, phenol dimerization/polymerization, and demethylation [40]. The substrate oxidation capacity of LiP includes depolymerization of synthetic lignin and transformation of TrOCs such as PAHs, chlorophenols, and TNT [50–52].

MnP (E.C. 1.11.1.13) catalyzes an H_2O_2-dependent oxidation of Mn^{2+} to Mn^{3+}. The catalytic cycle is initiated by binding of H_2O_2 or an organic peroxide to the native ferric enzyme and formation of an Fe–peroxide complex; the Mn^{3+} ions finally produced after subsequent electron transfers are stabilized via chelation with organic acids like oxalate, malonate, malate, tartrate, or lactate [53]. The chelates of Mn^{3+} with carboxylic acids cause one-electron oxidation of various substrates; thus, chelates and carboxylic acids can react with each other to form alkyl radicals, which after several reactions result in the production of other radicals. These final radicals are the source of autocatalytically produced peroxides and are used by MnP in the absence of H_2O_2.

VP (E.C. 1.11.1.16) was first described in *Pleurotus eryngii* [54] and *Bjerkandera* sp. [55]. VP is a heme-containing structural hybrid between MnP and LiP, as it is able to oxidize Mn^{2+}; veratryl alcohol; simple amines; phenolic, non-phenolic, and high-molecular-weight aromatic compounds; and high-redox potential dyes in reactions which are of Mn-independent character [56]. Therefore, this enzyme has a wider catalytic versatility as compared to LiP and MnP.

Laccase

Laccases (benzenediol:oxygen oxidoreductase; E.C. 1.10.3.2) are enzymes that contain four copper atoms, in different states of oxidation (I, II, and III) [57]. They are not only restricted to WRF as they can be found also in plants and some bacteria and recently reported in green algae too [58, 59]. Fungal laccases oxidize a broad range of compounds such as phenols, polyphenols, methoxy-substituted phenols, and amines [60] while reducing O_2 to H_2O (four-electron reduction). Other enzymatic reactions they catalyze include decarboxylations and demethylations [40]. The redox potential of specific lacasses can vary depending on the fungal strain and the isoenzyme.

The catalytic cycle of laccase includes several one-electron transfers between a suitable substrate and the copper atoms, with the concomitant reduction of an oxygen molecule to water during the sequential oxidation of four substrate molecules [60]. With this mechanism, laccases generate phenoxyl radicals that undergo nonenzymatic reactions [56]. Multiple reactions lead finally to polymerization,

alkyl–aryl cleavage, quinone formation, C_{α}-oxidation, or demethoxylation of the phenolic reductant [61].

Reported redox potentials of laccases are lower than those of non-phenolic compounds, and therefore these enzymes cannot oxidize such substances [62]. However, it has been observed that laccases are also able to oxidize non-phenolic structures in the presence of molecules capable to act as electron transfer mediators, such as *N*-hydroxyacetanilide (NHA), *N*-(4-cyanophenyl) acetohydroxamic acid (NCPA), 3-hydroxyanthranilate, 2,2′-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid) (ABTS), and 2,6-dimethoxyphenol (DMP) [63–65]. As part of their metabolism, WRF can produce several metabolites that play this role of laccase mediators [66].

2.1.2 Cytochrome P450 System

The intracellular cytochrome P450 system exerts a leading role in the degradation of xenobiotics in eukaryotic organisms. WRF are not an exception, and some TrOCs, for instance, PAHs [67] and chlorinated hydrocarbons [68, 69], can be transformed by fungal cytochrome P450. The cytochrome P450 system is monooxygenases that catalyze a broad range of reactions, which include hydroxylation, heteroatom oxygenation, dealkylation, epoxidation of C=C bonds and hydroxylation, reduction, and dehalogenation [70].

3 Treatment Approaches for PCP Degradation

The utilization of WRF and their LMEs for the treatment of pollutants has been widely reported [41, 71–74]. Several operational parameters, such as pH, temperature, additives, and the presence of inorganic salts and heavy metals, have been found to cause an impact on the WRF-mediated degradation of pollutants. These parameters influence the enzymatic activity, stability, and substrate specificity of the free LME or WRF strain employed. These features are important in the bioprocess design and optimization of whole-cell or enzymatic treatment of wastes. In general, tests were carried out in batch and preferably in aqueous media spiked with the selected contaminants at a certain concentration.

3.1 Removal by Whole Cell WRF

As stated before, some studies have been carried out with whole-cell cultures of several ligninolytic fungi strains. Most of the experiments have been carried out in submerged cultures due to the easiness of contaminants' quantification in comparison with studies in solid phase. Table 1 summarized the different fungi tested for

Table 1 Whole-cell WRF tested for the removal of PCPs in submerged cultures

Compound	PCP class	Fungus	Reference
TCS	Antimicrobial	*Irpex lacteus*	[45]
TCS	Antimicrobial	*Bjerkandera adusta*	[45]
TCS	Antimicrobial	*Phanerochaete chrysosporium*	[45]
TCS	Antimicrobial	*Phanerochaete magnoliae*	[45]
TCS	Antimicrobial	*Pleurotus ostreatus*	[45]
TCS	Antimicrobial	*Trametes versicolor*	[45]
TCS	Antimicrobial	*Pycnoporus cinnabarinus*	[45]
TCS	Antimicrobial	*Dichomitus squalens*	[45]
TCS	Antimicrobial	*Trametes versicolor*	[75]
BP1	UV filter	*Trametes versicolor*	[76, 77]
BP3	UV filter	*Trametes versicolor*	[75–77]
OC	UV filter	*Trametes versicolor*	[75]
4-MBC	UV filter	*Trametes versicolor*	[72, 73]
Iso-BP	Antimicrobial	*Trametes versicolor*	[78]

the removal of selected PCPs in liquid cultures. Up to eight different fungi were tested for the degradation of triclosan (TCS), i.e., *Irpex lacteus*, *Bjerkandera adusta*, *P. chrysosporium*, *Phanerochaete magnoliae*, *P. ostreatus*, *T. versicolor*, *Pycnoporus cinnabarinus*, and *D. squalens*. The results show that, under the applied conditions, all the tested fungi, with exception of *B. adusta*, were able to degrade the biocide within 14 days (d) of cultivation to 1–12% of the initial concentration (2.5 mg/L) with a fungal concentration of 0.1–0.25 g dry weight (dw)/L [44].

T. versicolor was also selected for the degradation of two UV filters, namely, benzophenone 3 (BP3) and octocrylene (OC), and TCS among other contaminants in a mixture of 30 compounds [75]. In that experiment, initial concentration of fungi and contaminants was 0.4 g dw/L and 50 μg/L, respectively, and removal only achieved values below 50% but as high as 80% for TCS. This particularly high removal for TCS is in agreement with the results reported by Kajthaml et al. (2009) in the abovementioned work [70]. The same authors, in the attempt to attain an efficient removal for recalcitrant contaminants under conventional biological treatments, explored a combination of technologies. A *T. versicolor*-augmented membrane bioreactor (MBR) was used for the biodegradation of the same contaminants [79]. Two identical MBR systems, one inoculated with *T. versicolor*-augmented sludge and the other with activated sludge, were operated for 110 days under the same operational conditions. Each MBR comprised a 5.5 L glass reactor and housed a PVDF hollow fiber membrane module, with a nominal pore size of 0.4 L m and a total effective membrane surface area of 0.074 m^2 (Fig. 1a). The initial mixed liquor suspended solid concentration in both MBRs was 3 g/L. Results from this study revealed that a mixed culture of bacteria and a WRF in a fungus-augmented MBR can achieve better removal for BP3, OC, and TCS (>80%) than a system containing fungus or bacteria alone.

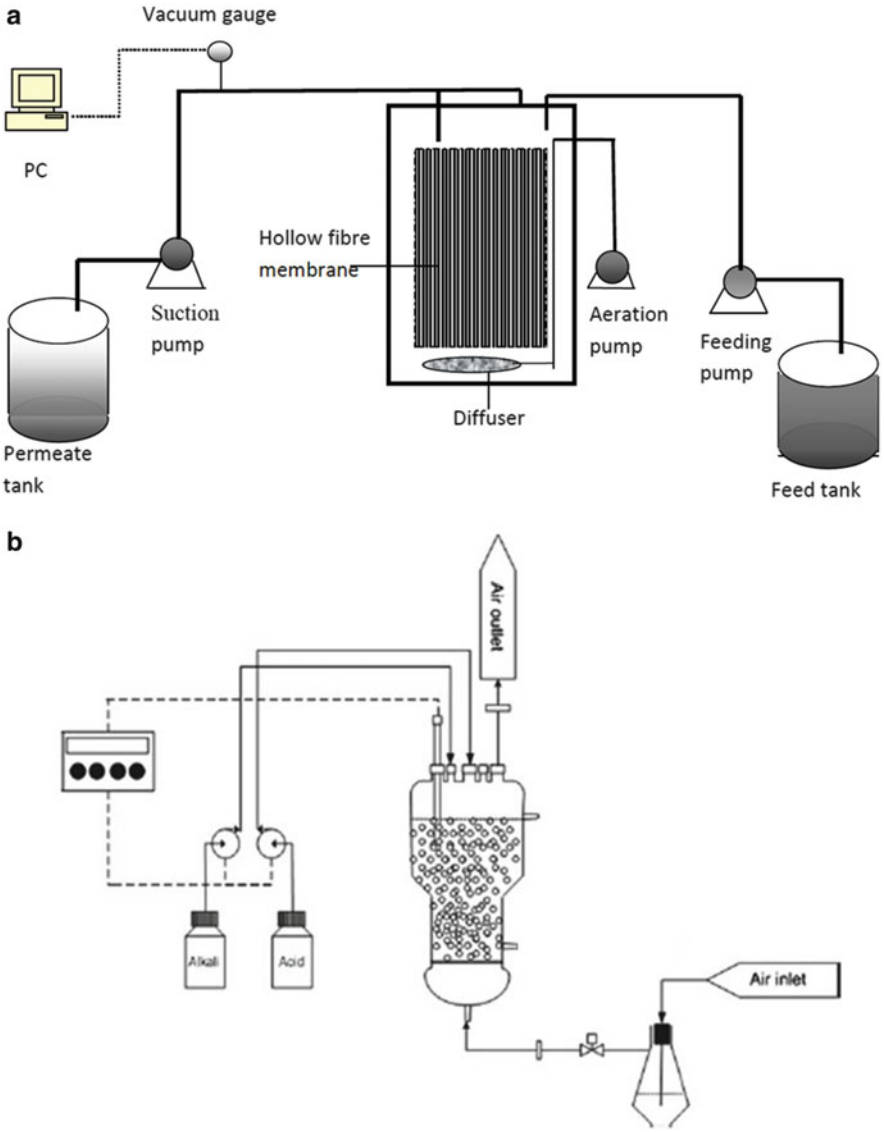

Fig. 1 (**a**) Schematic diagram of the fungal MBR reactor employed in the [45] (Adapted from Yang et al. (2012) [80]). (**b**) Schematic diagram of the fungal air-pulsed fluidized bioreactor employed in Badia-Fabregat et al. [76] (Adapted from Blánquez et al. (2007) [81])

On the other hand, Gago-Ferrero et al. obtained almost total removal of BP3 as well as for other UV filters (BP1 and 4-MBC) with a pure culture of another strain of *T. versicolor* under sterile conditions at erlenmeyer scale but also at 1.5 L bioreactor scale [76, 77]. In those studies, *T. versicolor* was inoculated at 2–5 g dw/L in the form of pellets instead of free mycelia, in order to improve the

fungal fluidization and to avoid the reactor clogging. The results at erlenmeyer scale pointed out that *T. versicolor* was able to completely degrade 4-MBC from an initial concentration of 10 mg/L in less than 24 h of treatment. In the experimental bottles, BP3 exhibited a high degree of elimination, reaching >99% removal rate between 6 and 24 h. Similarly, fungal degradation experiments were performed for BP1. Results showed a similar but faster degradation profile to that of BP3. High biodegradation rates were also observed in the bioreactors during 24 h batch operating. For those experiments, a 1.5 L air-pulsed fluidized glass bioreactor was used (Fig. 1b). Initial levels of BP3 (250 μg/L) dropped to non-detectable levels in 8 h. In the case of BP1, about 95% of the initial concentration was removed after 2 h of treatment and completely eliminated at 24 h.

Regarding the fungal degradation of certain commonly used parabens, Mizuno et al. reported 100% removal of iso-butylparaben (iso-BP), initially added at 19.4 mg/L, after 2 days of treatment with *T. versicolor* [78]. Besides that, possible future experiments for the evaluation of fungal degradation of fragrances should be carefully designed, as an attempt to assess degradation of celestolide, tonalide, and galaxolide in erlenmeyers found that removal was only due to volatilization [35].

Under the tested conditions in the literature, it appears that both degradation and sorption to biomass can be the responsible mechanisms for contaminant removal. To identify which one predominates, experiments with alive and inactivated fungi were performed [76, 77, 79]. The removal observed for many compounds was similar under both approaches when any extraction or solubilization step was included in the protocol. Therefore, further tests were carried out to confirm the fungal biodegradation of those compounds by means of including a solubilization or extraction step [76, 77] or comparing the removal attained with the whole-cell culture with that obtained with the crude enzyme extract [75]. In both cases, biodegradation was confirmed as the main mechanism of removal even for the very hydrophobic compounds, such as TCS and OC.

Degradation studies of several UV filters with *T. versicolor* in sterilized dry sewage sludge have been reported as well [76]. Solid-phase systems containing sterile sewage sludge and 38% (w/w, dry basis) *T. versicolor* inoculum (biopiles) were incubated for up to 42 days at 25°C, periodically homogenized and moisturized. The sterilization process consisted of autoclaving at 121°C for 30 min. It is noteworthy that degradation was evaluated on the real concentrations of PCPs found in the sludge. The removal observed for 4-MBC after solid-phase fungal treatment was 87%, whereas complete elimination was observed for the phenolic compounds BP3 and 4DHB. In the same study OC and EHMC were also tested, showing quite high removal rates of 89 and 93%, respectively. Sewage sludge treatment in bioslurry systems has been also evaluated, but removal efficiency was much lower for the UV filters analyzed as well as for many other emerging contaminants [82]. Based on those results, subsequent non-sterile biopiles treating dry sewage sludge were performed [83]. 80% removal of UV filters was achieved after 42 d of treatment with mycelia reinoculation at day 22.

Taking into account the good results of PCPs' degradation by whole-cell cultures of ligninolytic fungi, further studies under non-sterile conditions and real

effluent concentrations should be performed, especially in liquid treatments, where no data is available to date. That type of studies would represent a step forward in a potential full-scale application of the fungal treatment technology.

3.2 Removal by Lignin-Modifying Enzymes

Besides the application of whole-cell fungus cultures, a suitable alternative which decouples the fungal growth and chemical degradation stages is to use either the different individual enzymes as such (crude enzymes) or the extracellular enzymes previously purified or commercially available. However, it must be highlighted that because of the combined effect of intracellular, mycelium-bound, and extracellular enzymes as well as sorption of contaminants on the biomass, whole-cell fungal treatment may cover a wider range of compounds compared with enzymatic treatment.

The application of individual LMEs has been performed for the biodegradation of some PCPs such as TCS. Table 2 reports the enzymes investigated to degrade PCPs. A study involving the application of a laccase preparation extracted from the WRF *Coriolopsis polyzona* revealed a quite satisfactory removal of the phenolic biocide at pH 5 and 50°C [90]. TCS was degraded in a 65% after either 4 or 8 h treatment, indicating that longer exposition does not render better removal rate. Other two crude extracts from WRF *T. versicolor* and *P. cinnabarinus* were investigated for the biodegradation of TCS. After 48 h treatment, TCS began to disappear. Removal rates were not reported by the authors. Another study was conducted on the ability of laccase from *T. versicolor* to catalyze the oxidation of TCS [87]. Laccase was able to completely degrade the biocide under a variety of experimental conditions, but the optimal pH was found to be 5. Treatment could be achieved at elevated temperatures (optimum at 50°C), but at the expense of higher rates of inactivation.

N,*N*-Diethyl-*m*-toluamide (DEET), the active ingredient in most commercial insect repellent products against mosquitoes, ticks, flies, and other biting insects, has been found to be biodegraded by *T. versicolor* laccase [89]. The extent of degradation was medium dependent. In real wastewater, a higher degradation rate for DEET was observed (55% removal) as compared to that in acetate buffered solution (20% removal). This may be explained by the simultaneous presence of other compounds (for instance, phenolic substances) that can eventually serve as redox mediators in the degradation process. Anyway, these relatively low removal efficiencies for DEET may be due to the presence of the relatively strong withdrawing electron group (–CO–N [CH_2–CH_3]$_2$) in its chemical structure.

Removal of the antimicrobial preservatives iso-BP and *n*-butylparaben (*n*-BP) by partially purified laccase from cultures of *T. versicolor* achieved percentages of only 15 and 5%, respectively, despite their phenolic structure [78] UV filters BP3 and 4-MBC are also poorly removed by commercial laccase of *T. versicolor* [76, 88].

Table 2 Lignin-modifying enzymes (LMEs) tested for the removal of PCPs

Compound	PCP class	LMEs	Fungus	Reference
TCS	Antimicrobial	Crude laccase extract with ABTS, and with 1-HBT	*Coriolopsis polyzona*	[71]
TCS	Antimicrobial	Laccase	*Coriolopsis polyzona*	[71]
TCS	Antimicrobial	Crude extract	*Trametes versicolor*	[71]
TCS	Antimicrobial	Cross-linking of enzyme aggregates (CLEAs) of lacasse	*Coriolopsis polyzona*	[71]
TCS	Antimicrobial	Laccase immobilized on control porosity carrier (CPC)-silica beads	*Cerrena unicolor*	[84]
TCS	Antimicrobial	Covalently immobilized lacasse on a solid diatomaceous earth support	*Coriolopsis polyzona*	[85]
TCS	Antimicrobial	CLEAs of versatile peroxidase (VP)	*Bjerkandera adusta*	[86]
TCS	Antimicrobial	Glucose oxidase (GOD)	*Aspergillus niger*	[86]
TCS	Antimicrobial	Crude extract	*Pycnoporus cinnabarinus*	[87]
4-MBC	UV filter	Laccase	*Trametes versicolor*	[76]
BP3	UV filter	Laccase	*Trametes versicolor*	[88]
BP3	UV filter	Laccase	*Trametes versicolor*	[75]
OC	UV filter	Laccase	*Trametes versicolor*	[75]
TCS	Antimicrobial	Laccase	*Trametes versicolor*	[75]
DEET	Insect repellent	Laccase	*Trametes versicolor*	[89]
Iso-BP	Antimicrobial	Partially purified laccase	*Trametes versicolor*	[78]
n-BP	Antimicrobial	Partially purified laccase	*Trametes versicolor*	[78]

Despite the good performance of the use of free enzymes in some xenobiotics degradation, their low stability, low activity, and inhibition by high concentrations of substrates and products make this approach of little applicability in industrial processes [91]. To overcome such disadvantages, the several efforts during the past years have been made to design enzyme immobilization methods. Enzyme immobilization generally results in catalyst stabilization against thermal and chemical denaturation [92]. The most common procedures comprise the binding to a solid support, encapsulation, and cross-linking. For instance, the degradation of TCS with laccase immobilized on control porosity carrier (CPC)-silica beads (silica carrier silane-coated) was recently investigated [84]. Results of time-course

elimination experiments showed a gradual decrease of TCS of 50% initial concentration after 1 h of treatment. Data showed that in comparative study between free and immobilized laccase, the apparent Michaelis–Menten constant (K_m) was higher for the immobilized enzyme regardless the support used (3- to 19-fold). Carrier-free immobilization strategies, cross-linking of enzyme aggregates (CLEAs), has been proposed for the degradation of TCS. CLEAs of laccase from the WRF *C. polyzona* were placed in a fluidized bed reactor (FBR) which operated at pH 5 and at room temperature. After 50 min. treatment 90% TCS was eliminated. An additional treatment of 100 min. increased the degradation rate only by 5%. A similar study was conducted by the same authors using a packed bed reactor (PBR) filled with covalently immobilized laccase on a solid diatomaceous earth support. In this case after 200 min. treatment complete elimination of TCS was achieved [85]. Combined CLEAs of VP from *B. adusta* and glucose oxidase (GOD) from *Aspergillus niger* were tested to eliminate TCS [86]. A membrane reactor continuously operated with the combined CLEAs removed 26% of TCS after 10 min. of treatment. In comparative study with free VP (with H_2O_2 as enzymatic substrate) and free VP-GOD, it was proved that the combined CLEAS were not as effective as the free enzyme in degrading the biocide; the free VP was able to remove 36% of TCS, whereas the free VP with glucose oxidase achieved the highest removal rate, eliminating more than 40% of TCS. These results may be explained by the in situ oxidation of glucose which continuously produced H_2O_2 required by VP. However, glucose might not be a suitable substrate for a wastewater treatment process as it might serve as an unwanted growth substrate for microorganisms. Thus, further studies should be focused on the production of combi-CLEAs using other H_2O_2-producing enzymes with substrates that are more suitable in the scope of a water treatment process [93].

3.3 Redox Mediator-Catalyzed Removal

Many studies report on the application of low-molecular-weight oxidizable substances in the metabolic process to expand the activity of the fungi and enzymes, i.e., laccase. This mediated oxidation involves two oxidative steps. First, the enzyme oxidizes a primary substrate, the mediator, and this substance acts as an electron-transferring compound. The mediator finally transfers the electron to the substance of interest. In most studies, benzothiazoles and benzotriazoles are selected as the mediator substance [88]. In an earlier study, Cabana et al. compared [71] the ability of 2,2-azino-bis(3-ethylbenzthiazoline-6-sulfonic acid) (ABTS) and 1-hydroxybenzotriazole (1-HBT) to improve the elimination of TCS by a crude laccase extract from *C. polyzona*. The performance of both treatments was determined at 1 h treatment at 40°C, pH 4, enzyme preparation containing 10 U/L of laccase and 10 μM of mediator. Under these experimental conditions, ABTS allowed a total elimination for the chlorinated biocide. Treatment efficiency and reaction rates of TCS removal can be substantially improved

through the use of a protective additive, poly-(ethylene glycol) (PEG), and ABTS as mediator, reaching 100% removal as well [87].

1-HBT was also used as mediator to improve the removal of UV filters (BP3 and OC) as well as TCS [75]. A significantly improved degradation of BP3 with respect to that by the crude enzyme extract (from 4 to >60%) was observed, in contrast with the other substances for which removal did not improve or even decreased. The better performance achieved may be explained by the role played by the aminoxyl radical species generated from 1-HBT by laccase. As explained in a previous section, this enzyme promotes the oxidation of phenols [94], and BP3 has a phenolic structure. However, steric factors may hinder the approach of the substrate to the active site of laccase and, as a consequence, inhibit the oxidation of even phenolic substances. The aminoxyl radicals produced from HBT by laccase, due to their small size, can abstract H-atom from the –OH group in the phenolic moiety of the substrates forming the corresponding phenoxyl radicals [95]. These phenoxyl radicals, in turn, react with the substrate via a radical hydrogen atom transfer route [93] that improves the biodegradation potential. The addition of the same redox mediator to the fungal-augmented MBR system described in the previous section, however, did not provide any significant change in the removal efficiency for the three UV filters and TCS [79]. Garcia et al. performed a screening of mediators, and the best results were found for ABTS, obtaining a total removal of BP3 at pH over 7 [88]. Moreover, ABTS and 1-HBT significantly enhanced laccase crude enzyme degradation of the insect repellent DEET by two- and threefold, respectively. 1-HBT also allowed total removal of iso-BP and *n*-BP after 8 h of reaction [35]

The presence of ions including sulfite, sulfide, cyanide, chloride, Fe (III), and Cu (II) resulted in reduced treatment efficiency, likely due to the interruption caused by these substances in the electron transport system of laccase [96].

Summarizing, the use of mediators usually increases the spectrum of compounds that laccase can oxidize. However, the addition of extra molecules increases the cost of the treatment. Moreover, toxicity of the effluents usually increases after the treatment due to the toxicity of the mediators [87]. Therefore, alternatives to synthetic mediators should be found.

4 Identification of Intermediate and Metabolization Products

Few reports focused on the identification of intermediate and metabolization products formed by the action of whole WRT or free enzymes on PCPs. Among them TCS has been extensively investigated, as shown in Table 3. The production of phenoxyl radicals by the MnP, laccase, or laccase/mediator systems appears to result in coupling reactions. The polymerization products of TCS detected through mass spectrometry (MS) and tandem-mass spectrometry (MS/MS) analyses were

Table 3 Identified PCPs fungal metabolites

Compound	Fungus	Metabolite	Reference
TCS	*Coriolopsis polyzona*	TCS dimer	[71]
		TCS trimer	
		TCS tetramer	
TCS	*Trametes versicolor*	2-*O*-(2,4,4′-trichlorodiphenyl ether)-b-D-xylopyranoside	[97]
		2-*O*-(2,4,4′-trichlorodiphenylether)-b-D-glucopyranoside	
		2,4-dichlorophenol	
TCS	*Pycnoporus cinnabarinus*	2-*O*-(2,4,4′-Trichlorodiphenylether)-b-D-glucopyranoside	[97]
		2,4,4′-Trichloro-2′-methoxydiphenyl ether	
4-MBC	*Trametes versicolor*	Glucoconjugate of hydroxy-4-MBC with pentose	[76]
		Glucoconjugate of dihydroxy-4-MBC with pentose	
BP1	*Trametes versicolor*	4HB	[77]
		4DHB	
		Glucoconjugate with pentose	
BP3	*Trametes versicolor*	BP1	[77]
		4HB	
		4DHB	
		Glucoconjugates with pentose and hexose	

identified as dimers, trimers, and tetramers [71]. These high-molecular-weight chemicals detected suggest a reaction pathway involving the oxidative coupling of the primary oxidation product (formed by abstracting one electron from the OH group of the original molecule). Furthermore, the intermediate product identified as 2,4-dichlorophenol during the treatment of TCS by *T. versicolor* [97] indicates that the degradation of the biocide could occur in a manner similar to the bisphenol A reaction following two mechanisms, (1) a condensation phase resulting in the production of higher-molecular-weight metabolites and (2) a fragmentation phase at the C–O level. Due to the lack of detailed information on the structure of the oligomers formed, it was quite difficult to propose a precise transformation pathway. In the same study, the hydroxyl group of TCS was found to be methylated through the action of the fungus *P. cinnabarinus*, producing methyl-triclosan, a derivative of the biocide frequently found in the environment [98].

The transformation products of the UV filters 4-MBC, BP3, and BP1 originated through the action of *T. versicolor* were recently identified [77, 78]. The intermediate and transformation products of 4-MBC detected through MS/MS analyses were identified as the result of an hydroxylation in the aromatic ring or the methyl group next to the aromatic ring and, in lower amounts, a double hydroxylation [77]. Also, in the first hours of treatment, a compound with a MS/MS fragmentation pattern identical to that of 4-MBC was observed. This evidenced the transformation of the commercially available 4-MBC (E) into its isomer, 4-MBC (Z). This isomerization process was previously observed upon the action of other living organisms [99]. However, the main metabolite of 4-MBC produced by the fungi is the result of the conjugation of the mono-hydroxylated intermediate with a molecule of pentose by a glycosidic bond. The pentose-conjugated derivative of the di-hydroxylated intermediate was also identified, but to a lesser extent. In a similar study, BP1, 4DHB, and 4HB were identified as metabolites produced during the degradation experiments of BP3 with the fungus [78]. Further fungal degradation of BP1 resulted in the formation of 4HB and 4DHB, as in the case of BP3 metabolization. Similar to 4-MBC fungal degradation, the predominant metabolite may be produced by the addition of one pentose molecule to BP3. However, in this case the addition of one hexose molecule to BP3, likely glucose, via glycosidic bond also occurs. As it was reported for BP3, the addition of one pentose molecule to BP1 also produced the conjugated metabolite. On the other hand, the action of laccase/mediator systems generate oxidative coupling reactions, leading to transformation products of higher molecular weight than BP3 due to the coupling of BP3 to different oxidated forms of the mediators [88].

5 Concluding Remarks

The elimination of ingredients in personal care products by WRF-mediated treatments emerged as a promising environmental friendly degradation process. Compounds with strong electron-donating groups such as hydroxyl and amines are well

removed by WRF, whereas compounds with electron-withdrawing groups (e.g., halogen and nitro) are biodegraded mainly by WRF having all three major LME. Whole-cell WRF appears to effectively treat a wider spectrum of PCPs than crude cultures or purified enzymes, likely because of the combined effect of mycelium-bound, extracellular, and intracellular enzymes (as it usually is a multienzymatic process) and biosorption of the compound. Laccase has been the most studied LME for the degradation of PCPs. In the enzymatic treatments, the addition of redox mediators has been shown to be a good strategy to improve the degradation of recalcitrant compounds, whereas in the fungal degradation they are not usually needed because the fungus itself can generate radicals that act as natural mediators. Thus, the possible toxicity of treated effluents due to the release of the artificial mediators is avoided by the use of whole-cell fungal treatments. On the other hand, an alternative to improve the removal of PCPs by WRF is the combined use of a mixed culture of bacteria and WRF. This so-called fungus-augmented MBR proved to achieve better removal rates for several PCPs than the conventional systems using bacteria or a system containing the fungus (or the enzymes) alone.

So far, however, this innovative technology has not been tested in real wastewater effluents and under non-sterile conditions for the degradation of PCPs, neither in enzymatic nor in fungal reactors. From the few works dealing with non-sterile effluents, and with other purposes than degrading PCPs, it can be drawn that the main drawback of fungal reactors is the competition of the inoculated fungus with the other microorganisms and the enzyme deactivation in the case of enzymatic treatments. Thus, several factors need to be considered before their application as suitable treatments for bioremediation or decontamination in real situations can be done. Among them, the design of the bioreactor, the concentration of the biocatalyst (biomass or enzyme), the life cycle of the biomass or the half-life of the enzyme, the fermentation conditions, and the economic cost appear to be of outmost importance. Another important limitation for continuous flow treatment is to achieve and maintain the sufficient enzymatic activity inside the reactor for the degradation of PCPs. This can be achieved in the fungal bioreactors by means of adjusting the hydraulic and cellular residence times (HRT and CRT). In the enzymatic reactors, suitable activity can be achieved by continuously adding the enzyme or by means of an immobilization system. If mediators are needed, they should be continuously added. Out of the operational and design parameters, other issues need further research. In particular, the identification of the compounds formed during the fungal metabolization is critical in order to improve the understanding of the degradation mechanisms and to evaluate the ecotoxicological risk associated to the degradation process.

Acknowledgements This work has been financially supported by the Generalitat de Catalunya (Consolidated Research Group "2014 SGR 418 – Water and Soil Quality Unit").

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Removal of Personal Care Products in Constructed Wetlands

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Abstract This chapter is an overview of the occurrence of common personal care products in the influent and effluent of different types of constructed wetlands fed with domestic wastewaters, acting as primary, secondary, or tertiary steps and the corresponding removal efficiency achieved by these treatments. The reviewed personal care products belong to eight different classes: 3 antioxidants, 2 antiseptics, 1 deodorant, 1 insect repellant, 1 plasticizer, 3 sunscreen products, 5 synthetic musks, and 16 surfactants (seven anionic and nine nonionic).

Data are collated from 35 peer review papers, referring to investigations carried out in Europe (66%), America (28%), and Asia (6%). Of the 87 treatment lines reviewed, the most common constructed wetland type was the horizontal subsurface flow (49%) followed by the surface flow (38%) and, in a few cases, the vertical subsurface flow. Removal was mainly influenced by redox potential, temperature, hydraulic retention time, and influent concentration of the compound.

The highest values of removal were found for fragrances in secondary systems and fragrances and triclosan in polishing systems.

Due to the different and simultaneous removal mechanisms occurring within these systems and their buffer capacity, they might represent a reliable and feasible treatment which is able to control and reduce the spread of personal care products in the aquatic environment.

Keywords Constructed wetlands, Occurrence, Personal care products, Removal efficiencies, Removal mechanisms

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M.S. Díaz-Cruz and D. Barceló (eds.), *Personal Care Products in the Aquatic Environment*, Hdb Env Chem (2015) 36: 319–354, DOI 10.1007/698_2014_282,

Contents

1 Introduction

Every day we use products for our personal care and hygiene, in particular cosmetics (skin care products, hair sprays, and sunscreens), toiletries (bath additives, soaps, hair tonics, shampoos, oral hygiene products), and fragrances (perfumes, aftershaves). These products, commonly called personal care products (PCPs), contain synthetic organic chemicals with a specific function, the *ingredients*. They may be antimicrobial disinfectants (triclosan, triclocarban), preservatives (methylparaben, ethylparaben, butylparaben), or sunscreen agents (oxybenzone, avobenzone). In addition, some of them may contain synthetic surfactants (generally anionic and nonionic compounds). These are substances widely used in the formulation of many commercial PCPs not only for their wetting, cleaning, foaming, and emollient properties but also as they can create dispersed systems (suspension or emulsion), modify the cosmetic rheological properties, prolong the durability of the product, and control the release of active ingredients [1] which greatly improves the quality of the substance.

PCPs are used in the range of several thousand tons per year: parabens are used in more than 22,000 cosmetic products [2], approximately 350 tons of triclosan are

produced annually in Europe [3], and in 1998, 1,473 tons of galaxolide, 343 tons of tonalide, and 18 tons of celestolide were consumed in Europe [4].

These products are disposed of or discharged into the environment on a continuous basis via municipal/industrial sewage facilities and also directly by untreated discharges [5–7]. This means that their exposure potential may reach critical level for the environment, even for those compounds that might have a low persistence.

In recent years, increasing attention has been paid to the occurrence of some of them in aquatic environments, also due to the finding that some PCPs can induce known or suspected undesirable effects on humans and ecosystems (included endocrine disruptions) [8].

Limits of concentrations have been set for surfactants with regard to wastewater treatment plant discharges into surface water bodies or for the direct reuse of treated effluents. However, limits do not exist for many other PCPs occurring in wastewaters.

Environmental quality standards have also been set for some micropollutants in surface water bodies within the European Union [9].

In the European Union, USA, and other countries, a debate is open regarding the compilation of lists including *priority compounds* requiring monitoring in the aquatic environment [9–12]. However, due to the lack of information on toxicity and environmental impacts, a large number of contaminants, especially organic compounds, are not included in these lists. The number of compounds which could become priorities is therefore likely to grow.

Recent studies have remarked that due to the wide spectrum of characteristics of emerging contaminants, including PCPs, it is quite difficult to find a treatment able to remove most of them at a high percentage.

Recent studies [13, 14] pointed out that different groups of micropollutants can be removed at a medium-high extent only in those treatment trains where different removal mechanisms may occur. Multi-barrier treatment systems are necessary. As highlighted in Verlicchi et al. [15], constructed wetlands (CWs) are systems where oxic-anoxic-anaerobic environments may coexist, especially in subsurface flow beds or in sequence of different kinds of CW types. In surface flow systems, solar radiation may also contribute to the removal of micropollutants.

Increasing attention is being paid to the investigation of the occurrence and removal of common PCPs from wastewater but only a few studies deal with CWs. This chapter provides an overview of these issues, focusing on the different types of CWs acting as primary, secondary, or tertiary steps. Influent and effluent concentrations for 32 PCPs, belonging to eight different classes, were collected and discussed, along with their corresponding removal efficiencies achieved in the investigated types of CWs. The chapter concludes with an analysis of the influence of the main design parameters and operational and environmental conditions on the removal of the reviewed compounds.

2 Chapter Framework

This chapter is based on data collected from 35 peer reviewed papers published between 2001 and 2014, referring to 32 PCPs. All compounds are listed in Table 1, grouped according to their class. For each of them, chemical formula, CAS number and molecular structure are reported together with the references of the investigations included in the review dealing with it. A focus on surfactant classes is available in Table 2 where the nine most common ones are reported. Table 3 reports the schematics to which the investigated wetlands refer (i.e., if they act as a primary, secondary, or tertiary step) and Table 4 shows the CW types included.

The study continues with an analysis of the occurrence of the PCPs in the influent and effluent of CW acting as a primary, secondary, and tertiary step and a discussion of their removal achieved in the three steps distinguishing between the CW types (Figs. 1, 2, 3, 4, 5, 6, 7, 8, and 9). The characteristics and performance of restoration wetlands are then discussed, and finally data referring to occurrence (Figs. 10 and 11) and removal (Fig. 12) in hybrid systems complete the analysis of the different reviewed configurations. The final part of the chapter discusses how CW type, design parameters, and operational and environmental conditions influence the removal of investigated compounds on the basis of the collected literature data.

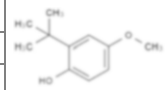
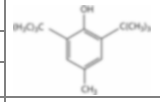
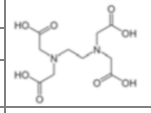
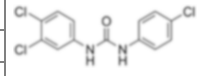
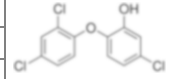
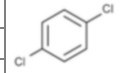
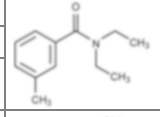
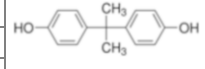
3 Personal Care Products in the Environment and Compounds Included in the Study

The chapter refers to 32 PCPs belonging to eight different classes: 3 antioxidants, 2 antiseptics, 1 deodorant, 1 insect repellant, 1 plasticizer, 3 sunscreen products, 5 synthetic musks, and 16 surfactants (seven anionic and nine nonionic ones).

Reviewed compounds are reported in Table 1 and classes of surfactants in Table 2. Their molecular structure is particularly complex due to the presence of aromatic and/or condensed rings, carboxylic and ketonic groups, double or triple bonds, and, in the case of surfactants, long hydrocarbon chains.

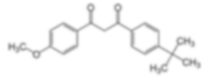
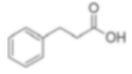
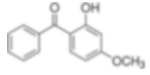
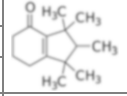
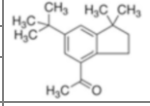
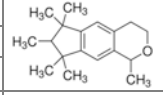
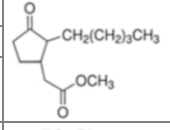
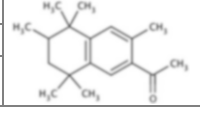
In Italy, NP and *p*-dichlorobenzene have been included among the substances to be monitored in the surface water [54]; in Switzerland, EDTA, NP, triclosan, DEET, and bisphenol A are included in the list of *relevant micropollutants in wastewater,* and they could be considered "target **c**ompounds" for which Swiss WWTPs, with a high environmental impact, should guarantee desired removal efficiencies [55]. At a European level, NP is included in the list of priority substances [9], requiring monitoring in water, and in the USA, BHA is included in the contaminant candidate List 3 U.S.EPA 2009 [10].

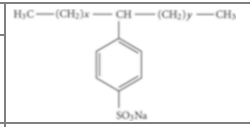
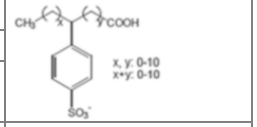
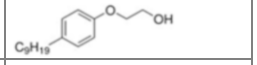
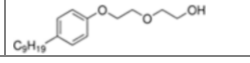
Table 1 List of reviewed PCPs, grouped according to their class with the corresponding references

	Class	Compound	Molecular structure	n. papers	References
1	Antioxidant	Butylated hydroxyanisole (BHA) $C_{11}H_{16}O_2$ 25013-16-5		1	[16]
2	Antioxidant	Butylated hydroxytoluene (BHT) $C_{15}H_{24}O$ 128-37-0		1	[16]
3	Antioxidant	Ethylenediaminetetraacetic acid (EDTA) $C_{10}H_{16}N_2O_8$ 60-00-4		1	[17]
4	Antiseptic	Triclocarban $C_{13}H_9C_{13}N_2O$ 101-20-2		3	[18–20]
5	Antiseptic	Triclosan $C_{12}H_7Cl_3O_2$ 3380-34-5		14	[16–29]
6	Deodorant	1,4-Dichlorobenzene (*p*-DCB) $C_6H_4Cl_2$ 106-46-7		1	[17]
7	Insect repellent	Diethyl-3-methylbenzoyl-amide (DEET) $C_{12}H_{17}NO$ 134-62-3		1	[20]
8	Plasticizer	4,4′-(Propane-2,2-diyl)diphenol (bisphenol A) $C_{15}H_{16}O_2$ 80-05-7		4	[17, 26, 31, 33]

(continued)

Table 1 (continued)

	Class	Compound	Molecular structure	n. papers	References
9	Sunscreen product	Avobenzone (Parsol) $C_{20}H_{22}O_3$ 70356-09-1		1	[33]
10	Sunscreen product	Hydrocinnamic acid $C_9H_{10}O_2$ 501-52-0		3	[25, 34, 35]
11	Sunscreen product	Oxybenzone $C_{14}H_{12}O_3$ 131-57-7		6	[24, 25, 27, 32, 34, 35]
12	Synthetic musk	Cashmeran $C_{14}H_{22}O$ 33704-61-9		1	[24]
13	Synthetic musk	Celestolide $C_{17}H_{24}O$ 13171-00-1		4	[24–27]
14	Synthetic musk	Galaxolide (HHCB) $C_{18}H_{26}O$ 1222-05-5		15	[16, 23–27, 33, 34, 36–42]
15	Synthetic musk	Methyl dihydrojasmonate (MDHJ) $C_{13}H_{22}O_3$ 24851-98-7		13	[16, 24–27, 33–37, 39, 42, 43]
16	Synthetic musk	Tonalide (AHTN) $C_{18}H_{26}O$ 1506-02-1		16	[16, 23–27, 31, 32, 34, 36–42]

17–20	Anionic surfactants	Linear alkylbenzene sulfonate (LAS)		2	[44, 45]
		$NaSO_3C_{10}H_{13}(CH_2)_{x+y}$			
		LAS C10	$x+y=7$		
		1322-98-1			
		LAS C11	$x+y=8$		
		27636-75-5			
		LAS C12	$x+y=9$		
		25155-30-0			
		LAS C13	$x+y=10$		
		26248-24-8			
21–23	Anionic surfactants	Sulfophenyl carboxylate		1	[44]
		SPC			
		$C_9H_9SO_5Na(CH_2)_{x+y}$			
		SPC-C9,	$x+y=6$		
		SPC-C10,	$x+y=7$		
		SPC-C11	$x+y=8$		
24	Nonionic surfactant	Nonylphenol (NP)		2	[46, 47]
		25154-52-3			
		$C_{15}H_{24}O$			
25–26	Nonionic surfactants	Nonylphenol-mono-ethoxylate (NP1EO)		2	[46, 47]
		Nonylphenol diethoxylate (NP2EO)			

(continued)

Table 1 (continued)

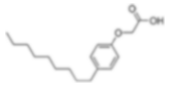
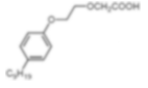
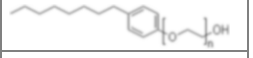
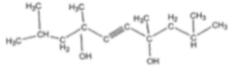
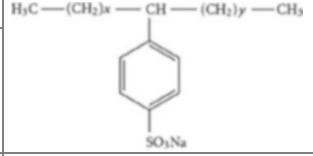
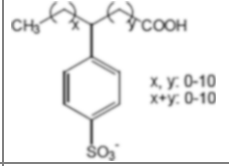
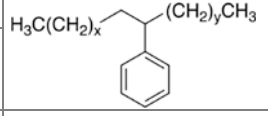
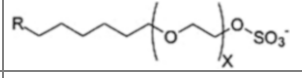
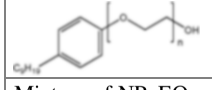
	Class	Compound	Molecular structure	n. papers	References
27–28	Nonionic surfactants	Nonylphenol-mono-ethoxycarboxylic acid (NP1EC)		1	[17]
		$C_{17}H_{26}O_3$			
		3115-49-9			
		Nonylphenol-di-ethoxycarboxylic acid (NP2EC)			
		$C_{19}H_{30}O_4$			
		106807-78-7			
29	Nonionic surfactant	4-Tert-octylphenol (OP)		1	[17]
		$C_{14}H_{22}O$			
		140-66-9			
30–31	Nonionic surfactants	4-Tert-octylphenolmono ethoxylate (OP1EO)		1	[17]
		$C_{16}H_{26}O_2$	$n = 1$		
		4-Tert-octylphenol-diethoxylate (OP2EO)	$n = 2$		
		$C_{18}H_{30}O_3$			
32	Nonionic surfactant	Surfynol 104		1	[33]
		$C_{14}H_{26}O_2$			
		8043-35-4			

Table 2 Classes of surfactants included in the chapter and corresponding references

	Type	Class	Molecular structure	n. papers	References
A	Anionic surfactants	Methylene blue active substances (MBAS)		3	[45, 48, 49]
B	Anionic surfactants	Linear alkylbenzene sulfonate (LAS)		3	[44, 45, 50]
		$NaSO_3C_9H_{11}(CH_2)_{x+y}$			
C	Anionic surfactants	Sulfophenyl carboxylate (SPC)		1	[44]
D	Anionic surfactants	Linear alkyl benzene (LAB)		1	[33]
		$C_6H_5CHR_1R_2$ where $R_1 = C_nH_{2n+1}$, $R_2 = C_mH_{2m+1}$ $m \geq 0$, $n \geq 1$ (typically 10–16)			
E	Anionic surfactants	Alkyl ethoxy sulfates (AES)		1	[50]
		$CH_3(CH_2)_y(O\ CH_2CH_2)_xOSO_3X$	$x = 0$–12		
			$y = 12$–13		
			X most often being Na		
F	Nonionic surfactants	NP(1–3)EO, NP(4–9)EO		2	[46, 47]
			Mixture of NPnEO		
			With $n = 1$–3		
			With $n = 4$–9		

(continued)

Table 2 (continued)

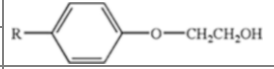
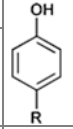
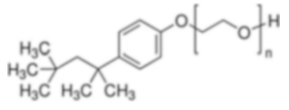
	Type	Class	Molecular structure	n. papers	References
G	Nonionic surfactants	4-Alkylphenol monoetoxylated (APE) $C_9H_{16}(CH_2)_nO_2$		1	[33]
H	Nonionic surfactants	Alkylphenols (AP) $C_7H_7O(CH_2)_n$		1	[33]
I	Nonionic surfactants	Triton X 100 (4-octylphenol polyethoxylate $C_{14}H_{22}O(CH_2\ CH_2O)_n$		3	[45, 51, 52]

Table 3 Schematics of wastewater treatments including CWs in different configurations, with the corresponding references

CW acting as	Schematic	References
Primary step	Raw influent → CW → Effluent	[22, 23, 45, 46, 49, 51]
Secondary step	Raw influent → Prim. Treat. → CW → Effluent	[31, 34–37, 39, 42, 44, 48]
Tertiary step	Raw influent → Prim. Treat. → Sec. Treat. → CW → Effluent	[16, 17, 19, 20, 24, 25, 27–30, 38, 40, 41]
Restoration wetland	WWTP 1 effluent; WWTP 2 effluent; WWTP n effluent; CW	[26, 33]
	Raw influent → CW → CW → Effluent	[18]
Hybrid system	Raw influent → Prim. Treat. → CW → CW → Effluent	[21, 32, 43, 47, 48, 50]
	Raw influent → CW → CW → CW → Effluent	[43]
	Step; Stage 1 … Stage n; CW → … → CW; Sampling point	[16, 17, 20, 21, 24, 25, 27, 28, 31, 37, 43, 47, 49]
Multistage step	Step; Stage 1; CW; …; CW; Stage n; Sampling point	[32, 43]

4 Classifications of Constructed Wetlands and Types Included in the Chapter

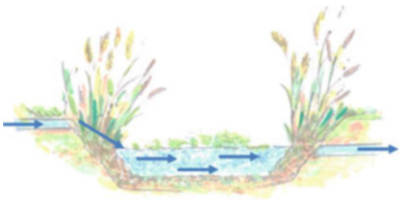
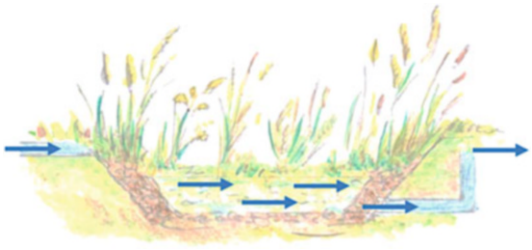
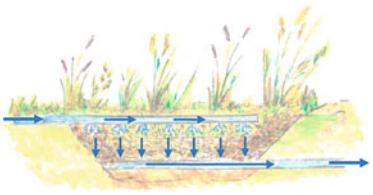
The CWs have been classified according to the treatment step and the main flow direction.

Depending on the treatment level, they have been divided into primary, secondary, or tertiary steps (Table 3). In cases where they were fed by a river whose water flow is primarily made up of a wastewater treatment plant effluent or even untreated wastewater, the system was called *restoration wetland*. If the treatment system includes two or three steps relying on CWs, it is called *hybrid plant*.

Finally, a step may also include more than one stage, either of the same type (monotypic) or of different types (polytypic), thus resulting in a *multistage system*.

Referring to the flow direction, CWs are classified in surface flow systems (SF) and horizontal and vertical subsurface flow beds, H-SSF and V-SSF,

Table 4 Classification of constructed wetlands and corresponding references

CW Type	Schematic	References
Surface flow (SF):		
Classic schematic (A)		[16][3], [17][3], [18][1+2], [19][3], [21][2+3], [22][1], [23][1], [24][3], [25][3], [26][a], [27][3], [28][3], [29][3], [30][3], [33][a,1], [36][2], [38][3], [40][3], [41][1], [42][2], [43][1], [43][1+2+3;2+3], [47][2+3], [48][2+3], [50][2+3]
Modified schematic (B)		
Horizontal subsurface flow (H-SSF)		[16][3], [21][2+3], [31][2], [32][2+3], [35][2], [36][2], [37][2], [39][2], [42][2], [43][2+3], [44][2], [46][1], [47][2+3], [48][2], [50][2+3]
Vertical subsurface flow (V-SSF)		[21][2+3], [35][2], [41][3], [44][2], [47][2+3], [49][1]

The numbers (1,2,3) reported as apex for each reference refer to the treatment steps of the investigated plants while the letter "a" means restoration wetland

respectively (Table 4). In SF basins, the majority of flow occurs through a water column overlying a benthic substrate, whereas the flow in H-SSF and V-SSF beds is through a porous medium (generally gravel) and classified as either horizontal, if the feed is from one side of the bed to the other part, or vertical, if the feed is spread over the surface of the bed, crossing it from the top to the bottom. Additionally, in H-SSF beds the feed is continuous, while in V-SSF beds it is intermittent. Surface flow systems investigated also include a modified system, Hijosa-Valsero et al. [36], where the effluent leaves the system after a passage through a stratum of

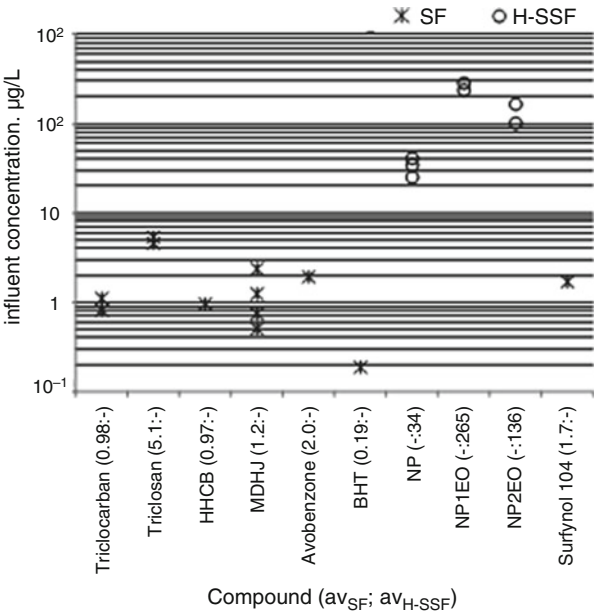


Fig. 1 Occurrence of investigated PCPs in the influent of CWs acting as a primary step. Data from: [18, 33, 43, 46]

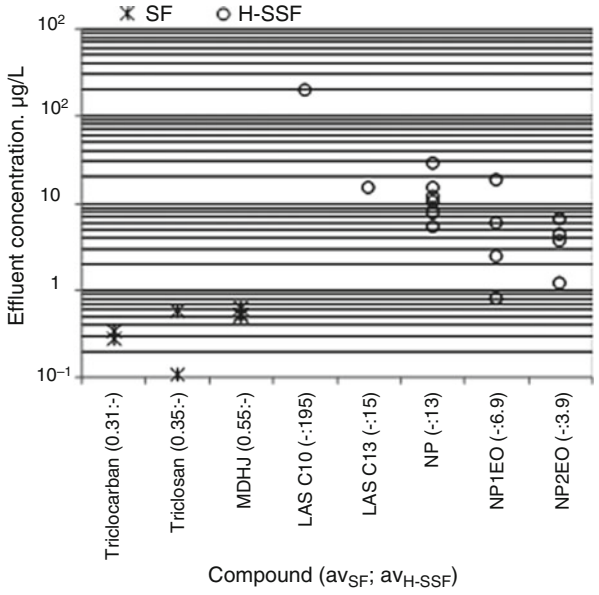


Fig. 2 Occurrence of investigated PCPs in the effluent of CWs acting as a primary step. Data from: [18, 22, 43, 46, 51]

materials at the bottom of the bed, resulting in a combination of surface and subsurface flow systems (Table 4).

In addition, there are two systems which are considered *nonconventional*. They are a pilot system fed by the secondary effluent of Empuriabrava WWTP, Spain,

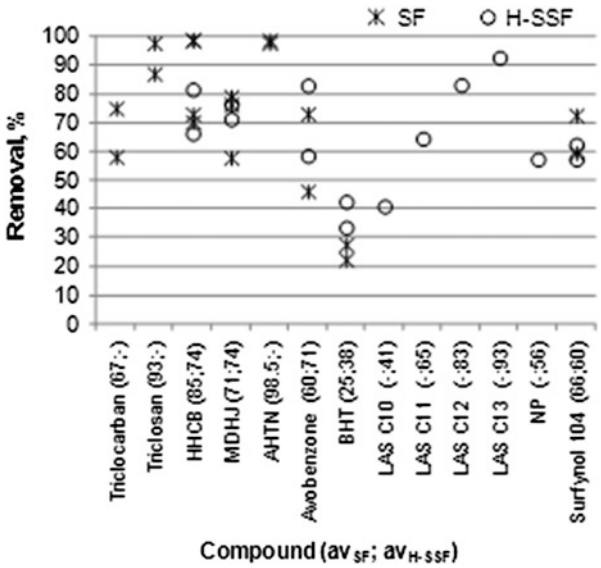


Fig. 3 Removal efficiencies observed in primary CWs for selected PCPs. Data from: [18, 23, 33, 43, 45, 46]

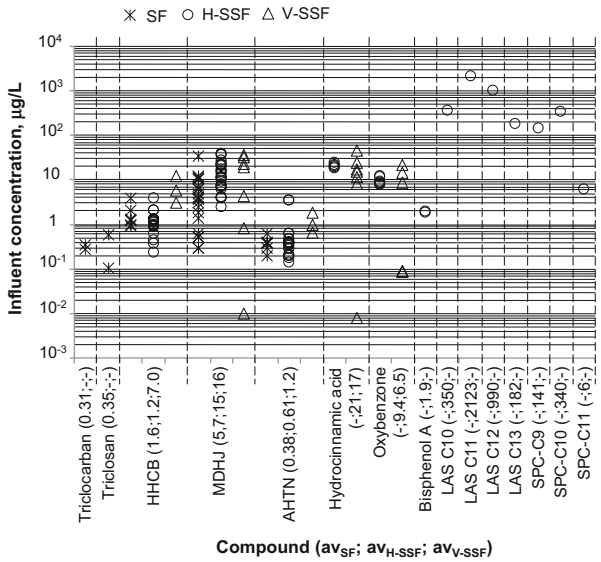


Fig. 4 Occurrence of investigated PCPs in the influent of CW acting as a secondary step. Data from: [18, 32, 34–37, 39, 42–44]

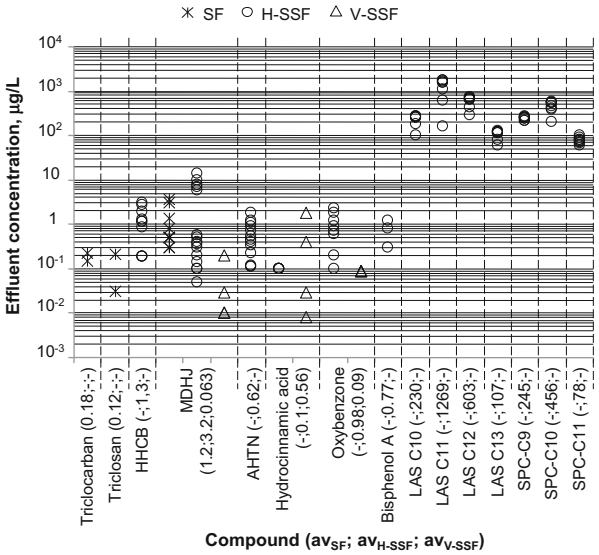


Fig. 5 Occurrence of investigated PCPs in the effluent of CW acting as a secondary step. Data from: [18, 32, 35, 37, 43, 44]

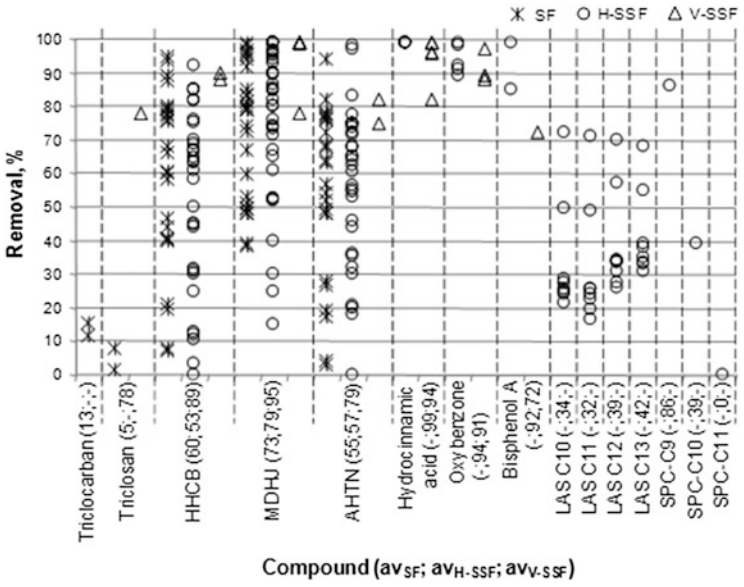


Fig. 6 Removal efficiencies for the investigated PCPs in different types of CWs acting as a secondary step. Data from: [18, 21, 31, 34–37, 39, 42–44]

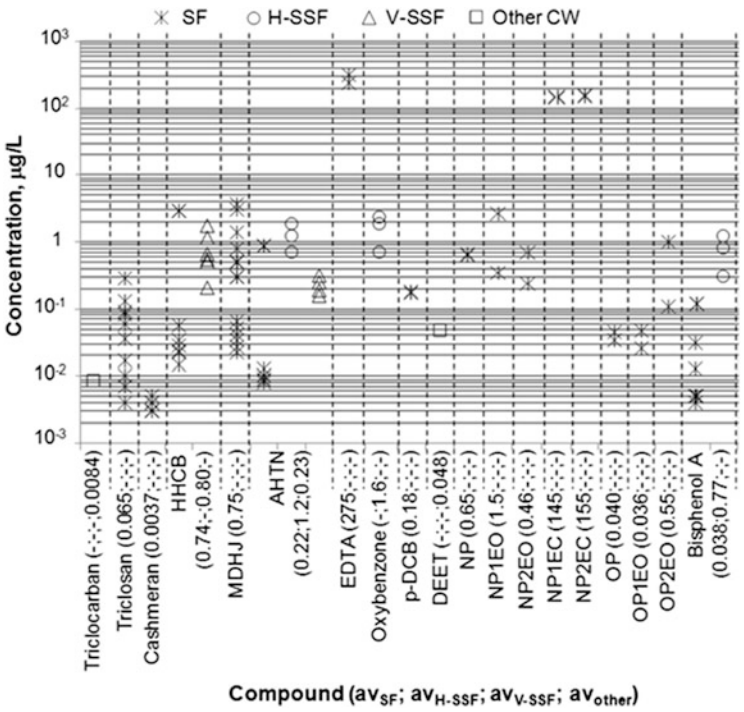


Fig. 7 PCP concentrations in the influent of CWs acting as a polishing step. Data from: [17, 26, 29, 30, 32, 38, 41, 43, 53]

which is operated in parallel with the full-scale reclamation plant consisting of surface flow basins [27] and a sequence of SF and H-SSF cells [20].

4.1 Main Features of the Investigated Plants

The chapter is based on investigations of PCP occurrence and removal in CWs carried out in Europe (64%: Spain, Denmark, England, and Czech Republic), America (28%: USA, Canada, and Mexico), and Asia (8%: Korea and China).

In the 35 peer reviewed papers, 87 treatment lines were investigated. They mainly include H-SSF beds (49%) and SF basins (38%) and in a few cases V-SSF systems (10%). The types of CW are not well specified in only 3% of the plants. Of the 87 treatment lines, 54 refer to pilot plants and 30 to full-scale plants, while the remaining 3 refer to full-scale plants followed by a pilot plant. Moreover, 12 treatment lines refer to hybrid systems.

In nine lines the investigated CW acted as a primary step, in 42 as a secondary step, in 15 as a tertiary one, and in nine to restoration wetlands.

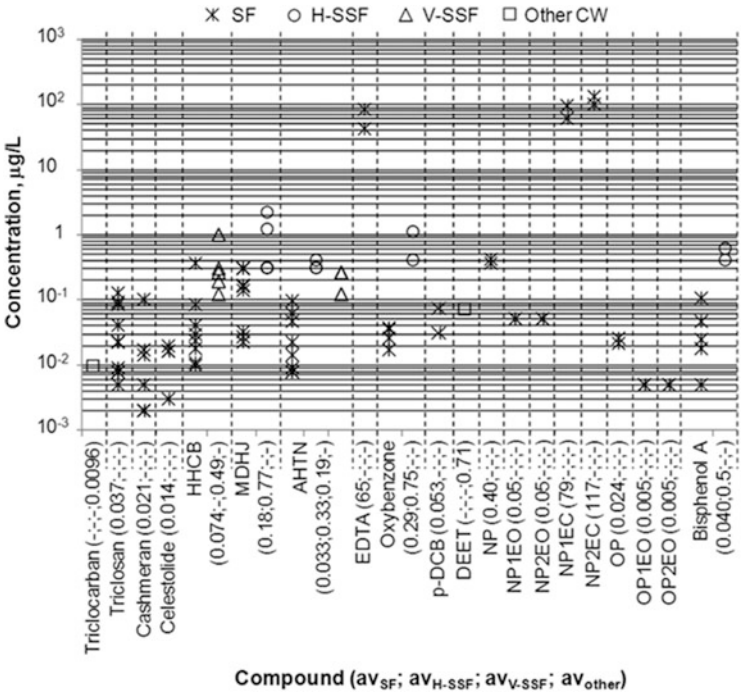


Fig. 8 PCP concentrations in the effluent of CWs acting as a polishing step. Data from: [17, 20, 26, 27, 29, 38, 41–43]

The feeding was always a real domestic wastewater, with a few cases where domestic wastewater was injected with selected PCPs at the desired concentration [21, 31, 32, 46] and one more where the influent contained a consistent percentage of industrial wastewater [33]. Two studies [49, 50] investigated occurrence and removal from grey water. All the treatment trains investigated were outdoor with the sole exception of the one investigated by Belmont et al. [47]. In nearly all studies, analyses were processed on grab samples of water.

5 Occurrence and Removal in the Different Treatments Steps

Figures 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, and 12 report concentrations observed in the influent and effluent of CWs acting as primary, secondary, and tertiary steps and in the case of hybrid systems. They also report removal efficiencies for the investigated compounds in the systems under study. In the *X*-axis of each graph, the numbers in brackets after the PCP name correspond to the average values of the collected data for each of the CW types considered.

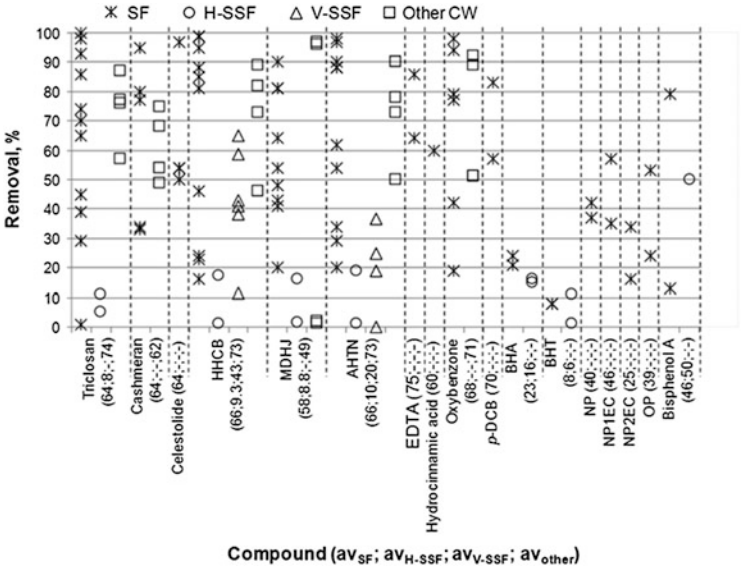


Fig. 9 Removal efficiencies for PCPs in different types of CWs acting as a polishing step. Data from: [16, 17, 24, 25, 27, 28, 30, 40, 41, 43]

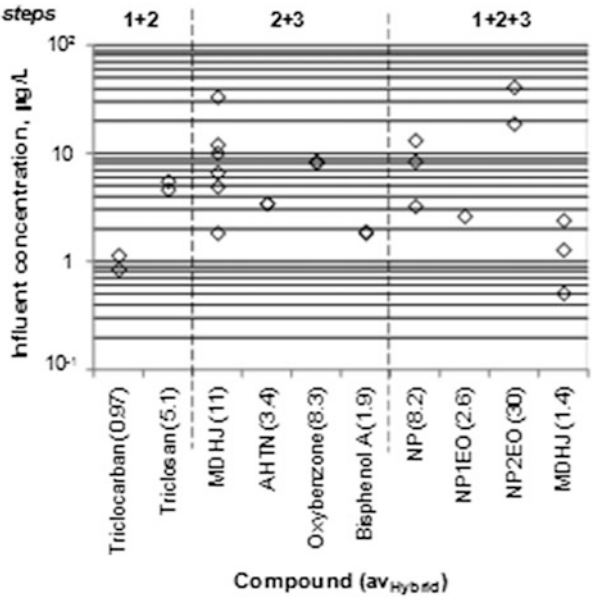


Fig. 10 Occurrence of investigated PCPs in the influent of hybrid CWs. Data from: [18, 42, 43, 47, 50]

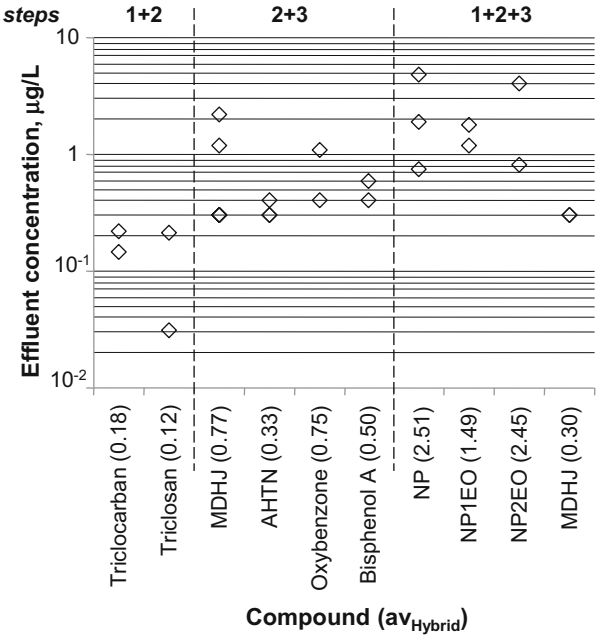


Fig. 11 Occurrence of investigated PCPs in the effluent of hybrid CWs. Data from: [18, 42, 43, 47, 50]

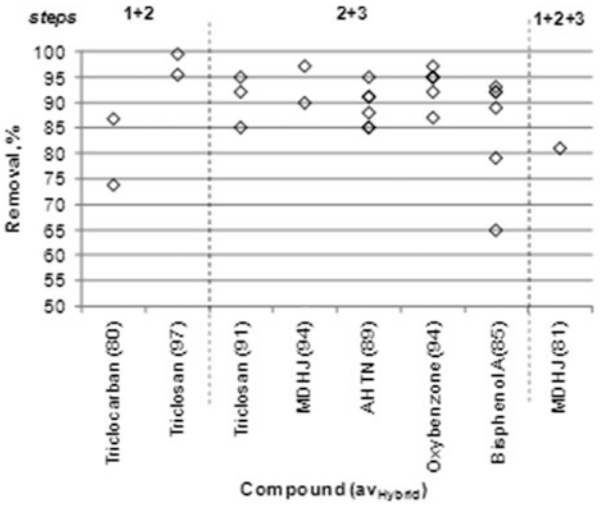


Fig. 12 PCP Removal in hybrid CWs. Data from: [18, 21, 32, 43]

Finally, ranges of concentration data for *groups* or *mixtures* of surfactants (MBAS, LAS, LAB, Triton X100; see Table 2) in the influent and effluent of some plants were reported in the discussion.

5.1 Primary Step: Occurrence and Removal of Selected PCPs

Only a few investigations reported PCP concentrations in the influent and effluent of CWs acting as a primary step. These are reported in Figs. 1 and 2, which show ten PCPs in the influent and eight in the effluent. The feeding was always only domestic wastewaters, with the exception of Navarro et al. [33] where the influent was a river receiving both untreated domestic as well as industrial wastewaters (see also Sect. 5.4).

Belmont and Metcalfe [46] and Sima and Holcová [51] investigated subsurface flow beds. All the other studies examined SF basins, which greatly differed for influent flow rate, geometry and size, configuration, and environmental and operational conditions. Hydraulic retention time (HRT) varied between 0.4 days [43] and 5 days [33].

The highest influent concentrations were found for the common nonionic surfactants NP1EO (289 μg/L), NP2EO (168 μg/L), and NP (41.5 μg/L), followed by triclosan (5.44 μg/L). The highest concentrations in the effluent were found for LAS C10 (195 μg/L), NP (28 μg/L), NP1EO (18 μg/L), and LAS C13 (15 μg/L). The same compounds exhibited the highest average values.

Referring to NP, NP1EO, and NP2EO, the effluent concentration is always lower than the corresponding influent one, but for NP the reduction is the smallest. This is due to the fact that NP1EO and NP2EO may transform into NP during anaerobic degradation throughout the system.

Classes of surfactants were found at very high concentrations both in the influent and effluent of primary CWs: MBAS (methylene blue active substances) 1,390–17,100 μg/L in the influent and 340–4,560 μg/L in the effluent [49], NP(1–3)EO 441 μg/L in the influent and 13 μg/L in the effluent [46], and Triton X100 978 μg/L in the influent and 99 μg/L in the effluent [45, 51]. These data point out that surfactants are present in a wide spectrum of substances commonly used in households, not only PCPs.

Removal – Figure 3 shows the observed removal efficiencies for selected PCPs in SF basins as well as H-SSF beds. In SF systems, high removals were observed for galaxolide and tonalide (both 99%, [23] and triclosan (98%, [18]), while these were very poor for BHT (less than 30%).

In H-SSF beds, the removal efficiencies for the reviewed compounds were in general lower than in SF systems and the best performances were found for LAS C13 (92.9%) and LAS C12 and avobenzone (both at 83%).

For the five substances investigated in both systems, higher average removals were observed in SF basins for HHCB and Surfynol 104, while avobenzone, BHT, and MDHJ were removed well in H-SSF beds. APE, AP, and LAB were removed to a greater extent in H-SSF beds than in SF systems [33], suggesting that removal was mainly due to sorption mechanisms. Moreover, APEs exhibited higher removal than APs, around 75 and 50%, respectively, which is correlated to the fact that APs may form during the biodegradation of APEs [33].

In H-SSF beds, nonionic surfactants were removed to a greater extent than anionic ones [45] and also more quickly [56].

Studies of the occurrence and degradation of LAS and SPC in CWs remarked that homologues with an alkyl chain shorter than C10 were rarely detected, as the alkyl chain is first preferably oxidized to carboxylic acid and then it is degraded [56].

5.2 Secondary Step: Occurrence and Removal of Selected PCPs

Figures 4 and 5 show concentrations in the influent and effluent of CWs acting as a secondary step and Fig. 6 shows the observed removal efficiencies for the reviewed 15 PCPs.

Synthetic musks were the most investigated in the influent, followed by sunscreen products, while in the effluent the most studied were surfactants followed by synthetic musks.

The highest influent concentrations were detected for the surfactants LAS C11 (2,123 μg/L), LAS C12 (990 μg/L), LAS C10 (350 μg/L), and SPC C10 (340 μg/L) [44]. It is worth noting that all the investigated surfactants were found at concentrations greater than 100 μg/L (with the only exception of SPC C11). The other PCPs were found below 45 μg/L (the highest values were due to hydrocinnamic acid [35] followed by the musk MDHJ (39 μg/L [39].

Regarding the effluent, the highest concentrations were detected for the same surfactants mentioned for the influent: LAS C11 (1,774 μg/L), LAS C12 (731 μg/L), SPC C10 (570 μg/L), and LAS C10 (264 μg/L) [44]. All the remaining investigated compounds exhibited concentrations at least one order of magnitude below.

A rapid glance at Figs. 4 and 5 shows that for each LAS compound, average effluent concentration is lower than the corresponding influent one, while this does not occur for SPCs as they were formed during the biodegradation of LAS in the system, and their formation was faster than their removal as pointed out in the work by Huang et al. [44]. For all the other compounds, a reduction of the average concentration was found from inlet to outlet of each type of CW.

Only for MDHJ is it possible to compare performance of the three kinds of CW on the basis of the measured concentrations. The lowest effluent concentrations were found in V-SSF systems leading to the supposition that the aerobic conditions of the bed favor its biodegradation [35].

Referring to oxybenzone and hydrocinnamic acid, similar performances were observed in H-SSF and V-SSF beds [34].

As remarked for primary CWs, much higher concentrations were found for classes of surfactants in the influent/effluent of secondary CWs: MBAS were detected around 15,000/2,500 μg/L [48], LAS around 3,600/2,900 μg/L, and

SPCs around 500/900 μg/L [44]. It is worth noting that only SPCs exhibited an increment in the concentrations due to the biodegradation of LAS, resulting in a formation of PCPs as discussed above.

Removals – Regarding collected removal efficiencies (Fig. 6), the most investigated compounds were the three fragrances in the SF and H-SSF basins. They exhibited a wide range of variability of removal values. This is also due to the fact that these studies were carried out with the aim of analyzing the influence which different factors have on PCP removal. These factors include design parameters [36], hydraulic loading rates (HLRs) [34, 35], operational conditions [21, 37], and environmental conditions [36, 42]. In addition, the investigated plants might have different ages and different sizes (lab, pilot, or full scale), they may be planted or unplanted, and they may also be affected by clogging, leading to a reduction in the HRT. These factors may greatly influence the removal of PCPs within the system, as discussed in Sect. 6.

All the investigated compounds were removed up to 95% with the only exceptions of the antiseptics triclosan and triclocarban and the surfactants.

In SF CWs, the best removals were achieved for the three fragrances. This occurred in the modified SF type reported in Table 4 [36], where the passage of the water through the filling media before discharge into the environment allowed the (lipophilic) pollutants to sorb onto filling materials.

In H-SSF beds, the highest average removals were found for hydrocinnamic acid (99%), oxybenzone (94%), and bisphenol A (92%) and also for fragrances, while surfactants generally exhibited lower removal levels.

In V-SSF beds the best performances were observed for MHDJ (95%), HHCB (89%), and AHTN (79%), suggesting that the intermittent feeding and the aerobic environment are beneficial to the removal of these micropollutants.

Figure 6 does not include negative removal values. These were rarely found, were limited to fragrances and SPCs, and were due to the internal generation of some compounds following the biodegradation of others (SPCs as intermediates of biodegradation of LAS or longer SPCs, Huang et al. [44]), release phenomena of selected compounds (HHTN and AHTN), and clogging conditions, resulting in HRT reduction and malfunctions including the release of compounds that could not be removed from the bed due to lack of time (i.e., MDHJ) [42]. Peculiar situations were reported in literature. Huang et al. [44], for example, found that in warm periods, suspended solids containing LAS retained within the bed quickly decomposed, resulting in a much higher quantity of SPCs generated compared to cold periods. In contrast, Reyes-Contreras et al. [42] found release phenomena for the three fragrances in winter in H-SSF beds but not in summer, perhaps due to an inhibition of the biological activity at low temperatures and a release of the biofilm within the system where fragrance molecules could be present.

5.3 Tertiary Step: Occurrence and Removal of Selected PCPs

Figures 7 and 8 refer to the concentrations of PCPs detected in the influent and effluent of CWs acting as a tertiary step, while Fig. 9 shows the removal efficiencies reported by the different authors in the polishing CWs. Nineteen PCPs were monitored in the influent and twenty compounds in the effluent (the same as the influent plus the fragrance celestolide), and removal values are available for seventeen compounds.

SF systems were the most studied CW type, followed by H-SSF beds. Different authors analyzed multistage polishing systems (see also Table 3). The investigated systems consisted of series of SF basins, with the exception of those studied by Reyes-Contreras et al. [16] and Hijosa-Valsero et al. [43], which were sequences of SF and H-SSF CWs. In addition, the multistage polishing plant investigated by Zhu and Chen [20] included 30 cells between SF and H-SSF types; this plant was classified as a nonconventional CW in Figs. 7, 8, and 9.

The highest influent concentration was detected for EDTA (310 μg/L [17]). This surprisingly high value is in accordance with those found in literature in the effluent of secondary WWTPs as reported by Kase et al. [55]. The second highest concentrations were for NP2EC with 160 μg/L and NP1EC with 150 μg/L. All the other PCPs exhibited influent concentrations of two orders of magnitude lower, the highest values being for MDHJ (3.7 μg/L) and galaxolide (2.9 μg/L).

The highest average influent concentrations were found for EDTA (275 μg/L), NP2EC (155 μg/L), NP1EC (145 μg/L), oxybenzone (1.6 μg/L), NP1EO (1.5 μg/L), and AHTN (1.23 μg/L). For the remaining investigated compounds, average values were always less than 1 μg/L.

Referring to CW effluent, the highest effluent concentrations were found for NP2EC (135 μg/L), NP1EC (97.5 μg/L), and EDTA (87 μg/L) [17], followed by MDHJ (2.2 μg/L) [43].

A comparison between Figs. 7 and 8 highlights that a general decrement in the concentrations occurs from influent to effluent.

Referring to cashmeran, average influent concentration is lower than that of the effluent, but an analysis of the investigations dealing with it reveals that some of the reviewed studies only provided effluent values and removal efficiencies, and in all of them a removal was always observed, as reported in Fig. 9, and no release occurred.

Only DEET exhibited a slight increase in the passage through the polishing system investigated by Zhu and Chen [20], but there is still little available data and it is not possible to conclude that a release would occur.

The only PCP investigated in surface and subsurface flow systems is AHTN – for this all three CW types showed a removal ability.

Removals – In SF systems, the highest values were found for triclosan (99.99%, [28]) and HHCB (99%, [24, 25]), AHTN and oxybenzone (both 98% [25]), celestolide (97% [25]), and cashmeran (95% [24]). All refer to two-stage systems. The high attenuation of EDTA (on average 75%) should be due to photolytic

reactions as the compound is quite resistant to biodegradation and has a low affinity for sorption [17]. Finally, very low removals are observed for NPs and NPnECs [17].

Modest removal values were observed in the V-SSF beds. Based on data reported by Reif et al. [41], they ranged between 65% (HHCB) and 0% (AHTN). The removals found in H-SSF beds are even poorer: Reyes-Contreras et al. [16] always found them to be less than 20% for triclosan, HHCB, MDHJ, AHTN, BHA, and BHT.

An interesting investigation was carried out by Sacco et al. [52] into the removal of the mixture of nonionic surfactants Triton X-100 dosed at 30 and 300 mg/L in the pilot H-SSF bed. Their mixture contained up to 13 EO groups in different percentages. They found that in the first 40 cm of the bed, OP and its monoethoxylate (EO = 1) had the biggest increment. The decrease (sometimes also the disappearance) in certain octylphenol ethoxylate (OPEO) oligomers seems to be correlated to increases in others (characterized by a shorter EO chain), and the biodegradation rate of those oligomers with a number of EO greater than 3 is higher than those observed for compounds with shorter chains.

Promising results were observed in the (nonconventional) biologically based filtration water reclamation plant investigated by Matamoros et al. [27] for oxybenzone, AHTN, HHCB, triclosan, and cashmeran, especially in summer time. MDHJ exhibited very high removal in summer (>96%), while in winter the removal was nearly absent.

In the multistage (SF + H-SSF) systems by Reyes-Contreras et al. [16], a consistent increment in the removal efficiencies of MDHJ, triclosan, AHTN, HHCB, and BHT was observed during the summer season with respect to the winter one (about 2–8 times higher).

The results obtained by Matamoros et al. [25] are quite interesting. They compared the removal for a group of PCPs in a tertiary pond and in a conventional tertiary treatment by UV radiation and chlorine disinfection. They found that solar radiation can degrade parental compounds in their intermediates both in the UV reactor and the pond. In most cases these reaction products are more toxic than the parental ones. However, in pond systems other mechanisms including biodegradation, sorption onto solids and sediments, and plant uptake may reduce their concentration.

5.4 Restoration Wetlands

Two restoration wetlands were included in this study. The first one, described in Matamoros et al. [26], is located in Denmark and is fed by two rivers – Aarhus (watershed 120 km^2) and Lyngbygaards (watershed 132 km^2) – which are impacted by urban sewage and agricultural runoff. The wetland is interconnected to a lake whose effluent discharges into the sea. The lake is used for recreational purposes and near it there are some of the city's water supply wells. The wetland was created

in 2003 to reduce the nutrient concentrations discharged into the lake and then into the sea and to preserve the downstream water environment conditions. It covers an area of 100 ha and consists of a surface flow basin with an average water depth of 0.5 m and a maximum depth of 2 m, an HRT ranging between 3 and 20 days, on average 7 days. Based on a mass balance between influent and effluent streams to the wetland, a consistent reduction was found in the effluent concentration (mitigation effect passing through the wetland) for most of the investigated PCPs (for triclosan, cashmeran, MDHJ, HHCB, AHTN, and bisphenol A, it was >40%). In winter, due to the low sunlight exposure and cold temperatures, bio- and photodegradation processes were limited. It is important to highlight that in the wetland outlet, the concentrations of all the investigated PCPs kept quite constant, although the influent values exhibited a wide variability confirming wetland buffer capacity.

The second restoration wetland is a pilot plant fed with the water of the Sordo River (in southeastern Mexico) which receives untreated urban sewage and industrial wastewaters [33]. The CWs consist of 8 cells: four are SF type (substrate upland soils, 0.4 m deep, free water surface flow column, 10 cm high) and four are H-SSF type (filled with 0.4 m of volcanic gravel, water flow 10 cm below the surface). Each of them has an HRT of 5 days. A high attenuation was found for galaxolide, MDHJ, parasol, and APE.

5.5 *Hybrid Systems: Occurrence and Removal of Selected PCPs*

Nine compounds were monitored in the influent (Fig. 10) and effluent (Fig. 11) of different types of hybrid systems, and data on observed removal efficiencies were provided for six of them (Fig. 12).

The most adopted CW type in the hybrid systems was SF basins, followed by H-SSF beds, and the most investigated sequences included SF + H-SSF systems [43, 50] and only H-SSF ones [32]. All three types were investigated in the hybrid systems by Avila et al. [21] and Belmont et al. [47].

A rapid glance at Figs. 10 and 11 highlights that for each substance a reduction was observed. The same was observed for classes of surfactants in the hybrid systems (steps 2 + 3) investigated by Conte et al. [48] and Jokerst et al. [50]. The first found that MBAS decreased from 3,200 and 16,000 μg/L in the influent to 2,000–2,500 μg/L in the effluent and the second that AES decreased from 50–16,500 μg/L in the influent to 15–50 μg/L in the effluent.

Avila et al. [21] investigated a hybrid system (V-SSF as secondary step and H-SSF + SF as tertiary step) fed by municipal wastewater where PCPs were injected at the desired concentrations. Their investigation also analyzed the operational characteristics inside the tank, in particular redox potential which resulted in the

range 110 + 128 mV in the V-SSF bed, in the range from −59 to −115 mV in the H-SSF bed, and between 156 and 171 mV in the SF basin.

Their investigation pointed out that the first stage, a V-SSF bed, was responsible for most of the removal of the selected PCPs, and the following polishing treatment contributed to the removal but to a smaller extent. In particular the effect of the SF stage on the removal of these compounds was quite negligible.

The highest removal efficiencies were found for triclosan in series of aerated lagoons (on average 97%, [18]) and in a hybrid-polytypic system (V-SSF acting as a secondary step followed by H-SSF + SF as a tertiary step); average removal 91%, Avila et al. [21], for MDHJ (97%) in the sequence SF + H-SSF beds [43], and for oxybenzone (97%) in the sequence of H-SSF beds by Reyes-Contreras et al. [42].

For triclosan, photodegradation greatly contributes to its removal followed by biodegradation, while for MDHJ photolysis is less important than biodecomposition. This fact is confirmed by the lower removal (81%) found by the same authors for MDHJ in a series of ponds (steps 1 + 2 + 3). Oxybenzone, instead, is mainly removed by biodegradation and then by sorption.

Many investigations confirmed that most of the removal of PCPs occurs in the first step. The comparison provided by Avila et al. [21] of the contributions in the accumulated average removal efficiencies achieved in each unit of the hybrid system for AHTN, oxybenzone, triclosan, and bisphenol A is quite interesting.

Referring to bisphenol A, the main removal mechanism is biodegradation and the lowest removal efficiencies (about 65%) were observed at the lowest redox values (anaerobic conditions in H-SSF beds by Avila et al. [32]).

6 Discussion of the Influence of the Main Design Parameters and Operational Conditions of PCP Removal Efficiencies

As already mentioned, for many reviewed compounds, the removal achieved in CWs exhibited a wide range of variability. In fact, in many cases the studies investigated the influence of some operational conditions (mainly HLR and temperature) and all the removal values observed were reported. As a consequence, the lowest values do not necessarily mean that these systems are not appropriate. In addition, removals are correlated to the influent concentrations. As will be discussed later, higher concentrations generally correspond to higher removal efficiencies.

The following paragraphs analyze the influence of the main design parameters as well as the operational and environmental conditions on the removal of the selected compounds.

6.1 Variation in the Influent Concentrations of PCPs

Higher influent concentrations often correspond to higher removal efficiencies, as reported by some authors (among them [24, 27, 40]). Variations in the influent could be attributed to a different consumption of the compound, infiltration in the sewage network by seawater [27] or groundwater, a malfunction in the upstream treatments (if CW acts as a secondary or a tertiary step) [24], or in the treatment itself.

Reyes-Contreras et al. [16] found a seasonal variation in the concentrations of the two fragrances: AHTN and HHCB occurred at concentrations three times higher in summer than in winter (tonalide: 1.5 μg/L against 0.44 μg/L and galaxolide 1.2 μg/L against 0.45 μg/L), and their removals were more than twice higher in summer than in winter.

6.2 Primary Treatment

The influence of two primary treatments – a septic tank and an anaerobic hydrolysis upflow sludge bed (HUSB) – on the removal of PCPs in the following H-SSF bed was compared by Hijosa-Valsero et al. [37]. The former produces an effluent of more constant quality during the year and therefore the effluent of a CW fed by a septic tank is slightly better than the effluent produced by a CW fed by a HUSB system.

Surfactants were removed at a consistent fraction in pretreatments. MBAS, for instance, was removed up to 20% in screens, horizontal sand traps, and sedimentation basins [51, 56].

6.3 HLR and HRT

A variation in the influent flow rate may be caused by a different wastewater flow, rainwater, snow melting, and seawater and groundwater infiltration. The main and most frequent disturbance is an increment of the HLR resulting in a shortening of HRT, with respect to the corresponding design values. Prolonged rain events (together with cleanup or reconstruction of the wetlands) may lead to a pulsed, albeit delayed release of the accumulated PCPs due to desorption.

Many studies agree with the fact that whatever the CW step, the higher the HRT, the higher the removal efficiencies achieved by the system for the investigated PCPs in wastewater (i.e., [40]).

Avila et al. [21] investigated ability in removing a selected group of PCPs (AHTN, oxybenzone, triclosan, and bisphenol A) at the three different HLRs (0.06, 0.13, and 0.18 m/day) in their treatment line, consisting of a V-SSF bed,

followed by an H-SSF bed and an SF basin as a polishing step. They found that the removal of triclosan decreased with the increase of HLR, while no clear patterns were found for AHTN, bisphenol A, and oxybenzone. The same increment of HLR applied to the H-SSF bed only affected the removal of AHTN that decreased, while for bisphenol A, oxybenzone, and triclosan, no correlation was found between HLR and observed removal.

In V-SSF beds an increment in the HLR (13–70 mm/day) did not result in a decrement of the removal of MDHJ, hydrocinnamic acid, oxybenzone, HHCB, and AHTN [34], while in SF basins, it resulted in a decrement in the removal efficiencies for oxybenzone and MDHJ [34] and in H-SSF beds for anionic [53] and nonionic surfactants [51].

6.4 Aging of the CW

The age of the CW may influence the removal of PCPs. In SF basins, biomass growth causes shading of the upper water layer resulting in a reduction of photodegradation processes. Moreover, clogging, matrix saturation, and hydraulic conductivity losses may be detrimental for removal mechanisms in (H- and V-) SSF beds, as found by Matamoros et al. [39] for MDHJ, HHCB, and AHTN. An H-SSF bed could work closer to as a SF basin if surface and volume clogging phenomena occur. In fact they may lead to a flooding of the bed, with a higher oxygen transfer from the air and a lower HRT, as remarked by Matamoros et al. [35] and Reyes-Contreras et al. [42]. Removal efficiencies are then affected by these phenomena and organic matter could be mainly removed by aerobic reactions.

6.5 Biomass Acclimatization

Some long experimental investigations on surfactant removal in H-SSF beds highlighted that microbial flora requires a period of time to adapt itself to the type of pollutant load. Sacco et al. [52] reported that in their pilot, H-SSF bed removal of Triton X 100 changed along the 12-month period of observation. A development of new bacteria strains appeared and others increased during the dosage of the mixture, suggesting that these bacteria were adapting to the presence of these surfactants and/or they used them as a source of nourishment.

6.6 Redox Conditions

The three types of CW differ not only in the main flow direction but also in their operational conditions. Avila et al. [21] reported the values of redox potential

measured in the three types of systems, confirming aerobic conditions in V-SSF beds and SF basins and anaerobic conditions in H-SSF beds. Hijosa-Valsero et al. [37] analyzed the seasonality variation of redox potential in H-SSF beds, and they found that in summer time redox may increase up to positive values, promoting the development of different microbial communities.

Redox potential within a system may vary during the life of the wetland, due to its aging and clogging phenomena and changes in the influent quality. It mostly influences the removal of PCPs as well as surfactants. Avila et al. [32], Navarro et al. [33], and Conkle et al. [57] remarked that higher redox values promote PCP removal with the exceptions of BHT and AP.

Huang et al. [44] and Sima et al. [45] agreed that anionic and nonionic surfactants can be degraded in a wide range of redox values. Referring to LAS, more oxidized conditions improve their removal, and in deeper SSF beds where the environment is characterized by sulfate-reducing methanogenic conditions, low LAS removals were observed [44].

In addition, redox conditions can also influence the degradation of PCPs bioaccumulated in sediments or gravel of a wetland. This influence was investigated by Conkle et al. [57] who found that DEET is appreciably degraded under aerobic sediments, while in anaerobic conditions this does not occur.

6.7 Removal Processes Along the System

Most of the removal occurs in the first meters of the system for many of the investigated compounds. The fragrances AHTN and HHCB mainly accumulated in the first section of the H-SSF bed investigated by Matamoros and Bayona [39] and a large fraction of nonionic surfactants (about 80%) and anionic ones (about 50%) degrade in the first meter of the H-SSF beds investigated by Sima and Holcová [51] and Sima et al. [53], respectively. The same profile was confirmed by the investigation of Zarate et al. [19] into the accumulation of triclosan and triclocarban on the sediments of a polishing SF basin.

Avila et al. [31] and Hijosa-Valsero et al. [37] investigated the removal of AHTN, HHCB, MDHJ, and bisphenol A in secondary multistage CWs consisting of two H-SSF beds in series.

They found that for AHTN, HHCB, and bisphenol A, most removal occurred in the first stage and near the inlet zone, probably due to the detention of most of the particulate matter with which all these compounds are associated. A different removal pattern was found for MDHJ as its main removal mechanism is biodegradation favored at high temperature.

6.8 H-SSF Bed Depth

Shallow H-SSF beds (0.3 m water depth) were found to be more efficient than deeper ones (0.5 m) in the removal of LAS due to differently oxidized conditions occurring on the two kinds of wetlands [44]. In the first, in fact, denitrification, sulfate reduction and methanogenesis occurred simultaneously, while in the second, the prevailing reactions were sulfate reduction and methanogenesis and denitrification is insignificant.

The effect of the depth of V-SSF beds on the removal of anionic surfactants was investigated by Kadewa et al. [49]. They found that in an *acclimatized* and vegetated 0.7 m-deep V-SSF bed, anionic surfactant removal was in the range of 76–85%, while in a cascade of three still-ripening and unplanted 0.2 m V-SSF beds, it was less, between 37 and 74%. These findings could be attributed to a more developed microbial community in the ripe higher V-SSF bed which could guarantee a complete biodegradation of the different surfactants, while in the cascade of shallow V-SSF beds, the more oxidized conditions promoted the alkyl chain shortening of the surfactants, but not their complete degradation.

Sima et al. [53] found that the removal of anionic surfactants in an H-SSF bed was faster in the upper 10 cm. At lower depths, anaerobic degradation of LAS occurs where sulfates were shown to be reduced. On the contrary, studies of nonionic surfactants showed that they can be effectively degraded at both depths, independent of aerobic or anaerobic conditions [51].

6.9 Filling Material in SSF Beds

Lower effluent concentrations were detected for LAS and SPCs in beds filled with finer gravel ($D_{60} = 3.5$ mm, $C_u = 1.7$) than in those containing coarse gravel ($D_{60} = 10$ mm, $C_u = 1.6$) [44].

6.10 Seasonality and Effect of Temperature

A seasonal variation was found for the removal efficiency of many compounds, but not for their occurrence. As a rule of thumb, removal efficiencies for dissolved-phase compounds are greatly influenced by temperature as biodegradation is their main removal mechanism, while depletion referring to compounds associated with particulate matter does not exhibit such a pronounced temperature variation since their removals are mainly due to physical mechanisms (sedimentation and adsorption).

For compounds such as MDHJ and oxybenzone, whose main removal mechanism is biodegradation, low temperatures directly reduce the physiological

activities of the microorganisms themselves, resulting in a slowing down of the degradation reactions that may occur [27, 42].

In H-SSF beds, summer removals were generally found to be very high (often greater than 80%) for HHCB, AHTN, and MDHJ, with a few exceptions related to unplanted H-SSF beds, where HHCB and AHTN were not removed at all, while MDHJ had variable removal efficiencies. The first two fragrances present a similar removal pattern as they have a great sorption potential due to their lipophilic properties, while MDHJ is mainly removed by biodegradation. The seasonality variation found in the removal of the investigated hydrophobic compounds can be explained by the release of these compounds in winter and accumulation in summer, when biofilm and plants are more active [37].

In SF basins, HHCB and AHTN exhibited the same (high) removal efficiencies in both seasons at around 85–90% [40].

For photodegradable compounds such as triclosan and cashmeran, lower values in their removal observed in SF basins in winter could also be due to lower levels of sunlight exposure [27].

6.11 Vegetation

Vegetation can insulate wetland surfaces and thus contribute to maintaining microbial activity; roots provide a surface for the development of microbial colonies and contribute to the creation of aerobic microenvironments within the bed, thus favoring biodegradation. Moreover, vegetation can contribute to the removal of micropollutants by plant uptake.

Higher removal levels of anionic surfactants were observed in planted and acclimatized V-SSF beds with respect to unplanted and non-acclimatized ones [49]. In SF basins covered by *Lemna minor*, the removal efficiencies of the photodegradable triclosan were found to be lower than in control unplanted SF wetlands [24].

Young CWs are more efficient when they are planted. When CWs get older, the efficiency of planted and unplanted systems is similar as many disturbing factors may occur (clogging, shading) causing a performance decrease in the planted CWs.

Reinhold et al. [58] found in their flask scale plants that duckweed can contribute to removing triclosan, while it is not efficient with respect to DEET. Zarate et al. [19] investigated bioconcentration patterns of triclosan and triclocarban among three different macrophytes (*Typha latifolia*, *Pontederia cordata*, *Sagittaria graminea*) and their concentrations in different sites of the investigated surface flow basin. They found that concentrations of the two analytes were higher in roots rather than in shoots and tended to decrease from the inflow to the outflow.

To complete this brief discussion, attempts to correlate observed removal efficiencies of the different PCPs with their $\mathrm{Log}K_{\mathrm{ow}}$, $\mathrm{Log}D_{\mathrm{ow}}$, and $\mathrm{p}K_{\mathrm{a}}$ were carried by different authors (among them [28, 30]) but unfortunately no significant correlations were found.

Referring to surfactants, Sima and Holcová [51] found similar removal efficiencies for BOD_5 and nonionic surfactants.

7 Conclusions

It is well known that CWs, if well designed, exhibit a good ability in removing common conventional pollutants. Their potential in removing emerging organic contaminants is, however, still under discussion. This chapter focuses on the ability of CWs in removing common PCPs, substances frequently used worldwide and with increasing levels of consumption. They are quite complex molecules, with different chemical and physical properties and are, in many cases, quite persistent to biodegradation.

On the basis of the collated data, in general a removal was observed for each reviewed compound with very few exceptions, mainly referring to groups of surfactants, such as SPCs, as their formation due to LAS degradation is faster than their removal.

The highest removal levels were found for the fragrances in all three treatment steps. These compounds were the most studied, while for many others there is still little data, and further investigations of their removal in the different types of CWs are necessary.

The coexistence of different microenvironments within each type of CW which guarantee different redox conditions and the simultaneous occurrence of biological, physical, and chemical removal mechanisms make CWs a potentially adequate system for the removal of PCPs, with limited operational costs.

The main weaknesses are the wide footprint of these systems – resulting in high investment costs – and the extremely long time required to reactivate the processes within them in the case of malfunctions which are mainly due to clogging phenomena and an influent which accidentally becomes highly polluted. These weaknesses lead to long rest periods (in the first case) or expensive maintenance interventions (in the second).

However, CWs, due to their buffer capacity, could represent a barrier to reducing the spread of these types of PCPs into the aquatic environment.

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Removal of Personal Care Products Through Ferrate(VI) Oxidation Treatment

Bin Yang and Guang-Guo Ying

Abstract Personal care products (PCPs) have been widely used in daily life and continually introduced to the aquatic environment, posing potential risks to the aquatic ecosystem and human health. Due to incomplete removal of PCPs in traditional wastewater and water treatment systems, advanced oxidation technologies can be applied to increase the removal efficiency of those PCPs. As a powerful oxidant, ferrate(VI) (Fe(VI)) has a great potential for removal of PCPs during water treatment. In this chapter, we firstly introduced the aqueous chemistry of Fe(VI); then critically reviewed the reaction mechanisms of Fe(VI) with typical PCPs by using removal rates, reaction kinetics, linear free-energy relationships, products identification, and toxicity evaluation; and finally discussed the removal of PCPs during water treatment by Fe(VI). Published phenolic and nitrogen-containing PCPs can be completely removed by Fe(VI) oxidation treatment except triclocarban. The reactions between the PCPs and Fe(VI) follows second-order reaction kinetics with the apparent second-order rate constants (k_{app}) ranging from 7 to 1,111 M^{-1} s^{-1} at pH 7.0. The reactivity of Fe(VI) species with the PCPs has the following decreasing order of $H_2FeO_4 > HFeO_4^- > FeO_4^{2-}$, through the electrophilic oxidation mechanism. The phenolic PCPs can be transformed by Fe (VI) oxidation based on phenoxyl radical reaction, degradation, and coupling reaction. More importantly, the oxidation of each phenolic PCPs by Fe(VI) leads to the loss of its corresponding toxicity. The coexisting constituents present in source water have significant effects on PCP removal during Fe(VI) oxidation treatment. In practical applications, in situ production of Fe(VI) solution appears to be a promising technology for removal of PCPs during pilot and full-scale water treatment.

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M.S. Díaz-Cruz and D. Barceló (eds.), *Personal Care Products in the Aquatic Environment*, Hdb Env Chem (2015) 36: 355–374, DOI 10.1007/698_2014_285,

Keywords Coexisting constituents, Ferrate(VI), In situ, Oxidation, Personal care products, Reaction mechanisms

Contents

Abbreviations

5CBT	5-Chloro-1H-benzotriazole
5MBT	5-Methyl-1H-benzotriazole
ABTS	2,2′-Azinobis-(3-ethylbenzothiazoline-6-sulfonate)
AHTN	7-Acetyl-1,1,3,4,4,6-hexamethyl-tetralin
BP-3	Benzophenone-3
BT	1H-benzotriazole
BTs	Benzotriazoles
DMBT	5,6-Dimethyl-1H-benzotriazole hydrate
DOC	Dissolved organic carbon
Fe(III)	Ferric hydroxide
Fe(V)	Ferrate(V)
Fe(VI)	Ferrate(VI)
GC–MS	Gas chromatography–mass spectrometry
HA	Humic acid
HBT	1-Hydroxybenzotriazole
HHCB	1,3,4,6,7,8-Hexahydro-4,6,6,7,8,8-hexamethylcyclopenta-γ-2-benzopyrane
I^-	Iodide
k_{app}	Apparent second-order rate constants
PCPs	Personal care products
pK_a	Acid dissociation constants
RRLC–MS/MS	Rapid resolution liquid chromatography–tandem mass spectrometry
$t_{1/2}$	Half-life
TCC	Triclocarban
TCS	Triclosan

1 Introduction

Personal care products (PCPs), including moisturizers, lipsticks, and fragrances to sunscreens, soaps, and anticavity toothpastes, make billions of people around the world to live a better and healthier lifestyle. These products are commonly used in large quantities, and after use, they are discharged directly or indirectly into receiving aquatic environments. Due to limited capacity for removal of these chemicals, environmental contamination by these chemicals has been reported [1–3]. Some of them were found to be environmentally persistent, bioactive, and bioaccumulative [4]. Moreover, some chemicals exhibited endocrine disruptive effects in vitro and in vivo and they have the potential to interfere with natural hormones, causing problems in the nervous and reproductive systems [5]. PCPs have received an increasing attention in recent years and they have been regarded as emerging contaminants. Therefore, it is necessary to remove PCPs from traditional water treatment effluents by using advanced oxidation technology.

Ferrate(VI) (Fe(VI)) is a powerful oxidant and its decomposition product is nontoxic ferric hydroxide (Fe(III)). Thus, Fe(VI) is regarded as an environmentally friendly oxidant in water treatment process [6–8]. Fe(VI) has been widely used to remove emerging organic contaminants [9–12], heavy metals [13, 14], and pathogens [15–18] during water treatment processes. Fe(VI) selectively reacts with electron-rich organic moieties of emerging organic contaminants, such as phenols, anilines, amines, and olefins through electrophilic oxidation mechanism [9, 10, 12, 19, 20]. The corresponding apparent second-order reaction rate constants range from >1 to 10^5 M^{-1} s^{-1} in aqueous solution [9, 12]. Besides, the coexisting constituents present in source water are also responsible for a rapid Fe (VI) consumption, which determine its ability to remove emerging organic contaminants.

This chapter aims to firstly introduce the aqueous chemistry of Fe(VI), then assess the potential for removal of typical PCPs during Fe(VI) treatment by chemical reaction kinetics, propose the reaction pathway of phenolic PCPs by Fe (VI) oxidation based on products identification, evaluate the safety of above treatment processes by toxicity tests, and finally clarify the impact of coexisting constituents in the source water on the removal processes. This chapter will provide a scientific basis for the removal of PCPs through ferrate(VI) oxidation treatment.

2 Aqueous Chemistry of Fe(VI)

Ferrate(VI) (K_2FeO_4, Fe(VI)) is a black-purple crystalline compound in which iron is in the +6 oxidation state. There are three main approaches for preparation of Fe (VI): wet oxidation, dry thermal, and electrochemical synthesis [6–8]. The concentration of Fe(VI) in aqueous solution can be determined by volumetric (chromite and arsenite), electrochemical (cyclic voltammetry and potentiometry), as well as

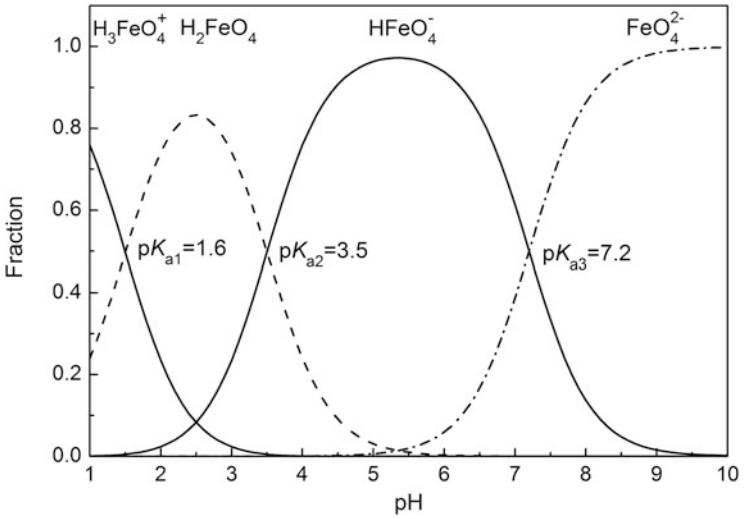

Fig. 1 Speciation of Fe(VI) in aqueous solution

spectrophotometric methods (FTIR, Mössbauer, UV–vis (direct 510 nm, iodide (I^-); 2,2′-azinobis-(3-ethylbenzothiazoline-6-sulfonate) (ABTS)), and fluorescence) [21]. For water treatment research, direct 510 nm ($\varepsilon_{510nm} = 1{,}150\ M^{-1}\ cm^{-1}$) and ABTS methods ($\varepsilon_{415nm} = 34{,}000\ M^{-1}\ cm^{-1}$) are the most suitable techniques for studying the reaction kinetics of Fe(VI) in aqueous solution [22–25]. Besides, phosphate buffer has been widely used as the reaction solution since not only it reacts very slowly with Fe(VI) but also it can prevent the precipitation of generated ferric ion from Fe(VI) decomposition which causes interference for optical monitoring of Fe(VI) concentration [8].

The rates of decay and changes in spectral features of Fe(VI) solution as a function of pH can be utilized to estimate the values of the acid dissociation constants (pK_a) [26]. Three pK_a values of Fe(VI) in aqueous solution of 1.6, 3.5, and 7.2 suggest the presence of four Fe(VI) species in the entire pH range, such as $H_3FeO_4^+$, H_2FeO_4, $HFeO_4^-$, and FeO_4^{2-} (Fig. 1). Therefore, $HFeO_4^-$ and FeO_4^{2-} are the predominant species in neutral and alkaline pH solution. Fe(VI) ion (FeO_4^{2-}) has tetrahedral structure, with four equivalent oxygen atoms covalently bonded to central iron atom [27].

Fe(VI) is the most powerful oxidant at acidic pH condition with the redox potential of 2.20 V (Table 1), but it becomes a relatively mild oxidant (0.57 V) at alkaline pH condition [6, 8, 20]. Due to its strong oxidizing property, Fe (VI) undergoes a rapid decomposition according to Eq. (1) in the presence of water, leading to the formation of molecular oxygen and a nontoxic by-product ferric hydroxide (Fe(III)), which makes Fe(VI) an environmentally friendly oxidant for water treatment. Additionally, the generated Fe(III) can act as an effective coagulant/precipitant during water treatment:

Table 1 Redox potential for the oxidants used in water treatment

Disinfectant/oxidant	Reaction	E^0(V)
Ferrate(VI)	$FeO_4^{2-} + 8H^+ + 3e^- \Leftrightarrow Fe^{3+} + 4H_2O$	2.20
	$FeO_4^{2-} + 4H_2O + 3e^- \Leftrightarrow Fe(OH)_3 + 5OH^-$	0.70
Chlorine	$Cl_2(g) + 2e^- \Leftrightarrow 2Cl^-$	1.36
	$ClO^- + H_2O + 2e^- \Leftrightarrow Cl^- + 2OH^-$	0.84
Hypochlorite	$HClO + H^+ + 2e^- \Leftrightarrow Cl^- + H_2O$	1.48
	$ClO^- + H_2O + 2e^- \Leftrightarrow Cl^- + 2OH^-$	0.84
Chlorine dioxide	$ClO_2(aq) + e^- \Leftrightarrow ClO_2^-$	0.95
Perchlorate	$ClO_4^- + 8H^+ + 8e^- \Leftrightarrow Cl^- + 4H_2O$	1.39
Ozone	$O_3 + 2H^+ + 2e^- \Leftrightarrow O_2 + H_2O$	2.08
	$O_3 + H_2O + 2e^- \Leftrightarrow O_2 + 2OH^-$	1.24
Hydrogen peroxide	$H_2O_2 + 2H^+ + 2e^- \Leftrightarrow 2H_2O$	1.78
	$H_2O_2 + 2e^- \Leftrightarrow 2OH^-$	0.88
Dissolved oxygen	$O_2 + 4H^+ + 4e^- \Leftrightarrow 2H_2O$	1.23
Permanganate	$MnO_4^- + 4H^+ + 3e^- \Leftrightarrow MnO_2 + 2H_2O$	1.68
	$MnO_4^- + 8H^+ + 5e^- \Leftrightarrow Mn^{2+} + 4H_2O$	1.51
	$MnO_4^- + 2H_2O + 3e^- \Leftrightarrow MnO_2 + 4OH^-$	0.59

$$4K_2FeO_4 + 10H_2O \rightarrow 4Fe(OH)_3 + 3O_2 \uparrow + 8KOH. \quad (1)$$

The decomposition of Fe(VI) in Eq. (1) is strongly dependent on the pH values of reaction solution, initial Fe(VI) concentration, temperature, and coexisting ions. The decomposition of Fe(VI) in solution follows the second-order kinetics with respect to its concentration. The decomposition rate of Fe(VI) dramatically decreases with the increasing pH, ranging from 10^5 M^{-1} s^{-1} (pH 1) to <1 M^{-1} s^{-1} (pH 8.2), indicating Fe(VI) has higher oxidation power at acidic pH conditions [8, 13]. The lowest rate of Fe(VI) decomposition occurs at pH 9.4–9.7. Besides, diluted Fe(VI) solutions are reported to be more stable than the concentrated ones. Increasing temperature would decrease the concentration of Fe(VI) in solution. The addition of KCl or KNO_3 as an impurity in solution accelerated the initial decomposition of the Fe(VI) but had the effect of stabilizing a small quantity of Fe(VI). NaCl and FeOOH as impurities caused complete decomposition of Fe (VI) in solution at a rapid rate [28].

3 Oxidation of Personal Care Products by Ferrate(VI)

3.1 Removal Rates

Removal of some PCPs by Fe(VI) has been investigated in the laboratory [29–31]. Figure 2 demonstrates the removal of eight typical PCPs by Fe(VI) oxidation individually under different molar ratios in buffered Milli-Q water at pH 7.0 or

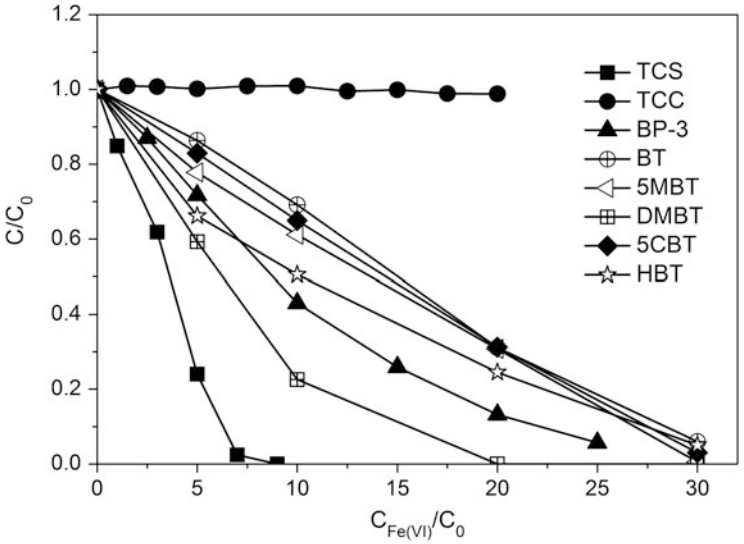

Fig. 2 Removal of typical PCPs by Fe(VI) oxidation in 10 mM phosphate buffer solution. Experimental conditions: $[TCS/TCC]_0 = 2$ μM, $[BP\text{-}3]_0 = 1$ μM, $[BTs]_0 = 10$ μM, $V = 25$ mL, $T = 24 \pm 1°C$, and contact time 3 h. The reaction of TCS and TCC was performed in pH 7.0 solution, and BP-3 and BTs in pH 8.0 solution

8.0 and $24 \pm 1°C$. The eight studied PCPs include antimicrobial triclosan (TCS) and triclocarban (TCC), UV filter benzophenone-3 (BP-3), and anticorrosion agents benzotriazoles (BTs; BT, 1H-benzotriazole; 5MBT, 5-methyl-1H-benzotriazole; DMBT, 5,6-dimethyl-1H-benzotriazole hydrate; 5CBT, 5-chloro-1H-benzotriazole; HBT, 1-hydroxybenzotriazole). With the dosage of Fe (VI) increasing, the concentration of each PCPs gradually decreased. However, TCC did not react with Fe(VI) at pH 7.0. When the molar ratio of Fe(VI) with PCPs increasing up to 30:1, the removal rate of each PCPs reached about >95% except TCC. Besides, the dosed amounts of Fe(VI) for complete removal of PCPs had the following increasing order: TCS < BP-3 < BTs << TCC, which illustrates the easier oxidation of TCS and BP-3 molecules than BTs and TCC by Fe(VI). Thus, the selected phenolic PCPs have higher reactivity with Fe(VI) than those nitrogen-containing PCPs.

Since Fe(VI) has been known to react with electron-rich organic moieties, such as phenols, anilines, amines, olefins, and organosulfur [9, 10, 12, 20], the reactivity of other categories of PCPs with Fe(VI) can be tentatively deduced as follows. Preservatives p-hydroxybenzoic esters (parabens) with the phenol moieties may be easily removed by Fe(VI) oxidation, but synthetic polycyclic musks (AHTN (7-acetyl-1,1,3,4,4,6-hexamethyl-tetralin) and HHCB (1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethylcyclopenta-γ-2-benzopyrane)) may not react with Fe(VI). The detailed removal of above PCPs by Fe(VI) oxidation still needs to be further confirmed.

3.2 Reaction Kinetics

Second-order reaction rate equation (Eq. (2)) is commonly used to describe the Fe (VI) oxidation of PCPs in phosphate buffer solutions. Kinetic experiments are conducted under pseudo-first-order conditions with either Fe(VI) or the PCPs in excess. For those with Fe(VI) in excess to PCPs, the decrease in concentrations for Fe(VI) and PCPs is measured as a function of the reaction time. The apparent second-order rate constants (k_{app}) are calculated by plotting the natural logarithm of the PCP concentrations with the Fe(VI) exposure (Fe(VI) concentration integrated over time, $\int_0^t [\mathrm{Fe(VI)}]\mathrm{d}t$), as shown in Eq. (3). For those with PCPs in excess to Fe (VI), Eq. (2) can be rewritten as Eq. (4). The values of k_{app} are then determined from the variation in k' as a function of PCP concentrations. The obtained values of rate constants k_{app} for the reaction of Fe(VI) with PCPs as a function of pH (6.0–10.0) are presented in Fig. 3 and Table 2 [29–31]. The determined k_{app} values range from 7 M^{-1} s^{-1} (5CBT) to 1,111 M^{-1} s^{-1} (TCS) at pH 7.0 and 24 ± 1°C with the half-life ($t_{1/2}$) ranging from 1,917 s to 12 s at a Fe(VI) concentration of 10 mg L^{-1}. The k_{app} values of TCS and BP-3 reaction with Fe(VI) are greater than those of BTs, which is consistent with the results of removal rates. Besides, the k_{app} of the reaction decreased with increasing pH values (Fig. 3). These pH-dependent variations in k_{app} could be explained by species-specific reactions between Fe (VI) species ($HFeO_4^- \Leftrightarrow H^+ + FeO_4^{2-}$, $pK_{a,HFeO4} = 7.23$ [26]), and acid–base species of an ionizable PCP species ($PCPs \Leftrightarrow H^+ + PCPs^-$, $pK_{a,PCPs}$) by Eqs. (5)–(11):

$$-\mathrm{d}[\mathrm{PCPs}]/\mathrm{d}t = k_{app}[\mathrm{Fe(VI)}][\mathrm{PCPs}], \tag{2}$$

$$\ln\left([\mathrm{PCPs}]/[\mathrm{PCPs}]_0\right) = -k_{app}\int_0^t [\mathrm{Fe(VI)}]\mathrm{d}t, \tag{3}$$

$$-\mathrm{d}[\mathrm{Fe(VI)}]/\mathrm{d}t = k'[\mathrm{Fe(VI)}] \quad \text{where} \quad k' = k_{app}[\mathrm{PCPs}], \tag{4}$$

$$k_{app}[\mathrm{Fe(VI)}]_{tot}[\mathrm{PCPs}]_{tot} = \sum_{\substack{i=1,2,3 \\ j=1,2}} k_{ij}\alpha_i\beta_j[\mathrm{Fe(VI)}]_{tot}[\mathrm{PCPs}]_{tot}, \tag{5}$$

$$\alpha_1 = \left[H_2FeO_4\right]/\left[\mathrm{Fe(VI)}\right]_{tot} = [H^+]^2/T, \tag{6}$$

$$\alpha_2 = \left[HFeO_4^-\right]/\left[\mathrm{Fe(VI)}\right]_{tot} = [H^+]K_{a,H2FeO4}/T, \tag{7}$$

$$\alpha_3 = \left[FeO_4^{2-}\right]/\left[\mathrm{Fe(VI)}\right]_{tot} = K_{a,H2FeO4}K_{a,HFeO4-}/T, \tag{8}$$

$$T = [H^+]^2 + [H^+]K_{a,H2FeO4} + K_{a,H2FeO4}K_{a,HFeO4-}, \tag{9}$$

$$\beta_1 = [\mathrm{PCPs}]/[\mathrm{PCPs}]_{tot} = [H^+]/([H^+] + K_{a,PCPs}), \tag{10}$$

$$\beta_2 = [\mathrm{PCPs}^-]/[\mathrm{PCPs}]_{tot} = K_{a,PCPs}/([H^+] + K_{a,PCPs}), \tag{11}$$

where $[\mathrm{Fe(VI)}]_{tot} = [H_2FeO_4] + [HFeO_4^-] + [FeO_4^{2-}]$, $[\mathrm{PCPs}]_{tot} = [\mathrm{PCPs}] + [\mathrm{PCPs}^-]$. α_i and β_j represent the respective species distribution coefficients for

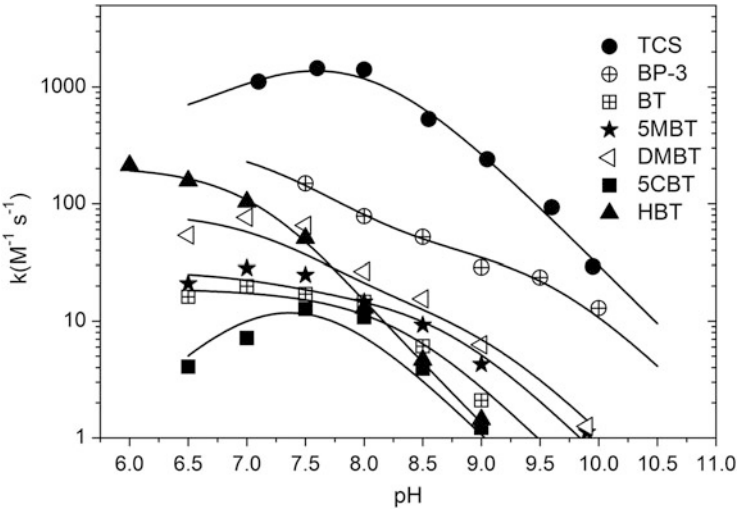

Fig. 3 Apparent second-order rate constants and associated model simulation for the reactions of PCPs with Fe(VI) as a function of pH (6.0–10.0) at the room temperature ($24 \pm 1°C$)

Fe(VI) and PCPs; *i* and *j* represent each of the three Fe(VI) species and PCP species, respectively; and k_{ij} represents the species-specific second-order rate constant for the reaction between the Fe(VI) species *i* with the PCP species *j*. Consequently, the k_{ij} is calculated from least-squares nonlinear regressions of the experimental k_{app} data by using SigmaPlot 10.0 (Systat Software Inc.). Table 2 summarizes the determined k_{12}, k_{21}, and k_{22} values for each PCPs. The k_{22} was magnitude higher than k_{21} because the deprotonated species are better electron donors. Thus, the reaction between $HFeO_4^-$ and the dissociated PCPs controls the overall reaction of Fe(VI) with PCPs. Besides, the k_{12} is 10^4 times higher than k_{22} for HBT, which indicates H_2FeO_4 has a higher reactivity than $HFeO_4^-$. However, reactions of the deprotonated Fe(VI) species (FeO_4^{2-}) with PCP species have a low contribution to the overall reactivity. Moreover, density functional theory (DFT) calculations have shown that the protonated species of Fe(VI) has a larger spin density on the oxo ligands than the deprotonated species of Fe(VI), which increases the oxidation ability of protonated Fe(VI) [32]. Above results demonstrate that the order of oxidizing power of Fe(VI) species for PCPs in aqueous solution is following $H_2FeO_4 > HFeO_4^- > FeO_4^{2-}$.

3.3 Linear Free-Energy Relationships

Linear free-energy relationships have been widely used in oxidation/disinfection reaction for the understanding of the reaction mechanisms and prediction of reaction rates [12, 22, 23, 25, 33, 34]. The Hammett-type correlations between

Table 2 Species-specific second-order rate constants for the reactions of Fe(VI) with selected PCPs

Chemical name	pK_a	$H_2FeO_4 + X^-$ (k_{12}, $M^{-1}\ s^{-1}$)	$HFeO_4^- + XH$ (k_{21}, $M^{-1}\ s^{-1}$)	$HFeO_4^- + X^-$ (k_{22}, $M^{-1}\ s^{-1}$)	k_{app} at pH 7.0 ($M^{-1}\ s^{-1}$)	$t_{1/2}$ (s)[a]
Triclosan (TCS)	8.1		$4.1\ (\pm 3.5) \times 10^2$	$1.8\ (\pm 0.1) \times 10^4$	1,111	12
Benzophenone-3 (BP-3)	9.57		$3.4\ (\pm 0.5) \times 10^2$	$8.5\ (\pm 0.7) \times 10^3$	228	60
1H-benzotriazole (BT)	8.37		$1.9\ (\pm 0.4) \times 10^1$	$1.9\ (\pm 0.2) \times 10^2$	20	690
5-Methyl-1H-benzotriazole (5MBT)	8.5		$2.7\ (\pm 0.5) \times 10^1$	$4.3\ (\pm 0.5) \times 10^2$	28	486
5,6-Dimethyl-1H-benzotriazole (DMBT)	8.98		$8.5\ (\pm 1.7) \times 10^1$	$7.3\ (\pm 1.4) \times 10^2$	77	180
5-Chloro-1H-benzotriazole (5CBT)	7.5		$2.0\ (\pm 0.2) \times 10^{\circ}$	$6.6\ (\pm 0.6) \times 10^1$	7	1917
1-Hydroxybenzotriazole (HBT)	7.39	$1.6\ (\pm 0.1) \times 10^6$		$7.7\ (\pm 0.6) \times 10^1$	104	132

[a]Estimated by assuming pseudo-first-order conditions with a Fe(VI) excess ([Fe(VI)] = 10 mg L^{-1}, pH 7.0)

the k_{ij} of the above PCP reaction with Fe(VI) and free-energy descriptors (σ_p^+ or σ_p) have been successfully established according to the relationship $\log(k_{ij}) = y_0 + \rho\sigma$ as shown in Eqs. (12)–(15) [30]. A negative Hammett slope (ρ) illustrated the electrophilic oxidation mechanism for Fe(VI) reaction with PCPs. The Hammett-type relationships of substituted phenols for TCS (Eqs. (12) and (13)) verify the dependence of TCS and Fe(VI) reaction kinetics on phenol substituent effects, illustrating the Fe(VI) reacts initially with TCS by electrophilic attack at the latter's phenol moiety. Similarly, 1,2,3-triazole moiety of BT can be initially electrophilic attacked by Fe(VI) (Eqs. (14) and (15)), but the initial attack site of HBT may be at the N–OH bond by Fe(VI).

Substituted phenols for TCS:

$$\log(k_{21}) = 2.30(\pm 0.08) - 2.20(\pm 0.26)\sigma_p^+ \quad R^2 = 0.91,\ n = 8, \tag{12}$$

$$\log(k_{22}) = 4.42(\pm 0.04) - 3.13(\pm 0.13)\sigma_p^+ \quad R^2 = 0.99,\ n = 8. \tag{13}$$

BTs:

$$\log(k_{21}) = 1.00(\pm 0.08) - 2.86(\pm 0.38)\sigma_p \quad R^2 = 0.95,\ n = 4, \tag{14}$$

$$\log(k_{22}) = 2.27(\pm 0.02) - 1.94(\pm 0.10)\sigma_p \quad R^2 = 0.99,\ n = 4. \tag{15}$$

3.4 Products Identification

During Fe(VI) oxidation treatment, numerous transformation products may be formed and persist even after the parent compound has been fully removed [35–39]. Thus, the oxidation products of some PCPs (i.e., TCS, BP-3, and BTs) reaction with Fe(VI) were tentatively identified by gas chromatography–mass spectrometry (GC–MS) and rapid resolution liquid chromatography–tandem mass spectrometry (RRLC–MS/MS) techniques [29–31]. For the reaction between Fe(VI) and TCS, four products of chlorophenol, 2-chlorobenzoquinone, 2,4-dichlorophenol, and 2-chloro-5-(2,4-dichlorophenoxy)benzene-1,4-diol were identified in the reaction solution by GC–MS and RRLC–MS/MS. In addition, the dimerization of some TCS degradation products, such as 5-chloro-3-(chlorohydroquinone)phenol, 4,6-dichloro-2-(2,4-dichlorophenoxy)phenol, and 3-chloro-2-(2,3-dichlorophenoxy)-6-(2,4-dichlorophenoxy)phenol, was also identified by RRLC–MS/MS. But, only two reaction products of 4-methoxybenzophenone and 4-methoxybenzoyl cation were found during Fe(VI) degradation of BP-3. However, no obvious transformation products were found in the Fe(VI) reaction with BTs.

According to the kinetic information, products identification, and the mechanism of Fe(VI) reaction with phenols [36, 40, 41], a plausible reaction scheme for Fe (VI) oxidation of phenolic PCPs (TCS and BP-3) is proposed in Fig. 4. Initially, the reaction mixture of Fe(VI) with phenol moiety of TCS and BP-3 may proceed through an associative type of mechanism and involve hydrogen bond formation in the activated complex accompanied by intermolecular electron transfer. Consequently,

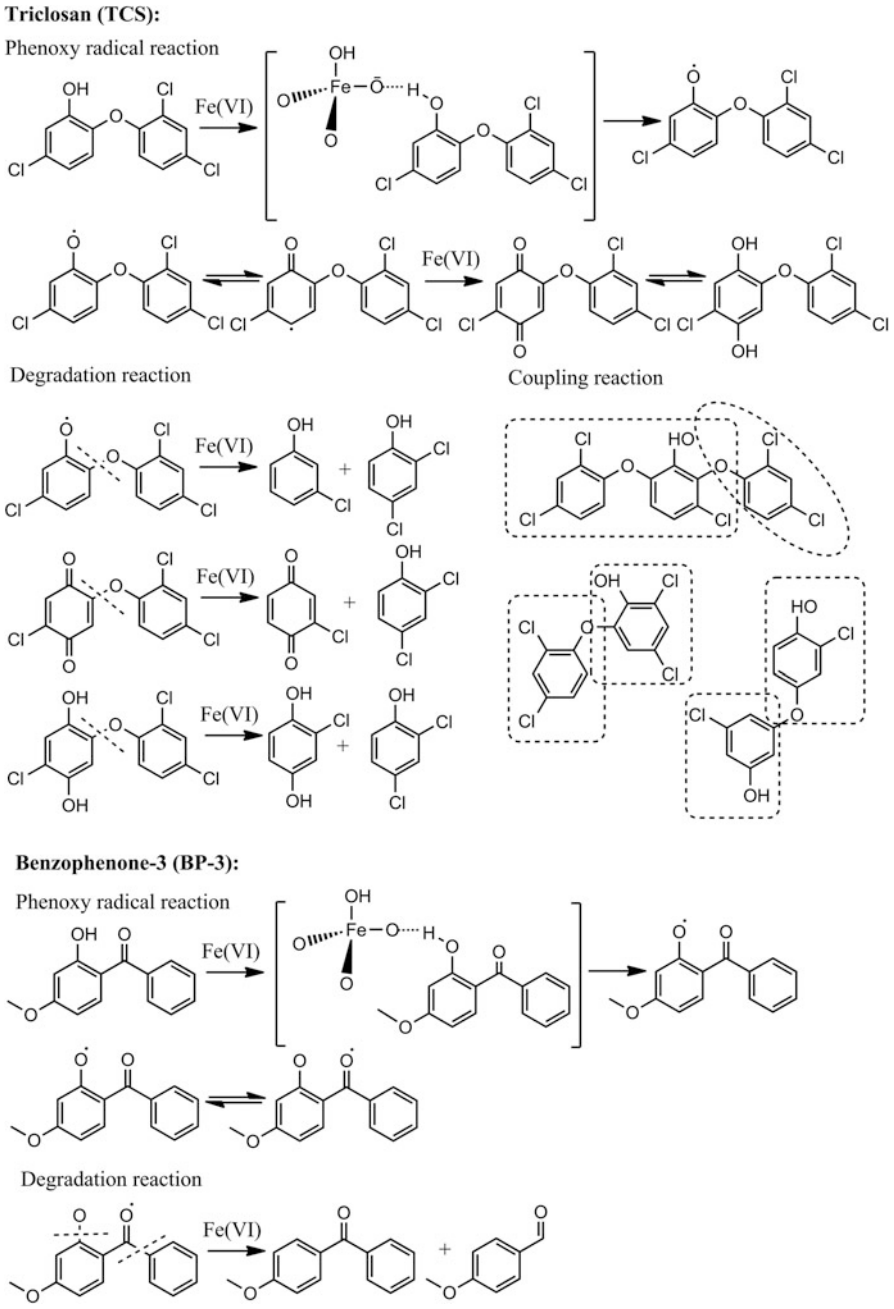

Fig. 4 Proposed reaction schemes for oxidation of TCS and BP-3 by Fe(VI)

Fe(VI) oxidizes the phenol moiety by one electron transfer generating corresponding phenoxyl radical and Fe(V) as the first step. For TCS, the phenoxyl radical transferred to the para-position of TCS molecule and reacts with ferrates (Fe(VI) and Fe(V)) generating 2-chloro-5-(2,4-dichlodichlorophenoxy)-[1,4] benzoquinone through two-electron oxidation. It can be converted into 2-chloro-5-(2,4-dichlorophenoxy) benzene-1,4-diol. Fe(VI) then goes on to break C–O bond leading to the formation of chlorophenol, 2,4-dichlorophenol, chlorocatechol, and 2-chlorobenzoquinone. Coupling reaction may also occur during Fe(VI) oxidation of TCS. This is especially likely given the large excess of phenol in the reaction mixture. Phenoxyl radical of 2,4-dichlorophenol reacted with another triclosan and 2,4-dichlorophenol forming products 3-chloro-2-(2,3-dichlorophenoxy)-6-(2,4-dichlorophenoxy) and 4,6-dichloro-2-(2,4-dichlorophenoxy)phenol. Phenoxyl radical of 2-chlorocatechol and m-chlorophenol produced 5-chloro-3-(chlorohydroquinone)phenol. For BP-3, the activated electron in phenoxyl radical could be transferred to the oxygen atom of phenyl methanone moiety. Ferrates (Fe(VI) or Fe(V)) then break C–O bond of phenol or eliminate benzene of BP-3 leading to the formation of 4-methoxybenzophenone and 4-methoxybenzoyl cation. But, coupling reaction of BP-3 products has not been found in the reaction solutions. Overall, transformation products could undergo further oxidation reactions with Fe(VI), yielding low molecular weight organic products.

3.5 Toxicity Evaluation

The Fe(VI) oxidation process will undoubtedly render the transformation products a different biological binding property [35, 37, 42]. For example, the antibacterial activity of the TCS molecule is derived primarily from its phenol ring, via van der Waals and hydrogen-bonding interactions with the bacterial enoyl–acyl carrier protein reductase enzyme [43]. Thus, oxidation of the TCS molecule by Fe (VI) leads to the breakage of C–O bond or phenol ring changing, which is considered to reduce or eliminate its toxicity. Using algae growth inhibition tests of TCS and its products to *Pseudokirchneriella subcapitata*, Yang et al. [29] demonstrated that the dose–response relationships of the Fe(VI) treated TCS samples and TCS standards are almost the same, indicating that the generated oxidation products of TCS did not exhibit any appreciable degree of inhibitory effect, only relative to TCS itself. Moreover, the Fe(VI) dosage used in this study did not appear to inhibit green algae growth, which reconfirms previous assumption that Fe(VI) can be an "environmentally friendly" oxidant for water treatment applications.

Similarly, the UV filter of BP-3 is an important representative hydroxylated benzophenone derivative which has potential endocrine-disrupting effects such as estrogenic and antiandrogenic activities [44–46]. However, the oxidation product of 4-methoxybenzophenone has been manifested to possess no estrogenic activity [47]. Thus, Fe(VI) oxidation treatment not only removes hydroxylated benzophenone derivatives in water but also produces by-products that are expected to have less endocrine-disrupting effects.

4 Removal of Personal Care Products During Water Treatment with Ferrate(VI)

4.1 Influence of Coexisting Constituents on PCP Removal

PCPs containing the electron-rich organic moieties mentioned above can be potentially removed during water treatment by Fe(VI) oxidation. Moreover, the coexisting constituents present in source water are also responsible for a rapid Fe (VI) consumption, which determine its ability to remove PCPs. The influence of coexisting constituents such as dissolved organic matter (humic acid (HA)), inorganic ions (Br^-, NH_4^+, and NO_3^-), metal cations (Cu^{2+}, Mn^{2+}, Fe^{3+}, and Fe^{2+}), or ionic strength (NaCl) on PCP removal during Fe(VI) treatment is discussed in the following with BP-3 as an example [31].

4.1.1 Dissolved Organic Matter

Humic substances are the principal component of dissolved organic matter in aquatic systems. HA can decrease the removal efficiency of BP-3 during Fe (VI) treatment [31]. When the spiked concentration of HA reached 15 mg L^{-1}, the removal efficiency of BP-3 reduced from 60% to 31% and 17% at pH 7.0 and 8.0, respectively. The significant consumption of Fe(VI) and the competition reaction with BP-3 by HA may be responsible for remarkably decreased removal efficiency. Besides, Lee and von Gunten [48] suggested that the competition can disappear rapidly after the electron-rich organic moieties present in effluent organic matter are consumed during Fe(VI) treatment.

4.1.2 Inorganic Ions

Selected Br^-, NH_4^+, and NO_3^- are important inorganic species in aquatic systems. The effect of Br^- on the Fe(VI) removal of BP-3 is related to the pH of the reaction solution [31]. When the reaction solution was at pH 7.0, Br^- significantly enhanced the removal efficiency of BP-3, from 58% to 84% at 100 μM of Br^-, but it showed no effect at pH 8.0. Besides, BP-3 removal is not affected by the presence of NH_4^+ and NO_3^-. This may be due to the low reactivity of Fe(VI) with NH_4^+ and NO_3^- [48, 49].

4.1.3 Metal Cations

The removal efficiency of BP-3 is slightly enhanced by the presence of Cu^{2+} [31]. At the Cu^{2+} concentration of 20 μM, the removal efficiency of BP-3 was increased from 60% to 83% and 79% at pH 7.0 and pH 8.0, respectively. However,

Mn^{2+} significantly decreases the removal efficiency of BP-3. This may be due to the reducing state of the manganese ion under the alkaline condition [50], which may accelerate the decomposition of Fe(VI). Besides, Fe^{3+} and Fe^{2+} have little effects on BP-3 removal.

4.1.4 Ionic Strength

NaCl is ordinarily used to adjust the ionic strength of aqueous solutions. NaCl only have a small effect on the removal efficiency of BP-3 during Fe(VI) treatment [31]. Even when the concentration of NaCl increased to 35 g L^{-1}, the removal efficiency of BP-3 decreased from 60% to 33% and 43% at pH 7.0 and 8.0, respectively. An explanation may be that the pH values of the reaction solution were decreased with the increasing NaCl which consumed more amount of Fe(VI), resulting in the decreased removal of BP-3.

The removal of BP-3 spiked in the natural water (groundwater, river water, and wastewater) during Fe(VI) treatment was also conducted in Fe(VI) excess to confirm the effects of coexisting constituents as shown in Fig. 5 [31]. With the increasing reaction times, the residual concentrations of BP-3 gradually decreased in all the natural water samples. Before complete removal of BP-3, the residual concentrations follow the decreasing order of wastewater > groundwater-1 > river water > groundwater-2, which is in accordance with the trends of dissolved organic

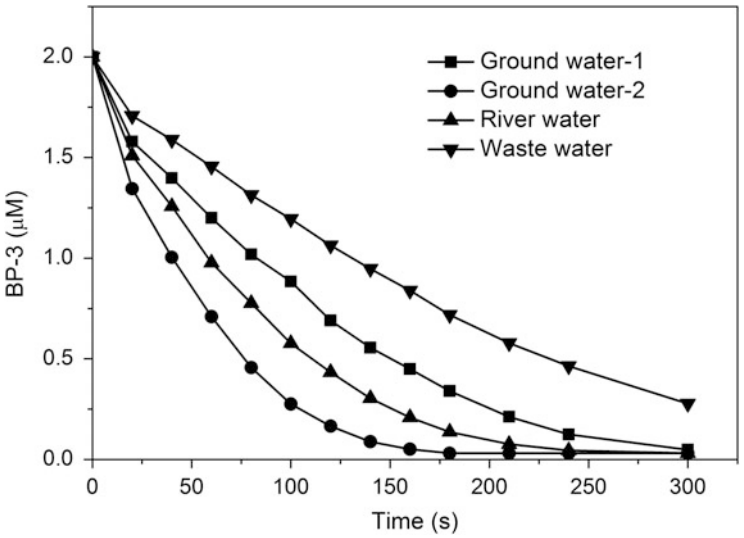

Fig. 5 Oxidation removal of BP-3 by Fe(VI) during the treatment of groundwater, river water, and wastewater. Experimental conditions: $[BP\text{-}3]_0 = 2$ μM, $[Fe(VI)]_0 = 100$ μM, pH 8.0 (20 mM borate buffer), $T = 24 \pm 1°C$

carbon (DOC) values: 2.51 mg L^{-1} (wastewater) > 0.78 mg L^{-1} (river water) > 0.24 mg L^{-1} (ground water). The residual concentrations of BP-3 in groundwater-1 are higher than in river water; this is because groundwater-1 has higher conductivity of 183.8 μS/cm than that of river water (49.4 μS/cm). So, the differences of water quality parameters caused mainly by the presence of coexisting constituents can significantly influence the removal efficiencies of BP-3 during Fe(VI) treatment. However, BP-3 can achieve complete removal in all natural water samples after 300 s (Fig. 5), indicating complete removal of BP-3 can be achieved by dosing more Fe(VI) in order to reduce the effects of coexisting constituents present in natural waters.

4.2 In Situ Production of Fe(VI) Solution for PCP Removal

The exploration of the use of Fe(VI) for removal of typical PCPs spiked in a natural water matrix has been well addressed in the laboratory studies. However, challenges still exist for the implementation of Fe(VI) oxidation treatment in a pilot or full-scale application for PCP removal during water treatment due to the instability of a Fe(VI) solution or high production cost of solid Fe(VI) products. Up to now, one promising approach is the in situ production of Fe(VI) in solution and its direct use in water treatment.

The Ferrator®, invented by Ferrate Treatment Technologies, LLC (FTT, Orlando, Florida), is a commercial reactor to synthesize liquid Fe(VI) in situ in bulk quantities for broad industrial use [51]. The Fe(VI) solution is synthesized based on wet oxidation method from commodity feedstocks such as alkali hydroxide, hypochlorite, and ferric chloride. Ferrator® reduces the production steps from 23 to 5 by eliminating the storage, handling, and transportation overheads required for a prepackaged product. Thus, the costs of production can be cut by 85% than traditional Fe(VI) deployment. But the disadvantage of this strategy is that addition of a sufficient amount of Fe(VI) solution leads to strong alkalization of the treated water to a pH of about 12; it has to utilize the ferric chloride, sulfuric acid, or CO_2 for adjusting the pH of treated water in actual applications.

Electrochemical Fe(VI) synthesis may be the most promising and economically competitive process on an industrial scale for the purpose of water treatment. Licht and Yu [24] proposed a schematic of online electrochemical Fe(VI) water purification system. Fe(VI) solution can be electrochemically prepared with a coiled iron wire anode immersed in 40 mL of 10 M NaOH at a constant oxidative current applied by Pine AFRDE5 bipotentiostat. The generated Fe(VI) was separated from the cathode by a Nafion 350 alkali-resistant, anion-impermeable membrane and then dosed into a continuous flow of effluent. This process also causes the strong alkalization of the treated water, but recent studies of pilot and full-scale trials demonstrated that with the use of highly concentrated NaOH, high current density, and anodic surface cleaning procedures, the yield efficiency of the in situ-generated Fe(VI) was up to 70%, and the concentration of the resulting Fe(VI) solution was as

high as 9 g L^{-1} [52–54]. Thus, very low volume dose of Fe(VI) solution is required for water treatment and the final pH value of treated water can be controlled below 9.

In summary, several attempts have been made to commercialize in situ Fe (VI) synthesis, but in situ production of Fe(VI) solution for removal of PCPs during water treatment needs to be further validated.

Conclusions

Fe(VI) has been demonstrated to have remarkable performance in the oxidative removal of PCPs in water. By Fe(VI) treatment, phenolic PCPs are more easily oxidized than those nitrogen-containing PCPs. The reactions between Fe(VI) and the above PCPs follow second-order reaction kinetics, with the determined k_{app} values ranging from 7 M^{-1} s^{-1} (5CBT) to 1,111 M^{-1} s^{-1} (TCS) at pH 7.0. The reactivity of Fe(VI) species with PCPs is following the decreasing order of $H_2FeO_4 > HFeO_4^- > FeO_4^{2-}$. Hammett-type relationships illustrate the electrophilic oxidation mechanism of the above reactions. Fe(VI) can transform the phenolic PCP molecules through phenoxyl radical reaction, degradation, and coupling reaction. More importantly, the oxidation of each phenolic PCPs by Fe(VI) leads to the loss of its corresponding toxicity. However, the coexisting constituents present in source water could have significant effects on PCP removal during Fe(VI) oxidation treatment. In situ production of Fe(VI) solution appears to be a promising technology for removal of PCPs during pilot and full-scale water treatment. The potential future research directions are proposed as follows:

1. The removal of other categories of PCPs through Fe(VI) oxidation treatment should be carried out in batch experiments, since the numerous PCPs ubiquitous in aquatic environment have different reaction mechanisms with Fe(VI).
2. The information on radical formation and valence of iron intermediates should be studied by the application of electron paramagnetic resonance spectroscopy and Mössbauer spectroscopic techniques, to advance our understanding of the oxidative chemistry of Fe(VI) with PCPs.
3. The potential transformation products of PCP reaction with Fe(VI) should be identified by GC–MS and LC–MS/MS techniques, and the toxicity of transformation products should be evaluated by using various bioassays.
4. The in situ production of Fe(VI) solution for PCP removal should be conducted in pilot and full-scale trials to validate the treatment performance obtained in the laboratory studies and evaluate economic suitability of using Fe(VI) oxidation treatment.

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Ozonation as an Advanced Treatment Technique for the Degradation of Personal Care Products in Water

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Abstract Water is the most essential element to life on Earth. However, the availability and quality of the global water resources are at risk because many stressors of human origin are putting pressure on it. The contamination of water bodies (lakes, rivers, aquifers and oceans) occurs when man-made chemicals are directly or indirectly discharged into water bodies without adequate treatment to remove harmful compounds, affecting organisms living in these aquatic ecosystems. As new compounds are produced and ultimately detected in the environment, improved water treatment techniques have to be available for their elimination. For the degradation of a wide range of emerging organic micropollutants, last year's

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M.S. Díaz-Cruz and D. Barceló (eds.), *Personal Care Products in the Aquatic Environment*, Hdb Env Chem (2015) 36: 375–398, DOI 10.1007/698_2014_298,

advanced oxidation techniques have proven to be quite effective. In this chapter, we focus on the capabilities of ozonation to eliminate personal care products (PCPs) from water. Fundamentals and major mechanisms of ozonation are presented, along with an overview of its main application for the removal of several PCPs, with a more detailed section on benzophenone-3 degradation and by-products. Finally, some considerations as regards the economic cost of implementing tertiary treatment techniques like ozonation in wastewater treatment plants are pointed out.

Keywords Advanced oxidation processes (AOPs), Benzophenones, By-products, Ozonation, Personal care products (PCPs)

Contents

1 Introduction

Access to clean water is one of human's first needs and a prerequisite for a healthy life. However, increased population and anthropogenic activities put a growing pressure on both the availability and quality of the global water resources. Although legislative frameworks, such as the European Water Framework Directive 2000/60/EC (WFD), have been developed to protect water bodies against pollution caused by a list of priority substances, a decade of advances in environmental analysis has resulted in the discovery and increased awareness of emerging, not-regulated anthropogenic organic micropollutants in the urban water cycle [1, 2]. These

include polar pesticides, pharmaceutical residues and drugs of abuse, personal care products, hormones and other endocrine disrupting compounds (EDCs), brominated and organophosphate flame retardants, perfluorinated compounds, plasticizers, surfactants, artificial sweeteners, algal and cyanobacterial toxins, disinfection by-products, etc., dispersed in the aquatic environment at very low concentrations (microgram down to nanogram per litre). Their continuous introduction into the environment, pseudo-persistence and intrinsic ability to interfere with organisms concern the scientific and public community because their potential toxic effects can threaten the good ecological status of water bodies as well as human health [3].

Commonly used municipal wastewater treatment plants (WWTPs), primarily operating through biological processes, were developed and designed to protect natural aquatic systems and water resources mainly by removing loads of carbon, nitrogen and phosphorous, present in the influent in the mg L^{-1} range [4, 5]. The increased detection of a wide range of organic micropollutants in the aquatic environment shows the limitations of conventional WWTPs in removing these often biorecalcitrant compounds. Since more than 90% of the wastewater is treated in centralized WWTPs in industrialized countries, they represent a major pathway through which micropollutants enter our water resources [6]. Therefore, the water industry is currently evaluating the need for upgraded WWTPs [7], necessitating the development, optimization and implementation of improved water treatment techniques.

In this context, advanced oxidation processes (AOPs) encompassing a number of physical–chemical techniques such as ozonation, UV/H_2O_2 processes, vacuum UV irradiation, heterogeneous photocatalysis and (photo-)Fenton and electrochemical processes are nowadays of main interest [5, 8–16]. Through different kinds of mechanisms, they all involve the production of highly reactive and non-selective hydroxyl radicals, being very strong oxidants transforming refractory (micro)pollutants into less complex compounds aiming at reducing toxicity and/or increasing biodegradability. According to Joss et al. [17], AOPs are a promising tool for the removal of recalcitrant organic pollutants at an acceptable cost (0.05–0.20 € per m^3 for ozonation). Among the different AOPs, ozonation is one of the most intensively investigated and most promising techniques [8, 18, 19].

Ozonation of drinking water and wastewater for disinfection purposes has a long tradition [4, 20]. In recent years, it has also come into picture because of its benefits as an advanced wastewater treatment technology in laboratory-, pilot- and some full-scale studies for micropollutant removal [21]. The results show that ozonation of various secondary wastewater effluents from Australia, Europe, Japan and the United States can achieve significant elimination (i.e. >80%) of many micropollutants at reasonable ozone doses (e.g. at mass-based ozone to dissolved organic carbon ratios of 0.6–1.0 g O_3 g^{-1} DOC). In conjunction with in vitro and in vivo test batteries, the toxicity of these wastewater effluents was also found to be significantly reduced after ozonation or ozonation followed by biological filtration [4]. With few exceptions, it can also be expected that municipal wastewater ozonation generally yields sufficient structural modifications of antibacterial

molecules to eliminate their antibacterial activity and oestrogenicity [11, 22, 23]. Overall, recent studies demonstrate that ozonation can be a useful, economically feasible polishing treatment to improve the quality of municipal wastewater effluents [7].

In this chapter, the goal is to provide the reader of this book with some data on the electronic structure and physical–chemical characteristics of ozone, as well as with some fundamentals and mechanisms taking place during ozonation reactions in (waste)water. In a second part, a rather comprehensive and broad overview is given of recent studies published in the open literature dealing with ozonation as an advanced oxidation technique to remove personal care products (PCPs) from water. Next, a more detailed case study is briefly presented in which the ozonation of the UV filter and model PCP compound benzophenone-3 (BP3) is studied with particular focus on the effect of operational variables and the identification of BP3 ozonation products. Finally, some economic considerations and conclusive comments are presented.

2 Ozonation: Fundamentals and Mechanisms

2.1 The Ozone Molecule and Its Reactivity

The ozone molecule, consisting of three oxygen atoms, exists as a hybrid of four possible resonance structures (Fig. 1), providing the molecule some degree of polarity.

Although the dipolar momentum of ozone is rather weak (0.53 D), different properties of the molecule – such as solubility and type of reactivity of bonds – are due to its polarity. Important for its application in AOP techniques is the fact that ozone is a very powerful oxidizing agent, with a standard redox potential of 2.07 V. The high reactivity can be attributed to the electron configuration of the molecule. Due to the absence of electrons at one part of the molecule and the excess at another part, ozone has an electrophilic as well as a nucleophilic character [24].

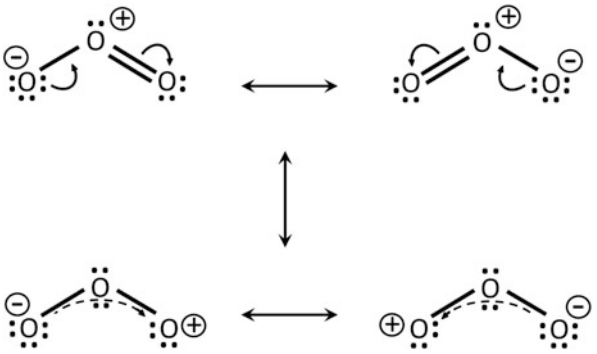

Fig. 1 Resonance structures of the ozone molecule

In aqueous medium, the ozone molecule is unstable, and autocatalytic decomposition occurs, giving rise to the formation of numerous free radical species, among which is the hydroxyl radical ($HO^{\bullet}$), being even a stronger (redox potential of 2.80 V) and much less selective oxidant than ozone. In fact, ozone reacts selectively with organic molecules at rate constants (k_{O3}) ranging between $<0.1\ M^{-1}\ s^{-1}$ and about $10^{10}\ M^{-1}\ s^{-1}$. It is particularly reactive towards functional groups with high electron density such as double bonds, activated aromatic systems, non-protonated secondary and tertiary amines and reduced sulphur species [4], but not towards aromatic rings with ethinyl, amide or carboxyl groups [25]. Hydroxyl radicals react unselectively via radical addition, hydrogen abstraction or electron transfer mechanisms at higher rate constants ($k_{HO\bullet}$) varying over four orders of magnitude with the major part being about $10^9\ M^{-1}\ s^{-1}$ [23, 26]. Therefore, hydroxyl radicals can contribute to the oxidation of ozone-recalcitrant compounds.

As a result, ozone may degrade organic micropollutants like PCPs in (waste) water by either of two oxidation mechanisms: direct (Sect. 2.2) or indirect (Sect. 2.3) ozonation reactions. In the presence of dissolved organic matter (DOM), the formation of hydroxyl radicals is enhanced compared to in pure water, which makes the indirect mechanism being the most prevalent in ozonation of highly loaded (DOM) (waste)waters [27]. Dodd et al. [28] suggest that compounds with $k_{O3}/k_{HO\bullet}$ ratios less than 10^5 will generally be transformed to a large extent by $HO^{\bullet}$ radicals rather than by molecular ozone during wastewater ozonation. Unfortunately, despite kinetic data are essential to evaluate the removal efficiencies of micropollutants from water during ozonation and AOPs, reaction rate constants are still unavailable for many emerging micropollutants like PCPs [29].

2.2 Direct Ozonation Reactions

Due to its electronic structure, ozone can react with aqueous compounds through mainly three different reaction mechanisms: (i) oxidation–reduction reactions, (ii) dipolar cycloaddition reactions and (iii) electrophilic substitution reactions.

Oxidation–reduction reactions are characterized by the transfer of electrons from one species (reductor) to another (oxidant). Because of its high standard redox potential, the ozone molecule has a high capacity to react with numerous compounds by means of this reaction mechanism. Nevertheless, this type of reactivity is particularly important for some inorganic species such as Fe^{2+} or I^- [24]. Oxidation of organic compounds in wastewater is typically associated with the formation of more oxygen-rich moieties (rather than their complete oxidation to produce inorganic carbon dioxide and water). These organic transformation products are typically more polar and biodegradable than the parent compounds [27, 30]. In case of olefinic compounds, having one or more carbon double bonds, cycloaddition reactions may occur. The general reaction pathway here is called the Criegee mechanism, where a primary unstable cyclic ozonide (1,2,3-trioxolane) is formed

which decomposes into a carbonyl compound and a carbonyl oxide. The latter undergoes further reaction with possible formation of a secondary ozonide (1,2,4-trioxolane), (hydro)peroxides and carbonyl compounds (ketones, aldehydes and carbonic acids). Also aromatic compounds can react with ozone through 1,3-cycloaddition leading to the break-up of the aromatic ring. However, because of the stability of the aromatic ring, the electrophilic attack of one terminal oxygen of the ozone molecule on any nucleophilic centre of the aromatic compound is more probable, resulting in the substitution of one part of the molecule. Whereas the cycloaddition reaction leads to the loss of aromaticity, the electrophilic substitution reaction retains the aromatic ring. An important consideration is the presence of substituting groups such as HO^-, NO_2^-, Cl^-, etc. in the aromatic molecule, since they can strongly affect (activate or deactivate) the reactivity of the aromatic ring with electrophilic agents, because of their increasing or decreasing effect on the stability of the carbocation involved during electrophilic substitution [24].

2.3 Indirect Ozonation Reactions

Indirect ozonation reactions are those between $HO^\bullet$ or other free radicals, formed through the decomposition of ozone or from other direct ozonation reactions, and compounds present in water.

The mechanism of Staehelin, Hoigné and Bühler (SHB model) is generally accepted for ozone decomposition in water at neutral pH conditions, whereas an alternative model is proposed by Tomiyasu, Fukutomi and Gordon (TFG) at rather alkaline pH [24]. Figure 2 gives a simplified representation of main reactions involved in the SHB model. Next to direct reactions of ozone with organic molecules (Sect. 2.2), ozone decomposition may be induced by OH^-, HO_2^- or other initiators. This will lead to $HO^\bullet$ through formation of $O_3^{\bullet-}$ and $HO_3^\bullet$. Hydrogen peroxide (H_2O_2) may be an important promotor for ozone decomposition. In the peroxone process, it is applied as reagent to enhance radical concentrations. It can also be formed through reactions between ozone and hydroxyl anions or between two hydroperoxyl radicals and/or during ozonation of organic impurities. H_2O_2 also acts as a $HO^\bullet$ scavenger. Buxton et al. [31] reported reaction constants of 7.5×10^9 and 2.7×10^7 M^{-1} s^{-1} between hydroxyl radicals and HO_2^- and H_2O_2, respectively. Therefore, H_2O_2/O_3 ratios for hydroxyl radical formation reveal an optimum, typically around 0.5 mol mol^{-1} [32].

In natural and wastewaters, the reaction system becomes even more complex than in pure water. Radical promotion as well as radical scavenging occurs. Carbonate ions are important radical scavengers since HCO_3^- and CO_3^{2-} have reaction constants with hydroxyl radicals of 8.5×10^6 and 4.2×10^8 M^{-1} s^{-1}, respectively [24]. Also DOM may act as a scavenger, although reactions between ozone and DOM are highly complex and affect ozone stability in several ways. Some DOM moieties directly react with ozone, and part of these reactions can give rise to superoxide radical anions or ozone radicals. As such, they initiate the chain

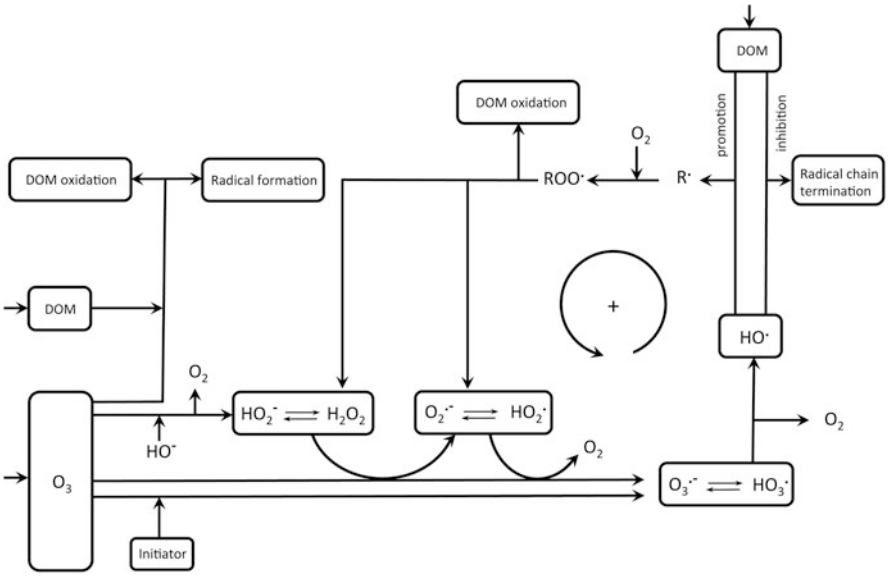

Fig. 2 Simplified scheme of reactions of ozone in water loaded with dissolved organic matter (DOM), according to the SHB model

reaction [26, 33]. DOM also indirectly affects ozone decomposition by interacting with $HO^{\bullet}$. This can have an inhibiting effect by terminating the radical chain mechanism, or it can promote the mechanism by peroxide formation. Part of these reactions lead to carbon-centred radicals which subsequently react with dissolved oxygen to finally produce superoxide radical anions. These radicals significantly promote ozone decomposition. Examples of compounds that produce superoxide radical anions upon reaction with ozone are phenols and secondary amines.

3 Ozonation and Ozone-Based Advanced Oxidation of PCPs

Ozonation studies of emerging organic micropollutants most often focus on pharmaceuticals (e.g. antibiotics, β-blockers, antineoplastic agents, etc.) and hormones (e.g. oestrone, oestradiol, diethylstilbestrol), while data on the ozonation of personal care products is relatively limited [34, 35]. Most of the studies dealing with ozonation or ozone-based advanced oxidation of PCPs do not particularly focus on this group of emerging contaminants, but include some PCPs in a mixture of a large number of other types of micropollutants. The main results obtained during ozonation of different types of PCPs are briefly summarized in Sects. 3.1–3.5.

3.1 Triclosan: A Widely Used Antimicrobial

Triclosan (2,4,4′-trichloro-2′-hydroxydiphenyl ether) is used as an antimicrobial agent in a large number of medical and personal care products (e.g. liquid soaps, deodorants, toothpaste, mouthwash) and in functional clothing, textiles and plastics (e.g. sportswear, bedclothes, shoes, carpets) to control the growth of disease- or odour-causing bacteria. It is also used as a stabilizing agent in a multitude of detergents and cosmetics [36–38]. Discharges of triclosan residues into surface water are undesirable because of toxic effects towards aquatic organisms (e.g. algae and fish), risks for unanticipated alterations in microbial communities, evolution of bacterial resistance and formation of 2,8-dichlorodibenzo-p-dioxin during triclosan photolysis in surface waters [36].

Although ozonation of organic pollutants in wastewater has been investigated in numerous studies, data on the removal of triclosan and eventual formation of by-products are scarce and incomplete [37]. In a dedicated study by Suarez et al. [36], reaction rate constants for each of triclosan's acid–base species with O_3 have been determined. Anionic triclosan was found to be highly reactive towards O_3, with a species-specific rate constant of 5.1×10^8 M^{-1} s^{-1}, while neutral triclosan reacts with a species-specific rate constant of 1.3×10^3 M^{-1} s^{-1}. As a consequence, triclosan ($pKa = 8.1$) is oxidized quite rapidly at circumneutral pH, with an apparent second-order rate constant of $k_{O3} = 3.8 \times 10^7$ M^{-1} s^{-1} at pH 7. A 10 times lower k_{O3} value (2.5×10^6 M^{-1} s^{-1}) was experimentally determined by Jin et al. [29]. The relatively high reactivity of triclosan with ozone can be explained by the donation of an electron by the hydroxyl group to the benzene ring, activating the aromatic system and thus facilitating the oxidative attack by ozone [25].

Biological assays of O_3-treated triclosan solutions indicate that ozonation yields efficient elimination of triclosan's antibacterial activity, which can be explained by the fact that O_3 reacts with triclosan by direct electrophilic attack of the phenol moiety, which is of primarily importance for the antibacterial activity of the molecule [36]. Chen et al. [37] identified 2,4-dichlorophenol, chlorocatechol, monohydroxy-triclosan and dihydroxy-triclosan as the main transformation products during triclosan ozonation at pH 7. The results of their study also indicate a reduced genotoxicity through transformation of triclosan into 2,4-dichlorophenol, although this latter compound (which has also been identified by Wu et al. [38] as the main oxidation product of triclosan during permanganate oxidation) is prioritized under the EU Council Directive 76/464/EEC on pollution caused by certain dangerous substances discharged into the aquatic environment and is classified to be harmful to aquatic organisms. Biological assessment data for the other transformation products are not provided.

During ozonation of effluent samples from two conventional WWTPs, nearly 100% triclosan (150 μg L^{-1}) removal was achieved with a 4 mg L^{-1} O_3 dose applied to a wastewater containing 7.5 mg L^{-1} of DOC, while removal efficiencies (RE) amounted to 58% for an ozone dosage of 6 mg L^{-1} to a wastewater with

12.4 mg L^{-1} of DOC [36]. At much lower concentrations, i.e. 48 ng L^{-1} of triclosan in aerobically treated grey water, Hernández-Leal et al. [34] obtained RE >87% at an ozone dose of 10 mg L^{-1}, being similar to the results obtained by Snyder et al. [39], Nakada et al. [25] and Rosal et al. [40]. Also Wert et al. [41] report RE >95% independent of the wastewater effluent quality. Less efficient ozonation of triclosan is reported by Giri et al. [19], who obtained better results with UV photolysis, H_2O_2/UV, TiO_2/UV and TiO_2/UV/O_3 processes. At O_3 doses larger than 1 mg L^{-1}, Suarez et al. [36] found that $HO^{\bullet}$ reactions accounted for less than 35% of the observed triclosan degradation in wastewaters ($k_{HO\bullet} = 5–10 \times 10^9$ M^{-1} s^{-1}; [7, 29]), supporting the importance of the direct O_3/triclosan reaction. As a possible strategy to reduce the O_3 dose without significantly decreasing the O_3 and $HO^{\bullet}$ exposures, Wert et al. [42] suggested an enhanced coagulation pretreatment, able to reduce the DOC content of the wastewater and thus the O_3 dose (the O_3/DOC ratio was maintained at 1) by 10–47%. At all conditions applied in this study, triclosan (68–170 ng L^{-1}) which was one of the 13 targeted micropollutants, was eliminated to concentrations below 25 ng L^{-1} (method reporting limit).

3.2 Parabens

Parabens (4-hydroxy-benzoate esters) and their salts are the most commonly used antimicrobial agents, antifungicidal agents and antioxidants in the cosmetic and pharmaceutical industries. These additives used in food, pharmaceuticals and PCPs have recently been demonstrated to have oestrogenic and anti-androgenic properties [43, 44]. Moreover, there seems to be a potential relationship between breast cancer and prolonged dermal exposure to paraben-containing products, since these compounds have been found in breast tumours [45]. Unfortunately, not much research has been carried out on the removal of parabens from aqueous solution [35, 46].

Tay et al. [46] investigated the degradation kinetics of a paraben mixture, containing methyl-, ethyl-, propyl-, butyl- and benzylparaben, using ozonation at different conditions of ozone dose, pH, initial concentration and temperature. Both pH and ozone dose favoured paraben removal, and the optimum temperature was 35°C. Second-order reaction rate constants of parabens with $HO^{\bullet}$ (6.8–9.2×10 M^{-1} s^{-1}) and ozone (10^2–10^9 M^{-1} s^{-1}) show a higher reactivity at increasing alkyl chain length [35]. Moreover, the rate constants for the reaction of ozone with dissociated parabens (order of 10^9 M^{-1} s^{-1}; pH 12) were found to be 10^4 times higher than those of undissociated parabens (pH 6), and 10^7 times higher than with the protonated parabens (pH 2), explaining the observed pH effect on the degradation rate [47]. The results also indicate that the formed ozonation by-products, which were identified to be mainly aromatic ring and ester chain hydroxylated parabens [47], are more resistant to further ozonation than the parent compounds. The same authors report a complete paraben removal from natural

water (pH 7) at ozone dosages of about 1 mg L^{-1}. Since, at this pH, their transformation is almost completely (>93%) due to direct reaction with ozone instead of indirect $HO^{\bullet}$ reactions, the ozonation performance is not much susceptible to the organic matter load in the aqueous matrix [35]. More recently, Hernández-Leal et al. [34] noticed a complete removal (>99%) of four parabens after 15 min of ozonation (total ozone consumption of 8.3 mg L^{-1}) in demineralized water, spiked at concentrations of about 1.5 mg L^{-1}.

3.3 Synthetic Musk Fragrances

Synthetic musk fragrances are commonly used in perfumery, shampoos, lotions and cleaning products [8]. They are of concern because of toxicity reasons and since they have been proven to cause anti-androgenic effects during in vitro and in vivo tests [48].

Data on their behaviour during ozonation processes are scarce. During treatment of aerobically treated grey water at an ozone dose of 15 mg L^{-1} [34], the polycyclic musk fragrances galaxolide (HHCB, 4,6,6,7,8,8-hexamethyl-1,3,4,6,7,8-hexahydrocyclopenta[*g*]isochromene) and tonalide (AHTN, 6-acetyl-1,1,2,4,4,7 hexamethyltetraline) were removed to below their limits of quantification (91 ng L^{-1} and 40 ng L^{-1}, respectively), yielding REs of at least 87% (galaxolide) and 79% (tonalide). These RE values fall in the range of removal previously shown by Rosal et al. [40], who report at similar conditions lower REs for two nitro-musk compounds, i.e. musk xylene (no removal) and musk ketone (RE = 38%). In a study by Molinos-Senante et al. [49], ozonation of galaxolide and tonalide in the permeate of a membrane bioreactor was slow and did, in contrast to some pharmaceuticals (e.g. diclofenac and sulfamethoxazole), not result in their complete removal within 10 min. Janzen et al. [50] found several stable transformation products during ozonation of polycyclic musk fragrances (no removal of musk xylene and musk ketone was obtained) and indicated that contact times of more than 15 min would be required to remove at least some of these transformation products. Accompanying analysis during an ozonation study by vom Eyser et al. [51], focusing on galaxolide and tonalide next to five pharmaceuticals, showed no genotoxic, cytotoxic or oestrogenic potential for the investigated compounds after oxidative treatment (ozonation, UV and UV/H_2O_2 treatment) of real wastewaters, indicating no hazardous impact of by-product formation from ozonation and other AOPs. Margot et al. [3] reported no removal of galaxolidone, a fragrance metabolite, during the ozonation of a WWTP effluent.

Overall, the ozonation efficiency towards this class of emerging organic micropollutants tends to be relatively low, which is in agreement with their low k_{O3} values, being 8–10 M^{-1} s^{-1} for tonalide and 67–140 M^{-1} s^{-1} for galaxolide [50, 52].

3.4 The Insect Repellent DEET

N,N-Diethyl-meta-toluamide (DEET) is a common active compound in insect repellents. It functions as a block to the insect's chemoreceptor that senses carbon dioxide and lactic acid in locating their host. The reported adverse effects of DEET to humans include seizures, brain damage and dermal toxicity [35]. Just like triclosan, DEET belongs to the 30 most frequently detected organic wastewater contaminants, as reported by the US Geological Survey [53]. Although DEET is readily biodegradable [54], concentrations in biologically treated wastewaters are ranging up to several hundreds of ng L^{-1} [55]. Also in drinking water, it is a commonly found micropollutant. Padhye et al. [56] report that the median concentrations of most detected pharmaceuticals, PCPs and EDCs during a year-long study of an urban drinking water treatment plant (DWTP) were below 5 ng L^{-1}, except for DEET and nonylphenol, which were at 12 and 20 ng L^{-1}, respectively. During the pre-ozonation step in the studied DWTP, the authors found that DEET was removed by only <30% at applied ozone dosages between 0.4 and 1.1 mg L^{-1} and a contact time of 3–4 min. During the same treatment, triclosan was removed by about 40%. During subsequent intermediate ozonation, a higher DEET removal (RE = 63%) was obtained at similar ozone dosages but at 5–10 times longer contact times.

In an operating WWTP, Nakada et al. [25] investigated the removal of 24 pharmaceuticals and PCPs during activated sludge treatment followed by sand filtration and ozonation (3 mg $O_3\,L^{-1}$, 27 min contact time) as posttreatment steps. They report efficient removal (>80%) of all the target compounds, except carbamazepine and DEET. The ozonation step contributed only to a very limited extent (<5%) to the overall DEET removal. At an ozone dosage of 5 mg L^{-1} and a contact time of 15 min, Sui et al. [55] obtained 50–80% DEET removal in secondary WWTP effluent. A somewhat lower removal (RE = 48%) has been obtained by Margot et al. [3]. During a 12-month evaluation of the removal of 19 pharmaceuticals and PCPs in a multi-treatment WWTP using primary clarification, activated sludge biological treatment, membrane filtration, granular media filtration, granular activated carbon (GAC) adsorption and ozonation, Yang et al. [54] found that ozonation oxidized most of the remaining compounds by >60%, except for primidone and DEET. The insect repellent was one of the four compounds that were frequently detected in the final effluent at concentrations in the order of <10–30 ng L^{-1}. Its RE during ozonation varied between 0% and 50% which might be attributable to variations in the ozone dose (ranging from 0.75 to 2.0 mg L^{-1} with an average value of 1 mg L^{-1}) or to variations in the influent water quality to the ozonation chamber.

The rather poor removal of DEET during ozonation, compared to many other organic micropollutants, is because of its low reactivity towards ozone (second-order reaction rate constant $k_{O3} = 5{,}2\ M^{-1}\ s^{-1}$; [35]), which can be explained by the electron-drawing nature of its amide function [3]. Therefore, DEET removal is mainly induced by $HO^{\bullet}$ reactions ($k_{HO\bullet} = 5{,}0 \times 10^9\ M^{-1}\ s^{-1}$) [7, 35, 42, 54], which

makes it also dependent on the aqueous total organic carbon (TOC) concentration. For example, at an ozone dosage of 2 mg L^{-1}, DEET removal efficiencies amounted to 98%, 96% and 86% in river water, secondary effluent and lake water having a TOC content of 13, 16 and 22 mg L^{-1}, respectively [35]. Lee et al. [7] showed that the elimination of ozone-refractory micropollutants like DEET can be well predicted by measuring the $HO^{\bullet}$ exposure via the decrease of the probe compound p-chlorobenzoic acid. On the basis of their results, a DOC-normalized ozone dose, the rate constants k_{O3} and $k_{HO\bullet}$ and the measurement of the $HO^{\bullet}$ exposure are proposed as key parameters for the prediction of the elimination efficiency of micropollutants during ozonation of municipal wastewater effluents with varying water quality.

3.5 UV Filters (Sunscreen Agents)

UV filters are used in personal care products such as cosmetics, beauty creams, lotions and shampoos or as an additive in polymeric materials that have to be protected from sunlight-initiated disruption [57, 58]. Recent studies [59, 60] indicate that these sunscreen agents are persistent, bioaccumulative compounds that show oestrogen-like activity in in vitro and in vivo assays [61–63]. Dermal and oral administration of benzophenone-3 (BP3), one of the most commonly used UV filter compounds, to rats and mice have shown alterations in liver, kidney and reproductive organs [62]. A recent study by Kunisue et al. [64] indicates that exposure to elevated levels of benzophenone-type UV filter compounds may be associated with oestrogen-dependent diseases such as endometriosis.

The feasibility of ozonation to remove UV filter compounds from sewage or treated grey water has been demonstrated in a few studies, but a detailed insight in the mechanisms is still lacking for most of these compounds, and also the data reported on removal efficiency are somewhat ambiguous. For example, Li et al. [65] and Rosal et al. [40] did not detect any or only a limited (RE $<30\%$ after 15–180 min) elimination during ozonation (ozone dosages of 5–16 mg L^{-1}) of the UV filters BP3, EHMC (ethylhexyl methoxycinnamate), octocrylene and 4-MBC (4-methylbenzylidene-camphor). In other work, however, much higher REs (from 65 up to 98%) were obtained for the same compounds at similar concentrations (order of ng L^{-1}), ozone doses and treatment times [3, 34, 39]. In a comparative study with benzophenone, spiked (10 mg L^{-1}) as a model compound in distilled water, Yan-jun et al. [66] noticed that the addition of Mn–Fe–K-modified ceramic honeycombs as a catalyst during ozonation may increase the removal rate of both benzophenone and the TOC content, which has been attributed to a larger $HO^{\bullet}$ generation. A more detailed study on the ozonation of BP3 is presented as a case study in Sect. 5.

4 A Point of Attention: Ozonation By-Product Formation

A concern related to the application of ozonation in water treatment is linked to the formation of potentially carcinogenic and/or toxic oxidation by-products from matrix components and transformation products from micropollutants [42, 67]. Recent research indicates that products of ozonation exhibit less oestrogenic activity than the original compounds, but toxicity assessment using bioassays indicates that in some cases the toxicity of the ozonated wastewater is increased, although this can be solved by a biological posttreatment [27, 68]. The formation of bromate can be relevant if bromide occurs in high concentrations, and also N-nitrosodimethylamine (NDMA) formation is reported during ozonation. In particular, quaternary amine-containing micro- and macroconstituents of PCPs (e.g. shampoos) have been suggested as contributors to NDMA formation [69]. Hollender et al. [4] detected NDMA ($\leq$14 ng L^{-1}) and bromate ($<$10 μg L^{-1}) during ozonation (0.6 g O_3 g^{-1} DOC) of a municipal WWTP secondary effluent containing 55 micropollutants ($>$15 ng L^{-1}), among which were some PCPs like galaxolidone (RE = 63%), DEET (RE = 62%) and BP3 (RE > 84%). However, their concentrations were below or in the range of the drinking water standards, and subsequent biological sand filtration showed to be an efficient additional technique for the elimination of biodegradable ozonation products such as NDMA. According to Kim et al. [70], O_3/UV and H_2O_2/UV processes might be a good solution to suppress or avoid bromate formation. For sure, the formation and mitigation of oxidation by-products have to be a point of attention in the further assessment of the full application potential of ozonation and related AOPs [7].

5 Benzophenone-3 Ozonation in Water: A Case Study for Benzophenone-Type Sunscreens

In order to gain better insight into the factors influencing PCPs' degradation during ozonation and peroxone (O_3/H_2O_2) oxidation, along with the identification of transformation products, Gago-Ferrero et al. [71] performed a detailed and particular study dealing with BP3 as a model compound for benzophenone-type UV filters. The ozonation experiments were conducted in a temperature-controlled bubble column. Ozone was generated in dry air and after flow adjustment dosed through a sintered glass plate at the bottom of the reactor. The reaction solution consisted of a saturated BP3 aqueous solution (dissolved concentration 5.0 mg L^{-1}). At the initial conditions, the ozone inlet concentration was 85.7 μmol L_{gas}^{-1}, the gas flow rate 120 mL min^{-1} and the reactor temperature 25°C. The experimentally estimated ozone mass transfer coefficient (k_La) in the column was 5.5 h^{-1} [72]. The water was buffered by a 10.12 mM phosphate buffer (pH 3 and 7) or a 2.5 mM borax buffer (pH 10).

At pH 7, BP3 showed a half-life time ($t_{1/2}$) of 12.6 min and a 95% removal after 40–50 min, indicating a good BP3 degradability by ozonation. Based on BP3 aqueous concentration data up to 5% of the initial BP3 concentration, a pseudo-first-order rate constant ($k_{1,BP3}$) of 0.056 min^{-1} was determined. From the ozone consumption profile (i.e. the ozone inlet minus the ozone outlet gas concentration as a function of time), it was estimated that 0.57 mmol of ozone was consumed after 60 min of ozonation, approximately a factor of 2 higher than in the absence of BP3.

5.1 *Effect of the Ozone Inlet Concentration on BP3 Degradation*

The effect of the ozone inlet concentration on the degradation of aqueous BP3 was investigated at ozone concentrations in the range 32.6–151 μmol L_{gas}^{-1} (ozone load 1.63–7.55 μmol min^{-1} L_{water}^{-1}). Other operational parameters, including the initial BP3 concentration (22.3 μmol L^{-1}), pH (buffered at 7) and temperature (25°C), were kept constant. The experimental results revealed a faster BP3 removal at higher inlet ozone gas concentrations, with $k_{1,BP3}$ values increasing from 0.023 to 0.12 min^{-1} (Fig. 3). This can be explained by an increased ozone concentration in the aqueous phase. Since BP3 is a non-volatile compound, reactions in the gas phase are negligible. After the mass transfer of ozone from gas to liquid phase, however, it may either directly react with BP3 or decompose to produce other reactive species which in turn react with BP3.

As Fig. 3 shows, a rather linear increase in the ozone consumption was observed after 60 min of ozonation, suggesting that within the concentration interval studied the ozone consumption is first order in the ozone inlet concentration. This increase might be explained not only by a faster BP3 degradation but also by the formed reactive species and BP3 degradation products.

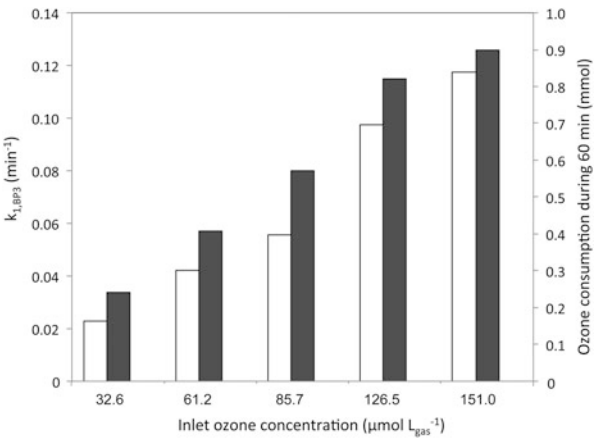

Fig. 3 Pseudo-first-order BP3 removal rate constants (*white*) and ozone consumption during 60 min of ozonation (*black*) for experiments at an initial BP3 concentration of 22.3 μmol L^{-1}, 25°C and pH 7

5.2 Effect of Temperature on BP3 Degradation

Ozonation processes might be influenced by reaction temperature in two aspects. On the one hand, Henry's law coefficient of ozone increases by more than a factor of 2 at higher temperature within the applied working range (25–65°C) [73], limiting the mass transfer from gas to liquid phase and thus negatively affecting the BP3 degradation efficiency. On the other hand, higher temperature may increase both the instability of ozone itself and the activation of the reactive species leading to the enhancement of the BP3 degradation rate [74]. The BP3 rate constants increased from 0.056 to 0.091 min^{-1} when increasing the temperature, whereas no significant effect in the consumption of ozone was observed. At these conditions, it appears that the second effect predominates. As at higher temperature the amount of ozone dissolved in the water phase is smaller, and the consumed amount of ozone is almost independent of temperature. This indicates a more efficient use of the aqueous ozone for BP3 degradation.

5.3 pH Effect on BP3 Degradation

Ozonation of BP3 at acid, neutral and alkaline conditions was investigated considering that pH may affect both the ozonation kinetics and mechanistic pathways of organic micropollutants [75]. Results show an increase of the BP3 removal rate at higher pH, especially between pH 7 and pH 10 (Fig. 4). This can be explained by the higher rate of ozone decomposition at higher pH as the hydroxyl ions catalyse

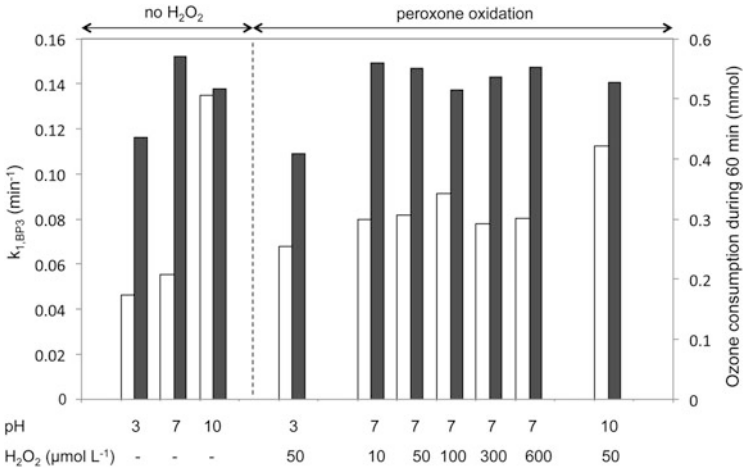

Fig. 4 Effect of pH and H_2O_2 addition on the pseudo-first-order BP3 removal rate constants (*white*) and ozone consumption during 60 min of ozonation (*black*) for experiments at an initial BP3 concentration of 22.3 µmol L^{-1}, 25°C and an inlet ozone concentration of 85.7 µmol L_{gas}^{-1}

the decay of ozone to form hydroxyl radicals serving as reactive species [76]. At acidic conditions, when no hydroxyl radical formation is expected and molecular ozone is presumed to be the most important reactive species, the decomposition of BP3 is slower than at neutral and basic conditions. At pH 10, the BP3 decomposition rate is more than twofold higher than at acid pH, showing the importance of the formed hydroxyl radicals. The reactivity of BP3 with $HO^{\bullet}$ is significantly higher than with ozone in aqueous phase, as is the case with most organic pollutants [77]. Furthermore, since BP3 has a pK_a of 8.06, it is mainly dissociated at higher pH, which might result into an enhancement of the reaction rate since ozone is an electrophilic reagent.

The important role of hydroxyl radicals during BP3 ozonation was confirmed by the increase in BP3 half-life time if t-butanol (TBU) was added as a strong hydroxyl radical scavenger. Whereas the effect was relatively small (10–16%) at pH 3 and pH 7, the BP3 half-life time increased from 5 to 8 min when TBU was added at pH 10, when the hydroxyl radical concentration is higher.

5.4 BP3 Oxidation by the Peroxone Process

Taking into account the significant contribution of hydroxyl radicals during BP3 ozonation, peroxone experiments were conducted. Various H_2O_2 dosages (10–600 μmol L^{-1}) were added in the aqueous phase as a source for $HO^{\bullet}$ radicals. The degradation of BP3 by using O_3/H_2O_2 still followed the pseudo-first-order decay. As a result of a promoted $HO^{\bullet}$ radical formation [78], an increment of the BP3 degradation rate is observed as the H_2O_2 concentration increases, to reach a maximum ($k_{1,BP3} = 0.091\ min^{-1}$) at 100 μmol L^{-1} H_2O_2, being 64% higher than without H_2O_2 (Fig. 4). At higher H_2O_2 dosages, however, the BP3 degradation rate decreased, showing similar values at 10 and 600 μmol L^{-1} H_2O_2. This inhibiting effect on the oxidation of BP3 may be explained by the scavenging behaviour of H_2O_2 towards hydroxyl radicals [79]. The ozone consumption as a function of H_2O_2 concentration followed an opposite trend to that of the BP3 degradation rate. The lowest ozone consumption was measured at 100 μmol L^{-1} H_2O_2, i.e. at the maximum BP3 removal rate. This fact may be attributed to the higher concentration of radicals present in the aqueous phase, reducing the ozone consumption due to direct reaction with BP3.

Peroxone experiments at different pH values revealed an opposite H_2O_2 effect at acid and neutral conditions than at alkaline conditions (Fig. 4). Adding 50 μmol L^{-1} H_2O_2 in the aqueous solution did increase the BP3 removal rate by 47% at pH 3, which is completely in line with the results obtained at neutral pH. In contrast, the BP3 degradation at pH 10 was almost 20% slower when H_2O_2 was added. Since in this case high concentrations of hydroxyl radicals and H_2O_2 are present simultaneously, the observed rate retardation most probably results from the consumption/scavenging of hydroxyl radicals by H_2O_2, yielding less reactive radicals (such as $HO_2^{\bullet}$) in the solution [80].

5.5 BP3 Ozonation By-Product Identification

HPLC-MS/MS data revealed that apart from BP3, several other chromatographic peaks were observed during full scan analysis with electrospray ionization in positive mode (ESI+) of samples collected during the first 25 min of BP3 ozonation. For four of the detected peaks, a molecular ion $[M+H]^+$ 245 was observed. Considering that the mass of these compounds is shifted 16 Da upwards relative to that of BP3, hydroxylation by $HO^{\bullet}$ attack is the most plausible explanation. Based on their identical fragmentation pattern with clear similarities with the MS/MS spectra obtained for BP3, three peaks represent the ortho- (confirmed by the analysis of a standard of 2,2′-dihydroxy-4-methoxybenzophenone, DHMB), meta- and para-hydroxylated forms. The fourth peak results from the hydroxylation of BP3 at the other moiety of the molecule. Next to hydroxylation, demethylation is suggested as a second BP3 degradation pathway, considering the spectral data on a peak with molecular ion $[M+H]^+$ 215. As confirmed by the analysis of the standard, this molecule corresponds to benzophenone-1 (BP1), which is also a commonly used UV filter. Although the detected concentrations of BP1 are relatively low compared to the initial BP3 concentration, its formation should be taken into account when considering the application of ozonation for BP3 removal from wastewater. A supporting experiment investigating BP1 ozonation revealed that BP1 degradation is slower than that of BP3, supporting its temporally accumulation during BP3 ozonation. Since yeast-based bioassay (ER-RYA) analysis showed that BP1 is about 200 times more oestrogenic than its parent compound BP3 [81], the ozonation time should be long enough in order to remove both BP3 and BP1 from the reaction medium. After 15 min of BP3 ozonation, another peak corresponding to the molecular ion $[M+H]^+$ 259 occurred with spectral information indicating the oxidation of the methyl group in one of the previously produced hydroxylated intermediates transforming the compound in an aldehyde derivative.

The analysis by HPLC-MS/MS with electrospray ionization in negative mode (ESI-) confirmed the detection of some by-products already identified in ESI + mode and yielded also additional information. A group of peaks corresponding to the molecular ion $[M\text{-}H]^-$ 259 were observed, all showing the same fragmentation pattern from which it was deduced that another non-specific $HO^{\bullet}$ oxidation of already hydroxylated reaction products is the most probable explanation. Finally, after 20 min of ozonation, three chromatographic peaks were observed related to the molecular ion $[M\text{-}H]^-$ 229. Due to the fact that this mass is 16 Da upwards relative to BP1 and since the obtained spectra are very similar, the peaks are representing the ortho-, meta- and para-hydroxylation products of BP1, resulting from a $HO^{\bullet}$ attack in the non-hydroxylated moiety of the molecule. The identity of the ortho-isomer was confirmed as 2,3,4-trihydroxybenzophenone (THB) by analytical standard analysis.

6 Economic Considerations

As long as there is no stringent legislation forcing the reduction of PCPs' concentrations to a predefined level during (waste)water treatment, economic considerations might be a hampering factor in extensively implementing tertiary treatment techniques like ozonation in WWTPs. While technical aspects about the removal of micropollutants from wastewater have been widely studied, the truth is that the assessment of the economics has been more limited [49]. The energy requirement for an additional post-ozonation step has been estimated to be about 0.035–0.09 kWh m^{-3} [4, 70, 82], being much more cost-effective than other AOPs such as O_3/UV (1.1 kWh m^{-3}) and H_2O_2/UV (0.54 kWh m^{-3}), and corresponding to ca. 12% of a typical medium-sized nutrient removal plant (5 g DOC m^{-3}) [4]. According to Molinos-Senante et al. [49], it is however not only important to evaluate the costs of the posttreatment, but also the environmental benefits should be quantified. Therefore, these authors calculated for the first time the shadow prices of three pharmaceuticals (ethinyl oestradiol, sulfamethoxazole, diclofenac) and two PCPs (tonalide and galaxolide) by treating effluent using a pilot-scale ozonation reactor. These shadow prices are to be interpreted as a proxy for the economic value of the environmental benefits for avoiding the discharge of contaminants into water bodies. For both PCPs, they ranged between −8 and −14 € kg^{-1}, being 3–10 times lower than that of the studied pharmaceuticals.

7 Conclusions and Perspectives

Although ozonation has become a widely applied technique for disinfection of drinking water and wastewater, its potential as a tertiary treatment to remove biorecalcitrant micropollutants has been recognized only much more recently. Among the studies dealing with the advanced oxidation of (emerging) organic micropollutants, most focus is put on pharmaceuticals and hormones, while the feasibility of ozonation and related AOPs for the removal of personal care products has only been demonstrated in a few studies, with most of them not particularly focusing on this class of recently considered contaminants. Depending on the nature of the PCP compound and the study considered, quite a large variability in removal efficiencies is reported which can be explained by differences in (i) treated water quality, (ii) conditions applied during ozonation and (iii) reactivity of the PCPs towards ozone. The main parameters affecting the ozonation performance show to be the ozone dose, temperature and pH. The latter parameter is particularly important for ionizable compounds since their dissociation state may affect their reactivity towards ozone. Higher pH also results into a faster ozone decomposition as hydroxyl ions catalyse the decay of ozone to form hydroxyl radicals, being stronger and less selective oxidants than ozone.

It is clear that certainly more research is needed to fully understand the mechanisms and to optimize the applicability of ozonation for PCPs' removal in full-scale applications. More dedicated research is required to investigate the ozonation or advanced oxidation of (mixtures of) PCPs at real conditions and to look for the best integration of these techniques in a complete treatment chain taking into account biodegradability and toxicity issues. In particular, the formation and mitigation of oxidation by-products have to be a point of attention in the further assessment of the full application potential of ozonation and related AOPs. Apart from the technical aspects, further research is also needed to estimate the economics taking into account the calculation of shadow prices of PCPs and other micropollutants to better assess the true environmental benefits of implementing tertiary treatments.

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Part V
Conclusions

Concluding Remarks and Future Research Needs

M. Silvia Díaz-Cruz and Damià Barceló

Abstract This chapter summarizes the main concluding remarks on analysis, fate, occurrence, and risk to the environment and to humans of personal care products. In addition removal technologies using different nonconventional wastewater treatment processes are being evaluated too. Finally, future research needs in this field will be summarized.

Keywords Chemical analysis, Ecotoxicity, Knowledge gaps, Occurrence, PCPs, Removal, Research trends

Contents

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M.S. Díaz-Cruz and D. Barceló (eds.), *Personal Care Products in the Aquatic Environment*, Hdb Env Chem (2015) 36: 401–408, DOI 10.1007/698_2015_358,

Abbreviations

BAF	Bioaccumulation factor
BMF	Biomagnification factor
GC-MS:	Gas chromatography coupled to mass spectrometry
HPLC-MS	High-performance liquid chromatography coupled to mass spectrometry
HRMS	High-resolution mass spectrometry
K_{ow}	Octanol-water partition coefficient
PCPs	Personal care products
UHPLC-MS	Ultrahigh-performance liquid chromatography coupled to mass spectrometry
WRF	White-rot fungi
WWTPs	Wastewater treatment plant

1 General Remarks

This final chapter presents an overview of analytical methodologies, occurrence data, effects on biota and humans, and removal technologies concerning personal care products (PCPs) in the aquatic environment. So far, many studies have focused on PCPs; however, likely because of the high number and diversity of substances included in such group or due to the limitations of the analytical capabilities (chemical and toxicological analysis), there are still many knowledge gaps that certainly need to be addressed to fully understand the fate and behavior of PCPs in the aquatic environment.

Chemicals used in PCPs comprise a diverse group of substances used in high proportion in daily use products. Many PCPs are bioactive, most are lipophilic, and all, when present in the environment, occur usually at trace concentrations (nanogram-microgram per liter, nanogram-microgram per gram). A number of them are persistent, bioaccumulative, and toxic, whereas others elicit endocrine disruption activity. This group of substances is considered a new class of emerging contaminants that have raised great concern in the last years. As far as we are aware, no PCP ingredients are yet considered in any priority contaminant list worldwide.

Considering the emerging risks posed by PCPs, we believe that this book will be a useful tool to encourage further research on the fate, risks, and mitigation of PCPs in the aquatic environment.

2 Occurrence

In this book we have made a picture of the current PCP distribution in the aquatic environment across the most industrialized areas of the planet: the USA, China, and Europe. Different regulatory frameworks and lifestyle are, therefore, included.

Most of the published literature on PCPs residues in aquatic ecosystems addressed the contamination of fresh surface water and wastewater. Nevertheless, to perform any sound survey on the impact of PCP contamination in the water cycle, groundwater, coastal waters, sediments, soils, and biota should also be included.

There is also a lack of studies concerning the formation of transformation products in the aquatic habitats following natural biotic and abiotic degradation as well as water treatment processes. There is documented evidence that the generated derivatives may pose enhanced toxicity to the ecosystem than the parent compound. Chlorine is essential in the disinfection process of water to prevent the exposure to pathogens, from tap water to swimming pool water. Chlorinated by-products are the most investigated PCP derivatives in the aquatic environment, but research on toxicity is still needed. In this respect, few of them were found to be genotoxic.

Given the temporal variability of a number of PCPs, surveys considering seasonal distribution are of outmost importance. Moreover, some PCPs, as observed in the Los Angeles (California) WWTP, have diurnal variability, such as triclosan. Different spatial patterns were also noticed; however, a large-scale distribution map is not yet possible because solely data from some hotspots in different countries is so far available. In particular, in China, where a dramatic difference between urban and rural areas is observed, data on PCPs pollution is really scattered.

We should realize that as the diversity and quantity of personal care products in use will be continuously increasing, the release of PCPs into the environment will be higher too.

3 Eco(toxicity) and Risk Assessment

The widespread occurrence of PCP residues in the environment is becoming of increasing concern, and improving their ecosystem and human risk assessment constitute a challenge for the scientific community. Still nowadays the majority of (eco)toxicological testing is done using acute toxicity assays. However, as it was demonstrated by other emerging contaminants, pharmaceuticals, for instance, acute toxicity cannot necessarily serve as a reliable substitute for chronic toxicity effects. It is well known that certain substances may elicit adverse effects even following exposure. Consequently, chronic exposure assessment should be promoted as part of overall planning of the proper (eco)toxicological characterization of PCPs. Another gap of knowledge relates to the (eco)toxicity assessment not only of single

substances but also of complex mixtures, how they are found in the environment. In particular, mixtures of PCPs are of concern as usually many of them are simultaneously added to the same formulation. UV filters is a typical example, where up to more than 8 sunscreen agents are mixed together to guarantee the protection within both the UVA and UVB radiation regions. Furthermore, for a more appropriate hazard characterization of PCPs, degradation products will need to be added too.

Another area where improvements are required is the bioavailability assessment of PCP residues by organisms. Generally, the n-octanol/water partition coefficient (Kow) or bioaccumulation (BAF) and biomagnification (BMF) factors are evaluated. However, no direct data on PCP uptake through the food web exist. Hydrophobicity, as measured by the log Kow, was found to be an important descriptor of toxicity, but more research is needed to get deeply insight into the toxicity mechanisms for a correct assessment of the potential ecological risk of PCPs.

Toxicity data, such as EC_{50} values, are typically obtained from the experimental tests using standardized protocols. However, due to cost and time limitations, it is unrealistic to identify all of the potentially harmful PCPs using the standardized animal test protocols. In such cases, the development of computational predictive models offers a good opportunity to fill gaps in data related to environmental risk assessments and regulatory concerns [1]. Additionally, predictive modeling circumvents the need to utilize animal models and thus ethical obligations [2] and has been proven to be an efficient tool for predicting the potentially adverse effects of other chemicals in terms of risk assessment, chemical screening, and priority setting [3–4].

Human exposure to PCPs only has been conducted from recently, in part thanks to the advance in the analytical methodologies. Urine is the most common sample of human origin analyzed, where not only parent but also metabolites have been assessed. Other biological fluids and tissues, breast milk, plasma, serum, placenta, amniotic fluid, and breast tumors have also been analyzed, but to a lesser extent. Epidemiological studies, therefore, appear to be necessary to find potential links between adverse health effects and bioaccumulation of PCPs in humans. Furthermore, information of exposure pathways and the factors affecting these exposures are still lacking.

4 Chemical Analysis

Currently, water analysis of PCPs is not a complex task; however, the preparation and analysis of solid samples is still a challenge. Among solid samples, sewage sludge and biota show the highest difficulty and are, thus, scarcely addressed. Most studies on aquatic biota have focused on fish and some on bivalves. Another relevant issue is the lack of reference materials for methods' validation, which hinders the development of new protocols. Besides, there are not always isotopic labeled compounds for use as surrogates/internal standards for all the target compounds, and those commercially available are rather expensive. Even more

complex is the analytical determination of transformation products. Nevertheless, there have been notorious efforts to identify and characterize derivative substances with the support of powerful high-resolution mass spectrometric (HRMS) techniques.

Over recent years, a number of methodologies for the analysis of chemicals used in PCPs have been developed. Some generic protocols have been described which permit the simultaneous determination of parent compounds and few transformation products. The latest trend has been the shift toward analysis automation through the coupling of sample preparation units and separation-detection platforms, such as online SPE coupled to chromatographic-MS systems, which minimize the sample volume, loss, and contamination during handling and improve repeatability and sensitivity.

The ingredients present in PCPs cover a wide range of physicochemical properties. Consequently, this fact involves both the selection of the proper extraction/purification techniques and the choice of the most suitable chromatographic and detection system. As already stated, PCPs generally appear in the environment at trace level, suggesting that sensitive and selective analytical methods are required for their reliable determination. Despite the analysis of PCPs, using both GC-MS and HPLC- or UHPLC-MS techniques are generally applied. The latest has gained relevance during the last years, when polar metabolites and other transformation products need to be determined. In this respect, matrix effects are relevant and can be a drawback for their quantitative determination. As for the analysis of other emerging contaminants, complex environmental matrices lead to the occurrence of interferences caused by the matrix components. For PCPs, in addition to the typical problems of signal enhancement or suppression observed when analyzing wastewater, sludge, etc, other complex matrices gain importance as a consequence of the use of PCPs. Among these environmental samples stand out seawater, due to the high saline content, and swimming pool waters, due to the high chlorine content.

In the future, bioaccumulation/biomagnification-focused studies should be carefully programmed in order to improve the quality and dimension of the obtained data for getting a more holistic picture of the distribution trends of the PCPs in the aquatic food web.

5 Removal Technologies

Removal efficiencies for organic pollutants in conventional wastewater treatment processes are limited. Considering the increasing use of PCPs and since it is commonly accepted that the major source of PCPs to the environment is WWTPs' effluents, improved elimination rates through the application of more efficient wastewater treatment technologies are urgently needed to avoid severe environmental problems. A number of new technologies to remove emerging pollutants have recently appeared in the wastewater treatment scene, showing the significant improvements achieved in this area in the last years. Among these

technologies, in this book we present some of the most promising ones for the elimination of PCPs.

Biologically based water treatment systems are considered a sustainable, cost-effective alternative to conventional wastewater treatment systems. In particular, constructed wetlands have revealed as a successful alternative solution for the removal of many PCPs from contaminated waters in small communities. However, to scale up wetland systems to big cities appears to be mostly impractical due to the large space requirements. Wherever possible, the easy landscape integration and low energy consumption constitute important advantages for decision-makers to take into consideration constructed wetlands, which make these systems competitive with other water treatment technologies for many specific applications. Nevertheless, systems' maintenance can become expensive if the influent wastewater is highly polluted. Other scarcely explored biologically based technology for the effective degradation of organic pollutants, despite being developed in the 1980s, involves the application of fungi, particularly white-rot fungi (WRF) and their ligninolytic enzymes. However, it has not been tested for the degradation of PCPs in real wastewater effluents and under non-sterile conditions. Several factors need to be considered before the application of this biotechnology as suitable treatments for decontamination in real situations can be done. Major issues involve the design of the bioreactor, the concentration of the biomass (or enzyme), the life cycle of the biomass (or the half-life of the enzyme), the fermentation conditions, and the economic cost. Besides them and as in previous many other technologies, the identification of the compounds formed during the fungal decontamination is critical. The unequivocal identification of these degradation products will improve the understanding of the degradation mechanisms as well as it will be a valuable tool for an improved ecological risk assessment.

Ozonation and advanced oxidation processes have found their place as a feasible replacement for the tertiary step in conventional wastewater treatments for the removal of emerging pollutants. Among them, however, few studies focused on PCPs. The promising results provided by ozonation point out that certainly more research is needed to fully understand the mechanisms and to optimize the major parameters affecting the ozonation performance (T^a, pH, and ozone concentration) for PCP removal in full-scale applications. The treatment using Fe (VI), also a powerful oxidant, has been shown a great potential for PCP removal, especially, for those compounds containing phenol and nitrogen. In the particular case of phenolic compounds, the oxidation by-products formed are no or less toxic than the parent substance, which constitutes a big advantage of this oxidation treatment toward ozonation, for instance. Furthermore, the ferric hydroxide ($Fe(OH)_3$) produced during the treatment is not toxic, contributing to the environmentally friendly characterization of this technology, extensively used in the degradation of other categories of emerging contaminants [5]. However, more research is expected for expanding the Fe (VI) oxidation treatment to the wide diversity of PCPs. Taking into account biodegradability and toxicity issues, the formation and elimination of oxidation by-products of PCPs is regarded as an issue of concern that has to be integrated in the safety evaluation of these technologies for their fully commercial

application as aforementioned for the other removal technologies. Economic suitability is other key aspect to be examined. Advanced treatment processes are still quite expensive to build and maintain and require a high level of energy.

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