

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.

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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

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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 ($<1 \mu\text{g L}^{-1}$) 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 $13,000 \mu\text{g kg}^{-1}$ total solids in suspended matter and $3,211 \mu\text{g kg}^{-1}$ 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.

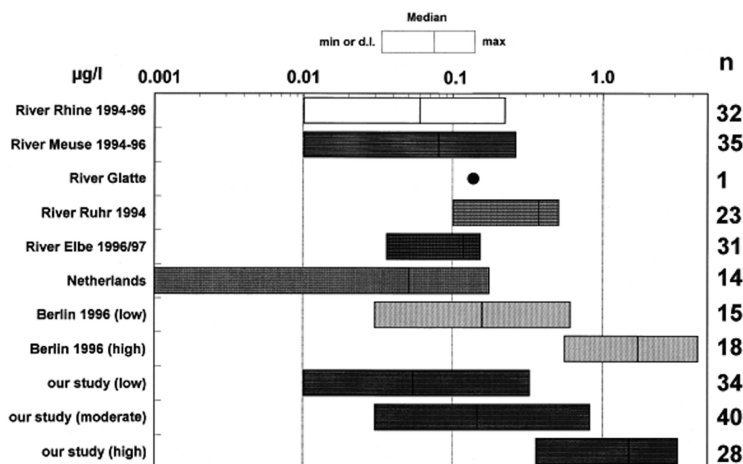


Fig. 1 Galaxolide (HHCB) in surface water samples from lakes and rivers. Low, moderate, and high relate to the proportion of sewage effluents in the aquatic system. Comparison with the results of another group, which examined representative sites in Berlin waters [28], showed good correlation with the 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 $\mu\text{g L}^{-1}$ level, with maximum values of 12.5, 6.8, and $0.52 \mu\text{g L}^{-1}$, 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 $6 \mu\text{g L}^{-1}$ of HHCB and $4.4 \mu\text{g L}^{-1}$ 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 $1.59 \mu\text{g L}^{-1}$ in surface water of areas strongly polluted with sewage, while a comparatively lower mean concentration of $0.07 \mu\text{g L}^{-1}$ 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 $20\text{--}470 \text{ ng L}^{-1}$ [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 $30\text{--}100 \text{ ng L}^{-1}$ [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 ($29\text{--}810 \text{ ng L}^{-1}$) 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'*-tetraacetylenethylenediamine, methoxycinnamic acid, 2-ethylhexylester, drometrizole, HHCB, AHTN, ADBI, AHMI, oxoisophorone, linal, 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 $10 \text{ } \mu\text{g L}^{-1}$) and in the river

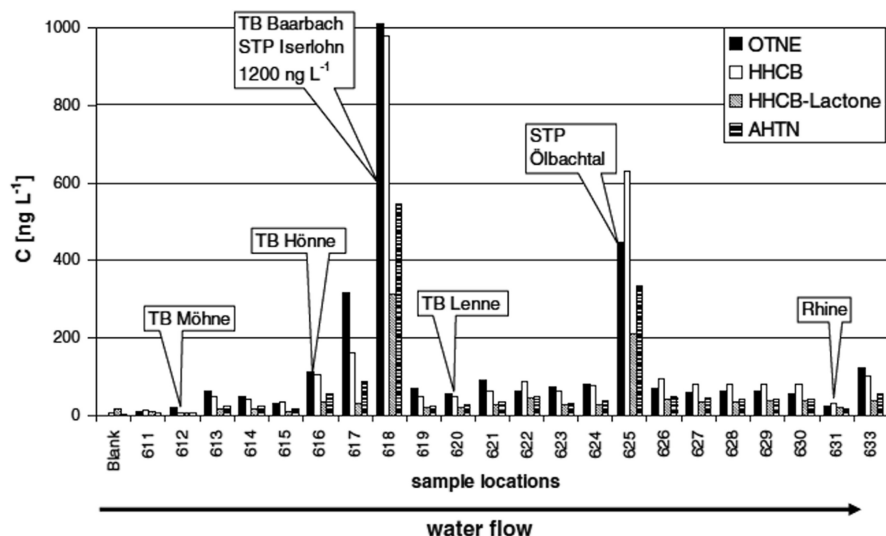


Fig. 2 Concentrations of synthetic fragrances (OTNE, HHCB, AHTN, and the metabolite HHCB-lactone) in surface waters from the Ruhr river basin (*TB* tributary). Picture taken from [33] with permission. The codes 611–633 represent location of sampling sites. OTNE concentrations in Ruhr river water showed 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.

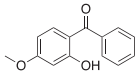
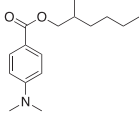
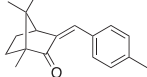
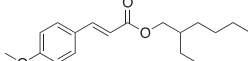
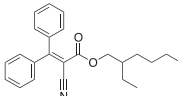
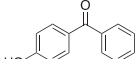
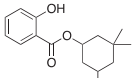
Terzic et al. determined fragrance compounds in municipal waters [42] of the region of Western Balkan (Bosnia and Herzegovina, Croatia, and Serbia). The concentrations measured ranged from $0.337 \mu\text{g L}^{-1}$ for traseolide (TRA) to $16.7 \mu\text{g L}^{-1}$ for amberonne (AMB). Among polycyclic 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 $0.13 \mu\text{g L}^{-1}$, 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 ($6\text{--}28 \text{ ng L}^{-1}$) were higher than those of AHTN ($3\text{--}10 \text{ ng L}^{-1}$); 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 $40\text{--}250 \text{ ng L}^{-1}$ [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

^aEPIWIN v3.12 database^bSoftware calculated value, from SciFinder Scholar Database 2006: <http://www.cas.org/products/sfacad/>^cSyracuse Research Corporation (SRC) database^dKOWWIN 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 $\mu\text{g L}^{-1}$ for BP-3 and OD-PABA, respectively, while shower water samples were in the range 8.2–9.9 and 5.3–6.2 $\mu\text{g L}^{-1}$, 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 ethylhexylmethoxycinnamate (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

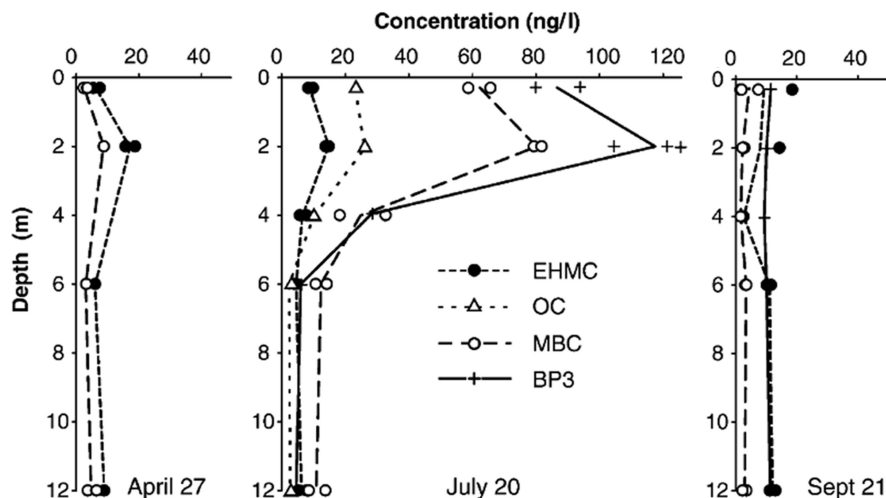


Fig. 3 Vertical concentration profiles of organic UV filters at Hüttnersee in 1998. Note the increased concentrations in July near the lake surface. Picture taken from [55] with permission. The first profile, measured in April 1998, shows low concentrations ($\approx 3\text{--}20\text{ ng L}^{-1}$) and 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 $80\text{--}125$, $60\text{--}80$, and $22\text{--}27\text{ ng L}^{-1}$, 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, $4.13 \times 10^5\text{ m}^3$) 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 $3\text{--}112\text{ ng L}^{-1}$ 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 $4,381\text{ ng L}^{-1}$ (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

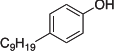
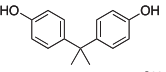
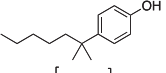
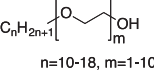
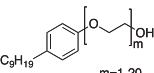
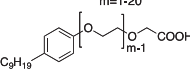
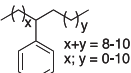
In the present section, phenolic compounds (mainly alkylphenols and their carboxylate and ethoxylate derivatives) and detergents are presented together; although phenols are released into the environment by different sources, they are widely used in the production of detergents. These are generally divided 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.

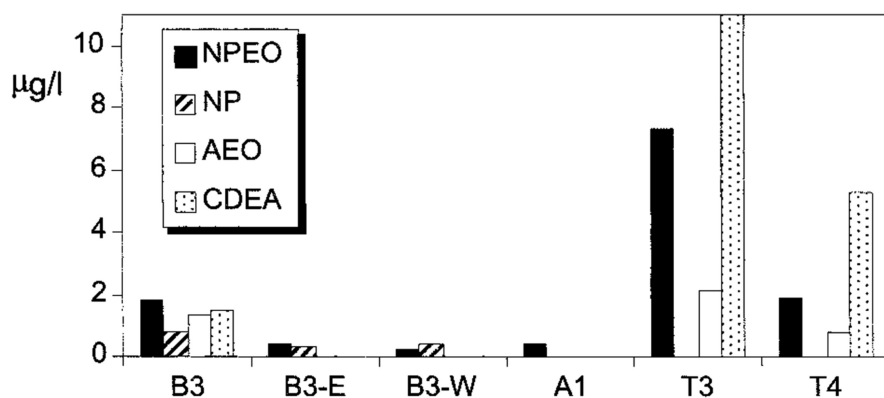
One of the first study on phenolic contaminants as a possible source of estrogenic effects in the aquatic environment was carried out in Germany by Bolz et al. [69]. They determined nine phenolic chemicals in various compartments, and data from 23 water samples (five streams and rivers) showed the predominance 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 nonylphenoethoxylates (NPEO) and NP near the points of wastewater discharges; NP was found in 47% of seawater samples, ranging from 0.15 to $4.1 \text{ } \mu\text{g L}^{-1}$. 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 $92 \text{ } \mu\text{g L}^{-1}$). 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	Nonylphenoethoxylates			4.2 ^d
NPEC	Nonylphenoxy-carboxylates			
LAS	Linear alkylbenzenesulfonates			3.32 for C11.6

^a[65]^b[66]^c[67]^d[68]**Fig. 4** Distributions of nonylphenoethoxylates (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 $31 \mu\text{g L}^{-1}$ for NPEOs, $15 \mu\text{g L}^{-1}$ for NP, and $35 \mu\text{g L}^{-1}$ for nonylphenoxy-carboxylate (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 $4.2 \mu\text{g L}^{-1}$ in eight of 705 screens.

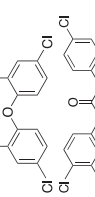
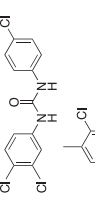
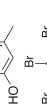
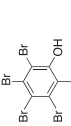
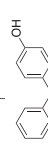
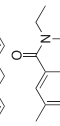
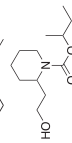
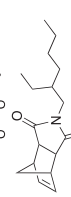
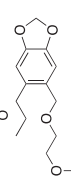
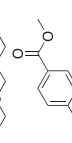
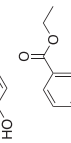
Another monitoring study was carried out in Austria; Hohenblum analyzed 400 ground and surface water samples and reported the concentration levels of various selected estrogenic compounds, including phenolic chemicals and their metabolites [72]. Results related to surface water showed that nonylphenoxycarboxylates 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 $1,500 \text{ ng L}^{-1}$ 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} .

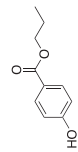
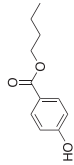
According to the recent pan-European survey on the occurrence of selected polar organic persistent pollutants in groundwater [73], BPA is one of the most relevant compounds detected in European groundwaters, either in terms of frequency of detection (40%) or maximum concentration level ($2.3 \mu\text{g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

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_{OW}
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- <i>o</i> -cresol		$C_7H_4Br_4O$	5.62 ^a
Repellents		<i>p</i> -Benzylphenol		$C_{13}H_{12}O$	3.54 ^a
	DEET	<i>N,N</i> -Diethyl- <i>meta</i> -toluamide		$C_{12}H_{17}NO$	2.18 ^a
	Icaridin	Bayrepel		$C_{12}H_{23}NO_3$	2.57 ^a
	MGK 264	<i>N</i> -Octylbicycloheptenedicarboximide		$C_{17}H_{25}NO_2$	3.76 ^a
Preservatives	PBO	Piperonylbutoxide		$C_{19}H_{30}O_5$	4.75 ^a
		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

^aSyracuse 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

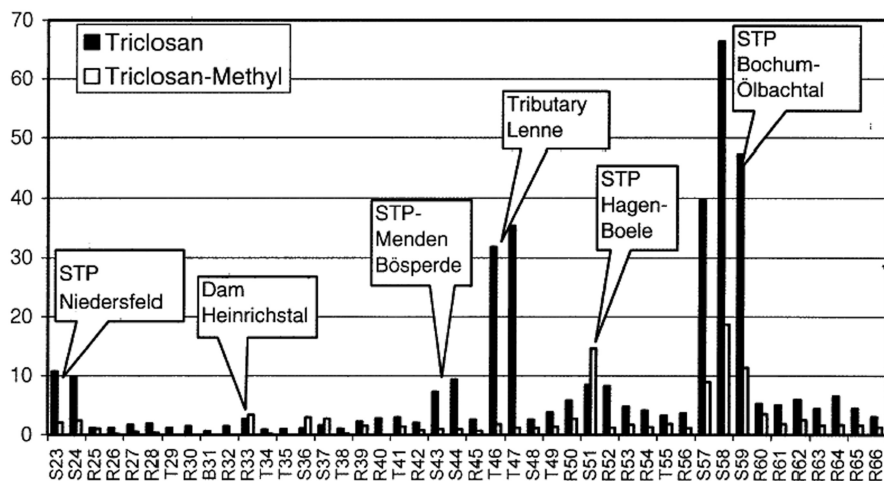


Fig. 5 Monitoring of TCS and MTCS in surface waters (concentrations in ng L^{-1}). *B* field blank, *R* riverine samples, *S* STP effluents, *STP* sewage treatment plant, *T* tributaries. Picture taken from [85] with permission. The concentrations of TCS ranged from <3 to 10 ng L^{-1} in surface water, 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 $38\text{--}57 \text{ ng L}^{-1}$ [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 $0.8\text{--}105 \text{ ng L}^{-1}$ [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

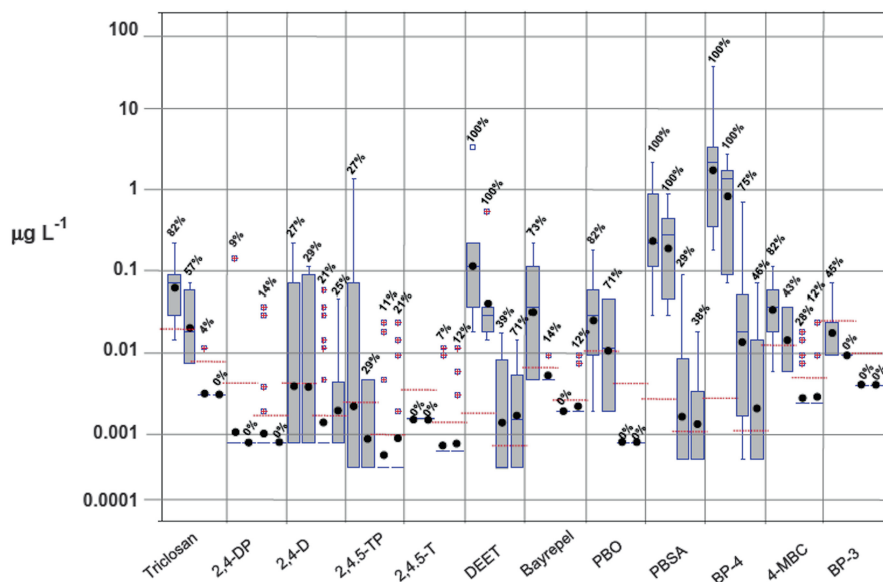


Fig. 6 Box-and-Whisker plots representing the concentrations of PCPs. From *left to right*: influent wastewater, effluent wastewater, surface water, and drinking water. Picture taken from [63] with permission. DEET was detected below 20 ng L^{-1} in both surface and tap water. The figure also shows the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

concentration range ($<0.3\text{--}400 \text{ ng L}^{-1}$) [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 $5,500 \text{ ng L}^{-1}$ 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 $0.4\text{--}13 \text{ ng L}^{-1}$ 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 ($6.7 \text{ } \mu\text{g L}^{-1}$) and Bayrepel ($2.2 \text{ } \mu\text{g L}^{-1}$) 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 $\text{LOQ}\text{--}40 \text{ ng L}^{-1}$. 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- <i>t</i> -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- <i>o</i> -cresol, <i>p</i> -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		
Germany	<i>N,N,N',N'</i> -Tetraacetylenediamine, methoxycinnamic acid, 2-ethylhexylester, drometrizole, HHCB, AHTN, ADBI, AHMI, oxoisophorone, lilial, viridine, dihydromethyljasmonate, cineol, DEET	–	River Aire River water	[91] [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	Groundwater	
		<LOQ (groundwater)		
Germany	AHTN	311 ng L ⁻¹	Surface water	[102]

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