Analytical methods for personal-care products in environmental waters

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Personal-care products (PCPs) are organic chemicals widely used in human life daily. Among the most recently studied PCPs, we can find ultraviolet filters, preservatives, antimicrobials, musk fragrances, insect repellents and siloxanes. PCPs are increasingly important emerging organic contaminants due to their presence in environmental waters.

We present a review of the most important extraction and chromatographic techniques used to determine PCPs in waters. We also review data regarding the occurrence of these compounds in different kinds of environmental waters and the removal of these compounds in sewage-treatment plants.

Keywords: Antimicrobial; Chromatography; Emerging organic contaminant; Environmental waters; Extraction; Musk fragrance; Personal-care product; Sewage-treatment plant; Siloxane; Ultraviolet filter

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1. Introduction

Pharmaceuticals and personal-care products (PPCPs) are included in the category known as the "emerging organic contaminants". Whereas pharmaceuticals have been extensively studied in environmental waters in recent years [1–3] and have been shown to occur widely, until recently, less attention has been paid to the presence of personal-care products (PCPs) in environmental waters. Although some critical reviews have covered research in PPCPs [4], only a few reviews have focused on PCPs.

Several compounds have been included in the group of PCPs. Although some of them (e.g., surfactants) have been widely studied, some groups of compounds were recently included as PCPs. Among these are organic ultraviolet (UV) filters (e.g., benzophenones), preservatives (e.g., parabens), antimicrobials (e.g., triclosan), musk fragrances (e.g., nitro musks), insect repellents [e.g. N,N-diethyl-m-toluamide (DEET)], and siloxanes [e.g., decamethylcyclopentasiloxane (D5)].

PCPs are organic chemicals included in different products widely used in daily human life (e.g., lotions, gels, cosmetics and even food), so considerable amounts of PCPs are used every day. After use, they may be absorbed by the body and excreted by urine or washed off after application [5]. As a consequence, significant amounts of these products and their metabolites go down the drain and reach sewage-treatment plants (STPs) [6,7]. Here, the PCPs are partly eliminated from influent wastewater during sewage treatment, so some of them are retained in the sewage sludge or are present in the effluents [8]. Because effluents are usually discharged into surface waters, PCPs can be present in the environment.

Some of these PCPs (e.g., organic UV filters and preservatives) have shown endocrine-disrupting effects [6]. Although, to date, there are few data on the fate and the behavior of these substances in the environment, several reports indicate the presence of all these compounds in sewage and river waters [9–11]. All these studies confirm some PCPs are not well removed and improved technologies are needed. Miège et al. [12] created a database regarding the fate of PPCPs in wastewaters and studied the removal of these compounds. STPs with conventional, activated sludge treatment showed a high removal efficiency for triclosan (>80%), whereas the removal efficiency was under 60% for

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several musk fragrances. Some authors have reported that UV-based processes (UV and UV/H_2O_2) are effective at removing several contaminants. Of these contaminants, DEET showed a high removal (>90%) [13].

Determining water quality is a priority for human health, especially given the interest in reusing wastewater, so selective, sensitive methods are needed to determine low levels of PCPs in environmental waters. One trend in extraction techniques is to decrease the consumption of organic solvents. For example, microextraction techniques or stir-bar sorptive extraction (SBSE) have been used to determine organic UV filters, fragrances and preservatives [14–16], but the variety of polar commercial materials is limited. Solid-phase extraction (SPE) presents a wide range of sorbents and is the extraction technique preferred by most authors [6,17,18]. The analytical methods for detecting and quantifying PCPs in waters are generally based on gas chromatography (GC) or liquid chromatography (LC) coupled to mass spectrometry (MS) or tandem MS (MS^2). The decision to use either GC or LC is based on to physico-chemical properties of the target analytes. The most apolar and volatile PCPs, such as musk fragrances and siloxanes, are best determined using GC-MS and GC-MS^2 [19–21], but other PCPs have to be derivatized before GC analysis can be applied. It is therefore better to use LC for determining these PCPs at low environmental levels [6,17,22].

We provide an overview of the most relevant analytical methods for determining some PCPs of recent interest and their occurrence in environmental waters.

2. Personal-care products

The name PCPs is a generic term that includes the organic compounds that are used in such products. All new contaminants are reviewed continually and, in recent years, new groups have appeared. The literature has classified PCPs into five groups according to the following areas in which they are used: organic UV filters; antimicrobials; preservatives; musk fragrances; and, insect repellents. Moreover, siloxanes were also recently classified as PCPs.

Not only PCPs but also their by-products need to be taken into account because, in some cases, these by-products are even more environmentally persistent [23].

2.1. Organic UV filters

Organic UV filters are very often found in sunscreen cosmetics and other PCPs as protection against UV radiation. Most of these compounds are lipophilic (log K_{ow} 4–8) with conjugated aromatic rings and are relatively stable against biotic degradation [24]. Regarding the toxicity of these compounds, it has been reported that the estrogenic activity of most of the commonly used organic UV filters is in the range of other well-characterized estrogenic chemicals (e.g., estradiol) [6,10,24]. The European Union (EU) Cosmetics Directive permits the commercial use of 26 organic UV filters. The organic UV filters most commonly found in water samples are:

- benzophenones (BP-1, BP-3, BP-4);
- 2-phenylbenzimidazole-5-sulfonic acid (PBSA);
- 4-methyl-benzylidene camphor (4-MBC);
- ethylhexyl methoxycinnamate (EHMC);
- isoamyl methoxycinnamate (IAMC);
- octocrylene (OC); and,
- octyl dimethyl-p-aminobenzoate (OD-PABA) [6,16, 22].

2.2. Antimicrobials

Antimicrobials are chemicals that kill or prevent the growth of microbes (e.g., bacteria, viruses, fungi or protozoa). Because of these properties, antimicrobials are widely used in PCPs. They have received increasing attention because of their pronounced microbial and algal toxicity, and their potential for fostering antimicrobial resistance [25]. The most commonly used are triclosan (TCS) and triclocarban (TCC), TCS having been reported in different kinds of water [25,26]. TCS is also known to undergo phototransformation in aqueous solution to form 2,8-dichlorodibenzo-*p*-dioxin (2,8-DCDD). Further, degradation products (e.g., methyl-TCS) have been studied in environmental waters [27].

2.3. Preservatives

Synthetic preservatives are widely included in consumer PCPs. The most commonly used are parabens [e.g., methylparaben (MPB), ethylparaben (EPB), propylparaben (PPB), benzylparaben (BzPB) and butylparaben (BPB)]. Parabens are *p*-hydroxybenzoate esters used to avoid spoilage and thus increase the shelf life of a wide variety of products (e.g., pharmaceuticals, soaps, gels, creams and food). They formulate well because they have neutral pH, no perceptible odor or taste, and do not cause discoloration or hardening. Until recently, parabens were commonly used as preservatives in cosmetics and pharmaceuticals because of their supposedly low toxicity, broad spectrum of activity, inertness, worldwide regulatory acceptance, biodegradability and low cost. Nowadays, there is an increasing trend to avoid using parabens because of growing evidence that they are endocrine disrupters [28].

2.4. Musk fragrances

Synthetic musk compounds are among the most important substances used in the fragrance industry. Nitro, polycyclic and macrocyclic musk fragrances are all used commercially. The EU decided to limit the use of