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Review

Advances in analytical methods and occurrence of organic UV-filters in the environment — A review

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HIGHLIGHTS

- Studies about analysis and occurrence of UV-filters in environment were reviewed.
- River water showed the highest and broadest UV-filter concentrations.
- UV-filters are poorly studied in soil and sediments, but detected in the μg/L range.
- Tens to thousands of ng/g of BP3 were detected in aquatic biota.
- Benzophenone derivatives are the most studied and detected compounds.

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ABSTRACT

UV-filters are a group of compounds designed mainly to protect skin against UVA and UVB radiation, but they are also included in plastics, furniture, etc., to protect products from light damage. Their massive use in sunscreens for skin protection has been increasing due to the awareness of the chronic and acute effects of UV radiation. Some organic UV-filters have raised significant concerns in the past few years for their continuous usage, persistent input and potential threat to ecological environment and human health. UV-filters end up in wastewater and because wastewater treatment plants are not efficient in removing them, lipophilic compounds tend to sorb onto sludge and hydrophilics end up in river water, contaminating the existing biota. To better understand the risk associated with UV-filters in the environment a thorough review regarding their physicochemical properties, toxicity and environmental degradation, analytical methods and their occurrence was conducted.

Higher UV-filter concentrations were found in rivers, reaching 0.3 mg/L for the most studied family, the benzophenone derivatives. Concentrations in the ng to μg/L range were also detected for the *p*-aminobenzoic acid, cinnamate, crylene and benzoyl methane derivatives in lake and sea water. Although at lower levels (few ng/L), UV-filters were also found in tap and groundwater. Swimming pool water is also a sink for UV-filters and its chlorine by-products, at the μg/L range, highlighting the benzophenone and benzimidazole derivatives. Soils and sediments are not frequently studied, but concentrations in the μg/L range have already been found especially for the benzophenone and crylene derivatives. Aquatic biota is frequently studied and UV-filters are

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Abbreviations: 1-Oc, 1-octanol; [C_4MIM]PF_6, 1-butyl-3-methylimidazolium hexafluorophosphate; [HMIM][FAP], 1-hexyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate; AcOH, acetic acid; Ac, acetone; ACN, acetonitrile; ASE, accelerated solvent extraction; BSTFA, N,O-bis(trimethylsilyl)trifluoroacetamide; CAS, Chemical Abstracts Service; CHL, chloroform; CYHex, cyclohexane; CYPN, cyclopentane; DAD, diode-array detection; DCM, dichloromethane; DI, direct-immersion; DLLME, dispersive liquid–liquid microextraction; EC_{50}, Half maximal effective values; EtOH, ethanol; Eth, ether; EA, ethyl acetate; GC–MS, gas chromatography coupled with mass spectrometry; GPC, gel permeation chromatography; HPLC, high performance liquid chromatography; HS, headspace; HAS, human serum albumin; Hep, heptane; Hex, hexane; IL, ionic liquid; IL-SDME, ionic liquid-based single-drop microextraction; IL-USAEME, ionic liquid based ultrasound-assisted emulsification microextraction; K_{OC}, organic carbon/water partition coefficient; K_{OW}, octanol–water partition coefficient; LC, liquid chromatography; LD, liquid desorption; LLE, liquid–liquid extraction; LODs, limits of detection; MAE, microwave assisted extraction; MALLE, membrane-assisted liquid–liquid extraction; MASE, membrane assisted solvent extraction; MeOH, methanol; MEPS, microextraction by packed sorbent; MME, micelle mediated extraction; MNPs-based dSPE, magnetic nanoparticles dispersive solid-phase extraction; MSTFA, N-methyl-N-(trimethylsilyl)trifluoroacetamide; MTB-STFA, N-methyl-N-(*tert*-butyldimethylsilyl)trifluoroacetamide; PCPs, personal care products; PDA, photodiode array detector; PDMS, poly(dimethylsiloxane); PLE, pressurized liquid extraction; POCIS, polar organic chemical integrative sampler; PrOH, propanol; Rec, recovery; SBSE, stir bar sorptive extraction; SEHSDT, sequential extraction with high-speed dispersion tool; SLE, solid–liquid extraction; SPE, solid-phase extraction; SPF, sun protection factor; SPLE, selective pressurized liquid extraction; SPMDs, semipermeable membrane devices; SPME, solid phase microextraction; TD, thermal desorption; TCE, tetrachloroethylene; THF, tetrahydrofuran; Tl, toluene; UPLC, ultra-performance liquid chromatography; USE, ultrasound extraction; UV, ultraviolet; WTP, water treatment plant; WWTP, wastewater treatment plant.

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found in the ng/g-dw range with higher values for fish and mussels. It has been concluded that more information regarding UV-filter degradation studies both in water and sediments is necessary and environmental occurrences should be monitored more frequently and deeply.

Contents

1. Introduction

In the past few years, concern for sunburns, premature skin aging and the risk of developing skin cancer has raised and ultraviolet (UV) radiation has been considered a public health threat. UV radiation can reach the earth surface in both UVA (315–400 nm) and UVB (280–315 nm) ranges, while solar light UVC (200–280 nm) is absorbed by ozone in the stratosphere (Kim and Choi, 2014).

UV-filters are compounds designed mainly to protect our skin against damage by UVA and UVB radiation. These compounds can either be organic (chemical) absorbers or inorganic (physical) blockers, depending on the basis of their mechanism of action. Organic UV-filters absorb UV radiation and the absorbed energy produces an excited state of the molecule, giving it higher energy content. The excess of energy is dissipated by emission of higher wavelengths or relaxation by photochemical processes, for example isomerisation and heat release (Abdelraheem et al., 2015). Inorganic sunscreens, like titanium dioxide and zinc oxide, protect the skin by reflecting and scattering UV radiation (Crista et al., 2014). In this review, only organic UV-filters are considered because of their frequent use at higher quantities.

Although UV-filters are mainly incorporated in cosmetics (such as sunscreen lotions, skin care, facial makeup and lip care products), they are also included in a wide range of products including plastics, adhesives, paint and rubber in order to protect from UV degradation (Brooke et al., 2008; Gackowska et al., 2014). Personal care products with a high sun protection factor (SPF) values are the most popular among consumers; however, the 'false' sense of protection leads to prolonged sun exposure. In order to enhance the SPF values, several combinations of UV-filters are used (both organic UVA and UVB and inorganic) and their total concentration in the final products increased. This results in an increased population exposure to a higher and greater diversity of UV-filters (Chisvert et al., 2001; Manova et al., 2013).

At some point, the majority of cosmetic products will find their way into wastewater (due to bathing and washing activities) and consequently into rivers, lakes and ocean, so it is not surprising that UV-filters are found in the environment (Abdelraheem et al., 2015; Duirk et al., 2013). A schematic of the major pathways of UV-filters in the environment was presented by Giokas et al. (2007) and can be completed with the understanding of the urban water cycle presented by Pal et al. (2014). UV-filters are very persistent in the environment due to their massive use and physicochemical properties (Liu and Wong, 2013; Rodil et al., 2009a) and their environmental issues are related mainly to their endocrine disrupting potential, systemic circulation and probable exposure of all tissues in the body in humans (Krause et al., 2012), mammals (Schlumpf et al., 2004), amphibian and also fish (Blüthgen et al., 2014).

The first review specifically oriented to UV-filters appeared in 1999 by Daughton and Ternes and the second in 2007 by Giokas et al. However, other reviews regarding specific topics under UV-filters also exist, such as BP3 (Kim and Choi, 2014), UV-filter transformation products (Santos et al., 2012) and UV-filter occurrence in biota (Gago-Ferrero et al., 2012). Overviews of analytical methods for determining UV-filters in cosmetic products (Salvador and Chisvert, 2005), human samples (Jiménez-Díaz et al., 2014) and advanced aspects of current LC–MS/MS methodology (Gago-Ferrero et al., 2013a) were also published, as well as regarding toxicity of few UV-filters in the aquatic environment (Brausch and Rand, 2011).

Therefore, the main objective of this review is to summarize the scattered information about the utilization of UV-filters and to explain why this class of compounds has raised so much concern in the past years. It is also expected to summarize and analyze the UV-filter profiles in several matrices (water, soil, sediments and biota), describe the analytical methods most used and analyze the overall distribution and fate of UV-filters in the environment.

2. UV-filter characterization

2.1. Chemistry

The most used UV-filters in today's worldwide industry and the most detected in environmental matrices are represented in Fig. 1, according to their chemical family. Those whose use in cosmetics is