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UV filters and benzotriazoles in urban aquatic ecosystems: The footprint of daily use products

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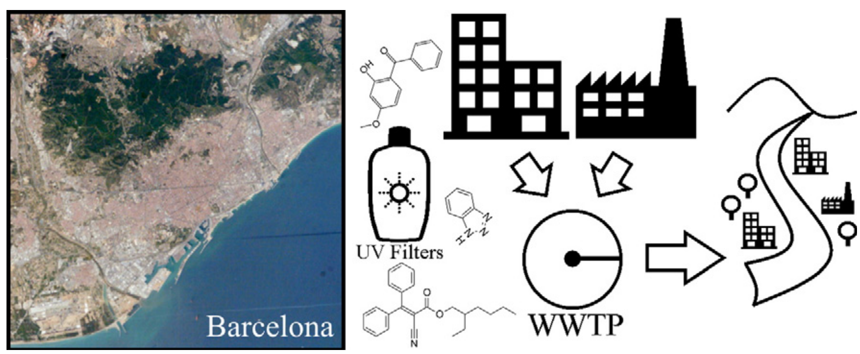
HIGHLIGHTS

- UV-filters (UV-Fs) and benzotriazoles were analysed in two rivers from a densely-developed area.
- UV-Fs and benzotriazoles were detected in all water, wastewater, and solid matrixes.
- The removal rates of UV-Fs and benzotriazoles in the WWTPs were highly variable.
- WWTPs effluents are pointed out as the major source of contamination.
- Estimated hazard quotients for wastewaters showed that benzotriazoles are a risk.

GRAPHICAL ABSTRACT



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ABSTRACT

The increased use of beauty and other daily use products, in particular those containing UV filters (UV-Fs) and benzotriazoles, results in their introduction in significant amounts into the aquatic environment. In this study, we aim to assess the occurrence and impact of UV-Fs and benzotriazoles in aquatic ecosystems in the metropolitan area of Barcelona, Spain. River water samples from the Llobregat and Besòs Rivers were analysed together with sediment, suspended particulate matter, and wastewater samples from 6 wastewater treatment plants (WWTPs) along their basins. The analysis of 6 UV-Fs and 2 benzotriazoles in water samples was performed using an automatized on-line solid phase extraction coupled to liquid chromatography tandem mass spectrometry (SPE-HPLC-MS/MS) method. The analysis of the target compounds in the suspended solids and in the sediments was performed by HPLC-MS/MS. The analysis of the water samples showed the ubiquitous presence of UV-Fs. Benzotriazole (BZT; partition coefficient octanol-water Log $K_{ow} = 1.23$) and methylbenzotriazole (MeBZT; Log $K_{ow} = 1.89$) had the highest levels in both river water and wastewater. Removal rates in the selected WWTPs were highly variable (4–100%). Concentrations of lipophilic UV-Fs (Log K_{ow} 4.95–7.53) in suspended particulate matter from wastewaters were high (up to 1,031,868.2 ng g^{-1}dry weight (dw)), whereas in sediment the concentrations were always below 300 ng g^{-1} dw. The risk assessment expressed in terms of hazard quotients (HQs) revealed that most UV-Fs were not likely to produce adverse ecotoxicological effects against the living organisms assayed in river waters and influent wastewaters at the concentrations observed. However, HQs above 1 were obtained for BZT and MeBZT in effluent wastewaters discharged to the river.

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1. Introduction

Excessive UV radiation exposure constitutes a well-known origin of pathological conditions such as skin burn, erythema, premature skin aging, photodermatoses, immunosuppression and skin cancer (Gasparro, 2000). As a consequence, nowadays UV radiation is considered a public health treat all over the world. UV filters (UV-Fs) are a wide group of chemicals that provide effective protection from UV radiation. These compounds are used in many consumers' goods, such as personal care products, and are also valuable additives in industrial products, where they prevent the deterioration of physical properties of materials, including decolouring and cracking (Fent et al., 2010). Benzotriazoles constitute a family of high production additives present in daily use products such as dishwasher detergents, corrosion inhibitors, and defrosting products as anti-icing agent. Benzotriazole is also a precursor of several derivatives which have UV light stabilizing capacities such as UV320 and UV327. These benzotriazole derivatives can be found for instance in textiles and plastic materials, including food and beverage containers, to preserve the integrity of materials and foodstuff (Molins-Delgado et al., 2015; Zhang et al., 2011).

These compounds are released into the environment through urban and industrial sewage waters or *via* recreational aquatic activities for UV-Fs or de-icing operations in aeronautics for benzotriazoles, making them ubiquitous. Previous studies have reported their occurrence in surface waters at concentrations in the range 1–862 ng l^{-1} (Ekpeghere et al., 2016; Gago-Ferrero et al., 2013a; Kasprzyk-Hordern et al., 2008; Tsui et al., 2014), in groundwater (Jurado et al., 2014; Serra-Roig et al., 2016) up to 55 ng l^{-1} and 1980 ng l^{-1}respectively, and in the range 1–8900 ng l^{-1} in wastewaters (Ekpeghere et al., 2016; Langford et al., 2015; Liu et al., 2012). UV-Fs have been found to adsorb onto sediments (Gago-Ferrero et al., 2011a; Langford et al., 2015) at concentrations in the range 3.2–870 ng g^{-1} dry weight (dw), and in sewage sludge (Gago-Ferrero et al., 2011b) between 260 and 970 ng g^{-1} dw. These studies also pointed out that the removal of these chemicals in wastewater treatment plants (WWTPs) was pretty variable, depending on the physical-chemical properties of the substances and the water treatment applied. The most lipophilic UV-Fs tend to bioaccumulate, for instance in fish (Fent et al., 2010; Gago-Ferrero et al., 2013c), mussels (Cunha et al., 2015), and dolphins (Gago-Ferrero et al., 2013b). The occurrence of these compounds has already been reported in human breast milk (Zafra-gómez et al., 2015), semen (León et al., 2010), and human placental tissue (Valle-Sistac et al., 2016; Vela-Soria et al., 2014).

There are little data currently available on the adverse effects the continuous exposure to these compounds may cause to living organisms. *In vitro* and *in vivo* assays have shown that these xenobiotics may interfere with the normal development in aquatic and terrestrial organisms (Klammer et al., 2007; Weisbrod et al., 2007). Some UV-Fs have been found to have similar estrogenic effects as those displayed by the natural sex hormone 17-β-estradiol (Fent et al., 2014; Klann et al., 2005; Kunz and Fent, 2006). Besides, the properties and environmental behaviour of the formed metabolites and other transformation products are yet mostly unknown. Data on the toxicity of benzotriazoles is scarce; they have been found to be toxic to aquatic organisms and slightly toxic to humans (Breedveld et al., 2002; Hem et al., 2003).

The aim of this study was to assess the occurrence of UV-Fs and benzotriazoles, in surface waters from the Besòs River and Llobregat River, in the wastewaters from 6 WWTPs along the two basins, in the suspended particulate matter and in the sediments from the urban aquatic environment of the large populated city of Barcelona, Spain. The compounds' removal rates in the WWTPs as well as the risk posed to selected aquatic species were also investigated.

2. Experimental

2.1. Reagents and materials

Highest purity (>99%) benzophenone-1 (BP1), benzophenone-3 (BP3), 4-hydroxybenzophenone (4HB), 4,4′-dihidroxybenzophenone (4DHB), ethylhexyldimethyl PABA (OD-PABA), octocrylene (OC), ethylhexyl methoxycinnamate (EHMC), ethyl PABA (EtPABA) and benzotriazole (BZT), were obtained from Sigma-Aldrich (Steinheim, Germany); 4-methylbenzylidene camphor (4MBC, 99% purity) was supplied by Dr. Ehrenstorfer (Augsburg, Germany) and 5-methyl benzotriazole (MeBZT, >99% purity) by TCI (Zwijndrecht, Belgium). Isotopically labelled standards 2-hydroxy-4-methoxy-benzophenone-2′,3′,4′,5′,6′-d_5 (BP3-d_5) and 3-(4-methylbenzylidene-d_4)camphor (99% purity) from CDN isotopes (Quebec, Canada) were used as internal standards.

Solvents HPLC-grade water, methanol (MeOH), acetone, ethanol (EtOH) and acetonitrile (ACN) were from J.T. Backer (Deventer, The Netherlands). Formic acid and alumina (aluminium oxide, 99%) were provided by Merck. The nitrogen (99% purity) used to evaporate samples was supplied by Air Liquide (Barcelona, Spain). The PURADISC syringe filters and the glass fibre filters (1 μm) and nylon membranes (0.45 μm) provided by Whatman International Ltd. (Maidstone, UK).

Standards and isotopically labelled internal stock standard solutions were prepared in MeOH at 200 mg l^{-1} and stored in the dark at −20 °C. From these solutions, a mixture standard solution containing all the UV filters and benzotriazoles was prepared in MeOH at 20 mg l^{-1}. Working solutions were freshly prepared by appropriate dilution of the mixed stock standards solution in MeOH. Table A1 in the Supporting Information summarises the name, abbreviation, and the Chemical Abstract Service (CAS) number of the selected UV-Fs.

2.2. Sampling area

In this study we performed a comprehensive analysis of environmental water and sediment samples collected in two Mediterranean river basins and in the WWTPs located in their basins close to Barcelona. Numerous cosmetic companies, as well as other kind of industries (pharmaceutical, pigments, textiles, plastic production…) are located along the basin of the studied rivers. The considered urban ecosystems constitute a good example of highly transformed environments, as a consequence of decades of human pressure, industrial contamination, resource depletion and natural ecosystem transformations.

Barcelona is the second biggest city in Spain, and one of the most industrialised cities in the Mediterranean coast (Palanques and Diaz, 1994). The city is enclosed by the mouths of the rivers Llobregat and Besòs and by the Serra de Collserola. Having 102.2 km^2, the metropolis has a permanent population of >1.6 million inhabitants (inhs) and a population density of 15,867 inhs. km^{-2} (Ajuntament de Barcelona, 2013). Besides, the surrounding Metropolitan Area of Barcelona (AMB), composed by 36 municipalities under direct influence of the city, has a population of 4.8 million inhs. with a density of 1926 inhs. km^{-2} (Institut d'Estadística de Catalunya, 2013).

The Llobregat River is a fast-flowing Mediterranean river that alternates from dry to torrential flows, with a mean flow rate of 19 m^3 s^{-1} (Agència Catalana de l'Aigua, 2013). Spreading along 5000 km^2, the river basin is composed of several tributary rivers, Cardener and Anoia Rivers being the most important ones, as shown in Fig. 1 (Rodríguez, 2001). The Llobregat's mouth constitutes the southwestern frontier of the city of Barcelona. Contamination is of great concern as this river is the main drinking water source to many municipalities of the AMB and part of Barcelona (Piedrafita, 1995).

Bounding Barcelona to the North, the Besòs River's mouth is at the end of a basin that occupies 1038 km^2. The main river has only 17.7 km, but its basin integrates several tributary drainage rivers, *i.e.* the Congost, Mogent, Tenes, Riera de Caldes and Ripoll Rivers which