Ecotoxicology and Environmental Safety 152 (2018) 98–103

Contents lists available at ScienceDirect

Ecotoxicology and Environmental Safety

journal homepage: www.elsevier.com/locate/ecoenv

Pollution patterns and underlying relationships of benzophenone-type UV-filters in wastewater treatment plants and their receiving surface water

Ming-hong Wu, Jian Li, Gang Xu, Luo-dan Ma, Jia-jun Li, Jin-song Li, Liang Tang*

Institute of Applied Radiation of Shanghai, School of Environmental and Chemical Engineering, Shanghai University, Shanghai 200444, PR China

ARTICLE INFO

Keywords:
BP-UV filters
Surface water
Wastewater treatment plant
Cosmetics factory
Environmental risk assessment

ABSTRACT

The environmental behaviors of emerging pollutants, benzophenone-type UV filters (BP-UV filters) and their derivatives were investigated in four wastewater treatment plants (WWTPs), and their receiving surface waters in Shanghai. The concentration level of selected BP-UV filters in the WWTPs was detected from ng L^{-1} to μg L^{-1}. BP (621–951 ng L^{-1}) and BP-3 (841-1.32 $\times$ 10^3 ng L^{-1}) were the most abundant and highest detection frequency individuals among the target BP-UV filters in influents, whereas BP (198–400 ng L^{-1}), BP-4 (93.3–288 ng L^{-1}) and BP-3 (146–258 ng L^{-1}) were predominant in effluents. BP-UV filters cannot be completely removed and the total removal efficiency varied widely (−456% to 100%) during the treatment process. It can be inferred that the usage of BP and BP-3 are higher than other BP-UV filters in the study area. The lowest and highest levels were BP-2 (ND-7.66 ng L^{-1}) and BP-3 (68.5-5.01 $\times$ 10^3 ng L^{-1}) in the receiving surface water, respectively. Interestingly, the seasonal variation of BP-3 is larger than those of other BP-UV filters in surface water from Shanghai. There is no obvious pollution pattern of BP-UV filters in the surface water from the cosmetic factory area. The correlation analysis of BP-UV filters between WWTPs effluents and nearby downstream water samples suggested that BP-UV filters emitted from some WWTPs might be the main source of receiving surface water. Preliminary risk assessment indicated that the levels of BP-UV filters detected by the effluent posed medium to high risk to fish as well as other aquatic organisms.

1. Introduction

Increasing use of UV filters as more and more people have recognized the damaging effects of UV (Ultraviolet) light from sunlight on human skin and other materials (Ekpeghere et al., 2016). In general, three to eight UV filters are added to commercial sunscreens to protect consumers from UV radiation and improve the light stability of the product (Li et al., 2007). It is reported these organic UV-shielding compounds that are used extensively in sunscreens and other cosmetic products in concentrations up to 10% (Fent et al., 2010). The most used UV-filters in today's worldwide industry and the most detected in environmental matrices are including benzophenone (BP), 2-hydroxy-4-methoxy benzophenone (BP-3), 5-Benzoyl-4-hydroxy-2-methoxybenzenesulfonicacid (BP-4), 2,2′,4,4′-Tetrahydroxybenzophenone (BP-2), 2,3,4-Trihydroxybenzophenone (2,3,4-OH-BP) and 2,4-dihydroxybenzophenone (BP-1), 4-Hydroxybenzophenone (4-OH-BP) (Ramos et al., 2015).

UV filters are presented in many products of daily use such as sunscreen products, skin creams, cosmetics, hair sprays, body lotions, hair dyes, shampoos, and other personal care products (PCPs) (Li et al., 2007). The UV filters will be finally discharged into the environment in their entire life of a wide range of applications. Recently, many studies have reported on BP-UV filters in water system (Bluthgen et al., 2012; Cuderman and Heath, 2007; Rodil et al., 2009; Tsui et al., 2014b), sediment (Gago-Ferrero et al., 2011a; Zhang et al., 2011), sewage sludge (Gago-Ferrero et al., 2011b; Nieto et al., 2009), fish (Sang and Leung, 2016; Zenker et al., 2008), and even in human urine (Kunisue et al., 2012).

It is worth our attention that some UV-filters may act as endocrine disruptors. BP-2, BP-1 and 4-OH-BP exhibit estrogenic activity in human *breast cancer cell line MCF-7* (Suzuki et al., 2005). BP-3 at concentration of 1.0 g L^{-1} could increase *catalase (CAT)* activities in *tetrahymena thermophila cells* (Gao et al., 2013). 2,3,4-OH-BP shows little effects on the *androgenic* activity of dihydrotestosterone in *rat fibroblast cell line NIH3T3* presumably because of sterichindrance (Suzuki et al., 2005). BP4 displays *antiandrogenic antiestro-genic, and estrogenic* activities in vitro testing of fish (Kunz et al., 2006). Moreover, BP-4 not only interferes with the expression of genes involved in hormonal pathways and steroidogenesis, but also interferes with the *sex hormone system* of fish (Zucchi et al., 2011).

* Corresponding author.
E-mail address: tang1liang@shu.edu.cn (L. Tang).

https://doi.org/10.1016/j.ecoenv.2018.01.036
Received 26 November 2017; Received in revised form 10 January 2018; Accepted 16 January 2018

UV filters enter into the aquatic environment directly as a result of water recreational activities when they are washed off from the skin and/or clothes, as well as production link (Gago-Ferrero et al., 2011b). The migration of UV-filters through urban drainage systems and wastewater treatment plants (WWTPs) to the receiving waters is an important pathway for contamination of the aquatic environment (Kupper et al., 2006). However, the treatment of traditional WWTPs for UV-filters is not really effective; meanwhile the treated wastewater will be ultimately discharged into adjacent surface water, leading to high occurrence of UV filters in the surrounding environments. To date, there are still some knowledge gaps need to be further clarified in their environmental behaviors, including occurrence, mass loading, environmental risk assessment in WWTPs and their underlying interrelationships with the receiving waters. Besides, the cosmetics factory may be another potential source of surface emissions; however, study focuses on this is scarce until now, and such significant information is urgent to be clarified.

The investigation is conducted to monitor and analyze the occurrence of selected BP-UV filters in Shanghai, including influents and effluents in WWTPs and their receiving waters, Huangpu River (the largest river in Shanghai flows through urban and suburban areas), Suzhou River and Yunzao Brook (The second and third largest river in Shanghai, flow through the cosmetics industry area), and the removal of these analytes in WWTPs were studied at the same time. In addition, we estimated the mass loading and the underlying relationships of benzophenone-type UV-filters in wastewater treatment plants and their receiving surface water. Furthermore, preliminary assessment of the environmental risks of the target BPs to aquatic species based on the calculation of risk quotients (RQs) were assessed. The results will provide background data in pollution patterns of benzophenone-type UV-filters in the study area.

2. Materials and methods

2.1. Chemicals and materials

Standards of benzophenone-2 (purity of 98%) and benzophenone-3 (99%) were obtained from Chemservice (West Chester, PA, USA) and AccuStandard Inc. (New Haven, CT, USA), respectively. BisphenolA-d16 (98%), benzophenone (99.5%), benzophenone-4 (99.5%) were obtained from Dr. Ehrenstorfer GmbH (Augsburg, Germany). Benzophenone-1 (98%) and 2,3,4-Trihydroxybenzophenone (98%) were obtained from Anpel Scientific Instrument Corporation (Shanghai, China). 4-Hydroxybenzophenone (98%) was obtained from Toronto Research Chemicals (North York, Canada). Caffeine-C_{13} (98%) was purchased from Cerilliant Corp. (Austin, TX, USA). Molecular structures and physicochemical properties of the seven targeted BP-UV filters are summarized in Table S1. HPLC grade dichloromethane and methanol were obtained from Merck (Darmstadt, Germany). Caffeine-C_{13} and BPA-d16 were used as internal standards. 1 mg of individual standard (BP, BP-1, BP-2, BP-3, BP-4, BPA-d16, 4-OH-BP and 2,3,4-OH-BP) was accurately weighed and transferred in amber glass flasks, and then diluted with methanol to 10 mL.

2.2. Sample collection and preparation

The samplings were divided into two parts in June of 2017. The first part, water samples were collected from influents and effluents of four WWTPs. The Second part, surface water samples were collected from Huangpu River, Suzhou River and Yunzao Brook. The waste treatment plant samples were collected on the first day, the surface water samples were collected on the second day. Sampling sites on the rivers and the locations of the WWTPs are labeled in Fig. 1, and 22 specific sampling points are georeferenced in Table S2. At each sample point, samples were collected in clean dry amber glass flasks, which were pre-rinsed with methanol followed by Milli-Q water and rinsed again with sample

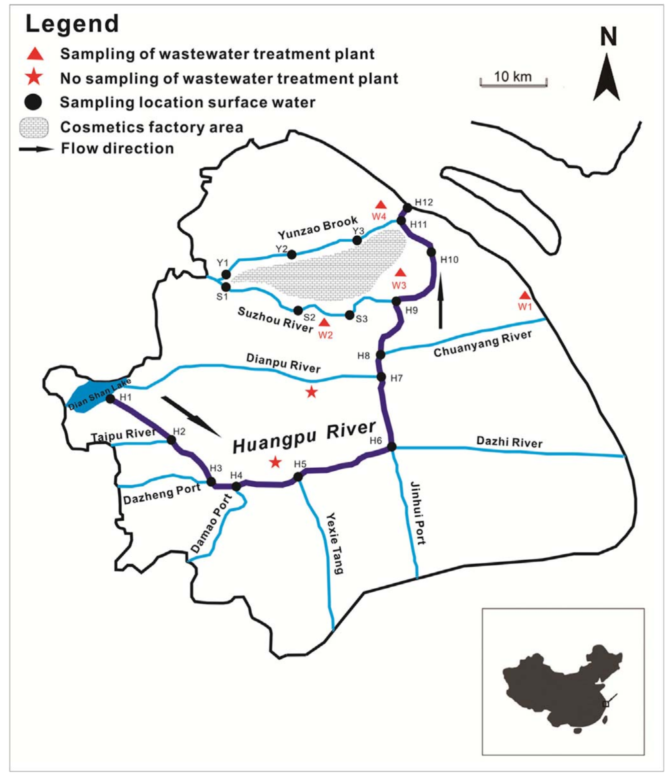

Fig. 1. Specific locations of the WWTPs (W1-W4) and other sites in Huangpu River (H1-H12), Suzhou River (S1-S3) and Yunzao Brook (Y1-Y3).

water before sample collection. Each sample was wrapped with aluminum foil to avoid contamination and photo-degradation of the target compounds. All samples were transported to the laboratory in the dark at 4 °C prior to analysis.

2.3. Sample extraction and purification

The extraction method of solid phase extraction is slightly modified as described in previous literatures (Pedrouzo et al., 2009; Purra et al., 2014; Wu et al., 2017). All water samples analyzed in this study were previously filtered with rapid qualitative filter paper to remove large particles and the pH was adjusted to 3 using HCl. After that, samples were filtered with GF/F (Whatman International Ltd., Maidstone, England) glass fiber filter, 200 mL water samples of WWTPs and 400 mL surface water samples was spiked with 0.1 mL/1 ppm internal standard BPA-d_{16}. Solid phase extraction (SPE) cartridges (200 mg/6 mL Strata-X, Phenomenex, USA) were performed. Before extraction, the cartridges were conditioned initially with 5 mL methanol followed by 5 mL ultra-pure water. Then, the samples were percolated through cartridges with a flow rate of 2 mL min^{-1}. After extraction, the cartridges were rinsed with 5 mL ultra-pure water and kept dry for about 15 min in vacuum. The target compounds were eluted from cartridge with 3 mL methanol followed by 3 mL dichloromethane (Anpel, China) into 15 mL conical tubes. The extracts were evaporated to dryness under a gentle stream of nitrogen, then spiked with 0.1 mL/1 ppm internal standard Caffeine-C_{13} and reconstituted to 1 mL with methanol, filter through a 0.2 µm PTFE filter (Anpel，China) and transferred into sample vials for analysis by high performance liquid chromatography-tandem mass spectrometry (HPLC-MS/MS).

2.4. LC-MS/MS quantitative approach

The analysis of BP-UV filters were performed on an Agilent 1260 liquid chromatograph coupled to an Agilent 6460 triple quadrupole