WATER RESEARCH 67 (2014) 55–65

Available online at www.sciencedirect.com

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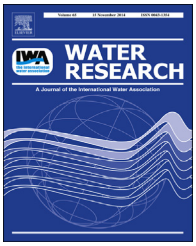

Occurrence, distribution and ecological risk assessment of multiple classes of UV filters in surface waters from different countries

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ARTICLE INFO

Article history:
Received 17 July 2014
Received in revised form
1 September 2014
Accepted 6 September 2014
Available online 18 September 2014

Keywords:
Ultraviolet filters
Marine environment
Surface water
Risk assessment
Personal care products
Seasonal variation

ABSTRACT

Organic UV filters are common ingredients of personal care products (PCPs), but little is known about their distribution in and potential impacts to the marine environment. This study reports the occurrence and risk assessment of twelve widely used organic UV filters in surface water collected in eight cities in four countries (China, the United States, Japan, and Thailand) and the North American Arctic. The number of compounds detected, Hong Kong (12), Tokyo (9), Bangkok (9), New York (8), Los Angeles (8), Arctic (6), Shantou (5) and Chaozhou (5), generally increased with population density. Median concentrations of all detectable UV filters were <250 ng/L. The presence of these compounds in the Arctic is likely due to a combination of inadequate wastewater treatment and long-range oceanic transport. Principal component analysis (PCA) and two-way analysis of variance (ANOVA) were conducted to explore spatiotemporal patterns and difference in organic UV filter levels in Hong Kong. In general, spatial patterns varied with sampling month and all compounds showed higher concentrations in the wet season except benzophenone-4 (BP-4). Probabilistic risk assessment showed that 4-methylbenzylidene camphor (4-MBC) posed greater risk to algae, while benzophenone-3 (BP-3) and ethylhexyl methoxycinnamate (EHMC) were more likely to pose a risk to fishes and also posed high risk of bleaching in hard corals in aquatic recreational areas in Hong Kong. This study is the first to report the occurrence of organic UV filters in the Arctic and provides a wider assessment of their potential negative impacts in the marine environment.

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http://dx.doi.org/10.1016/j.watres.2014.09.013

1. Introduction

Organic ultraviolet (UV) filters are widely used as UV radiation-absorbing substances in personal care products (PCPs) to protect human skin from the negative effects of sunlight as well as in materials and paints to prevent product photodegradation. Authorized contents of organic UV filters in PCPs vary according to regulations in the countries/regions of their manufacture, where they may comprise up to 20% of product mass (Chisvert and Salvador, 2007). Owing to their large annual production quantities and widespread usage, particularly because of greater awareness of skin cancer risks in recent decades, organic UV filters can enter the aquatic environment (i) indirectly from wastewater treatment plants (WWTPs) after entering sewage systems following bathing or from industrial discharge due to incomplete removal as well as surface runoff and (ii) directly from recreational activities (e.g. swimming) (Giokas et al., 2007).

As a result of their extensive application and continuous release into aquatic systems, organic UV filters are regarded as pseudo-persistent environmental contaminants, and their ubiquity has raised concerns about their potential environmental impacts (Giokas et al., 2007). They have been found in various environmental samples including surface water, wastewater and sediment (e.g. Tsui et al., 2014; Kameda et al., 2011) generally at ng/L to sub-ug/L levels for aqueous matrices and sub-ng/g levels for solid matrices. However, only a few studies have reported the occurrence of UV filters in the marine environment, and only a limited number of globally authorized compounds have been investigated; for example, benzophenone-3 and -4 (BP-3 and BP-4), ethylhexyl methoxycinnamate (EHMC) and octocrylene (OC) were detected in surface waters in some European countries and Japan (Tashiro and Kameda, 2013; Tovar-Sánchez et al., 2013; Rodil et al., 2008).

Many organic UV filters have high lipophilicity, with octanol-water partition coefficients (log K_{ow}) values generally greater than 3. They have been detected in various aquatic organisms such as brown trout (*Salmo trutta fario*) up to 1800 ng/g (4-methylbenzylidene camphor, 4-MBC) and 2400 ng/g (OC) lipid weight (lw) in Swiss rivers (Buser et al., 2006) and in marine mussels (*Mytilus edulis*) up to 256 ng/g (EHMC) and 7112 ng/g (OC) dry weight (dw) along the French Atlantic and Mediterranean coasts (Bachelot et al., 2012). Moreover, Fent et al. (2010b) suggested food chain accumulation of EHMC, reporting its concentrations in fish and cormorants (*Phalacrocorax* sp.) from six Swiss rivers up to 337 and 701 ng/g lw, respectively. Accumulation of these compounds in organisms is a concern because organic UV filters and their metabolites have been shown to interfere with endocrine function by acting as environmental estrogens both *in vitro* and *in vivo* (Schlumpf et al., 2001; Kunz and Fent, 2006). Moreover, they have been shown to induce bleaching in corals by promoting viral infections (Danovaro et al., 2008).

Data on the occurrence of organic UV filters in fresh surface waters are available for several developed countries (e.g. Kameda et al., 2011; Fent et al., 2010b), but relevant information is lacking for the marine environment in countries outside of Europe or Japan for certain uniformly approved and widely consumed UV filters (e.g. butyl methoxydibenzoylmethane (BMDM) and homosalate (HMS)). Moreover, previous studies have reported the occurrence of UV filters at beaches, but little information is known about coastal waters. In contrast to other organic contaminants (e.g. perfluoroalkyl substances (PFAS) and pharmaceuticals) which have been studied in detail (Richardson and Ternes, 2014), information on the occurrence, distribution, transport pathways and risks of organic UV filters in the aquatic environment is lacking. Therefore, it is of crucial importance to study the environmental distribution and concentrations of these emerging contaminants in order to evaluate their ecological risks.

In light of these considerations, the objectives of this study were to (i) determine the concentrations and spatial occurrence of twelve commonly consumed UV filters, including benzophenone-1, -3, -4 and -8 (BP-1, -3, -4 and -8), ethylhexyl salicylate (EHS), isoamyl p-methoxycinnamate (IAMC), octyl dimethyl-p-aminobenzoic acid (ODPABA), BMDM, EHMC, HMS, 4-MBC and OC in surface water samples collected from different countries including China (Hong Kong, Shantou and Chaozhou), the United States (New York City and Los Angeles), Japan (Tokyo Bay), Thailand (Bangkok) and the Arctic region, as well as their seasonal variation in Hong Kong over the course of one year; and (ii) conduct an ecological risk assessment by using the measured environmental concentrations and available toxicity data.

2. Materials and methods

2.1. *Chemicals and materials*

Information on chemical standards and preparation of standard solutions can be found in the Supplementary material. Standard purities were all ≥97%. Detailed information on the targeted UV filters is shown in Table A1.

2.2. *Sampling*

Surface water samples were collected from eight locations (Hong Kong, $n = 60$; Tokyo, $n = 8$; New York, $n = 6$; Los Angeles, $n = 4$; Shantou, $n = 4$; Chaozhou, $n = 3$; Bangkok, $n = 2$) and the Arctic ($n = 14$) from 2012 to 2013 using plastic or stainless steel buckets or glass bottles which were pre-cleaned by rinsing (in sequence) with methanol, Milli-Q water, and water from the specific location. All samples were marine surface water samples except those collected from Bangkok which were freshwater samples. Most of the selected cities are metropolitan areas featuring both commercial and industrial development. Temporal and spatial samples were collected in Hong Kong in both the wet and dry seasons; spatial samples were collected from Tokyo Bay, Los Angeles, New York City and the Arctic, while only a single location was sampled in Bangkok. Detailed information on the sampling locations is shown in Supplementary material Table A2 and Figs A1–5.

Surface water samples were collected from 20 points in Hong Kong in August 2012, February and June 2013; June and August samples represented the wet season, while the February samples represented the dry season. The sampled