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Environmental occurrence and distribution of organic UV stabilizers and UV filters in the sediment of Chinese Bohai and Yellow Seas☆

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ABSTRACT

Organic UV stabilizers and UV filters are applied to industrial materials and cosmetics worldwide. In plastics they prevent photo-induced degradation, while in cosmetics they protect human skin against harmful effects of UV radiation. This study reports on the occurrence and distribution of organic UV stabilizers and UV filters in the surface sediment of the Chinese Bohai and Yellow Seas for the first time. In total, 16 out of 21 analyzed substances were positively detected. Concentrations ranged from sub-ng/g dw to low ng/g dw. The highest concentration of 25 ng/g dw was found for octocrylene (OC) in the Laizhou Bay. In the study area, characteristic composition profiles could be identified. In Korea Bay, the dominating substances were OC and ethylhexyl salicylate (EHS). All other analytes were below their method quantification limit (MQL). Around the Shandong Peninsula, highest concentrations of benzotriazole derivatives were observed in this study with octrizole (UV-329) as the predominant compound, reaching concentrations of 6.09 ng/g dw. The distribution pattern of UV-329 and bumetrizole (UV-326) were related (Pearson correlation coefficient $r > 0.98$, $p \ll 0.01$ around the Shandong Peninsula), indicating an identical input pathway and similar environmental behavior.

1. Introduction

UV absorbing compounds are widely used in personal care products, textiles, plastics, paints, adhesives, rubber, and other industrial products (Avagyan et al., 2015; Kim et al., 2011b; Ramos et al., 2015). Depending on their purpose, they can be divided into two categories as described by Langford et al. (2015): i) UV stabilizers are added to plastic products (and other materials) to prevent UV-induced degradation and discoloring of the product and ii) UV filters are used in personal care products (PCPs) such as sunscreens and cosmetics to protect human skin and hair against UV radiation. Some compounds are used for both purposes, whereby a strict differentiation is not possible. Therefore, the term "UV stabilizer" is used for all compounds in the following.

UV stabilizers used in PCPs are regulated worldwide. In Europe, Annex VI of the Cosmetic Regulation No. 1223/2009 (European Commission, 2017) provides a positive list of substances allowed in cosmetic products. In China, the same substances are permitted as in Europe.

The input pathways of UV stabilizers to the marine environment are mainly indirect, through wastewater treatment plant discharges, or direct, through recreational activities such as bathing and swimming (Poiger et al., 2004; Ramos et al., 2016). Microplastic and plastic debris are also discussed as potential sources of plastic additives (Cole et al., 2011; Rani et al., 2015, 2017).

Some UV stabilizers are currently listed as High Production Volume Chemicals (HPVC) by the OECD (2017). Due to the widespread usage and high production volumes, UV stabilizers are present in various environmental matrices. UV stabilizers have been reported worldwide in water (Balmer et al., 2005; Cunha et al., 2015b; Kameda et al., 2011; Liu et al., 2014; Tsui et al., 2014), suspended particulate matter (Wick et al., 2016), house dust (Kim et al.,

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2012), sediment (Kameda et al., 2011; Langford et al., 2015; Nakata et al., 2009; Wick et al., 2016), and biota (Cunha et al., 2015a; Gago-Ferrero et al., 2012; Langford et al., 2015; Nakata et al., 2012; Peng et al., 2015; Sang and Leung, 2016; Wick et al., 2016). For example, Huang et al. (2016) had identified three UV stabilizers in sediment samples from China's Pearl River estuary with the highest concentrations of ethylhexyl methoxycinnamate (EHMC) and octocrylene (OC) (around 0.5 μg/g dw) in fishing harbors. Most UV stabilizers are hydrophobic compounds with high octanol-water partition coefficients ($\log K_{ow} > 3$) and show significant accumulation potentials in suspended matter, sediments, and biota. Some substances show persistent, bioaccumulative, and toxic (PBT) properties. For this reason, four benzotriazole UV stabilizers are currently listed as Substances of Very High Concern (SVHC) under the EU legislation REACH (ECHA, 2017a). Namely, these substances are 2-(Benzotriazol-2-yl)-4,6-di-tert-butylphenol (UV-320), 2,4-di-tert-Butyl-6-(5-chlorobenzotriazol-2-yl) phenol (UV-327), 2-(Benzotriazol-2-yl)-4,6-bis-(1,1-dimethyl-propyl) phenol (UV-328), and 2-(Benzotriazol-2-yl)-6-butan-2-yl-4-tert-butylphenol (UV-350). In addition, EHMC is included in the Watch List to be monitored under the Water Framework Directive (European Commission, 2015).

The widespread contamination and the resulting potential exposure of UV stabilizers have raised increasing concern about their impact on ecosystems and human health. There is increasing evidence to the adverse effects of UV stabilizers. Many UV stabilizers, such as benzophenones, camphor and cinnamate derivatives, have been identified as potential endocrine disruptors (Balazs et al., 2016; Wang et al., 2016). Several compounds are a major cause of coral bleaching (Danovaro et al., 2008) and show hormonal activity and toxicity in *in vivo* rat model systems (Rainieri et al., 2017). So far, for benzotriazole UV stabilizers no estrogenic and androgenic activities have been observed in zebrafish eleuthero-embryos (Fent et al., 2014), but exposure to UV-P and UV-326 may lead to metabolic imbalance and developmental toxicity (Fent et al., 2014). At environmental concentration levels, benzotriazole UV stabilizers were shown to have no acute toxicity in Daphnia (Kim et al., 2011a). Toxicity studies showed that direct contact with UV-P might cause acute effects such as dermatitis and skin irritation (Yamano et al., 2001). Benzotriazole UV stabilizers interacted with the human serum albumin (Zhuang et al., 2016) and showed activity toward the human aryl hydrocarbon receptor (AhR), which could adversely affect the immune response (Nagayoshi et al., 2015).

While the widespread occurrence of UV stabilizers is known, only few studies focused on the marine environment. The main aim of this study was to assess the significance of UV stabilizers as emerging contaminants in the sediment of the Chinese Bohai and Yellow Seas.

The Bohai Sea is surrounded by the Bohai Economical Rim (BER), which is the largest economic engine in North China. It includes megacities such as Beijing and Tianjin and comprises parts of the Hebei, Shandong, and Liaoning provinces. Many chemical pollutants, such as per- and polyfluorinated substances (Heydebreck et al., 2015; Wang et al., 2014) and organophosphate esters (Wang et al., 2015) are transported by rivers into the Bohai Sea and pose a great risk for aquatic wildlife (Zhang et al., 2017). Large volumes of domestic and industrial discharges are entering the Bohai Sea as well as the Yellow Sea, significantly deteriorating the water quality (Wang et al., 2015; Zhong et al., 2018).

In this work, surface sediment samples were collected and analyzed for 20 UV stabilizers and one hindered amine light stabilizer (HALS) to i) evaluate the current pollution status, ii) characterize regions, iii) identify potential contamination sources, and iv) give a preliminary risk evaluation of UV stabilizers in the Bohai and Yellow Seas.

2. Material and methods

2.1. Chemicals

Enzacamene (4-MBC), Iscotrizinol (DBT), Ethylhexyl triazone (EHT), Ethylhexyl methoxycinnamate (EHMC), Octocrylene (OC), Bumetrizole (UV-326), 2,4-di-tert-Butyl-6-(5-chlorobenzotriazol-2-yl) phenol (UV-327), 2-(Benzotriazol-2-yl)-4,6-bis-(1,1-dimethyl-propyl) phenol (UV-328), Ethylhexyl methoxycinnamate-d_{15} (EHMC-d_{15}), Homosalate-d_4 (HMS-d_4), Octocrylene-d_{15} (OC-d_{15}), and Benzophenone-d_{10} (BP-d_{10}) were purchased from Sigma-Aldrich (Germany). Oxybenzone (BP-3), Octabenzone (BP-12), Ethylhexyl salicylate (EHS), Bis[4-(2-phenyl-2-propyl) phenyl] amine (HALS-445), Homosalate (HMS), Amiloxate (IAMC), Padimate O (OD-PABA), Drometrizole (UV-P), 2-(5-tert-butyl-2-hydroxyphenyl) benzotriazole (UV-PS), Octrizole (UV-329), and 2-(Benzotriazol-2-yl)-4,6-bis-(2-phenylpropan-2-yl) phenol (UV-234) were obtained from TCI Deutschland GmbH (Germany). 2-(Benzotriazol-2-yl)-6-butan-2-yl-4-tert-butylphenol (UV-350), 2-(Benzotriazol-2-yl)-4,6-di-tert-butylphenol (UV-320), and 2-(Benzotriazol-2-yl)-4-methyl-6-(2-propenyl) phenol (Allyl-bzt) were supplied by amchro GmbH (Germany). Enzacamene-d_4 (4-MBC-d_4) and Oxybenzone-$^{13}C_6$ (BP-3-$^{13}C_6$) were distributed by EQ Laboratories GmbH (Germany) and LGC Standards GmbH (Germany), respectively. 2-(2-Hydroxy-5-methylphenyl)-benzotriazole-d_4 (UV-P-d_4), 2-(Benzotriazol-2-yl)-4,6-bis-(1,1-dimethyl-propyl) phenol-d_4 (UV-328-d_4), and Perfluoro-1-[$^{13}C_8$]-octanesulfonamide (FOSA-$^{13}C_8$) were supplied by CAMPRO Scientific GmbH (Germany). Further information such as structures, CAS-No., chemical names, and purities can be found in Tables S1 and S2 of the Supplementary Material.

Dichloromethane (Picograde) was purchased from LGC Standards (Germany). Both methanol (LiChrosolv, hypergrade for LC-MS) and toluene (LiChrosolv, for liquid chromatography) were purchased from Merck (Germany). Deionized water was supplied from a Milli-Q Integral 5 system (Germany).

2.2. Study area and sample collection

The Bohai and Yellow Seas are semi-enclosed marginal seas in the northwest Pacific Ocean. The Yellow Sea is surrounded by the west coast of the Korean Peninsula and the east coast of China. It has an area of approximately 380,000 km^2 (Song, 2010) and an average depth of 44 m (Song, 2010). Its northern extension is referred to as Korea Bay and in the northwest, the Yellow Sea is connected to the Bohai Sea through the Bohai Strait. The Bohai Sea has an area of approximately 77,000 km^2 (Song, 2010) and features three bays, one of them being Laizhou Bay in the south.

Surface sediment samples from the Bohai and Yellow Seas were collected in June and July 2016 on the Chinese research vessel *Dongfanghong 2* sampling campaign. Surface sediment samples from Laizhou Bay were collected in July 2016 on the *Chuangxin 1* sampling cruise. On both campaigns the samples were taken using a stainless-steel box corer and the top 10 cm of sediment was collected. Samples were put afterward into pre-cleaned (cleaned with acetone and baked out at 250 °C) aluminum bowls and stored at −20 °C until sample preparation. Detailed sampling information can be found in Table S7 of the Supplementary Material.

2.3. Sample preparation

The wet sediment samples were freeze-dried (Christ Alpha 1–4 LDplus, Germany) and homogenized using a laboratory mortar. Large pieces (such as seashells and stones) were removed. Afterward, extraction and clean-up were performed simultaneously