

Occurrence and Concentrations of Persistent Personal Care Products, Organic UV Filters, in the Marine Environment

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Abstract—The benzotriazol organic UV filters, such as UV-320 (CAS# 3846-71-7), UV-326 (CAS# 3896-11-5), UV-327 (CAS# 3864-99-1), and UV-328 (CAS# 25973-55-1), were detected in marine organisms collected from the Ariake Sea, western Japan. The high concentrations of UV filters were found in oysters and tidal flat species, at the concentrations of several ten ng/g (wet wt. basis). It is interesting to know that marine mammals and seabirds accumulate UV-326, 328 and UV-327, respectively. These results suggest the significant bioaccumulation of UV filters through the marine food-webs. Benzotriazole UV filters were also detected in surface sediments from the Ariake Sea, at the average concentrations of several ng/g (dry wt.). Significant correlations were found between UV filters concentrations and organic carbon contents in sediments, which implies an adsorption of these contaminants to organic carbon. In order to understand the geographical distribution of UV filters, blue and green mussels from 10 Asian countries and region were analyzed. UV filters were detected in most mussel samples, indicating the widespread use of these compounds in Asian coastal regions. The high concentrations of UV filters were found in mussels from Korea, Hong Kong, and Japan. Further investigations and global monitoring survey for organic UV filters are necessary to understand their contamination, fate and risks in the ecosystems.

Keywords: organic UV filters, contamination, marine organisms, bioaccumulation, sediment, mussels, Asian coastal waters

INTRODUCTION

There is increasing public concerns in the occurrence and contamination of pharmaceuticals and personal care products (PPCPs) in the environment. Because most PPCPs are water-soluble, the contamination and concentrations of PPCPs have been studied in the aquatic matrices, such as drinking water, ground water and river water. While the levels of PPCPs in natural waters are generally low, high concentrations of pharmaceuticals were found in influent and effluent of

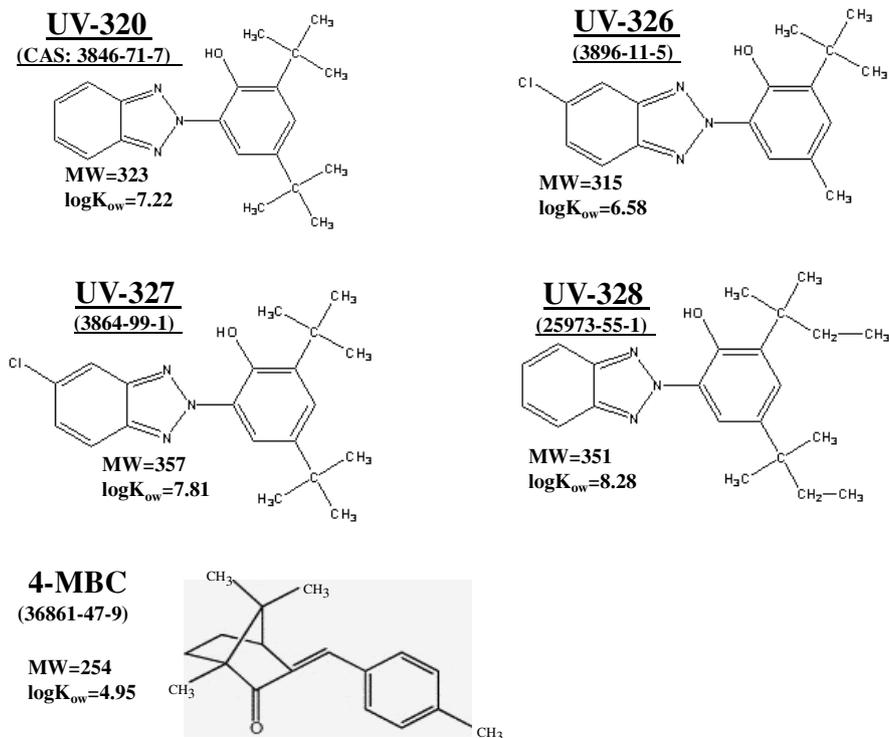


Fig. 1. Benzotriazole UV filters (UV-320, 326, 327, 328) and 4-MBC analyzed in this study.

wastewater treatment plant (WWTP). This indicates that WWTP is a significant source of PPCPs in the environment.

On the other hand, some PPCPs are lipophilic, and therefore have a potential for bioaccumulation in the environment. For examples, synthetic musks, HHCB (1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethylcyclopenta[g]-2-benzopyrane) and AHTN (7-acetyl-1,1,3,4,4,6-hexamethyl-tetrahydronaphthalene), which are present in cosmetic products of daily use, have been detected in marine organisms, such as mussels, oysters, fish, marine mammals, and seabirds collected from Japanese coastal waters (Nakata *et al.*, 2005, 2007). The occurrence of HHCB was also reported in seals and dolphins, top predators of the marine food web, in the US coastal waters (Kannan *et al.*, 2005). These results suggest significant bioaccumulation of HHCB through the marine food-webs, although the bioconcentration factors in fish were relatively low (HHCB: 1584, AHTN: 597) under laboratory exposure conditions (Balk and Ford, 1999).

Organic UV filters have been used in various kinds of cosmetics and sunlight protection products to protect skin and to preserve the properties of polymers from high damages of UV beams. While large amount of UV filters have been

produced in the world, some compounds, such as 4-methylbenzylidene camphor (4-MBC; CAS#: 36861-47-9) and benzophenone derivatives are of particular interests, due to their estrogenic activity and depression of thyroid hormones (Schlumpf *et al.*, 2001; Morohoshi *et al.*, 2005; Klammer *et al.*, 2007). Recently, organic UV filters has been detected in the aquatic environment (Giokas *et al.*, 2007). The concentrations of 4-MBC and octocrylene (OC) in river and lake waters ranged from several to several ten ng/L, whereas high concentrations of these compounds were found in fish tissues ($>1 \mu\text{g/g}$ lipid wt.; Buser *et al.*, 2006). This indicates bioaccumulation of UV filters in the aquatic ecosystems, due to their lipophilic properties (logKow: 5.1 for 4-MBC, 6.9 for OC). However, little information is available on the contamination and concentrations of more lipophilic organic UV filters, benzotriazole compounds. The logKows of benzotriazole UV filters generally range from 6.0 to 8.5, and they also have a potential for bioaccumulation in the aquatic ecosystems.

Based on these backgrounds, this study have investigated the occurrence, concentrations and bioaccumulation profiles of benzotriazole UV filters, such as UV-320 (2-(3,5-di-*t*-butyl-2-hydroxyphenyl)-benzotriazole), UV-326 (2-(3-*t*-butyl-2-hydroxy-5-methylphenyl)-5-chlorobenzotriazole), UV-327 (2,4-di-*t*-butyl-6-(5-chloro2*H*-benzotriazol-2-yl) phenol), and UV-328 (2-(2*H*-benzotriazol-2-yl)-4,6-di-*t*-pentylphenol), and 4-MBC (3-(4-methylbenzylidene)-camphor) (Fig. 1), in the marine organisms collected from Ariake Sea, western Japan. In addition, blue and green mussels collected from Asian countries were analyzed to examine the contamination and geographical distribution of organic UV filters in Asian coastal waters.

MATERIALS AND METHODS

Chemicals

Four benzotriazole standards, UV-320, UV-326, UV-327, and UV-328 were obtained from Wako Pure Chemicals (Japan). 4-MBC were purchased from AVOCADO Co. Ltd. The purities of standards were 97, 97, 97, 98, and 99% for UV-320, UV-326, UV-327, UV-328, and 4-MBC, respectively. Deuterated polycyclic aromatic hydrocarbon (d_{10} -phenanthrene) was obtained from Cambridge Isotope Laboratory (Andover, USA) as surrogate standard during UV filter analysis in this study.

Samples

Fifty-one marine organisms, such as lugworms, mussels, oysters, crustaceans, fish, birds, and marine mammals were collected from the Ariake Sea during 2001 and 2005. Twelve sediments were also collected from same region in December, 2007. Forty-five green mussels (*Perna viridis*) and blue mussels (*Mytilus edulis*) were collected from Asian coastal countries and region, such as Cambodia, China, Hong Kong, India, Indonesia, Japan, Korea, Malaysia, the Philippines, and Vietnam during 1998 and 2005.

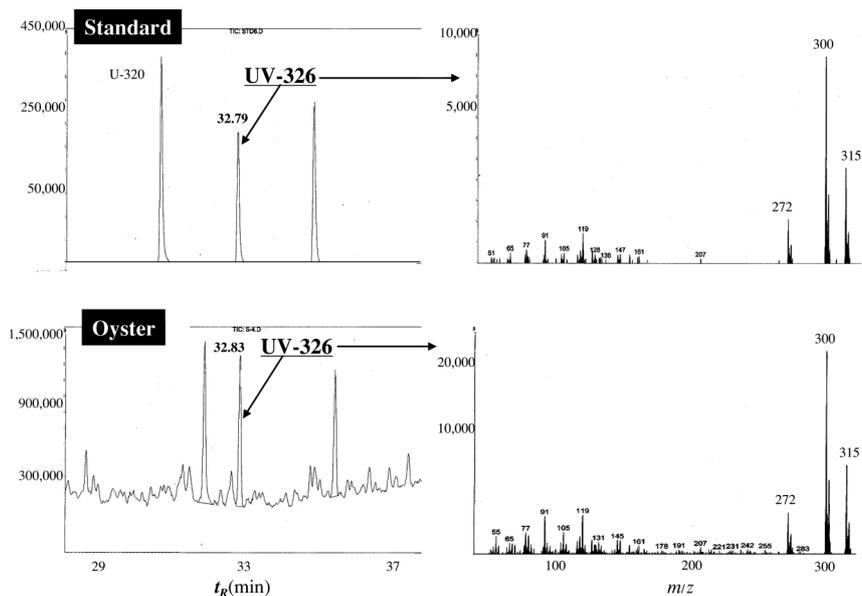


Fig. 2. GC-MS chromatograms (SCAN mode) and fragment patterns of UV-326 in oysters from Japanese coastal water and a standard mixture.

Analytical procedures

Approximately 2–20 g of tissues were ground with sodium sulfate and extracted with a mixture of dichloromethane and hexane (8:1) for 5 hrs using a Soxhlet apparatus. A portion of the extract was used for lipid measurement. Sediments are freeze-dried, followed by Soxhlet extraction. The deuterated phenanthrene was spiked into the extract as surrogate standard. To remove lipid from the sample extract, it was subjected to gel permeation chromatography (GPC) packed with a Bio-beads S-X3 (Bio-Rad Laboratories, Hercules, CA, USA) in glass column (400 mm × 30 mm i.d.). A mixture of 50% hexane in dichloromethane (DCM) was used as the mobile phase at a flow rate of 5 ml/min. The first 110 ml of eluate was discarded, and the following 90 ml fraction, which contained all UV filters analyzed as well as surrogate was obtained. The eluted solvent was concentrated, and passed through a 5 g of 5% deactivated silica gel (Wakogel C-200, Wako Pure Chemical Co. Ltd., Japan) for further clean-up. A solvent of 50 ml 5% diethyl ether in hexane was eluted in a glass column. The eluate was concentrated to 200 μ L and injected into a gas chromatograph interfaced with a mass spectrometer (GC-MSD, Agilent 6890 and 5973 Series). Injections were made both in Scan and SIM modes. The selected ions were monitored at m/z 254, 211, 239 for 4-MBC, 308, 323, 252 for UV-320, 300, 315, 272 for UV-326, 342, 344, 357 for UV-327, 322, 351, 336 for UV-328 and 188

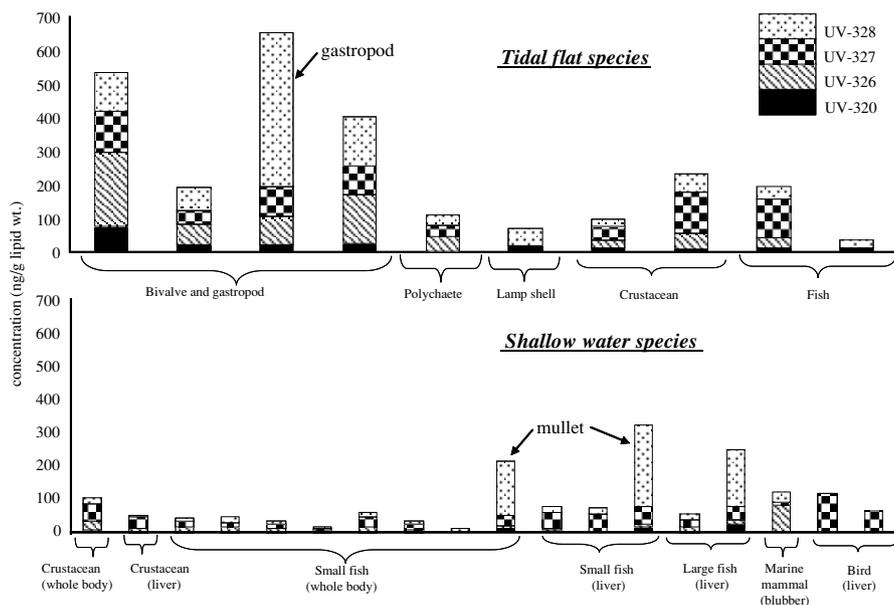


Fig. 3. Concentrations of UV filters in tidal flat and shallow water species from the Ariake Sea, Japan.

and 94 for d_{10} -phenanthrene. The GC column used was HP-5MS (Agilent Technologies USA) fused silica capillary column (30 m \times 0.25 mm i.d., 0.25 μ m of film thickness). The oven temperature was programmed from 80°C to 160°C at a rate of 10°C/min and held for 10 min, and the temperature was increased to 300°C at a rate of 3°C/min, with a final hold time of 15 min. The temperatures of injector and detector of GC-MSD were set at 270 and 300°C, respectively. Helium was used as a carrier gas.

Quality control

A standard mixture containing all UV filters analyzed in this study was used to determine recovery rates of the compounds before sample analysis. Non-contaminated salad oil (0.5 g) was spiked with 50 ng of the standard mixture. Three replicate analyses were performed, and the average recoveries of 4-MBC, UV-320, UV-326, UV-327, and UV-328 were 93, 114, 122, 114, and 110%, respectively.

A procedural blank was analyzed with every set of six samples to confirm interfering peaks in chromatograms and to correct sample values. Blank peaks were observed in the chromatograms, as discussed below. The concentrations were reported as below the detection limit if the peak height was not greater than the specified threshold (signal to noise ratio of 3 in the blank chromatogram).

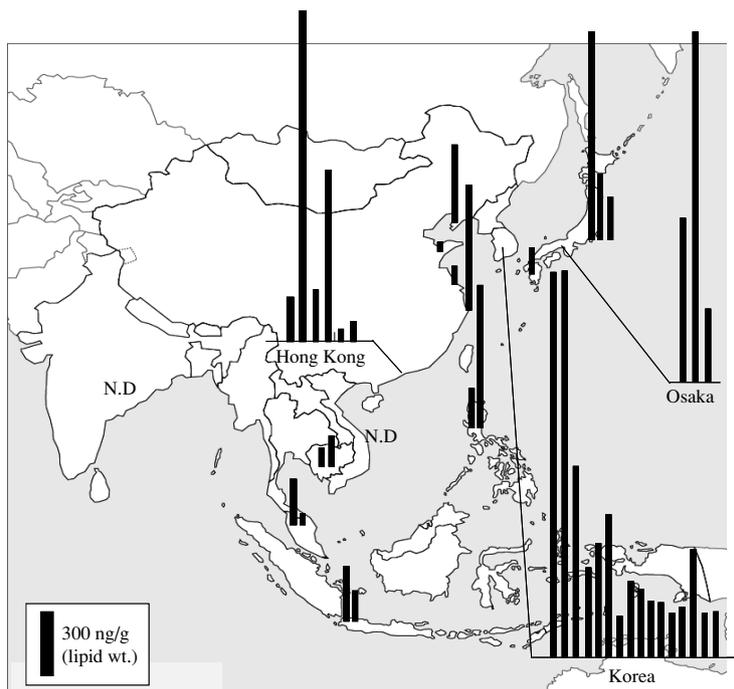


Fig. 4. Geographical distributions of UV filter concentrations in mussels collected from Asian coastal waters.

RESULTS AND DISCUSSION

The total ion chromatograms and fragment patterns of UV-326 in oyster were shown in Fig. 2. The retention times of UV-326 (32.79 min) in samples were well agreed with those in the standard solutions. As for fragment patterns, the dominant m/z of UV-326 were 300, 315, and 272 in samples, which were also similar to those of standards. These results strongly indicate the occurrence and accumulation of benzotriazole UV filters in oyster samples. To our knowledge, this is the first report to determine benzotriazole UV filters in wildlife.

To understand the bioaccumulation profiles of UV filters, tidal flat and shallow water species from the Ariake Sea were analyzed. As the results, UV filters were detected in most marine organisms in this study (Fig. 3). In general, the highest concentrations of UV filters (lipid wt. basis) were found in lower benthic organisms, gastropods, collected from tidal flat area of the Ariake Sea. UV-328 and UV-326 were the dominant components in these organisms. In shallow water species, elevated residue levels of UV filters were found in the liver of mullet, benthic fish analyzed in this study. In addition, higher trophic species, such as sharks, marine mammals and birds accumulate organic UV filters in their bodies. UV-328 and UV-327 were dominant in finless porpoises and mallards,

respectively. The different compositions of UV filters might be due to species specific metabolism of these compounds. These results suggest the persistent and less biodegradable features of benzotriazole UV filters in the marine ecosystem.

UV filters were detected in sediments from the Ariake Sea, at the concentrations of several ng/g (dry wt.). High concentrations of UV filters were found in the Omuta River sediments, at the levels ranging from 2.3 to 320 ng/g dry wt. basis. It has been reported that Omuta River is heavily contaminated by persistent organic pollutants, such as PCBs, organochlorine pesticides and polycyclic hydrocarbons (PAHs) (Nakata *et al.*, 2004). Significant correlations were found between UV filters concentrations and organic carbon contents in sediments. This implies an adsorption of UV filters to sediment organic particles, which is similar to those of persistent organochlorines, such as DDT, in the environment (Nakata *et al.*, 2005).

To understand the geographical distribution of UV filters in Asian coastal regions, mussels were analyzed in this study. Benzotriazole UV filters were detected in most samples analyzed (Fig. 4). In general, UV-326 was the dominant compounds, whereas UV-320 was detected only several samples collected from Japan. The UV filters concentrations were high in mussels from Korea, Japan, and Hong Kong. In contrast, low residue levels of UV filters were found in samples from India and Vietnam. These results suggest different usage volumes of UV filters among countries and regions in Asia. The UV filters concentrations in mussels showed great spatial variations in Korea, and Japan, which may due to the distance between the sampling points and the sources of UV filters, such as wastewater treatment plants. Significant positive correlation was determined in concentrations between UV-327 and UV-328 in mussels. This suggests that the sources of HHCB and AHTN are almost same.

To our knowledge, this is the first report to identify organic UV filters in the marine ecosystems. Further investigations and global monitoring survey of persistent organic UV filters are necessary to understand the contamination, fate, and risks in the environment.

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