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Tissue Distribution, Growth Dilution, and Species-Specific Bioaccumulation of Organic Ultraviolet Absorbents in Wildlife Freshwater Fish in the Pearl River Catchment, China

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Abstract: Tissue distributions and body-size dependent and species-specific bioaccumulation of 12 organic ultraviolet absorbents (UVAs) were investigated in 9 species of wildlife freshwater fish from the Pearl River catchment, South China. The concentrations of the 12 UVAs were from 109 to 2320 ng/g lipid weight in the fish tissue samples. The UVAs 2-hydroxy-4-methoxybenzophenone (BP-3), octocrylene (OCR), UV531, and 5 benzotriazole UV stabilizers (UVP, UV329, UV234, UV328, and UV327) were detected in more than half of the fish tissue samples. The UVA UV531 showed an obvious potential for bioaccumulation in the wild freshwater fish, with an estimated bioaccumulation factor (log BAF) and a biota–sediment accumulation factor (BSAF) of 4.54 ± 0.55 and 4.88 ± 6.78, respectively. Generally, liver (989 ± 464 ng/g lipid wt) contained the highest level of UVAs, followed in decreasing order by belly fat (599 ± 318 ng/g lipid wt), swimming bladder (494 ± 282 ng/g lipid wt), dorsal muscle (470 ± 240 ng/g lipid wt), and egg (442 ± 238 ng/g lipid wt). The bioaccumulation of UVAs in the freshwater wild fish was species specific and compound dependent. Bottom-dwelling detritus-ingesting omnivorous fish contained obviously higher UVA concentrations, suggesting that detritus/sediment ingestion is a significant pathway for exposure of the wild freshwater fish to the UVAs. The UVAs UV531 and BP-3 demonstrated a potential for growth dilution. Metabolism might play a significant role in elimination of the UVAs in the fish tissues, with the highest rate of metabolism in the liver. The UVAs did not demonstrate obvious trophic magnification in the freshwater ecosystem of the Pearl River catchment. More research is warranted to elucidate maternal transfer of the UVAs. *Environ Toxicol Chem* 2020;39:343–351. © 2019 SETAC

Keywords: Bioaccumulation; Trophic transfer; Bioaccumulative compounds

INTRODUCTION

Organic ultraviolet absorbents (UVAs), including UV filters (UVFs) and UV stabilizers (UVSs), are widely used in consumer and industrial products (such as personal care products, textiles, paints, and plastics) to minimize UV radiation–induced harm. As a result, various UVAs have been detected pervasively in the environment (Balmer et al. 2005; Nakata et al. 2009, 2012; Kameda et al. 2011; Kim et al. 2011; Gago-Ferrero et al. 2013, 2015; Groz et al. 2014; Lai et al. 2014; Tsui et al. 2014, 2015; Langford et al. 2015; Monforte et al. 2015; Sang and Leung 2016; Wick et al. 2016; Peng et al. 2017a; Liao et al. 2018; Mao et al. 2018; Parajulee et al. 2018; Tovar-Sanchez et al. 2019).

Some UVAs have been found to be bioaccumulative. For instance, 2-hydroxy-4-methoxybenzophenone (BP-3), octocrylene (OCR), 2-ethylhexyl-4-methoxycinnamate (EHMC), and benzotriazole UV stabilizers (BZT-UVSs) have been detected in various organisms including invertebrates, fish, birds, and marine mammals (Balmer et al. 2005; Buser et al. 2006; Nakata et al. 2009, 2012; Fent et al. 2010; Kim et al. 2011; Groz et al. 2014; Langford et al. 2015; Lu et al. 2016, 2017, 2018; Wick et al. 2016; Peng et al. 2017b). In addition, these UVAs have been proved and/or suspected to be endocrine disrupting in fish and mammals (Fent et al. 2010, 2014; Downs et al. 2016; Liang et al. 2017). Some BZT-UVSs have been considered to be persistent, bioaccumulative, and toxic chemicals and are managed as substances of very high concern in Europe (Lu et al. 2018).

However, little is known at present about tissue distribution of the UVAs in organisms, nor is species-specific bioaccumulation of the UVAs well understood (Wick et al. 2016).

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Maternal transfer and trophic magnification of the UVAs are also unclear, although some BZT-UVSs have been detected in herring gull eggs from the Great Lakes (USA/Canada; Lu et al. 2018). Clarifying these issues is essential to elucidate mechanisms of accumulation, elimination, and biotransfer of the UVAs in organisms and subsequent proper evaluation of relevant ecotoxicological risks.

In this context, the present study comprehensively investigated the occurrence of 12 commonly used UVAs in edible freshwater wildlife fish from the Pearl River catchment, South China. Species-specific and body-size dependent bioaccumulation of the UVAs was studied to illustrate the mechanisms potentially affecting bioaccumulation and elimination of the UVAs in the fish. Tissue distribution and seasonal and spatial patterns were studied in depth, to better understand bioaccumulation and elimination of the UVAs. The potential for trophic magnification and maternal transfer of the UVAs is discussed, in terms of a more accurate assessment of relevant ecological risks. We provide a full picture of UVA contamination in the freshwater ecosystem.

MATERIALS AND METHODS

Sampling and analysis

Located on the south edge of the subtropical zone, the Pearl River Delta, China has a warm, pluvious climate with an average annual temperature of 21 to 23 °C and an annual precipitation of >1500 mm, mostly in April to September. Details of the study area and sample collection have been described previously (Peng et al. 2018), and a map of the study area with the sampling sites is provided in the Supplemental Data, Figure S1.

Nine species of wild freshwater fish were collected from 7 sites in the main stream of the Pearl River and its 3 tributaries, Xijiang, Dongjiang, and Beijiang (Supplemental Data, Figure S1). Species names along with habitats and feeding habits have been previously described in detail (Peng et al. 2018) and are provided in the Supplemental Data, Table S1. Sampling time, sampling sites, and body size of the fish are also detailed in the Supplemental Data, Table S1. The river water samples were collected concurrently. Considering the climatic and meteorological characteristics of the study area, samplings were performed in dry (October to the following March) and wet (April–September) seasons. The water samples were concentrated with solid-phase extraction within 24 h after arrival at the laboratory, where the fish were stored in a freezer at –20 °C until treatment.

A total of 174 fish were analyzed. The fish samples were carefully washed and physically measured before being skinned and dissected. The weight and length of the fish ranged from 30.6 to 1232.4 g and from 12.5 to 49.0 cm, respectively. Dorsal muscles, belly fat, and livers were collected and treated separately. Swimming bladders were collected and analyzed for some barbell chub and mud carp. Ovaries of female fish were also collected and analyzed if available. As a consequence, 448 biota samples were analyzed including 174 dorsal muscles, 172 belly fat, 67 livers, 18 swimming bladders, and 17 ovaries.

Treatment and analysis of the biota samples have been detailed previously (Peng et al. 2015) and are also provided in the Supplemental Data. The biota samples were lyophilized, homogenized, and spiked with internal standards (benzophenone-d_{10} and 4-methyl-benzylidene camphor-d_4) prior to being extracted with ultrasonic assisted extraction (USE). The USE extracts were cleaned up with gel permissible chromatography followed by silica gel column chromatography. The sample was finally brought to dryness and reconstituted in methanol for ultra-high–performance liquid chromatography coupled with tandem mass spectrometry (UHPLC–MS/MS) analysis. Lipid contents of the biota samples were determined by the gravimetric method. The UVA concentrations in biota samples were reported based on lipid weight.

Trophic level determination

Stable nitrogen ($\delta^{15}N$) and carbon ($\delta^{13}C$) isotope analyses were conducted using dorsal muscles and a FlashEA 1112 series elemental analyzer coupled with a Finnigan MAT ConFlo III isotope ratio MS device (Thermo Scientific). The analyzing procedure and precision have been detailed previously (Peng et al. 2018) and are also provided in the Supplemental Data. The $\delta^{15}N$ and $\delta^{13}C$ of the freshwater fish from the Pearl River catchment ranged from 4.87‰ to 12.78‰ and from –29.03‰ to –18.43‰, respectively (Peng et al. 2018).

Trophic levels of the fish were then determined using grass carp (*Ctenopharyngodon idella*, $\delta^{15}N$ of 5.32‰) as the baseline organism (trophic level = 2.0), as detailed in the Supplemental Data; the levels were 2.0 to 3.6 for freshwater fish (Peng et al. 2018).

Bioaccumulation factors (BAFs), biota–sediment accumulation factors (BSAFs), and trophic magnification factors (TMFs) were estimated for the UVAs to reveal their potential for bioaccumulation and trophic magnification, which have also been detailed previously (Peng et al. 2018) and in the Supplemental Data.

Quality assurance and quality control

Quality assurance followed procedures described previously (Peng et al. 2015) and provided in detail in the Supplemental Data. Recoveries of the UVAs from the biota samples ranged from 70 to 120%. The limits of quantification were generally 0.003 to 1.0 ng/g dry weight. Trace amounts of 3-(4-methylbenzylidene)-dl-camphor (4-MBC), UV-531, UVP, UV329, UV326, UV-234, UV328, and UV327 were found in procedural blanks and were appropriately subtracted in the reported results. Random replicate samples were used to monitor analytical performance, and the results were subsequently expressed as mean ± standard deviation.

Data analysis

Data processing was conducted using Microsoft Excel 2010, Origin Ver 8.0 (OriginLab), and IBM SPSS Statistics Ver 19.0. Differences were analyzed using Kruskal–Wallis tests because

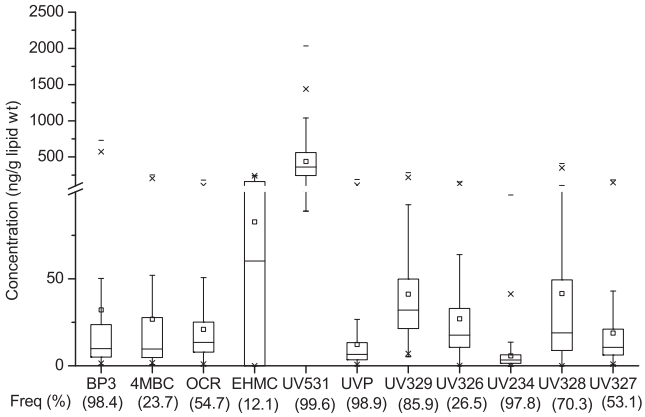

FIGURE 1: Boxplot of the organic ultraviolet absorbents in wildlife freshwater fish from the Pearl River catchment, China. PB3 = 2-hydroxy-4-methoxybenzophenone; 4-MBC = 3-(4-methylbenzylidene)-dl-camphor; OCR = octocrylene; EHMC = 2-ethylhexyl-4-methoxycinnamate.

the UVA concentrations were not normally distributed or homogeneous. The statistical significance level was set at $p \le 0.05$.

RESULTS AND DISCUSSION

Occurrence and bioaccumulation of the UVAs in the wild freshwater fish

The ∑UVAs concentrations ranged from 109 to 2320 ng/g lipid weight. Eight UVAs, including 2 UVFs (BP-3 and OCR), UV531, and 5 BZT-UVSs (UVP, UV329, UV234, UV328, and UV327) were detected in >50% of the biota samples ($n = 448$). The most abundant was UV531, with a concentration of 353 ± 300 ng/g lipid weight. The BZT-UVSs were widely present in the fish tissues except for UV326 (Figure 1). This UVA distribution pattern was basically consistent with that in marine organisms from the Pearl River Estuary (Peng et al. 2017b). The detected level of the BZT-UVSs (not detected – 377 ng/g lipid wt) fell in the range of levels reported in freshwater fish from a Canadian urban creek, the Great Lakes, and German rivers (Lu et al. 2016, 2018; Wick et al. 2016). However, the distribution pattern showed certain geographic differences. For example, UV329 and UV327 were not detected in fish and herring eggs from a Canadian urban creek and the Great Lakes, whereas UV327 and UV329 were widely detected in fish from the German rivers (Wick et al. 2016) and from the Pearl River catchment in the present study (Figure 1). The UVFs (including EHMC, 4-MBC, BP-3, and OCR) were widely found at rather high levels in invertebrates (e.g., mussels and crustaceans) and vertebrates (e.g., fish and birds) from Swiss lakes and rivers (Balmer et al. 2005; Busher et al. 2006; Fent et al. 2010). In fish from Iberian river basins (Spain), EHMC was also frequently detected, with a maximum concentration of 241.7 ng/g dry weight (Gago-Ferrero et al. 2015). However, in the present study, EHMC and 4-MBC were only occasionally detected in wild freshwater fish from the Pearl River catchment (Figure 1). These differences in UVA distributions in freshwater ecosystems worldwide might be mainly due to differences in use and subsequently differences in emission of the UVAs in geographically different regions. In addition, differences in fish body sizes (Supplemental Data, Table S1) between the present study and others might also be a reason for the differences in UVA distribution because bioaccumulation of some UVAs appeared to be body size dependent, which will be discussed in detail later.

Log BAFs of the UVAs were 1.61 to 4.54, 2.15 to 4.74, 3.24 to 5.24, 1.32 to 4.74, and 0.51 to 4.60 for dorsal muscle, belly fat, liver, egg, and swimming bladder, respectively, based on the detected UVA concentrations in the fish tissues and the ambient river water (Table 1, Figure 2, and Supplemental Data, Table S2), indicating slight to moderate tendencies toward bioaccumulation, except for UV531, which was obviously bioaccumulative, with log BAFs of 4.54 ± 0.55, 4.74 ± 0.59, and 5.24 ± 0.35 in fish dorsal muscle, belly fat, and liver, respectively. An average BAF of 762 was reported for EHMC in fish from Swiss rivers (Fent et al. 2010). It is of particular interest to note that the estimated log BAFs for the benzophenone-type UVAs, especially UV531, were obviously

TABLE 1: Bioaccumulation factor (BAF), biosediment accumulation factor (BSFA), and trophic magnification factor (TMF) of the organic ultraviolet (UV) absorbents (bold face means bioaccumulative)

		Log BAF				
Compound	Log K_{OW}	Predicted[a]	Measured[b]	BSAF measured[b]	Bio–half-life (d)[a]	TMF estimated[b,c]
BP-3	3.52	1.82	2.06 ± 0.93	0.49 ± 0.71	0.17	1.3 ± 0.1
4-MBC	5.9	4.7	—[d]	—[d]	19	—[d]
OCR	6.88	2.49	—[d]	0.5 ± 0.55	1.26	0.7 ± 0.04
EHMC	5.8	2.8	—[d]	—[d]	1.6	—[d]
UV531	6.96	2.58	**4.54 ± 0.55**	**4.88 ± 6.78**	1.46	1.0 ± 0.3
UV329	6.2	4.07	3.02 ± 0.63	0.34 ± 0.56	8	0.9 ± 0.1
UVP	3	2.56	1.61 ± 0.45	0.25 ± 0.41	1.02	0.7 ± 0.1
UV326	5.6	3.07	—[d]	—[d]	3	—[d]
UV234	7.7	4.73	2.23 ± 0.59	0.1 ± 0.16	13	1.6 ± 0.1
UV328	7.3	4.97	—[d]	1.36 ± 1.96	14	1.2 ± 0.1
UV327	6.9	3.86	—[d]	—[d]	13	1.4 ± 0.3

[a]By Estimation Program Interface (EPI) Suite (Ver 4.11) modeling.
[b]Calculated on dorsal muscle.
[c]With no significance.
[d]Could not be calculated due to low detection.
Bold text means bioaccumulative.
PB3 = 2-hydroxy-4-methoxybenzophenone; 4-MBC = 3-(4-methylbenzylidene)-dl-camphor; OCR = octocrylene; EHMC = 2-ethylhexyl-4-methoxycinnamate; UVP = ultraviolet stabilizers.

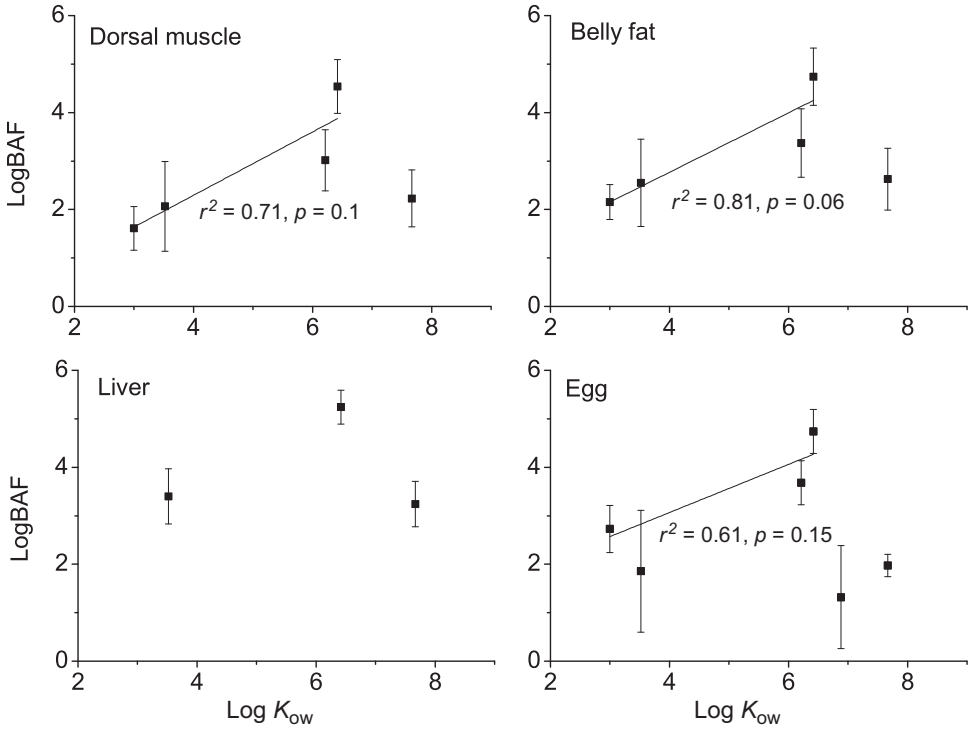

FIGURE 2: Relationships of the bioaccumulation factors (log BAF) with log K_{OW} values.

higher than the predicted values using EPI Suite Ver 4.0, whereas for the BZT-UVSs, the measured log BAFs were lower than the predicted values (Table 1). This finding suggests potential differences in bioaccumulation and metabolism between benzophenone-type and benzotriazole-type UVAs in fish. As for polychlorinated biphenyls, polybrominated diphenyl ethers (PBDEs), and phenolic endocrine-disrupting contaminants (Sun et al. 2015; Peng et al. 2018), a parabolic relationship was observed between the estimated log BAF and the log octanol/water partition coefficient (K_{OW}) of the UVAs in wild freshwater fish (Figure 2), which might be related to poor bioavailability of strongly hydrophobic chemicals (Sun et al. 2015). A similar phenomenon has also been observed for UVAs in marine organisms from the Pearl River Estuary (Peng et al. 2017b).

The estimated BSAFs based on measured concentrations in fish and the river bed sediment (Peng et al. 2017a) were mostly <1.7, except for UV531 (4.9–7.6; Table 1 and Supplemental Data, Figure S2), indicating a slight tendency of the UVAs to partition from sediment to organisms (except for UV531). A similar result was reported for the UVFs in fish from Swiss rivers, with BSFAs of 0.04 to 0.3, which was ascribed to excretion of the UVFs by fish (Fent et al. 2010). However, higher BSAFs were reported for UV328 (0.22–31.2) and UV234 (1091 ± 337) in fish from a Canadian urban creek, which was ascribed to nonequilibrium conditions caused by unknown sources (Lu et al. 2016).

Lifetime bioaccumulation patterns of UVAs in wild freshwater fish

Body size- and/or age-dependent accumulation has been reported for various organic contaminants in fish and other organisms (Wan et al. 2007; Van Ael et al. 2013; Su et al. 2017; Peng et al. 2018; Lyons et al. 2019). Overall, the concentrations of UV531 ($r = -0.13$, $p < 0.001$) and BP-3 ($r = -0.2$, $p < 0.001$) were slightly negatively correlated with fish weight, suggesting potential effects of growth dilution in wild freshwater fish. Specifically by species, in barbell chub and redbelly tilapia, the concentrations of UV 531, BZT-UVSs, and BP-3 showed decreasing trends as fish weight increased, except for BP-3 in the dorsal muscle of barbell chub (Supplemental Data, Figures S3 and S4). In contrast, Lu et al. (2017) found a significantly positive correlation between the concentration of UV234 in chub and fish body weight and length, which was ascribed to a significantly negative correlation between chub body size and lipid content and sufficiently slow release of UV234 for its increase as the fish grew. However, negative but not significant correlations were found between the lipid contents and the weight for both barbell chub and redbelly tilapia in the present study. Therefore, lipid variations did not seem to account for the decrease in UVA concentrations with increasing weight of barbell chub and redbelly tilapia. In the dorsal muscle of common carp, however, a parabolic correlation was observed between the BZT-UVS concentrations and fish weight (Supplemental Data, Figure S5), probably suggesting predominance of accumulation and metabolism of the BZT-UVSs in early and adult growth stages of fish, respectively. On the other hand, a U-shaped pattern of lifetime accumulation was observed for organochlorine contaminants in Mako sharks, with decreasing contaminant concentrations from 53 to approximately 100 cm fork length due to growth dilution, which was relatively stable from 100 to 200 cm fork length owing to a balance between accumulation, and sharply increasing

concentrations after approximately 200 cm fork length as a result of accumulation rather than elimination and/or growth dilution (Lyons et al. 2019). The results of the present study also suggest important roles for metabolism in elimination of the UVAs in all the fish tissues. Metabolism as a mechanism of elimination of 4-MBC, benzophenone-4, and BTZ-UVSs in biota has been described previously (Fent et al. 2010; Wick et al. 2016). Similar results were also observed for some endocrine-disrupting personal care products in the same fish species in our previous research (Peng et al. 2018).

Tissue distribution

Generally, the UVA concentrations in the fish decreased on the order of liver, belly fat, swimming bladder, dorsal muscle, and egg (Supplemental Data, Figure S6). Hepatic concentrations were significantly higher than those in the other tissues ($p < 0.001$), indicating that the liver is a major organ of UVA accumulation in wild freshwater fish, which was consistent with results obtained for the BZT-UVSs and other organic contaminants (Wan et al. 2009; Wu et al. 2009; Peng et al. 2012, 2018; Dominguez-Romero et al. 2016; Lu et al. 2017).

The tissue-specific partition coefficient between liver and other tissues has been used to evaluate the extent of liver accumulation of chemicals. A log partition coefficient near 0 indicates an equal distribution between the liver and the other tissues, whereas coefficients of >1 indicate enrichment in the liver over other tissues (Lu et al. 2017). The log partition coefficients for the UVAs were mostly <0.5 except for the log (liver/dorsal muscle) values for BP-3 (0.7 ± 0.5) and UVP (0.7 ± 0.4; Figure 3), suggesting no significant accumulation in the liver over that in the dorsal muscle and belly fat of the wild freshwater fish for most of the UVAs. Furthermore, the log (liver/belly fat) values of BZT-UVSs were close to 0, particularly for UV234 (0.002 ± 0.5) and UV328 (0.011 ± 0.3), suggesting a higher metabolism of the BZT-UVSs in the liver than in belly fat of freshwater fish. Higher rates of biotransformation and clearance in the liver than in ovary and muscle have been reported for pharmaceuticals and personal care products in zebrafish (Chen et al. 2017). The tissue-specific partition coefficients were negatively correlated with the log K_{OW} value (Figure 3), suggesting that stronger hydrophobic UVAs are more likely to undergo hepatic metabolism in wild freshwater fish.

Species-specific accumulation

Overall, mud carp contained the highest UVA concentrations, followed by common carp, whereas silver carp had the lowest UVA concentrations (Figure 4). Specifically, the concentrations of BP-3 and OCR were obviously lower ($p < 0.03$) in mud carp and Guangdong black bream than in the other species. In contrast, UV531 and the BTZ-UVS concentrations were obviously higher ($p < 0.05$) in mud carp and common carp than in the other species. Species-specific and compound-dependent accumulation of the UVAs was also observed in marine organisms from the Pearl River Estuary (Peng et al. 2017b).

In terms of habitat, the UVA concentrations were obviously higher in demersal fish than in pelagic species ($p < 0.04$), particularly for UV531 and the BTZ-UVSs, which might be related to higher availability of these compounds in sediment due to their strong hydrophobicity. Lu et al. (2016) reported that UV328 was more frequently detected in bottom-dwelling crayfish, whereas UV234 was more frequently detected in pelagic chub and shiner in a Canadian urban creek, which was ascribed to different partition processes of UV234 from water or sediment to different species and/or different metabolic

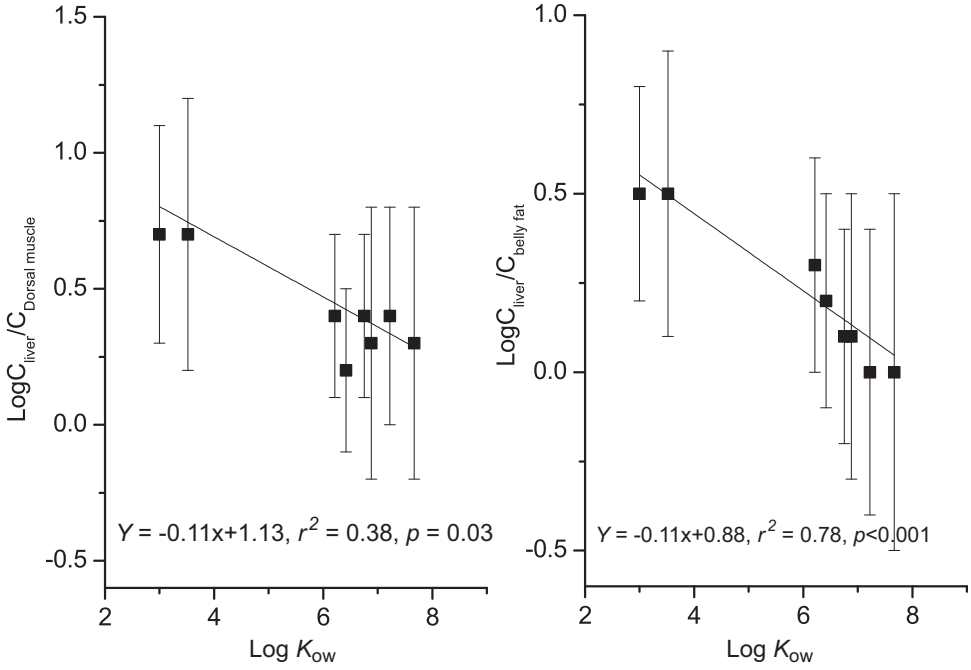

FIGURE 3: Tissue-specific partition coefficient between liver and dorsal muscle (left) and belly fat (right) of the ultraviolet absorbents (UVAs) and their relationships with log K_{OW} values.

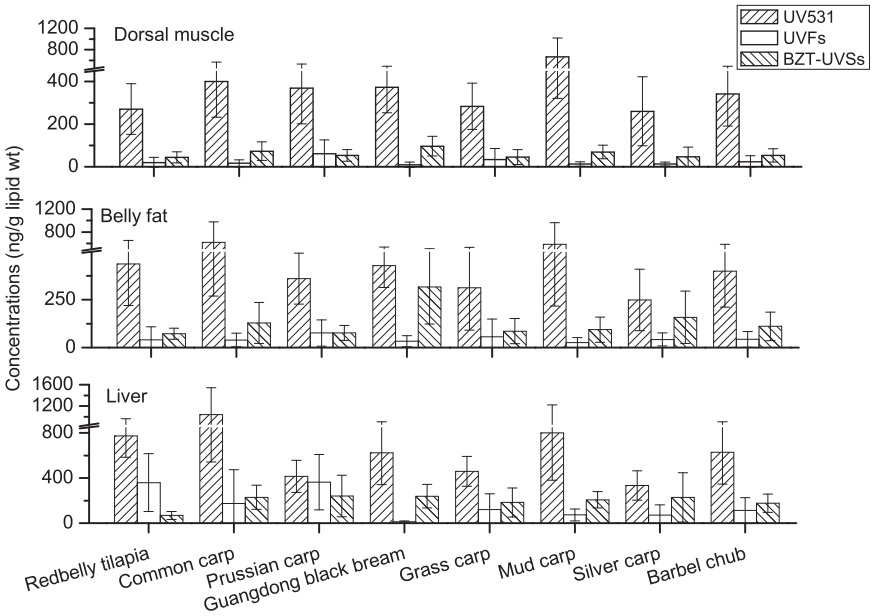

FIGURE 4: Species-specific patterns of the ultraviolet asorbents (UVAs) in wildlife freshwater fish. UVFs = UV filters; BZT-UVSs = benzotriazole UV stabilizers.

processes in different species of organisms. The OCR concentration was also relatively higher in the bottom dwellers, which was consistent with wide presence of OCR in sediment of the Pearl River catchment (Peng et al. 2017a). Furthermore, the lowest OCR concentration was found in mud carp and Guangdong black bream, which live in mid-water to bottom (Figure 4). No habitat differences were found for BP-3, probably associated with its wide presence at low concentrations in both the riverine water and sediment (Peng et al. 2017a). Species-specific bioaccumulation of the other UVFs, such as EHMC and 4-MBC, cannot be discussed in the present study due to limited detections. Fent et al. (2010) reported obviously higher (~5-fold) concentrations of EHMC in sediment-dwelling barb than in chub, which prefers open water.

In terms of feeding habits, omnivores, especially detritus-ingesting omnivores, contained obviously higher UVA concentrations ($p < 0.02$). Concentrations of BP-3, UV531, and BTZ-UVSs were clearly higher in detritus-ingesting omnivores, suggesting that detritus ingestion is an important pathway for exposure of fish to UVAs in the environment. In addition, BP-3 was also relatively abundant in the vegetarian grass carp. However, the OCR concentration did not show an obvious difference according to feeding habits of the fish.

Spatial and seasonal distribution

The concentrations of UV531 ($p = 0.02$) and BP-3 ($p = 0.008$) in freshwater fish were obviously higher in the dry season than in the wet season, as illustrated by mud carp from Beijiang and Xijiang (Supplemental Data, Figures S7 and S8), which was consistent with the results in river water (Peng et al. 2017a). In contrast, the concentrations of OCR and BZT-UVSs were (nonsignificantly) higher in fish collected during the wet season than in those collected during the dry season (Supplemental Data, Figures S7 and S8), probably related to the fact that detritus and sediment ingestion is a major exposure route of fish to OCR and BZT-UVSs.

Spatial patterns of UVA bioaccumulation in the wild freshwater fish differed by species to a certain degree. For instance, the concentrations of UV531 and BZT-UVSs were obviously higher in silver carp from Dongjiang than from the other tributaries (Supplemental Data, Figure S9), whereas in Guangdong black bream, the UVA concentrations did not exhibit an obvious spatial difference (Supplemental Data, Figure S10). The sampling sites in Dongjiang (R7 and R8; Supplemental Data, Figure S1) are located near Dongguan City, an important manufacturing center that is much more industrialized and more densely populated than the areas near the Xijiang (R1) and Beijiang (R2) tributaries. Thus Dongguan City would have a higher release of toxins to the Dongjiang tributary, which would subsequently cause higher concentrations of UVAs in pelagic silver carp, especially the compounds UV531 and BZT-UVSs that are commonly used in industrial products. Similar data have been reported for UVFs in fish from Swiss rivers and BZT-UVSs in organisms from the Great Lakes (Fent et al. 2010; Lu et al. 2018). Higher concentrations and loads of BZT-UVs in highly urban rivers compared with rural rivers have also been observed during both snowmelt and rainfall events in Canada (Parajulee et al. 2018).

In aquatic systems, plastic debris has been considered an important source of UVSs, which are commonly used as additives in plastic products (Rani et al. 2017; Parajulee et al. 2018). Ingestion of plastics by birds has been suggested to increase their exposure risks to plastic additives including BZT-UVSs (Lu et al. 2018). Our previous research revealed more abundant plastic debris in the water, sediment, and freshwater fish from Dongjiang than from Xijiang and Beijiang (Fan et al. 2019; Zheng et al. 2019), which was consistent with the spatial

distribution of UVAs in wild freshwater fish. Therefore, plastic debris ingestion might also be an important route of exposure to UVAs for wild freshwater fish in the Pearl River catchment.

Trophic magnification and human exposure

Based on the detected UVA concentrations and trophic levels (2.0–3.6) of the fish, the calculated TMFs for the UVAs were 0.7 to 1.4 and 0.6 to 2.4 in dorsal muscle and belly fat, respectively. Some UVAs (e.g., BP-3 and UV327) showed a slight, nonsignificant tendency toward trophic magnification in belly fat of freshwater fish (Supplemental Data, Figures S11 and S12). The TMFs in liver, egg, and swimming bladder could not be obtained due to limited detection, which indicated no obvious trophic magnification of the UVAs in the freshwater ecosystem of the Pearl River catchment, probably related to the metabolism of UVAs in the fish. The UVA UV531 did not biomagnify, with TMFs of 0.8 in dorsal muscle (Supplemental Data, Figure S11) and 1.1 in belly fat (Supplemental Data, Figure S12), although it was obviously bioaccumulative (log BAF = 4.54 ± 0.55) and was the most abundant UVA in freshwater fish. However, UV531 was found to biomagnify in marine organisms from the Pearl River Estuary, with a TMF of 1.7 (Peng et al. 2017b). Previous research has reported that the BAFs for personal care products were different in freshwater organisms compared with the BAFs in marine organisms (Chen et al. 2017), which might also explain the difference in trophic magnification of UV531 between marine organisms and freshwater fish. It has been speculated that some of the UVFs, such as EHMC and OCR, biomagnified to a certain degree based on their concentrations in the predator/prey pairs (Fent et al. 2010; Gago-Ferrero et al. 2015).

Ratios of chemical concentrations in ovary versus those in paired maternal liver (E/L) were used to evaluate maternal transfer potential (Russell et al. 1999; Wu et al. 2009, 2013; Peng et al. 2012). The E/L values of the UVAs in freshwater fish ranged from 0.27 ± 0.19 (UV531) to 0.7 ± 0.65 (UV329; Supplemental Data, Figure S13); these values are in the range of those reported for various halogenated compounds and personal care products such as PBDEs and parabens in fish and frogs (Serrano et al. 2008; Van den Steen et al. 2009; Wu et al. 2009, 2013; Peng et al. 2018). The E/L values were not closely correlated with log K_{OW} or hepatic concentrations (Supplemental Data, Figure S13). In addition to the lipophilicity of the compounds, several other factors, such as contaminant levels and the ecology and physiology of organisms, may have effects on maternal transfer of contaminants (Wu et al. 2013; Lyons et al. 2019). More data are needed to fully elucidate maternal transfer and related mechanisms of UVAs in wild freshwater ecosystems.

Assuming an average body weight of 60 kg for adults and an average consumption of 105 g fish/person in the study area, as adopted previously (Peng et al. 2017b), the estimated average daily intake of the 12 UVAs via freshwater fish consumption were 19.2 g/kg/d based on the detected concentration in the dorsal muscle. Because of limited information on the relevant toxicological effects of these chemicals on human beings, it is difficult to evaluate the adverse effects resulting from consumption of wild freshwater fish. Future studies are needed on the long-term and mixed effects of organic UVAs co-occurring with various contaminants in the environment.

CONCLUSIONS

The commonly used organic UVAs were widely present in wild freshwater fish from the Pearl River catchment, with UV531 being the most abundant. The UVA UV531 was obviously bioaccumulative, whereas the other UVAs showed slight to moderate tendencies toward bioaccumulation in wild freshwater fish. The UVA concentrations in the fish generally decreased on the order of liver > belly fat > swimming bladder > dorsal muscle > egg. Bioaccumulation of the UVAs was species specific, depending on the feeding habits and habitats of the fish and the compound. Detritus-ingesting, bottom-dwelling omnivorous fish contained obviously higher UVA concentrations, indicating that detritus/sediment ingestion is a significant pathway for exposure of fish to the UVAs. The compounds BP-3 and UV 531 demonstrated a potential for growth dilution in freshwater fish. Metabolism played a significant role in UVA elimination in all fish tissues, with a higher metabolism rate in the liver. The UVAs did not demonstrate obvious trophic magnification in the freshwater ecosystem of the Pearl River catchment.

Supplemental Data—The Supplemental Data are available on the Wiley Online Library at DOI: 10.1002/etc.4616.

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Data Availability Statement—Data, associated metadata, and calculation tools are available by request via pengx@gig.ac.cn.

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