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Personal care products in wild fish in two main Chinese rivers: Bioaccumulation potential and human health risks

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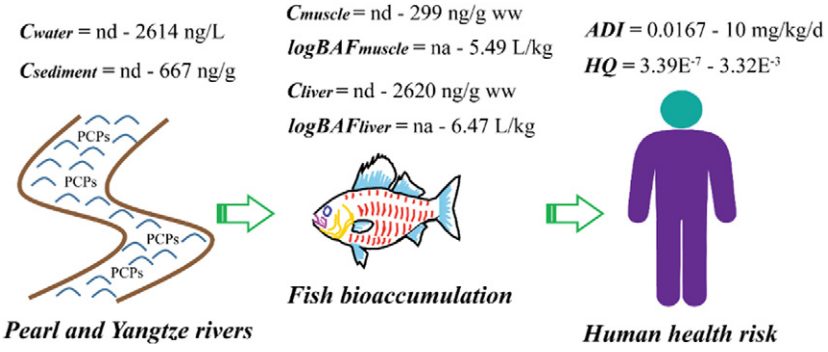
HIGHLIGHTS

- Levels of personal care products (PCPs) in wild fish tissues were investigated.
- Thirteen PCPs were found in muscle/liver tissues up to thousands ng/g wet weight.
- The log BAF displayed good linear relationships with log K_{ow} and log D_{ow}.
- No appreciable health risk to human via the consumption of wild fish muscle

GRAPHICAL ABSTRACT



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ABSTRACT

Personal care products (PCPs) are widely applied in our daily life, however, little is known about their occurrence in wild fish. We investigated the bioaccumulation and potential risks of 24 PCPs in muscle and liver tissues of wild fish collected from two large rivers of Pearl and Yangtze Rivers in China. The results showed the detection of a total of 13 PCPs including 9 biocides, 2 synthetic musks and 2 benzotriazoles in at least one type of fish tissue from 12 fish species. The compounds with high detection frequencies (>50%) in fish muscle or liver tissues were *N*,*N*-diethyl-3-methylbenzamide, carbendazim, climbazole, miconazole (MCZ), methylparaben, propylparaben, triclosan (TCS), tonalide, galaxolide (HHCB) and 5-methyl-1H-benzotriazole (5-TT). Among biocides, synthetic musks and benzotriazoles, TCS, HHCB and benzotriazole showed the maximum concentrations of 79.5 ng/g wet weight (ww), 299 ng/g ww and 3.14 ng/g ww, respectively, in muscle tissue, while MCZ, HHCB and 5-TT showed the maximum concentrations of 432 ng/g ww, 2619 ng/g ww and 54.5 ng/g ww, respectively, in liver tissue. The median values of logarithm of bioaccumulation factors (BAF) for the detected 13 PCPs were ranged 0.8–3.35 in muscle and 0.85–4.58 in liver. The log BAF values of the PCPs displayed good linear relationships with log K_{ow} and log D_{ow} (pH-dependent K_{ow}). The health hazard assessment of 10 detected PCPs in the muscle indicated no appreciable risk to human via consumption of the wild fish.

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1. Introduction

The active ingredients of personal care products (PCPs) including biocides, synthetic musks and benzotriazoles have received increasing attention as emerging contaminants due to their ubiquitous existence in the environment (Chen and Ying, 2015; Lee et al., 2010; Giger et al., 2006). The sources of PCPs in the environment are from the widespread use of personal and household care products (Wieck et al., 2016). In the whole of United States, the annual usage of *N,N*-diethyl-3-methylbenzamide (DEET) was approximately 1100 tons for the year of 2009 (Aronson et al., 2012), while that of benzotriazole (BT) was approximately 9070 tons for the year of 2003 (Hart et al., 2004). In the whole of China, the annual usage of climbazole (CBZ) was estimated to be 345 tons, according to the market sales data for the year of 2011 (Zhang et al., 2015), while the annual total usage of triclocarban (TCC) and triclosan (TCS) was estimated to be 1220 tons based on the consumption statistics of commodities at the period around the year 2011 (Zhao et al., 2013). In 2004, the global production volumes of synthetic musks were approximately 5000 and 1000 tons for tonalide (AHTN) and galaxolide (HHCB), respectively (Lange et al., 2015).

After use, these PCPs end up in domestic wastewaters, which are usually treated in wastewater treatment plants (WWTPs) or directly released into the receiving environment (Ternes et al., 2004). Due to the incomplete removal of PCPs in WWTPs (Chen and Ying, 2015), PCPs were still detected in the effluents (Liu et al., 2012), and also found in surface water and sediments (Venkatesan et al., 2012; Wolschke et al., 2011). These emerging PCPs were reported to cause acute or chronic toxicity to aquatic organisms. For biocides, the reproduction of algae was inhibited by CBZ, with the lowest median effective concentrations (EC_{50}) of 0.013 mg/L (Richter et al., 2013). The behavior of daphnia can be influenced by miconazole (MCZ), with the EC_{50} of 0.4 mg/L (Minguez et al., 2016). The lethal concentration (LC_{50}) and lowest observed effect concentration (LOEC) of butylparaben (BP) to daphnia were 5.3 mg/L and 0.2 mg/L, respectively (Dobbins et al., 2009). The toxicity of TCC and TCS fish were extensively reported, with the LC_{50} of TCC and TCS to fish (*Oryzias latipes*) of 85 μg/L and 210 μg/L, respectively (Tamura et al., 2013; Nassef et al., 2010). For synthetic musk, HHCB showed weak acute toxicity to daphnia, with the EC_{50} value of 3.33 mg/L using behavior as endpoints (Pablos et al., 2015). Benzotriazoles also showed a weak toxicity to aquatic organisms. The behavior of *daphnia* was affected by BT and 5-TT, with EC_{50} values of 107 mg/L and 51.6 mg/L, respectively (Seeland et al., 2012).

PCPs would also be taken up by aquatic organisms lived in the aquatic environment. Among various PCPs, AHTN, HHCB, TCC, TCS and parabens were frequently reported to be found in fish homogenates or specific tissues (Jakimska et al., 2013; Ramirez et al., 2009; Subedi et al., 2012). The tissue specific investigations indicated that most of PCPs showed higher bioaccumulation potential in fish liver than that in fish muscle (Tanoue et al., 2015; Xue and Kannan, 2016).

For two large rivers of Pearl River and Yangtze River in China, which receive large quantities of treated and untreated domestic sewage from the fast developing cities like Huizhou, Dongguan, Wuhan and Nanjing (W.R. Liu et al., 2015; Zhao et al., 2015), the occurrence of PCPs such as DEET, CBD, CBZ, parabens, TCC and TCS in the surface water and sediments have been reported in our previous works (F. Chen et al., 2014; W.R. Liu et al., 2015). The bioaccumulation of synthetic musks were widely reported in other areas (Ramirez et al., 2009; Subedi et al., 2012) but not in the Pearl and Yangtze River, and the bioaccumulation characteristics of benzotriazoles have not been reported. Thus, the objectives of this study were to investigate the occurrence of a variety of PCPs (16 biocides, 4 synthetic musks and 4 benzotriazoles) in wild fish (muscle and liver tissues) from the Pearl River and Yangtze River, and to assess the bioaccumulation potential of these PCPs in wild fish, and to calculate their exposure risks to human via wild fish consumption.

2. Materials and methods

2.1. Study area

As shown in Fig. 1, for the Pearl River, sites S1–S2 are located in the Danshui River, site M1 is located in the Shima River, while sites S3, S4 and M2 are located in the mainstream of Dongjiang River, the reference site S5 is located in the Xizhijiang River, which was less influenced by human activities. For Yangtze River, sites C1 and C2 are located in the middle reach of the mainstream, while sites C3–C4 are located in the lower reach. Detailed information of geographic location, population, gross domestic product (GDP) are listed in Table 1, and the quality parameters of surface water and sediment in sampling sites are summarized in Tables S1 and S2.

2.2. Sampling collection

Sampling campaigns were carried out in July 2012 (wet season) and in November 2012 (dry season) for the Pearl River (S1–S5, M1 and M2), and in July 2013 (wet season) and November 2013 (dry season) for the Yangtze River (sites C1–C4). One liter surface water samples (three replicates for each site) were collected and stored in amber glass bottles, then 50 mL of methanol and 400 μL of 4 M H_2SO_4 (adjust pH to 3.0) were added immediately into each bottle to inhibit microbial growth. Sediment samples (approximately 200 mL slurry of each with three replicates) were collected in clean amber bottles. Sodium azide (approximate 1 g/L slurry) was then added into the bottle to suppress potential microbial activity. The collected water and sediment samples were transported to the laboratory in cool containers and then stored in a cold room (4 °C) before further processing within 24 h. Sediment samples were freeze-dried and stored at 4 °C for further extraction. Fish samples were collected by electroshocking with a pulsed direct current or by fish trawls from selected sampling sites. The collection fish were transferred to bucket filled with surface water of sampling sites, and then immediately transported to the laboratory with sufficient aeration to keep fish alive. Once arrival, the alive fish were anesthetized by tricaine methanesulfonate (100 mg/L) and then sacrificed by rapid dissection. The liver was separated from viscera, followed by muscle in abdomen and back after fish skin and bone were removed, and all the muscle in different part of each fish sample was cut up and mixed together. All tissues were immediately stored at −20 °C until extraction. All of the procedures for fish dissection followed the Guidelines reported by Nickum et al. (2004). They were also permitted by the Animal Care and Use Committee of South China Agricultural University (license number 2012-SCAU-X05).

The fish species, including tilapia (*Tilapia aurea*), snakehead (*Ophicephalus argus*), mud carp (*Cirrhinus molitorella*), mullet (*Mugil cephalus*), common carp (*Cyprinus carpio*), chub (*Hypophthalmichthys molitrix*), crucian (*Carassius auratus*), bream (*Parabramis pekinensis*), bullhead (*Ameiurus nebulosus*), snapper (*Lutjanus erythopterus*), grass carp (*Ctenopharynodon idellus*) and catfish (*Clarias fuscus*) were collected in the present study. The descriptive information for fish samples is listed in Table S3. Liver samples were not obtained from each fish due to the difficulty of dissection and the complexity of viscera. Hence, totally 81 fish muscle tissue and 74 liver tissue samples from the two rivers were obtained.

2.3. Sample extraction and instrumental analysis

Three groups of PCPs including biocides, synthetic musks and benzotriazoles were selected as target compounds. Among them, 16 biocides include 3 insect repellents (thiabendazole, DEET and icaridin), 7 antifungals [fluconazole (FCZ), carbendazim (CBD), ketoconazole (KCZ), CBZ, clotrimazole (CTZ), MCZ, itraconazole], 4 preservatives of MP, ethylparaben (EP), propylparaben (PP) and BP, and 2 disinfectants (TCC and TCS). Four synthetic musks are AHTN, HHCB, musk xylene and

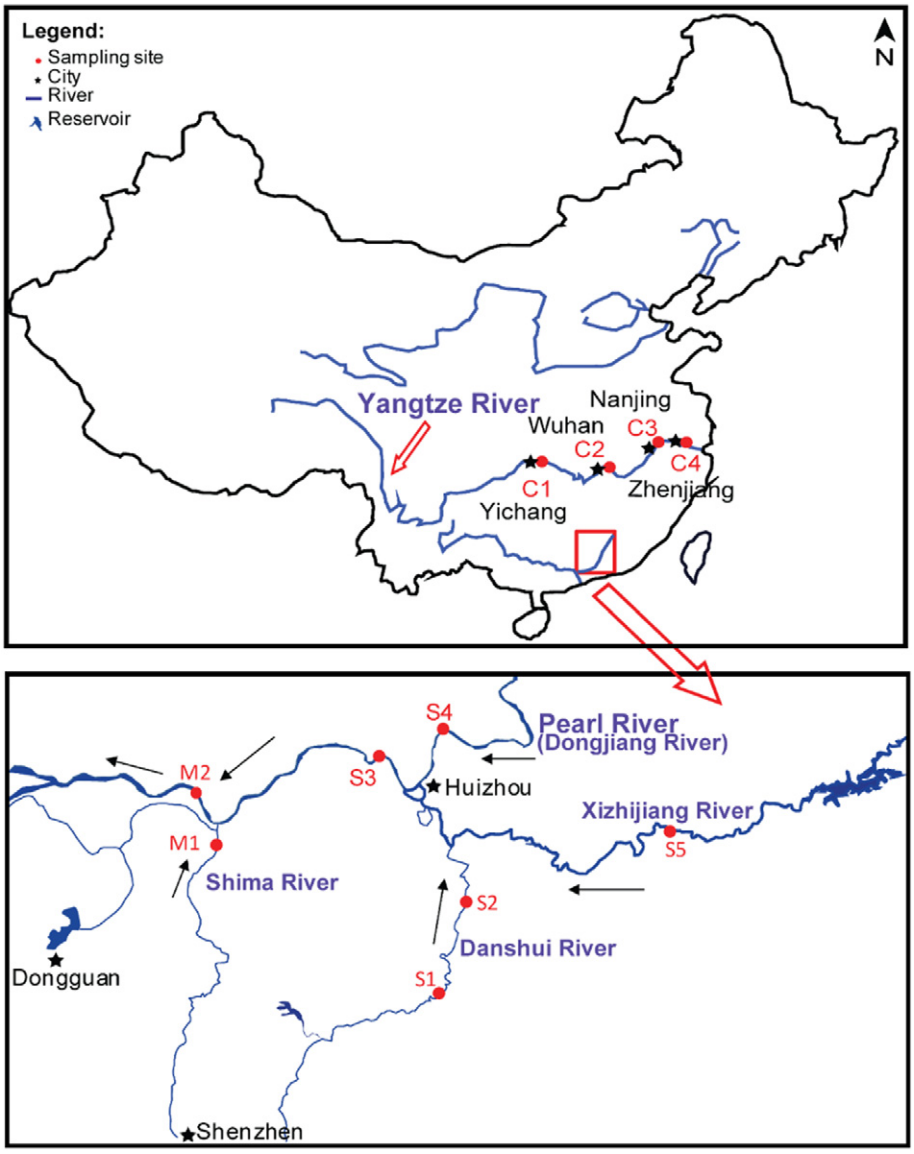

Fig. 1. Map of study area in the Pearl River and Yangtze River showing the sites of water, sediments and fish samples collected.

Table 1
Detail informations for the sampling sites in this study.

Sampling site	Geographic location (N, E)		Site location	Flow (m3/s)		Population (10,000 person)	GDP (100 million yuan)	Site characteristics
				Wet	Dry			
Pearl River								
S1	114°27′13″	22°47′59″	Danshui River	29.1[a]	21.5	20.00[c]		Middle reach
S2	114°29′28″	22°56′38″	Danshui River	246	109	4.00		Lower reach
S3	114°21′42″	23°08′53″	Dongjiang River	608[6]	367	14.88		Middle reach
S4	114°27′19″	23°10′51″	Dongjiang River	593	322	5.90		Upper reach
S5	114°94′39″	23°03′41″	Xizhijiang River	483	91.7	2.20		Reference site
M1	114°06′39″	23°01′11″	Shima River	32.6	45.4	12.29		Lower reach (Tributary)
M2	114°05′30″	23°04′38″	Dongjiang River	1400	403	8.90		Lower reach
Yangtze River								
C1	111°20′41″	30°38′25″	Xiling District	31,000[b]	7410	144.65[d]	710.45[d]	Upper reach
C2	114°19′11″	30°36′50″	Hankou Marshland	33,300	10,400	433.04	2489.04	Middle reach
C3	118°42′59″	32°5′47″	Pukou Dock			342.51	2280.36	Lower reach
C4	119°50′51″	32°16′23″	Erdungang			122.49	999.25	Lower reach

[a] Flow of S1, S2 and M1 was calculated based on the flow rate, river depth and river width, and flow of S3, S4 and M2 cited from previous reported work (Zhao et al., 2013).
[b] Flow of Yangtze River basin from the hydrological information web of China http://xxfb.hydroinfo.gov.cn/ssIndex.html.
[c] The population of sites located in Pearl River basin were estimated according to the population of corresponding towns.
[d] The population and GDP of sites located in Yangtze River basin were obtained from the local "Statistical Yearbook" of 2013.

musk ketone. Four benzotriazoles are BT, 5-methyl-1H-benzotriazole (5-TT), 5-chloro-1H-benzotriazole (CBT) and 5,6-dimethyl-1H-benzotriazole (XT). Their basic physicochemical properties can be found in Table S4. Supplier of the standards, their corresponding internal standards and reagents used in this study are described in Supplementary materials (Text S1).

The extraction methods for target PCPs in water, sediments and fish samples have been developed in our previous studies (Chen et al., 2012; Liu et al., 2011; Z.F. Chen et al., 2014; Yao et al., 2016). Detailed description of the extraction method can be found in Text S2–S4. Briefly, water samples were extracted by the solid-phase extraction, using Waters Oasis HLB cartridges (500 mg, 6 mL). The sediment samples were extracted by ultrasonic extractor (for 16 biocides) or accelerated solvent extractor (for 4 synthetic musks and 4 benzotriazoles). The target PCPs in fish muscle and liver tissues were extracted by QuEChERS (quick, easy, cheap, effective, rugged, and safe) method, and the lipid content of muscle tissues was measured with gravimetric method by following a previous study (Wu et al., 2008). The target PCPs in the extracts of water, sediment and biological samples were analyzed by UPLC-MS/MS (Agilent 1200 series ultra-pressure liquid chromatography coupled to Agilent 6460 triple quadrupole mass spectrometer with electrospray ionization (ESI) source) in multiple reaction monitoring (MRM) mode and GC–MS (Agilent 6890N series gas chromatography integrated with Agilent 5975B mass spectrometer with electron impact (EI) source) in selective ion monitoring (SIM) mode. A Zorbax SB-C18 (Agilent, 100 mm × 3 mm, 1.8 μm particle size) column and DB-5MS column (Agilent, 30.0 m × 0.25 mm, 0.25 μm thickness) were used for the chromatographic separation on UPLC and GC system, respectively. The detail instrumental conditions are described in our previous studies (Chen et al., 2012; Z.F. Chen et al., 2014; Lai et al., 2014).

For each batch of samples, a solvent blank and a check standard (the standard solution with each target PCPs at the concentration of 100 μg/L) were run in sequence to check carryover and system performance. No PCPs were detected in the solvent blanks. Independent check standard was injected approximately every twenty injections, and the expected concentration value was required to be within 20%. The recoveries of 24 PCPs in water, sediment and fish tissues (muscle and liver) were summarized in Table S5.

2.4. Data analysis

For the calculation of concentration ranges, median and mean values, the data with values less than method quantification limits (MQLs) were substituted by a half of MQL (Zhao et al., 2015), and the data of "nd" was substituted by zero. When calculating the detection frequency, data below MQL were also counted, while data of "nd" were not counted. The specific MQL values were also given for the PCPs when the concentrations were lower than MQLs (<MQL) in the text and tables. The differences of concentrations or logarithm of bioaccumulation factors (log BAF) values between two rivers and seasons were examined with the nonparametric tests of Kolmogorov–Smirnov (K-S test). Differences in the concentrations and logarithm of bioaccumulation factors (log BAF) values of detected PCPs for various fish species were examined with the nonparametric of Kruskal-Wallis tests (K-W test). The p-value of <0.05 was considered to be statistically significant. Descriptive statistics and linear regression were performed with the software of Microsoft Excel 2013 and SPSS 16.0.

2.5. Parameters calculation and human exposure risk assessment

The BAF values for target compounds were calculated based on the wet weight (ww) concentrations of each compound in muscle or liver tissues, and the corresponding surface water concentrations at each sampling site. Due to the continue discharge of PCPs into the receiving environments (Zhao et al., 2015), the calculation of bioaccumulation can be assumed at a pseudo steady state, with the following equations:

$$\mathrm{BAF} = \frac{C_{muscle}}{C_w} \times 1000,$$

$$\mathrm{BAF} = \frac{C_{liver}}{C_w} \times 1000.$$

where BAF (L/kg) is the bioaccumulation factor; C_W (ng/L) is the concentration of PCPs in corresponding surface water; C_{liver} (ng/g) or C_{muscle} (ng/g) are the concentrations of PCPs in fish muscle or liver. The log BAF values were also simulated in fish muscle based on the Arnot and Gobas model and conducted with the BCFBAF program of the software Epi Suite 4.1 released from U.S. Environmental Protection Agency (U.S. EPA, 2014). Chemical name and SMILES (simplified molecular-input line-entry system) structure were inputted as the basic parameters.

The pH – dependent octanol – water partition coefficient (D_{ow}) of some detected PCPs were calculated, to examine the influence of pH to the bioaccumulation of PCPs in wild fish, with the following equation (Tanoue et al., 2015; Meredith-Williams et al., 2012):

$$f_{ion} = f_{neutral} \times 10^{i\ (pH-pK_a)},$$

$$\log K_{ow\ (ion)} = log\ K_{ow\ (neutral)} - 3.5,$$

$$D_{ow} = f_{neutral}\ K_{ow(neutral)} + f_{ion}\ K_{ow(ion)}.$$

where $f_{neutral}$ and f_{ion} are the fraction of neutral and ionic species of contaminants at study pH, respectively, $K_{ow\ (neutral)}$ and $K_{ow\ (ion)}$ are the K_{ow} values for neutral and ionic species, respectively.

Potential intake (mg/kg/d) of the PCPs by human consumers was assessed based on the average intake of fish muscle and the observed contaminant concentrations (Dunnivant and Anders, 2006), with the following equation:

$$\mathrm{Intake} = \frac{C_{fish} \times \mathrm{IR} \times \mathrm{FI} \times \mathrm{EF} \times \mathrm{ED}}{\mathrm{BW} \times \mathrm{AT}}.$$

where C_{fish} is the concentration of one compounds of PCPs in fish muscle with unit of mg/kg ww, IR is the fish ingestion rate (0.054 kg/d), FI is the fraction of the daily fish intake from the polluted source (assume to 1.00), EF is the exposure frequency (350 d/y), ED is the duration of exposure (30 y), BW adult body weight (70 kg) and AT the time period over which exposure is averaged (30 y × 365 d/y).The human intake risks were assessed by hazard quotient (HQ) which is derived from the ratio between the intake rate and the acceptable daily intake by adult (Boonsaner and Hawker, 2013). The HQ value equal or above 1.0 indicates high risk of an adverse health effect, and conversely the HQ value below 1.0 indicates low risk.

3. Results

3.1. Concentrations of PCPs in surface water, sediments and wild fish

In surface water, 18 out of 24 PCPs including DEET, FCZ, CBD, CBZ, CTZ, MCZ, MP, EP, PP, BP, TCC, TCS, AHTN, HHCB, BT, 5-TT, CBT and XT were detected in the Pearl River and Yangtze River (Fig. 2a, Table S6). Among the three classes of PCPs (biocides, synthetic musks and benzotriazoles), DEET, HHCB and BT were detected at relatively high levels with the maximum concentrations up to 166, 133 and 2614 ng/L, respectively. While in sediments, TCC, HHCB and BT were detected at the maximum concentrations of 667, 57.7 and 63.1 ng/g, respectively (Fig. 2b, Table S7). It can be seen that chemicals frequently detected in surface water samples were also commonly found in sediments, except for FCZ, BP and XT were only found in surface water

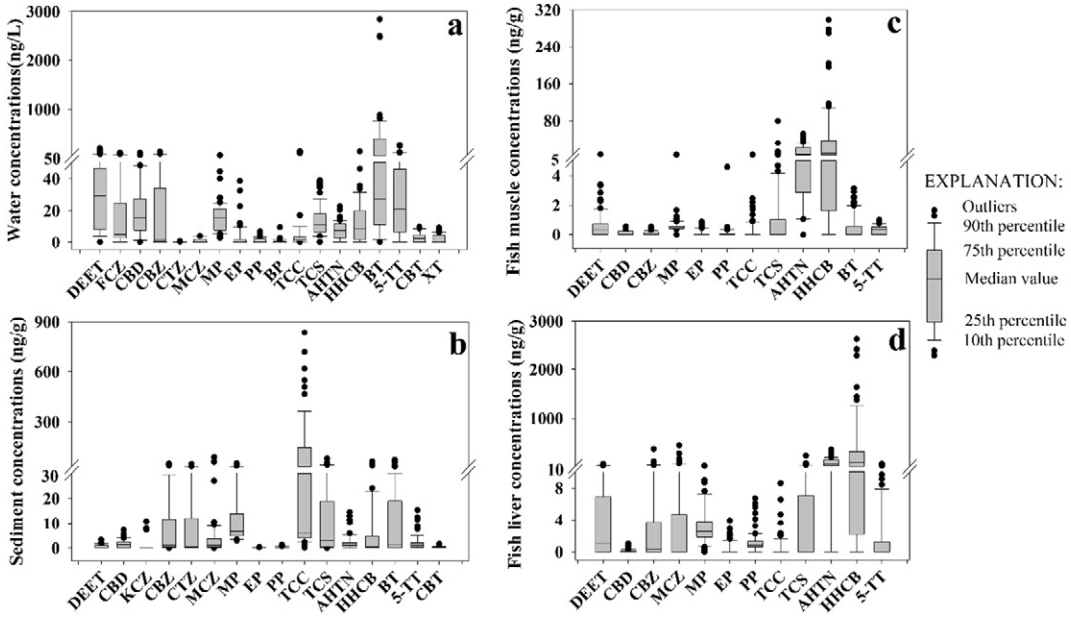

Fig. 2. The concentrations of personal care products in surface water (a), sediment (b), fish muscle (c) and fish liver (d). The box plot graphically depicts the distribution of the concentrations using five number summaries (the smallest observation, lower quartile, median, upper quartile and the largest observation).

samples, and KCZ were only detected in sediment samples. Besides, only 10 PCPs were occasionally detected in the surface water or sediment samples of reference site S5, except for DEET (61.4 ng/L), the concentrations of detected PCPs were lower than 9.50 ng/L (AHTN) in surface water and 4.81 ng/g (MP) in sediment (Table S8).

In fish tissues, 13 out of the 24 target PCPs, including 9 biocides (DEET, CBD, CBZ, MCZ, MP, EP, PP, TCC and TCS), 2 synthetic musks (AHTN and HHCB) and 2 benzotriazoles (BT and 5-TT), were detected at least once in fish muscle or liver samples collected from the sampling sites of Pearl River and Yangtze River (Tables 2, 3). Overall, the target compounds detected in muscle tissues with high frequencies were also frequently found in liver tissues. And for most of the detected compounds (except for EP and TCC), their concentrations in liver were higher than those in muscle (K-S test, $p < 0.05$). For example, the mean concentrations of DEET, CBZ, HHCB and 5-TT in liver were dozens of times higher than those in muscle tissues, and the mean concentrations of MP, TCS and AHTN in liver tissues were also several times higher than those in muscle tissues. At the reference site, only MP and AHTN were found in the fish tissues, with the maximum concentrations of 0.61 ng/g (MP) and 1.06 ng/g (AHTN) in muscle, and 4.48 ng/g (MP) and 6.47 ng/g (AHTN) in liver (Table S8).

For fish muscle (Table 2, Fig. 2c), the mean concentrations of 12 PCPs ranged from <0.08 ng/g ww (EP) to 51.4 ng/g ww (HHCB) in the Pearl River and Yangtze River. Two synthetic musks (AHTN and HHCB) had the relatively high detection frequencies and concentrations in both Pearl River and Yangtze River, followed by biocides (DEET, MP, PP and TCS). For synthetic musks, AHTN and HHCB were detected at maximum concentrations of 52.1 ng/g ww (common carp, S2) and 299 ng/g ww (common carp, S2), respectively. For biocides, only a sporadic detection of TCS was found with a maximum concentration of 79.5 ng/g ww (common carp, S3). The maximum concentrations of other biocides compounds ranged from 0.54 ng/g ww for CBZ (common carp, S3) to

Table 2
Summary of concentrations (ng/g ww) of detected target compounds in fish muscle samples from Pearl River and Yangtze River.

Compound	Pearl River								Yangtze River							
	Wet season				Dry season				Wet season				Dry season			
	D.F[a]	Range	Mean	Median	D.F	Range	Mean	Median	D.F	Range	Mean	Median	D.F	Range	Mean	Median
Biocides																
DEET	61%	0–3.33	0.64	0.50	45%	0–6.46	1.00	nd	63%	0–1.17	0.38	0.40	88%	0–1.80	0.41	0.32
CBD	36%	0–0.28	<0.09[c]	nd[b]	45%	0–0.37	0.12	nd	63%	0–0.31	0.14	0.20	65%	0–0.55	0.16	0.20
CBZ	54%	0–0.54	<0.30	nd	20%	0–<0.3	<0.30	nd	31%	0–0.43	<0.30	nd	35%	0–<0.30	<0.30	nd
MP	79%	0–1.06	0.47	0.52	100%	0.39–1.09	0.64	0.57	100%	0.36–0.70	0.47	0.46	100%	0.39–5.66	0.92	0.45
EP	7%	0–0.35	<0.08	nd	0%	nd	nd	nd	38%	0–0.79	0.17	nd	41%	0–0.88	0.24	nd
PP	64%	0–0.35	<0.20	nd	40%	0–0.44	<0.20	nd	94%	0–0.24	<0.20	<0.20	100%	0.29–4.58	1.80	0.52
TCC	14%	0–2.45	<0.22	nd	35%	0–5.63	0.66	nd	13%	0–<0.22	<0.22	nd	24%	0–0.57	<0.22	nd
TCS	39%	0–79.5	3.82	nd	30%	0–31.2	2.11	nd	38%	0–12.4	1.52	nd	47%	0–2.59	0.50	nd
Synthetic musk																
AHTN	89%	0–52.1	11.9	4.97	80%	0–31.8	7.35	3.00	100%	10.4–40.3	23.5	23.7	100%	1.81–40.7	8.53	6.99
HHCB	86%	0–299	29.5	5.46	80%	0–278	43.8	9.50	100%	3.01–270	51.4	29.5	76%	0–110	19.8	6.27
Benzotriazoles																
BT	54%	0–3.14	0.72	nd	50%	0–2.92	0.90	<0.40	31%	0–<0.40	<0.40	nd	41%	0–<0.40	<0.40	nd
5-TT	54%	0–1.00	0.31	0.30	40%	0–1.01	0.27	nd	75%	0–0.84	0.39	0.45	76%	0–0.53	0.30	0.34

[a] D.F: Detection frequency.
[b] nd: Not detected.
[c] <0.09: <MQLs.

Table 3
Summary of concentrations (ng/g ww) of detected target compounds in fish liver samples from Pearl River and Yangtze River.

Compounds	Pearl River								Yangtze River							
	Wet season				Dry season				Wet season				Dry season			
	D.F[a]	Range	Mean	Median	D.F	Range	Mean	Median	D.F	Range	Mean	Median	D.F	Range	Mean	Median
Biocides																
DEET	64%	0–34.3	7.72	1.04	68%	0–53.9	8.84	2.85	88%	0–44.3	9.17	4.11	65%	0–5.54	1.11	0.67
CBD	32%	0–0.33	<0.22[c]	nd	26%	0–1.02	<0.22	nd	44%	0–0.63	<0.22	nd	82%	0–0.93	0.25	0.25
CBZ	68%	0–358	33.5	8.97	58%	0–103	12.7	1.78	13%	0–2.19	<1.16	nd	53%	0–6.45	1.27	nd
MCZ	41%	0–88.9	6.21	nd	16%	0–9.73	<2.30	nd	81%	0–432	83.7	15.7	24%	0–16.1	<2.30	nd
MP	100%	0.60–17.2	4.70	3.11	100%	0.60–18.6	3.84	2.48	100%	1.61–11.6	3.99	3.36	100%	1.58–5.22	2.37	2.05
EP	0%	nd[b]	nd	nd	0%	nd	nd	nd	19%	0–2.13	0.31	nd	59%	0–3.94	1.10	1.11
PP	77%	0–6.72	1.20	0.89	74%	0–5.62	1.32	0.73	94%	0–6.10	1.17	0.82	100%	0.51–2.28	0.94	0.75
TCC	9%	0–6.57	<1.17	nd	47%	0–8.60	1.45	nd	25%	0–<1.17	<1.17	nd	12%	0–<1.17	<1.17	nd
TCS	23%	0–39.4	3.66	nd	37%	0–51.7	8.33	nd	63%	0–221	26.1	11.6	24%	0–8.91	1.30	nd
Synthetic musks																
AHTN	86%	0–349	72.4	46.8	74%	0–265	40.1	16.6	100%	23.5–336	148	156	100%	3.85–179	67.9	54.1
HHCB	77%	0–2619	471	117	79%	0–2402	498	57.1	100%	12.2–1439	293	172	76%	0–359	80.9	21.2
Benzotriazoles																
5-TT	45%	0–54.5	4.38	nd	47%	0–31.0	4.21	nd	31%	0–15.5	<2.48	nd	41%	0–<2.48	<2.48	nd

[a] D.F: Detection frequency.
[b] nd: Not detected.
[c] <0.22: <MQLs.

6.46 ng/g ww for DEET (common carp, M2). As for benzotriazoles, BT and 5-TT were detected with the maximum concentrations of 3.14 ng/g ww (tilapia, S2) and 1.01 ng/g ww (tilapia, S1).

For liver tissues, 12 out of the 24 target PCPs compounds were found with the mean concentrations ranged from <0.22 ng/g ww (CBD) to 498 ng/g ww (HHCB) in the Pearl River and Yangtze River (Table 3, Fig. 2d). Similar to fish muscle tissues, two synthetic musks (AHTN and HHCB) showed the high detection frequencies and concentrations in fish liver samples from two rivers, followed by biocides (DEET, CBZ, MCZ and TCS). The maximum concentrations of AHTN and HHCB were 349 ng/g ww (common carp, S2) and 2619 ng/g ww (common carp, S2), respectively. For biocides, the maximum concentrations of DEET, CBZ, MCZ and TCS were 53.9 ng/g ww (bullhead, M2), 358 ng/g ww (mud carp, S2), 432 ng/g ww (grass carp, C4) and 221 ng/g ww (bream, C4), respectively. The MCZ was only found in liver tissues but not detected in muscle tissues. For benzotriazoles, 5-TT was found the maximum concentration of 54.5 ng/g ww (tilapia, S2).

3.2. Temporal and spatial variations of PCPs in water, sediment and fish

The temporal variations of the detected PCPs were examined. For surface water, the mean concentrations of the most detected PCPs in wet season were lower than or close to those in dry season except for AHTN in the Pearl River. As a comparison, the mean concentrations of most PCPs in wet season were higher than or close to those in dry season (Fig. S1), but the mean concentrations of 3 benzotriazoles (BT, 5-TT and CBT) in wet season were obviously lower than those in dry season in the Yangtze River. This may due to the consumption of vehicle antifreeze (with benzotriazoles added) in the winter of Pearl River, as similar result reported in other study (Qi et al., 2014). For sediment, the mean concentrations of the most detected PCPs in wet season were lower than (except for MP) those in dry season in the Pearl River, and the mean concentrations of the detected PCPs did not show much seasonal variation in the Yangtze River (Fig. S1). For fish tissues, the concentrations distribution of the most detected PCPs did not show obvious seasonal deviations in the Pearl River whether in muscle or liver (K-S test, $p > 0.05$). While in the Yangtze River, the fish muscle concentrations of AHTN and HHCB in wet season were obviously higher than those in dry season (K-S test, $p < 0.05$). And fish liver concentrations of MCZ in wet season were higher than those in dry season (K-S test, $p < 0.05$). In general, the seasonal deviation for the concentrations of the detected PCPs in fish was not exactly same to those in surface water.

Spatial variations for the concentrations of some PCPs in surface water, sediment and fish samples can be observed between Pearl River and Yangtze River (Fig. S1). For surface water, the concentrations of many PCPs (FCZ, CBZ, MCZ, HHCB, BT and XT) in the Pearl River were higher than those in the Yangtze River (K-S test, $p < 0.05$), only the concentrations of PP and BP in the Pearl River were lower than those in the Yangtze River (K-S test, $p < 0.05$). Specially, the mean concentration of BT in the Pearl River was 473 ng/L, which was dozens of times higher than those in the Yangtze River (19.5 ng/L). For sediment, the concentrations of most detected PCPs in the Pearl River were higher than those in the Yangtze River, except for DEET and 2 parabens (EP and PP) which were not detected in the Pearl River (K-S test, $p < 0.05$). Similar as the result of surface water, the concentrations of 2 parabens (EP and PP) in the fish muscle of Pearl River were lower than those in the Yangtze River, and the concentration of BT in the fish muscle of Pearl River were obviously higher than that in the Yangtze River (K-S test, $p < 0.05$). For fish liver samples, higher concentration of CBZ and lower concentration of MCZ were distributed in the Pearl River than those in the Yangtze River (K-S test, $p < 0.05$), and no obvious spatial variation were observed for other detected PCPs.

3.3. Fish bioaccumulation factors

The log BAF values for detected PCPs in fish muscle and liver were summarized in Tables S9–10. For fish muscle tissues, the log BAF values for 12 detected PCPs were ranged from 0.04 to 5.49, with the maximum value for TCC at site S4 (crucian carp). The mean and median log BAF values for most of the PCPs were higher than 1, except that BT had the mean and median values of 0.73 and 0.80, respectively. The order of the mean log BAF values for the detected PCPs was: HHCB > AHTN > PP > EP > TCC > TCS > MP > CBZ > DEET > 5-TT > CBD > BT. For fish liver, the range of log BAF values for 12 detected PCPs was 0.18 to 6.47, with the maximum values for MCZ at site S2 (tilapia). The mean and median log BAF values for most of the PCPs were higher than 1, except that CBD had the mean and median values of 0.87 and 0.85, respectively. The mean values of log BAF for those PCPs followed the order: MCZ > HHCB > AHTN > PP > EP > TCS > CBZ > TCC > MP > 5-TT > DEET > CBD. For the tissue type, the mean log BAF values in liver tissues were higher than those in muscle tissues for most of the detected PCPs, except for CBD. Besides, though MCZ was not detected in muscle

tissues, the mean log BAF values of MCZ in liver tissues were high up to 4.61.

For five commonly found fish species of tilapia, common carp, bream, crucian and chub (n ≥ 6), significant difference in the log BAF values of DEET, CBZ, AHTN and HHCB in muscle tissues were observed (K-W test, $p < 0.05$). The mean log BAF values of DEET and CBZ in different fish species followed the order of common carp > chub > bream > tilapia > crucian, and the mean log BAF values of AHTN and HHCB in different fish species ordered as: crucian > bream > common carp > tilapia > chub. The significant difference in the log BAF value of MCZ and PP in liver tissues were observed (K-W test, $p < 0.05$). The mean log BAF values of MCZ in different fish species ordered as: bream > crucian > common carp > tilapia > chub, and the mean log BAF values of PP in different fish species ordered as: crucian > tilapia > chub > bream > common carp, respectively. There was no obvious difference in the log BAF values of other detected PCPs among different fish species in muscle or liver tissues (Fig. 3). The results indicated that fish species or trophic position might not be an important factor for the distribution of PCPs in wild fish.

As shown in Table S11, the simulated log BAF values in muscle tissue for 12 target PCPs were at the range of 0.38–4.06 and 0.59–6.31 for the calculation of with and without biotransformation, respectively. Only the determined log BAF values of DEET, TCC, HHCB and BT were at the same order of magnitude as the simulated values with biotransformation. For other PCPs, the detected log BAF values were clearly one or two orders of magnitudes higher or lower than those of modeled log BAF values with biotransformation. This may due to the limitations of sampling sites among two rivers which flow through large area, and the concentrations of PCPs in surface water and fish tissues also influenced by complex factors, such as sampling depth and time, which may result in the variations of BAFs values.

3.4. Human health risk from fish consumption

The exposure risks of 10 frequently detected PCPs (DEET, CBD, MP, EP, PP, TCC, TCS, AHTN, HHCB and BT) via consumption of fish muscle were assessed, with the maximum concentrations in each fish species used as the worst-case scenario. The highest HQ values of these compounds in all fish species were in the range of 3.39×10^{-7}–3.32×10^{-3}, with HQ values of AHTN and HHCB relatively higher than those of the others (Table S12). For those 10 PCPs, no obvious difference in the maximum HQ values were observed among five commonly found fish species of tilapia, common carp, bream, crucian and chub (K-W test, $p > 0.05$), despite the maximum HQ values usually found in tilapia and common carp. Which indicated that the health risks of PCPs to human is not affiliated with the intake of different fish species.

4. Discussion

4.1. Occurrence of PCPs in wild fish

For the sampling sites of Pearl River and Yangtze River, PCPs which were frequently detected in surface and sediment samples were also found in fish tissues, such as DEET, MP, PP, AHTN, HHCB and BT. For the middle and lower stream of Pearl River, the antibiotics detected in the surface water with concentration to 1578 ng/L, were reported to widely found in the wild fish (Zhao et al., 2015). For the highly urbanized region of Yangtze River, some pharmaceuticals widely detected in surface water with relatively low concentrations (≤85.3 ng/L), were also reported to bioaccumulated by wild fish (J.C. Liu et al., 2015). In a stream of Ehime of Japan, which receives effluent from WWTPs, some PCPs (DEET, parabens, TCC and TCS) detected in the surface water with concentration to 870 ng/L, were also commonly found in wild fish muscle, liver, plasma and bile samples (Tanoue et al., 2015). The results indicated that some contaminants in environment can be accumulated by the aquatic organism living there (Subedi et al., 2012).

Notably, FCZ was not detected in fish tissues although it was frequently detected in the surface water with the maximum concentration to 99.2 ng/L (site M1, dry season) in the present study. This is because the bioaccumulation potential of hydrophilic FCZ (log $K_{ow} = 0.4$) is low in aquatic organisms (Chen and Ying, 2015). Due to the strong lipophilic properties, synthetic musks of AHTN (log $K_{ow} = 5.2$) and HHCB (log $K_{ow} = 5.9$) were frequently detected in fish tissues with high concentrations, despite their relatively low concentrations in surface water (mean values <40 ng/L) in this study. Which were similar to the results in Hudson River of United States and Haihe River of China (Reiner and Kannan, 2011; Hu et al., 2011). For 4 hydrophilic benzotriazoles (log

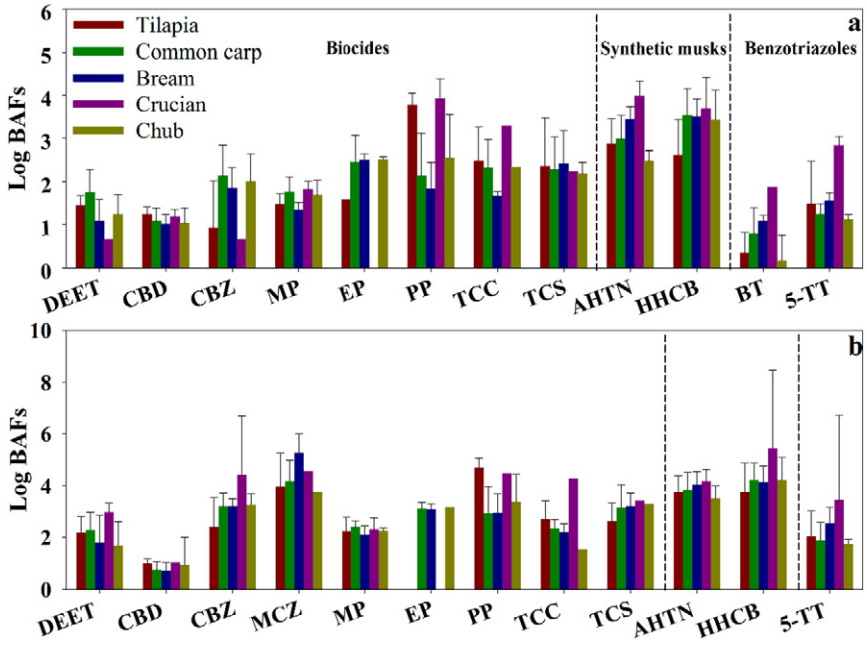

Fig. 3. The mean value of log bioaccumulation factors (BAFs) of personal care products in fish muscle and liver tissues, with fish species (5 commonly found fish were listed, n ≥ 6 for each kind of fish species) deviation.

K_{ow} = 1.4–2.26), they mainly existed in the water phase (Liu et al., 2012), despite the log K_{ow} value of BT and 5-TT were almost one order of magnitudes lower than those of CBT and XT. Hence, high concentrations of BT and 5-TT in surface water led to their detections in fish tissues. The results indicated that the bioaccumulation potential of these PCPs were affected by both surface water concentrations and their hydrophilic-lipophilic properties.

For muscle tissues, the concentrations of MP and EP in the present study were lower than those of fish collected from Mediterranean rivers of Spain (Jakimska et al., 2013), Manila Bay of Philippines (Ramaswamy et al., 2011; Kim et al., 2011), and the inland lakes of United States (Xue and Kannan, 2016), and in the same range of those fish collected from the stream of Ehime in Japan (Tanoue et al., 2015). The measured values of TCC and TCS in this study were higher than those fish in Manila Bay of Philippines (Ramaswamy et al., 2011; Kim et al., 2011), and the rivers of Germany (Rüdel et al., 2013), and TCS were in the same order of magnitude of those fish from the rivers Mediterranean rivers of Spain (Jakimska et al., 2013) and the stream of Ehime in Japan (Tanoue et al., 2015). The concentrations for AHTN and HHCB of this study were at the same level of fish collected the rivers of Denmark (Duedahl-Olesen et al., 2005), but lower than the fish collected from the pond receiving the effluent of WWTPs (Gatermann et al., 2002), the rivers in the United States (Ramirez et al., 2009), and higher than those in fish the shallow water areas of Japan (Nakata et al., 2007), the rivers of Germany (Subedi et al., 2012), and the Taihu Lake of China (Zhang et al., 2013). For liver tissues, the concentrations of most detected PCPs (DEET, MP, EP, PP, AHTN HHCB) in this study were higher than those in fish from the stream of Ehime in Japan (Tanoue et al., 2015).

4.2. Bioaccumulation patterns of PCPs in wild fish

Generally, the log BAF values of liver tissues were higher than those of muscle tissues in the present study, especially for two azole antifungal agents (CBZ and MCZ), as the same results for pharmaceuticals and parabens in various wild fish species from the steam or rivers (Ramirez et al., 2009; Tanoue et al., 2015; Xue and Kannan, 2016). This may be related to the difference in exposure mechanism between liver and muscle to contaminants. Bioaccumulation in the field is the competing process of all routes of uptake (dietary, respiratory and dermal adsorption) and elimination (respiratory exchange, fecal egestion, metabolic biotransformation and growth dilution) (Arnot and Gobas, 2006; Lahti et al., 2011), which means that contaminants existed in food can be directly accumulated by liver but not muscle. It was reported that many PCPs like CBZ, MP, PP, TCC, and TCS can be taken up by various aquatic plants (Richter et al., 2013; Aznar et al., 2016). Since the uptake efficiency of contaminants usually higher than the elimination efficiency in liver (Liu et al., 2014), such as the uptake and depuration concentrations for TCS in *Poecilia* (at 200 ng/L for 168 h) were 63.75 ng/g ww and 6.42 ng/g ww, respectively (Escarrone et al., 2016); Thus the PCPs in food can directly bioaccumulated and only partly metabolized by liver, which results in the relatively high log BAF values of some PCPs in liver.

For the detected PCPs in all collected fish species, no relationship with body weight and log BAF values of muscle or liver tissues were observed (Pearson, $p > 0.05$), same results for TCC and TCS in common and crucian from the stream of Ehime in Japan were reported (Tanoue et al., 2015). And no relationship with body lipid (0.07%–4.8%) and log BAF values of detected PCPs in muscle were observed (Pearson, $p > 0.05$), similarly, no significant correlation between lipid content (0.13%–

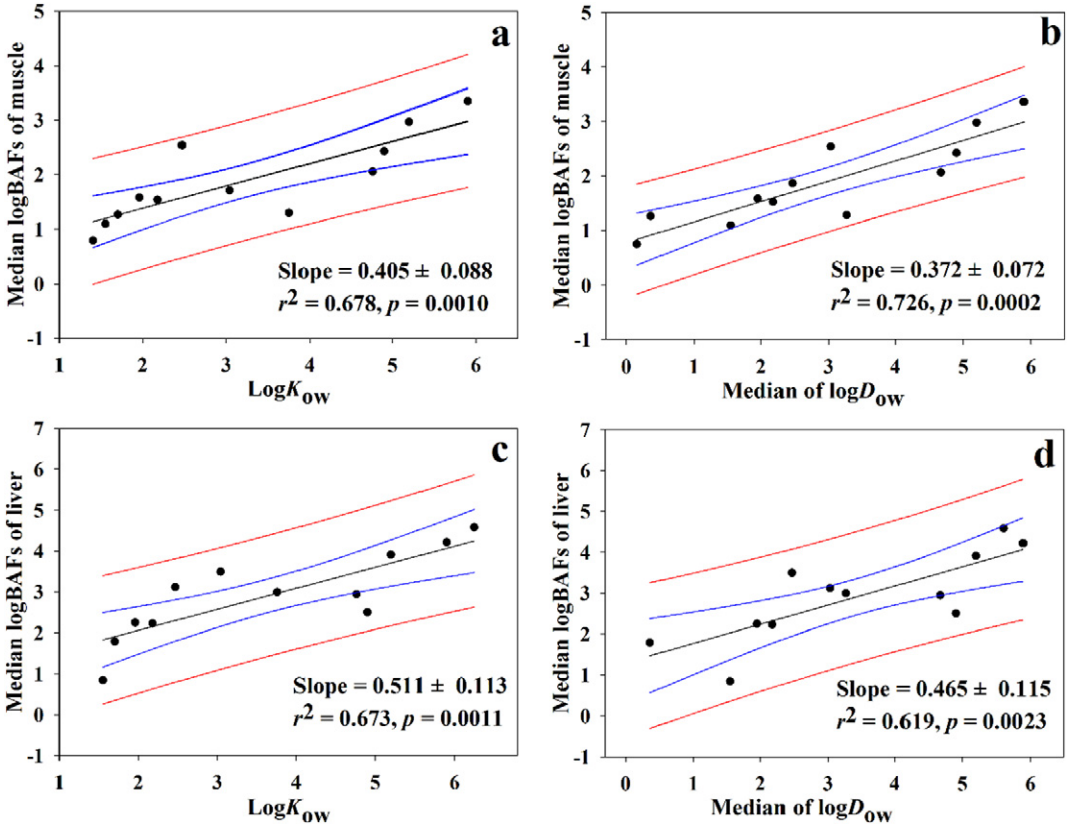

Fig. 4. Linear regression comparison of median of log BAF value with chemical lipophilic parameters (a & c, log K_{ow}; b & d, log D_{ow}) for each detected compounds (one dots represents one compound, AHTN and HHCB were also listed with log D_{ow} = log K_{ow}) in muscle and liver. Blue and red dashed lines surrounding linear regression represent the 95% confidence interval and the 95% prediction band of the linear regression. r^2 is linear regression coefficient; p is the probability for the observed linear regression to be caused by random sampling.

2.61%) and bioaccumulation of parabens, TCC and TCS in wild fish from Manila Bay of Philippines observed (Ramaswamy et al., 2011).

However, good linear relationship between measured log BAF values and the log K_{ow} values of all detected 12 PCPs were observed whether in muscle ($r^2 = 0.678$, $p < 0.05$) or liver ($r^2 = 0.673$, $p < 0.05$) tissues, as the results shown in Fig. 4. The results indicated that the bioaccumulation potency of PCPs was closely related to their physicochemical properties (Tanoue et al., 2015). Recent studies indicated that the ionization characteristic of chemicals at the environmental pH should be considered to evaluate their bioavailability (Nakamura et al., 2008). For most of the detected PCPs in this study, after the environmental pH of each sampling sites were considered, the median log D_{ow} were close to their log K_{ow}, except that BT and 5-TT with almost one order of magnitudes variation (Table S13). And the linear relationships between the median values of log BAF and the median values of log D_{ow} of PCPs were similar to that of log BAF and log K_{ow}, whether for muscle ($r^2 = 0.726$, $p < 0.05$) or liver ($r^2 = 0.619$, $p < 0.05$) tissues (Fig. 4). In fact, despite 11 (DEET, CBD, CBZ, MCZ, MP, EP, PP, TCC, TCS, BT and 5-TT) out of those 13 detected PCPs in fish muscle and liver tissues are ionizable compounds, their ionization properties are not quite obvious as some pharmaceuticals (Tanoue et al., 2015). The results indicated that the bioaccumulation potential of target PCPs were not obvious influenced by environmental pH.

4.3. Human health implications by fish consumption

Because the values of HQ for 10 PCPs (DEET, CBD, MP, EP, PP, TCC, TCS, AHTN, HHCB and BT) were far below 1, thus there were no immediate health risks associated with the consumption of these wild fish in the two rivers. The results in the present study were similar to previous study of AHTN and HHCB in the Catalonia of Spain (Trabalon et al., 2015). However, the assessment performed in the present study did not consider the joint risks of PCPs mixtures, since multiple PCPs residues were shown to be present in wild fish (Ramirez et al., 2009; Lange et al., 2015). Besides, some of these PCPs tend to be transformed into other metabolites, which are probably more persistent and hydrophobic than the parent compounds, such as methyl-TCS or HHCB-lactone (Balmer et al., 2004; Santiago-Morales et al., 2012). Therefore, further research is needed to assess the exposure risks of PCP mixture and their transformation products from the fish consumption.

5. Conclusion

Eleven PCPs were detected in wild fish muscle and liver tissues from Pearl River and Yangtze River, with AHTN and HHCB most frequently detected at high concentrations. For each detected PCPs, the concentrations and log BAF values in liver were usually higher than those in muscle tissues, which may related to the higher lipid content of liver than those of muscle. However, the lipid content were not detected in this study due to the amount limitation of liver tissue, so the influence of lipid content to the concentrations of PCPs in different tissues should be investigated in the future. The bioaccumulation potential of PCPs was mainly influenced by their log K_{ow} values. Simple exposure risk assessment indicated no appreciable human health risks associated with the consumption of these wild fish. The results from this study may help to the understanding of the bioaccumulation of the PCPs in fish and their possible human health risks.

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Compliance with ethical standards

Conflict of interest

The authors declare that they have no competing interests.

Ethical approval

All the animals received human care and all experimental protocols in this study were performed in conformity with Animal Care Quality Assurance in China.

Appendix A. Supplementary data

Additional information about extraction methods of water, sediments and fish samples, the description of sampling sites and fish, basic physicochemical properties of analytes, statistical data of log BAF values, modeled log BAF values and calculated log BAF values, the concentration of PCPs in water and sediment samples are also available in Supplementary materials. Supplementary data associated with this article can be found in the online version, at https://doi.org/10.1016/j.scitotenv.2017.10.117.

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