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Baseline

PCBs and OCPs in fish along coastal fisheries in China: Distribution and health risk assessment

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ABSTRACT

PCBs and OCPs were analyzed in fish (bass) taken along Chinese coastal fisheries. In the bass muscle, PCB, DDT and HCH concentrations were in the range of 1.02–2.2 ng/g, 0.44–1.74 and 2.84–106.11 ng/g ww, respectively. Spatial distribution showed that the concentrations of target contaminants in bass from south fisheries were in general much lower than those from north fisheries in China. The ratios of OCP congeners suggested that technical DDT was not the main input and a recent usage of lindane or old technical HCH residuals could be the source of HCHs. The OCC concentrations in liver (127–442.43 ng/g ww) from selected samples were 8–12 and 10–14 times higher than those in gills and muscles, respectively. Based on the maximum allowable fish assumption rate (CR_{lim} and CR_{mm}), it could cause human health risk, by consuming bass samples taken from highly contaminated fisheries including QD and ST.

Organochlorine compounds (OCCs), including polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs), were a group of persistent organic pollutants (POPs). These compounds have caused significant global concern because of their persistence, bioaccumulation and toxicity. PCBs and OCPs had been widely utilized in past decades due to their high efficiency, low cost, and broad-spectrum pesticidal efficacy. PCBs had been banned or restricted to produce since 1974, and although DDTs and HCHs have been forbidden since 1983, DDTs have still been used in low amounts to control certain insects in tropical and subtropical countries, including China (Zhao et al., 2013). In general, due to their degradation resistance and environmental persistence, OCCs were found in different aquatic environments, such as river water, sludge, surface sediment and aquatic organisms (Mai et al., 2005b; Zhou et al., 2000; Jin et al., 2007).

With high K_{ow} values, PCBs and OCPs can enter the aquatic organisms, be bio-accumulated into higher trophic level via food chain, and eventually be uptake by human beings, posing adverse effects on human health. Fish are particularly vulnerable to exposure to aquatic contaminants, and 50% of the pesticides can be retained in the body for >30 days, making fish as an environmental bioindicator to monitor a level of aquatic contaminants (Guo et al., 2008a,b; Sucman et al., 2006). The consumption of fish could be one of the predominant exposure sources of persistent organic pollutants to humans, such as PBDEs (Ohta et al., 2002; Meng et al., 2007). Especially, it has been reported that fish had higher levels of OCCs than any other food category (Yim et al., 2005).

With rapid development of urbanization and industrial activities, eastern coastal area of China is under serious stress of contaminations, including PCBs and OCPs (Jonsson et al., 2003; Zhang et al., 2014). For example, PCB usage in coastal area accounted for 45% of the total amount used in China (Zhang et al., 2010). Moreover, coastal area is the important area of seafood fisheries in China, among which bass accounts for 11.4% of the total amount of the sea framed fish (Ministry of Agriculture of China, 2012). Several studies have investigated the POP level of seafood products in selected Chinese coastal areas, such as Zhoushan, demonstrating that DDTs and PCBs were the two main POPs in fish, and particularly DDTs contributed to about 75% of the POPs in seafood in these areas (Jiang et al., 2005; Klumpp et al., 2002; Nakata et al., 2002). However, in previous studies, limited numbers of coastal fisheries were involved and seldom researches paid attention to the bass, one of the most important marine farmed fish. Up to our knowledge, it is the first time to evaluate the residual level of OCCs in bass taken along coastal fisheries in China. In this study, bass was therefore selected to represent the marine farmed fish. The objectives of the present study are (1) to study the residue level and spatial distribution of PCBs and OCPs in bass along coastal fishery areas of China; (2) to compare their concentrations in different tissues and further (3) to assess the potential human health risk by uptake bass daily based on the joint exposure of PCBs and OCPs.

Standards of PCBs (PCB28, PCB52, PCB101, PCB118, PCB153, PCB138, PCB180), DDTs (p,p′-DDD, o,p′-DDT, p,p′-DDT, p,p′-DDE, o,p′-DDE, o,p′-DDD) and HCHs (α-BHC, β-BHC, γ-BHC, δ-BHC) were purchased from O2si Smart Solution (South Carolina, USA). O,p'-DDE d_8, PCB65, PCB82, and PCB209 were used as internal standards, supplied by Dr. Ehrenstrofer GmbH (Augsburg, Germany). Separate stock solution

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(1000 mg/L) of individual compound and internal standards were prepared by dissolving in n-hexane. A 10 mg/L mixture of working standards containing each compound was prepared by diluting the stock solution with n-hexane. All standard solutions were stored at −20 °C. All the solvents used, including dichloromethane and n-hexane, were of pesticide analysis grade.

The fish samples were collected in January 2013 and 2014 from thirteen coastal fisheries along eastern coastal area of China, including Tianjin (TJ), Qingdao (QD), Lianyungang (LYG), Zhoushan (ZS), Ningbo (NB), Wenling (WL), Ningde (ND), Quanzhou (QZ), Shantou (ST), Shenzhen (SZ), Fangchenggang (FCG), Sanjiang (SJ) and Wanning (WN) (Fig. 1) and the detailed sampling information was summarized in Table 1. In the present study, all the fisheries selected were bass-based because of the high yield and consumption of bass in China. Bass samples were refrigerated after collected and then transported to the laboratory immediately.

After measuring the weight, length, and then dissecting the fish samples, the different tissues including muscle, liver and gill were separated and homogenized respectively, and then stored at −20 °C. All the samples were freeze-dried and treated as described by Geng et al. (2015). In brief, samples (fish muscle, liver and gill) were ground into powder and extracted using an accelerated solvent extractor (ASE 350, DIONEX, USA) by a mixture of n-hexane and dichloromethane (1:1, v:v, 40 ml). The extraction cell (stainless steel, 33 ml) was filled with microfiber filters (GF/B, Whatman), Florisi gel, sample mixed with quartz sand sequentially, and extracted under 1500 psi at 100 °C for 3 cycles in a static mode for 5 min. Before extraction, each cell was spiked with 20 ng internal standards. All collected extraction were reduced to 2 ml by rotatory evaporation at 37 °C, and then concentrated to 1 ml under gentle N_2 stream. 2 ml of concentrated sulfuric acid (98%) was added to remove the lipid and the concentrated supernatant was subjected to GC–MS/MS analysis.

The PCBs and OCPs were quantitatively analyzed by gas chromatograph–tandem mass spectrometry (GC–MS/MS, Quaffro micro GC, Waters) system in an Electron Impact Ionization (EI) Mode. The GC column used was DB-5MS (30 m × 0.25 mm × 0.25 μm, Agilent Technologies Inc.). The column oven temperature was programmed as follows: 60 °C for 2 min, increasing to 180 °C at the rate of 20 °C/min followed by 5 °C/min to 250 °C, then increased to a final 310 °C for 5 min. Helium was used as the carrier gas. 1 μl of sample bulk was injected and the injection port temperature was 250 °C. In the present study, o,p′-DDT and p,p′-DDD showed similar retention time and unseparated peak, and therefore, the concentration of (o,p′-DDT + p,p′-DDD) was quantified instead of individual o,p′-DDT and p,p′-DDD. The linear calibration curves were constructed by analyzing standard solutions of different concentrations including 1, 3, 5, 10, 20, 50 ng/ml. The limit of detection (LOD) and the limit of quantification (LOQ) for PCBs and OCPS were defined as the concentrations corresponding to the signal-to-noise (S/N) of 3 and 10, respectively. The LOD and LOQ of PCBs and OCPS in fish samples were 0.044–0.126 ng/g dw and 0.148–0.421 ng/g dw, respectively, and the recoveries of 21 target compounds were between 84.67% and 117.5%. Analysis of reagent blanks suggested that the analytical system and glassware were free of contamination. The relative standard deviation of all the parallel samples was within 20%.

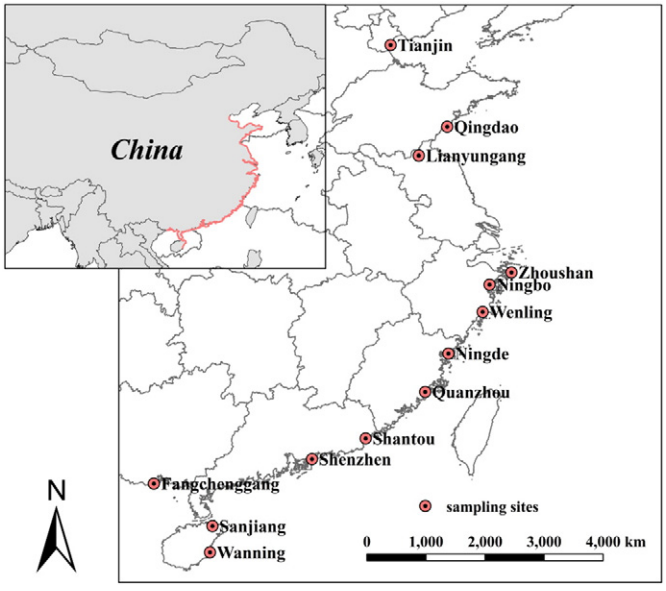

Fig. 1. Sampling coastal fisheries along coastal area of China.

The lipid content of each bass sample was extracted by ASE and the parameters are as follows: 3 extractions with n-hexane solvent at 125 °C and static extractions for 5 min. The collected extraction was reduced to nearly dry under rotatory evaporation at 45 °C and then put into the oven for completely dried at 102 ± 2 °C for 2 h. The lipid content was calculated by the ratio of weight loss and sample weight.

People are simultaneously exposed to multi-contaminants, and the United States Environmental Protection Agency (USEPA, 2011) has developed a risk-based method to multiple-chemical exposure for assessing carcinogenic and non-carcinogenic effects caused by PCBs, DDTs and HCHs. In the present study, we used this method with an acceptable risk level of 1 in 100,000 (10^{-6}) to derive consumption advisories for consuming bass samples taken from thirteen coastal fisheries.

$$CR_{lim} = \frac{ARL * BW}{\sum_{m=1}^{x} C_m * CSF} \quad (1)$$

where CR_{lim} represents maximum allowable fish assumption rate (kg/d); *ARL* is maximum acceptable individual lifetime risk level; *BW* is consumer body weight which is set as 59.6 kg (Meng et al., 2007); C_m is the chemical concentration of the contaminant in fish (mg/kg) and *CSF* is defined as cancer slope factor, where the *CSF* of γ-HCH (1.3 mg/kg/d) was used for HCHs and the *CSF* is 2.0 and 0.34 mg/kg/d for PCBs and DDTs, respectively. In the present study, only one fish species is involved, so CR_{mm} can be simplified as Eq. (2)

$$CR_{mm} = \frac{CR_{lim} * T_{ap}}{MS} \quad (2)$$

where CR_{mm} represents maximum allowable fish assumption rate (meal/month), T_{ap} is time- averaging period of one month, expressed as 30.44 d/mo; *MS* is the fish meal size, which was set as 227 g/meal.

OCCs, including PCBs, DDTs and HCHs were all detected in bass muscles taken from thirteen coastal fisheries, suggesting that the ubiquitous occurrence and continuous accumulation of these compounds in bass. The total concentrations of selected PCBs and OCPs were 1.02–2.2 ng/g and 5.63–106.84 ng/g on a wet weight basis, respectively (Table S1). The highest concentration of OCCs was found in QD, and the lowest one was in QZ. The distribution pattern of selected contaminants at each sampling site was similar (Fig. 2), showing DDTs > PCBs > HCHs.

The concentrations of DDT were in the range of 2.84–106.11 ng/g ww, and were 1–2 orders of magnitude higher than those of ∑HCHs and ∑PCBs, which could be attributed to the extensive utilization in history and high lipophilicity of DDTs ($logK_{ow} = 6.5$) (Xia et al., 2011). ∑DDT concentrations in bass from thirteen coastal fisheries showed significant spatial difference ($p < 0.05$). The highest value was found in QD bass muscles, which was about 37 times higher than the lowest one in QZ. Antifouling paint for fishing ships was proven to have technical DDTs of about 500 μg/g, regarded as an important source of DDT (Li et al., 1998). Moreover, high levels of o,p′-DDT have also been found in dicofol, resulting in elevated DDT levels in the environment (Di Muccio et al., 1988; Gillespie et al., 1994). In China, about 000 8770 tons of DDTs entered the environment from 1882 to 2002 due to the usage of dicofol in agriculture (Xia et al., 2011). In addition, Dicofol had been