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Assessment on dioxin-like compounds intake from various marine fish from Zhoushan Fishery, China

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HIGHLIGHTS

- 32 Fish species were measure for 29 dioxin-like compounds.
- The factors effecting the accumulation of the compounds in sea fish were discussed.
- A risk-based consumption advice for sea fish was developed.

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ABSTRACT

Sea fish consuming is an important intake source of dioxin-like compounds, especially for the coastal residents. To assess the intake levels of these contaminants from sea fish and to provide risk-based consumption advice, concentrations of 17 polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) and 12 dioxin-like polychlorinated biphenyls (dl-PCBs) were measured in 32 commonly consumed fish species from Zhoushan Fishery, China. Due to the different accumulation influenced by fat content, feed habits and living zone in the sea area, the levels of PCDDs, PCDFs and dl-PCBs in different fish species varied significantly ranging from 0.002 to 0.078 pg WHO-TEQ/g fresh weight, from 0.002 to 0.553 pg WHO-TEQ/g fresh weight and from 0.003 to 2.059 pg WHO-TEQ/g fresh weight, respectively. Based on mean fish consuming rate in China, the estimated maximum possible dioxin-like compounds intake through different fish species ranged from 0.26 to 65.61 pg TEQ kg^{-1} bw $month^{-1}$. *Bullet mackerel* has the highest monthly intake level which was much higher than other fish species and very close to the provisional tolerable monthly intake (70 pg TEQ kg^{-1} bw $month^{-1}$) proposed by the Joint FAO/WHO Expert Committee on Food Additives. Hence, comparing to other fish species, the consumption of *Bullet mackerel* from Zhoushan Fishery should be cautious to reduce the potential health risk.

1. Introduction

Polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) and dioxin-like polychlorinated biphenyls (dl-PCBs) are the broad class of environmental pollutants which are ubiquitous in the environment worldwide. PCDD/Fs are unwanted by-products mainly from incomplete combustion as well as manufacture of certain chemicals (Dannenberger et al., 1997; Kim et al., 2005). Dl-PCBs mainly stemmed from the production and usage of the commercial PCBs mixtures, which has been banned in 1970s, as well as leakage from the container (Baars et al., 2004). The great concern on PCDD/Fs and dl-PCBs by humans is their potential risk to human health (Clapp and Ozonoff, 2000; Oh et al., 2003). In literature, effects on the reproductive-, immune- and nervous system have been reported (Safe, 1990; USEPA, 2010).

For humans, the exposure pathways to PCDD/Fs and dl-PCBs are dermal contact, inhalation and food intake. Among them, the dietary intake is the main pathway for general population, accounting for more than 90% (van Leeuwen et al., 2000; Wang et al., 2009; Fernandes et al., 2010; Grassi et al., 2010). There are

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many studies reporting fish as main food contributor (Kim et al., 2007; Zhang et al., 2008; Lorber et al., 2009). In China, especially in southeast China, aquatic foods corresponded to the dominant contribution to the dietary intake of PCDD/Fs and PCBs (Li et al., 2007; Zhang et al., 2013). These findings revealed the importance of fish as a source of potential exposure to toxic pollutants such as PCDD/Fs and PCBs. This is of great concern taking into account the nutritional role of fish as a part of a healthy diet, whose relevance has notably increased in recent years. In order to monitor the levels of PCDD/Fs and dl-PCBs in seafood and assure the health of humans, data on these compounds in sea fish and other sea food were reported gradually during recent years in China (Liu et al., 2011; Shen et al., 2009; Zhang et al., 2008). In the developed area of China, especially in southeast China, the high level body burden of dioxin-like compounds may be due to high consumption of aquatic food such as sea fish in these areas (Li et al., 2009; Zhang et al., 2013). Therefore, the detailed advices on edible fish selection regarding to dioxin-like compounds level could be essential to reduce the dietary intake of these contaminations in these area.

In the present study, 32 fish species from Zhoushan fishery which is the largest fishery in southeast China were selected. These species are the most consumed by the local general population. Through analyzing the levels of the dioxin-like compounds and characterizing the factors affecting accumulation in these fishes, risk assessment on dioxin-like compounds from fish consumption for general population was conducted and the risk-based consumption advice for fish species selection was recommended.

2. Materials and methods

2.1. Sample collection

Zhoushan, the only city on the sea composed of archipelago, is located at the junction of the southeast seashore and the entrance to the sea of Yangtze River, backing Shanghai, Hangzhou and Ningbo City, facing the Pacific Ocean. Zhoushan Fishery is the biggest fishery in China, known as "East China Sea fish warehouse". The annual output of aquatic products is around 1.3 million tons. The offshore ocean fishing output is more than one tenth of the country's total. During the months of September and October 2011, the 32 fish species which are most consumed by local residents from the Zhoushan Fishery were acquired. Three individual fish were collected for each fish species. Samples were frozen at −20 °C until analysis. More information of these fish is shown in Table A1.

2.2. Standard solutions and chemical reagents

The quantification standard solutions of PCDD/Fs and dioxin-like PCBs containing 15 congeners of $^{13}C_{12}$-labeled PCDD/Fs and 12 congeners of $^{13}C_{12}$-labeled-dioxin-like PCBs respectively and the 2 congeners of $^{13}C_{12}$-labeled injection standard for PCDD/Fs and 3 congeners of $^{13}C_{12}$-labeled injection standard for PCBs were all purchased from Wellington Laboratories (Guelph, Canada). The solvents including n-hexane, toluene, ethyl acetate, dichloromethane and acetone were purchased from J T Baker (Philipsburg, USA). All solvents were pesticide-grade. In addition, both diatomite and silica gel were bought from Merk (Darmstadt, Germany). The certified fish reference material of WMF-01 was supplied by Wellington Laboratories.

2.3. Sample preparation and clean-up

The edible filet tissues were dissected from each fish, mixed and homogenized by species, weighed and then freeze-dried. The purification procedure for PCDD/Fs and dl-PCBs was described previously (Li et al., 2007). In brief, after freeze-drying, the 15 congeners of $^{13}C_{12}$-labeled PCDD/Fs and 12 congeners of $^{13}C_{12}$-labeled-dioxin-like PCBs were spiked in the samples, followed by Soxhlet-extracted with a mixture n-hexane/dichloromethane (1:1) and the bulk fat was removed by shaking with acid-modified silica-gel. Sample cleanup was performed using a through Power Prep instrument (Fluid Managment Systems, Waltham, MA, USA). The eluting fractions were concentrated to about 10 μL and the $^{13}C_{12}$-labeled injection standard for PCDD/Fs and PCBs was added into the concentrated solutions respectively prior to analysis.

2.4. HRGC/HRMS analysis

The seventeen most toxic congeners of PCDD/Fs and twelve congeners of dioxin-like PCBs were analyzed by HRGC/HRMS (MAT95XP, ThermoFinnigan, German) equipped with DB-5MS capillary column (60 m × 0.25 mm × 0.25 μm) at 10000 resolution using the splitless injection mode and multiple ion monitoring (MID). The temperature program for the analysis of PCDD/Fs started with 1 min at 120 °C, raised to 220 °C at 44 °C min^{-1} holding for 15 min, and then to 250 °C at 2.3 °C min^{-1} and from 250 °C to 260 °C at 0.9 °C min^{-1}, lastly, ultimately to 310 °C at 20 °C min^{-1} holding for 11 min. In addition, the temperature was held for 1 min at 90 °C and programmed to 180 °C at 20 °C min^{-1} holding for 1 min, then further to 300 °C at 3 °C min^{-1} and held for 2 min for the analysis of dioxin-like PCBs. The temperatures of injector, transfer line, ion source and interface temperatures were 260 °C, 270 °C, 260 °C and 280 °C, respectively, ionization energy 60 eV and trap current 1.00 mA.

2.5. Quality control and assurance

The laboratory performance was validated by successfully participating interlaboratory comparison of POPs in food organized by the Norwegian Institute of Public Health in 2012. In this study, the laboratory method blanks were performed every eight samples. Certified fish reference material WMF-01 (Wellington Laboratories) was analyzed for method validation and as a quality control sample. The method detection limits ranged from 0.001 pg g^{-1} fresh weight (fw) to 0.008 pg g^{-1} fw for PCDD/Fs and ranged from 0.020 pg g^{-1} fw to 0.034 pg g^{-1} fw for dl-PCBs. The recoveries of the labeled compounds were between 30% and 115% for all samples, which were in the range of the USEPA limits (USEPA-1613, 1994; USEPA-1668A, 1999).

2.6. Estimation of dietary intake of PCDD/Fs and DL-PCBs

To assess the potential health risk from fish consumption, the possible maximum intakes from each fish species was calculated by multiplying the fish consumption rate (50 g d^{-1}) acquired from the Guide to Chinese Diet (Chinese Nutrition Society, 2007) by TEQs concentration of PCDD/Fs and PCBs in each fish species followed by dividing by the standard body weight about 60 kg (Song et al., 2011).

3. Results and discussion

3.1. PCDD/Fs and dl-PCBs congener's patterns

In this study, all of 17 PCDD/Fs and 12 dl-PCBs can be detected. As shown in Figs. 1–3, the predominating congeners of PCDDs are OCDD followed by 1,2,3,7,8-PeCDD and 1,2,3,4,6,7,8-HpCDD and the most abundant congeners of PCDFs are OCDF, 2,3,4,7,8-PeCDF as well as 2,3,7,8-TCDF and the PCB118 is found as the main dl-PCB congener, similar to some other studies (Isosaari et al.,