Chemosphere 89 (2012) 944–949

Contents lists available at SciVerse ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Polychlorinated biphenyls (PCBs) in marine fishes from China: Levels, distribution and risk assessment

Chonghuan Xia [a,b], James C.W. Lam [b], Xiaoguo Wu [c], Zhouqing Xie [a,*], Paul K.S. Lam [b,*]

[a] Institute of Polar Environment, School of Earth and Space Sciences, University of Science and Technology of China, Hefei, Anhui 230026, China
[b] State Key Laboratory in Marine Pollution and Department of Biology and Chemistry, City University of Hong Kong, Tat Chee Avenue, Kowloon, Hong Kong, China
[c] School of Environmental Science and Engineering, Anhui Normal University, Wuhu, Anhui 241003, China

HIGHLIGHTS

- PCBs in food fish from nine coastal cities of East China were studied.
- Risks to human associated with exposure to dl-PCBs in fish may be of concern.
- No significant difference in total PCB levels among the cities was observed.
- PCA indicated that PCB pollution came from similar sources in the sampling areas.

ARTICLE INFO

Article history:
Received 7 September 2011
Received in revised form 3 May 2012
Accepted 30 June 2012
Available online 3 August 2012

Keywords:
Polychlorinated biphenyls (PCBs)
Fish
China
Coastal
Human health risk assessment

ABSTRACT

Muscle tissues of large yellow croakers (*Pseudosciaena crocea*) and sliver pomfret (*Pampus argenteus*) from nine coastal cities of East China including Dalian, Tianjin, Qingdao, Shanghai, Zhoushan, Wenzhou, Fuzhou, Quanzhou and Xiamen were analyzed for polychlorinated biphenyl (PCB) concentrations. Thirty-six PCB congeners were quantified in the fishes, of which 11 congeners were dioxin-like PCBs. The total PCB concentrations of the present study were at the low end of the global range, which may be related to the smaller usage and shorter consumption history of PCBs in China. PCBs 18, 29, 52, 66, 101, 104, 138, 153, 180 and 194 were the major constituents found in the fish samples. Regression analysis showed a strong positive correlation ($R^2 = 0.800$; $p < 0.001$) between total dioxin-like PCBs and total PCB concentrations, and that total PCB concentrations explain 80% of the variability in total dioxin-like PCB concentrations. Among the species investigated, significantly higher concentrations of total PCBs were found in croakers than in pomfrets, which may be attributed to their different feeding and living habits. No significant difference in total PCB concentrations among the cities was observed; principal component analysis (PCA) of PCB profiles indicated that PCB pollution came from similar sources in the sampling areas and that there may be other PCB sources in Dalian and Wenzhou. The calculated carcinogenic risks (CRs) from the two species based on a low consumption group and high consumption group were all greater than 10^{-6}, suggesting that daily exposure to dioxin-like PCBs via fish consumption results in a lifetime cancer risk of greater than one in one million. In contrast, the hazard quotients (HQs) of noncancer risks were all less than unity.

1. Introduction

Polychlorinated biphenyls (PCBs) are a class of organic compounds with 1–10 chlorine atoms attached to a biphenyl molecule. They were commercially produced as complex mixtures since 1929, and have been widely used as dielectric fluids in transformers, capacitors, coolants and for other applications based on their chemical stability and physical properties (Safe, 1994; Frame et al., 1996; Diamond et al., 2010). The total amount of PCBs manufactured worldwide was estimated to be 1.5 million metric tons (t) (Ivanov and Sandell, 1992). In China, approximately 10,000 t of PCBs were produced in the decade from 1965 to 1975, and were known as PCB3 and PCB5 (Fu et al., 2003). PCB3 and PCB5 were reported to be similar to Aroclor 1242 and Aroclor 1254, respectively (Jiang et al., 1997).

The toxicity of the individual PCB congeners depends on the chlorine substitution pattern. Coplanar PCBs, especially the non- (PCB 77, 81, 126 and 169) and mono-ortho PCBs (PCB 105, 114, 118, 123, 156, 157, 167 and 189) are the most toxic congeners. These non- and mono-ortho PCBs share a structural similarity

* Corresponding authors. Tel.: +852 2788 7681 (P.K.S. Lam), +86 551 3601415 (Z.Q. Xie).
E-mail addresses: zqxie@ustc.edu.cn (Z. Xie), bhpksl@cityu.edu.hk (P.K.S. Lam).

0045-6535/$ - see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.chemosphere.2012.06.048

and common toxic mechanism with the most toxic dioxin compound (i.e., 2,3,7,8-tetrachlorodibenzo-*p*-dioxin; 2,3,7,8-TCDD) (Giesy and Kannan, 1998; Van den Berg et al., 1998). The World Health Organization (WHO) toxic equivalency factor (TEF) scheme includes 12 of the 209 PCB congeners that have the propensity to disrupt the endocrine system, cause neurobehavioral deficits and possibly cause cancer (Van den Berg et al., 1998, 2006). One notorious poisoning event occurred in Japan in 1968, in which PCB-contaminated rice bran oil was used as chicken feed, resulting in a mass poisoning known as Yushō disease in over 15,000 people (Umeda, 1972). From then on, PCBs attracted considerable attention from the scientific community because of their toxicity, resistance to degradation, potential for long-range transport and their tendency to bioaccumulate through food chains (Harrad et al., 1994; Olsson et al., 1994). The production and/or usage of PCBs have been banned or restricted since the early 1970s, and under the 2001 Stockholm Convention, PCBs are classified as persistent organic pollutants (POPs), and are subject to international restrictions on their production and use (UNEP, 2001; Mai et al., 2005). Although the concentrations of PCBs in various environmental matrices have decreased dramatically since peaking in the 1970s (Jones et al., 1992; Mason, 1998; Schneider et al., 2001; Schuster et al., 2010), they continue to bioaccumulate in organisms and be categorized as major global contaminants. Jonsson et al. (2003) estimated that human exposure to PCBs is expected to continue for decades and perhaps centuries because of the very long global environmental mean residence times of these pollutants.

The coastal regions of eastern China are characterized by intensive urban development and industrial activities. It was estimated that the PCB usage in the eastern part of China contributed 45% of the total amount used in the country (Zhang et al., 2010). Leaks and spills of PCBs, illegal disposal of PCB-containing products, municipal solid waste incineration, and historical contamination of bottom sediments could be potential PCB emission sources (Zhang et al., 2007; Lakshmanan et al., 2010). Coastal environments serve as a sink for PCBs and thus may be greatly affected by PCBs (Jonsson et al., 2003). Fishes are good bioindicators to elucidate the contamination status and distribution of POPs (Ueno et al., 2003). Furthermore, the consumption of fishes and fish products is a major route of human exposure to POPs, and may pose a risk to the Chinese population. In order to assess the extent and patterns of PCBs contamination in the coastal environment in China, this study investigated the presence and concentrations of PCBs in muscle tissues of two species of marine fishes collected from nine coastal cities.

2. Materials and methods

2.1. Collection of samples

The marine fish samples were randomly collected and purchased from fishing boats and local fish markets in nine coastal cities of East China including Dalian, Tianjin, Qingdao, Shanghai, Zhoushan, Wenzhou, Fuzhou, Quanzhou, and Xiamen in 2008 (Fig. 1). Two species of fishes, large yellow croaker (*Pseudosciaena crocea*) and sliver pomfret (*Pampus argenteus*), were caught in local waters as confirmed by local fishermen. Procedures for sample preparation have been described previously (Xia et al., 2011).

2.2. Chemicals

Standards used in this study were purchased from Wellington Laboratories (Guelph, Ontario, Canada). All solvents used throughout the study were of HPLC- and pesticide-grade.

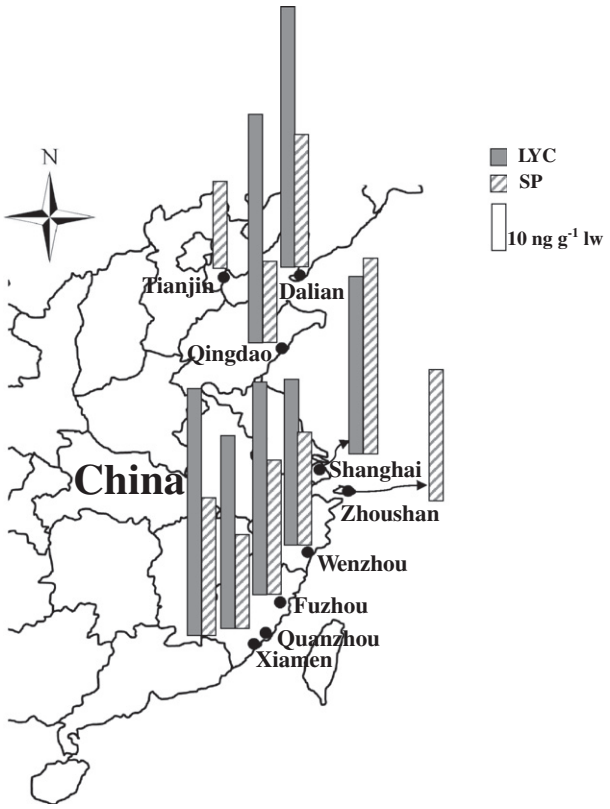

Fig. 1. Map showing sampling locations and mean ΣPCB concentrations in marine fishes analyzed in this study (LYC-large yellow croaker; SP-silver pomfret).

2.3. Sample treatment and chemical analysis

Analysis of PCBs was accomplished by use of previously established methods with modifications (Lam et al., 2008). Briefly, freeze-dried muscles were ground into fine powder, homogenized with anhydrous sodium sulfate, and placed in pre-cleaned extraction cells and extracted by accelerated solvent extraction (ASE 200, DIONEX Inc.) using a mixture of dichloromethane (DCM) and hexane (4:1 v/v, 40 mL) at 1500 psi and 110 °C for 6 min for two cycles. Before extraction, PCB 30 was added as an internal surrogate standard. All extracts were concentrated to 5 mL with a rotary evaporator. An aliquot of 0.5 mL was used for gravimetric determination of lipid content. Lipids were removed from extracts using a gel permeation chromatography column (GPC; 25 mm (i.d.) × 500 mm (L); Bio-Beads S-X3, Bio-Rad Laboratories, Hercules, CA) by elution with an equivalent mixture of DCM in hexane (1:1 v/v) at a flow rate of 5 mL min^{-1}. The concentrated extract was then transferred and further purified by elution with 90 mL of hexane and 110 mL of DCM and hexane mixture (1:1 v/v) through activated silica gel (60 Å average pore size) and deactivated alumina. 2,4,5,6-Tetrachloro-m-xylene (TCMX) was spiked into the concentrated fraction and the volume was further reduced to 0.1 mL prior to GC/MS analysis.

Quantification of PCBs was performed using a GC (Agilent 7890A) equipped with a mass-selective detector (Agilent 5975c) in the negative chemical ionization (NCI) mode with methane used as the reactant gas. The GC column used for quantification was a DB-XLB fused silica capillary column (J&W Scientific Inc., Folsom, CA) with 0.25 mm i.d. × 60 m × 0.25 μm film. PCB standards were measured and the samples were analyzed separately in selective ion monitoring (SIM) mode. The most abundant ions were selected for quantification and two reference ions were used for

confirmation of each analyte in SIM mode. In the present study, 36 PCB congeners were monitored (Table S1).

2.4. Quality control

Procedural blanks were analyzed simultaneously with every batch of five samples to check for cross-contamination. PCB concentrations in the procedural blanks were <0.01 ng g^{-1}, indicating no significant interferences or contamination from the processing of samples. The limit of quantification (LOQ), defined as three times the procedural blank was 0.01 ng g^{-1} of lipid for each PCB congener. Congener concentrations below LOQ were treated as half of the LOQ for statistical analyses. Surrogate recovery (n = 53, including 44 fish samples and nine laboratory blanks) was 92 ± 11% for PCB 30. The recovery rates of analytes ranged between 70% and 120% (n = 3).

2.5. Statistical analysis

All statistical tests were performed with SPSS software (SPSS 17.0 for Windows, SPSS Inc.). Nonparametric Kruskal–Wallis tests were used to analyze overall differences among the cities in lipid content and Σ_{36}PCB concentrations. Nonparametric Mann–Whitney tests were used to compare interspecies differences for the lipid proportion and the PCB concentrations. Statistical significance was accepted at $p < 0.05$.

3. Results and discussion

3.1. PCB concentrations and global comparison

PCBs were detected in all the fish samples collected from coastal waters in China. Due to the lipophilic nature of PCBs, they are generally well correlated to the lipid content in biota samples (Svendsen et al., 2007; Walters et al., 2008). In this study, Σ_{36}PCBs (wet weight) were significantly positively correlated with lipids (Fig. S1, R^2 = 0.786, $p < 0.001$). Considering that the lipid contents of fish samples were significantly different across the species ($p < 0.01$) and the coastal cities ($p < 0.05$), PCB concentrations were normalized to lipid weight (Table S1). Σ_{36}PCB concentrations in all fish samples varied between 13.3 and 78.3 ng g^{-1} lipid weight (lw), with an average (±SD) concentration of 35 ± 15 ng g^{-1} lw. The wet weight basis results are shown in Table S2.

PCBs are important global pollutants that have been measured at high concentrations in marine fishes worldwide. In order to facilitate comparisons (Table S2), only data from the muscle tissues of fishes sampled after the year of 2000 were used in consideration of the temporal trend of PCB concentrations. Comparable results from other studies were reported in coastal regions such as Shanghai (Nakata et al., 2002) and the Pearl River Estuary (Nie et al., 2005), China. Overall, the concentrations of PCBs in fishes were at the low end of the global range. Lower residues of PCBs were also reported in coastal sediments, surface water and bivalves from China (Zhou et al., 2000; Mai et al., 2005; Jin et al., 2007). These lower concentrations may be related to the limited usage and shorter consumption history of PCBs in China—the total amount of technical PCBs produced from 1965 to 1975 in China (10,000 t) accounted for 0.6% of the total global production. Although a number of PCB-containing transformers and capacitors were imported from industrialized countries, the quantities of PCBs in this equipment amount to only approximately 10,000 t (Zhang et al., 2010). Notably, PCB in fishes from the Arctic (i.e. Alaska) were present at extremely high concentrations, supporting the role of long-range atmospheric transport of PCBs as an important component of their environmental fate and also indicating that the Arctic acts as a sink for PCBs as suggested by other studies (i.e. MacDonald et al. (2000)).

3.2. Congeneric composition of PCBs

Concentrations of individual PCB congeners ranged from <0.01 to 23 ng g^{-1} lw in yellow croakers, and from <0.01 to 10.7 ng g^{-1} lw in pomfrets (Table S1). The occurrence frequencies for PCB 1, PCB 8 and PCB 50 in pomfrets were the lowest—26%, 52% and 30%, respectively—while these congeners were detected in all of the croakers. The rates of detection for PCB 81 in both species were relatively lower: 38% in yellow croakers and 65% in pomfrets. The concentration patterns of individual PCB congeners were similar between the two species, although the concentrations were higher in croakers than in pomfrets (Fig. 2). The contributions of individual PCB congeners to Σ_{36}PCBs were also investigated (Fig. S2). The tri-, tetra-, penta- and hexa-CBs contributed relatively higher proportions than the other congeners, accounting for 80% of Σ_{36}PCBs. Concentrations of PCBs 18, 29, 52, 66, 101, 104, 138, 153, 180 and 194 were greatest in both species (Fig. 2).

Similar PCB congener patterns to those analyzed in fishes in the present study have been reported elsewhere: in a study investigating fishes from the Pearl River Estuary region, penta- and hexa-CBs were the most abundant (Nie et al., 2005); and a study of shellfish from the coastal areas of Xiamen Island and Minjiang Estuary in China reported that PCBs 101, 138, 149, 153, 180 contributed considerably to ΣPCB concentrations (Chen et al., 2002). This pattern could have arisen from historic use and subsequent environmental release of domestically-produced commercial PCB mixtures (i.e. usage of tri-formulations such as PCB3 and penta-formulations such as PCB5), in which tri- to penta-chlorinated congeners were the important constituents. Previous studies on PCB contamination in sediments from the Haihe Estuary and the Pearl River Estuary in China found that lower chlorinated homologues, tri- to penta-CBs, predominated (Mai et al., 2005; Zhao et al., 2010), a pattern which is consistent with the commercial PCB formulations. However, hexa-CBs accounted for a relatively higher proportion of Σ_{36}PCBs in fishes in the present study. It is possible that higher-chlorinated congeners have lower chemical degradation rates than those with lower chlorination and thus are retained to a greater degree in aquatic systems, where they may bioaccumulate in fishes. For example, the global environmental mean residence times of PCB 153 and PCB 180 were estimated to be in the order of 110 and 70 years (Jonsson et al., 2003).

The proportions of total dioxinlike PCBs (Σdl-PCBs hereafter, include non-ortho PCB 81, 126, 169, and mono-ortho PCB 105, 114, 118, 123, 156, 167, and 189) to Σ_{36}PCBs varied slightly among individual fish of both species, and their average values were similar (Fig. S2). Bhavsar et al. (2007) found that the dl-PCB composition in fishes was relatively constant (mean: 8.5%; interquartile range: 5.2–10.6%) regardless of the fish species and ΣPCB level using the largest known dl-PCB fish dataset, and also that the abundance of dl-PCBs was generally in the order of PCB 118 > 105 > 156 > 167 > 123 > 157 ≈ 114 > 189 > 77 > 126 > 81 ≈ 169. In this study, we measured the concentrations of 11 dl-PCB congeners in fishes, omitting PCB 77, which contributed only 0.018–0.093% to ΣPCBs as reported previously (Bhavsar et al., 2007). The mean relative abundance of Σdl-PCBs to ΣPCBs in this study was 9.9% (interquartile range: 8.7–11.3%), which was a little higher than the value reported in the literature. In addition, the dl-PCB congener profile in fishes in the present study was somewhat different from that described previously, i.e., PCB 118 > 123 > 156 > 105 > 167 > 157 > 189 > 114 > 81 ≈ 126 ≈ 169 (Fig. S3). In agreement with the findings of Bhavsar et al. (2007), all non-*ortho* congeners including PCB 81, 126, and 169 accounted for the lowest proportion of ΣPCBs in fishes. The linear relationship between

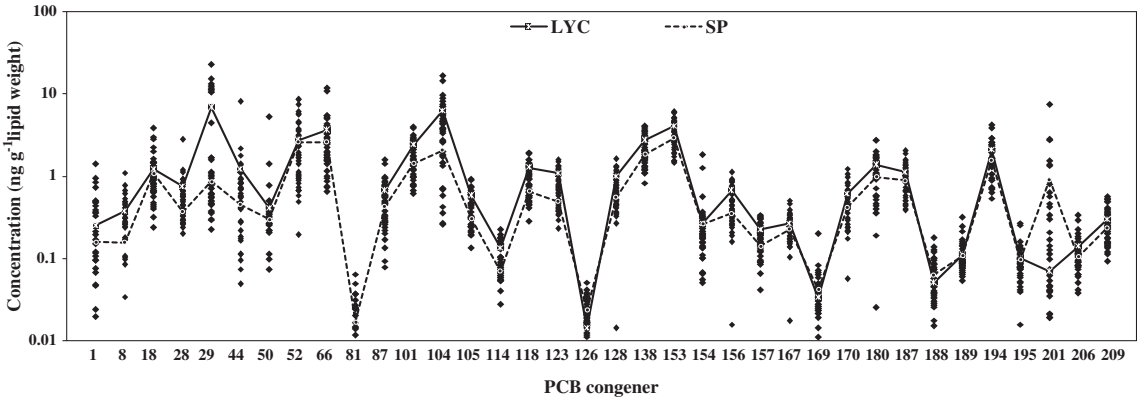

Fig. 2. Concentrations and mean values (ng g^{-1} lipid weight) of PCB congeners determined in marine fish samples from the coast of East China (LYC-large yellow croaker; SP-silver pomfret).

dl-PCBs and ΣPCBs was also investigated to determine whether the dl-PCB congeneric composition was constant in these two fish species from coastal China (Fig. S4). The regression analysis showed a strong positive correlation ($R^2 = 0.800$; $p < 0.001$, $n = 44$) between concentrations of Σdl-PCBs and ΣPCBs. PCBs 118, 123, 156, 105, 167, 157 and PCB 114 also showed strong linear relationships with ΣPCBs ($R^2 > 0.5$, Fig. S4), while other congeners (i.e. PCB 81, 126, 169, 189) showed weaker correlations ($R^2 < 0.5$, results not shown). A weaker correlation was found for lower levels of dl-PCBs, which was probably due to higher analytical errors for the lower dl-PCB concentrations. These results were consistent with an earlier study indicating that the contributions of dl-PCBs to ΣPCBs were constant in fishes (Bhavsar et al., 2007).

3.3. Interspecies differences and geographical distribution

Significant interspecies differences were found with regard to ΣPCB concentrations in the nine coastal cities ($p < 0.01$), and higher concentrations of ΣPCBs were found in croakers. However, in Shanghai, relatively higher PCB concentrations were found in pomfrets than croakers (Fig. 1), probably because the lipid content was greatest in croakers and lowest in pomfrets from Shanghai compared to other cities. In general, croakers contained higher concentrations of ΣPCBs than pomfrets, which may be attributed to their different feeding and living habits, as many studies have provided evidence of the biomagnification of PCBs along marine food webs (Fisk et al., 2001; Hop et al., 2002; Hoekstra et al., 2003; Ramu et al., 2006). Pomfrets are omnivorous species, mainly feeding on ctenophores, medusae and other plankton groups (Abdurahiman et al., 2006), whereas yellow croakers are carnivorous fish (Ai et al., 2006) that occupy a higher trophic level than pomfrets, which is a likely reason for the higher concentrations of ΣPCBs present. Furthermore, croakers, which are bottom-feeding species, are likely to have a much higher level of exposure to PCBs in the bottom sediment than pomfrets which are characterized by a more pelagic diet; benthic fishes have been found to show higher concentrations of PCBs in a study in the US (Morgan and Lohmann, 2010).

Principal component analysis (PCA) was performed to provide additional information about interspecies differences based on the bioaccumulation properties of individual PCB congeners. PCA analyses were carried out for each species separately using concentrations of seven indicator PCBs, PCBs 28, 52, 101, 118, 138, 153 and PCB 180, and lipid content as eight variables in the correlation matrix. A component matrix was obtained after varimax rotation (Table S3). The first two principal components (PCs) of PCA together explained 79.7% and 85.9% of the total variance in croakers and pomfrets, respectively. In both species, the medium- and higher-chlorinated PCBs (i.e. PCB 101, 118, 138, 153, 180) were related to PC1, indicating that they are characterized by similar accumulation features in the two species. The lower-chlorinated congener PCB 28 was related to PC1 in croakers and to PC2 in pomfrets, reflecting that PCB 28 accumulated in the two species via different mechanisms. PCB 52 in both species was related to PC2, indicating different accumulation behavior compared to higher-chlorinated congeners. The concentrations of penta-CBs to hepta-CBs were negatively correlated to lipid content in pomfrets, but not in croakers.

Geographically, no significant differences in ΣPCB concentrations among the cities were observed ($p > 0.05$). The highest concentration of ΣPCBs in croakers was found in Dalian and Xiamen, while the highest ΣPCB concentration in pomfrets occurred in Shanghai. The different distribution pattern in the two species may be caused by the age of the fishes, lipid content, as well as other physiological differences among the fish species. PCA was applied to identify differences and similarities in PCB profiles among the nine cities using concentrations of mono- to deca-chlorinated PCB congeners as the variables. The first three PCs accounted for 74.5% of the variance in ΣPCB concentrations (Fig. S5). Fishes from different sampling sites grouped together, except for a few samples (Fig. S6a) and most samples from Dalian and Wenzhou (Fig. S6b), indicating that PCB pollution originated from similar sources in most of the sampled areas but that there may be other PCB sources in Dalian and Wenzhou.

3.4. Toxic equivalents (TEQs) and estimated human intake of dioxin-like PCBs and non dioxin-like PCBs

Toxic equivalency factors (TEFs) were developed to assess and compare the toxic potencies of polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and PCBs, by which the toxicity of an individual compound is compared to that of 2,3,7,8-TCDD. TEFs for dioxin-like compounds, including some PCBs, were reevaluated at a WHO International Programme on Chemical Safety expert meeting held in Geneva in June 2005. The total toxic equivalent (TEQ) is defined by the sum of the products of the concentration of each compound multiplied by its TEF value and is given by the following equation (Van den Berg et al., 2006):

$$\mathrm{TEQs} = \Sigma(C_i \times \mathrm{TEF}_i)$$

In this study, TEQs is the total toxic equivalent of dl-PCBs (pg TEQ g^{-1} ww); C_i is the concentration of dl-PCB congener i (pg g^{-1} ww); TEF_i is the toxic equivalent factor value of congener i.

Estimated daily intakes (EDIs) were calculated by multiplying per capita fish consumption values with the PCB residue levels

measured in the present study assuming a typical body weight of 60 kg. The equation is as follows:

$$EDI = C \times FCR/BW$$

in which, EDI is the estimated daily intake; C is the concentration of chemical contaminant; BW is the consumer body weight (60 kg); FCR is the per capita fish consumption (g d^{-1}). In the present study, an absorption fraction of one was applied to both dl- and non-dl-PCBs.

The rates of the consumption of fishes for the Chinese population were estimated to be 11 g d^{-1} per capita for the low fish consumption group and 119 g d^{-1} per capita for the high consumption group in order to deduce the lower and higher exposure concentrations of PCBs, respectively (Fung et al., 2004). In order to be able to estimate the contribution of each dl-PCB to TEQs, their concentrations were reported on a wet weight basis (Table S4). The ΣPCB concentrations were much less than the maximum concentration (2000 ng g^{-1} ww) of ΣPCBs in edible seafood allowed by the US Food and Drug Administration (FDA). The intakes of dl-PCBs from croakers and pomfrets ranged between 0.09 and 0.93 pg TEQ kg^{-1} bw d^{-1}, and 0.07 and 0.76 pg TEQ kg^{-1} bw d^{-1}, respectively. Intake values of non-dl-PCBs were between 1.14 and 12.32 ng kg^{-1} bw d^{-1} via consumption of croakers, and 0.34 and 3.67 ng kg^{-1} bw d^{-1} via consumption of pomfrets. TEQ exposure from both species was comparable though slightly greater from croakers, whereas intake of non-dl-PCBs was significantly higher from croakers than pomfrets. A tolerable daily intake (TDI) of 1–4 pg TEQ kg^{-1} bw was established by WHO in 1998, a tolerable weekly intake of 14 pg TEQ kg^{-1} bw (corresponding to a TDI of 2 pg TEQ kg^{-1} bw) was proposed by the European Commission in 2001, and a tolerable monthly intake of 70 pg TEQ kg^{-1} bw was proposed by the Joint FAO/WHO Expert Committee on Food Additives in 2001 (Baeyens et al., 2007). Estimated daily intakes of dl-PCBs in this study were all lower than these levels, indicating that dietary consumption of these fishes does not represent a perceptible human health risk.

3.5. Evaluation of human health risks

In order to screen for the potential public health significance of the estimated exposure levels, risk due to both carcinogenic and noncarcinogenic effects was assessed.

For carcinogens, risks are estimated as the incremental probability of an individual developing cancer over a lifetime as a result of exposure to the potential carcinogen. The carcinogenic risk equation is described as follows (USEPA, 1989):

$$CR = EDI \times CSF$$

where CR is the carcinogenic risk, a unitless probability of an individual developing cancer; EDI is the estimated daily intake (pg TEQ kg^{-1} d); and CSF is the cancer slope factor (pg kg^{-1} $d)^{-1}$.

A CSF of 1.56×10^{-4} (pg kg^{-1} $d)^{-1}$ (USEPA, 2000) was used in this study.

The cancer risk set to one in one million due to lifetime exposure was used as the generally acceptable risk level. The principle is that if CR values obtained from the low fish consumption group were greater than 10^{-6}, some appropriate control or management strategies will need to be taken, while if CRs obtained from the high consumption group were lower than 10^{-6}, dl-PCBs are unlikely to cause adverse health effects to human consumers, and thus should be accorded a lower priority.

The potential risks of noncarcinogenic effects are evaluated by comparing an exposure level over a specified time period (e.g., lifetime) with a reference dose derived for a similar exposure period (USEPA, 1989). This ratio of exposure to toxicity is a hazard quotient (HQ) and is described as follows:

$$HQ = EDI/RfD$$

where HQ is hazard quotient; EDI is the estimated daily intake (ng kg^{-1} d); and RfD is the reference dose (ng kg^{-1} d).The RfD applied in this study was 20 ng kg^{-1} d (USEPA, 2000).

A HQ greater than unity indicates that the exposure level exceeds the effects threshold, and therefore there may be concern for potential noncancer effects. Generally, greater HQ values indicate greater levels of concern.

The cancer risk from two species based on low consumption group and high consumption group were all greater than 10^{-6}, suggesting that daily exposure to dioxin-like PCBs via fish consumption would result in a lifetime cancer risk of greater than one in one million (Table S5). These results imply that lifetime cancer risk is a possibility for coastal residents who are likely to consume more seafood than those living inland. Dl-PCBs may be of particular concern. In contrast, the noncancer risks associated with fish consumption of PCBs for both the low and high consumption groups were all less than unity. A similar result was found in a previous study undertaken in Zhoushan, which reported that the HQs of noncancer risk based on 50th and 95th percentile concentrations were also less than unity (Jiang et al., 2005). However, the HQs obtained from consumption of croakers were relatively higher than those of pomfrets, especially for the high consumption groups. This suggests that pomfrets were safer for consumption than croakers based on their contributions to the EDI of PCBs.

4. Conclusion

Risk estimation indicated that PCBs may pose a health risk to heavy fish consumers. However, there were a number of sources of uncertainty introduced in the risk assessment, such as the relatively small number of fish species analyzed and the sample sizes used for chemical analysis, as well as potential variation in actual risk among human consumers in different age groups and due to differences in fish consumption rates. Nevertheless, this preliminary health risk assessment of PCBs to human consumers due to fish consumption in coastal cities of China indicates that dl-PCBs may be of concern.

Acknowledgments

This study was partially supported by grants from the Area of Excellence Scheme under the University Grants Committee of the Hong Kong Special Administrative Region, China (Project No. AoE/P-04/2004) and the National Natural Science Foundation of China (Project No. 41025020).

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.chemosphere.2012.06.048.

References

Abdurahiman, K.P., Zacharia, P.U., Nayak, T.H., Mohamed, K.S., 2006. Diet and trophic ecology of silver pomfret, Pampus argenteus (Euphrasen, 1788) exploited from the Southeast Arabian Sea. J. Marine Biol. Assoc. India 48, 206–212.

Ai, Q.H., Mai, K.S., Tan, B.P., Xu, W., Duan, Q.Y., Ma, H.M., Zhang, L., 2006. Replacement of fish meal by meat and bone meal in diets for large yellow croaker, Pseudosciaena crocea. Aquaculture 260, 255–263.

Baeyens, W., Leermakers, M., Elskens, M., Van Larebeke, N., De Bont, R., Vanderperren, H., Fontaine, A., Degroodt, J.M., Goeyens, L., Hanot, V., Windal, I., 2007. PCBs and PCDD/FS in fish and fish products and their impact on the human body burden in belgium. Arch. Environ. Contam. Toxicol. 52, 563–571.

Bhavsar, S.P., Fletcher, R., Hayton, A., Reiner, E.J., Jackson, D.A., 2007. Composition of dioxin-like PCBs in fish: an application for risk assessment. Environ. Sci. Technol. 41, 3096–3102.

Chen, W.Q., Zhang, L.P., Xu, L., Wang, X.H., Hong, L.Y., Hong, H.H., 2002. Residue levels of HCHs, DDTs and PCBs in shellfish from coastal areas of east Xiamen Island and Minjiang Estuary. China. Mar. Pollut. Bull. 45, 385–390.

Diamond, M.L., Melymuk, L., Csiszar, S.A., Robson, M., 2010. Estimation of PCB Stocks, emissions, and urban fate: will our policies reduce concentrations and exposure? Environ. Sci. Technol. 44, 2777–2783.

Fisk, A.T., Hobson, K.A., Norstrom, R.J., 2001. Influence of chemical and biological factors on trophic transfer of persistent organic pollutants in the northwater polynya marine food web. Environ. Sci. Technol. 35, 732–738.

Frame, G.M., Wagner, R.E., Carnahan, J.C., Brown, J.F., May, R.J., Smullen, L.A., Bedard, D.L., 1996. Comprehensive, quantitative, congener-specific analyses of eight aroclors and complete PCB congener assignments on DB-1 capillary GC columns. Chemosphere 33, 603–623.

Fu, J.M., Mai, B.X., Sheng, G.Y., Zhang, G., Wang, X.M., Peng, P.A., Xiao, X.M., Ran, R., Cheng, F.Z., Peng, X.Z., Wang, Z.S., Tang, U.W., 2003. Persistent organic pollutants in environment of the Pearl River Delta, China: an overview. Chemosphere 52, 1411–1422.

Fung, C.N., Lam, J.C.W., Zheng, G.J., Connell, D.W., Monirith, I., Tanabe, S., Richardson, B.J., Lam, P.K.S., 2004. Mussel-based monitoring of trace metal and organic contaminants along the east coast of China using Perna viridis and Mytilus edulis. Environ. Pollut. 127, 203–216.

Giesy, J.P., Kannan, K., 1998. Dioxin-like and non-dioxin-like toxic effects of polychlorinated biphenyls (PCBs): implications for risk assessment. Crit. Rev. Toxicol. 28, 511–569.

Harrad, S.J., Sewart, A.P., Alcock, R., Boumphrey, R., Burnett, V., Duartedavidson, R., Halsall, C., Sanders, G., Waterhouse, K., Wild, S.R., Jones, K.C., 1994. Polychlorinated-biphenyls (PCBS) in the British environment – sinks, sources and temporal trends. Environ. Pollut. 85, 131–146.

Hoekstra, P.F., O'Hara, T.M., Fisk, A.T., Borga, K., Solomon, K.R., Muir, D.C.G., 2003. Trophic transfer of persistent orgranochlorine contaminants (OCs) within an Arctic marine food web from the southern Beaufort-Chukchi Seas. Environ. Pollut. 124, 509–522.

Hop, H., Borga, K., Gabrielsen, G.W., Kleivane, L., Skaare, J.U., 2002. Food web magnification of persistent organic pollutants in poikilotherms and homeotherms from the Barents Sea. Environ. Sci. Technol. 36, 2589–2597.

Ivanov, V., Sandell, E., 1992. Characterization of polychlorinated biphenyl isomers in sovol and trichlorodiphenyl formulations by high-resolution gas-chromatography with electron-capture detection and high-resolution gas-chromatography mass-spectrometry techniques. Environ. Sci. Technol. 26, 2012–2017.

Jiang, K., Li, L.J., Chen, Y.D., Jin, J., 1997. Determination of PCDD/Fs and dioxin-like PCBs in Chinese commercial PCBs and emissions from a testing PCB incinerator. Chemosphere 34, 941–950.

Jiang, Q.T., Lee, T.K.M., Chen, K., Wong, H.L., Zheng, J.S., Giesy, J.P., Lo, K.K.W., Yamashita, N., Lam, P.K.S., 2005. Human health risk assessment of organochlorines associated with fish consumption in a coastal city in China. Environ. Pollut. 136, 155–165.

Jin, Y.N., Hong, S.H., Li, D.H., Shim, W.J., Lee, S.S., 2007. Distribution of persistent organic pollutants in bivalves from the northeast coast of China. In: 5th International Conference on Marine Pollution and Ecotoxicology, Hong Kong, PEOPLES R CHINA, pp. 775–781.

Jones, K.C., Sanders, G., Wild, S.R., Burnett, V., Johnston, A.E., 1992. Evidence for a decline of PCBs and PAHs in rural vegetation and air in the United Kingdom. Nature 356, 137–140.

Jonsson, A., Gustafsson, O., Axelman, J., Sundberg, H., 2003. Global accounting of PCBs in the continental shelf sediments. Environ. Sci. Technol. 37, 245–255.

Lakshmanan, D., Howell, N.L., Rifai, H.S., Koenig, L., 2010. Spatial and temporal variation of polychlorinated biphenyls in the Houston Ship Channel. Chemosphere 80, 100–112.

Lam, J.C.W., Murphy, M.B., Wang, Y., Tanabe, S., Giesy, J.P., Lam, P.K.S., 2008. Risk assessment of organohalogenated compounds in water bird eggs from South China. Environ. Sci. Technol. 42, 6296–6302.

MacDonald, R.W., Barrie, L.A., Bidleman, T.F., Diamond, M.L., Gregor, D.J., Semkin, R.G., Strachan, W.M.J., Li, Y.F., Wania, F., Alaee, M., Alexeeva, L.B., Backus, S.M., Bailey, R., Bewers, J.M., Gobeil, C., Halsall, C.J., Harner, T., Hoff, J.T., Jantunen, L.M.M., Lockhart, W.L., Mackay, D., Muir, D.C.G., Pudykiewicz, J., Reimer, K.J., Smith, J.N., Stern, G.A., Schroeder, W.H., Wagemann, R., Yunker, M.B., 2000. Contaminants in the Canadian Arctic: 5 years of progress in understanding sources, occurrence and pathways. Sci. Total Environ. 254, 93–234.

Mai, B.X., Zeng, E.Y., Luo, X.J., Yang, Q.S., Zhang, G., Li, X.D., Sheng, G.Y., Fu, J.M., 2005. Abundances, depositional fluxes, and homologue patterns of polychlorinated biphenyls in dated sediment cores from the Pearl River Delta. China. Environ. Sci. Technol. 39, 49–56.

Mason, C.F., 1998. Decline in PCB levels in otters (Lutra lutra). Chemosphere 36, 1969–1971.

Morgan, E.J., Lohmann, R., 2010. Dietary uptake from historically contaminated sediments as a source of PCBs to migratory fish and invertebrates in an urban estuary. Environ. Sci. Technol. 44, 5444–5449.

Nakata, H., Kawazoe, M., Arizono, K., Abe, S., Kitano, T., Shimada, H., Li, W., Ding, X., 2002. Organochlorine pesticides and polychlorinated biphenyl residues in foodstuffs and human tissues from China: status of contamination, historical trend, and human dietary exposure. Arch. Environ. Contam. Toxicol. 43, 473–480.

Nie, X.P., Lan, C.Y., Wei, T.L., Yang, Y.F., 2005. Distribution of polychlorinated biphenyls in the water, sediment and fish from the Pearl River estuary. China. Mar. Pollut. Bull. 50, 537–546.

Olsson, M., Karlsson, B., Ahnland, E., 1994. Diseases and environmental contaminants in seals from the baltic and the swedish west-coast. Sci. Total Environ. 154, 217–227.

Ramu, K., Kajiwara, N., Lam, P.K.S., Jefferson, T.A., Zhou, K.Y., Tanabe, S., 2006. Temporal variation and biomagnification of organohalogen compounds in finless porpoises (Neophocaena phocaenoides) from the South China Sea. Environ. Pollut. 144, 516–523.

Safe, S.H., 1994. Polychlorinated-biphenyls (PCBS) – environmental-impact, biochemical and toxic responses, and implications for risk assessment. Crit. Rev. Toxicol. 24, 87–149.

Schneider, A.R., Stapleton, H.M., Cornwell, J., Baker, J.E., 2001. Recent declines in PAH, PCB, and toxaphene levels in the northern Great Lakes as determined from high resolution sediment cores. Environ. Sci. Technol. 35, 3809–3815.

Schuster, J.K., Gioia, R., Sweetman, A.J., Jones, K.C., 2010. Temporal trends and controlling factors for polychlorinated biphenyls in the UK atmosphere (1991–2008). Environ. Sci. Technol. 44, 8068–8074.

Svendsen, T.C., Vorkamp, K., Ronsholdt, B., Frier, J.O., 2007. Organochlorines and polybrominated diphenyl ethers in four geographically separated populations of Atlantic salmon (Salmo salar). J. Environ. Monit. 9, 1213–1219.

Ueno, D., Takahashi, S., Tanaka, H., Subramanian, A.N., Fillmann, G., Nakata, H., Lam, P.K.S., Zheng, J., Muchtar, M., Prudente, M., Chung, K.H., Tanabe, S., 2003. Global pollution monitoring of PCBs and organochlorine pesticides using skipjack tuna as a bioindicator. Arch. Environ. Contam. Toxicol. 45, 378–389.

Umeda, G., 1972. PCB poisoning in Japan. AMBIO 1, 132–134.

UNEP, 2001. United Nations Environment Programme; Stockholm Convention on Persistent Organic Pollutants; UNEP/POPs/CONF/4.

USEPA, 1989. Risk Assessment Guidance for Superfund Volume I: Human Health Evaluation Manual (Part A). Office of Emergency and Remedial Response, Washington, DC.

USEPA, 2000. Guidance for Assessing Chemical Contaminant Data for Use in Fish Advisories, volume 2: Risk Assessment and Fish Consumption Limits, third ed. Washington, DC: US Environmental Protection Agency (USEPA).

Van den Berg, M., Birnbaum, L., Bosveld, A.T.C., Brunstrom, B., Cook, P., Feeley, M., Giesy, J.P., Hanberg, A., Hasegawa, R., Kennedy, S.W., Kubiak, T., Larsen, J.C., van Leeuwen, F.X.R., Liem, A.K.D., Nolt, C., Peterson, R.E., Poellinger, L., Safe, S., Schrenk, D., Tillitt, D., Tysklind, M., Younes, M., Waern, F., Zacharewski, T., 1998. Toxic equivalency factors (TEFs) for PCBs, PCDDs, PCDFs for humans and wildlife. Environ. Health Perspect. 106, 775–792.

Van den Berg, M., Birnbaum, L.S., Denison, M., De Vito, M., Farland, W., Feeley, M., Fiedler, H., Hakansson, H., Hanberg, A., Haws, L., Rose, M., Safe, S., Schrenk, D., Tohyama, C., Tritscher, A., Tuomisto, J., Tysklind, M., Walker, N., Peterson, R.E., 2006. The 2005 World Health Organization reevaluation of human and mammalian toxic equivalency factors for dioxins and dioxin-like compounds. Toxicol. Sci. 93, 223–241.

Walters, D.M., Fritz, K.M., Johnson, B.R., Lazorchak, J.M., McCormico, F.H., 2008. Influence of trophic position and spatial location on polychlorinated biphenyl (PCB) bioaccumulation in a stream food web. Environ. Sci. Technol. 42, 2316–2322.

Xia, C., Lam, J.C.W., Wu, X., Sun, L., Xie, Z., Lam, P.K.S., 2011. Levels and distribution of polybrominated diphenyl ethers (PBDEs) in marine fishes from Chinese coastal waters. Chemosphere 82, 18–24.

Zhang, Q.H., Wang, Y.W., Li, A., Jiang, G.B., 2007. Polychlorinated Dibenzo-p-dioxins, Dibenzofurans, and Biphenyls, and Polybrominated Diphenyl Ethers in China. In: Li, A., Tanabe, S., Jiang, G.B., Giesy, J.P., Lam, P.K.S. (Eds.), Persistent Organic Pollutants in Asia: Sources, Distributions, Transport, and Fate. Elsevier Publications, Amsterdam, London (Chapter 2004).

Zhang, Z., Tian, C.G., Jia, H.L., Li, Y.F., 2010. Gridded Chinese polychlorinated biphenyis (PCBs) usage inventories. Journal of Natural Science of HeiLong Jiang University 27, 111–116.

Zhao, L., Hou, H., Zhou, Y.Y., Xue, N.D., Li, H.Y., Li, F.S., 2010. Distribution and ecological risk of polychlorinated biphenyls and organochlorine pesticides in surficial sediments from Haihe River and Haihe Estuary Area, China. Chemosphere 78, 1285–1293.

Zhou, J.L., Hong, H., Zhang, Z., Maskaoui, K., Chen, W., 2000. Multi-phase distribution of organic micropollutants in Xiamen Harbour. China Water Res. 34, 2132–2150.