Chemosphere 86 (2012) 242–247

Contents lists available at SciVerse ScienceDirect

Chemosphere

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

Polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), dioxin-like polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs) in waterbird eggs of Hong Kong, China

Yuan Wang [a,b], James C.W. Lam [a,*], M.K. So [a], Leo W.Y. Yeung [a], Zongwei Cai [c], Craig L.H. Hung [a], Paul K.S. Lam [a]

[a] State Key Laboratory in Marine Pollution, Department of Biology and Chemistry, City University of Hong Kong, Tat Chee Avenue, Kowloon, Hong Kong SAR, People's Republic of China
[b] Jiangsu Academy of Environmental Science, No. 241 Fenghuang West Road, Nanjing 210036, People's Republic of China
[c] Dioxin Laboratory, Department of Chemistry, Hong Kong Baptist University, Hong Kong, People's Republic of China

ARTICLE INFO

Article history:
Received 24 May 2011
Received in revised form 19 August 2011
Accepted 22 September 2011
Available online 22 October 2011

Keywords:
PCDD/Fs
Coplanar PCBs
PBDEs
Waterbirds
Egg
Hong Kong

ABSTRACT

Concentrations of PCDD/Fs, PCBs and PBDEs were measured in 56 egg samples collected from waterbirds of different species (Great Egret, Little Egret, Night Heron and Chinese Pond Heron) from different regions of Hong Kong (Ho Sheung Heung, Mai Po Village and Mai Po Lung Village) during 2000 and 2006. Dominance of 2,3,4,7,8-PeCDF indicates a signature associated with commercial usage of PCBs. Although no significant variations were observed within- and between-site in the levels of PCDD/Fs, coplanar PCBs and PBDEs, the concentrations of coplanar PCBs were much higher than PCDD/Fs. Similarity in composition profiles of PCDD/F and coplanar PCBs from different egretries is possibly associated with non-point sources of these contaminants to Hong Kong. Predominant accumulation of BDE-47, BDE-99 and BDE-100 suggested the penta-BDE technical mixtures usage in Hong Kong and its vicinity. Toxic equivalency and Monte Carlo simulation technique showed potential risks on waterbirds due to their exposure to PCDD/Fs.

1. Introduction

Polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), coplanar polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs) are environmental contaminants which have ubiquitous distribution in various environmental matrices including sediment, wildlife and human tissue (Alcock and Jones, 1996; de Wit, 2002). Because of their persistent, bioaccumulative nature and potential toxic characteristics, PCDD/Fs, coplanar PCBs, tetra-BDE and penta-BDE have been be listed as an additional global persistent organic pollutant (POP) under the Stockholm Convention in 2009 (UNEP, 2009). PCDD/Fs are commonly classified as unintentional by-products which come from various combustion and industrial processes, while co-planar PCBs were widely used as insulation material for electrical equipment such as PCB-containing transformers and capacitors (Alcock and Jones, 1996; Lam et al., 2008). High concentrations of PCDD/Fs have been often detected in the sediment (Wu et al., 2001; Micheletti et al., 2007). For PBDEs, rapid industrialization, urbanization, and unregulated disposal of electronic wastes (e-wastes) have been recognized as a cause of increased release of these environmental contaminants (Widmer et al., 2005). High consumption of brominated flame retardants (BFRs) in Asia particularly in China has been reported recently (Covaci et al., 2011). Thus, it is probable that huge amounts of BFRs may have been released and discharged into the coastal environment in the vicinity of the Pearl River Delta (PRD). Hong Kong is situated at the lower reach of PRD and is inevitably influenced by the pollution sources. A number of monitoring studies carried out in the PRD estuary and Hong Kong waters indicated significant loadings of PBDEs in various environmental matrices of this region (Zheng et al., 2004; Liu et al., 2005; Mai et al., 2005; Ramu et al., 2005).

Waterbirds have been commonly used as sentinel species for monitoring the effects and levels of POPs in the aquatic environment as they are widespread and sensitive to the environmental changes as well as often occupy high position in the food web. Thus they may be exposed to relatively higher concentrations of these environmental contaminants and are able to integrate pollutant levels over a large area by bioaccumulation. Bird egg has been reported as a good biomonitoring tools to measure levels of different POPs because it is an isolated and independent metabolic system. In addition, collection of eggs is a relatively non-invasive technique that can minimize the adverse effects on the bird community (Connell et al., 2003). In Hong Kong, concentrations of POPs

* Corresponding author. Tel.: +852 3442 4126; fax: +852 2194 2281.
E-mail address: james.lam@cityu.edu.hk (J.C.W. Lam).

0045-6535/$ - see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.chemosphere.2011.09.032

and heavy metals were monitored in eggs of Little Egrets (*Egretta garzetta*), Black-crowned Night Herons (*Nycticorax nycticorax*) and Bridled Terns (*Sterna anaethetus*) and the corresponding potential risks to the breeding success of these waterbirds were assessed (Connell et al., 2003; Lam et al., 2005), however, there is a lack of information about the levels and possible adverse effects of dioxin-like compounds (including PCDDs, PCDFs and coplanar PCBs) and PBDEs on waterbirds. Hence the aim of the present study is to assess the risk of adverse biological effects on selected waterbird species of Hong Kong due to their prolong exposure to PCDD/Fs, coplanar PCBs and PBDEs by using the derived concentrations of these compounds in their eggs.

2. Materials and methods

2.1. Collection of eggs

Egg samples were collected from five egretries in Hong Kong following conditions stipulated by Agriculture, Fisheries and Conservation Department (AFCD) over the period from March to April in 2006. They are: 16 Great Egret eggs (*Egretta alba*) and 16 Night Heron (*N. nycticorax*) eggs from A Chau, 12 Chinese Pond Heron eggs (*Ardeola bacchus*) from Ho Sheung Heung, four Little Egret eggs (*E. garzetta*) from Mai Po Village, five Chinese Pond Heron eggs from Mai Po Lung Village (Fig. S1). In addition three Little Egret eggs collected from Mai Po Village during 2000 were also analyzed for dioxin and coplanar PCBs. Only one egg was collected from each nest as collection of a single egg early in the breeding season allows birds the opportunity to lay another egg in replacement. Eggs collected were wrapped in aluminum foil, and individually labeled. The eggs were transferred to pre-cleaned glass jars and stored at −20 °C in the laboratory for subsequent analyses.

2.2. Chemical analysis

Quantification of dioxins, furans, coplanar PCBs and PBDEs was accomplished by use of previously established methods (Liu et al., 2006; Lam et al., 2008) with modifications; details can be found in the Supplementary material.

2.3. Quality control and quality assurance

A sequence table was established for each batch of samples, which comprised of a standard mixture, five samples, one procedural blank and one solvent blank. For analyses of PCDD/Fs and coplanar PCBs, 2000 pg and 1000 pg of ^{13}C-labeled PCDD/F and ^{13}C-labeled PCBs were added respectively as the internal standards to each sample prior to the instrumental analysis. ^{13}C-labeled PCBs and PCDD/F recovery standards were spiked into all samples before the extraction step. Recoveries for PCDD/Fs and coplanar PCBs were within 60–110%. Recovery of $^{13}C_{12}$-labeled BDE ranged between 60% and 120%.

2.4. Statistical analysis

Differences in the concentrations of PCDD/Fs, coplanar PCBs and PBDEs among egretries/locations were statistically analyzed, and the details can be found in the Supplementary material.

3. Results and discussion

3.1. PCDD/Fs

Concentrations of PCDD/Fs and coplanar PCBs in the eggs of Night Herons, Little Egrets and Chinese Pond Herons from egretries in Hong Kong (A Chau, Ho Sheung Heung and Mai Po Village) are summarized in Table 1. Due to close proximity among locations and the similarity in the environment of Mai Po Village and Mai Po Lung Village, and lack of significant differences in PCDD/F and coplanar PCB concentrations, the data for the egg samples collected in 2006 from these sites were pooled together under "Mai Po Village" for comparison.

The highest average of sum of PCDD/F concentration was found in egg samples of Night Heron from A Chau (PCDDs: 1020 pg g^{-1} - lipid wt. and PCDFs: 165 pg g^{-1} lipid wt.), whereas lower concentrations were observed in egg samples of Little Egret and Chinese Pond Heron from Mai Po Village (PCDDs: 520 pg g^{-1} lipid wt. and PCDFs: 167 pg g^{-1} lipid wt.), and egg samples of Chinese Pond Heron from Ho Sheung Heung had the least (PCDD: 484 pg g^{-1} lipid wt. and PCDF: 80.1 pg g^{-1} lipid wt.). However, there were no significant differences in the concentrations of PCDD/Fs in eggs collected during 2006 among Mai Po Village, A Chau, and Ho Sheung Heung. Hence it is suggested that point source pollution, such as contamination from discharges to the Pearl River, may be less important than non-point source pollution, such as atmospheric deposition. Similar results have also been observed with the eggs of double-crested cormorants and herring gulls collected from different colonies of the Great Lakes. PCDDs/Fs in the atmosphere were shown to be the possible source leading to the similar composition and magnitude of PCDD/F levels in the eggs between colonies (Kannan et al., 2001). Similar profiles of PCDD/Fs congeners were observed in eggs between egretries (Fig. S2).

Total PCDD concentrations were significantly greater than those of total PCDFs in all eggs collected in 2006. This could probably be due to greater exposure to dioxin than furans in the environment; or a higher metabolic rate for PCDFs than PCDDs in birds. Greater $\sum$PCDD concentrations were also detected in eggs of Audouin's Gull and Yellow-legged Gull from western Mediterranean (Pastor et al., 1995); and Herring Gull eggs from the Great Lakes (Kannan et al., 2001).

The dominance of 2,3,4,7,8-PeCDF in the PCDF patterns for all samples suggests a signature associated with commercial sources. The predominance of this congener has been attributed to the exposure to technical grade PCB mixtures containing this PeCDF as an impurity (Elliott et al., 1996). Technical PCBs have been reported to be the most important source of 2,3,4,7,8-PeCDF in the environment (Wakimoto et al., 1988). Technical PCBs were widely applied in transformers and capacitors in China and Hong Kong over the last few decades (Morton, 1989; Philips, 1989), so urban areas are a source of technical PCBs through their use in electrical equipment and its disposal after completion of its usage. The low TCDF concentrations in bird eggs could be due to the rapid excretion of the chemical from birds (Braune and Norstrom, 1989). In contrast OCDD was the predominant PCDD congener found in all egg samples. Similar observations were also found in eggs of gull species from the western Mediterranean (Pastor et al., 1995). The author attributed the result to the selective retention of PCDDs and PCDFs in females during yolk formation, as well as to the biomagnification potential of OCDD and its ability to resist metabolism (Braune and Norstrom, 1989). There are natural sources of OCDD, such as combustion, but it is possible that there can be a local pollution source of OCDD leading to its enrichment in the background air in Hong Kong (Tung et al., 2005).

Generally, PCDD concentrations in eggs from Hong Kong were greater than those from Canada, China and Japan; but were comparable to those found in eggs from Great Lakes (Table S1). In contrast, PCDF concentrations in eggs from Hong Kong were lower than those from other regions such as Canada, China, Great Lakes in the United States, Torishima Island in Japan and Midway Atoll, however they were found to be higher than some of the osprey eggs collected from the Pacific Northwest (Table S1).