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Levels and bioaccumulation of organochlorine pesticides (OCPs) and polybrominated diphenyl ethers (PBDEs) in fishes from the Pearl River estuary and Daya Bay, South China

Lingli Guo [a], Yaowen Qiu [a,b], Gan Zhang [a,*], Gene J. Zheng [c], Paul K.S. Lam [c], Xiangdong Li [d]

[a] State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou, Guangdong 510640, China
[b] Key Laboratory of Tropic Marine Environmental Dynamics, South China Sea Institute of Oceanology, Chinese Academy of Sciences, Guangzhou 510301, China
[c] Department of Biology and Chemistry, Centre for Coastal Pollution and Conservation, City University of Hong Kong, Tat Chee Avenue, Kowloon, Hong Kong SAR, China
[d] Department of Civil and Structural Engineering, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong SAR, China

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Bioconcentration was suggested to be responsible for the accumulation of OCPs and PBDEs in the lower trophic organisms of subtropical waters.

Abstract

Fifty fish samples were collected from the Pearl River estuary (PRE) and Daya Bay, South China and were analyzed for DDTs, HCHs, chlordanes and polybrominated biphenyl ethers (PBDEs). Except the high concentrations of DDT observed in fishes, the concentrations of HCHs, chlordanes and PBDEs were low when compared to other regions. BDE-47 was the predominant PBDE congener and the BDE-209 concentrations were relatively low, despite its high concentration in surface sediments. The absence of significant increase of DDT, HCH, chlordane and PBDE concentrations towards higher δ^{15}N values, as well as the lack of a significant correlation ($p < 0.1$) between log concentrations (lipid normalized) and δ^{15}N, may indicate a weak biomagnification of these chemicals in the food webs. Good agreement was observed between their concentrations and lipid contents of the organisms. Bioconcentration was suggested to be responsible for the accumulation of OCPs and PBDEs in the lower trophic organisms in the studied subtropical waters.

Keywords: Polybrominated diphenyl ethers (PBDEs); Organochlorine pesticides (OCPs); Fishes; Pearl River estuary; Daya Bay; South China

1. Introduction

Organochlorine pesticides (OCPs) are among the most widely applied chemicals in the world. They have been used for pest and insect control in more than half a century, owing to their negative impact on the ecosystem and human health (Colborn et al., 1993; Patlak, 1996). The agricultural uses of most OCPs, in particular, technical DDT and HCH, have been banned worldwide since the late 1970–1990s. However, these chemicals are hard to be degraded and hence are capable of remaining in the environment up to decades. In the meantime, some specific OCPs are still allowed to be used, for instance, γ-HCH as an effective component in lindane, chlordane for termite control, and DDT for malaria control (in some tropical and subtropical countries). There have been few studies in China concerning chlordane contamination in organisms and used as a termiticide in China as early as in 1945 (Nakata et al., 2002). In general, the environmental

* Corresponding author. Tel.: +86 20 8529 0178; fax: +86 20 8529 0706.
E-mail address: zhanggan@gig.ac.cn (G. Zhang).

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persistence and the use of some OCPs make it a long-term challenge for the international community to control and finally phase out in the environment.

Polybrominated diphenyl ethers (PBDEs) are a class of flame-retardants widely used in plastics, textile, electronics and other materials. PBDEs were put into use in 1970s and its global annual consumption in 1999 reached *ca*. 70,000 tons. PBDEs can impair attention, learning, memory and behavior in laboratory animals (Fowles et al., 1994). PBDE concentrations in biota are estimated to have been doubling every 5 years (de Wit, 2002) and were reported to have increased by 60-fold in human breast milk in Sweden between 1972 and 1997 (Meironyte and Bergman, 1999). Compared with the well known OCPs, PBDE contamination has become an emerging environmental thrust in the recent years which is attracting more and more attention from the public and environmental community.

Both OCPs and PBDEs are hydrophobic organic compounds (HOCs) capable of accumulating in the organisms. In aquatic environments, HOCs can enter into an organism, for instance, a fish, mainly *via* two pathways, *i.e*. bioconcentration directly through the water environment (LeBlanc, 1995), and/or biomagnification through foodweb preys (Thomann, 1989; Kiriluk et al., 1995). Lipid content (Bentzen et al., 1996), depuration rates (LeBlanc, 1995), size and exposure duration of the organism (Harding et al., 1997), as well as the structure of the food web (Evans et al., 1991) and the environmental concentrations of the chemicals are all potential factors influencing bioaccumulation of HOCs in an aquatic organism. Pelagic organisms were found to be more subjected to HOC bioaccumulation than biota relying upon benthic primary production (Kidd et al., 1998).

Stable nitrogen ratio (δ^{15}N) of biota has been widely employed to characterize an organism's trophic position and enabling a quantitative assessment of biomagnification of HOCs in aquatic environments, though it does not allow for specific identification of prey and relative proportion of ingestion (Kidd et al., 1995).

The Pearl River Delta, geographically including Hong Kong and Macau, is located in southern China. It has a population of more than 38 millions and a land area of approximately 40,000 km^2. DDT and HCH have been applied for agricultural usage in the Pearl River Delta until 1983. As a region with severe termite problem, chlordane has been widely used as a termiticide. DDT concentrations in human breast milk from Guangzhou and Hong Kong were reported as the highest in the world (Wong et al., 2002). While no significant historical decrease of DDT concentrations was observed in the sediments from the Pearl River estuary (Zhang et al., 2002), it was inferred that there are still current fresh inputs of DDT to the aquatic environment of the Pearl River Delta (Zhou et al., 2001; Luo et al., 2004). In addition, the PBDEs were widely detected in riverine and coastal sediments of the regions, characteristic of high concentrations of the congener BDE-209 (Zheng et al., 2004; Mai et al., 2005).

There have been limited reports on OCP and PBDE levels in the aquatic organisms of the Pearl River Delta. The OCP concentrations were reported in mussels from Hong Kong waters (Phillips, 1985; Fang et al., 2001), fishes from the Hong Kong markets (Chan et al., 1999), inland waters (Zhou et al., 1999) and from aquacultural fishponds in the Pearl River Delta (Zhou and Wong, 2004). As for the PBDE is concerned, their concentrations in green-lipped mussels from the Hong Kong waters were reported as the highest in the world (Liu et al., 2005).

The present study aims to investigate the levels and concentrations of OCPs and PBDEs in aquatic organisms in Pearl River estuary and Daya Bay, as well as to know their bioaccumulation in the subtropical waters using stable nitrogen isotope techniques.

2. Materials and methods

2.1. Sampling

The Pearl River is the second largest river (331.9×10^9 m^3 yr^{-1}) in China and the largest river system flowing into the South China Sea (Zhao, 1990). The Pearl River estuary (PRE), which has a characteristic of fresh-salt water and supports a large habitation of marine organisms (Fig. 1). Daya Bay, a separate sea bay to the east of the PRE, was selected as a reference site and listed as a member of "China Ecosystem Research Network" (CERN) since 1983.

Organisms were collected using fish trawls from the above mentioned waters (Fig. 1) during November 2003 (Daya Bay) and February 2004 (PRE). The samples were stored in polyethene bags and frozen at −20 °C prior to treatment.

The collected samples were identified in South China Institute of Oceanology, CAS. Their dietary habits ranged from planktonivorous, omnivorous to carnivorous. They are 34 species of fishes (*Mugil cephalus*, *Clupanodon thrissa*, *Clupanodon punctatus*, *Apogon quadrifasciatus*, *Apogon semilineatus*, *Sardinella aurita*, *Syngnathus acus*, *Callionymus richardsoni*, *Thryssa dussumieri*, *Sillago japonica*, *Ilisha elongata*, *Leiognathus bindus*, *Leiognathus ruconius*, *Glossogobius giuris*, *Trypauchen vagina*, *Odontamblyopus rubicundus*, *Inimicus cuvieri*, *Siganus fuscescens*, *Collichthys lucidus*, *Aseraggodes kobensis*, *Cynoglossus robustus*, *Cynoglossus lingua*, *Johnius belengerii*, *Nibea acuta*, *Platycephalus indicus*, *Dasyatis zugei*, *Polynemus sextarius*, *Therapon jarbua*, *Therapon theraps*, *Acanthopagrus latus*, *Saurida undosquamis*, *Plotosus anguillaris*, *Muraenosox cinereus*, *Lophiomus setigerus*); four shrimps (*Penaeus orientalis*, *Penaeus merguiensis*, *Metapenaeus ensis*, *Oratosquilla oratoria*); and six crabs (*Portunus pubescens*, *Portunus sanguinolentus*, *Portunus pelagicus*, *Portunus brockii*, *Portunus granulatus*, *Charybdis feriata*).

2.2. Chemical analysis

The whole samples were analyzed for organic pollutants. Prior to extraction, fish tissues were homogenized and freeze-dried. Subsamples were dried to constant weight to determine the water contents. Dry mussels were then ground into powder with a stainless steel blender. A 5 g of dry powder was Soxhlet extracted with 150 ml of dichloromethane (DCM) and acetone (2:1 V/V) for 48 h. Activated copper granules were added to remove elemental sulfur. 2,4,5,6-Tetrachloro-*m*-xylene (TC*m*X), decachlorobiphenyl (PCB209), $^{13}C_{12}$-PCB138 and $^{13}C_{12}$-PCB180 were added as surrogates prior to the extraction. The extract solution was concentrated to 10 ml with a rotary evaporator. An aliquot of 1 ml was used for gravimetric determination of the lipid content (Borgå et al., 2001). For clean-up, the left solution was first treated with concentrated sulfuric acid (5 ml × 3) to remove the bulk of lipids (Olsson et al., 2000) and further cleaned on a glass column (1 cm i.d.) packed with 5 g of silica gel impregnated with sulfuric acid (1:1 W/W). OCPs and PBDEs were eluted from the column with 30 ml of DCM:*n*-hexane (1:1 V/V). The solution was solvent exchanged to *n*-hexane and reduced to a final volume of 200 μl under a gentle nitrogen stream. A 20 ng of pentachloronitrobenzene (PCNB) was added to the sample vial as internal standard prior to GC–MS analysis.