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# Organochlorine Pesticides in Muscle of Wild Seabass and Chinese Prawn from the Bohai Sea and Yellow Sea, China

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**Abstract** Muscle samples from wild seabass and Chinese prawn collected from the Bohai Sea and the Yellow Sea, China were analyzed for 22 organochlorine pesticides. DDTs were the predominant contaminants in all samples. The concentration of DDTs in seabass was 247 μg kg$^{-1}$ wet wt (from 4.30 to 2,089 μg kg$^{-1}$ wet wt). Significantly, concentration of DDTs in seabass was much higher than that in prawn (6.51 μg kg$^{-1}$ wet wt). Very high concentrations of DDTs and high DDT/DDTs ratio were found in seabass samples from some locations, which imply there might be new inputs of DDT into the marine environment.

**Keywords** Organochlorines pesticides · Wild seabass · Bohai Sea · Yellow Sea

Organochlorine pesticides (OCPs) are toxic, mobile and the biodegrability is relatively low in the environment and organisms (Wania and Mackay 1996). As a result of agricultural and industrial activities, OCPs are found in several ecosystems worldwide. It has been suggested that oceans act as a final sink for OCPs, and these compounds can be biomagnified in marine food webs and subsequently induce various toxic effects in humans after consumption (Binelli and Provini 2003). Fish generally contain higher levels of OCPs than any other food category (Roots 2001), residents of coastal cities are more likely to be exposed to toxic contaminants via the consumption of seafood than inland populations.

Since the early 1980s, rapid industrial and agricultural development along the coastline of the Bohai and Yellow seas (China) has resulted in discharge of large amounts of OCPs to the offshore environment, and subsequent deterioration of the coastal environment (Ma et al. 2001; Klumpp et al. 2002). Wild fish and Chinese prawn are popular seafood with residents in coastal cities of the Bohai and Yellow seas. However, little information is available on OCPs contamination in wild seafood from this region. The present work surveyed the levels and distribution of OCPs in wild seabass and Chinese prawn from this special marginal area.

## Materials and Methods

Samples of seabass and Chinese prawn were collected along the coast at 11 sampling sites in the Bohai Sea and Yellow Sea area on April 2007. Details of the sampling locations were obtained from the fisherman or fishmonger. Sampling locations and details of the fish samples are shown in Table 1. Length and weight of biological samples were analyzed individually before frozen. All the samples were wrapped in aluminum foil, sealed in polyethylene bags and stored at −20°C until analysis.

The head, bones and internal organs of the seabass and prawn were removed. Muscle tissue (100 g) was then minced with a food processor. Minced muscle tissue (5 g) was placed in a homogenizer with 100 μL of 0.2% butylated hydroxytoluene (BHT), 50 mL of acetonitrile and 20 μL of $^{13}$C-labeled *p*,*p*′-DDT(5 μg mL$^{-1}$). The sample was homogenized for 5 min and then filtered into a 500 mL separating funnel. Water (350 mL), NaCl (17 g)

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**Table 1** Information for samples collected from the Bohai Sea and Yellow Sea in China from 13 to 17 April 2007

| NO | Location | Seabass (individual) | | | | Spawn (average) | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | N | Length (cm) | Weight (g) | Remarks | N | length (cm) | Weight (g) | Remarks |
| Bohai Sea | | | | | | | | | |
| B1 | Dalian | 3 | 26/27/29 | 212/221/307 | Netting | 5 | 22.0 | 63.9 | Purchased |
| B2 | Yingkou | 1 | 46 | 1,466 | Netting | 6 | 22.8 | 94.7 | Purchased |
| B3 | Xingcheng | 1 | 53 | 1,775 | Netting | 5 | 21.0 | 46.3 | Purchased |
| B4-1 | Jingtanggang | 1 | 37 | 539 | Netting | 6 | 20.1 | 43.4 | Purchased |
| B4-2 | Jingtanggang | 1 | 48 | 1,113 | Purchased | NA | NA | NA | NA |
| B5-1 | Tianjing | 1 | 27 | 251 | Angling | 4 | 22.5 | 64.2 | Purchased |
| B5-2 | Tianjing | 1 | 89 | 6,500 | Purchased | NA | NA | NA | NA |
| B6 | Huanghua | 1 | 88 | 6,310 | Purchased | 7 | 19.6 | 47.0 | Purchased |
| B7-1 | Dongying | 1 | 37 | 530 | Netting | 4 | 17.8 | 42.4 | Purchased |
| B7-2 | Dongying | 1 | 46 | 1,806 | Netting | NA | NA | NA | NA |
| Yellow Sea | | | | | | | | | |
| H1 | Yantai | 1 | 71 | 4,200 | Purchased | NA | NA | NA | NA |
| H2 | Qingdao | 1 | 40 | 724 | Netting | 6 | 19.7 | 45.4 | Purchased |
| H3 | Rizhao | 2 | 26/27 | 203/225 | Netting | 7 | 18.6 | 35.4 | Purchased |
| H4 | Lianyungang | 2 | 30/39 | 364/651 | Netting | NA | NA | NA | NA |

*NA* not available, *N* number of samples

and 40 mL of n-hexane/ethyl acetate (3:2, v/v) were added to the separating funnel and the solution shaken for 10 min. The lower layer was extracted twice with this procedure, and the two upper layers combined. Water was removed using $Na_2SO_4$ and the solution was concentrated to approximately 1 mL by rotary evaporator.

The concentrated extract was passed through a $NH_2$ solid phase extraction (SPE) cartridge (2 g, 6 mL, Supelco, USA). The $NH_2$ SPE was conditioned with 25 mL of n-hexane. After the sample was transferred onto the cartridge, it was eluted with 50 mL of n-hexane. The eluate was concentrated to about 1 mL using rotary evaporator.

The concentrated eluate was then passed through a silica solid phase extraction (SPE) cartridge (2 g, 6 mL, Supelco, USA) that had been conditioned with 10 mL of acetone/n-hexane (2:98, v/v). The sample was eluted with 12 mL of acetone/n-hexane (2/98, v/v), and the eluate was concentrated to about 1 mL using a centrifugal vacuum evaporator system (CVE3100, Eyala, Japan). A mixed solution of deuterated phenanthrene, deuterated pyrene, and deuterated chrysene (Accu Standard, Inc., USA) was added to the solution as an injection internal standard prior to transfer to a glass microvial for injection to gas chromatography-mass spectrometry (GC–MS).

The determination of OCPs was performed on a Shimadzu GCMS-QP2010 equipped with a fused silica capillary DB-5MS column (30 m × 0.25 mm i.d., film thickness: 0.25 μm) using electron ionization with selective ion monitoring mode. High purity (99.999%) helium was used as carrier gas at 0.98 mL $min^{-1}$. The injector, transfer line, and ion source temperature were 250, 260, and 230°C respectively. The oven temperature program was as follows: initial temperature 70°C held for 1 min, increased to 180°C at 20°C $min^{-1}$, then to 260°C at 4°C $min^{-1}$, to 300°C at 15°C $min^{-1}$, and held at 300°C for 6 min. Two microlitres of each sample was injected in spiltless mode.

All the data were subject to strict quality control procedures, including the analysis of procedural blanks, analytical reliability, recovery efficiency and accuracy. None of the target compounds were detected in the procedural blanks. Spiked samples were determined with a good precision Recoveries of added pesticides (100 ng OCPs) in muscle samples ranged from 66.8% to 149% ($\delta$-HCH was not detected in this method). Surrogate compounds will be used to ensure the quality of the monitoring data, $^{13}C$-labeled *p*,*p*′-DDT was added to all the samples before extraction, and the recoveries ranged from 71.5% to 130%. 10.0 ng of OCPs mixture was added in 5.0 g of Sea bass muscle and analyzed with every set of six samples. The standard deviation (SD) was calculate, 3SD were defined method detection limit. The method detection limit ranged from 0.040 to 0.182 μg $kg^{-1}$ for compounds of OCPs.

## Results and Discussion

OCPs were detected in all samples analyzed (Tables 2, 3). However, only some OCPs, including HCB, DDTs and

**Table 2** OCPs residues in sea bass muscle samples (μg $kg^{-1}$ wet wt)

| Sites | α-HCH | HCB | *o,p′*-DDE | *p,p′*-DDE | *o,p′*-DDD | *p,p′*-DDD | *o,p′*-DDT | $^{13}$C *p,p′*-DDT | *p,p′*-DDT |
|---|---|---|---|---|---|---|---|---|---|
| B1 | nd | 0.156 | nd | 8.08 | 0.909 | 8.64 | 1.01 | 128 | 6.66 |
| B2 | nd | 0.147 | nd | 1.22 | nd | 1.92 | nd | 110 | 1.16 |
| B3 | nd | 0.304 | nd | 3.00 | 0.746 | 5.59 | 0.724 | 114 | 5.00 |
| B4-1 | nd | 0.179 | nd | 8.12 | 0.819 | 8.48 | 0.612 | 111 | 6.56 |
| B4-2 | nd | 0.246 | nd | 5.99 | 0.835 | 5.32 | 0.946 | 92.8 | 8.05 |
| B5-1 | nd | 2.70 | nd | 3.38 | 0.720 | 6.66 | 1.32 | 100 | 5.95 |
| B5-2 | nd | 1.46 | 13.8 | 83.7 | 5.05 | 29.3 | 7.21 | 115 | 21.5 |
| B6 | nd | 0.326 | 0.851 | 7.96 | 0.66 | 5.55 | 1.05 | 114 | 4.82 |
| B7-1 | nd | 0.717 | 0.816 | 9.25 | 1.49 | 10.5 | 1.43 | 117 | 6.45 |
| B7-2 | nd | 0.806 | 0.806 | 21.3 | 4.55 | 26.0 | 6.73 | 105 | 30.8 |
| H1 | nd | 0.783 | 1.38 | 46.7 | 6.00 | 67.6 | 10.7 | 130 | 57.6 |
| H2 | nd | 0.336 | 1.22 | 229 | 12.9 | 220 | 22.3 | 116 | 255 |
| H3 | 3.43 | 0.192 | 4.62 | 189 | 62.3 | 526 | 131 | 116 | 1,176 |
| H4 | nd | 0.785 | nd | 6.18 | 1.19 | 10.4 | 1.87 | 71.5 | 13.6 |

Heptachlor, heptachlor epoxide, methoxychlor, aldrin, dieldrin, endrin, and mirex were below the quantification limit, and these compounds are not listed in the table

*nd* less than the detection limit

DDTs = DDT + DDE + DDD; DDT = *p,p′*-DDT + *o,p′*-DDT; DDE = *p,p′*-DDE + *o,p′*-DDE; DDD = *p,p′*-DDD + *o,p′*-DDD

**Table 3** OCPs residues in Chinese prawn samples (μg $kg^{-1}$ wet wt)

| Sites | HCB | *p,p*’-DDE | *o,p*’-DDD | *p,p*’-DDD | $^{13}$C *p,p*’-DDT | *p,p*’-DDT |
|---|---|---|---|---|---|---|
| B1 | nd | 1.55 | nd | nd | 93.7 | nd |
| B2 | nd | 1.61 | nd | nd | 108 | nd |
| B3 | 0.215 | 0.447 | 0.324 | 0.701 | 78.1 | 0.698 |
| B4 | nd | 0.760 | nd | nd | 112 | nd |
| B5 | nd | 1.61 | nd | 1.35 | 110 | 4.47 |
| B6 | nd | 1.19 | nd | 0.23 | 92.5 | nd |
| B7 | nd | 0.28 | nd | nd | 107 | nd |
| H2 | 0.127 | 8.21 | nd | 4.47 | 103 | 16.0 |
| H3 | nd | 10.6 | nd | 1.48 | 103 | 2.74 |

HCHs were detected. Other OCPs, including heptachlor, heptachlor epoxide, methoxychlor, aldrin, dieldrin, endrin, and mirex were below the method detection limit. The total OCPs concentrations for seabass ranged from 4.45 to 2,090 μg $kg^{-1}$ wet wt (average 248 μg $kg^{-1}$ wet wt), while those in Chinese prawn ranged from 0.28 to 28.8 μg $kg^{-1}$ wet wt (average 6.56 μg $kg^{-1}$ wet wt). DDT and its metabolites were the predominant contaminants in all samples, and made up 86.9%–100% of the total OCPs in each sample.

HCHs were only detected in seabass muscle samples from station H3, and α-HCH was the only HCHs detected in this sample. Concentrations of HCHs in samples were much lower than those of DDTs. This trend is consistent with the previous observations on the contamination of OCPs in sediments and fish in East China Sea (Ma et al. 2001; Nakata et al. 2005). There is no quantitative information to prove that the amount of technical HCH used was smaller than that of DDT. A most likely explanation for the current relatively lower concentrations of HCHs in samples was due to the differences in physicochemical and biochemical properties, wherein HCHs have higher vapor pressure and biodegradability, and lower lipophilicity and particle affinity compared to other OCPs, leaving fewer residues in environment. In addition, the absence of new input sources may contribute to low levels of HCHs residues in the study region.

The average concentration of HCB in seabass samples was <1.0 μg $kg^{-1}$ wet wt (range 0.147–2.70 μg $kg^{-1}$ wet wt) at all sites except stations 5–1 and 5–2, which were

2.70 and 1.46 μg kg$^{-1}$ wet wt, respectively. A similar concentration (0.07–2.0 μg kg$^{-1}$ wet wt) was reported in fish samples from the East China Sea (Jiang et al. 2005). HCB is not presently used directly in agriculture, but it is used for producing other pesticides in China (Zhang et al. 2009). In addition, it can be released into the environment by incineration during industry processes. However, the potential sources of HCB in China are still not clear. Compared to the other stations, relatively high HCB levels were observed at stations B5-1 and B5-2, which are close to a sewage outfall from the Hai River. These results suggest that there are various sources of HCB to coastal waters, such as untreated sewage discharge from urban areas and dumping of toxic industrial wastes from others locations.

The levels of DDTs in seabass were much higher than those in prawn. The average concentration of DDTs in seabass was 247 μg kg$^{-1}$ wet wt (range 4.30–2,089 μg kg$^{-1}$ wet wt). Compared with an average of 6.51 μg kg$^{-1}$ wet wt (range 0.280–28.7 μg kg$^{-1}$ wet wt) in prawn. Due to different ecological characteristics for different aquatic species such as feeding habits, bioaccumulation of DDTs in aquatic was highly species-specific (Yang et al. 2006). Prawn and seabass have a pradator/prey feeding relationship, the concentrations of DDTs in seabass generally are higher over one or two orders of magnitude than in spawn. The highest concentration of DDTs was found in seabass at station H3 in the Yellow Sea (2,089 μg kg$^{-1}$ wet wt). In general, the DDTs levels in seabass from the Yellow Sea (763 μg kg$^{-1}$ wet wt) were higher than in seabass from the Bohai Sea (41.0 μg kg$^{-1}$ wet wt). A similar pattern was observed in the Chinese prawn samples, with average DDTs concentrations of 2.17 μg kg$^{-1}$ wet wt in the Bohai Sea and 21.8 μg kg$^{-1}$ wet wt in the Yellow Sea. An earlier study also observed these patterns in sediments (Ma et al. 2001), and proposed that DDTs contamination in Yellow Sea was worse than in the Bohai Sea due to industrial effluent. Due to the small number of samples analyzed in our study, additional research is required to evaluate the reasons for the differences in DDTs concentrations between the Yellow and Bohai seas.

The estimated environmental half-life for DDT from aquatic studies is more than 10 years, and DDT is transformed to DDE and DDD in this order (Sericano et al. 1990). Consistently high proportions of DDT in the form of the parent compound suggest recent release of this chemical to the environment (Doong et al. 2002). Therefore, DDT/DDTs or DDE/DDTs ratios can be used as an indicator of the chronology of DDT-based pesticides entering the ecosystem. Because the concentrations and detection rates of DDTs in Chinese prawn were low, only the sources of DDTs in seabass were evaluated. The ratios of DDT/DDTs, DDD/DDTs and DDE/DDTs differed greatly between the seabass samples from different locations (Fig. 1). On average DDT made up 36.0% of total DDTs with a range of 17.9%–62.6%. The highest ratio of DDT/DDTs (62.6%) and the highest concentration of DDTs (2,089 μg kg$^{-1}$ wet wt) were found at station H3 on the coast of Rizhao, Yellow Sea. The compositions and residue

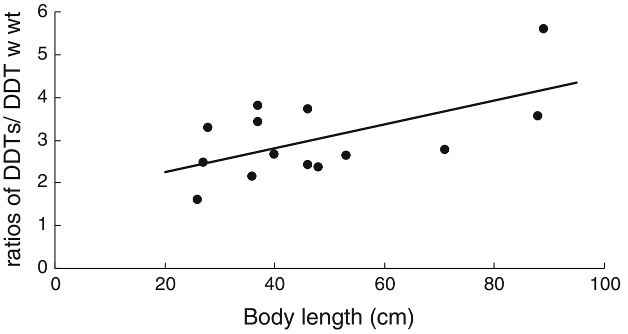

**Fig. 2** Relationship between DDT/DDTs ratio and body length in seabass collected from the Bohai Sea and Yellow Sea

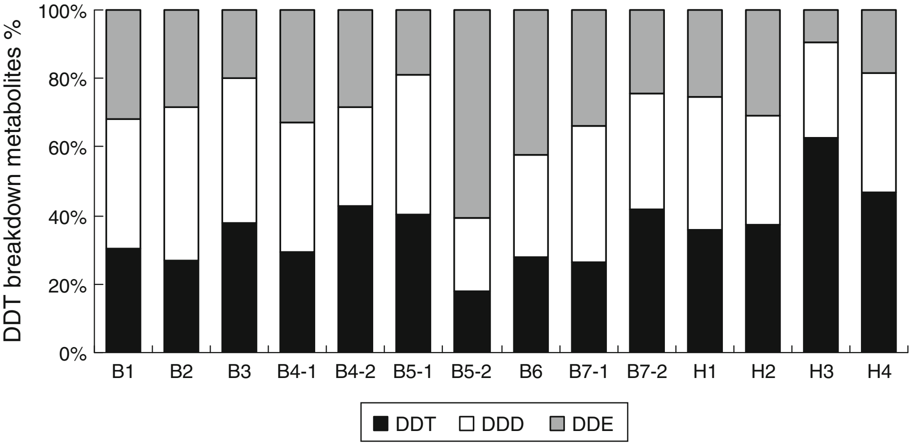

**Fig. 1** Ratios of DDT and derivatives in muscle of seabass from the Bohai Sea (B samples) and Yellow Sea (H samples)

concentrations of DDTs in seabass in this study imply DDT use has not been eradicated in China, and that there might be new DDT inputs in the study area. The sources of DDTs in this area are riverine exports of agricultural chemicals and atmospheric deposition. Furthermore, although DDTs have been banned for many years in China, they are still be used as antifouling chemicals on many boats (Guo et al. 2009). The ratio of DDT/DDTs in this study was slightly higher than that reported in a previous study for fish collected from the East China Sea (average 29.0%, range 9.27%–42.2%) (Jiang et al. 2005), but similar to that reported for fish collected from the Xiamen Sea, China (average 35.0%, range 21.4%–44.7%) (Klumpp et al. 2002). All studies make the same conclusion that there were new inputs of DDTs in the coastal zone of China.

**Table 4** Range of DDTs concentrations in fish from other parts of China (μg $kg^{-1}$ wet wt)

| Sampling time | Area | Fish | Tissue | Length (cm) | Weight (g) | Remarks | Concentration | References |
|---|---|---|---|---|---|---|---|---|
| 1997 | Hongkong, South China Sea | Sea bream | Muscle | NA | 614 ± 343 g | Fish market | 76 | Chan et al. (1999) |
| 1999 | Xiamen, Eastern Sea | Various fishes | Muscle | 29–37 | 410–630 | Aquaculture cages | <0.5–220 | Klumpp et al. (2002) |
| 2001, 2002 | Pearl River delta, South China Sea | Various fishes | Muscle | 6–66 | NA | NA | 1.5– 62 | Kong et al. (2005) |
| 2003 | Zhoushan East Sea | Various fishes | Muscle | 19–62 | 16–380 | Fish market | 0.45–8.6 | Jiang et al. (2005) |
| 2007 | Bohai Sea and Yellow Sea | Seabass | Muscle | 26–89 | 203–6,500 | Fish market, net | 4.3–2,089 | This study |

*NA* not available

No clear correlation between DDTs concentrations and length in seabass was found. In contrast, significant linear correlation was observed between the ratios of DDTs/DDT and the body length of seabass (Fig. 2). It is well known that DDT can be transformed to DDE and DDD in fish (Sericano et al. 1990). With the increase of length/age of seabass, more new intake DDT is metabolized to DDE or DDD, hence the ratios of DDT/DDTs was decreased. Furthermore, the feeding habit is an important factor determining the bioaccumulation of DDTs. The food of large seabass (carnivorous: fish) is generally at the upper layers of food chain, which contained higher concentrations of DDEs than that of small seabass (filter feeder: zooplankton). This factor may also attribute to the decreased DDT/DDTs in large seabass. This result also indicates that there were suspected new inputs of DDT in this area.

DDTs were the predominant contaminants in the samples analyzed in this study. These results provide a general overview of the residual levels of DDTs in fish from a coastal region of China (Table 4). Among the samples studies, wild sea bass showed comparatively high levels of DDTs. The maximum admissible concentration for marine biological quality established by the Chinese government (standard GB-18421-2001) is 10 μg $kg^{-1}$ wet wt, and 7.14% of our samples were over this limit.

Therefore, some seabass might not be suitable for continual consumption in large amounts.

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