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Organochlorine pesticide content and distribution in coastal seafoods in Zhoushan, Zhejiang Province

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ABSTRACT

Thirteen types of seafoods were collected from four counties (districts) of Zhoushan, Zhejiang Province, China and analyzed for organochlorine pesticides (OCPs). The average concentrations of OCPs in seafoods ranged from 258.3 ng g^{-1} (lw) to 3459.6 ng g^{-1} (lw). Hexachlorocyclohexanes (HCHs) and dichlorodiphenyltrichloroethanes (DDTs) were the most abundant compounds in these environments and in total accounted for 8.2–62.2% and 32.1–89.0% of the total OCPs in seafoods, respectively. The total OCP contents were higher in seafoods from Shengsi and Putuo and lower in those from Dinghai and Daishan. The ratios of (DDE + DDD)/DDTs reflected a mixed input of accumulated and fresh DDTs in Shengsi, Putuo. The ratios of o,p′-DDT/p,p′-DDT in seafoods of Shengsi ranged 0.10–0.60 (mean 0.33), indicating that DDTs in seafoods of Shengsi may partly contain dicofol products and other pollutants accumulated in Yangtze Estuary. DDTs are a greater concern for ecotoxicological risk in the study area.

Organochlorine pesticides (OCPs), especially dichlorodiphenyltrichloroethanes (DDTs) and hexachlorocyclohexanes (HCHs), are persistent organic pollutants with stable chemical properties and long residue times in the environment. The pesticides enter the water environment through surface runoff and atmospheric deposition (Park et al., 2001). From the environment, these pesticides accumulate within aquatic animals and thereby propagate through the food chain (Thomann, 1989; Kirrluk et al., 1995). OCPs can enter the human body through respiration, skin contact, and food intake, with food intake being the main route for OCP entry (Dougherty et al., 2000). Long-term exposure to OCPs elicits adverse health effects such as developmental defects, cancer, and endocrine disruption in both wildlife and humans (Kelce et al., 1995; Birnbaum and Staskal, 2004; Lee et al., 2006; Ha et al., 2007), and therefore, OCPs represent a potential hazard to the environment and human health. Although OCPs have not been produced since their use was restricted at the Stockholm Convention in 2001, high levels of these contaminants remain in coastal environments (Sudaryanto et al., 2008; Moon et al., 2008, 2009; Won et al., 2009).

Many seafoods are important food resources and thus constitute an important link from lower marine organisms to humans. Seafoods can accumulate OCPs, and their consumption can amplify the effects of OCPs. In the coastal areas of China, 75% of the DDTs that enter humans comes from edible seafoods (Nakata et al., 2002). The Zhoushan Islands (Fig. 1) of the Zhejiang Province are situated at the mouth of the Yangtze River, the largest river in China. In the Yangtze River estuary, which is the largest agricultural

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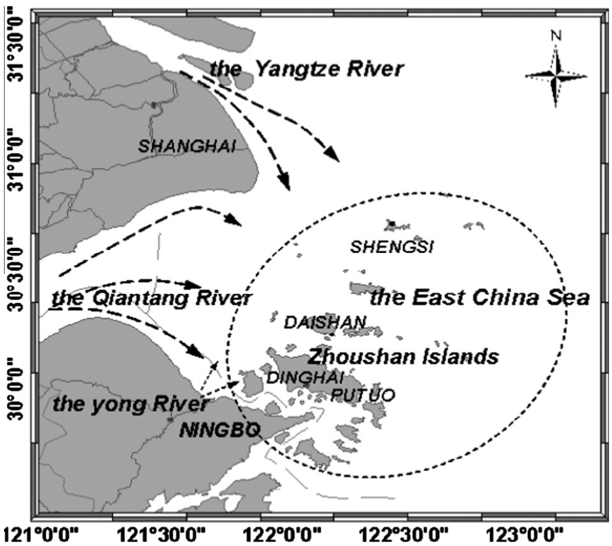

Fig. 1. Map of Zhejiang Zhoushan Islands: located in the intersection of Yangtze River, Qiantang River and Yong River. Zhoushan is the largest fishing ground in China.

production base in China (Zhang et al., 2007), OCPs were applied in large quantities for a long time. The Zhoushan fishing ground, the largest fishing ground in China, receives the most OCPs through surface runoff. In addition, seafoods compose a high proportion of the diet of the local residents. Therefore, with its unique geographical position and the dietary structure of the local residents, this region presents a representative area for the study of OCPs in seafoods. However, while the contamination status of OCPs in other tropical regions have been intensively studied (Cai et al., 1998; Ma et al., 2001; Liu et al., 2008; Zhang et al., 2009, Daya Bay Qiu et al., 2007), information about OCP contamination in seafoods of the Zhoushan regions has not been reported.

The objective of this study was to understand the actual pollution situation of high residue OCPs in the Yangtze River estuary areas in order to provide basic data and a scientific foundation for the management of a highly polluted area and for the guarantee for human health.

Thirteen types of seafoods were collected from four counties (districts) of Zhoushan, Zhejiang Province, China in September of 2011. The four counties were Shengsi, Daishan, Dinghai, and Putuo, and four samples were collected for each seafood in each county ($4 \times 13 \times 4 = 208$ samples). The types of seafoods collected were representative of populations in the coastal waters of Zhoushan, and samples were collected from the seas offshore from each county. The types collected included 9 species of fish, 3 species of crustacean, and 1 species of mollusk. The fish species were *M. cinereus*, *T. japonicus*, *P. argentata*, *P. polyactis*, *P. sinensis*, *E. japonicas*, *S. taty*, *H. nehereus*, and *O. rubicundus*. The crustacean species included *S. crassicornis*, *L. gracilis*, and *O. oratoria*, and the mollusk species was *L. chinensis*. The collected samples were rinsed with deionized water and placed in clean polyethylene plastic bags for freezing. Then they were sent to the laboratory for analysis.

For the Soxhlet extraction-concentrated sulfuric acid method, samples of 5.00 g were weighed precisely, and the tracing standard (TCMX) was added. The Soxhlet extraction was performed for 24 h with the anhydrous Na_2SO_4 five times the mass of the sample, followed by addition of an appropriate amount of copper powder and petroleum ether. The extract was transferred to a separatory funnel, and 10 mL concentrated H_2SO_4 was added. The mixture was allowed to stand, and then the H_2SO_4 layer was removed. The operation was repeated once. The mixture was concentrated to 1–2 mL using a rotary evaporator. For extract purification, the chromatographic column (20 cm, 10 mm) was purified from bottom to top by solid-phase extraction. Then it was eluted with 100 mL N-hexane and dichloromethane (7:3, V/V). The eluent was collected and concentrated to a constant volume of 0.5 mL by dilution in N-hexane. PCB103 (2,2′,4,5′,6-pentachlorobiphenyl) was added as the internal standard for GC–MS analysis.

OCPs were analyzed on an Agilent-5975 GC-MSD system with a HP-5MS capillary column (30 m, 0.25 mm, 0.25 μm), operating under a single ion monitoring (SIM) mode with a detector voltage of 500 V, a scan range of m/z 30–500 and a dwell time of 50 ms for each ion. Helium was used as carrier gas at 1.0 mL/min under constant-flow mode. The oven temperature began at 80 °C and was increased to 200 °C (2-min hold time) at a rate of 15 °C min^{-1}. It was then increased to 250 °C (1-min hold time) at a rate of 10 °C min^{-1} before being raised to 290 °C (5-min hold time) at 20 °C min^{-1}. Then splitless injection was performed with an injection volume of 1 μL.

The recovery rates (%) of OCPs were calculated according to the selected sample treatment method and the determination method described above. The determination was repeated six times for each sample. The relative standard deviations (RSDs) were calculated (%). The result showed that the standard recovery rates of

Table 1
Average concentrations of OCPs in seafoods from the coastal waters of four counties in Zhoushan, Zhejiang Province (ng g^{-1} lw).

Sample/Items	*M.c*	*T.j*	*A.a*	*P.p*	*P. s*	*S.c*	*S.t*	*E.j*	*L.g*	*O.o*	*H.n*	*L.c*	*O.r*
α-HCH	17.3	8.3	4.1	4.8	10.2	63.3	2.8	27.1	11.6	ND	10.5	ND	79.8
β-HCH	21.9	36.6	90.5	91.0	48.8	312.2	17.2	131.3	125.0	154.5	164.0	60.2	430.9
γ-HCH	1.9	3.8	ND	ND	6.1	109.2	9.9	16.7	14.6	22.7	ND	ND	33.0
δ-HCH	33.1	26.7	24.1	23.7	48.3	215.3	14.8	102.1	73.8	36.4	49.1	9.7	293.6
Hexachlorobenzene	13.1	6.8	11.2	13.6	16.6	25.5	5.7	36.5	51.8	39.4	21.9	ND	168.1
Quintozene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Heptachlor	13.3	18.8	4.9	17.4	34.6	24.5	6.7	66.7	34.1	43.9	36.8	32.3	242.6
Heptachlor epoxide	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Trans-chlordane	3.2	1.2	1.7	2.7	2.0	6.1	1.5	12.5	2.4	4.5	3.5	ND	47.9
Cis-chlordane	1.7	1.0	0.9	1.5	1.7	9.2	1.1	ND	ND	ND	ND	4.3	37.2
o,p′-DDE	42.0	17.5	26.3	9.8	27.3	14.5	18.6	31.5	8.4	24.6	52.6	4.3	78.7
p,p′-DDE	226.4	141.3	383.6	131.3	256.8	112.5	149.7	298.4	49.7	324.2	367.1	27.4	539.4
o,p′-DDD	40.5	25.8	9.3	7.3	31.6	55.1	22.6	56.8	8.8	69.7	46.1	10.8	270.2
p,p′-DDD	100.5	84.4	129.2	68.8	138.3	4.1	69.3	204.4	25.9	273.1	216.2	31.5	407.4
o,p′-DDT	62.9	74.7	65.5	86.9	87.4	20.2	49.3	29.7	7.3	42.0	95.8	7.8	200.0
p,p′-DDT	185.8	200.3	254.9	226.5	286.3	154.6	174.3	268.8	61.0	297.0	397.8	74.5	630.9
∑OCPs	763.6	647.4	1006.4	685.3	996.0	1126.3	543.5	1282.3	474.5	1332.2	1461.6	258.3	3459.6
Average lipid (%)	6.47	5.76	4.65	4.13	3.44	0.98	11.35	0.96	1.64	0.66	1.14	0.93	0.94

M.c: *M. cinereus*; *T.j*: *T. japonicus*; *A.a*: *A. argentatus*; *P.p*: *P. polyactis*; *P. s*: *P. sinensis*; *S.c*: *S. crassicornis*; *S.t*: *S. taty*; *E.j*: *E. japonicus*; *L.g*: *L. gracilis*; *O.o*: *O. oratoria*; *H.n*: *H. nehereus*; *L.c*: *L. chinensis*; *O.r*: *O. rubicundus*.