

## Enantiomeric Signatures of Chiral Organochlorine Pesticides in Consumer Fish from South China

XIANG-ZHOU MENG,<sup>†,‡</sup> YING GUO,<sup>†,§</sup> BI-XIAN MAI,<sup>†</sup> AND EDDY Y. ZENG<sup>\*,†</sup>

<sup>†</sup>State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China, <sup>‡</sup>State Key Laboratory of Pollution Control and Resources Reuse, School of Environmental Science and Engineering, Tongji University, Shanghai 200092, China, and <sup>§</sup>Graduate School, Chinese Academy of Sciences, Beijing 100049, China

Despite the importance of chiral organochlorine pesticide enantiomers in terms of environmental effects, no relevant data have been acquired in consumer fish. The present study determined the residual levels and enantiomer fractions (EFs) of  $\alpha$ -HCH, *o,p'*-DDT, and *o,p'*-DDD in 11 consumer fish species from South China, including 6 freshwater farmed fish, 3 seawater farmed fish, and 2 wild marine fish. The mean concentrations of  $\alpha$ -HCH, *o,p'*-DDT, and *o,p'*-DDD were 0.27, 4.4, and 3.5 ng/g wet, respectively, in all fish samples measured ( $n = 125$ ). The EFs of  $\alpha$ -HCH varied widely, from below the racemic EF of 0.5 to above it. For *o,p'*-DDT, the (+)-enantiomer dominated in all fish species. On the other hand, all EFs of *o,p'*-DDD, a metabolite of *o,p'*-DDT, were below 0.5, suggesting the (–)-enantiomer was preferentially enriched in fish. In addition, all three target analytes showed species dependence of EFs, consistent with results from other previous studies. Moreover, no significant correlations were found between the EFs and concentrations of  $\alpha$ -HCH, *o,p'*-DDT, and *o,p'*-DDD in red drum, snubnose pompano, and crimson snapper, with the exception of *o,p'*-DDD in snubnose pompano, in which weak correlations were detected. Nevertheless, more studies are needed to explore the residual levels and toxicity of chiral contaminants in consumer fish or other foodstuff to further develop the human risk assessment framework based on chiral signatures.

**KEYWORDS:** Enantiomer; chirality; organochlorine pesticides; consumer fish; South China

### INTRODUCTION

Approximately 25% of the pesticides were chiral in nature in 1996, which are primarily used in the form of racemates (1). For example, hexachlorocyclohexane (HCH) and dichlorodiphenyltrichloroethane (DDT) are two main organochlorine pesticides (OCPs), which have been widely used in agriculture and forestry and as a wood preservative in China and throughout the world (2–5). The main components of these two OCPs,  $\alpha$ -HCH and 1,1,1-trichloro-2-(*o*-chlorophenyl)-2-(*p*-chlorophenyl)ethane (*o,p'*-DDT), are chiral and thus occur in two enantiomeric forms (2, 3). One of the metabolites of *o,p'*-DDT, 1,1-dichloro-2-(*o*-chlorophenyl)-2-(*p*-chlorophenyl)ethane (*o,p'*-DDD), is also chiral (3). Upon release into the environment, one enantiomer may be preferentially depleted or enriched compared with the other by stereospecific enzymatic processes in organisms (6–9). As a result, nonracemic signatures of chiral chemicals have been found in various environmental compartments (9). On the contrary, abiotic processes including physical (e.g., air–water exchange, sorption) and chemical processes (e.g., abiotic transformation) do not alter enantiomeric composition (10).

Generally, enantiomers may exhibit different biological and toxicological activities (11, 12); for example, (–)-*o,p'*-DDT is a more active estrogen-mimic in rats and humans than (+)-*o,p'*-DDT (11). Yet the concentrations of organic contaminants in the racemic form have often been used to assess human exposure via diet (13–16), which may either overestimate or underestimate the potential health risk. Thus, it is desirable to consider the level and toxicity of each enantiomer to achieve the best possible results from the assessment of human exposure to chiral contaminants (17, 18). Moreover, the European Union has developed a framework (Directive 91/414/EEC) to evaluate the pesticide active substances constituted by enantiomeric and other stereoisomeric mixtures (19). Several studies have investigated the enantiomeric compositions of selected chiral polychlorinated biphenyls in cow's, goat's, and ewe's milk and dairy products (20, 21). On the other hand, no enantiomeric signatures of chiral contaminants have been acquired for consumer fish, the main route of human exposure to OCPs. With these considerations, the present study was set out to determine the enantiomer fractions (EFs) of several chiral pesticides, that is,  $\alpha$ -HCH, *o,p'*-DDT and *o,p'*-DDD, in consumer fish collected from South China, which was then used to examine the species dependency of EFs and the relationship between the EFs and concentrations of the target analytes.

\*Corresponding author (telephone 86-20-85291421; fax 86-20-85290706; e-mail eddyzeng@gig.ac.cn).

**Table 1.** Mean Enantiomeric Fractions with Standard Deviation (SD) and Range of Chiral Organochlorine Pesticides ( $\alpha$ -HCH,  $o,p'$ -DDT, and  $o,p'$ -DDD) in Consumer Fish from South China<sup>a</sup>

species	$\alpha$ -HCH				$o,p'$ -DDT				$o,p'$ -DDD			
	<i>n</i>	mean	SD	range	<i>n</i>	mean	SD	range	<i>n</i>	mean	SD	range
racemic standard	17	0.495	0.003	0.490–0.500	13	0.501	0.004	0.490–0.517	17	0.504	0.009	0.486–0.523
tilapia	3	0.651	0.283	0.487–0.978	nd				6	0.229	0.137	0.070–0.389
grass carp	1	0.688			1	0.529			1	0.194		
bighead carp	3	0.447	0.033	0.423–0.485	4	0.566	0.069	0.477–0.640	5	0.331	0.059	0.253–0.387
largemouth bass	6	0.515	0.172	0.264–0.775	6	0.605	0.088	0.492–0.762	6	0.266	0.035	0.217–0.310
mandarin fish	4	0.523	0.070	0.435–0.582	4	0.510	0.109	0.367–0.620	4	0.169	0.080	0.052–0.230
northern snakehead	3	0.446	0.183	0.314–0.655	5	0.624	0.057	0.551–0.705	5	0.337	0.037	0.274–0.365
red drum	21	0.335	0.105	0.135–0.590	28	0.562	0.041	0.502–0.675	28	0.057	0.049	0.009–0.178
snubnose pompano	17	0.461	0.211	0.124–0.845	26	0.559	0.055	0.486–0.672	26	0.148	0.030	0.101–0.240
crimson snapper	22	0.353	0.159	0.146–0.757	29	0.535	0.058	0.448–0.663	29	0.035	0.060	0.005–0.308
hairtail	8	0.519	0.134	0.379–0.726	12	0.569	0.043	0.502–0.658	12	0.210	0.061	0.136–0.324
common mullet	2	0.645	0.167	0.526–0.763	2	0.600	0.193	0.459–0.733	3	0.120	0.110	0.048–0.247

<sup>a</sup> nd, not detected.

## MATERIALS AND METHODS

**Sample Collection.** Detailed sample information has been described in a previous study (13). In the present study, a subset of the fish samples with abundant concentrations of  $\alpha$ -HCH,  $o,p'$ -DDT, and  $o,p'$ -DDD were selected for chiral analysis. The total sample number is 125, including tilapia (*Tilapia*;  $n = 6$ ), grass carp (*Ctenopharyngodon idellus*;  $n = 1$ ), bighead carp (*Aristichthys nobilis*;  $n = 5$ ), largemouth bass (*Micropterus salmoides*;  $n = 6$ ), mandarin fish (*Simiperca chuatsi*;  $n = 4$ ), northern snakehead (*Ophicephalus argus*;  $n = 5$ ), red drum (*Sciaenops ocellatus*;  $n = 28$ ), snubnose pompano (*Trachinotus blochii*;  $n = 26$ ), crimson snapper (*Lutjanus erythropterus*;  $n = 29$ ), hairtail (*Trichiurus lepturus*;  $n = 12$ ), and common mullet (*Mugil cephalus*;  $n = 3$ ).

**Sample Preparation and Extraction.** Details of sample preparation and extraction have been previously published (13). Briefly, fish samples were extracted with a mixture of acetone and hexane (1:1, v/v). Each extract was subsequently cleaned by a gel permeation chromatography column to remove lipid content and further purified with a 10 mm i.d. silica/alumina column. The internal standard (PCB 82) was added to the final extract for instrumental analysis.

**Instrumental Analysis.** Achiral analyses were performed using a Hewlett-Packard (HP) 5890 gas chromatograph (GC) coupled to a 5972 mass spectrometer (MS), in the selective ion monitoring (SIM) mode. With a signal/noise ratio of better than 3, the limits of detection (LOD) for  $\alpha$ -HCH,  $o,p'$ -DDT, and  $o,p'$ -DDD ranged from 10 to 20 pg/g on a wet weight basis. Detailed procedures are provided in a previous study by Meng et al. (13). After achiral analyses, the same extracts were analyzed for enantiomers of  $\alpha$ -HCH,  $o,p'$ -DDT, and  $o,p'$ -DDD using a Varian 3800 GC interfaced with a Saturn 2000 MS and a 30 m  $\times$  0.25 mm i.d.  $\times$  0.25  $\mu$ m BGB-172 column (BGB analytik AG, Switzerland). Splitless injection of 1  $\mu$ L sample was conducted at an injector temperature of 220 °C. The GC oven was programmed from 120 °C (1 min hold) to 220 at 2 °C/min (5 min hold). Ultrahigh-purity helium was used as the carrier gas at a flow rate of 1.3 mL/min. Target/qualifier ions 181/183 and 235/237 were monitored for  $\alpha$ -HCH and  $o,p'$ -DDT/ $o,p'$ -DDD, respectively. Enantiomer data are expressed as EFs (22), that is, EF = peak areas of the (+)/(+ + (-)) enantiomers. EFs were calculated from the measured enantiomer ratio (ER) using the following equation: EF = ER/(1 + ER). Eluting sequences of enantiomeric  $\alpha$ -HCH,  $o,p'$ -DDT, or  $o,p'$ -DDD were taken from the literature (23). As for the eluting order of  $o,p'$ -DDT and  $o,p'$ -DDD enantiomers, we made the decision on the basis of the results from ref 3. In that study, the authors examined the eluting order of the two enantiomers of  $o,p'$ -DDD and  $o,p'$ -DDT, respectively, using a 20 or 28 m OV1701/BS- $\beta$ -CD fused silica column (0.25 mm i.d.) (BS- $\beta$ -CD = *tert*-butyldimethylsilyl- $\beta$ -cyclodextrin; 30% w/w), the same chiral stationary phase as that used in BGB-172 column. The result showed that the *R*-(-)-enantiomer eluted earlier than the *S*-(+)-enantiomer for  $o,p'$ -DDT. For  $o,p'$ -DDD, the elution order was reversed, with the (+)-enantiomer coming out earlier than the (-)-enantiomer. Recently, Wang et al. (24) also reported the

eluting order of the enantiomers of  $o,p'$ -DDT on BGB-172, which is the same as what we adopted.

**Quality Assurance/Quality Control.** For achiral measurements of  $\alpha$ -HCH,  $o,p'$ -DDT, and  $o,p'$ -DDD, quality assurance/quality control measures were described in the previous study by Meng et al. (13). For chiral analyses, racemic standards were injected repeatedly to determine the reproducibility of EF measurements (Table 1). Average EF values of the standards were  $0.495 \pm 0.003$  (standard deviation;  $n = 17$ ) for  $\alpha$ -HCH,  $0.501 \pm 0.004$  ( $n = 13$ ) for  $o,p'$ -DDT, and  $0.504 \pm 0.009$  ( $n = 17$ ) for  $o,p'$ -DDD. These EFs were not significantly different from 0.500 (all  $p > 0.05$ ). In the present study, decisions as to whether a particular sample contained racemic or nonracemic residues of the target compounds were made by determining if the EF value fell within or outside the  $\pm 95\%$  confidence interval for the standards (the range was 0.482–0.518).

**Data Analysis.** Statistical analyses were performed using SPSS version 13.0 (SPSS, Chicago, IL) with statistical significance for all test set at  $p = 0.05$ . The normality of the distribution was tested using nonparametric test (Kolmogorov–Smirnov Z). To examine the difference between means, a one-way analysis of variance (ANOVA) was used. Tukey's multiple-comparison tests were used when a difference by ANOVA was observed.

## RESULTS AND DISCUSSION

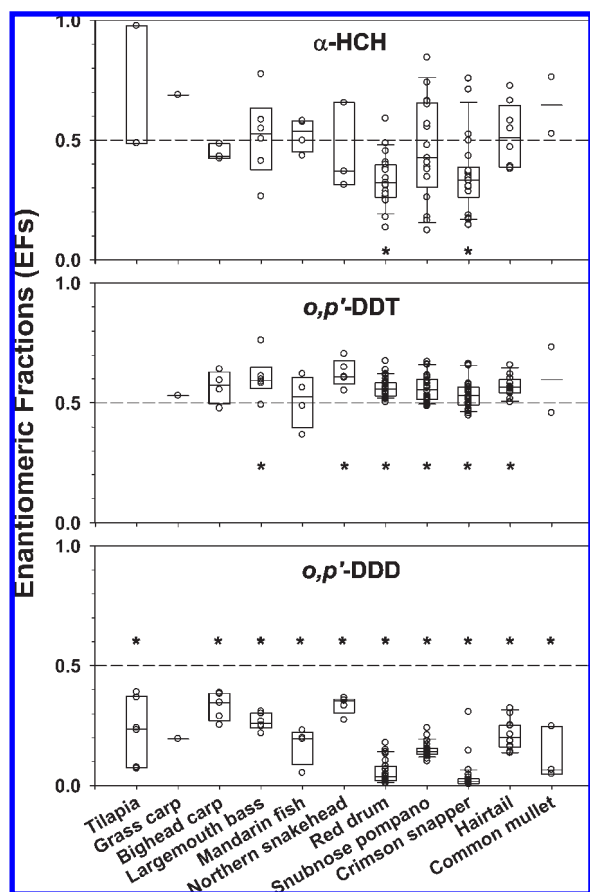
**Residual Levels of the Total Target Analytes.** The concentrations of total  $\alpha$ -HCH,  $o,p'$ -DDT, and  $o,p'$ -DDD in 11 fish species from South China are summarized in Table 2. In all samples analyzed ( $n = 125$ ), the detection frequency of  $\alpha$ -HCH was 72% with a mean concentration of 0.27 ng/g of wet weight (ww). The highest concentration of  $\alpha$ -HCH was 5.8 ng/g of ww, which occurred in a largemouth bass sample. For  $o,p'$ -DDT, the detection frequency was 94% with a mean value of 4.4 ng/g of ww (ranging from 0.03 to 32.3 ng/g of ww). As one of the metabolites of  $o,p'$ -DDT,  $o,p'$ -DDD was detected in all selected fish samples. The levels of  $o,p'$ -DDD ranged from 0.02 to 34.6 ng/g of ww with a mean value of 3.5 ng/g of ww, similar to the levels of  $o,p'$ -DDT in the present study.

**Profiles of Enantiomer Fractions.** Detailed EF values of  $\alpha$ -HCH,  $o,p'$ -DDT, and  $o,p'$ -DDD are given in Table 1 and graphically displayed in Figure 1; these results are discussed in detail below.

**$\alpha$ -HCH.** The enantiomeric composition of  $\alpha$ -HCH varied widely (Figure 1). In the samples containing detectable  $\alpha$ -HCH ( $n = 90$ ), the (+)-enantiomer was enriched in 26 samples (EF > 0.5). In contrast, the (-)-enantiomer enrichment occurred in 62 samples (EF < 0.5). If enantiomers with EF values from 0.482 to 0.518 are assumed to be racemic or

**Table 2.** Mean Concentrations (Nanograms per Gram of Wet Weight) with Standard Deviation (SD) and Range of Chiral Organochlorine Pesticides ( $\alpha$ -HCH,  $o,p'$ -DDT, and  $o,p'$ -DDD) in Consumer Fish from South China<sup>a</sup>

species	Latin name	$\alpha$ -HCH				$o,p'$ -DDT				$o,p'$ -DDD			
		<i>n</i>	mean	SD	range	<i>n</i>	mean	SD	range	<i>n</i>	mean	SD	range
tilapia	<i>Tilapia</i>	3	1.3	1.1	0.10–2.3	nd				6	0.14	0.14	0.03–0.37
grass carp	<i>Ctenopharyngodon idellus</i>	1	0.08			1	1.2			1	2.2		
bighead carp	<i>Aristichthys nobilis</i>	3	0.17	0.10	0.11–0.29	4	0.33	0.10	0.23–0.46	5	0.48	0.24	0.25–0.87
largemouth bass	<i>Micropterus salmoides</i>	6	1.1	2.3	0.13–5.8	6	0.59	0.71	0.15–2.0	6	0.37	0.33	0.12–1.0
mandarin fish	<i>Siniperca chuatsi</i>	4	0.35	0.10	0.25–0.48	4	0.42	0.66	0.08–1.4	4	1.5	1.0	0.37–2.8
northern snakehead	<i>Ophicephalus argus</i>	3	0.25	0.04	0.22–0.29	5	0.07	0.03	0.03–0.11	5	0.64	0.37	0.19–1.2
red drum	<i>Sciaenops ocellatus</i>	21	0.12	0.05	0.07–0.24	28	1.9	2.3	0.53–12.2	28	0.16	0.14	0.04–0.78
snubnose pompano	<i>Trachinotus blochii</i>	17	0.24	0.09	0.09–0.44	26	13.4	9.3	0.92–32.3	26	15.0	10.0	0.65–34.6
crimson snapper	<i>Lutjanus erythropterus</i>	22	0.13	0.04	0.06–0.19	29	1.7	1.8	0.08–6.6	29	0.11	0.10	0.02–0.40
hairtail	<i>Trichiurus lepturus</i>	8	0.11	0.04	0.07–0.21	12	4.6	4.2	1.1–12.8	12	1.6	2.6	0.18–8.5
common mullet	<i>Mugil cephalus</i>	2	0.26	0.02	0.24–0.27	2	0.22	0.14	0.12–0.32	3	0.19	0.11	0.07–0.26

<sup>a</sup> nd, not detected.**Figure 1.** Box plots of enantiomer fractions (EFs) of  $\alpha$ -HCH,  $o,p'$ -DDT, and  $o,p'$ -DDD in consumer fish from South China. The horizontal lines in each diagram represent the 10th, 50th, and 90th percentiles, and the horizontal box edges represent the 25th and 75th percentiles. Circles are EF values for individual samples. The lines at 0.5 represent the racemic EF. Asterisks above or below the boxes indicate that the measured EFs in the fish species are significantly different from 0.5.

near-racemic, racemic  $\alpha$ -HCH occurred in nine samples, 10% of the total with detectable  $\alpha$ -HCH. Moreover, the EFs of  $\alpha$ -HCH in red drum (with a mean of 0.335;  $n = 21$ ) and crimson snapper (with a mean of 0.353;  $n = 22$ ) were significantly ( $p < 0.01$ ) different from that of the racemic standard. For other fish species, no significant ( $p > 0.05$ ) difference was found compared with the racemic standard (Figure 1). It should be noted that sample size was limited for some fish species, which may

compromise the quality of the EF data; for example, there were only one and two samples, respectively, for grass carp and common mullet.

Some previous studies have reported racemic or near-racemic composition of  $\alpha$ -HCH in fish. Wong et al. (10) examined  $\alpha$ -HCH in selected Standard and Certified Reference Materials and obtained mean EFs of  $0.500 \pm 0.003$  ( $n = 5$ ) and  $0.500 \pm 0.003$  ( $n = 8$ ) in SRM 1588a (organics in cod liver oil) and CRM trout, respectively. Near-racemic composition was also found in Arctic cod (*Boreogadus saida*) from the Arctic marine environment (25) and in salmon (*Salmo salar*) (EF =  $0.48 \pm 0.02$ ) from the Baltic Sea (26). Hoekstra and co-workers reported near-racemic compositions of  $\alpha$ -HCH in Arctic cod and char (*Salvelinus alpinus*) from the coastal Beaufort–Chukchi Seas food web near Barrow, AK (27). Also, an EF of close to 0.50 was determined in Atlantic cod (*Gadus morhua*) liver from the North Atlantic (SRM 1588) (28). On the other hand, nonracemic profiles of  $\alpha$ -HCH have been found in fish tissue. The EFs in herring (*Clupea harengus*) from the Swedish coastline ranged from 0.44 to 0.45, similar to those in dissolved  $\alpha$ -HCH in the Baltic Sea (29). The likely explanation is bioconcentration from water or trophic transfer from water to phyto/zooplankton to herring (29). In the liver of flounder (*Platychthys flesus* L.) from the German Bight (North Sea), EFs ranged from 0.44 to 0.48 (28). The average EF in Arctic cod from the Arctic marine food web of the Northwater Polynya was 0.45 (30). Koske and co-workers analyzed Atlantic cod liver oils and fish oils from different countries and found that EFs were nearly 0.5 in fish oils and significantly different from 0.5 in Atlantic cod liver oils (31).

$o,p'$ -DDT. The (+)-enantiomer was dominant in 84% of the total measured samples (Figure 1). The EFs of  $o,p'$ -DDT in bighead carp (0.566;  $n = 4$ ), largemouth bass (0.605;  $n = 6$ ), northern snakehead (0.624;  $n = 5$ ), red drum (0.562;  $n = 28$ ), snubnose pompano (0.559;  $n = 26$ ), crimson snapper (0.535;  $n = 29$ ), and hairtail (0.569;  $n = 12$ ) were significantly ( $p < 0.05$ ) different from that of the racemic standard (Table 1). This is consistent with the results from other previous studies. The mean EFs were  $0.371 \pm 0.013$  and  $0.415 \pm 0.081$  in SRM 1588a ( $n = 5$ ) and CRM trout ( $n = 8$ ), respectively (10). In the Atlantic cod liver oils and fish oils as noted above, EFs were also distinctly different from 0.5 (31).

$o,p'$ -DDD. The EFs were lower than 0.500 with a range of 0.005–0.389 (Table 1 and Figure 1), indicating preferential enrichment of the (–)-enantiomer. Only one sample of grass carp was analyzed, and the EF was 0.19. For other species, EFs were significantly ( $p < 0.05$ ) different from that of the racemic

standard. To the best of our knowledge, few chiral data on *o,p'*-DDD in the environment, especially in biota, are available in the literature. Buser and Müller (3) for the first time isolated *o,p'*-DDD racemates using enantioselective high-resolution gas chromatography (HRGC) with silylated  $\beta$ -cyclodextrin and enantioselective high-performance chromatography (HPLC) with permethylated  $\gamma$ -cyclodextrin. They further determined the configurations of (+)-*o,p'*-DDD and (-)-*o,p'*-DDD and reported enantiomeric ratios (ERs) in the technical and the synthetic reference materials (both ERs  $\approx$  1.0) (3). Garrison et al. (18) obtained a range of EFs from 0.29 to 0.44 in fish, similar to our findings. Venier and Hites (32) yielded a mean EF of 0.44 in air samples collected from Indiana, Arkansas, and Louisiana in 2002–2003. Shen et al. (33) measured the ERs of *o,p'*-DDD (expressed as the ratio of the first eluting enantiomer to the second enantiomer) in 112 placentas from mothers of Finnish boys collected between 1997 and 2001, which varied with the total concentration of *o,p'*-DDD.

**Preliminary Analysis of Enantioselective Origins.** One possible source for the occurrence of nonracemic  $\alpha$ -HCH, *o,p'*-DDT, and *o,p'*-DDD in fish tissues is enantioselective biotransformation within fish, which has been confirmed through previous in vivo experiments (6–8, 34). Wong et al. (7) found that immature rainbow trout (*Oncorhynchus mykiss*) preferentially eliminated (-)-*trans*-chlordane and (+)-PCB 136, whereas PCB 95 and  $\alpha$ -HCH residues remained racemic throughout the experiment. Using naturally contaminated mummichog (*Fundulus* sp.), Vetter et al. detected enantioselective elimination of 2-*exo*, 3-*endo*, 6-*exo*, 8,9,10-hexachlorobornane (34). Konwick et al. (6) reported that juvenile rainbow trout was able to enantioselectively biotransform fipronil, PCB 84, and PCB 132 rapidly, but could not alter the EFs of  $\alpha$ -HCH, heptachlor epoxide, PCB 174, *o,p'*-DDT, and *o,p'*-DDD. Wiberg et al. (8) examined the fate of chiral  $\alpha$ -HCH, *cis*-chlordane,  $^{13}\text{C}_4$ -heptachlor, *o,p'*-DDT, PCB 95, PCB 132, and PCB 136 in exposed Arctic char (*Salvelinus alpinus*) via peritoneal cavity injection and indicated that  $\alpha$ -HCH, *cis*-chlordane, *o,p'*-DDT, PCB 132, and PCB 136 could be enantioselectively eliminated by Arctic char. They also observed the formation of the chiral heptachlor metabolite  $^{13}\text{C}_4$ -heptachlor-*exo*-epoxide in Arctic char. The detection of nonracemic *o,p'*-DDD in the present study supports the notion that some chiral organochlorine compounds can be enantioselectively biotransformed by fish.

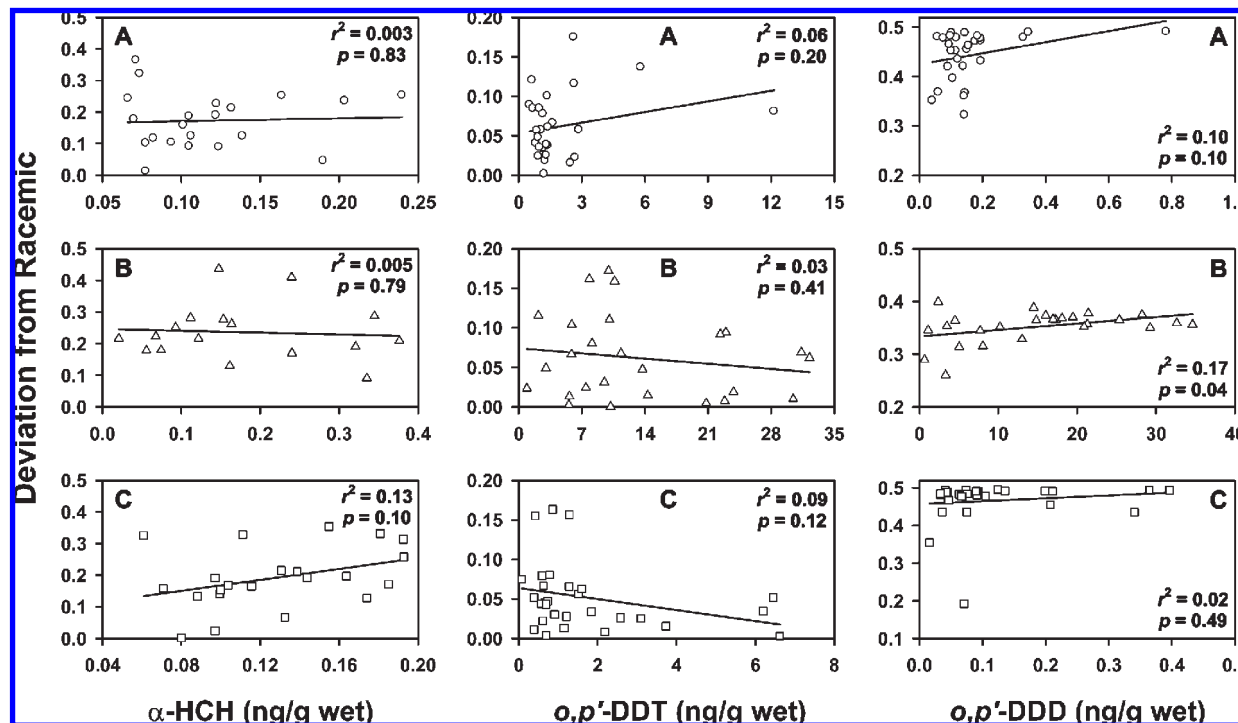
On the other hand, the general view is that fish have only limited biotransformation capacity, because fish have lower levels and activities of cytochrome P-450 type enzymes than do mammals (7, 8, 17, 35). In addition, other main routes for uptake and elimination of OCPs in fish, including uptake and loss via gills, dietary ingestion, and excretion, have been shown to be controlled mainly by diffusive processes with no stereospecificity and enantioselectivity involved (7, 8, 17, 26, 27). As a result, some field studies further inferred that bioaccumulation of these OCPs in fish body occurred without inducing enantioselectivity because no significant difference between the EFs of fish and water or sediment was observed (25, 27, 30, 36). For example, Moisey et al. (30) obtained EFs of  $\alpha$ -HCH in zooplanktons and Arctic cod similar to that in water collected from the Northwater Polynya. Given these assessments, direct uptake of nonracemic contaminants from environmental media (e.g., water, suspended particulate matter, and feeds) may have been a possible route for the occurrence of nonracemic compounds in fish (17). Unfortunately, data acquired in South China are insufficient to allow an adequate test of such a possibility. In the only study conducted so far in the region, Li et al. (37) found that the EFs of  $\alpha$ -HCH and *o,p'*-DDT

ranged from  $<0.5$  to  $>0.5$  in 74 soil samples from the Pearl River Delta, South China.

**Species Dependence of Enantiomer Fractions.** As noted above, fish can enantioselectively enrich or eliminate chiral compounds with cytochrome P-450 type enzymes. As a result, EFs may vary with fish species because enzymes capable of biotransforming chiral compounds also differ in stereoselectivity that dictates the interaction with chiral chemicals (17). In the present study, EFs of  $\alpha$ -HCH were significantly different among 11 fish species ( $p = 0.002$ ); that is, the (+)-enantiomer was depleted in bighead carp, northern snakehead, red drum, snubnose pompano, and crimson snapper, whereas the (-)-enantiomer was depleted in tilapia, grass carp, largemouth bass, mandarin fish, hairtail, and common mullet (Figure 1). In addition, red drum had significantly lower EFs of  $\alpha$ -HCH than tilapia ( $p = 0.048$ ), but no significant difference was observed for other species ( $p > 0.05$ ). Likewise, significantly different EFs of *o,p'*-DDT and *o,p'*-DDD ( $p = 0.038$  and  $p < 0.01$ , respectively) were found among 11 fish species. The average EF of *o,p'*-DDT in largemouth bass (0.624;  $n = 5$ ) was significantly ( $p = 0.042$ ) higher than that in crimson snapper (0.535;  $n = 29$ ), and no significant difference was found among other fish species (all  $p > 0.05$ ). For *o,p'*-DDD, crimson snapper had the lowest average EF (0.035;  $n = 29$ ), followed by snubnose pompano (0.057;  $n = 28$ ) and common mullet (0.120;  $n = 3$ ), and there was no significant difference between crimson snapper and snubnose pompano ( $p = 0.92$ ) or common mullet ( $p = 0.34$ ). On the other hand, mandarin fish had the highest average EF (0.337;  $n = 7$ ), which was significantly higher than those in all species except bighead carp (0.331;  $n = 5$ ;  $p = 0.085$ ), tilapia (0.229;  $n = 6$ ;  $p = 1.00$ ), and largemouth bass (0.266;  $n = 6$ ;  $p = 0.60$ ).

Several previous studies also reported species dependence of EFs in fish. Wong et al. (17) noted significant species dependence of EFs for PCB 91, 95, 136, and 149 in largemouth bass, bluegill sunfish (*Lepomis macrochirus*), crayfish (*Procambarus* sp.), water snakes (*Nerodea sipedon sipedon*), and barn swallows (*Hirundo rustica*) collected from Lake Hartwell. For example, the EFs of PCB 91 were significantly lower in bluegills than in the other four species and were highest in water snakes. Wiberg et al. (8) also found that Arctic char could enantioselectively biotransform  $\alpha$ -HCH. However, no enantioselective elimination of  $\alpha$ -HCH was found in rainbow trout upon 56 days of exposure (7).

**Correlation between EFs and Concentrations of Enantiomers.** Red drum, snubnose pompano, and crimson snapper with large sample sizes were selected to examine the correlation between the deviation of EFs to the racemic value and concentrations of enantiomers on the basis of wet weight. Clearly, only weak correlations were found between the deviation of EFs to the racemic value and concentrations of *o,p'*-DDD in snubnose pompano ( $r^2 = 0.17$ ,  $p = 0.04$ ), and no significant correlations were found for other species or target analytes (all  $p > 0.05$ ) (Figure 2). Also, the relationships between the concentrations and EFs of  $\alpha$ -HCH, *o,p'*-DDT, and *o,p'*-DDD were tested for all species as a single data set (data not shown). Similarly, no significant correlations were found for all fish species or target analytes (all  $p > 0.05$ ). A previous study also reported no significant correlation between the EFs and concentrations of chiral PCB atropisomers in fish samples collected from Lake Hartwell (17). In contrast, several studies suggested that EFs of chiral compounds were negatively related to their concentrations. Tanabe et al. (38) reported the enantiomeric ratios of  $\alpha$ -HCH were linearly related to the relative abundance of  $\beta$ -HCH to total HCH in blubber of small cetaceans from the



**Figure 2.** Relationships between the deviation of enantiomer fractions (EFs) from the racemic value and concentrations (ng/g wet) of  $\alpha$ -HCH,  $o,p'$ -DDT, and  $o,p'$ -DDD in consumer fish from South China (**A**, red drum; **B**, snubnose pompano; **C**, crimson snapper).

North Pacific and Bay of Bengal. Hoekstra et al. (39) found that the EF values for PCB 91 were inversely correlated with its concentrations and total PCB burdens in blubber of male bowhead whale (*Balaena mysticetus*) collected from Barrow, AK. Ross et al. (40) collected glaucous gulls (*Larus hyperboreus*) and their eggs from Svalbard (Norwegian Arctic) and observed that EFs of PCB 183 and heptachlor epoxide in egg yolk varied negatively with total PCB and chlordane concentrations.

In conclusion, some chiral OCPs under investigation in the present study were nonracemic in consumer fish from South China. Therefore, more studies are needed to determine the distribution of chiral OCPs in the fish-farming environment, for example, water, sediment, air, and fish feed, which is the key to understanding the bioaccumulation and biotransformation processes of these contaminants in fish. On the other hand, human exposure to OCPs via fish consumption should be assessed on the basis of enantioselective toxicity. As mentioned above, ( $-$ )- $o,p'$ -DDT is a more active estrogen-mimic in humans than ( $+$ )- $o,p'$ -DDT (11). As a result, human exposure via fish consumption will be overestimated if the total concentration of  $o,p'$ -DDT is used, because the mean EFs of  $o,p'$ -DDT in fish samples were higher than 0.5, indicating ( $+$ )- $o,p'$ -DDT was more abundant than ( $-$ )- $o,p'$ -DDT in fish tissue from South China.

#### ACKNOWLEDGMENT

We thank Xiang-Fei Sun for assistance in GC-MS analysis.

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Received for Review January 5, 2009. Revised manuscript received March 14, 2009. Accepted March 18, 2009. This research was financially supported by the National Natural Science Foundation of China (40532013 and 40821003), and the Foundation of the State Key Laboratory of Pollution Control and Resource Reuse, China (No. PCRRYL09001). This is contribution IS-1052 from GIGCAS.