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Biomagnification and enantiomeric profiles of organochlorine pesticides in food web components from Zhoushan Fishing Ground, China

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ABSTRACT

Trophodynamics and chiral signatures of organochlorine pesticides (OCPs), including dichlorodiphenyltrichloroethanes (DDTs), hexachlorocyclohexanes (HCHs), and chlordanes in a food web from Zhoushan Fishing Ground, China, were studied. Residues of OCPs in all teleost fishes were within food safety levels. Strong positive correlations were found between trophic levels (TLs) and wet weight concentrations of target chemicals, with trophic magnification factors (TMFs) from 4.17 to 9.77. Lipid contents and TLs significantly correlated, which indirectly affect the bioaccumulation processes of OCPs. The consistently racemic EF values of α-HCH, as well as invariability of the relative proportions of HCH isomers in different marine species implied that HCHs in animals originate directly from the surrounding environment. However, in vivo biotransformation and/or elimination of *o,p′*-DDT cannot be precluded. TMFs of the individual enantiomers further suggest that the influence of achiral biotransformation is too minor to induce enantioselective biomagnification of chiral OCPs through the studied food web.

1. Introduction

Organochlorine pesticides (OCPs), such as dichlorodiphenyltrichloroethanes (DDTs), hexachlorocyclohexanes (HCHs), and chlordanes (CHLs), are typical persistent organic pollutants of great concern. The production and use of these OCPs have been prohibited in most parts of the world due to their potential acute and chronic health effects (e.g., cancer, disruption of the developmental and endocrine systems, and neurological damage) on non-target organisms, including humans (UNEP, 2001). As a result, concentrations of OCPs in the abiotic and biotic matrices initially decreased but have begun to show signs of leveling off or even increasing recently in marginal sea areas because of land–sea migration (Zhou et al., 2014a, 2014b).

The high lipophilicity and stability of OCPs allow these compounds to bioaccumulate and biomagnify along food chains (Nfon et al., 2008). Since the detection of OCPs in biotic samples in the 1960s, numerous studies related to biomagnification profiles have been conducted (Ikemoto et al., 2008; Hop et al., 2002; McKinney et al., 2012; Ruus et al., 2002; Ryan et al., 2013). Increases in concentrations of many OCPs from prey to predator were observed, and the highest residues of these compounds were found in top predators, such as marine mammals (Ruus et al., 2002). However, the trophodynamics of OCPs from field studies, which are evaluated by trophic magnification factors (TMFs), vary with the studied organisms and chemicals. It has been suggested that a number of factors, such as the lipid content and trophic position of organisms, may influence the biomagnification process of OCPs (Borgå et al., 2004; Fisk et al., 2001; Kidd et al., 2001). Sometimes, collinearity may exist between the lipid contents and trophic levels of the organisms, which complicates the relative contribution of these variables to the contaminant burdens (Kucklick and Baker, 1998; Stapleton et al., 2001). Nevertheless, few studies have addressed the correlations among these variables, and such correlations need to be further clarified.

Several OCPs and their metabolites, such as *cis*-chlordane, *trans*-chlordane, α-HCH, *o,p′*-DDT, and *o,p′*-DDD, are chiral and exist as two mirror-image forms called enantiomers. Each pair of enantiomers has identical physicochemical properties and abiotic degradation rates. However, they can exhibit stereoselectivity in biotransformation pathways, which may affect the relative accumulation of the enantiomers in biota and result in changes in the enantiomeric fractions (EFs). Thus, the discrepancy of EF values may partly explain the biotransformation and bioaccumulation process up the food web (Wong et al., 2004).

Zhoushan Fishing Ground (ZFG) is the largest fishing ground in China. The annual catch of fish at ZFG can run up to 800,000 tones,

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Table 1
Basic characteristics and trophic levels for organisms collected from Zhoushan Fishing Ground, China (mean/SD).

Species	*n*	Body size (cm)	Body weight (g)	Lipid (% ww)	$\delta^{15}N$	$\delta^{13}C$	TL	Habitat and diets
ZPK(mixed)	2	–	–	1.9/0.8	6.70/0.25	−21.06/1.30	2.00/0.07	Plankton, Herbivorous
Crustacea								
TC	8	–	–	0.9/0.1	7.80/0.65	−17.91/0.60	2.32/0.19	Benthos, omnivorous
OP	3	18.5/1.3	125.8/12.4	1.7/0.1	9.85/1.10	−17.12/0.52	2.92/0.32	Benthos, omnivorous
PS	2	19.0/2.1	113.3/26.5	1.5/0.1	10.10/0.74	−16.65/0.30	3.00/0.22	Benthos, omnivorous
PT	2	19.3/2.7	132.3/37.8	1.3/0.0	10.28/0.80	−16.78/0.43	3.05/0.24	Benthos, omnivorous
Cephalopoda								
SES	6	–	253.7/45.4	3.00/0.4	9.72/1.32	−17.74/0.36	2.88/0.39	Nekton, omnivorous
Teleost fishes								
EJ	9	8.5/2.7	10.4/2.9	2.8/0.6	8.65/0.47	−19.92/0.33	2.57/0.14	Nekton, planktivorous
CL	4	12.7/2.2	27.3/3.0	3.0/0.5	9.22/0.68	−18.15/0.32	2.74/0.20	Nekton, planktivorous
HN	11	26.3/2.4	110.7/24.6	1.3/0.4	9.53/0.50	−17.36/0.99	2.83/0.15	Benthos, omnivorous
SEL	5	10.7/1.4	10. 6/4.9	2.2/0.1	9.55/0.87	−17.55/0.36	2.84/0.26	Benthos, carnivorous
PP	7	18.5/1.4	63.4/14.2	7.4/0.9	10.26/1.09	−18.86/0.42	3.04/0.32	Benthos, omnivorous
CS	6	20.8/1.6	87.6/22.5	1.9/0.2	10.29/0.80	−17.06/0.60	3.05/0.24	Benthos, carnivorous
PA	5	24.6/1.7	246.0/43.2	4.0/0.4	11.13/0.58	−18.51/0.43	3.30/0.17	Nekton, carnivorous
CR	10	32.2/2.2	191.7/30.5	3.5/1.3	11.69/0.49	−16.24/0.22	3.46/0.14	Benthos, carnivorous
MM	7	36.2/1.8	416.4/54.9	2.7/0.4	11.98/0.76	−16.34/0.32	3.55/0.22	Benthos, carnivorous
TLL	9	77.0/5.5	263.3/55.2	11.6/1.0	12.78/0.52	−18.74/0.73	3.78/0.15	Nekton, carnivorous
Elasmobranch fish								
MG	10	63.9/7.8	1070/221.5	0.9/0.4[a] 41.3/5.4[b]	13.06/0.66	−15.74/0.59	3.87/0.20	Nekton, carnivorous
Cetacean								
TT	2	185–220	150–171 kg	1.2/0.4	12.87/0.91	−16.01/0.45	3.81/0.27	Nekton, carnivorous

ZPK, Zooplankton; TC, *Trachypenaeus curvirostris*; OP, *Ovalipes punctatus*; PT, *Portunus trituberculatus*; PS, *Portunus sanguinolentus*; SES, *Sepia esculenta*; EJ, *Engraulis japonicus*; CL, *Collichthys lucidus*; HN, *Harpadon nehereus*; SEL, *Saurida elongata*; PP, *Pseudosciaena polyactis*; CS, *Chelidonichthys spinosus*; PA, *Pampus argenteus*; CR, *Cynoglossus robustus*; MM, *Miichthys miiuy*; TLL, *Trichiurus lepturus*; MG, *Mustelus griseus*; TT, *Tursiops truncatus*.

[a] Lipid contents of shark muscle.

[b] Lipid contents of shark liver.

which represents almost one-third of the national output (Liu et al., 1991). ZFG is adjacent to the Yangtze River Delta (YRD), a traditional agriculture area with the heaviest use of OCPs in China (Li et al., 2001). As a result, high levels of OCP residues as well as their upward trends have been observed in different environmental media and animal samples from ZFG (Nakata et al., 2002; Yang et al., 2006; Zhou et al., 2014a, 2014b). In coastal cities, dietary uptake of contaminated seafoods may be a major route of OCP exposure in humans (Nakata et al., 2002). And the biomagnification through the marine food web could amplify the effects and risks of OCPs. Nevertheless, to our knowledge, little information about the trophodynamics of OCPs can be available for ZFG, not alone the enantioselective patterns.

The main purposes of the present study were (a) to investigate the concentrations and accumulation status of OCPs in ZFG; (b) to use stable isotope ratios ($\delta^{13}C$ and $\delta^{15}N$) to assess the biomagnification potentials of OCPs in the food web, from zooplankton to cetaceans; (c) to explore the relative importance of animal lipid contents and trophic levels to the biomagnification processes of OCPs through the studied food web; and (d) to address the enantiomer-specific accumulation of chiral OCPs in the marine species from ZFG.

2. Materials and methods

2.1. Sampling collection and preparation

A total of 17 marine species were collected in November 2011 in the waters at 29.5°N-30.0°N and 124.0°E-125.0°E, one of the conventional fishing areas in ZFG (Supplementary material, Fig. S1). Zooplankton (ZPK) samples were obtained from vertical tows (bottom to surface) using medium-sized zooplankton nets (50 cm mouth diameter, 2.8 m in length, 505 μm mesh). Bottlenose dolphin (*Tursiops truncatus*, TT) was collected by local fishermen as a by-catch during a commercial fishery operation. Other organisms, including four crustaceans (white-hair rough shrimp (*Trachypenaeus curvirostris*, TC) and 3 crabs (three-spot swimming crab (*Ovalipes punctatus*, OP), redspot swimming crab (*Portunus sanguinolentus*, PS), and Japanese blue crab (*Portunus trituberculatus*, PT))), one cephalopod (golden cuttlefish (*Sepia esculenta*, SES)), and ten teleost fishes (Japanese anchovy (*Engraulis japonicus*, EJ), bombay duck (*Harpadon nehereus*, HN), lizardfish (*Saurida elongata*, SEL), small yellow croaker (*Pseudosciaena polyactis*, PP, now renamed as *Larimichthys polyactis*), bluefin searobin (*Chelidonichthys spinosus*, CS), light maigre (*Collichthys lucidus*, CL), silvery pomfret (*Pampus argenteus*, PA), robust tonguefish (*Cynoglossus robustus*, CR), brown croaker (*Miichthys miiuy*, MM), Atlantic cutlassfish (*Trichiurus lepturus*, TLL)), were collected by trawling. After field collection, the collected organisms were cleaned of epibionts and transported to the laboratory in precleaned glass jars (ZPK) or polyethylene bags (all other organisms) stored on ice. We also collected ten specimens of dog shark (*Mustelus griseus*, MG) from the same sea areas in April 2011. Our previous report discussed the OCP distributions in tissues of dog sharks from ZFG (Zhou et al., 2013). In the present study, lipid contents and pollution levels of OCPs in muscle and liver samples were used.

In the laboratory, all organisms were weighed and measured, and species identification was completed for the organisms when possible. Zooplanktons were composite samples of organisms of mixed sizes. Subsamples of the zooplankton indicated that these samples were primarily of *Sagitta bedoti*, *Sagitta enflata*, *Calanus sinicus*, and *Eucalanus subcrassus*. For crustaceans, whole soft tissues were extracted from the shell, and 30 (shrimp) or 5 (crab) individuals were pooled for analysis. For all of the teleost fishes, a clean stainless steel knife was used to remove the head, and the remains were pooled together. Conversely, for cuttlefish and the bottlenose dolphin, only muscle tissues were used. For most samples, the whole teleost fishes and the muscle tissues of cuttlefish and bottlenose dolphin were homogenized individually; however, 5–12 whole bodies of bluefin searobin, lizardfish, Japanese anchovy, and small yellow croaker were pooled because these species