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Residues and chiral signatures of organochlorine pesticides in mollusks from the coastal regions of the Yangtze River Delta: Source and health risk implication

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HIGHLIGHTS

- The levels of the DDTs and HCHs in mollusks may increase cancer risk.
- The DDTs increased and the HCHs decreased compared to historical data.
- Fresh sources and non-racemic proportions of OCPs ubiquitously existed.
- The OCP residues in mollusks primarily originate from the surrounding environment.
- The *in vivo* biotransformation in mollusks cannot be rule out for DDTs.

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ABSTRACT

The residues and enantiomeric fractions of organochlorine pesticides (OCPs) were measured in 11 mollusk species collected from the coastal areas along the Yangtze River Delta to evaluate the status, potential sources, and health risks of pollution in these areas. The concentrations of DDTs, HCHs, and chlordanes ranged from 6.22 to 398.19, 0.66–7.11, and 0.14–4.08 ng g^{-1} based on wet weight, respectively; DDTs and HCHs have the highest values, globally. The DDTs increased and the HCHs decreased compared to historical data. Both the box-and-whisker plots and the one-way ANOVA tests indicated that the OCP levels varied little between sampling locations and organism species. The compositions of the DDTs and HCHs suggested a cocktail input pattern of fresh and weathered technical products. The comparative EF values for the α-HCH between the sediments and mollusks, as well as the lack of any discernible difference in the relative proportions of HCH isomers among different species from the same sampling site implied that the HCH residues in the mollusks came directly from the surrounding environment. However, the biotransformation of DDTs in mollusks cannot be precluded. The assessments performed based on several available guidelines suggested that although no significant human health risks were associated with the dietary intake of OCPs, the concentrations of DDTs exceeded the maximum residual limits of China and many developed nations. Moreover, an increased lifetime cancer risk from dietary exposure to either DDTs or HCHs remains a possibility. Because non-racemic OCP residues are common in the mollusk samples, our results suggest a need to further explore the levels and toxicity of the chiral contaminants in mollusks and other foodstuff to develop the human risk assessment framework based on chiral signatures.

1. Introduction

Organochlorinated pesticides (OCPs) are typical persistent organic pollutants that continue to attract considerable scientific and regulatory interest due to their large amounts of historical production, persistence, bioaccumulation, and potentially negative impact on non-target organisms (Jones and de Voogt, 1999). Although the application of these chemicals has been either banned or restricted in many countries, some developing countries continue to use these compounds due to their low associated costs and excellent versatility in industry, agriculture and public health

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(UNEP, 2003). OCPs can be transferred from original sources to marine ecosystems in various ways, such as through the release of effluents, wet/dry deposition, and surface runoff. Due to their hydrophobic properties, OCPs are easily absorbed by particulate organic matters and deposited in sediments, enabling their re-release when the sediment layer is disturbed (Eggleton and Thomas, 2004); these compounds also bioaccumulate in sediment-dwelling organisms, particularly in sessile mollusks with limited metabolic defenses against xenobiotic chemicals due to their relatively low *P*450 activities (Livingstone et al., 1989; Solé et al., 1994). In addition to their high xenobiotic chemical accumulation and sedentary behavior, mollusks have other unique characteristics, such as their abundance in marine environments and a tolerance toward contaminant stress and salinity changes, making these organisms useful potential bioindicators for monitoring the levels of OCPs in the marine environment (Farrington et al., 1983). Moreover, many mollusk species are popular types of seafood that are targeted for consumption by higher animals and human beings via direct predation and/or the indirect food chain, thus representing an important exposure pathway of the pollutants (Cao et al., 2011; Guo et al., 2010; Yu et al., 2012).

Several OCPs and their metabolites are chiral compounds comprised of two enantiomers. Enantiomers are identical in composition and connectivity but possess different 3D structures that are not superimposable. Some common chiral OCPs include *a*-HCH, *o*,*p*′-DDT, *o*,*p*′-DDD and the main components of technical chlordane, such as *cis*-chlorodane (CC) and *trans*-chlordane (TC). The proportions of the two enantiomers in the technical mixtures are 1:1, *i.e.*, racemic. Enantiomers have identical physicochemical properties and abiotic degradation rates. However, because of their different molecular configurations, their ability to bind to structure–sensitive biological receptors may be different. Therefore, they may undergo biotic degradation at different rates, preferentially enriching one enantiomer in the environment and in organisms (Müller and Kohler, 2004). Thus, enantiomers are important markers of biological activity and can be used to interpret the environmental fate of organic pollutants (Covaci et al., 2010; Moisey et al., 2001; Wiberg et al., 2000). Numerous studies have identified non-racemic mixtures of chiral OCPs in various organisms, such as crustaceans (Hoekstra et al., 2003; Moisey et al., 2001), fish (Meng et al., 2009; Wiberg et al., 2000; Wong et al., 2002), birds (Ross et al., 2008; Yang et al., 2010a) and mammals (Wiberg et al., 2000; Yang et al., 2010a). And some reports also have suggested that chiral biotransformation can occur in organisms at higher trophic levels (Wong et al., 2002; Wiberg et al., 2000; Yang et al., 2010a; Ross et al., 2008). Despite of the important role of mollusks during the transfer of dissolved and particle-bound persistent pollutants to higher levels in the aquatic food web, information regarding the chiral signature of OCPs in these organisms still remains scarce (Pfaffenberger et al., 1992).

China is one of the largest and most prominent producers and consumers of OCPs in the world. The amounts of technical HCH and DDT were estimated to be 4.9 and 0.4 million tons, accounting for 33% and 20% of the total global production, respectively (Zhang et al., 2002). The Yangtze River Delta (YRD) is located in eastern China, comprising the triangular-shaped territory of Shanghai, southern Jiangsu province and northern Zhejiang province of China. As one of the most urbanized and industrialized regions in China, the YRD accounts for a quarter of China's GDP, nearly half of its foreign direct investment, and more than a third of its foreign trade. This area is also an important production base for foodstuffs and historically has the highest use of OCPs in the country (Li et al., 1999, 2001; Wang et al., 2013). The total consumption of technical HCH, DDT and chlordane in Zhejiang and Jiangsu provinces were 800 kt, 60 kt and 1.3 kt, accounting for approximately 1/5, 1/4, and 1/2 of the nation's applications, respectively (Li et al., 1999, 2001; Wang et al., 2013). The total usage density of OCPs in Shanghai was 4.8 kg h m^{-2} (Wu et al., 2007), or approximately 2 times that of the national average consumption of total pesticides (Wang et al., 2005a,b). Some studies have confirmed that OCPs contribute significantly toward the pollution of the environment (Qiu et al., 2004; Zhang et al., 2011; Zhao et al., 2009) and biota (Nakata et al., 2005; Zhao et al., 2009) in this region. And these contaminants from the YRD may subsequently enter into the adjacent sea areas (*i.e.*, the Northern East China Sea) through surface runoff, creating long-term adverse effects on the coastal resources.

Mollusks, including bivalves and gastropods, are one of the most important commercial seafood products from the coast along the YRD. According to a statistical report in 2012, the mariculture of mollusk products in the above-mentioned coastal areas reached 1409 kha and a total output of 1403 kt, accounting for approximately 10% of the national amounts (NFBC, 2012). Mollusks are heavily consumed in the daily life of individuals, particularly for those who live in coastal regions. With the rapid economic development and accelerating urbanization processes, the daily dietary habits of the YRD residents have changed significantly. For example, the consumption of shellfish, shrimp and crabs by Shanghai citizens increased from 7.2 g d^{-1} in 2000 to 11.8 g d^{-1} in 2011 (SMSB, 2012). Large-scale farming and the increasing market demand of marine mollusks should generate more concern on the health consequences of mollusk consumption because historical and potential new sources of OCPs are likely to adversely impact the quality of mollusk products from the YRD coastal areas (Fung et al., 2004; Ma et al., 2008; Li et al., 2010; Ren et al., 2006; Wang et al., 2005a,b; Yang et al., 2006). However, information on the residual levels of OCPs in the mollusks from this area has not been updated, and earlier investigations have not examined the risks to human health that are associated with the measured levels of pollutants. Moreover, no studies regarding the enantiomeric proportions of OCPs in mollusks have been published.

The present study investigated the contents and distribution of OCPs in 11 species of mollusks from 12 locations in the coastal areas along the YRD. Both the composition and enantiomeric profiles were used to trace the possible pollution sources and identify the biotransformation of OCPs in mollusks. Furthermore, a hazard assessment was also carried out to determine their potential risks to both the aquatic ecosystem and human health.

2. Materials and methods

2.1. Chemicals

A mixture of standard solution containing α-, γ-, β- and δ-HCH, *p*,*p*′-DDT, -DDD, and -DDE, *o*,*p*′-DDT, -DDD, and -DDE, CC, and TC were purchased from the National Research Center for Certified Reference Materials of China. Seven individual standards of OCPs including α-HCH, *p*,*p*′-DDT, *o*,*p*′-DDT, *p*,*p*′-DDD, *o*,*p*′-DDD, CC and TC were obtained from Dr. Ehrenstorfer GmbH (Augsburg, Germany). Decachlorobiphenyl (PCB 209), and 2,4,5,6-tetrachloro-*m*-xylene (TC*m*X), were purchased from Sulpelco Company (Augsburg, Germany). Two stationary phases for column chromatography, *i.e.*, ultrapure neutral silica gels (70–230 meshes) and neutral aluminium oxide (50–200 μm) were activated at 180 °C for 12 h, and 450 °C for 2 h, respectively before used. Anhydrous sodium sulfate was washed with hexane, and heated at 450 °C for 12 h. Super-purified copper powder was activated in diluted hydrochloride acid and stored in methanol. All solvents used were of HPLC or glass-distilled grade.