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Extensive organohalogen contamination in wildlife from a site in the Yangtze River Delta☆

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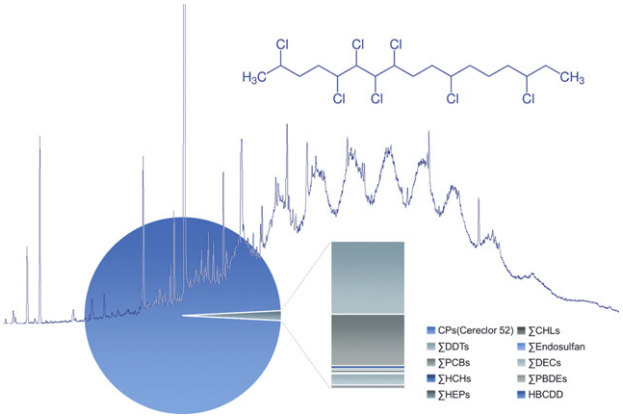
HIGHLIGHTS

- Six wildlife species of amphibians, fish and birds were sampled and screened for organohalogen contaminants (OHCs) in a paddy field in Yangtze River Delta, China.
- High contaminations of chlorinated paraffins were found particularly in terrestrial species.
- A novel pattern of PCBs with relatively high contribution from octa-CBs to decaCB was observed.
- A new group of OHCs, with 5–8 chlorines, were found but are not yet structurally confirmed.
- DDTs was the major organochlorine pesticide contaminant in wildlife; HBCDD level in wildlife was comparable to PBDEs in the present study.
- The results show an extensive contamination of OHCs in wildlife in Yangtze River Delta, calling for further (eco)toxicology study and environmental monitoring.

GRAPHICAL ABSTRACT



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ABSTRACT

The environmental and human health concerns for organohalogen contaminants (OHCs) extend beyond the 23 persistent organic pollutants (POPs) regulated by the Stockholm Convention. The current, intense industrial production and use of chemicals in China and their bioaccumulation makes Chinese wildlife highly suitable for the assessment of legacy, novel and emerging environmental pollutants. In the present study, six species of amphibians, fish and birds were sampled from paddy fields in the Yangtze River Delta (YRD) were screened for OHCs. Some extensive contamination was found, both regarding number and concentrations of the analytes, among the species assessed. High concentrations of chlorinated paraffins were found in the snake, Short-tailed mamushi

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(range of 200–340 μg g^{-1} lw), Peregrine falcon (8–59 μg g^{-1} lw) and Asiatic toad (97 μg g^{-1} lw). Novel contaminants and patterns were observed; octaCBs to decaCB made up 20% of the total polychlorinated biphenyls (PCBs) content in the samples and new OHCs, substituted with 5–8 chlorines, were found but are not yet structurally confirmed. In addition, Dechlorane 602 (DDC-DBF) and numerous other OHCs (DDTs, hexachlorocyclohexanes (HCHs), polybrominated diphenyl ethers (PBDEs), hexbromocyclododecane (HBCDD), chlordane, heptachlor, endosulfan and Mirex) were found in all species analyzed. These data show extensive chemical contamination of wildlife in the YRD with a suite of OHCs with both known and unknown toxicities, calling for further in-depth studies.

1. Introduction

Exposure to persistent organic pollutants (POPs) is a risk for human health and wildlife and has led to the Stockholm Convention which today regulates 26 POPs (Stockholm Convention, 2015a). However, numerous other chemicals are identified as both persistent (Green and Bergman, 2005) and bioaccumulative in humans and wildlife although their toxicological and ecotoxicological impacts are not yet well established. There is worldwide occurrence of such persistent and bioaccumulative chemicals, particularly in intense chemical production and application areas, i.e. fast growing economies like China. These chemicals, appearing as organohalogen contaminants (OHCs), are originally from the manufacturing of well-established chemicals, but also of new chemicals (Chen et al., 2009a; Ruan et al., 2015; Shi et al., 2009; Sun et al., 2012a), including byproducts and impurities (Qiu et al., 2005), all of which undergo biotic and abiotic transformations once released into the environment. In the past, China produced approximately 0.4 and 4.9 million metric tons (MTs) of technical dichlorodiphenyltrichloroethane (DDT) and hexachlorocyclohexanes (HCHs) from the 1950s to 1983 (Zhang et al., 2002), and an estimated 10,000 MTs of polychlorinated biphenyls (PCBs) between 1965 and1974 (Chen et al., 2009b). From 1988 to 2002, an additional 54,000 MTs of DDT was used to manufacture dicofol for mite control, resulting in an estimated amount of almost 9000 MTs of DDTs as an impurity in commercial dicofol and its release to the environment (Qiu et al., 2005). Decabromodiphenyl ethane (DBDPE), dechlorane plus (DDC-CO) and chlorinated paraffins (CPs) have been produced in China as emerging flame retardants in addition to polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecanes (HBCDD), and detected in various environmental compartments (Newton et al., 2015; Vorkamp et al., 2015; Zheng et al., 2015). Commercial CP mixtures include short chain CPs (SCCPs) with a chain length of 10–13 carbons and 30–70% relative chlorine content by weight; they are currently under review for inclusion in the Stockholm Convention (Stockholm Convention, 2015b) and are on the candidate list of substances of very high concern within the European Chemical Agency (ECHA, 2008).

China started their CP production at the end of the 1950s (Zeng et al., 2013) and has become the world's largest CP producer (Wang et al., 2013). The production volume had grown to about 1 million MTs in 2009 (Wu et al., 2013). Most manufacturing and usage occurred in the coastal regions of China, and CPs in marine sediments have recently been found to be more abundant in nearshore areas of East China Sea compared to outer shelf, suggesting a direct influence of riverine inputs and the proximity to land-based sources (Zeng et al., 2013). CP-42, CP-52 and CP-70 are the main commercial CP products in China with almost 80% of national production as CP-52 (Zhang et al., 2013a). The applications of CPs in China are disperse, including use as flame retardant, plasticizer, rubbers, sealant, paint and lubrication (Zeng et al., 2015).

Numerous researchers have reported contamination of OHCs in the Chinese environment, primarily in abiotic media (i.e., air, water, soil and sediment), but the studies are not even distributed on a national scale and limited for wildlife in Yangtze River Delta (YRD). Still, exposure data have been published for birds (Chen et al., 2007, 2009b; Dong et al., 2004; Gao et al., 2009; Lam et al., 2008; Luo et al., 2009; Sun et al., 2012a, 2013; Zhang et al., 2011a, 2011b), fishes (Hu et al., 2010; Sun et al., 2015; Yang et al., 2010), amphibians (Wu et al., 2009, 2012b), and other species (Yin et al., 2015). In China, studies on OHCs in birds began about 10 years ago, focusing on Pearl River Delta (Liu et al., 2010; Luo et al., 2009; Shi et al., 2009; Sun et al., 2012a, 2012b, 2012c, 2013; Zhang et al., 2011a, 2011b) and north China (Chen et al., 2007, 2009b; Gao et al., 2009; Yu et al., 2011, 2013). Of the OHCs measured, 4,4′-DDE had the highest concentrations (Chen et al., 2009b; Gao et al., 2009), BDE-209 was the most abundant PBDE (Chen et al., 2007) and many POPs and some emerging pollutants were detected in birds in China (He et al., 2010; Luo et al., 2009; Shi et al., 2009; Sun et al., 2012a; Sun et al., 2012b; Sun et al., 2013; Zhang et al., 2011a). In addition to birds, frogs collected from an Electronic-waste (E-waste) site in Pearl River Delta had a unique PBDE congener profile that was intermediate between aquatic and terrestrial species (Wu et al., 2009). However, there is a major lack of information regarding the situation of such compounds in wildlife from YRD.

The YRD is an important area of economic growth in China. It supports extensive industrial activities, business, trade, transportation, agriculture and aquaculture, contributing 20% of the Chinese Gross domestic production in 2014 (China NBS, 2014). With rapid economic development and high energy consumption, the regional environment is deteriorating (Shao et al., 2006; Zhang et al., 2013c). A recent report showed high concentrations of OHCs in YRD air (Suzhou, Wuxi, Nantong) (Zhang et al., 2013c). Total discharges of chlorinated compounds, aromatic hydrocarbons, phenols, and polycyclic aromatic hydrocarbons in Yangtze River water, were estimated to range between 500 and 3500 kg d^{-1} (Müller et al., 2008) and represent a threat to wildlife and humans. The YRD is well known as “a town of rice and fish” in China. Rice is one of the most common staple food for Chinese, especially in South of China and paddy field is the typical feature of rice farming in many Asian countries. The paddy field environments are complex ecosystems including both aquatic and terrestrial environments (Tojo, 2014).

The aim of the present study is to screen for OHCs in wildlife from paddy field environments in the YRD and to quantify selected OHCs in order to establish a baseline for future environmental monitoring efforts.

2. Materials and methods

2.1. Samples

Two amphibian, two bird, one fish and one reptile species were collected from paddy fields in YRD, China, located in the junction between Jinshan District in Shanghai and Jiaxing City in Zhejiang province, close to Hangzhou Bay (Supplemental Material (SM), Fig. S1). The sampling site is also adjacent to Jianshan second industrial park. Hence, it may be impacted by both agriculture and industrial activities. The amphibian species were Dark-spotted frog (*Pelophylax nigromaculatus*, n = 5 in pool) and Asiatic toad (*Bufo gargarizans*, n = 8 in pool); the two bird species were Chinese pond heron (*Ardeola bacchus*, n = 3) and Peregrine falcon (*Falco peregrinus*, n = 3); the fish species was Rice field eel (*Monopterus albus*, n = 5 in pool) and the reptile species was