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Persistent halogenated compounds in captive Chinese alligators (*Alligator sinensis*) from China

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HIGHLIGHTS

- DDTs were the most dominant PHCs in Chinese alligators.
- Both neonates and eggs had significantly higher ∑PCBs and ∑DDTs than adult muscles.
- DDTs in Chinese alligator eggs could cause sex reversal.
- First report on PBDEs in crocodilia and first study on PHCs in Chinese alligators.

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ABSTRACT

While a number of studies have reported residual levels of persistent halogenated compounds (PHCs) in crocodilia, there is still a dearth of information on the Chinese alligator, a critically endangered crocodilian species. In the present study, several PHCs, including polybrominated diphenyl ethers (PBDEs), polychlorinated biphenyls (PCBs), and dichlorodiphenyltrichloroethane and its metabolites (DDTs), were detected in the adult tissues, neonates, and eggs of captive Chinese alligators from China. The concentrations of ΣPBDEs, ΣPCBs, and ΣDDTs in Chinese alligators ranged from 0.11 to 16.1, 1.12 to 22.2, and 6.03 to 1020 ng g^{-1} wet weight, respectively, with higher levels of ΣPCBs and ΣDDTs in the neonates and eggs than in muscle tissues. The ΣDDT residues in the studied Chinese alligators were at the high end of reported ranges from crocodilia around the world, and some results exceeded levels known to cause a female-biased sex ratio in crocodilians.

1. Introduction

Toxic persistent halogenated compounds (PHCs), such as polybrominated diphenyl ethers (PBDEs), polychlorinated biphenyls (PCBs), and dichlorodiphenyltrichloroethane and its metabolites (DDTs), are of great concern due to their environmental persistence, bioaccumulative properties, and potentially adverse effects on both wildlife and humans (Snedeker, 2001; de Wit, 2002; Beyer and Biziuk, 2009). Moreover, PCBs, DDT and its main metabolites, and components of the penta-BDE and octa-BDE mixtures have been added to the list of persistent organic pollutants (POPs) that are now regulated under the Stockholm convention. Although the production and use of these PHCs have been officially banned, they are still present in most environmental matrices long after their use and remain a potential health hazard to ecosystems (Snedeker, 2001; de Wit, 2002; Beyer and Biziuk, 2009).

While a number of studies have addressed the bioaccumulation of PBDEs in wildlife (de Wit, 2002), there is still a dearth of information on their presence in reptiles. To date, studies on the occurrence of PBDEs in reptiles have primarily focused on turtles (de Solla et al., 2007; Alava et al., 2011; Stewart et al., 2011) and water snakes (Wu et al., 2008). The available data suggest that PBDE 47 is often the predominant PBDE congener in turtles and water snakes, followed by PBDEs 99, 100, 153, and 154 (Wu et al., 2008; Alava et al., 2011; Stewart et al., 2011), which is in accordance with typical patterns of PBDE congeners in aquatic organisms (de Wit, 2002; Wu et al., 2008; Gao et al., 2009). How-

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ever, a unique PBDE pattern with a predominance of PBDE 100 was reported in the plasma of two freshwater turtles (*Sternotherus odoratus* and *Trachemys scripta troosti*) from the Tennessee River Gorge (Moss et al., 2009). Furthermore, an atypical PBDE pattern dominated by PBDEs 153 and 100 instead of PBDEs 47 and 99 was observed in fat biopsies and plasma samples from diamondback terrapins in New Jersey (Basile et al., 2011). These atypical patterns have been attributed to the biotransformation or metabolism of certain PBDE congeners, which are location-specific rather than species-specific (Basile et al., 2011).

Crocodilia is an order of large reptiles that has been used extensively as sentinel organisms for monitoring the levels and effects of PHCs in local environments because crocodilians are long-lived, non-migratory and top-level carnivores (Stoker et al., 2011). The Chinese alligator (*Alligator sinensis*) is one of only two alligator species in the world. These alligators are currently endemic to the lower Yangtze River in China and prefer freshwater habitats such as streams, swamps, ponds, lakes, and rice paddies. In the past decade, very few wild nests have been found, and even fewer have produced viable offspring. At present, the estimated wild population consists of less than 130 individuals (Thorbjarnarson et al., 2002). Thus, the Chinese alligator is listed as a critically endangered species on the International Union for Conservation of Nature (IUCN) red list of threatened species (http://www.aquaticcommunity.com/alligators/chinese.php). As indicated by a previous study, environmental pollution may be associated with the decline of wild Chinese alligator population (Thorbjarnarson et al., 2002). Several previous studies have found organochlorine pesticides, including DDT-related chemicals, in the tissues of American alligators (*Alligator mississippiensis*) (Delany et al., 1988; Heinz et al., 1991; Cobb et al., 1997; Rauschenberger et al., 2004a; Garrison et al., 2010), broad-snouted caimans (*Caiman latirostris*) (Stoker et al., 2011), Morelet's crocodiles (*Crocodylus moreletii*) (Pepper et al., 2004; Rainwater et al., 2007; Wu et al., 2000a, 2000b, 2006), American crocodiles (*Crocodylus acutus*) (Hall et al., 1979; Rainwater et al., 2007), Nile crocodiles (*Crocodylus niloticus*) (Skaare et al., 1991), Australian freshwater crocodiles (*Crocodylus johnstoni*), and saltwater crocodiles (*Crocodylus porosus*) (Yoshikane et al., 2006), and a few studies have further measured PCB levels in the eggs (Cobb et al., 1997, 2002; Stoker et al., 2011), muscles (Delany et al., 1988), and serum (Guillette et al., 1999) of American alligators (*A. mississippiensis*). However, there is no current information on the levels and distribution of PHCs in Chinese alligators. It has been suggested that some PHCs are endocrine-disrupting compounds, which can be maternally transferred to developing alligator eggs, leading to reduced hatchling success, increased embryonic mortality, and sex reversal (Guillette et al., 2000; Rauschenberger et al., 2004a, 2004b, 2007; Stoker et al., 2011). Therefore, monitoring the concentrations of PHCs in Chinese alligators is important for understanding the distribution and potential impact of these compounds on this species.

In the present study, we examined the levels and patterns of several PHCs including PBDEs, PCBs, and DDT and its metabolites in the adult tissues, neonates, and eggs of captive Chinese alligators (*A. sinensis*) from the Anhui Research Center for Chinese alligator reproduction. Furthermore, we assessed the potential toxicological effects of these chemicals on Chinese alligators.

2. Materials and methods

2.1. Sample collection

Eleven adult tissue samples from five female Chinese alligators (2 skin samples, 4 muscle samples, 1 liver sample, 3 spleen samples, and 1 kidney sample), three neonate samples, and five egg samples were collected from the Anhui Research Center for Chinese Alligator Reproduction between 2006 and 2007. Detailed sample information is provided in Supplementary Materials (SM; Table S1 and Fig. S1). All samples were collected from dead captive Chinese alligators. The collected samples were packed with aluminum foil, sealed in polyethylene bags, and then frozen at −20 °C for chemical analysis.

2.2. Sample preparation and chemical analysis

The extraction procedures, instrumental conditions, quantitation procedures, and quality assurance/quality control (QA/QC) measures and outcomes were provided in the SM.

2.3. Data analysis

All concentrations were expressed on both wet weight (ww) basis and lipid weight (lw) basis to minimize the inter-individual variation of different tissue types and to facilitate the comparison of results with other studies. The PBDEs, PCBs and DDTs are defined as the sum of 17 PBDE congeners (PBDEs 28, 47, 85, 99, 100, 138, 153, 154, 183, 196, 197, 202, 203, 206, 207, 208 and 209), the sum of 52 PCB congeners (PCBs 18, 28/31, 52, 64, 66, 70, 74, 92, 95, 99, 101, 107/123, 110, 115/87, 117, 118, 128, 130, 131, 135, 137, 138, 141, 146/161, 149, 151, 153/132, 156, 158, 164/163, 170/190, 171, 172, 174/181, 175, 178, 180/193, 183, 199, 202, 207, 208 and 209), and the sum of DDT and its metabolites (*o,p′*- and *p,p′*-DDT, *o,p′*- and *p,p′*-DDE, *p,p′*-DDD, *p,p′*-DDM and *p,p′*-DDMU), respectively (Table 1). 1-Chloro-2,2-bis(4-chlorophenyl)ethylene (*p,p′*-DDMU) and bis(4-chlorophenyl)methane (*p,p′*-DDM) are two secondary metabolites of *p,p′*-DDT. *p,p′*-DDMU can be generated by either reductive dechlorination from *p,p′*-DDE or dehydrochlorination from *p,p′*-DDD (Quensen et al., 1998; Guo et al., 2009). Data analysis was performed using SPSS 16.0 (SPSS Inc., Illinois). Linear correlation analysis was used to investigate the relationship between eggshell thickness and DDT concentrations in the eggs of Chinese alligators. One-way analysis of variance (ANOVA) was used to determine the differences in chemical concentrations and compositions among the adult tissues, neonates and eggs. In each case, statistical significance was set at $p < 0.05$.

3. Results and discussion

3.1. Residual levels

The concentrations of ∑PBDEs, ∑PCBs and ∑DDTs and the levels of major congeners or isomers of PBDEs, PCBs and DDTs in the adult tissues (sum of 5 tissue types), neonates and eggs of Chinese alligators were summarized in Table 1. The concentrations of ∑PBDEs ranged from 0.14 to 16.1 (median = 0.65), 0.26 to 0.73 (median = 0.70) and 0.11 to 0.16 (median = 0.15) ng g^{-1} ww for the adult tissues, neonates, and eggs, respectively. No data on PBDE concentrations in alligators or crocodiles are available for comparison. ∑PBDE concentrations have been reported in the muscles and eggs of other reptiles such as water snakes and turtles. The median ∑PBDE concentrations (0.60 ng g^{-1} ww) in the muscles of Chinese alligators were 4 orders of magnitude lower than those (1090 ng g^{-1} ww) in water snakes from an electronic waste recycling site in South China (Wu et al., 2008). The concentrations of ∑PBDEs found in the eggs of Chinese alligators (Tables 1 and 2) was similar to that observed in loggerhead sea turtle egg yolks from western Florida (median 0.664 ng g^{-1} lw) and eastern Florida (median 1.44 ng g^{-1} lw) (Alava et al., 2011), but it was 4 and 7 times and 1–2 orders of magnitude lower than those detected in leatherback turtle eggs from Juno Beach, Florida (median 0.689 ng g^{-1} ww) (Stewart et al., 2011), loggerhead sea turtle egg