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Human exposure to PCDDs and their precursors from heron and tern eggs in the Yangtze River Delta indicate PCP origin ☆

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ABSTRACT

Polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) are highly toxic to humans and wildlife. In the present study, PCDD/Fs were analyzed in the eggs of whiskered terns (*Chlidonias hybrida*), and genetically identified eggs from black-crowned night herons (*Nycticorax nycticorax*) sampled from two lakes in the Yangtze River Delta area, China. The median toxic equivalent (TEQ) of PCDD/Fs were 280 (range: 95–1500) and 400 (range: 220–1100) pg TEQ g^{-1} lw (WHO, 1998 for birds) in the eggs of black-crowned night heron and whiskered tern, respectively.

Compared to known sources, concentrations of PCDDs relative to the sum of PCDD/Fs in bird eggs, demonstrated high abundance of octachlorodibenzo-*p*-dioxin (OCDD), 1,2,3,4,6,7,8-heptaCDD and 1,2,3,6,7,8-hexaCDD indicating pentachlorophenol (PCP), and/or sodium pentachlorophenolate (Na-PCP) as significant sources of the PCDD/Fs. The presence of polychlorinated diphenyl ethers (PCDEs), hydroxylated and methoxylated polychlorinated diphenyl ethers (OH- and MeO-PCDEs, known impurities in PCP products), corroborates this hypothesis. Further, significant correlations were found between the predominant congener CDE-206, 3′-OH-CDE-207, 2′-MeO-CDE-206 and OCDD, indicating a common origin.

Eggs from the two lakes are sometimes used for human consumption. The WHO health-based tolerable intake of PCDD/Fs is exceeded if eggs from the two lakes are consumed regularly on a weekly basis, particularly for children. The TEQs extensively exceed maximum levels for PCDD/Fs in hen eggs and egg products according to EU legislation (2.5 pg TEQ g^{-1}lw). The results suggest immediate action should be taken to manage the contamination, and further studies evaluating the impacts of egg consumption from wild birds in China. Likewise, studies on dioxins and other POPs in common eggs need to be initiated around China.

1. Introduction

Polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) are among the most well-known environmental contaminants, as they are highly persistent, bio-accumulative, and associated with toxic effects to both humans and

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wildlife (Hites, 2011). PCDD/Fs are released into the environment via natural pathways e.g. forest fires (Baker and Hites, 2000; Zheng et al., 2008) but more heavily through anthropogenic activity. For example, PCDD/Fs are present in chlorinated chemical products (e.g. polychlorinated phenols) as impurities and by-products. Other sources include combustion of chlorine-containing material, coal and oil industries, municipal and medical waste incineration, vehicle exhaust emission, crop burning, and steelworks. In China specifically, seven PCDD/Fs hotspots have been identified (Zheng et al. (2008)), primarily indicating pentachlorophenol (PCP) manufacturing and use (Lee et al., 2006a, 2006b), and electronic-waste (e-waste) recycling activities (Leung, 2006) as principal sources.

PCP has been a widely used pesticide globally, yet has continuously been attributed to myriad adverse effects on human health, including toxicity such as thyroid disrupting effects (Dallaire et al., 2009) and carcinogenicity (Cheng et al., 2015). Technical grade PCP also includes many toxic by-products, primarily tetrachlorophenol (TeCP), PCDDs, PCDFs, polychlorinated diphenyl ethers (PCDEs), hydroxylated polychlorinated diphenyl ethers (OH-PCDEs), further known as polychlorinated phenoxyphenols (PCPPs), hexachlorobenzene (HCB) and polychlorinated biphenyls (PCBs) (GmbH, 2010). OH-PCDEs are considered as main impurities in technical (poly-)chlorophenol formulations, and 2′-OH-CDE-206 (also presented as nona-C_2PP) (Holt et al., 2008) is suggested as a precursor to octachlorodibenzo-*p*-dioxin (OCDD) (Holt et al., 2008; Jensen and Renberg, 1972; Nilsson and Renberg, 1974; Rappe and Nilsson, 1972). Published data on PCP impurities, such as PCDEs and OH-PCDEs, are scarce compared to reports on PCDD/Fs. Within the last 20 years, PCDE environmental contamination data originate primarily from Finland and remain related to the commercial chlorophenol formulation Ky-5, consisting of 80% TeCP (Koistinen et al., 1997, 1995a, 1995b). Recently, He et al. (2015) reported PCDEs in sediment and water from Nanjing, China, which to date, remains the only research on PCDEs in the Yangtze River Delta (YRD) area that we are aware. In addition, of the few studies conducted thus far, most evaluate soil and sediment, whereas knowledge on the environmental fate of OH-PCDEs and methoxylated polychlorinated diphenyl ethers (MeO-PCDEs) in biota are lacking (Holt et al., 2008; Persson et al., 2007; Zhou et al., 2016b).

In China, PCP and Na-PCP have been particularly widely used in the southern area across the YRD from the mid-1950s, primarily as a response to protect people from the *Schistosomiasis japonica* parasite (Ge et al., 2007). It was estimated that until 2005, the production of PCP and sodium pentachlorophenolate (Na-PCP) in China was 10 000 metric tons per year, contributing almost 20% of its global annual production (Chen et al., 2013; Yu et al., 2005; Zheng et al., 2012). Despite its adverse effects, PCP remains one of the most effective ways to protect human from the serious schistosomiasis, and the combined effect of the YRD heavy industrialization and expansive agriculture production to support the large and growing population, makes for a potentially dangerous combination.

Bird eggs have been reported as one of the most ideal surrogates for contaminant monitoring, mirrored through numerous previous and ongoing programs (Bignert and Helander, 2015; Braune et al., 2015; Dittmann et al., 2012; Elliott and Elliott, 2013; Miller et al., 2014). Birds at a high trophic level tend to accumulate lipophilic environmental contaminants, often to considerably high concentrations. A high and relatively stable fat content contributes to make organic contaminant concentrations in bird egg less variable compared to other organisms such as fish, hence increasing statistical power to detect contaminant temporal trends (Miller et al., 2014).

In a previous study, levels of organochlorine pesticides (OCPs), industrial chemicals (PCBs and PBDEs), and a novel pattern of highly chlorinated PCBs (octa-, nona- and decaCB) were assessed in black-crowned night heron (*Nycticorax nycticorax*) and whiskered tern (*Chlidonias hybrida*) egg samples from YRD (Zhou et al., 2016a). Known to be commonly consumed by humans in the region, our present study will focus on PCDD/Fs and related compounds in eggs from these two widely distributed bird species.

Our specific aims include *i:* investigating PCDD/F levels and congener profiles in collected bird eggs; *ii:* to quantify PCP, and PCP impurities, in those samples, and discuss potential sources of PCDD/Fs and *iii:* to evaluate risk on the human intake of PCDD/Fs based on the study result. To our knowledge, this research is the first study focusing on impurities in PCP, particularly dioxin precursors within the Chinese environment.

2. Material and methods

2.1. Sample collections

Eggs from twenty black-crowned night herons (*Nycticorax nycticorax*) and thirty-four whiskered terns (*Chlidonias hybrid*) were collected from Tianmu Lake and East Tai Lake, respectively, in April and May 2014, respectively. Both black-crowned night herons and whiskered terns are summer breeders in the YRD. The black-crowned night herons feed in paddy fields, pastures, and along the shores where they form nesting colonies in trees during the breeding season. The whiskered terns generally forage in open water-bodies by skimming over, or plunging into the water. Primary dietary items of both species include fish, shrimp, and aquatic insects. Because the nests of black-crowned night herons generally mix with other Ardeidae species, in Tianmu Lake, DNA barcoding was used to distinguish the eggs of black-crowned night herons from other species (see Supplementary Material, *SM*). After species identification, ten eggs from each species were used for chemical pollutant analysis. Detailed information about transportation and preservation of eggs has been described elsewhere (Zhou et al., 2016a).

2.2. Species identification

Although knowledge of the habitat and geographical location allowed the taxonomic origin of these heron eggs to be restricted to approximately 10 sympatric aquatic bird species with similar egg morphological characteristics (mean ± S.D.; mass 31.95 ± 3.91 g, length 4.84 ± 0.19 cm, width 3.53 ± 0.17 cm), a mixture of yolk, albumen, amniotic fluid, chalazan, and membrane from each egg was genetically analyzed for accurate species identification. Further details of the analysis are presented in the *SM*, where species identification is done for 20 eggs.

Of the twenty putative night heron eggs from Tianmu Lake, one egg was broken with its yolk and amniotic mixture expelled, rendering it useless for contamination free DNA analysis. One additional sample could not be successfully sequenced after three replicate amplification trials. In total, we successfully amplified and sequenced 18 eggs (Table S1). Using a BLAST search in the NCBI database (blast.ncbi.nlm.nih.gov/Blast.cgi), it was determined that 17 eggs originated from the black-crowned night heron, and one egg from the little egret, *Egretta garzetta* (both representing predatory opportunists associated with wetlands in Asia). From this information, ten of the genetically identified black-crowned night heron eggs were used for chemical analysis.

2.3. Chemical analysis

Yolk and albumen of the egg were analyzed individually. For