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Accumulation and exposure assessment of persistent chlorinated and fluorinated contaminants in Korean birds

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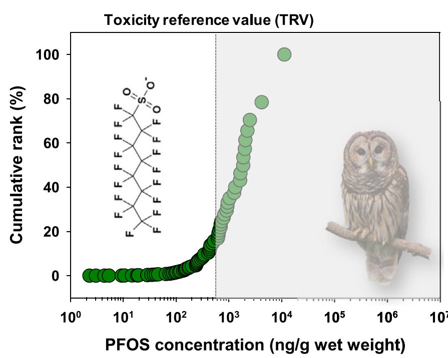
HIGHLIGHTS

- Concentrations of PCBs, OCPs, and PFASs varied in several bird species from Korea.
- PFOS concentration found was highest for a bird species on a global scale.
- Accumulation levels and profiles of OHCs varied by trophic position and migration pattern.
- Organochlorines biomagnified in residential predatory birds.
- PFOS concentrations in most of the predatory birds exceeded threshold values for adverse health effects.

GRAPHICAL ABSTRACT



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ABSTRACT

To date, information is scarce on the accumulation and potential risks of persistent chlorinated and fluorinated contaminants in birds. In this study, organohalogen contaminants (OHCs), such as polychlorinated biphenyls (PCBs), organochlorine pesticides (OCPs), and perfluoroalkyl substances (PFASs), were measured in the liver tissues of 10 bird species ($n = 69$) from Korea. Among the OHCs, PFASs showed the highest concentration, ranging from 5.40 to 11,300 (median: 294) ng/g wet weight. The median concentrations of OCPs and PCBs in all the bird samples were 147 and 81.9 ng/g lipid weight, respectively. The maximum concentration of perfluorooctane sulfonate (PFOS) observed in our bird samples was highest reported so far. Concentrations of OHCs in predatory birds were significantly greater than those measured in non-predatory birds, indicating the importance of diet and trophic position for bioaccumulation of these contaminants. In addition, different accumulation patterns of OHCs were found between predatory and non-predatory birds. Significant correlations were found between organochlorine concentrations and stable nitrogen isotope ratio ($\delta^{15}N$) measurements, whereas no correlation was found between PFASs and $\delta^{15}N$. Although the concentrations of PCBs and DDTs in birds were lower than the threshold levels, 25% and 49% of birds exceeded the toxicity reference value and predicted no effect concentration for PFOS, respectively, implying potential health risks to Korean birds.

1. Introduction

Organohalogen contaminants (OHCs) are of global concerns due to their widespread contamination, toxicity, and potentials for

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bioaccumulation and long-range transport. Polychlorinated biphenyls (PCBs), organochlorine pesticides (OCPs), and per- and polyfluoroalkyl substances (PFASs) are representative OHCs, which have been widely used for agriculture and industry (Loganathan, 2012; Kodavanti and Loganathan, 2017). In particular, PFASs have been applied as surfactants and surface protectors in industrial and commercial products including food container, textiles, and fire retardants for 60 years (Paul et al., 2009). PCBs and several OCPs (e.g., DDTs) were listed by the United Nations Environmental Programme (UNEP) as persistent organic pollutants (POPs) under the Stockholm Convention in 2001. In addition, PFOS and its related compounds were also nominated as new POPs under the Stockholm Convention in 2009 (UNEP, 2017).

Birds of prey have been utilized as bioindicators of environmental pollution, because of their vulnerability and low metabolic capacity for organic contaminants (Van Drooge et al., 2008; Yohannes et al., 2017). To date, various types of bird tissues such as muscle, blood, liver, and feathers have been used to evaluate the accumulation extent and profiles of persistent contaminants (Dahmardeh Behrooz et al., 2009; Jin et al., 2016; Zheng et al., 2018). Liver tissues of birds are an accumulation repository associated with external exposure of POPs and later undergo metabolic transformations and redistribution (Falkowska et al., 2016). In particular, liver tissues of wildlife species have shown several orders of magnitude for PFASs higher than concentrations in other biological compartments due to high level of protein (Conder et al., 2008; Custer et al., 2012).

Exposure to OHC in various bird species causes negative health effects on reproduction, immune function, hormone and vitamin homeostasis, and biotransformation enzymes (Grasman et al., 1996; Schuur et al., 1998; Lau et al., 2003; Sonne et al., 2012; Ortiz-Santaliestra et al., 2015). More recent studies have reported the induction of oxidative stress due to OHC exposure in birds (Sletten et al., 2016; Abbasi et al., 2017). In addition, exposure to PFASs has been positively associated with an increase in total thyroxin (TT4) in plasma (Nøst et al., 2012) and alanine aminotransferase activity (LAT) in nestlings (Hoff et al., 2005).

Our recent study showed the highest accumulation levels of bis (2-ethylhexyl)-3,4,5,6-tetrabromo-phthalate (BEHTBP), 1,2-bis(2,4,6-tribromophenoxy) ethane (BTBPE), and dechlorane plus (DP) in liver tissues of Korean birds compared with those found in previous studies (Jin et al., 2016). Among those contaminants, BEHTBP, and DP showed biomagnification potentials with an application of nitrogen stable isotope ratio in predatory birds. In addition, the historical trends in PFASs in the coastal environment of Korea as well as several other countries showed a clear increase since the 1980s (Zushi and Masunaga 2012; Shen et al., 2018). These findings suggest that emerging contaminants could be of environmental concern in Korea (Hong et al., 2014; Abbasi et al., 2016; Jin et al., 2016). Considering rapid industrialization, historical trends, and adverse health effects, it is essential to provide baseline information on OHCs, in wildlife, including Korean birds. To date, earlier studies on OHCs in Korean birds have generally investigated the levels and profiles of contaminants with limited numbers of avian species, while the influencing factors for bioaccumulation of OHCs have rarely been studied (Kannan et al., 2002; Yoo et al., 2008; Hong et al., 2014). In the present study, the concentrations and accumulation profiles of PCBs, OCPs, and PFASs were investigated in the livers of 10 bird species collected from Korea. To understand the factors influencing bioaccumulation of OHCs in birds, several variables such as habitat, diet, trophic level, and migration patterns were investigated. Moreover, the ecotoxicological risks were assessed for the observed concentrations of OHCs in various bird species based on toxicity reference values for birds.

2. Materials and methods

2.1. Sample collection

Bird samples (10 species and 69 individuals), collected during the period of 2010–2011, were obtained from the National Science Museum in Daejeon, Korea. Most bird species were collected from Paju, Gyeonggi-do ($n = 57$), while the other individuals were collected from Gyungsangbuk-do ($n = 1$), Jeollabuk-do ($n = 3$), Jeollanam-do ($n = 2$), Dokdo Island ($n = 3$), or Ulleung Island ($n = 3$) (Figure S1). Eurasian eagle owl (*Bubo bubo*; $n = 5$), common kestrel (*Falco tinnunculus*; $n = 4$), collared scops owl (*Otus lempiji*; $n = 6$), and black-tailed gull (*Larus crassirostris*; $n = 8$) are classified as residential predatory birds. Brown hawk owl (*Ninox scutulata*; $n = 9$), northern goshawk (*Accipiter gentilis*; $n = 6$), cinereous vulture (*Aegypius monachus*; $n = 7$) and common buzzard (*Buteo buteo*; $n = 7$) are classified as migratory predatory birds. Spot-billed duck (*Anas poecilorhyncha*; $n = 6$) and oriental turtle dove (*Streptopelia orientalis*; $n = 11$) are classified as residential herbivore and insectivore birds, respectively (Won and Kim, 2012; Jin et al., 2016). All bird samples were found dead due to causes such as vehicle collision, poisoning, and starvation. A previous study reported that most poisoning by insecticides to wild birds of Korea was associated with the misuse of carbamates (e.g., monocrotophos and phosphamidon) and organophosphates (Kim et al., 2016a, b), which are not target contaminants in the present study. Collected bird samples were transported to the National Science Museum laboratory and stored at −20°C before dissection. All of the bird samples were dissected, and liver tissue was collected. Biometric information such as body weight and body length were recorded, and sex was determined by DNA examination (Jin et al., 2014). Most birds were adults, but a few specimens (e.g., black-tailed gull) were nestlings. Detailed biological and ecological information on the avian species investigated in our study are summarized in Table S1.

2.2. Standards and reagents

Twenty-five PCB congeners (IUPAC No. CBs 8, 18, 28, 29, 33, 44, 52, 70, 87, 101, 105, 110, 118, 128, 138, 153, 170, 180, 187, 194, 195, 199, 200, 205, and 206), DDTs (*o,p′*-DDT, *p,p′*-DDT, *o,p′*-DDE, *p,p′*-DDE, and *o,p′*-DDD), hexachlorocyclohexanes (HCHs; α-, β-, γ-, and δ-HCH), chlordanes (CHLs; *cis*-, *trans*-, and *oxy*-chlordanes, *cis*- and *trans*-nonachlor, and heptachlor), and chlorobenzenes (CBz; tetra-, penta-, and hexa-CBz) were measured in the bird liver tissues. Sixteen PFASs, comprising perfluoropentanoic acid (PFPeA), perfluorohexanoic acid (PFHxA), perfluoroheptanoic acid (PFHpA), perfluorooctanoate (PFOA), perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA), perfluoroundecanoic acid (PFUnDA), perfluorododecanoic acid (PFDoDA), perfluorotridecanoic acid (PFTrDA), perfluorotetradecanoic acid (PFTeDA), perfluorohexadecanoic acid (PFHxDA), perfluorooctadecanoic acid (PFOcDA), perfluorobutane sulfonate (PFBS), perfluorohexane sulfonate (PFHxS), perfluorooctane sulfonate (PFOS), and perfluorodecane sulfonate (PFDS) were also measured in the samples. PCBs (CBs 103, 198, and 209; AccuStandard, New Haven, NJ, USA) were spiked as surrogate standards for OC analysis before extraction. ^{13}C-labelled PCBs (CBs 28, 52, 118, 153, 180, 202, 206, and 209; EC-9605-SS, Wellington Laboratories; Guelph, ON, Canada), ^{13}C-labelled CBz (MCBS; 1,2,3,4-TeCBz, penta- and hexa-CBz; Wellington Laboratories), and ^{13}C-labelled PFASs ($^{13}C_4$-PFOA, $^{13}C_5$-PFNA, $^{13}C_2$-PFDA, $^{13}C_2$-PFUnDA, $^{13}C_2$-PFDoDA, and $^{13}C_4$-PFOS; MPFAC-MXA, Wellington Laboratories) were used as internal standards for the quantification of PCBs, OCPs, and PFASs. Ultra-residue grade dichloromethane (DCM) and hexane, and HPLC-grade methanol and methyl tert-butyl ether (MTBE) were purchased from J.T. Baker (Phillipsburg, NJ, USA). Pesticide analysis grade nonane was purchased from Sigma-Aldrich (St. Louis, MO, USA). Anhydrous Na_2SO_4 (pesticide analysis grade) and neutral silica gel were purchased from GL Sciences (Tokyo, Japan).

2.3. Experimental procedure

The determination of OCs in the liver samples was conducted following the methods described previously (Moon et al., 2009). In brief,