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The first exposure assessment of legacy and unrestricted brominated flame retardants in predatory birds of Pakistan☆

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ABSTRACT

The exposure to legacy polybrominated diphenyl ethers (PBDEs), hexabromocyclododecanes (HBCDDs) and unrestricted 1,2-bis (2,4,6-tribromophenoxy) ethane (BTBPE), bis (2-ethylhexyl)-2,3,4,5-tetrabromophthalate (BEH-TEBP) and 2-ethylhexyl-2,3,4,5-tetrabromo-benzoate (EH-TBB) was examined in tail feathers of 76 birds belonging to ten predatory species inhabiting Pakistan. In addition, different feather types of six individuals of Black kite (*Milvus migrans*) were compared for their brominated flame retardant (BFR) levels. Black kite was found to be the most contaminated species with a median (minimum-maximum) tail feather concentration of 2.4 (0.70–7.5) ng g^{-1} dw for ∑PBDEs, 1.5 (0.5–8.1) ng g^{-1} dw for ∑HBCDDs and 0.10 (<LOQ-0.1) ng g^{-1} dw for BTBPE. Among unrestricted BFRs, BTBPE was detected only in Black kite and Little owl (*Athene noctua*), whereas BEH-TEBP and EH-TBB were not detected in any species. BDE-47 was found to be the most prevalent BFR compound in aquatic species, while BDE-99 and -153 were more abundant in terrestrial species. For HBCDDs, α-isomer was generally recorded as the most prevalent BFR in both terrestrial and aquatic species. The concentrations of BFRs differed significantly (all $P < 0.01$) among species, trophic guilds and between habitats, the latter for PBDEs only ($P < 0.04$), whereas differences among taxonomic affiliations and groups with different feeding regimes were not significant ($P > 0.05$ for both). Similarly, no significant concentration differences were observed among different feather types (all $P > 0.05$) suggesting their similar exposure. While variables such as species, trophic guild and $\delta^{15}N$ values were evaluated as major predictors for BFR accumulation in the studied species, we predict that combined effects of just mentioned factors may govern the intra- and interspecific differences in BFR contamination profiles. We urge for further investigation of BFR exposure and potential toxicological effects in predatory birds from Asia with a more extensive sample size per species and location.

1. Introduction

To meet the criteria of fire safety regulations, production of flame retarding chemicals has been observed as a growing industry since the 1960s (Dasari et al., 2013). To date, several groups of brominated flame retardants (BFRs) have been commercially used

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in textiles, paints, thermoplastics, rubbers, polyurethane foams, building materials and a variety of electronic equipment to improve the fire resistance of products (de Wit, 2002; Alaee et al., 2003). There is a growing environmental concern for BFR contamination because these compounds have the capacity to persist and undergo long range transport in the environment, bioaccumulate in biota and biomagnify in food chains, and pose various health risks to humans and wildlife (Darnerud, 2003; Ezechiáš et al., 2014). Polybrominated diphenyl ethers (PBDEs) constitute a major and most concerning group of BFRs because of their large-scale use since the 1970s (Chen and Hale, 2010). Two of the commercially available mixtures, i.e. Penta- and Octa-BDE, have been listed as persistent organic pollutants (POPs) under the Stockholm Convention (Zhang et al., 2011) and are restricted in the European Union, China, Canada and USA while the use of Deca-BDE has diminished worldwide (UNEP, 2011). After the restrictions on PBDEs, alternative BFRs such as hexabromocyclododecanes (HBCDDs; also commonly referred to HBCDs) and a variety of other non-PBDE BFRs have been introduced to the global market (Wu et al., 2012). While HBCDDs have also recently been included in Annex A of the Stockholm convention (BSEF, 2016), the brominated compounds 1,2-bis (2,4,6-tribromophenoxy) ethane (BTBPE), bis (2-ethylhexyl)-2,3,4,5-tetrabromophthalate (BEH-TEBP) and 2-ethylhexyl-2,3,4,5 tetrabromobenzoate (EH-TBB) remain unrestricted as alternatives of legacy PBDEs (Covaci et al., 2011). All mentioned BFRs are used as additive FRs and thus readily leach from consumption products into the environment (Alaee et al., 2003; Covaci et al., 2006, 2011). Although few studies has been reported from China and Japan (Chen and Hale, 2010), very little is known about the contamination of birds through BFRs from the Asian continent, particularly from South Asian countries (Abbasi et al., 2016a).

Biomonitoring of environmental contaminants is best carried out through reliable sentinel species. Historically, predatory birds have been proven to be excellent sentinels for anthropogenic pollution (Chen et al., 2010; Gómez-Ramírez et al., 2014; Janák et al., 2008). Being at the top of their food chain, having relatively large home ranges and long life spans, as well as being dependent on various aquatic and terrestrial prey species, predatory birds are highly susceptible to contamination with BFRs and hence regarded as useful sentinels (Chen et al., 2007; Chen and Hale, 2010). Variation in levels of organohalogenated compounds (OHCs) including BFRs, among various tissues and feather types has also remained a topic of interest in recent avian ecotoxicological studies (Eulaers et al., 2014a, b; Jaspers et al., 2008; Voorspoels et al., 2006). Sacrificing living predatory birds for research purposes encounters various ethical and practical impediments. Therefore, non-invasive sampling, particularly the use of feathers as a biomonitoring tool, is highly encouraged (Dauwe et al., 2005; Eulaers et al., 2011a, b; García-Fernández et al., 2013; Jaspers et al., 2007).

In a number of recent studies, factors influencing intra- and interspecific variations of BFR concentrations in predatory birds have been highlighted (Eulaers et al., 2013, 2014b; Elliot et al., 2009, Kocagöz et al., 2014). Intra- and interspecific variation of BFR exposure in predatory birds is usually found to be associated with various ecological, biological and spatiotemporal variables (Eulaers et al., 2013, 2014b). In addition, the position of a species in the trophic food chain and dietary exposure are elucidated as major factors explaining the overall burden of BFRs in birds (Elliott et al., 2009; Ruus et al., 2002; Wu et al., 2009). The use of stable nitrogen and carbon isotopes (SIs) to quantify the feeding ecology of species are found as a valuable tool for exposure assessment studies (Jardine et al., 2006). The ratio of stable nitrogen SIs (^{15}N:^{14}N; $\delta^{15}N$) infers the trophic position of an individual, typically increasing 2–5‰ with each succeeding trophic level (Zhang et al., 2011). The ratio of stable carbon SIs (^{13}C:^{12}C; $\delta^{13}C$) then again typically delineates food chain-specific dietary carbon sources (Jardine et al., 2006; Yu et al., 2011).

During the last few decades, sharp declines in the population of predatory birds including some important vulture species have been observed in Pakistan (Prakash et al., 2003). Toxicity through OHC exposure has been suggested as a potential factor contributing to this population decline (Abbasi et al., 2016a, b). So far, there is merely a single report on the levels of PBDEs in colonial waterbirds of Pakistan (Malik et al., 2011). Seeing the scarcity of baseline data on exposure of BFRs in predatory birds, the current study was designed to investigate the levels of the legacy PBDEs and HBCDDs along with some of their unrestricted alternatives, such as BTBPE, BEH-TEBP and EH-TBB, in predatory bird species of Pakistan. Further, we evaluated several factors governing the interspecific variation for BFR concentrations in predatory birds, while intraspecific variations in BFR levels was studied using carbon ($\delta^{13}C$) and nitrogen ($\delta^{15}N$) SIs. Finally, we have also evaluated the suitability of different feather types based on their specific accumulation of BFRs.

2. Materials and methods

2.1. Field sampling

Sampling was carried out between June 2012 and September 2014 at different localities, i.e. Punjab, Sind and Northern Pakistan (Fig. 1). Information about sampling of species and number of individual samples at each site is given in Table S1. Feather samples from 76 different individuals belonging to 10 species of predatory birds were collected. The investigated species included Black kite (*Milvus migrans*, $n = 13$), Eurasian sparrowhawk (*Accipiter nisus*, $n = 10$), Common kestrel (*Falco tinnunculus*, $n = 4$), Red-necked falcon (*Falco chicquera*, $n = 2$), Indian vulture (*Gyps indicus*, $n = 9$), White-rumped vulture (*Gyps bengalensis*, $n = 12$), Spotted owlet (*Athene brama*, $n = 10$), Little owl (*Athene noctua*, $n = 6$), Great cormorant (*Phalacrocorax carbo*, $n = 4$) and Grey heron (*Ardea cinerea*, $n = 6$). Except for three species which were sampled from two different sites (Table S1, Fig. 1), i.e. Black kite (S7, S11), Eurasian sparrowhawk (S5, S8) and Spotted owlet (S6, S12), all species were sampled at only one sampling site. Most of the samples were collected from the birds captured at outskirts of small or large cities and towns of the Punjab province (S3 to S12), and are therefore possibly influenced by anthropogenic BFR sources. Samples from two Vulture species were obtained from their isolated colonies at Nagar Parker, Sindh province (S1 and S2) which is a relatively remote location. Similarly, Grey herons were sampled at Lulusar Lake (S13), considered to be a pristine water reservoir in northern Pakistan. A special permit from CITES (Convention on international trade of endangered species) was obtained for shipping and transport of samples of two critically endangered Vulture species. While tail feathers were collected from all birds, six individuals of Black kite were sampled for body, tail, primary and secondary feathers as well, in order to compare concentrations among different types of feather. After collection, feathers were packed in plastic zipped bags and stored at −20 °C prior to analysis.

2.2. Analysis for brominated flame retardants

The targeted BFR compounds were extracted from feathers at the Bird Ecotoxicology laboratory, Norwegian University of Science and Technology (NTNU, Trondheim, Norway), and quantified at the Toxicological Centre, University of Antwerp (Wilrijk, Belgium). The procedure for the analysis of BFRs was adapted from the method previously reported by Eulaers et al. (2011a, b, 2014a, b). Briefly, all feathers were vigorously rinsed with distilled water, using stainless steel tweezers, and subsequently dried overnight at ambient

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