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Legacy and current-use brominated flame retardants in the Barn Owl

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HIGHLIGHTS

- Reactive (TBBPA) and additive BFRs (PBDEs, HBCD) bioaccumulate differently.
- TBBPA was only sporadically detected in tissues, but present in body feathers.
- All tissues showed regional variation in HBCD and PBDE, but not TBBPA, exposure.
- HBCD levels in feathers, but not in tissues, surpassed those of legacy PBDEs.
- PBDE and HBCD levels in body feathers closely reflected those in liver and muscle.

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ABSTRACT

The present study investigated the current-use brominated flame retardants (BFRs) tetrabromobisphenol A (TBBPA) and hexabromocyclododecane (HBCD), simultaneously with legacy polybrominated diphenyl ethers (PBDEs), in Barn Owls (*Tyto alba*) collected from two regions with a contrasting degree of urbanisation and vicinity to point sources (Flanders in Belgium versus Normandy in France). Both tissues (muscle, liver, adipose and preen gland) and feathers (primary, tail and body feathers) showed elevated HBCD concentrations in Flanders, close to Europe's sole HBCD production plant in the Netherlands, and identified Normandy as a historical source region for PBDEs. In sharp contrast, the reactive BFR TBBPA bioaccumulated poorly (2.3%) in tissue samples, but was present in 96% of all body feather samples (0.36–7.07 ng g^{-1} dw), equally in both regions. PBDE concentrations in tissues (7.46–903 ng g^{-1} lw) were considerably lower in the investigated Flemish Barn Owls, collected in 2008/2009, compared to specimens collected in 2003/2004 (46–11,000 ng g^{-1} lw), possibly suggesting the effectiveness of the 2004 European ban of Penta- and Octa-BDE mixtures. Feathers showed a similar trend and additionally exhibited HBCD concentrations (0.02–333 ng g^{-1} dw) surpassing those of PBDEs (0.50–10.4 ng g^{-1} dw). While body feathers were a reliable matrix to predict both internal PBDE ($0.21 \leq R^2 \leq 0.67$) and HBCD body burdens ($0.20 \leq R^2 \leq 0.37$), the suitability of primary and tail feathers appeared to be confounded by external contamination and moult. In conclusion, the present study clearly showed that the reactive versus additive use of BFRs results in contrasting exposure scenarios in a species higher up the food chain, and therefore may have profound implications for environmental health. In addition, the presented results extend the promising use of feathers as a non-destructive sampling strategy for current-use BFRs, and show that birds of prey are valid early-warning systems for environmental contamination.

1. Introduction

Since the 1970s, brominated flame retardants (BFRs) have been chemically incorporated in consumption products in order to increase their fire resistance. The growth of their cumulative production volume, from 150,000 t y^{-1} in 1992 (de Wit, 2002) to exceeding 200,000 t y^{-1} in 2007 (Bergman et al., 2012), illustrates their increasing presence in consumption products, such as plastics, textiles, insulation materials and electrical and electronic equipment (Covaci et al., 2006, 2009; de Wit, 2002). Presently, the larger part of the BFR production volume is composed of the high volume tetrabromobisphenol A (TBBPA), covering about 60% (Covaci et al., 2009), and hexabromocyclododecane (HBCD; Kemmlein et al., 2009). Aside from their specific use, both are possible alternatives in some applications for the legacy polybrominated diphenyl ethers (PBDEs; Covaci et al., 2006, 2009). At present day, their production and use are restricted on a European (Directive, 2003/11/EC; ECJ, 2008) and largely worldwide scale (SC, 2013) due to

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their persistent, bioaccumulative and toxic (PBT) properties (de Wit, 2002). Like PBDEs, HBCD is an additive BFR, and its PBT properties as well as its ubiquitous environmental occurrence have been evidenced (Covaci et al., 2006; Sun et al., 2012). In contrast, TBBPA is likely to leak less into the environment as it is produced in closed systems and is largely (58%) used as a reactive BFR, being covalently bound to the polymeric backbone of the resin (Covaci et al., 2009). Although HBCD and TBBPA are suspected to be PBT and degradation products have been identified (de Wit, 2002; de Wit et al., 2010), their production and use are currently not restricted. However, both are currently under review of REACH (Kemmlein et al., 2009) and their emissions are voluntarily being reduced (BSEF, 2013). Furthermore, the UNEP Stockholm Convention on Persistent Organic Pollutants has commended the elimination of HBCD, with specific exemptions (SC, 2013).

Historically, birds of prey have shown their validity as early warning systems for anthropogenic pollution (Furness, 1993; Ratcliffe, 1970) and several recent studies have shown their sensitivity to HBCD and TBBPA exposure at the reproductive, hormonal and immunological functioning (Fernie et al., 2009, 2011; Marteinson et al., 2011, 2012). Nevertheless, the existing exposure data are not yet as substantial as for PBDEs (reviewed by Chen and Hale, 2010). HBCD has been analysed in eggs of White-tailed Eagle (*Haliaeetus albicilla*; Janak et al., 2008; Nordlöf et al., 2010), Peregrine Falcon (*Falco peregrinus*; Guerra et al., 2012; Janak et al., 2008; Johansson et al., 2009, 2011; Leslie et al., 2011; Lindberg et al., 2004; Vorkamp et al., 2005) and different owl species (Bustnes et al., 2007; Jaspers et al., 2005). Although HBCD has also been successfully analysed in tissues of non-predatory bird species (He et al., 2010; Hong et al., 2013; Lundstedt-Enkel et al., 2005, 2006; Morris et al., 2004; Sørmo et al., 2011; Verreault et al., 2007; Vorkamp et al., 2012), to present day; only muscle of the predatory Eurasian Sparrowhawk (*Accipter nisus*) has been analysed for HBCD (Leslie et al., 2011). Tissue concentrations of TBBPA in birds of prey are similarly underrepresented, although such analysis seems analytically and ecologically feasible given positive results for lower tropic level species (He et al., 2010; Morris et al., 2004). Egg concentrations for Peregrine Falcon, White-tailed Eagle, Osprey (*Pandion haliaetus*) and Golden Eagle (*Aquila chrysaetos*) were nonetheless reported, albeit below the limit of quantification or in very low concentrations (Herzke et al., 2005; Vorkamp et al., 2005). In conclusion, to the best of our knowledge, data on internal body burdens in predatory bird species are very limited and the tissue distribution of HBCD or TBBPA in any bird species is virtually unknown.

The Barn Owl (*T. alba*) has been shown a valuable model species to study exposure to and effects of a wide variety of environmental pollutants, amongst which rodenticides (Sheffield, 1997), radionuclides (Kitowski et al., 2008; Sheffield, 1997), toxic metals (Dauwe et al., 2003; Sheffield, 1997), and organohalogenated compounds (OHCs; Jaspers et al., 2006, 2013; Sheffield, 1997). Its wide geographical distribution facilitates the study of larger-scale variation, while concurrently offering a high spatial resolution due to its residential foraging behaviour (Birdlife International, 2013). Samples can be relatively easily obtained from road-kill or from nest-boxes, which generally show high occupancy rates (Meyrom et al., 2009). Lastly, their use in pest management is economically and ecotoxicologically advantageous over the use of rodenticides, which cause secondary poisoning in non-target species (Paz et al., 2013).

Sampling birds of prey is often impeded by practical and ethical aspects. Therefore non-destructive sampling strategies are greatly encouraged. The present study employed two such strategies, i.e. necropsy of road-kill specimens and the sampling of feathers. While good necropsy practices are established (Eurapmon, 2013), certain aspects of using feathers, although a promising strategy, still require validation (Eulaers et al., 2011a; Garcia-Fernandez et al., 2013). While feathers reflect internal body burdens for a wide range of OHCs (Eulaers et al., 2011b; Jaspers et al., 2007, 2013), their suitability for current-use BFRs has not yet been evaluated. In addition, Jaspers et al. (2011) compared recently the suitability of different types of White-tailed Eagle feather and concluded that the levels in body feathers were 10-fold higher than those in primary and tail feathers. A similar investigation on terrestrial species is required, as we hypothesise different preening behaviour, and consequently external contamination. Finally, above-mentioned investigations of feathers as bio-indicators of internal concentrations remained correlative, rather than reporting parameters on which predictions of the internal body burden can be made.

The present study investigated how the contrasting reactive versus additive use of TBBPA and HBCD affects internal body burdens (muscle, liver and adipose) in a terrestrial bird of prey, the Barn Owl, and how they benchmark against legacy PBDEs. Lower detection of and exposure to TBBPA were expected as its reactive use should result in less environment leaching and consequently lower wildlife exposure (Covaci et al., 2009), in sharp contrast to the additive HBCD (Covaci et al., 2006). In order to answer the need to investigate regional variation in (assumed) background exposure (Covaci et al., 2006), the Barn Owls were collected in two regions with variable degree of urbanisation and vicinity to Europe's sole HBCD production plant. Due to their additive use, regional variation in HBCD and PBDE exposure was expected, in contrast to similar regional exposure for the reactive TBBPA. In addition to this spatial aspect, a temporal comparison of PBDE levels will be made with those reported for Barn Owls collected in 2003/2004 (Jaspers et al., 2006, 2007), in order to contribute to the recently prioritised evaluation of the effectiveness of the ban of PBDEs (SC, 2013). Further, the suitability of different types of feather (primary, tail and body feathers) as non-destructive bio-indicators for internal body burdens will be investigated. In this respect, the possible influence of external contamination and feather moult will be investigated.

2. Material and methods

2.1. Sampling

During 2008 and 2009, the Barn Owl Study Group (Kerkuilwerkgroep) collected road-killed Barn Owls ($n = 15$), in Flanders, Belgium while the Association of CHENE (Centre d'Hebergement et d'Etude sur la Nature et l'Environnement) operated similarly in Normandy, France ($n = 11$; Fig. 1). In this regional comparison, Flanders has an intermediate degree of urbanisation (<50% of the inhabitants live in rural grid cells), which is higher compared to thinly populated Normandy (>50% of the inhabitants live in rural grid cells; EC Eurostat, 2013). Furthermore, Flanders is situated closer to Europe's sole HBCD production plant in the Netherlands (BSEF, 2013; Fig. 1).

All collected specimens were stored frozen at −20 °C until necropsy. Those collected in Flanders were dissected for pectoral muscle and liver, and, when possible, preen gland and adipose tissue were obtained as well. An identical effort by the Association of CHENE was supplemented with the collection of brain tissue, for which, due to the limited sample size ($n = 7$) and the impossibility for regional comparison, concentrations are only reported in the Supplementary information but were not further discussed (Table SI-1). Dissections were performed using stainless steel tools rinsed thoroughly with acetone between tissues and individuals. Different types of feathers were collected as well: sternal and dorsal body feathers (pooled for Normandy), and the right outermost primary and tail feathers. Tissues were preserved in polystyrene containers at −20 °C, feathers in paper envelopes at ambient temperature.

2.2. Chemical analyses

The tissue analysis was adapted from the protocol earlier described by Roosens et al. (2010). Briefly, subsamples of tissues were weighed (Table 1), homogenised and mixed with anhydrous Na_2SO_4, and subsequently spiked with internal standards (100 pg μL^{-1} BDE 77 + 400 pg μL^{-1} ^{13}C-α-HBCD + 100 pg μL^{-1} ^{13}C-β-HBCD + 200 pg μL^{-1} ^{13}C-γ-HBCD + 100 pg μL^{-1} ^{13}C-TBBPA). The tissues were extracted for