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Detailed analysis of polybrominated biphenyl congeners in bird eggs from Norway

Walter Vetter [a,*], Roland von der Recke [a], Dorte Herzke [b], Torgeir Nygård [c]

[a] University of Hohenheim, Institute of Food Chemistry, Garbenstrasse 28, DE-70593 Stuttgart, Germany
[b] Norwegian Institute for Air Research (NILU), NO-9296 Tromsø, Norway
[c] Norwegian Institute for Nature Research (NINA), Tungasletta 2, NO-7485 Trondheim, Norway

We provide for the first time detailed information on the PBB congeners present in eggs of bird of prey, and quantified three hexabromo congeners.

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ABSTRACT

Individual eggs of six species of birds from Norway representing different food chains were analysed for residues of polybrominated biphenyls (PBBs). In all species, the residue pattern was dominated by hexaBBs. The dominating congeners were PBB 153, PBB 154, and PBB 155. Whereas PBB 153 is present in technical hexabromobiphenyl, PBB 154 and PBB 155 are formed by the reductive debromination of decabromobiphenyl. This was evidenced by the detection of several heptaBBs and octaBBs all of which are typical degradation intermediates of PBB 209. Hepta- and octaBBs were more than one order of magnitude less abundant than the hexaBBs. The second most prevailing homologue group was pentaBBs. The most relevant pentabrominated isomers were PBB 99 and PBB 101. Concentrations of the three hexaBBs – PBB 153, PBB 154, and PBB 155 – amounted to 1.3–13 ng/g wet weight or 3–23% of the contamination with polybrominated diphenyl ethers.

1. Introduction

Polybrominated biphenyls (PBBs) have been extensively applied as flame retardants in textiles, electronic equipment and plastics (de Boer et al., 2000). Three different technical mixtures have been produced and distributed: technical hexabromobiphenyl (THBB), technical octabromobiphenyl (TOBB), and technical decabromobiphenyl (TDBB). PBBs exist in a theoretical variety of 209 congeners but the technical products contained only limited numbers of congeners (de Boer et al., 2000). THBB which contains ~54% PBB 153 (Robertson et al., 1984) was marketed under the trade names Firemaster BP-6 and Firemaster FF-1. TOBB (e.g. Bromkal 80 and FR 250 14A) mainly constituted of PBB 194 and PBB 206 whereas TDBB (e. g. Flammex-B and Adine 0102) consisted of ~97% decabromobiphenyl (PBB 209).

An accidental contamination of cattle feed with PBBs in Michigan (1973) revealed the environmental risk of this group of flame retardants (Getty et al., 1977; Kay, 1977). As a consequence, the worldwide annual production continuously decreased since the late 1970s. Nevertheless, PBB levels in the environment were only slightly declining since then. Moreover, the ubiquitous presence of PBBs has been documented in a wide range of samples (Luross et al., 2002; Herzke et al., 2005; de Wit et al., 2006; Hites, 2006). Noteworthy, most of the data available is based on PBB 153 (Jansson et al., 1993). Depending on species, the concentration of PBB 153 alone amounted for up to 13% of the sum of PBDEs in eggs of bird of prey (Herzke et al., 2005). As a consequence, a global ban is under discussion for "hexabromobiphenyl" (UNEP, 2006).

However, an assessment of residues of brominated pollutants in wild bird eggs indicated the presence of several other abundant PBB congeners (Herzke et al., 2005). Occasionally, PBB 101 (Braune et al., 2007; Herzke et al., 2005), PBB 155 (Watanabe et al., 2004), PBB 132 and PBB 149 (Götsch et al., 2005) were determined as well. However, both Watanabe et al. (2004) and Herzke et al. (2005) mentioned the presence of several unknown penta- to octaBBs in bird eggs. In another study, PBBs could not be quantified in samples because PBB standards were not available (Karlsson et al., 2006). All studies have in common that the analysis of PBBs was suffering from a lack of environmentally relevant reference standards.

* Corresponding author. Tel.: +49 711 459 24016; fax: +49 711 459 24377.
E-mail address: w-vetter@uni-hohenheim.de (W. Vetter).

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Recently, it was found that PBB residues in marine mammals mainly originated from hexabromo isomers followed by pentabromo isomers (von der Recke and Vetter, 2008a). Furthermore, it was shown that residues in North American marine mammals mainly consisted of PBB 153 whereas in European samples, this key congener of THBB was little abundant (von der Recke and Vetter, 2008a). Thus, attempts were undertaken to identify a range of PBB congeners formed by anaerobic and photolytic degradation of higher-brominated biphenyls (von der Recke and Vetter, 2007, 2008b). In the present study, we explored the full range of PBBs in bird egg samples from Norway. Birds of prey are important indicator organisms for anthropogenic pollution, owing to their high trophic position in the food web.

2. Materials and methods

2.1. Bird egg samples

Eggs of white-tailed sea eagle *Haliaeetus albicilla* were collected along the Norwegian coast between 61 and 68° north (latitude). The peregrine falcon *Falco peregrinus* eggs came from the southern and western coast 60–65° north. Eggs of the European shag (*Phalacrocorax aristotelis*) were from Sklinna, a seabird sanctuary at 65°15′ north. Merlin *Falco columbarius* eggs were sampled from both inland and coastal sites from south to north. The golden eagle *Aquila chrysaetos* eggs were sampled from most of Norway's mountain range, 62–69° north. The goshawk *Accipiter gentilis* eggs were from the central part of the country, mainly between 63 and 64° north. All eggs were analysed separately (see Herzke et al., 2005, for details). Since the eggs analysed were addled eggs, no information on egg number is known. The age of the mother bird remained unknown as well.

2.2. Chemicals

Synthesis, isolation, and/or peak assignment of individual PBB congeners (for structures, see below) have been described in details elsewhere (von der Recke and Vetter, 2007, 2008b; Berger et al., 2002). 4,6-Dibromo-2-(2′,4′-dibromo)-phenoxyanisole (2′-MeO-BDE 68, BC-2) was previously synthesized in our research group and used as internal standard for GC/MS analysis (Vetter and Wu, 2003). Technical hexabromobiphenyl (THBB) and technical octabromobiphenyl (TOBB) were purchased from ULTRA Scientific (North Kingstown, USA). Solutions with PBB congeners which could not be weighed were calibrated by GC/FID as recently described (von der Recke and Vetter, 2007).

2.3. Sample preparation

Sample clean-up was performed according to Herzke et al. (2002). In brief, homogenized eggs were blended with a 10-fold amount of dry Na_2SO_4 and cold-extracted with cyclohexane/acetone (v/v, 3:1). Aliquots were taken for the gravimetric determination of the lipid content. The bulk of the sample was purified using gel-permeation chromatography followed by fractionation on a florisil column. $^{13}C_{12}$-BDE 77 was used as internal standard. Octachloronaphthalene (10 ng in isooctane) acting as a recovery standard was added prior to quantification (Herzke et al., 2002).

2.4. Gas chromatography coupled with electron capture negative ion tandem mass spectrometry in the selected reaction monitoring mode (GC/ECNI-MSMS-SRM)

Analyses were carried out with a CP-3800/1200 triple–quadrupole system (Varian, Darmstadt, Germany) using the parameters described elsewhere in details (von der Recke and Vetter, 2007; von der Recke et al., 2005). The key settings were as follows: methane and argon were used as reagent and collision gases, respectively. A DB5-like 30 m × 0.25 mm i.d. × 0.25 μm film thickness Factor Four CP-Sil 8MS column (Varian) was installed in the GC oven (von der Recke and Vetter, 2008b). GC/ECNI-MSMS-SRM (collision voltage 12 V, and detector voltage 2000 V) analyses were based on the most abundant isotope peak (peak width ± 3 u) of the molecular ions of di- to octabromobiphenyls as precursor ion and the bromide ion isotopes (m/z 78.5–81.5) as product ions (von der Recke and Vetter, 2007). NonaBBs and PBB 209 were determined using m/z 785.4 ± 3.0 as precursor ion (isotopic peaks of $[M-Br]^-$ and $[M-2Br]^-$, respectively) due to the upper mass limit of the instrument (m/z 800) (von der Recke and Vetter, 2007). GC/ECNI-MSMS was used for the assignment of PBB structures to peaks in the chromatograms as well as for the calibration of a solution with PBB 153, PBB 154, and PBB 155 (von der Recke and Vetter, 2008a).

2.5. Gas chromatography coupled with electron ionization mass spectrometry in the selected ion monitoring mode (GC/EI-MS-SIM)

Analyses were performed with an 8560 Mega gas chromatograph (CE Instruments, Milan, Italy) in combination with an MD 800 mass spectrometer (Finnigan, San Jose, CA, USA) using the parameters described by Herzke et al. (2005). A 30 m DB5-MS column (0.25 mm i.d. and 0.25 μm, film thickness; J&W, Folsom, USA) fitted with a guard column (0.53 mm i.d., 2.5 m length deactivated, J&W) and a restriction capillary (0.18 mm i.d., 1.5 m length deactivated, J&W) was installed in the GC oven. In the SIM mode, m/z 547.6 was used for quantification and m/z 549.6 for verification of hexaBBs. Representative fragment ions of other degrees of bromination were monitored as well (Herzke et al., 2005). The method detection limits (signal/noise ratio of three) for PBBs ranged between 1 and 2 ng/g wet weight. PBB 153 was quantified against a quantitative solution of this congener, whereas GC/EI-MS-SIM results of PBB 154 and PBB 155 were corrected by the relative response as determined with GC/FID and GC/ECNI-MSMS-SRM (see above).

3. Results and discussion

3.1. PBB congener pattern in bird eggs

A first pre-screening of the samples showed that virtually the same PBBs were present in all species albeit at different relative abundances (see below). A white-tailed sea eagle egg was chosen for a detailed determination of PBB congeners because this species was found to bear the highest PBB load among the bird eggs analysed so far in Norway (Herzke et al., 2005). A range of penta- through octaBBs was detected in this sample (Fig. 1a–d).

3.1.1. OctaBBs

Neither nonaBBs nor PBB 209 were observed in this egg. However, the presence of octaBBs (Fig. 1a) unequivocally verified that some of the pollution was caused by the previous release of TOBB or TDBB into the environment because octaBBs were not detected in THBB (von der Recke and Vetter, 2008b). In addition, the octabromo congeners PBB 197, PBB 201, and PBB 202 are neither present in TOBB nor can they be formed from any precursor in this mixture except PBB 209, i.e. the principal compound of TDBB (von der Recke and Vetter, 2007). These octaBBs were identified for the first time in bird eggs (Fig. 1a) and this alone proves that some of pollution originated from weathered PBB 209.

The commercial synthesis of PBBs is driven by the subsequent introduction of Br at specific positions. Thus, the dominating congeners in THBB acted as precursors of the PBBs found in TOBB, and these in turn are precursors of PBB 209 (Fig. 2). On the other hand, the anaerobic or photolytical debromination of BDE 209 is following a completely different route. As a consequence, the isomer spectrum obtained in both processes was completely different (Fig. 2). If the debromination took place prior uptake by the mother bird or *in situ* in the mother organism or later in the egg is not known.

3.1.2. HeptaBBs

That significant proportion of the PBBs in the birds originated from previous release of TDBB into the environment was further evidenced by the heptaBB pattern. None of the heptaBBs labelled in Fig. 1b are present in TOBB but all of them were identified as debromination products of PBB 207, PBB 208 and PBB 209 (von der Recke and Vetter, 2007). These heptaBBs were identified for the first time in environmental samples. Although the peak intensities were one order of magnitude lower than the dominating hexaBBs, their presence in bird eggs is remarkable because octaBBs were only low abundant in marine mammals (von der Recke and Vetter, 2008a). Recently, it was shown that debromination of PBBs mainly occurs in *meta*- and *para*-positions (von der Recke and Vetter, 2007, 2008b). This relative enrichment in poly-*ortho*-substituted PBBs is accompanied with a shift of the elution range of groups of homologues to shorter retention times on nonpolar GC stationary phases. For instance PBB 180 – the major heptaBB and second most abundant congener in THBB – has a retention time similar to the octabromo isomer PBB 202, i.e. much later than the heptaBBs detected in the bird egg sample (Table 1). That PBB 180 was not