PBDEs in Heron Adipose Tissue and Eggs from the United Kingdom

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Introduction

Polybrominated diphenyl ethers (PBDEs) are flame retardants used extensively in a variety of materials. They have been shown to be ubiquitously distributed, persistent and toxic[1]. Fish-eating birds are, in particular, subject to accumulation of persistent organic pollutants[2] through ingestion of contaminated food. Herons (*Ardea cinerea*) are top-predators, typically feeding on fish, but they will also eat amphibians, molluscs, insects and even small rodents and birds[3].

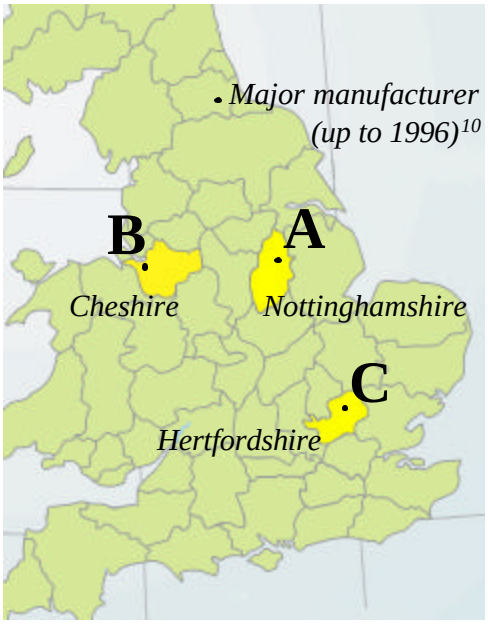


Figure 1. Sampling Sites

Bioaccumulation of certain environmental contaminants may result in deformities in growing birds and thinning of egg shells[4]. Recent investigations have detected elevated levels of mortality and bone disease in herons at a nesting site in the United Kingdom[5] (U.K.). This prompted a pilot study into assessing the level of environmental contaminants, such as PBDEs, in heron tissue and eggs from three sites across the U.K. (Figure 1). The sampling sites included an established heronry in Nottinghamshire (Site A), as well as nests in Cheshire (Site B) and Hertfordshire (Site C). Site A is located on a flood plain on the eastern bank of the River Trent, which flows through densely populated and industrialised areas, from the west midlands to the Humber estuary. Nests at site B were located in rural woodland, and site C is located nearby a reservoir neighbouring the Grand Union Canal.

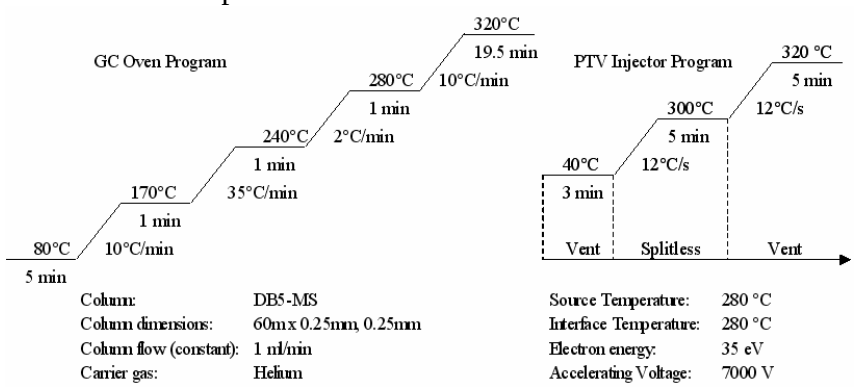
Methods

Adipose samples were collected during 2002-2003 from dead, or euthanised, juveniles and chicks from a heronry at site A, further samples were taken from adult birds found dead from gunshot wounds near site A. Eggs were collected under licence from nests at sites A, B, and C during 2003. At each site adipose tissue samples and eggs were pooled into groups corresponding to nest location or the physiological condition of the bird, i.e. diseased or deformed.

The accredited (ISO 17025) analytical method used is outlined in more detail elsewhere[6]. In short, the freeze dried samples were fortified with $^{13}C_{12}$ mass labelled PBDEs 28, 47, 99, 153, 154, 183 (Wellington Labs). The samples were extracted using hexane with high speed blending followed by open column chromatography on acid modified and base modified silica gel. Further purification was carried out using acid and base modified silica followed by alumina chromatography.

Sixteen PBDEs were determined, namely PBDE 17, 28, 47, 49, 66, 71, 77, 85, 99, 100, 119, 126, 153, 138, 154 & 183. ∑PBDE levels quoted are the sum of all 16 congeners determined, analytes detected at less than LOD (0.05 µg/kg lipid) were recorded as upper bound. Determination was by high resolution gas chromatography - high resolution mass spectrometry (HRGC-HRMS, Autospec Ultima, Micromass). The instrument was operated in selected ion monitoring mode, two ions monitored for each analyte, mass resolution typically 10,000 at 10% peak height. Extracts were chromatographed on a 60m DB5-MS column (Figure 2). A cryogenically cooled programmed temperature vaporisation (PTV) injector was used (Gerstel CIS4), injection volumes typically 10µl. Acceptance criteria followed were analogous to those used for the analysis of chlorinated dioxins and furans[7].

Figure 2. Instrumental parameters



Results and Discussion

PBDEs were detected at varying levels in all of the heron fat and egg samples. ∑PBDE levels were typically higher in heron fat than eggs from the same area (Figure 3). Interestingly the percentage contribution of higher brominated (hexa to hepta) congeners was higher in the eggs (ca. 20%) than the fat (ca. 11%). This could be due to variations in environmental levels between sampling dates. Another hypothesis is that the more lipophilic, higher brominated congeners accumulate in the fat rich egg sac. Levels in adipose tissue from site A ranged from ∑PBDE 1.36-2.27 µg/g lipid. Levels in adult birds from near site A were higher; ∑PBDE 2.91 µg/g lipid (Figure 4). Different food sources (e.g. tributary or reservoir), localised point sources or bioaccumulation may explain the elevated levels observed in the adult birds.

The appreciable levels found in adipose and eggs were in the same order as those found in other predatory species, such as Peregrine Falcon and Sparrowhawk from mainland

Europe[8]. To the authors knowledge this is the first time PBDEs have been reported in heron samples and the levels detected are among the highest reported in avian egg samples from the United Kingdom. Average congener profiles for both egg and fat samples were similar to those reported for cormorants from the U.K.[9]. Typically BDE-47 was the dominant congener and contributed ca. 40-50% of the total PBDE detected in eggs and fat.

The highest levels were detected in eggs from site C (Figure 5); ∑PBDE 4.12 µg/g lipid. Interestingly, BDE-183 contributed a higher proportion (>1%) of ∑PBDE from the Cheshire site than seen at the other three sites (typically <0.2%). BDE-183 is a 'marker' congener for both the OctaBDE and DecaBDE commercial formulations.

Figure 3. Comparison of PBDEs in Heron fat and Eggs from the same site (Site A)

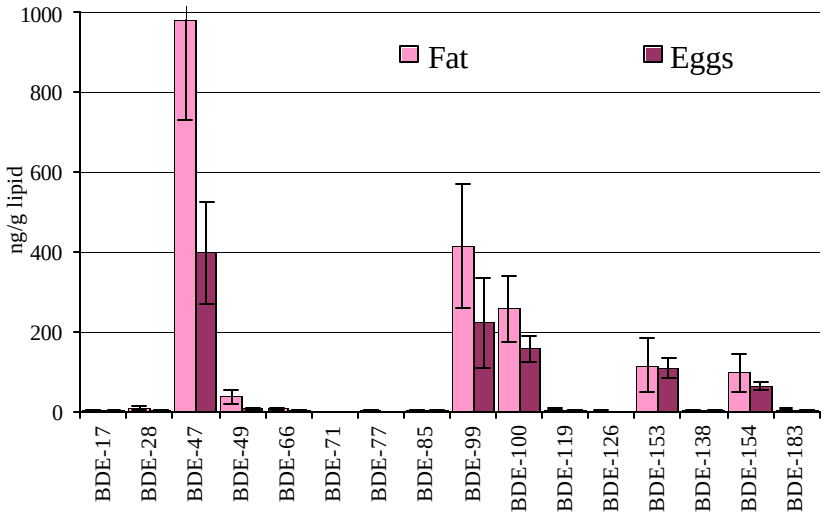
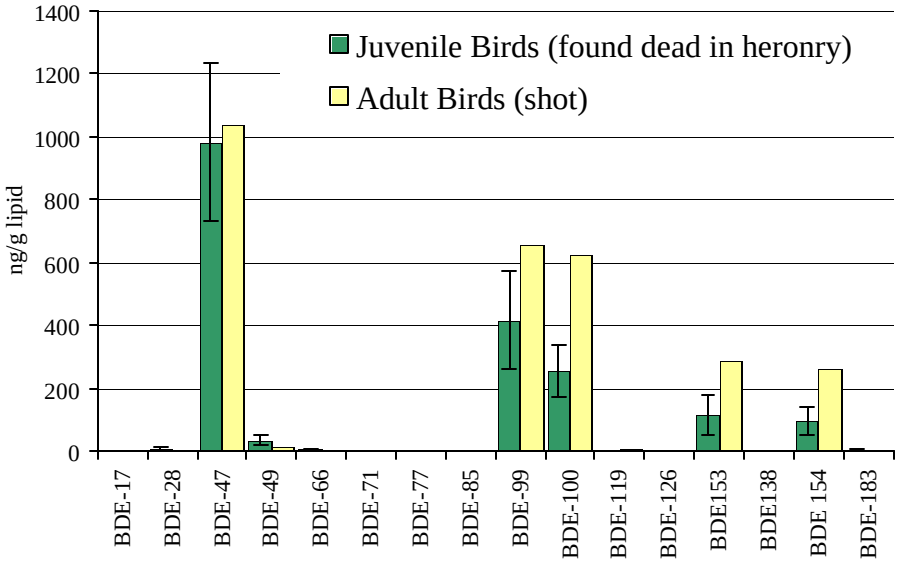


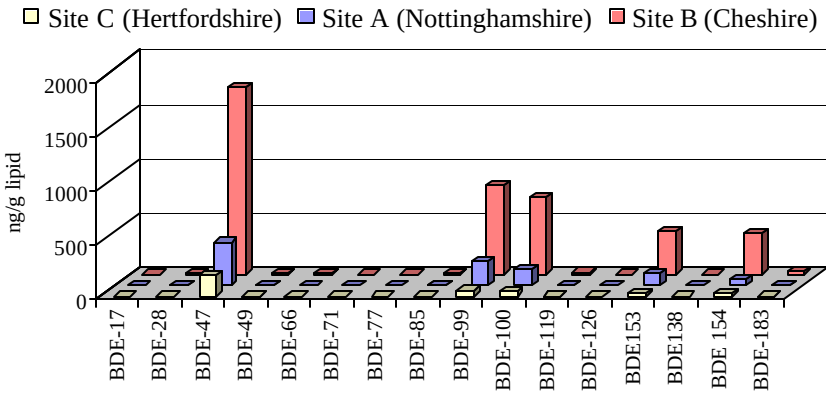
Figure 4. Comparison of mean PBDE levels in Heron fat from the Trent valley



Conclusions

PBDEs are prevalent as contaminants in herons from the U.K., typically at the low parts per million (ppm) lipid weight range. When corrected for lipid weight, levels detected were in agreement with those reported for cormorant livers from U.K[9]. It is uncertain why the highest levels detected were in Cheshire, further investigations are planned. To date PBDEs have only been manufactured at a single site in the U.K., located in the North East[10] (Figure 1). However, heavy manufacturing industry in Cheshire, especially surrounding the River Mersey, could well explain the high levels detected. Further research is required to established if the levels detected are toxicologically significant to herons and other avian species. Research is planned to assess possible relationships between PBDEs and other environmental contaminants upon bone deformities and eggshell thinning in herons.

Figure 5. Average PBDE levels in Heron Eggs from UK nesting sites



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