# POLYBROMINATED DIPHENYL ETHERS (PBDEs) IN BIRD EGGS FROM SOUTH AFRICA

Polder A[1], Bester B[2], Skaare JU[1,3]. Bouman H[2]

[1]The Norwegian School of Veterinary Science, P.O. Box 8146 Dep., N- 0033 Oslo, Norway.
[2]North-West University, P.B. X6001, Potchefstroom 2520, South Africa.
[3]National Veterinary Institute, P.O. Box 8156 Dep., N-0033 OSLO, Norway

## Introduction

Brominated flame retardants (BFRs) and in particular polybrominated diphenyl ethers (PBDEs) are used worldwide in combustible materials, such as plastics, electronic equipment, and textiles, to prevent fire[1]. Since the chemical structures are very similar to those of polychlorinated biphenyls (PCBs), these substances have been transported in similar ways to places far from the production sites and have contaminated different food chains. As a result of this BFRs are found in wild living species in industrialized countries as well as in remote areas around the North Pole where their presence is well documented[2,3]. The PBDEs, and especially penta- and octa-BDEs have been shown to be toxic[4]. Countries of the European Union (EU) have therefore banned these mixtures[5]. In the United States, the industry voluntary discontinued the production of penta- and octa-BDEs in 2005[6].

Very little is known about the environmental contamination with BFRs in the Southern Hemisphere. This lack of knowledge includes humans as well as wild life. As far as we know, no other studies have so far been carried out on PBDEs in avian wild life in South Africa and this study presents therefore the first findings of levels of PBDEs in eggs of different bird species in South Africa.

## Materials and Methods

*Sampling of eggs*

Prior to the field season necessary permissions and export/import licenses were obtained from the appropriate authorities concerning the sampling of eggs of some endangered species, and for local and international transport of the eggs (Convention on International Trade in Endangered Species of Wild Fauna and Flora (CITES)). During a period of five months (the summer period from November 2004 to March 2005), 43 eggs from eight different bird species were collected from different localities in South Africa (Table 1). Collection of eggs along the Vaal River were done downstream of the most industrialized area in South Africa which stretches far around Johannesburg. Barberspan Bird Sanctuary is situated 300 km to the west of Johannesburg, whereas the place Koppies, characterized by agricultural activities is situated near a side river of the Vaal, about 150 km south of Johannesburg. Velddrif is a place located along the coastline in the Western Cape Province, about 1500 km from Johannesburg. The eggs were kept cool while transporting to the laboratory at Potchefstroom, where the total weight and dimensions were noted for further reference. The eggs were then wrapped in aluminum foil and frozen at $-20^0$ C. For the transport to Norway per courier the eggs were packed in individual plastic bags in a cooler box, supplied with 4 kg of dry ice, which guaranteed a temperature below 0 C until arrival.

Table 1 Description of the bird species and sampling sites in South Africa

| **English name** | **Latin name** | **Geography** |
|---|---|---|
| African darter | *Anhinga rufa* | Vaal River |
| Cattle egret | *Bubulcus Ibis* | Vaal River and Barberspan Bird Sanctuary |
| Reed cormorant | *Phalacrocorax africanus* | Vaal River |
| Sacred ibis | *Threskiornis aethiopicus* | Vaal River (Mimosa) |
| Crowned plover | *Vanellus coronatus* | Koppies (Ground dam) |
| Dabchick | *Tachybaptus ruficollis* | Koppies (Ground dam) |
| Whitefronted plover | *Charadrius marginatus* | Velddrif, Western Cape Province Salt pan |
| Kelp gull | *Larus dominicanus* | Velddrif, Western Cape Province Salt pan |

*Chemical analyses and determination of BDEs:*
Samples preparation and chemical analyses of BDEs were done in the Laboratory of Environmental Toxicology at the Norwegian School of Veterinary Science. The laboratory is accredited by Norwegian Accreditation for testing BFRs in biological material of animal origin according to the requirements of the NS-EN ISO/IEC 17025 (TEST 137). After the samples had defrosted the eggs were opened and the contents were homogenized using a small blender. The method for BDE determination included liquid extraction, clean up with sulphuric acid and GC-MS analysis. BDE-119, BDE-181 and $^{13}$C-BDE-209 (Cambridge Isotope Laboratories, Inc., Andover, MA, USA) were used as internal standards. The lipid determination was done gravimetrically. Aliquots (1µl) of the concentrates were automatically injected (Agilent Auto sampler, Agilent Technologies, Avondale, PA, USA) and the gas chromatographic separation of BFRs was performed by a Hewlett Packard 6890 Series, equipped with a pulsed splitless injector (at 250°C) connected to a MS quadrupol detector (Agilent Technologies, Avondale, PA, USA). The mass spectrometer was operated in the electron capture mode with methane as buffer gas. The PBDEs were monitored using negative chemical ionization (NCI) in selected ion monitoring (SIM) at m/z ratios 79 and 81. The detection limits of BDE-28, -47, -100, -99, -154 and -209 in the egg samples were from 0.020 to 0.028 ng/g ww. Estimated uncertainty (95 % confidence interval) of the internal standards, blanks and international calibrating standards were within the acceptance range of the laboratory. More details of the analytical method are described elsewhere[7,8].

**Results and discussion**
This study shows that BDEs were present in bird eggs from bird species living along the Vaal River, in the other areas in the North-West and in species from the Western Cape Province. Highest levels of ∑BDEs were measured in eggs of one of the sacred ibis (120 ng/g lipid weight (lw)), which is comparable to levels found in eggs of Atlantic puffin (*Fratercula arctica*) at Hornøya, Northern Norway in 2003[9]. The high BDE levels in the sacred ibis might be explained by the habit of this wading bird to forage in waste dumps. Other sources of food are fish, frogs and insects, found in muddy places. The mean ∑BDEs measured in sacred ibis were approximately two times higher compared with findings in eggs of Arctic tern (*Sterna paradisaea*), that migrates to Southern African areas (37 ng/g lw), but lower than corresponding levels in little Auk (*Alle alle*) (108 ng/g lw) living in Arctic areas all year round[10]. ∑BDEs levels found in eggs of African darter and Reed cormorant (both inland species) were 1/20 of ∑BDEs found in egg yolk of the coastal European shag (*Phalacrocorax aristotelis*) (251 ng/g lw)[11].

**Table 2.** Concentrations of BDE-28, -47, -99, -100, -154, -209 and ∑ BDEs (ng/g lw) in bird eggs from South Africa

| **Bird species** | *N* | Lipid % | BDE-28 | BDE-47 | BDE-99 | BDE-100 | BDE-154 | BDE-209 | ∑BDE |
|---|---|---|---|---|---|---|---|---|---|
| African darter | 14 | 5.92 | n.d. | 1.34 | 0.64 | 3.00 | 6.65 | 0.32 | 11.96 |
| Cattle egret | 20 | 6.47 | n.d. | 0.40 | 0.67 | 0.88 | 0.83 | 0.44 | 3.19 |
| Reed cormorant | 3 | 4.29 | n.d. | 2.02 | 1.05 | 2.33 | 4.71 | 0.43 | 10.54 |
| Sacred ibis | 2 | 9.89 | n.d. | 6.53 | 28.22 | 11.79 | 12.00 | 18.03 | 76.56 |
| Crowned plover | 1 | 4.84 | n.d. | 3.01 | 1.56 | 0.34 | 3.05 | 2.79 | 10.75 |
| Dabchick | 1 | 5.83 | n.d. | 8.43 | 7.17 | 1.26 | 1.00 | n.d. | 17.86 |
| Whitefronted plover | 1 | 10.8 | n.d. | 2.72 | 2.21 | 0.50 | 0.600 | n.d. | 6.03 |
| Kelp gull | 1 | 9.96 | n.d. | 5.33 | 1.26 | 1.36 | 1.08 | n.d. | 9.04 |

BDE-28 was not measured in any of the eggs (Table 2). As many other authors who studied BDEs in birds in the Northern Hemisphere, Knudsen et al. 2005, found a higher proportion of BDE-47 compared to the other BDE congeners in eggs of different seabirds from Northern Norway and Svalbard. In this study, only in dabchick, whitefronted plover, and kelp gull the BDE-47 (tetra-BDE) was the most abundant congener which contributed 47, 45 and 59 % to ∑BDEs. The different BDE profile between the studied species (Figure 1) is probably depending on the birds place in the food chain, different diets and migratory behaviour. Furthermore we found that in sacred ibis, dabchick and whitefronted plover BDE-99 contributed 37, 40 and 37 % to ∑BDEs, whereas the other penta-BDE, BDE-100, contributed 25, 27 and 22 % to ∑BDEs in African darter, cattle egret and Reed cormorant. Hexa-BDE, BDE-154, contributed 56, 25, 45 and 28 % to ∑BDEs in African darter, cattle egret, Reed cormorant and crowned plover. Deca-BDE (BDE-209) was present in 5/8 studied species and highest levels were found in one of the sacred ibis (26.3 ng/g lw). Highest contribution of BDE-209 to ∑BDEs was found in sacred ibis and crowned plover (24 and 26 %) respectively. Law et al. 2003[12] suggests that birds feeding

in the terrestrial environment may be more highly exposed to higher brominated congeners than marine species. In South Africa there is no documentation about usage of BDEs available at this moment and a more detailed explanation of the BDE- patterns found in the bird eggs is therefore difficult. Compared to the PCB levels measured in the same eggs[13], the BDE levels were much lower.

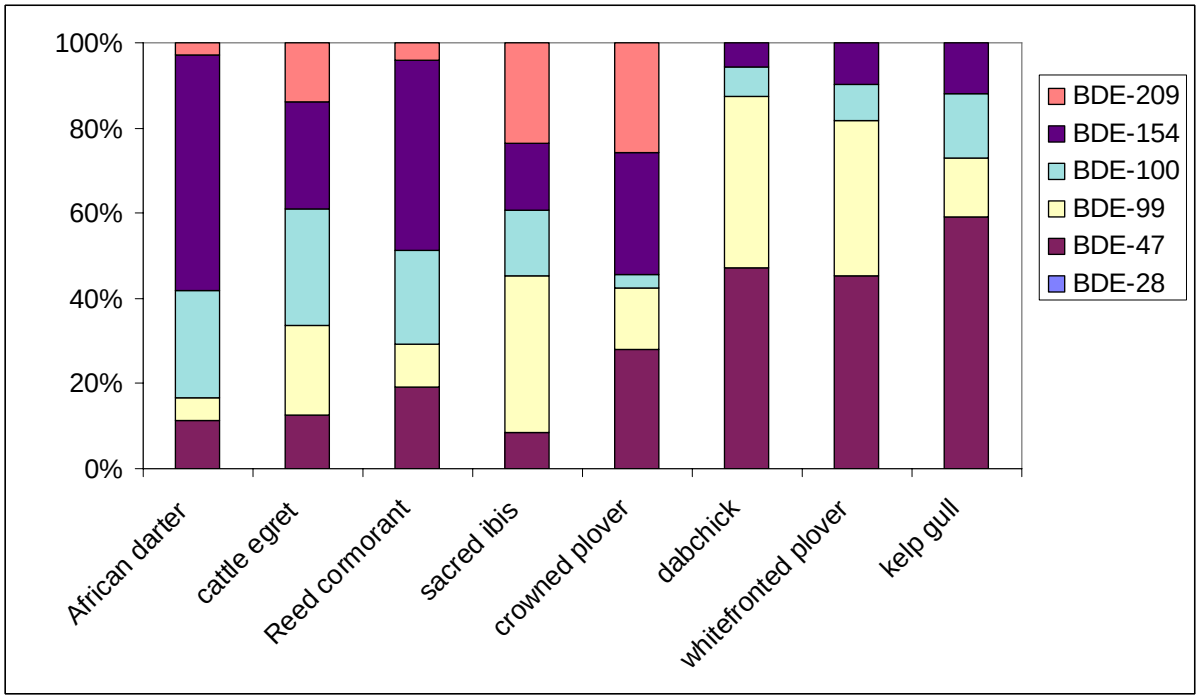


**Figure 1.** Relative distribution of BDE-28, -47, -99, -100, -154 and -209 to ∑BDEs in eggs of different bird species from South Africa.

**Conclusion**

This study shows for the first time the presence of BDEs in bird eggs from birds living in different parts of South Africa, and demonstrates that the contamination of BDEs is not only concentrated around industrialized areas, but also has entered the food chain along the western coastline. The needs for further studies of the environmental contamination with brominated flame retardants in South Africa are obvious.

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