Chemosphere 82 (2011) 88–95

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

# Decabromodiphenylether and hexabromocyclododecane in wild birds from the United Kingdom, Sweden and The Netherlands: Screening and time trends

Heather A. Leslie [a,*], Pim E.G. Leonards [a], Richard F. Shore [b], Lee A. Walker [b], Philippe R.C. Bersuder [c], Steve Morris [d], Colin R. Allchin [c], Jacob de Boer [a]

[a] Institute for Environmental Studies, VU University, Amsterdam, The Netherlands, Netherlands Institute for Fisheries Research, IJmuiden, The Netherlands[1]
[b] NERC Centre for Ecology and Hydrology, Lancaster Environment Centre, Library Avenue, Bailrigg, Lancaster, LA1 4AP, UK
[c] Centre for Environment, Fisheries, and Aquaculture Sciences (Cefas), Lowestoft, Suffolk, UK
[d] Centre for Environment, Fisheries, and Aquaculture Sciences (Cefas), Weymouth, Dorset, UK

ARTICLE INFO

*Article history:*
Received 27 May 2010
Received in revised form 24 September 2010
Accepted 27 September 2010
Available online 1 November 2010

*Keywords:*
Decabromodiphenylether
Hexabromocyclododecane
Diastereomers
Birds
Time trend
Europe

ABSTRACT

The brominated flame retardant decabromodiphenylether (DBDE) was analysed in wild birds to identify the most suitable species for monitoring time trends in DBDE contamination. This information was later used for the design of a 10-year trend study on DBDE in the European Union. DBDE was measured in muscle tissue, liver, and eggs from 10 terrestrial and four aquatic bird species. DBDE was detected in 47% of the terrestrial bird samples (nine species) and in 9% of the aquatic bird samples (six species). Peregrine falcon and sparrowhawk specimens were selected as most suitable species to determine temporal trends of DBDE. For sparrowhawks, no significant change in DBDE concentrations between 1973 and 2001 was found, although in later years more DBDE concentrations were above the detection limit. Peak DBDE levels measured in peregrines in 1995, were followed by a decline in concentrations until 2001. The same species were used for a trend study on hexabromocylcododecane (HBCD). Twenty-four percent of peregrine falcon eggs and 12% of sparrowhawk muscle samples demonstrated measurable HBCD residues. Three diastereomers of HBCD were analysed and the α-diastereomer was the predominant one in most samples. No clear time trends were observed for HBCD in either species. This study demonstrated that these DBDE and HBCD are bioavailable to birds of Northern Europe, although bioaccumulation seems to occur to a limited extent.



## 1. Introduction

Brominated flame retardants (BFRs) such as polybrominated diphenylethers (PBDEs), tetrabisphenol-A and hexabromocyclododecane (HBCD) are used in high quantities in many different materials, such as electrics and electronics (E&E), upholstered furniture, building materials, and many others. They are being produced in high volumes in The Netherlands, UK and USA. Many BFRs can be transported over long distances and they have been detected all over the globe including polar areas (Verreault et al., 2005; Gauthier et al., 2008; Helgason et al., 2009). Due to environmental concern some PBDE mixtures (Penta and Octa-mix) have been banned in Europe (European Union, 2003). In the USA the bromine industry has voluntarily terminated the production of these mixtures. Based on their bioaccumulative, persistent and toxic properties, these two mixtures have been officially labelled as persistent organic pollutants (POPs) by the United Nations under the Stockholm Convention. The 'political fate' of decabromodiphenylether (DBDE, produced as Deca-mix) and HBCD is currently under discussion. As of June 2008 HBCD has entered a screening procedure under the European legislation REACH (Registration, Evaluation, Authorisation and Restriction of Chemical Substances). The use of DBDE in E&E applications has already been banned in Europe (Umweltbundesamt, 2008).

Although DBDE is a large, water-insoluble molecule, traces have been detected in a variety of organisms including peregrine falcons (Lindberg et al., 2004), glaucous gulls and polar bears (Verreault et al., 2005), sparrowhawks (Leslie et al., 2007), fish (Leonards et al., 2004), foxes (Voorspoels et al., 2006) and humans (Sjödin et al., 2001; Thuresson et al., 2006). DBDE concentrations well above levels reported elsewhere were reported in common kestrel tissues from China (Chen et al., 2007). Many endpoints in toxicity studies on DBDE have been negative (Hardy et al., 2003). However, investigations on toxic effects are ongoing (Cantón et al., 2006). These observations, together with the persistent nature and wide environmental distribution of DBDE, justify a continuous awareness for this substance.

* Corresponding author. Address: Institute for Environmental Studies (IVM), VU University, De Boelelaan 1085, 1081 HV Amsterdam, The Netherlands. Tel.: +31 20 5989597; fax: +31 20 5989553.
*E-mail address:* heather.leslie@ivm.falw.vu.nl (H.A. Leslie).
[1] Address when was study initiated.

0045-6535/$ - see front matter © 2010 Published by Elsevier Ltd.
doi:10.1016/j.chemosphere.2010.09.073

Unlike DBDE, HBCD is known to bioaccumulate, and appears to have potential to biomagnify (Covaci et al., 2006). HBCD has been detected in marine (Leonards et al., 2004, Morris et al., 2004, Zegers et al., 2005) and freshwater food webs (Tomy et al., 2004). Reports of increasing concentrations in marine top predators are a cause for concern (Law et al., 2005; Vorkamp et al., 2005). Several studies to date have reported HBCD in birds, (Jaspers et al., 2005; Verreault et al., 2005; Vorkamp et al., 2005; Fernie and Letcher, 2010) and the generation of more and reliable (internal) exposure data is necessary.

Risk assessments are dependent on analytical data of high quality to accurately characterize exposure (Hansson, 2008). DBDE concentrations in biota tend to be low, making analytical sensitivity critical for detection. A large number of precautions required when analysing DBDE have been reported (De Boer et al., 2001; Leonards et al., 2001; De Boer and Wells, 2006). In the current study, particular attention was paid to these factors.

Exposure assessment of HBCD can use measurements of ∑HBCD, with a relatively small number of publications reporting environmental data for HBCD in biota and sediments using GC–MS (Sellström et al., 1998, 2003; Allchin and Morris, 2003; Watanabe and Sakai, 2003; Eljarrat et al., 2004; Lindberg et al., 2004, Morris et al., 2004, Covaci et al., 2003, 2006). Individual diastereomers are not separated by GC but LC–MS enables separation of the diastereomers and analysis without thermal destabilization and interconversion (Budakowski and Tomy, 2003, Morris et al., 2004, Morris et al., 2006). This technique is, therefore, preferred. Sample analysis with LC–MS has shown that the α-diastereomer is generally the most abundant in HBCD body residues of aquatic biota (Morris et al., 2004, Tomy et al., 2004; Zegers et al., 2005; Janák et al., 2008). This is in contrast to the technical mixtures where γ-HBCD is the dominant diastereomer (Peled et al., 1995; Simonsen et al., 2000). Some enantiomeric selectivity of HBCD bioaccumulation has also been reported (Janák et al., 2005, 2008), which has led to increased interest in the characterization of HBCD stereochemistry (Arsenault et al., 2007), and extra challenges for scientists and regulators (Law et al., 2006). In the present study, it was considered important to measure the individual HBCD (i.e., α-, β- and γ-) diastereomers in the avian samples, as differences in diastereomer profiles were expected.

### 1.1. Objectives

The present study had three objectives: (i) screening of DBDE in a range of species of wild birds of prey ($n = 14$) including both terrestrial and aquatic birds; (ii) identification of temporal trends of DBDE and HBCD in archived specimens of bird samples; from part (i) (screening study) it appeared that peregrine falcon (*Falco peregrinus*) eggs and sparrowhawk (*Accipiter nisus*) muscle tissue showed the highest DBDE concentrations, so these were selected for the time trend study under (ii); samples from the period mid 1970s to 2002 were used; (iii) information from both studies was used to select one suitable bird species for monitoring future time trends of DBDE in a 10-year monitoring program in Europe (Leslie et al., 2007).

## 2. Materials and methods

### 2.1. Avian samples

Most of the avian samples used for the screening study were from the Predatory Bird Monitoring Scheme (PBMS) frozen archive held by the Centre for Ecology and Hydrology (CEH), United Kingdom. The tissue samples were from birds found dead all over Britain by members of the public who, in response to advertised requests, submitted the carcasses to the PBMS. Egg contents were from addled eggs collected under licence by volunteers and these samples were also from various locations throughout Britain. The Department of Applied Environmental Science (ITM) of Stockholm University provided 20 peregrine falcon eggs from south-Sweden (south of Lake Vättern, including 10 previously analysed eggs (Lindberg et al., 2004)) and cormorant (*Phalacrocorax carbo*) samples were from the river Rhine delta (Biesbosch, Hollands Diep), The Netherlands (Fig. A1). Muscle and liver samples were acquired from seven species: barn owl (*Tyto alba*), great crested grebe (*Podiceps cristatus*), Grey heron (*Ardea cinerea*), kestrel (*Falco tinnunculus*), peregrine falcon, sparrowhawk and cormorant. Addled egg samples came from 12 species: barn owl, peregrine falcon, sparrowhawk, cormorant, gannet (*Morus bassanus*), golden eagle (*Aquila chrysaetos*), merlin (*Falco columbarius*), marsh harrier (*Circus aeruginosus*), Montagu's harrier (*Circus pygargus*), osprey (*Pandion haliaetus*), red kite (*Milvus milvus*) and white-tailed eagle (*Haliaeetus albicilla*) (Table A1). Part of the bird species selected occur normally in surface water dominated areas and, consequently, have a fish diet (osprey, cormorant, great crested grebe, heron, gannet, white-tailed eagle), whereas another part normally has a terrestrial habitat and, consequently, has a mammal/bird/reptile/insect diet (red kite, barn owl, kestrel, peregrine falcon, sparrowhawk, Montagu harrier, marsh harrier, merlin, golden eagle). All samples were collected between 2000 and 2002. Some eggs showed an early embryo development. Given the low numbers of samples these were included as yet.

The archived peregrine falcon eggs ($n = 58$) analysed for the time trend study were collected between 1973 and 2002, and archived sparrowhawk muscle tissue samples ($n = 69$) between 1975 and 2001 (Table A2). Six of these sparrowhawk muscle tissue samples were composite samples consisting of two to three individuals.

### 2.2. DBDE analysis

The DBDE analysis was carried out using methods described by de Boer et al. (2001). In summary, all samples were blended, dried with sodium sulphate and Soxhlet-extracted with hexane:acetone (v/v 1:1). A separate aliquot of the extract was used for the extractable lipid determination. Co-extracted lipids were removed by gel permeation chromatography (GPC) or alumina columns. Sulphuric acid treatment followed by silica gel column chromatography was used for additional clean up. The final extracts were concentrated to 200 μL (in iso-octane), and analysed by an GC–ECNI–MS (Agilent 6890/5973, Agilent, Amstelveen, The Netherlands).

### 2.3. HBCD analysis

HBCD was measured in the same extracts of peregrine falcon eggs and sparrow hawk muscle used for the time trend study of DBDE. The extraction, clean up and LC–MS method followed that reported by Morris et al. (2006). The extracts were evaporated to dryness and 120 μL (at Cefas) or 200 μL (at RIVO) methanol were added. The LC/MS analysis was carried out on a Perkin Elmer LC/ion-trap MS with electrospray ionisation (ESI) and in the negative ionisation mode.

### 2.4. QA/QC

All samples were equally divided over the Cefas (Centre for Environment, Fisheries and Aquaculture Sciences) laboratory (Burnham on Crouch, UK) and The Netherlands Institute for Fisheries Research (RIVO) (IJmuiden, The Netherlands) for analysis. Six selected samples from the UK, two peregrine falcon eggs and four sparrowhawk muscle tissues were analysed by Cefas and RIVO for