



OSPAR Background Document on  
certain brominated flame retardants



### **OSPAR Convention**

The Convention for the Protection of the Marine Environment of the North-East Atlantic (the “OSPAR Convention”) was opened for signature at the Ministerial Meeting of the former Oslo and Paris Commissions in Paris on 22 September 1992. The Convention entered into force on 25 March 1998. It has been ratified by Belgium, Denmark, Finland, France, Germany, Iceland, Ireland, Luxembourg, Netherlands, Norway, Portugal, Sweden, Switzerland and the United Kingdom and approved by the European Community and Spain.

### **Convention OSPAR**

La Convention pour la protection du milieu marin de l'Atlantique du Nord-Est, dite Convention OSPAR, a été ouverte à la signature à la réunion ministérielle des anciennes Commissions d'Oslo et de Paris, à Paris le 22 septembre 1992. La Convention est entrée en vigueur le 25 mars 1998. La Convention a été ratifiée par l'Allemagne, la Belgique, le Danemark, la Finlande, la France, l'Irlande, l'Islande, le Luxembourg, la Norvège, les Pays-Bas, le Portugal, le Royaume-Uni de Grande Bretagne et d'Irlande du Nord, la Suède et la Suisse et approuvée par la Communauté européenne et l'Espagne.

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## Executive Summary

Brominated flame retardants are a diverse group of chemicals, whose common points are that they all contain bromine and are all used to retard the combustibility of commercial goods. Two substances – decabromodiphenyl ether (DecaDBE) and Tetrabromobisphenol A (TBBP-A; this is subject of a separate Background Document) – account for about 50% of world use of brominated flame retardants. Two other polybrominated diphenyl ethers (PolyBDE) – octabromodiphenyl ether (OctaDBE) and pentabromodiphenyl ether (PentaDBE) – are used commercially, but in much smaller quantities than DecaDBE. Hexabromocyclododecane (HBCDD) is also used in large volumes. Polybrominated biphenyls (PBB) have also been used, but production was stopped in September 2000. Some PolyBDE are toxic, especially those with smaller molecules. PentaDBE may disrupt the oestrogenic system. PBB have similar effects to polychlorinated biphenyls, and may also produce hypothyroidism. Some of these chemicals are bioaccumulated. Brominated flame retardants were given priority in the 1992 OSPAR Action Plan, and therefore included in 1998 in the List of Chemicals for Priority Action.

The quantities of PolyBDE used in the EU in 1994 were estimated as: DecaBDE (8210 tonnes) as a general-purpose flame retardant, especially in polymers, polypropylene fabric and other textiles (other than clothing fabrics); OctaBDE (2550 tonnes) in acrylonitrile-butadiene-styrene plastics (often used for casings of electrical and electronic equipment), nylon and other plastics and in adhesives and coatings; PentaBDE (125 tonnes) mainly in flexible polyurethane foam for furniture, as well as epoxy and phenolic resins, some polyesters and textiles. About 9200 tonnes of HBCDD was used in the EU in 1999, 85% of it in polystyrene.

Since the products containing these chemicals are widely dispersed, their possible release from waste disposal routes may be of concern, together with their potential role in producing dioxins and furans during waste incineration. The degradation of DecaBDE to the more toxic and bioaccumulative lower levels of PolyBDE is also of concern. The overwhelming majority of samples of marine biota have not shown detectable quantities of DecaBDE; however, OctaBDE has been found in fish and molluscs (up to 325 µg/kg wet weight) and PentaBDE has been found in fish and marine mammals (up to 7700 µg/kg in white-beaked dolphins). All these chemicals have been found in river or marine sediments.

Action has been taken through voluntary commitments by industry within the framework of the OECD. The risk assessment for PentaBDE under the EC existing substances regulation concluded that risk reduction measures were needed, and hence a ban on the substance is in force in the European Union. The PolyBDEs are included as priority substances in the list of priority substances under the EC Water Framework Directive, and pentaBDE as a priority hazardous substance.

The action recommended is: to note the inclusion of PBB in the EC Directive on Waste from Electrical and Electronic Equipment and the EC harmonised restrictions on PentaBDE, OctaBDE and DecaBDE; to support risk reduction measures for HBCDD and seek appropriate risk-reduction strategies.

## Récapitulatif

Les retardateurs de flamme au brome représentent un groupe de produits chimiques diversifié, dont les points communs sont qu'ils contiennent tous du brome et servent tous à retarder la combustion de produits vendus dans le commerce. Deux substances – l'éther décabromodiphénylique (DecaDBE) et le tétrabromobisphénol A (TBBPA – lequel est l'objet d'un document de fond distinct) – représentent environ 50% de la consommation mondiale de retardateurs de flamme au brome. Deux autres éthers polybromodiphényliques (PolyBDE) – l'éther octabromodiphénylique (OctaDBE) et l'éther pentabromodiphénylique (PentaDBE) – sont utilisés dans le commerce, mais en quantités nettement inférieures au DecaDBE. L'hexabromocyclododécane (HBCDD) est aussi utilisé en gros volumes. Les polybromobiphényles (PBB) ont aussi été utilisés, mais leur fabrication a été arrêtée en septembre 2000. Les PolyBDE sont toxiques, surtout ceux dont les molécules sont petites. Le PentaDBE est susceptible de perturber le système œstrogénique. Les PBB ont des effets analogues à ceux des polychlorobiphényles, et peuvent aussi provoquer une hyperthyroïdie. Le HBCDD est aussi toxique. Tous ces produits chimiques ont tendance à s'accumuler biologiquement. La priorité a été donnée aux retardateurs de flamme au brome dans le Plan d'action OSPAR 1992, et ils ont donc été inscrits en 1998 sur la Liste des produits chimiques devant faire l'objet de mesures prioritaires.

Les quantités de PolyBDE consommées en 1994 dans l'Union européenne ont été estimées comme suit : DecaBDE (8210 tonnes), comme agent ignifuge général, surtout dans les polymères, les tissus de polypropylène et autres textiles (autres que les tissus d'habillement) ; OctaBDE (2550 tonnes) dans les matières plastiques acrylonitrile-butadiène-styrène (dont sont souvent faits les boîtiers dans le matériel électrique et électronique), le nylon et autres matières plastiques ainsi que dans les adhésifs et revêtements ; PentaBDE (125 tonnes) surtout dans la mousse de polyuréthane souple destinée au mobilier, ainsi que dans les résines époxy et les résines phénoliques, certains polyesters et textiles. Environ 9200 tonnes de HBCDD ont été consommées dans l'Union européenne en 1999, dont 85% dans du polystyrène.

Les produits contenant ces produits chimiques étant très répandus, leurs émissions par les voies d'élimination des déchets sont très préoccupantes, ceci parallèlement au fait qu'ils sont susceptibles de produire des dioxines et des furanes pendant l'incinération des déchets. La dégradation du DecaBDE jusqu'aux niveaux inférieurs de PolyBDE, plus toxiques et s'accumulant plus dans les tissus biologiques, est elle aussi préoccupante. Dans la très vaste majorité des cas, l'on n'a pas constaté la présence de DecaBDE en quantités décelables dans les échantillons de biote marin ; toutefois, l'on a observé la présence d'OctaBDE chez le poisson et les mollusques (pouvant atteindre 325 µg /kg du poids à l'état humide) de même que du PentaBDE chez les poissons et dans les mammifères marins (jusqu'à 7700 µg/kg chez les lagénorhynques à bec blanc). La présence de tous ces produits chimiques a été constatée dans des sédiments fluviaux ou marins.

Les mesures prises consistent en engagements volontaires de l'industrie, contractés dans le cadre de l'OCDE. Le résultat de l'évaluation des risques suscités par les PentaBDE, effectuée en conséquence du Règlement communautaire européen sur les substances existantes, est qu'il a été conclu que des mesures de réduction des risques s'imposaient. De ce fait, une interdiction de cette substance est en vigueur à travers de l'Union européenne. Les PolyBDE sont inscrits en tant que substances prioritaires sur la Liste des substances prioritaires dans le contexte de la Directive communautaire européenne cadre relative aux eaux, les pentaBDE comme substances prioritaires dangereuses.

Les mesures recommandées sont les suivantes : prendre note de l'inscription des PBB dans la Directive communautaire européenne relative aux déchets de matériel électrique et électronique et des restrictions harmonisées au niveau communautaire aux PentaBDE aux OctaBDE et aux DecaBDE ; soutien aux mesures de réduction des risques pour les HBCDD, et à la lumière de ses conclusions, mettre en place les stratégies de réduction des risques adéquates.

# 1. Identification of sources and pathways to the marine environment

## 1.1 Brominated flame retardants

Brominated flame retardants (BFRs) is a chemically diverse group of substances. Brominated flame retardants as a class include aromatic diphenyl ethers, cyclic aliphatics, phenolic derivatives, aliphatics, phthalic anhydride derivatives and others. Their major common points are that they are used to flame retard items in commerce and all contain bromine. The approach to establish a background document for “certain brominated flame retardants” is therefore more of a pragmatic way to handle these compounds in the framework of OSPAR strategy for hazardous substances. Of the 75 commercially recognised BFRs, tetrabromobisphenol-A (TBBPA), hexabromocyclododecane (HBCDD) (mainly used in polystyrene), and decabromodiphenyl ether (DecaBDE) (mainly used in plastics, textile such as upholstery fabric, and synthetic carpets), used to constitute more than 97% of the BFRs used in Europe (BSEF 2003). A number of different brominated flame retardant structural types may potentially be used, but the two other commercial polybrominated diphenyl ether (PBDE) flame retardants: octabromodiphenyl ether (octaBDE) and pentabromodiphenyl ether (pentaBDE) have been banned in the European Union and other alternative BFRs have not yet gained commercial importance. The production of polybrominated biphenyls (PBB) ceased already in September 2000. This background document does not cover TBBP-A since a separate background document has been prepared by the United Kingdom (UK) for this substance. In the case alternative BFRs will gain commercial importance, OSPAR may choose to include other BFR substances in this background document.

## 1.2 PBDEs production and use

The world production of PBDEs were estimated at 40 000 tonnes in 1992 (including 4000 tonnes of pentaBDE). The use of PBDEs in the European Union (EU) in 1994 was estimated at 11 000 tonnes. In its risk assessments carried out under Council Regulation (EEC) No 793/93 of 23 March 1993 on the evaluation and control of the risks of existing substances, the UK (Member State Rapporteur) assumed the following EU quantities for the individual PBDEs: pentaBDE 125 tonnes/year, octaBDE 2550 tonnes/year, and decaBDE 8210 tonnes/year. The Bromine Science and Environmental Forum estimated total market demand for major brominated flame retardants for 1999. In Europe the demand was estimated to be: pentaBDE 210 tonnes/year, octaBDE 450 tonnes/year and decaBDE 7500 tonnes/year. The total demand for PBDEs in the world was estimated to about 67 000 tonnes/year. PBDEs are used in many different applications, which may give rise to diffuse losses of the substances in the “technosphere”, for example in electrical and electronic equipment, furniture, and cars. The ban on penta- and octaBDE in the EU suggests insignificant use of these substances, but continued presence in imported goods cannot be totally excluded, although import of articles treated with penta- and octaBDE are covered by the ban.

The major use of pentaBDE is as a flame retardant additive in flexible polyurethane foam for furniture and upholstery. Other reported uses include as a flame retardant additive in epoxy resins, phenolic resins (e.g. in printed circuit boards), unsaturated polyesters and textiles.

Around 95% of the octaBDE supplied in the EU was used as a flame retardant in acrylonitrile-butadiene-styrene (ABS) plastics (often used in covers and casings for electrical or electronic equipment). Other reported uses included nylon and low density polyethylene, polycarbonate, phenol-formaldehyde resins and unsaturated polyesters and in adhesives and coatings.

DecaBDE is used as a flame retardant, mostly in applications in the plastics and textile industries. It is a general purpose flame retardant and is thus used in a variety of polymer applications. Industry information indicates that decaBDE is widely used for flame retarding polypropylene drapery and upholstery fabric. DecaBDE may also be used in some synthetic carpets. It is not used as a flame retardant in textiles used for clothing. In the UK it is thought that around 95% of all upholstery materials are flame retarded, and estimated that over 50% of the total PBDE use is in the textile industry. In most other countries the amounts used in this application would be much lower. The ban on the whole PBDE group of substances (including decaBDE) in the so called "RoHS Directive" 2005/95/EC however came into force during 2008, meaning that the use of decaBDE is changing substantially in the EU at present. It has previously been estimated that about 80% of the use of decaBDE in the EU can be attributed to electronic articles, of which a substantial part is covered by the RoHS Directive.

### 1.3 PBBs production and use

DecaBBs were produced in France until 30 September 2000. The use of PBB will cease when the stock has been consumed. The yearly production was around 1000 tonnes. PBBs are sold exclusively as technical decaBB, which consists of at least 94% decaBB and up to 6% nonaBB, with traces of octaBB. PBBs are used mainly for electrical and electronic equipment. PBBs are used in many different applications, which may give rise to diffuse losses of the substances.

### 1.4 HBCDD production and use

HBCDD is both manufactured in and imported into the EU. HBCDD is used industrially as an additive flame retardant in polymers. End products containing HBCDD are used both professionally and by consumers. The EU use of HBCDD in 1999 was 9200 tonnes/year according to the EU risk assessment. 85% of HBCDD is used in polystyrene (PS). The predominant use of PS is in rigid insulation panels/blocks for building construction; 10% is used in textile back coating and 5% is used in high impact polystyrene (HIPS) in electric housings, e.g. housings for videocassette recorders.

### 1.5 Waste and recycling of brominated flame retardants

The waste stage is a source of at least losses of PBDE and PBB both into the working environment and into the natural environment. Once an article has reached the end of its service life, it can be recycled, incinerated or landfilled. In most countries large quantities of PBDE and PBB occur in plastic parts in electric and electronic equipment. There are various modes of disposal. In the case of goods handled by electronics disposal firms, covers are often burned in incineration plants. There may be a risk of the formation of halogenated dioxins. Printed circuit boards can be sent to metal smelting plants or treated in connection with fragmentation. There are insufficient data to assess the magnitude of the various flows of PBDE and PBB and the resulting releases.

### 1.6 Pathways to the marine environment

A detailed analysis of the specific pathways to the marine environment of the sources mentioned above in paragraphs 1.2 to 1.5 is generally beyond the scope of this background document. Brominated flame retardants reach the marine environment from these sources generally via rivers and via the atmosphere. However, there is a lack of data. It has not been possible to estimate which is the dominant pathway. Several research programs are however studying the pathways of BFRs to the marine environment. PBDE has e.g. been selected as one of totally 10 hazardous substances in the EU project SOCOPSE - Source control of priority substances in Europe ([www.socopse.eu](http://www.socopse.eu)). The

overall objective of this project is to support the implementation process for the Water Framework Directive by providing guidelines and decision support system for the management of priority substances.

## 2. Monitoring data and quantification of sources

### 2.1 PBDEs

#### 2.1.1 Monitoring data

The UK risk assessments contain several monitoring data that are summarised below.

Recent monitoring data published after 2004 is also summarised below.

#### **Concentrations in the marine environment**

##### *PentaBDE*

No levels of pentaBDE have been reported in water. In Japan, water samples have been analysed for hexaBDE, but it has not been detected in any sample.

Components of commercial pentaBDE have been measured in sediments in several EU countries and also in Japan. The results are reported for various isomers of the commercial mixtures. Thus the measured results can be used only to obtain an approximate indication of the levels found in sediment.

Levels of commercial pentaBDE of 561 - 1271  $\mu\text{g}/\text{kg}$  dry weight have been measured in a river and heavily industrialised estuary close to a pentaBDE production site in the UK. The highest levels were found in the heavily industrialised estuary, which may indicate that sources other than the production site contribute to these levels. No production currently occurs in the EU. Higher levels of 1400  $\mu\text{g}/\text{kg}$  dry weight have been measured near to a factory in Sweden. Surficial sediment samples taken from the southern part of the Baltic Sea (Baltic Proper) were found to contain 0.21 to 1.1  $\mu\text{g}/\text{kg}$  dry weight as the sum of two congeners. PentaBDE was not detected in samples taken from the northern part of the Baltic Sea (Bothnian Bay).

Levels of pentaBDE of 0.04 - 1.5 ng/g dry weight have been measured in sediments along the Norwegian coast (Fjeld *et al.*, 2004).

A one-off survey was carried out in 2003 in the Dutch Marine and Coastal waters. Concentrations of tetra- and pentaBDE (penta-mix) in sediments were present in the coastal zone and at open sea in concentration of 0.65 - 2.2 ng/g dry weight. Levels were slightly higher around the Haringvlietsluizen and the Nieuwe Waterweg and rather similar throughout the Dutch continental shelf (SIME 2005).

Passive samplers for monitoring of pentaBDE in 91 coastal/marine and limnic sites were used in a screening study performed in Sweden in 2006 - 2007 (SWECO VIAK 2007). PentaBDE was measured in generally low concentration all over Sweden with sporadically high concentrations even close to or above EQS (0.68 - 57 pg/l).

PentaBDE was measured in the topmost sediment (0 - 1 cm) from the National Swedish Status and Trends Monitoring Program (SSTMP) stations in North Sea and Baltic Sea in 2003. The levels of PentaBDE varied between <0.02 - 1.1 ng/g dry weight in samples from Skagerrak and Bothnian Bay. In Kattegat and the southern and western Baltic Sea no PentaBDE was detected (Cato and Kjellin 2008).

PBDE (BDE 28, 47, 99, 100, 138, 153 and 154) were measured in levels of 0.0015 - 0.3 ng/g dry weight in bottom sediments from the Barents Sea in 2007, with highest levels found in the central and eastern part of the Barents Sea (Bakke *et al.*, 2008).

#### *OctaBDE*

The levels of octaBDE in water have been analysed in Japan, but it has not been detected.

Levels of octaBDE of up to 3030 µg/kg dry weight (wt) have been detected in sediments in industrialised areas in the UK. The measured levels in other industrialised areas are generally 20 - 200 µg/kg dry wt.

#### *DecaBDE*

DecaBDE has not been reported in water samples, which is consistent with its low water solubility (<0.1 µg/L). DecaBDE was not detected in 15 water samples collected in Japan in 1977 (DL= 0.2 - 2.5 µg/L). DecaBDE was not detected in 75 water samples collected in 1987 (DL= 0.1 µg/L) and was not detected in 141 samples collected in 47 locations in 1988 - 89 in Japan (DL= 0.06 µg/L). DecaBDE was not detected in 12 samples from the Kino River water in Japan (DL= 0.1 µg/L). The samples were taken from several industrial, urban and rural areas of Japan and are thought to be representative of the country as a whole (EU 1999).

Levels of decaBDE in sediments in the UK near possible sources of release ranged from less than the detection limit (DL, 0.6 µg/kg dry wt) to 3190 µg/kg dry wt. Results from 11 out of 24 of these samples were reported as less than the DL. Sediments from two streams, collected downstream of landfills receiving brominated wastes, also reported results as less than the DL. Ten out of 11 samples collected in a second study in the UK near possible sources of release reported all values <200 or 500 µg/kg dry wt, which are the presumed detection limits. One sample was reported to possibly contain decaBDE at ~850 µg/kg, but interference in the analysis did not allow confirmation (EU 1999).

A recent survey of marine sediments in estuaries discharging in to the North Sea has been carried out. DecaBDE concentrations in 22 samples ranged from less than the DL (0.51 µg/kg dry wt) to 1700 µg/kg dry wt. The highest level, 1700 µg/kg dry wt, was detected in the Mersey Estuary, a site used formerly for dumping sewage sludge. The next highest level, 200 µg/kg, was detected in the Schelde estuary. The lowest levels reported in this survey were samples collected 100 km off Terschelling (less than the DL of 0.51 µg/kg dry wt), from the Glomma Estuary (<DL of 0.52 µg/kg), from the Otria Estuary (0.71 µg/kg), and from the Elbe estuary (0.83 µg/kg dry wt) (EU 1999).

DecaBDE levels up to 0.2 mg/kg wet weight in sediment collected in Sweden were reported. Surface sediment (0 - 2 cm) collected at 8 locations in the River Viskan and other nearby water systems ranged from <1.1 to 241 µg decaBDE/kg wet wt. Five of the nine samples analysed had decaBDE concentrations <1.7 µg/kg wet wt. The highest levels were generally found downstream from industry (EU 1999).

A number of sediment monitoring studies were conducted in Japan between 1977 and ~1989. In 15 sediment samples collected in Japan in 1977, decaBDE was not detected (DL=25 - 870 µg/kg dry wt). Marine, estuarine and river sediment samples were collected at different locations in Japan in 1981 - 83; decaBDE was detected in 7 out of 15 samples in the range of 20 - 375 µg/kg dry wt. Further decaBDE was identified at 20 µg/kg dry wt in one of 3 estuarine sediment samples from Osaka. However it was not detected in samples from Tokyo, Matsuyama, or Hiroshima. DecaBDE was detected in 16 out of 60 sediment samples at concentrations ranging from 10 to 1370 µg/kg in 1987 and was detected in 39 out of 129 samples collected at 43 locations at concentrations ranging from 4 - 6000 µg/kg in 1988 - 89. The upper sediment layer of the Second Neya River in Osaka, Japan was found to contain ~0.2 mg decaBDE/kg dry wt in 1983. Twenty sediment samples from the Kino River in Japan contained decaBDE ranging from 0.003 - 11.6 mg/kg dry wt (EU 1999).

Near its manufacture in the U.S. in 1978, sediment levels of decaBDE were reported to range from not detectable up to 14 mg/kg (EU 1999).

A one-off survey was carried out in 2003 in the Dutch Marine and Coastal waters. DecaBDE was detected in sediments in the coastal zone and the open sea and the concentration varied between 0.92 and 130 ng/g dry weight (SIME 2005).

DecaBDE was measured in levels of <0.01 - 1.1 ng/g dry weight in bottom sediments from the Barents Sea in 2007 (Bakke *et al.*, 2008).

### **Concentration in biota**

#### *PentaBDE*

There is a consistent pattern in the levels of commercial pentaBDE measured in biota in Europe. The major isomer detected is 2,2',4,4'-tetraBDE which typically makes up >70 % of the total components detected. Levels in freshwater fish are generally slightly higher than in marine fish, possibly reflecting the proximity to likely sources of pentaBDE. On a lipid basis, levels of up to 88 mg/kg on a formulation basis have been measured in fish liver in Sweden. High levels have been measured in marine fish in the UK in industrialised areas near to a pentaBDE production site. Analyses of a number of PBDE congeners (BDE-47, BDE-99, BDE-100) in flounder collected in the Scheldt Estuary in 2000 showed values ranging from <0,2 - 260 and 0,4 - 7,8 µg/kg wet weight in liver tissue and muscle tissue, respectively (data from RIVO transmitted by Mr. van Zeijl, NL).

The total tetra- and pentaBDE concentration in sperm whale blubber were found to be about 100 µg/kg. The concentrations found in whitebeaked dolphins and harbour seals were 7700 µg/kg and 1400 µg/kg respectively. The presence of tetra- and pentaBDE in sperm whales suggests that these compounds have reached deep ocean waters (de Boer 1998). This indicates the stability and long-range transportation of the substance.

In human samples, the presence of the various components of commercial pentaBDE has been shown in many samples of adipose tissue and milk. The levels found, when expressed on a lipid weight basis, show a remarkably consistent picture between the various surveys and samples with the levels generally being 2 - 4 µg/kg lipid in both milk and adipose tissue with up to around 100 µg/kg lipid in adipose tissue and 11 µg/kg in human milk being measured in some samples.

BDE 28, 47, 99 and 100 were detected in blue mussel and cod liver from the coastal area of southern Norway (Greater North Sea) at levels of 0.16 - 0.59 and 13 - 140 ng/g wet weight respectively (Schlabach *et al.*, 2002).

PBDE (47, 49, 71, 99, 100, 153 and 154) have been measured in blue mussel sampled along the Norwegian coast in levels of 0.03 to 0.73 ng/g wet weight (Fjeld *et al.*, 2004)

BDE-47 has been detected in biota samples of herring muscle in levels of 4.5 - 21, 1.8 - 3 and 1.7 - 4.3 ng/g lipid weight respectively at sites Utlängan (southern Baltic Proper), Fladen (Kattegat) and at Väderöarna (Skagerrak) in year 2006/2007. BDE-47 has also been measured in cod liver at Fladern in levels of 7.7 - 24 ng/g lipid weight (Bignert *et al.*, 2008).

PBDE<sub>7</sub> (28, 47, 99, 100, 153 and 154) were recently detected in samples of blue mussel, shrimps, capelin and cod liver from Barents Sea in levels < DL-1.2, 0.001 - 0.0017, 0.047 - 0.18 and 4.3 - 29 ng/g wet weight respectively (Bakke *et al.*, 2008).

*OctaBDE*

OctaBDE has been detected in biota samples of dab, flounder, plaice and mussels. The highest level, 325 µg/kg wet weight, was found in dab liver off River Tees, UK. The monitoring data indicated that commercial octaBDE were only found in biota at measurable concentrations in industrial areas, particularly where sources of octaBDE were thought to be present.

*DecaBDE*

Biomonitoring studies have previously only exceptionally been able to demonstrate the presence of decaBDE in biota. Over 270 biological samples collected in the environment (fish, marine mammals) were analysed for decaBDE and DecaBDE was only detected in one of these 270 samples at a level of 0.001 mg/kg wet wt. In the EU, decaBDE was not detected in dab, whiting, flounder, plaice, winkles, mussels, pike, sperm whale, dolphin, minke whale, harbour seal, mackerel or mussels. In Japan, decaBDE was not detected in 229 samples from different aquatic species, but was detected at 0.001 mg/kg wet wt in 1 mussel (EU 1999). DecaBDE was however found in eggs of Peregrine Falcons breeding in Sweden which indicated that decaBDE nevertheless could be taken up by biota and possibly bioaccumulate (Sellström 2001).

Later studies have however confirmed the presence of decaBDE in several biological samples. DecaBDE was measured in samples of blue mussel and cod liver from the inner and outer Oslo fjord and the Skagerrak coast in levels of <0.5 - 0.16 ng/g wet weight (Schlabach *et al.*, 2002) and in cod liver samples from the Norwegian coast in levels up to 1.5 ng/g wet weight (Fjeld *et al.*, 2004).

DecaBDE was detected in herring gull eggs and kittiwake eggs at Hornöya (Arctic Sea, Northern Norway) in levels of 11 and 0.2 ng/g wet weight respectively. DecaBDE was also measured in herring gull eggs and Atlantic puffin eggs at Röst (Arctic Sea, Northern Norway) at levels of 0.1 - 14 and 0.2 ng/g wet weight respectively (Knudsen *et al.*, 2005).

DecaBDE was not detected in dab liver samples from the North Sea and Baltic Sea (Lepom *et al.*, 2006), in blue mussel from the Atlantic - Pen Be' (Johansson *et al.*, 2006) and in the blubber of twelve species of marine mammals stranded in the UK (Law *et al.*, 2005).

DecaBDE was measured in levels up to 0.96 ng/g dry weight in blue mussel from the English Channel, Villerville (Johansson *et al.*, 2006).

Different concentrations of PBDE mixtures in biota are summarised in Table 1.

**Table 1.** Levels of PBDE in biota samples

Compound	Site	Species	Concentration range and unit	Reference
Sum 8 BDE	Northern Norway- Hornöya	Herring gull eggs	39 - 91 ng/g ww	Knudsen <i>et al.</i> , 2005
Sum 8 BDE	Northern Norway- Hornöya	A. puffin eggs	9.0 - 21 ng/g ww	Knudsen <i>et al.</i> , 2005
Sum 8 BDE	Northern Norway- Hornöya	Kittikawe eggs	7.3 - 24 ng/g ww	Knudsen <i>et al.</i> , 2005
Sum 8 BDE	Northern Norway- Röst	Herring gull eggs	45 - 83 ng/g ww	Knudsen <i>et al.</i> , 2005
Sum 8 BDE	Northern Norway- Röst	A. puffin eggs	7.0 - 25 ng/g ww	Knudsen <i>et al.</i> , 2005
Sum 8 BDE	Northern Norway- Röst	Kittikawe eggs	18 - 32 ng/g ww	Knudsen <i>et al.</i> , 2005
Sum 9 BDE	Northern Norway- Bear Island	Glaucous gulls plasma (male)	7.4 - 76 ng/g ww	Verreault <i>et al.</i> , 2004

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Sum 9 BDE	Northern Norway- Bear Island	Glauous gulls plasma (female)	27 - 53 ng/g ww	Verreault <i>et al.</i> , 2004
Sum 9 BDE	Northern Norway- Bear Island	Glauous gulls eggs	24 - 104 ng/g ww	Verreault <i>et al.</i> , 2004
Sum 9 BDE	Northern Norway- Bear Island	Glauous gulls (brain)	220 - 11000 ng/g lw	Knudsen <i>et al.</i> , 2007
Sum 9 BDE	Northern Norway- Bear Island	Glauous gulls (liver)	1800 - 103000 ng/g lw	Knudsen <i>et al.</i> , 2007
Sum 10 BDE	UK coast	Bottlenose dolphin	0.85 - 11 ng/g ww	Law <i>et al.</i> , 2005
Sum 10 BDE	UK coast	Sowerby's beaked whale	0.11 - 0.85 ng/g ww	Law <i>et al.</i> , 2005
Sum 10 BDE	UK coast	Killer whale	0.61 - 16 ng/g ww	Law <i>et al.</i> , 2005
Sum 10 BDE	UK coast	Pugmy sperm whale	0.3 - 0.37 ng/g ww	Law <i>et al.</i> , 2005
Sum 10 BDE	UK coast	Hooded seal	0.005 - 0.005 ng/g ww	Law <i>et al.</i> , 2005
Sum 10 BDE	UK coast	Other whales and dolphin (7 st)	<DL-0.41 ng/g ww	Law <i>et al.</i> , 2005
Sum 10 BDE	the Atlantic (Pen Be')	Blue mussel	0.19 - 1.4 ng/g dw	Johansson <i>et al.</i> , 2006
Sum 10 BDE	English Channel (Villerville)	Blue mussel	4.8 - 25 ng/g dw	Johansson <i>et al.</i> , 2006
Sum 12 BDE	Norway Drammens Fjord	Eel, trout, orfe, perch	1.1 - 18 ng/g ww (12 - 170 ng/g lw)	Fjeld <i>et al.</i> , 2004
Sum 12 BDE	Norway - coast	Cod liver	7.2 - 25 ng/g ww	Fjeld <i>et al.</i> , 2004
Sum 13 BDE*	North Sea	Dab liver	2.8 ng/g ww	Lepom <i>et al.</i> , 2006
Sum 13 BDE	Norway Lake Mjösa/Lake Losna	Perch, pike, trout and burbot	2.4 - 980 ng/g ww (49 - 22000 ng/g lw)	Fjeld <i>et al.</i> , 2004
Sum 14 BDE	England	Cormorant liver	1.8 - 140 µg/kg ww	Law <i>et al.</i> , 2002
Sum 14 BDE	England	Porpoise blubber	<DL-6900 µg/kg ww	Law <i>et al.</i> , 2002
Sum 40 BDE	Svalbard	Polar bears	0.015 - 0.048 ng/g ww	Gabrielsen <i>et al.</i> , 2004
Sum 8 BDE (28, 47, 100, 99, 154, 153, 183, 209)				
Sum 9 BDE (28, 47, 100, 99, 154, 153, 138, 183, 209)				
Sum 10 BDE (28, 47, 66, 85, 100, 99, 138, 154, 153, 183)				
Sum 12 BDE (28, 47, 49, 71, 77, 100, 99, 119, 138, 153, 154, 183)				
Sum 13 BDE* (28, 47, 66, 71, 75, 85, 100, 99, 138, 154, 153, 183, 190)				
Sum 13 BDE (28, 47, 49, 71, 77, 100, 99, 119, 138, 153, 154, 183, 209)				
Sum 14 BDE (28, 47, 66, 71, 75, 77, 85, 99, 100, 119, 138, 153, 154, 190)				
Sum 40 BDE (7 - 209)				

### 2.1.2 Releases

The UK risk assessments contained a number of release estimations, made by using various models and assumptions. Following this study, BFR producers launched the Voluntary Emissions Control Action Program (VECAP). VECAP aims to manage, monitor and minimize industrial emissions of the high production volume BFRs Deca-BDE, TBBPA and HBCDD into the environment through

partnership with the supply chain. VECAP has most likely considerably reduced the emissions of BFRs from the production sites and industrial users. There has however been no updated comprehensive European estimation of emissions and hence the estimations from the UK risk assessment are still a valuable source of information. In summary, the UK risk assessment indicated the following releases in the EU:

- PentaBDE: 39 tonnes/year to air (from polyurethane foam use), 5 tonnes/year to surface and waste water (from polyurethane foam manufacture), 14 tonnes/year to industrial soil and 932 tonnes/year to landfills (or incineration) (from polyurethane foam disposal).
- OctaBDE: 13 tonnes/year to air (mainly from service life of polymers), 1 tonne/year to waste water (mainly from compounding and conversion of polymers), and 2 295 tonnes/year to landfill/disposal (from polymers).
- DecaBDE: 26 tonnes/year to air (mainly from service life of polymers), 245 tonnes/year to waste water (mainly from washing of textiles), and 7476 tonnes/year to landfill/incineration (mainly from polymers).

### 2.1.3 Exposure to pentaBDE

According to the UK risk assessment, occupational exposure may occur during the production of polyurethane foams and subsequent manufacture of equipment. It is estimated that several thousands of workers in the EU could be exposed to materials containing pentaBDE. Dermal exposure may occur during the handling of receptacles containing pentaBDE, and when coming into contact with vessels and surfaces that have been contaminated from spillage. Regarding consumers, the current use pattern provided by industry is that pentaBDE is only used in polyurethane foam and that consumers do not come into direct contact with these foams.

The daily human intake of pentaBDE through environmental routes is estimated as:

- Local sources (polyurethane foam production): 0.043 - 0.048 mg/kg bw/day.
- Regional sources: 0.0008mg/kg bw/day.

The time trend data indicate that the levels in human breast milk increased markedly over the period 1972 - 1997. In biological samples collected in the environment the time trend indicates declining levels (de Wit 2000).

In the human health risk assessment the UK concludes that although further information should be gathered in order to refine the risk assessment, in the light of the properties of pentaBDE and the time it would take to gather the information, consideration should be given at a policy level to the need to take risk reduction measures now. Regarding the environment it is further concluded by the UK that there is a need to limit the risks. This applies to the assessment of secondary poisoning arising from use in polyurethane foams. High levels of pentaBDE have been both predicted and measured in fish and earthworms near to sources of release, and lead to a risk of secondary poisoning that is linked to local releases from foam production sites. A possible risk of secondary poisoning has also been identified at the regional level (linked to diffuse releases arising from use of the foam) for the earthworm-based food chain. The widespread environmental occurrence and bioaccumulative nature of the substance also lend support to the overall concern for this end-point.

#### 2.1.4 Exposure to octa- and decaBDE

The draft environmental risk assessment concludes for the aquatic compartment that the risk from exposure via surface water is thought to be low. Exposure to organisms via sediment is thought to be much more relevant for these substances and a risk to sediment dwelling organisms could not be ruled out using the available data in the local scenario for polymer processing (octa) and the estimated concentrations from local and regional sources (deca). Measured levels near to sources of release also indicate a possible concern for sediment (octa). For the terrestrial compartment, a risk could not be ruled out using the available data in the local (octa, deca) and regional (deca) scenarios where sewage sludge containing the substances is applied to agricultural soil. Toxicity studies on sediment and soil are being investigated further. The results will be available during spring 2001.

A possible concern is the formation of lower brominated diphenyl ethers from the photochemical degradation of octaBDE in the environment, since these compounds, particularly tetra- and pentaBDE have been found extensively in the environment and are potentially more toxic and bioaccumulative. No information is currently available on this point for octaBDE. Limited data are available on the direct photolysis of decaBDE in water, which show that it does not appear to form significant amounts of lower brominated congeners, such as penta- and tetraBDE, on exposure to sunlight in environmentally relevant media. However, this is currently being investigated further. Photolysis and anaerobic biodegradation tests under environmentally relevant conditions have been initiated.

Another area of possible concern with regard to secondary poisoning (and also direct toxicity) is the formation of brominated dibenzo-p-dioxins and dibenzofurans during combustion or other high temperature processes (e.g. incineration, landfill where fires could occur), metal recycling (if the metal is contaminated with plastic containing octa- or decaBDE), or accidental fires involving articles containing PBDEs. These brominated dioxins and furans have been identified in flue gas from municipal waste incineration. However, they have not been identified in the very limited number of environmental samples analysed so far.

## 2.2 PBB

Human and environmental exposure may occur in connection with the use of products, in the recycling of plastics containing PBBs and after disposal to landfills. Emission is probably very slow, but PBBs may be released after degradation of PBB-bearing material.

DecaBB and hexaBB have been found in several sediment samples from the estuaries of large rivers in western Europe. Outside the PBB production plant in France, biphenyls with between five and ten bromines have been found in mussels, algae and seaweed. HexaBB has been identified in edible fish from northern Europe (Jansson *et al.*, 1993). Although hexaBB has previously been used as a flame retardant, the possibility of their resulting from the debromination of decaBB cannot be ruled out. DecaBB are persistent, but there are studies to suggest that debromination can take place in UV light. Microbial debromination in an anaerobic environment is also a possible transformation path. DecaBB may have a potential for airborne distribution, but it is not likely that decaBB will undergo significant long-range airborne distribution.

There are great similarities between less brominated PBBs such as hexaBB and certain PCB compounds as regards biological effects, chemical structure and occurrence in the natural environment. If, therefore, decaBB is debrominated to less brominated PBBs of this kind, there is a risk of detrimental effects, resembling those which PCB has caused, occurring in human beings and in the environment.

Studies of industrial workers exposed to decaBB and decaBDE have pointed to effects on the thyroid system (hypothyroidism) resembling those seen in experimental animals (Bahn *et al.*, 1980).

PBB compounds are fat-soluble and persistent. Some PBB compounds metabolise very slowly in the body and therefore accumulate in the fat of organisms. After release into the environment they can reach the food chain and accumulate there.

Bioaccumulation of different PBB compounds increases with increasing bromination up to at least tetraBB. Uptake will be less efficient, however, if the molecule is too large, as for example in the case of decaBB. Bioaccumulation of decaBB in fish, therefore, is unlikely to occur to any significant extent ( $BCF < 5$ ). Molecular size can be one reason for low uptake through the gill membranes. Bioavailability through food or for other aquatic organisms is regarded as a possible exposure path.

Few toxicity data are available from short-term tests on aquatic organisms. These data suggest moderate toxicity. Studies carried out in 1992 by MITI (Japan) found the 48 hr LC<sub>50</sub> of DBB to be 250 and >66 mg/L in *Oryzias latipes* and *Daphnia magna*, respectively.

PBB (14, 49, 52) was measured in blue mussel and cod (liver) sampled along the Norwegian coast in levels of <0.01 - 0.13 and <0.2 - 0.45 ng/g wet weight respectively (Schlabach *et al.*, 2002).

PBB-101 was found in plasma samples of male individuals of glaucous gulls from Bear Island (Northern Norway) in concentration of 0.09 - 0.76 ng/g wet weight. The PBB concentration in plasma of female individuals was slightly lower (0.09 - 0.56 ng/g wet weight). In the eggs of glaucous gulls, the levels varied between 0.06 - 0.54 ng/g wet weight (Verreault *et al.*, 2004).

PBB-15 and 153 have been detected in liver of northern fulmars from Björnøya (Northern Norway), in levels of 0.21 - 0.44 ng/g wet weight (Gabrielsen *et al.*, 2005).

## 2.3 HBCDD

### 2.3.1 Monitoring data

#### Concentrations in the marine environment

Very few data used to be available on HBCDD in water. HBCDD was monitored in marine and river sediment in Japan. Three out of 69 sediment samples contained HBCDD in the range 0.02 – 0.09 mg/kg dry weight.

In sediments taken in a river in Sweden down-stream from a possible point source HBCDD was found. The approximate wet weight concentrations ranged from 0.04 to 0.37 mg/kg (Sellström *et al.*, 1998).

HBCDD was measured in sediments along the Norwegian coast. The levels up to 14 ng/g dry weight was measured (Fjeld *et al.*, 2004).

$\alpha$ - and  $\gamma$ -HBCDD was measured in sediments (1 - 2 cm) from Lake Ellasjøen on Björnøya (Arctic Sea region) in levels up to 4.3 ng/g dry weight.  $\beta$ -HBCDD was not detected in any of the samples (Christensen *et al.*, 2004).

A one-off survey was carried out in 2003 in the Dutch Marine and Coastal waters. HBCDD was measured in sediments from the coastal zone and at open sea at levels of 0.04 - 30 ng/g dry weight. HBCDD was also detected in suspended matter in levels of 6 - 310 ng/g dry. Generally, the concentrations of HBCDD tended to be higher in the coastal zone (SIME 2005).

In a report from Cefas (2006) monitoring data concerning HBCDD in sediments from the North Sea was reported. The results are summarised in Table 2.

**Table 2.** Concentration of HBCDD in sediments from North Sea (Cefas 2006).

Site	Concentration range and unit
Scheldt basin	<0.2 - 260 ng/g dw
Western Scheldt	<0.1 - 128 ng/g dw
Netherlands (Estuarine + riverine)	<0.5 - 34 ng/g dw
England (Estuarine + riverine)	<2.4 - 1680 ng/g dw
Dublin Bay, Ireland	<1.7 - 12 ng/g dw

HBCDD has been found in sediments from Barents Sea in levels up to 190 ng/g dry weight. This study showed that HBCDD in the Barents Sea sediments do not represent an environmental risk (Bakke *et al.*, 2008).

### Concentrations in biota

HBCDD has been found in fish (pike) muscle in Sweden at concentrations of 4000 to 8000 ng/g lipid weight. This corresponds to 0.02 to 0.06 mg/kg wet weight (Sellström *et al.*, 1998). HBCDD was also found in four out of 66 fish samples analysed in the Japanese study mentioned above (0.01 – 0.023 mg/kg fresh weight).

Fjeld *et al.*, (2004) reported levels of HBCDD in cod liver of 0.7 - 4.9 ng/g wet weight.

HBCDD has been detected in liver samples of Northern fulmars from - Bjørnøya (Northern Norway) in levels of 0.2 - 2.2 ng/g wet weight (Gabrielsen *et al.*, 2005). HBCDD was also measured in blood and adipose tissues of polar bears from Svalbard in concentration of 0.001 - 0.045 ng/g wet weight (Gabrielsen *et al.*, 2004).

HBCDD was measured in the blubber harbour porpoise (*Phocoena phocoena*) stranded or bycaught in the U.K during the period of 1994 to 2003. The levels varied between 10 to 19200 ng/g wet weight (Law *et al.*, 2006).

In a report from Cefas (2006) monitoring data concerning HBCDD in biota from the North Sea was reported. The results are summarised in Table 3.

**Table 3.** HCBDD concentration in biota from the North Sea (Cefas, 2006).

Site	Species	Concentration range and unit
North Sea	Common whelk (whole)	29 - 47 ng/g lw
Western Scheldt	Sea star (digestive system)	<DL-84 ng/g lw
North Sea	Hermit crab (abdomen)	<DL
North Sea	Whiting (muscle)	<DL
North Sea	Cod (liver)	<DL
Scheldt basin Belgium	Eel	<DL-33000 ng/g lw
Netherlands - Rivers	Eel	12 - 850 ng/g lw
Western Scheldt	Common Tern (eggs)	330 - 7100 ng/g lw
W. Wadden Sea	Harbour seal (blubber)	63 - 2055 ng/g lw
North Sea	Harbour porpoise (blubber)	440 - 6800 ng/g lw
North Sea - E. England	Harbour porpoise (blubber)	<DL-1020 ng/g lw
England	Cormorant (liver)	140 - 1300 ng/g lw
Atlantic - S. Ireland	Hake (liver)	<DL

HBCDD was measured in plasma samples of glaucous gulls from the Bear Island (Northern Norway). The concentration varied between 0.1 - 1.5 ng/g wet weight for male individuals and was slightly higher for the female individuals (0.2 - 2 ng/g wet weight). The levels of HCBDD in eggs of glaucous gulls varied between 2 - 70 ng/g wet weight (Verreault *et al.*, 2004). In another study from the Bear Island, HCBDD was detected in brain and liver samples of glaucous gulls in levels of 5.1 - 48 and 195 – 15 000 ng/g lipid weight respectively (Knudsen *et al.*, 2007).

In a recent study, trend analysis of HCBDD concentration in biota from the Swedish national monitoring programme until year 2006 was performed. Biobank samples of guillemot eggs showed that the concentration of HCBDD increased with 3% per year with a statistically significant trend for the period from 1968 - 2006. A similar trend was also found in samples of herring muscle at some sites in the southern Baltic Sea, but the number of samples was not sufficient to accurately estimate long-term trends. Samples from the Kattegat (site Fladern) showed a concentration of HCBDD of 0.031 – 58 ng/g lipid weight but no trend analysis was made (Bignert *et al.*, 2008).

### 2.3.2 Releases

According to the EU risk assessment, humans may be exposed from many different sources owing to the wide use of HBCDD in products in society. Inhalation of vapour and airborne dust and via dermal contact is considered relevant at the workplace while producing, formulating and processing HBCDD or the polymer containing HBCDD. Exposure occurs via inhalation and dermal contact during industrial and consumer use of products containing HBCDD. Indirectly, exposure can also occur via food, soil, water and air.

Exposure to HBCDD may be equated with long-term (during the entire human lifetime) and low dose exposure.

In view of the potential ability of HBCDD to be transported long range, releases from diffuse sources are likely to influence areas remote from point sources and in that way exposure to humans.

Inhalator exposure during the manufacture (packing, filling of sacks) of HBCDD is considered to be 5 mg/m<sup>3</sup> in a reasonable worst-case scenario. Short-term exposure may be twice as high or 10 mg/m<sup>3</sup>.

Dermal exposure levels have been calculated in reasonable worst-case scenarios. During manufacture (packing, filling of sacks) and during industrial use of HBCDD as an additive the exposure level will be 840 mg/day.

The amount of waste containing HBCDD will increase in the future. Up until now mostly end products with a service life shorter than 20 years have been wasted. It is not known to what extent end products containing HBCDD are landfilled, incinerated, left in the environment or recycled. Municipal waste is likely to be landfilled or incinerated. Construction material used on or under the soil could be left or is used as filling material *e.g.* for road construction. In the case of incineration the generation of polybrominated dibenzofurans and dibenzo-*p*-dioxins will have to be considered.

Recycling of expanded polystyrene, EPS, does occur in several European countries. Wasted EPS blocks are ground and put in the moulding process together with virgin EPS to form new blocks. However it is not clear to what extent a distinction is made between streams of flame retarded and non-flame retarded material. It is possible that HBCDD will end up in applications where fire resistance is not needed nor wanted and the substance flow will be out of control.

## 2.4 Further considerations

The EU Technical Guidance Document for risk assessment of chemicals has since the last update of this background document been supplemented with a section about marine risk assessment and methods for the identification of PBT substances in the marine environment. The results from the risk assessments within the EU Existing Substances Programme has also led to the current ban on all uses of penta and octaBDE and the ban on decaBDE in electronic products. HBCDD has also been identified as a PBT substance for which risk reduction measures should be taken. The three BDEs therefore must be considered to be severely restricted, and restrictions most likely will be introduced for HBCDD in the future. Since alternative BFRs however may replace these substances in the future the following information may therefore still be relevant when discussing the need for future measures:

- a. releases from articles in use.

The widespread distribution of these persistent substances in society via articles makes sources of exposure hard to locate. A slow release of some PBDE from articles is known to occur. The fact that octaBDE has been measured in the blood of workers employed on premises where computers and TV sets are used could be an indication of that. No single exposure source, however, can be reliably identified. The source may be computers and TV sets emitting octaBDE, but food may also be a source of uptake;

- b. releases from waste.

There is a general background exposure to PBDE. This can be elevated in the case of occupational exposure, including waste handling. Among occupational categories employed in the dismantling of electronics, the blood concentration of heptaBDE (the most common compound in technical octaBDE) was 65 times higher than among hospital cleaning staff. This suggests a connection between professional handling of products containing PBDE and concentrations of these PBDE found in the bloodstream. Elevated concentrations of nona- and decaBDE were also found. Releases to the environment, *e.g.* from landfills, have also to be considered;

- c. cumulative exposure during a lifetime.

Exposure from these chemicals occurs during the whole life. Quantitative information is lacking concerning the magnitude of exposure, and concerning consequences of lifetime exposure for human health. However, recent data have shown that in Sweden the concentration of tetraBDE and pentaBDE in breast milk has been increasing exponentially since 1972, with concentrations doubling every five years; and a decrease as from around year 2000.

- d. marine environment.

Both PBDE and PBB occur in the marine environment. HexaBB and tetra- and pentaBDE have been found in many animal species from a wide variety of regions, including marine organisms like seal from Svalbard, and pike, perch and eel from more industrialised regions. Their occurrence in areas where exposure sources are lacking suggests long-distance transport of PBDE and PBB. Experience from substances of this type, *e.g.* PCB, has shown that exposure reduction takes a long time. Once the environmental concentrations have reached a level giving rise to serious effects, slow degradation of these substances may sustain such levels.

One recent *in vitro* study indicates that a few of the congeners in pentaBDE may interact with the estrogenic system by binding to the oestrogen receptor (Meerts *et al.*, 2001). Although this interaction has not been confirmed *in vivo*, it supports the need for a proper evaluation of the potential reproductive toxicity of pentaBDE.

Another complicating factor for assessments is that most PBDE data refer to tetraBDE and pentaBDE. The occurrence of octaBDE and decaBDE are less well known. One explanation may be that analyses often are lacking. Analyses of highly brominated compounds are more complicated and require additional analytical stages. Recent monitoring data however show that decaBDE also occur in biota in areas not directly affected by point sources.

Finally, some data also indicated behavioural effects on mice and further studies have later supported this effect. A single, low dose of tetraBDE or pentaBDE given to new-born mice has been found to affect these animals' behaviour in adulthood. In similar animal experiments, PCB has affected the animals' behaviour in the same way. In the case of PCB these effects are accompanied by biochemical changes in the brain of the experimental animals, and there is strong evidence that the behavioural effects induced in animals can also occur in human beings. In addition, it is possible that these persistent compounds may have synergic effects on the brain.

### 3. Desired reduction

Brominated flame retardants are on the OSPAR List of Chemicals for Priority Action since 1998 (see the OSPAR Strategy with regard to Hazardous Substances). The OSPAR objective with regard to hazardous substances on this list is to prevent pollution of the maritime area by continuing to reduce discharges, emissions and losses of hazardous substances, with the ultimate aim of achieving concentrations in the marine environment near background values for naturally occurring substances and close to zero for man-made synthetic substances. Every endeavour will be made to move towards the target of cessation of discharges, emissions and losses of hazardous substances by the year 2020.

In the Esbjerg Declaration of the 4<sup>th</sup> North Sea Conference (1995), Ministers agreed to take concerted action within the framework of the competent international forum to substitute the use of brominated flame retardants by less hazardous or preferably non-hazardous substances where these alternatives are available.

Occurrence in the environment, high persistence, potential for long-range air transport are reasons for concern relating to certain PBDEs and PBBs. For some of the substances, high bioaccumulation and high toxicity are also of concern. Based on available data these substances seem to be the most important substances for risk reduction. HBCDD is used in large volumes, has a very high potential to bioaccumulate and is not readily biodegraded.

The aim is to achieve the 2020 target of the cessation of discharges, emissions and losses of brominated flame retardants. At present only decaBDE (CAS no. 1163-19-5) and HBCDD (CAS nos. 25637-99-4, 3194-55-6) are commercially significant among the BFRs discussed in this background document. The need for further measures may therefore first of all be discussed for these two substances.

## 4. Identification of possible measures

### 4.1 Ongoing activities

The work of the OECD has involved discussions of how industry has performed on its commitment to reduce the hazards of PBDE, PBB and TBBP-A. This commitment includes *e.g.* the use of best available technique when manufacturing the substances, but not a phase-out. With the exception of decaBB, industry made the commitment that PBB will not be further produced. The exemption for decaBB was later no longer needed because the manufacturer made a statement to cease production on 30 September 2000. The use of all PBBs have also later been severely restricted in the EU.

The risk assessment for pentaBDE within the framework of the Existing Substances Regulation (EEC) 793/93 concluded that there was a need for specific measures to limit the risks. This was justified by the particular characteristics of this substance, especially its environmental persistency, potential for bioaccumulation, toxicity, levels in biota and occurrence in breast milk in concentrations that may be increasing with time.

A ban on marketing and use, has consequently been enforced for penta and octaBDE. These measures will as far as possible contribute to achieving the 2020 target.

In the framework of Directive 2000/60/EC of the European Parliament and of the Council of establishing a framework for Community action in the field of water policy (Water Framework Directive). The Directive has established a list of priority substances including substances identified as priority hazardous substances. Brominated diphenyl ethers are included in this list with an indication that only pentabromobiphenyl ether is identified as a priority hazardous substance. With respect to the priority substances, the European Commission shall submit proposals of controls for the progressive reduction of discharges, emission and losses of substances concerned, and, in particular the cessation or phasing out of discharges, emissions and losses of priority hazardous substances. Hazardous substances are defined in the Water Framework Directive as “substances or groups of substances that are toxic, persistent and liable to bio-accumulate, and other substances or groups of substances which give rise to an equivalent level of concern”. In drawing up the above list in its proposal, the European Commission has taken into account OSPAR work on the prioritisation of hazardous substances.

All PBBs are at present banned for use in electronic equipment according to the RoHS Directive, 2005/95/EC, and may not be used in textiles intended for coming into direct contact with the skin.

HBCDD was on the 2<sup>nd</sup> priority list of existing chemicals within the EU programme on Existing Chemicals. A risk assessment report according to Regulation (EEC) 793/93 has been finalised and Sweden has proposed the following risk reduction measures:

- to impose restrictions on the marketing and use of HBCDD in general, *i.e.* in textiles, High Impact Poly Styrene (HIPS), Expanded polystyrene foam (EPS) and Extruded polystyrene foam (XPS) under the Limitations Directive (76/769/EEC);
- to consider the need for time limited exemptions for certain uses of HBCDD in EPS and XPS under the Limitations Directive;
- to impose compulsory marking of exempted uses of HBCDD in EPS and XPS products under the Limitations Directive;
- to classify used material and products containing HBCDD as hazardous waste under the Hazardous Waste Directive;

- to include HBCDD as a priority hazardous substance in Annex X of the Water Framework Directive;
- to develop a proposal for the inclusion of HBCDD in the Stockholm Convention on POPs.

HBCDD has subsequently been selected as a Substance of Very High Concern (SVHC) based on it being a PBT substance. Further use in the EU will require authorisation.

The directive concerning Waste from Electric and Electronic Equipment (WEEE), and the directive concerning restrictions on use of hazardous substances in electric and electronic equipment (RoHS) have been finalised. The latter directive includes provisions for the substitution of the brominated flame retardants PBDE and PBB. The WEEE Directive includes systems for collecting electric and electronic waste as well as improved handling of waste. These measures have most likely already contributed to achieving the 2020 target, and a reduction in the use of these brominated flame retardants. Monitoring data show that BFRs are still present in detectable concentrations but the decreasing trends for especially PBDEs indicate the efficiency of a combination of voluntary emission limit programmes and legislative measures. The monitoring data for HBCDD however still indicate increasing trends, which might be directly connected to the continuous use of the substance for certain applications.

A broader work than that at present conducted within the EU will still be needed to be able to reach the cessation target described in Chapter 3. There is increasing evidence for the PBT properties of decaBDE, including the possibility of debromination of decaBDE. There has recently been an agreement on the PBT properties of HBCDD among the EC member states and risk-reduction measures will have to be applied. The use of BFRs outside the OSPAR area is also a matter of concern due to the risks for long-range transport and the import of flame-retarded articles.

## 4.2 Alternatives

A large number of compounds may be considered as alternatives. Substitution can take place at three levels:

- brominated flame retardants can in some applications be replaced by another flame retardant without changing the base polymer;
- the plastic material, *i.e.* the base polymer containing flame retardants and other additives, can be replaced by another plastic material;
- a different product can replace the product, *e.g.* the plastic material is replaced by another material, or the function can be fulfilled by the use of a totally different solution.

Alternatives mentioned under the first indent for electric and electronic equipment are *e.g.* aluminium trihydroxide, magnesium hydroxide, red phosphorus or organic phosphorus compounds. These substances may not be viable for equipment which needs to meet certain demands with respect to technical and safety standards.

The flame retarded plastics used for switches, sockets and other applications where the material is in direct contact with live parts of electronic and electrical appliances are mainly made of thermoplastic polyester and polyamides. According to the Danish Environmental Protection Agency decaBDE has been substituted by TBBP-A and brominated styrene, but diarylphosphonate, melamine cyanurate or red phosphorus may be used as well.

Flame retardants for rigid polyurethane foams may be based on ammonium polyphosphates or red phosphorus. For flexible foams chlorinated phosphate esters, in some cases combined with melamine, ammonium polyphosphates and reactive phosphorus polyols are used.

Polysulfone, polyaryletherketone and polyethersulfone are plastics that are self-extinguishing and can be used without the addition of flame retardants. Less flammable materials e.g. wood and metals can also replace plastic material. Another example of the substitution of material is using wool instead of a more flammable fabric.

Available data show that there are less hazardous alternatives e.g. aluminium trihydroxide. But it cannot be disregarded that less suitable substances might be among the alternatives. When industry selects a method to inhibit fire, data has to be generated in order to allow a good choice from an industrial/product and environmental point of view.

## 5. Choice for action/measures

According to CEFIC/European Brominated Flame Retardant Industry Panel and the European manufacturer (Bakés 2000), the production of PBB ceased during 2000. They also state that there is no production of PBB outside Europe. This seems to have been the case for at least some decades. Provided there are no hidden sources, such as products coming from non-EU countries, no further action by OSPAR is considered necessary. Therefore,

- OSPAR is recommended to note that production of PBB has ceased;
- OSPAR Contracting Parties that are also EU Member States are recommended to note that PBBs are included in the EC Directive on Waste from Electric and Electronic Equipment and the RoHS Directive on the use of hazardous substances in electric and electronic equipment.

Work within the EU Existing Substances Regulation on pentaBDE and octa BDE provided a sufficient basis for restricting the uses that give rise to the major part of emissions and discharges. An amendment to Council Directive 76/769/EEC banned all marketing and use of pentaBDE and octa BDE (Directive 2003/11/EC). On this basis,

- no further OSPAR action will be necessary, but
- Contracting Parties may consider the need for continuous monitoring and market surveillance, especially on imported products.

For decaBDE, Contracting Parties should note the decision, underlining that decaBDE is (among other PBDEs) banned in electronic equipment put on the EU market. This will most likely considerably reduce the use of decaBDE in the European Union. Remaining areas of use may however also need to be scrutinized since monitoring data support the presence of decaBDE in biota.

For HBCDD, risk assessments within the framework of the Existing Substances Regulation has been completed and concern for the marine environment has been shown for a number of uses.

- in the light of the conclusions of that risk assessment, OSPAR Contracting Parties should note the proposals on risk-reduction strategies for HBCDD, including the identification as a SVHC under the REACH regulation. The use of HBCDD will need authorisation and contracting parties may in the meantime support voluntary substitution of HBCDD with less harmful alternatives.

Under the EC Water Framework Directive a list of priority substances, including the identification of priority hazardous substances, has been established. PentaBDE is included on this list as a priority hazardous substance. Following the formal adoption of the first revision of this list, and in the light of the conclusions of the risk assessments of other PBDEs, OSPAR Contracting Parties that are also EU Member States should note:

- that all PBDEs are included on that list. Member States may establish national environmental quality standards for all PBDEs except for pentaBDE where a common EC EQS apply.

In order to provide a sound basis both for future decisions and assessments of the quality status of the marine environment, OSPAR should note the monitoring strategy for the brominated flame retardant covered by this Background Document annexed to this background document.

The 2009 update of this background document shows that major steps have been taken to enable the OSPAR 2020 target to be achieved for brominated flame retardants in general.

OSPAR should however continue to follow the developments regarding HBCDD, taking a common position in support of introduction of risk reduction measures. OSPAR may also note that the Helsinki Commission (HELCOM) including Russia and the European Union have recently agreed on the identification of HBCDD as a priority substance for measures in order to protect the Baltic Sea.

OSPAR CPs may also note the current revision of the EC Regulation for building products and support the proposals of introducing a system of declaration of content for environmentally harmful substances like HBCDD.

OSPAR should also continue to review the need for further risk reduction measures for decaBDE, *e.g.* the use of decaBDE as a flame retardant in textiles.

To ensure that the information in this background document and the conclusions reached by OSPAR are formally communicated to the European Commission, OSPAR should write to the European Commission expressing its views on additional measures to be taken in order to reach the OSPAR 2020 target.

OSPAR should also note the possibility that some brominated flame retardants might be replaced with others, being equally persistent and with insufficient ecotoxicity and monitoring data. OSPAR should therefore investigate the possibility to agree on a recommendation in view of avoiding increased release of new BFRs in the OSPAR area. One example of possible substituting BFRs is the substance TBBPA-DBPE (CAS no. 21850-44-2). This substance is subject to industry's VECAP program on voluntary emission control. It was on the OSPAR List of Substances of Possible Concern but the Informal Group of Experts (IGE) has concluded that the available scientific evidence is insufficient to support keeping TBBPA-DBPE selected. TBBPA-DBPE is nevertheless subjected to the VECAP program on voluntary emission control. IGE noted<sup>1</sup> that the Dynamec mechanism does not provide for uncertainty as a basis for selection but OSPAR CPs may in the future provide new data and support a renewed evaluation.

To ensure that the information in this background document can be considered in the context of other international agreements, which deal with hazardous substances and to, which Contracting Parties are associated.

- OSPAR should send copies of this background document to the appropriate bodies dealing with those agreements and invite Contracting Parties who are common parties to OSPAR and those other agreements to promote action to take account of this background document by those other international bodies in a consistent manner.

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<sup>1</sup> Some IGE members expressed concern over the possibility that present studies on TBBPA-DBPE do not fully reflect the potential toxicity and bioaccumulation properties of the substance.

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## Appendix 1: Monitoring strategy for certain brominated flame retardants

As part of the Joint Assessment and Monitoring Programme (OSPAR agreement 2003-22), OSPAR 2004 adopted an Agreement on monitoring strategies for OSPAR Chemicals for Priority Chemicals (OSPAR agreement 2004-15) to implement the following monitoring for tracking progress towards the objectives of the OSPAR Hazardous Substances Strategy (OSPAR agreement 2003-21) with regard to certain brominated flame retardants. The Monitoring Strategy for certain brominated flame retardants will be updated as and when necessary, and redirected in the light of subsequent experience.

This monitoring strategy covers those brominated flame retardants (BFRs) covered by the recommendations of the OSPAR Background Document on certain brominated flame retardants - pentabrominated diphenyl-ether, octabrominated diphenyl-ether, decabrominated diphenyl-ether, hexabromocyclododecane and decabromobiphenyl. Penta- and octabromodiphenyl ether will be banned in 2004. Hexabromocyclododecane is still in use and may be increasingly used as a substitute for the banned diphenyl ethers.

There are a number of relevant controls (e.g. regulations, directives, recommendations and decisions) on a) marketing and/or use, b) emissions and/or discharges of BFRs which have been agreed by Contracting Parties both in OSPAR and in other international forums and have been highlighted as important measures for achieving the OSPAR Hazardous Substances objective with respect to BFRs in the “choice for actions” chapter of the Background Document. Evidence from reports on the implementation of such measures will be used to make an initial judgement of the extent to which the amounts of these substances emitted or discharged are reduced.

Bearing in mind the widely dispersed and diffuse sources of BFRs, environmental monitoring may offer a better option than the source oriented approach for tracking the progress towards the 2020 cessation target. Methodologies for monitoring BFRs in the environment are available. Monitoring that has been carried out in the marine environment shows concentrations above the detection limit in biota and sediment.

On the evidence available, it would not appear to be sensible to include BFRs in the RID or CAMP programmes.

Since the laboratories of several Contracting Parties have developed sufficient analytical capability to measure BFRs they appear to be good candidates to be included in the review of the CEMP in 2005 - 06. Any future proposal for inclusion of BFRs in the CEMP, should take into account:

- a. the possible need for monitoring in relation to agreed Ecological Quality Objectives (organochlorine concentrations in seabird eggs). The Swedish long-term monitoring programme using guillemot eggs as an indicator of the reductions of BFRs in the Baltic marine environment could be shown as a good example;
- b. brominated diphenyl ethers are included as a priority hazardous substances under the EC Water Framework Directive, and OSPAR will seek to make use of the results of Water Framework Directive monitoring. The Water Framework Directive catchment assessments may assist the identification of monitoring locations.

In the meantime Contracting Parties are urged to extend their monitoring programmes to cover BFRs and to report results on a voluntary basis through the data-handling mechanism operated by ICES for the CEMP.

OSPAR will consider the need to developing an EAC for certain BFRs, taking into account the development of an environmental quality standard under the WFD.

Some BFRs may disrupt the oestrogenic system, and biological effects monitoring may also need to be considered. Available information on the occurrence of BFRs and their biological effects in marine biota will be evaluated to gauge whether there is a gap in knowledge which OSPAR should seek to fill, prior to the 2009 Quality Status Report for the Convention Area.

<b>CERTAIN BROMINATED FLAME RETARDANTS MONITORING STRATEGY<sup>2</sup></b>	
<i>Implementation of actions and measures</i>	<ul style="list-style-type: none"> <li>Examination of progress in the implementation of regulations on marketing and/or use or emission and/or discharge which have been agreed, or are endorsed, by the Background Document</li> </ul>
<i>Concentrations in sediments</i>	<ul style="list-style-type: none"> <li>The review of the CEMP in 2005 - 06 will consider whether to add an additional appendix on these substances</li> <li>Before [2006] the lead country will collate information on concentration of these substances in the marine environment in order to assess whether this is a gap in knowledge which OSPAR should fill prior to the 2009 QSR</li> <li>The need for EACs and BRCs will be considered</li> </ul> <p>Additional voluntary monitoring</p> <ul style="list-style-type: none"> <li>In the meantime, Contracting Parties will be encouraged to extend their monitoring programmes to cover brominated flame retardants and to report results on a voluntary basis through the data-handling mechanism operated by ICES for the CEMP</li> </ul>
<i>Concentrations in biota</i>	<ul style="list-style-type: none"> <li>The review of the CEMP in 2005 - 06 will consider whether to add an additional appendix on these substances. Any proposal for such an appendix should consider possible synergies with monitoring related to the North Sea Pilot Project EcoQO on organochlorine concentrations in seabirds' eggs</li> <li>Before 2006 the lead country will collate information on concentration of these substances in order to assess whether this is a gap in knowledge which OSPAR should fill prior to the 2009 QSR</li> </ul> <p>Additional voluntary monitoring</p> <ul style="list-style-type: none"> <li>In the meantime, Contracting Parties will be encouraged to extend their monitoring programmes to cover brominated flame retardants and to report results on a voluntary basis through the data-handling mechanism operated by ICES for the CEMP</li> </ul>
<i>Biological effects</i>	<ul style="list-style-type: none"> <li>Before 2006 the lead country will collate information on concentration of these substances in order to assess whether this is a gap in knowledge which OSPAR should fill prior to the 2009 QSR</li> </ul>

<sup>2</sup> That is, pentabrominated diphenyl-ether, octabrominated diphenyl-ether, decabrominated diphenyl-ether, hexabromocyclododecane and decabromobiphenyl.



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