



Background Document on Tetrabromobisphenol-A



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 Union 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 l'Union européenne et l'Espagne.

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Executive Summary

Tetrabromobisphenol-A (CAS No. 79-94-7) is a brominated organic compound (C₁₅H₁₂Br₄O₂), and is primarily used as a reactive intermediate in the manufacture of flame-retarded epoxy and polycarbonate resins. It may also be used as an additive flame retardant, for example in the manufacture of acrylonitrile-butadiene-styrene resins and phenolic resins, or in the manufacture of derivatives, although there is presently no evidence of this latter use in the EU. Tetrabromobisphenol-A was added to the OSPAR List of Chemicals for Priority Action in 2000.

Tetrabromobisphenol-A is produced in the USA, Israel, Jordan and Japan but not in the EU. The current total amount of tetrabromobisphenol-A produced is estimated in the order of 120 000 to 150 000 tonnes/year. The amounts of tetrabromobisphenol-A imported into the EU both as the substance itself and in partly finished and finished products are estimated to be in the order of 40 000 tonnes/year.

Tetrabromobisphenol-A is considered to meet all three of the OSPAR criteria for the PBT assessment, although it should be acknowledged that it is a borderline case for the bioaccumulation criterion. However, tetrabromobisphenol-A does not meet the criteria for a PBT or a vPvB substance that are used under REACH/ESR (it would be considered P (persistent) or vP (very persistent) only); it is not B (bioaccumulating) or vB (very bioaccumulating), but potentially meets the toxicity criterion on the basis of a fish study that gave inconclusive results.

Tetrabromobisphenol-A poses a potential risk to water and sediment from the compounding step for its additive uses in ABS. The manufacture and processing of epoxy and polycarbonate resins, and the conversion step for ABS, do not appear to present a risk. None of the major manufacturing sites in the EU using tetrabromobisphenol-A as a reactive flame retardant, or compounding sites using tetrabromobisphenol-A as an additive flame retardant, are situated close to coastal areas, and the sole ABS plant in the EU where a risk was identified has been closed. There is also indication for the potential of tetrabromobisphenol-A to degrade under anaerobic conditions to form bisphenol-A whose adverse effects on aquatic molluscs at low concentrations remain uncertain, although the risk arising from bisphenol-A for the marine compartment is considered to be low. The extent of the risk arising from tetrabromobisphenol-A bis(methyl ether), which may be formed by degradation and is very persistent and very bioaccumulative, is unclear but likely to decline in light of actions taken; nevertheless, it remains a potential concern.

Actions so far have been limited. EC Directive 2002/96/EC on Waste Electrical and Electronic Equipment (WEEE Directive) requires Member States to set up separate collection schemes and ensure the proper treatment, recovery and disposal of WEEE and this will encourage producer responsibility for separation of plastic containing brominated flame retardants from collected WEEE. The main producers/suppliers of tetrabromobisphenol-A in the EU have instigated a VECAP with the aim of reducing emissions to the environment through a better understanding and better management of chemical substances throughout the supply chain.

The actions recommended are: to ensure that the information in this background document and the conclusions reached by OSPAR are generally taken into account in the approach of the European Community; to encourage the substitution of tetrabromobisphenol-A through the development and identification of safer substitutes which pose less risk; to invite the relevant industries to work with Contracting Parties to improve the estimates of emissions, environmental levels, and, if necessary, the estimation of PNEC values and clarification of PBT properties of relevant degradation products, in order to allow re-evaluation of the risks posed by tetrabromobisphenol-A releases when further information has been collected; to communicate this background document to other international agreements that deal with hazardous substances.

A monitoring strategy for tetrabromobisphenol-A is attached to this background document.

Récapitulatif

Le tétrabromobisphénol-A (N° CAS. 79-94-7) est un composé organique bromé (C₁₅H₁₂Br₄O₂), et est principalement employé comme intermédiaire réactif dans la fabrication des résines époxy et de polycarbonates ignifuges. Il peut aussi servir d'adjuvant retardateur de flammes, par exemple dans la fabrication des résines acrylonitriles-butadiènes-styrènes et des résines phénoliques, ou dans la fabrication de produits dérivés, bien qu'à l'heure actuelle l'on ne dispose d'aucun indice prouvant cette dernière application dans l'Union européenne. Le tétrabromobisphénol-A a été inscrit en 2000 sur la liste OSPAR des produits chimiques devant faire l'objet de mesures prioritaires.

Le tétrabromobisphénol-A est fabriqué aux Etats Unis, en Israël, en Jordanie et au Japon, mais pas dans l'Union européenne. La quantité totale fabriquée à l'heure actuelle est estimée se situer entre 120 000 et 150 000 tonnes/an. La quantité de tétrabromobisphénol-A importée dans l'Union européenne, que ce soit sous la forme de la substance elle-même, ou dans les produits finis ou en partie finis, est destinée être de l'ordre de 40 000 tonnes/an.

On considère que le tétrabromobisphénol-A respecte les critères OSPAR pour l'évaluation PBT, bien que l'on doive reconnaître qu'il s'agit d'un cas limite quant au critère de bioaccumulation. Le tétrabromobisphénol-A ne respecte cependant pas les critères pour une substance PBT ou vPvB, utilisés dans le cadre de REACH/ESR (il ne serait seulement considéré P (persistant) ou vP (très persistant)); il n'est pas B (bioaccumulant) ou vB (très bioaccumulant), mais il respecte potentiellement le critère de toxicité selon une étude halieutique dont les résultats ne sont pas concluants.

Le tétrabromobisphénol-A présente un risque potentiel pour l'eau et les sédiments au cours de l'étape de production pour ses usages en tant qu'additif aux ABS. La fabrication et le traitement de résines époxy et polycarbonées et l'étape de transformation pour les ABS, ne semblent pas présenter de risque. Aucun site principal de fabrication de l'UE utilisant le tétrabromobisphénol-A comme retardateur de flamme réactif, ou de production utilisant le tétrabromobisphénol-A en tant que retardateur de flamme additif, n'est situé près de zones côtières et la seule usine d'ABS de l'UE qui présentait un risque a été fermée. Il semble également que, potentiellement, le tétrabromobisphénol-A puisse se dégrader, dans des conditions anaérobiques, en bisphénol-A dont les effets préjudiciables sur les mollusques aquatiques à faible concentration sont incertains, bien que l'on considère que le risque posé par le bisphénol-A pour le milieu marin soit faible. Il n'est pas clair dans quelle mesure le risque que présente le tétrabromobisphénol-A bis(éther méthylique), qui peut se former par dégradation et qui est très persistant et bioaccumulatif, pourrait diminuer à la lumière des mesures prises; il continue cependant à causer des préoccupations potentielles.

Jusqu'à présent, les actions ont été limitées. La Directive 2002/96/CE sur les déchets de matériel électronique et électrique (Directive WEEE) exige que les Etats membres mettent sur pied des régimes de collecte séparée, et fasse en sorte que les déchets de matériel électrique et électronique soient convenablement traités, récupérés et éliminés, ce qui renforcera la responsabilité qu'ont les fabricants de séparer les matières plastiques contenant des retardateurs de flammes au brome dans les déchets de matériel électrique et électronique qui auront été ainsi recueillis. Les principaux fabricants/fournisseurs de tétrabromobisphénol-A de l'UE ont envisagé un VECAP dans le but de réduire les émissions dans l'environnement grâce à une meilleure compréhension et une meilleure gestion des substances chimiques dans l'ensemble de la chaîne d'approvisionnement.

Les actions recommandées sont les suivantes : faire en sorte que les renseignements figurant dans le présent document de fond ainsi que les conclusions tirées par OSPAR soient généralement pris en compte dans l'approche adoptée par la Communauté européenne ; encourager la substitution du tétrabromobisphénol-A, ceci par la création et l'identification de substituts moins dangereux, présentant un risque moindre, inviter les industries concernées à travailler avec les Parties contractantes afin d'améliorer les estimations des émissions, les niveaux environnementaux, et, si nécessaire, l'estimation des valeurs PNEC et la clarification des propriétés des produits de dégradation pertinents, ceci afin de réévaluer les risques présentés par les émissions de tétrabromobisphénol-A lorsque de nouveaux éléments d'information

auront été recueillis ; communiquer le présent document de fond aux autres accords internationaux traitant des substances dangereuses.

Une stratégie de surveillance sur le tétrabromobisphénol-A est jointe à ce document de fond.

1. Basis and rationale for action

The objective stated in the OSPAR Strategy with regard to Hazardous Substances ('the Strategy'), which was adopted in Sintra in 1998, updated at the 2003 Ministerial Meeting and endorsed by Ministers 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".

The Strategy also includes a timeframe which states that:

"every endeavour will be made to move towards the target of cessation of discharges, emissions and losses of hazardous substances by the year 2020".

Tetrabromobisphenol-A (CAS No.79-94-7) is on the OSPAR List of Chemicals for Priority Action (cf. Annex 2 of the Strategy), and the OSPAR Action Plan for 1998 – 2003 shows that the UK is the lead country for drawing up a background document on tetrabromobisphenol-A.

This background document addresses this obligation and has the following aims:

- identifying the main sources of tetrabromobisphenol-A and its various pathways into the marine environment;
- reviewing the various controls to limit discharges, emissions and losses of tetrabromobisphenol-A;
- assessing the extent of the risk posed by tetrabromobisphenol-A to the marine environment;
- assessing what further activities should be undertaken by OSPAR, or other relevant international organisations, in order to achieve the various OSPAR commitments.

This background document takes into account the "Interim Guidance on how to address Hazardous Substances for Priority Action" agreed at OSPAR 1999 (cf. Annex 7 of the Summary Record OSPAR 99/15/1) and follows the structure for OSPAR background documents outlined in that document.

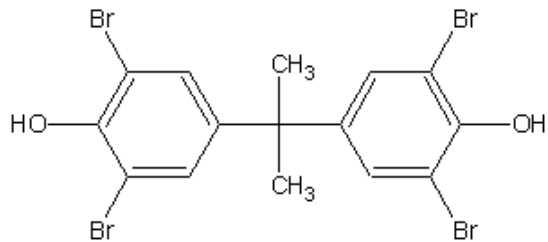
Tetrabromobisphenol-A has undergone a detailed risk assessment (including the marine compartment) under the EU Existing Substances Regulation (EC) no. 793/93 (ESR). Much of the information used here is taken from the final agreed risk assessment report (ECB, 2008).

2. Identification of all sources of the substance and pathways to the marine environment

2.1 Properties of Tetrabromobisphenol-A

This assessment considers the following commercial substance:

CAS No:	79-94-7
EINECS No:	201-236-9
IUPAC Name:	2,2',6,6'-Tetrabromo-4,4'-isopropylidenediphenol (tetrabromobisphenol-A)
Molecular formula:	$C_{15}H_{12}Br_4O_2$
Molecular weight:	543.9 g/mole
Structural formula:	



Tetrabromobisphenol-A is very toxic to aquatic organisms, does not degrade readily in the environment and accumulates in fish. The detailed properties of tetrabromobisphenol-A, including numerical values for toxicity, persistence and bioaccumulation are set out in the fact sheet at Annex 2. This fact sheet includes the more recent values reported in ECB (2008) and selected monitoring data that have become available since that report was finalised. A full literature search has not been carried out for this document, so it is possible that additional data are available.

2.2 Identification of sources of Tetrabromobisphenol-A

The primary use of tetrabromobisphenol-A is as a reactive intermediate in the manufacture of flame-retarded epoxy and polycarbonate resins. This means that the substance is chemically reacted with, and becomes part of, the polymer matrix. It may also be used as an additive flame retardant, for example in the manufacture of acrylonitrile-butadiene-styrene (ABS) resins and phenolic resins, where free tetrabromobisphenol-A will be present in the final polymer. Where tetrabromobisphenol-A is used as an additive flame retardant, it is generally used with antimony oxide for maximum performance (Hakk, 2001). Antimony oxide is generally not used in conjunction with tetrabromobisphenol-A in reactive flame retardant applications (Industry Consortium, 2002).

Tetrabromobisphenol-A is also used in the manufacture of derivatives. The main derivatives are tetrabromobisphenol-A dimethyl ether, tetrabromobisphenol-A dibromopropyl ether, tetrabromobisphenol-A bis(allyl ether), tetrabromobisphenol-A bis(2-hydroxyethyl ether), tetrabromobisphenol-A brominated epoxy oligomer, and tetrabromobisphenol-A carbonate oligomers (IPCS, 1995). The main use of these derivatives is as flame retardants, usually in niche applications. As far as is known, tetrabromobisphenol-A is not currently used to manufacture any derivatives within the EU (the Industry Consortium for tetrabromobisphenol-A has indicated that none of its members currently manufacture derivatives in the EU (Industry Consortium, 2003; ECB, 2008)).

2.3 Pathways to the marine environment

Tetrabromobisphenol-A is likely to reach the marine environment largely through industrial waste waters from land-based industrial activities. A smaller contribution to releases to water comes from particulate losses from products containing the substance over their lifetime. Emissions to air are smaller than those to water, and most such emissions are expected to be deposited close to the sources of emission. There are however some indications of possible transport over longer distances, possibly adsorbed to particulate matter, which could lead to a contribution to the marine environment through this route.

3. Quantification of sources

3.1 Manufacture of tetrabromobisphenol-A

Tetrabromobisphenol-A is produced in the USA, Israel, Jordan and Japan but not in the EU (it is possible that other suppliers exist in Asia, but this has not been confirmed). The current total amount of tetrabromobisphenol-A produced is estimated at >120,000 tonnes/year (Hakk, 2001) and 150,000 tonnes/year (Arias, 2001).

The amounts of tetrabromobisphenol-A imported into the EU have been estimated in ECB (2008). Tetrabromobisphenol-A is imported as the substance itself. It is also imported as partly finished products (in the form of masterbatch, epoxy resins) and in finished products and components. **Table 1** summarises the estimated amounts for each of the routes. It should be noted that there are a number of assumptions involved in the derivation of these figures, particularly for the amounts imported as partly finished or as finished products. These assumptions are described in ECB (2008).

Table 1: EU imports of tetrabromobisphenol-A

Route	Amount (tonnes/year)	
	late 1990s	2003/2005
Tetrabromobisphenol-A imported into the EU as the substance	13,800	6,500
Tetrabromobisphenol-A imported into EU as partly finished products (e.g. masterbatch, epoxy resins)		6,000
Amount of tetrabromobisphenol-A imported into the EU in finished products and components		27,500
Total		40,000

3.2 Quantification of uses

A breakdown of use world-wide was provided by Leisewitz *et al.* (2000), who indicated that around 70% is used for epoxy resins in printed circuit boards, 15% is used additively in HIPS for casing materials, 10% is used for the production of derivatives and 5% is used as additives for other polymers such as ABS and thermoplastic polyesters. Industry has since indicated that they are unaware that tetrabromobisphenol-A is (or has ever been) used as an additive in HIPS, and in their experience, it is not an effective flame retardant for HIPS (Industry Consortium, 2003). No current use in HIPS was therefore assumed in ECB (2008).

Private information from industry indicates that the ratio between reactive and additive flame retardant use in the EU is around 9:1, with ABS being the main additive use of tetrabromobisphenol-A.

4. Monitoring data on discharges, emissions and losses

4.1 Aquatic inputs to the marine environment

No data are available on loads of tetrabromobisphenol-A entering the OSPAR Convention Waters and the Greater North Sea.

A Voluntary Emissions Control Action Programme (VECAP) was introduced by the members of the European Brominated Flame Retardant Industry Panel (EBFRIP) in Europe in 2004 for another substance (EBFRIP, 2006). Tetrabromobisphenol-A was added to the VECAP in 2006 (EBFRIP, 2007). The aim is to reduce emissions through a better understanding and management of chemical substances throughout the supply chain. At present the VECAP covers producers, their immediate customers and a number of customers further down the supply chain who use the flame retardant in their products or articles. At present the VECAP does not deal with potential emissions from articles during and at the end of their service life (EBFRIP, 2009). The progress of the VECAP is reported annually (EBFRIP, 2006, 2007, 2008 and 2009, and BSEF, 2007). A summary of the main points and progress made for tetrabromobisphenol-A is given in **Table 2**. The survey carried out in 2008 (based on the 2007 consumption volume) showed a total potential emission of 815 kg/year (32 kg/year to air, 59 kg/year to water and 724 kg/year to land) from companies involved in the programme. This had been reduced by around 77% in the 2009 survey (based on the 2007 consumption volume) to a total potential emission of 189 kg/year (0.5 kg/year to air, 0.4 kg/year to water and 188 kg/year to land). The reduction reflects the measures introduced to limit emissions (particularly in relation to disposal of packaging residues) and also partly reflects the use of worst case assumptions in the 2008 survey that were refined in the 2009 survey. There was also a 33% reduction in the sales volume of tetrabromobisphenol-A between the two surveys, and one user site with a relatively significant emission to water was closed between the two surveys. The data show that the direct inputs of tetrabromobisphenol-A from point sources in the EU into water are low and decreasing. However, it should also be noted that companies that do not take part in the VECAP might have higher emissions.

The 2010 VECAP survey results for TBBPA volume sold in Europe in 2009 will be published in early 2011. The preliminary findings from this survey have demonstrated that potential emissions to water remain very low while an increase in land emissions has been noticed. This increase is linked to the packaging waste disposal mode at a few users (the VECAP methodology always considers the worst case when non-VECAP compliant disposal practices are used). Recommendations on the use of Best Available Techniques have been provided and it is hoped that improvements will be made in 2011¹.

¹ The emissions estimated in ECB (2008) imply that local scenarios for production and use make a much higher contribution (by two orders of magnitude) to regional emissions than volatile and particulate losses over the service life of articles, and release during recycling and disposal. However, there is significant uncertainty in the magnitude of releases arising from articles and waste disposal for additive uses.

Table 2: Summary of the VECAP for tetrabromobisphenol-A

Year	Summary	Source
2006-2007	89% of European users (by volume ^a) of the substance as an additive had committed to reducing their emissions and establishing an emissions base-line.	EBFRIP, 2007
2007-2008	A survey reported a total volume sold of 4,165 tonnes in 2007 and a total potential emission of 815 kg from the 2008 survey (corresponding to an emission factor of around 200 g/tonne). The potential emissions to air, water and land were: Air 32 kg/year [8 g/tonne] Water 59 kg/year [14 g/tonne] Land 724 kg/year [175 g/tonne]	EBFRIP, 2009
2008-2009	89% of the tetrabromobisphenol-A consumption volume ^a , corresponding to 17 out of 23 user sites, was covered by the VECAP survey in Europe. Users of 84% of the consumption volume ^a in Europe had committed to the VECAP programme. The survey reported a total volume sold of 3,224 tonnes in 2008 and a total potential emission of 189 kg from the 2009 survey (corresponding to an emission factor of around 60 g/tonne). The potential emissions to air, water and land were: Air 0.5 kg/year [0.2 g/tonne] Water 0.4 kg/year [0.1 g/tonne] Land 188 kg/year [58 g/tonne]	EBFRIP, 2009

Note: a) As a percentage of the volumes supplied by EBFRIP member companies. Volumes supplied by non-EBFRIP members are not included. A commitment to the programme means that the company has signed up to the relevant codes of practice and agrees to take whatever steps they can to reduce the levels of potential emissions.

4.2 Atmospheric inputs

No data are available on atmospheric inputs of tetrabromobisphenol-A into the marine environment but considering its low vapour pressure and tendency to adsorb to soils and sediments it can be expected that atmospheric concentrations will be extremely low. A very low, and decreasing, emission to air from point sources in the EU is indicated from the results of the VECAP summarised in **Table 2**. The total emissions to air in 2008-2009 were reported to be 0.5 kg/year (although companies that do not take part in the VECAP might have higher emissions). Available measurements in air mainly relate to indoor and workplace situations and so are not relevant to this background document. The available information on the long-range atmospheric transport of this substance indicates that the substance has a low, but not zero, potential to be transported over long distances via the atmosphere. The substance is thought to adsorb strongly onto atmospheric particulates and that it is the transport behaviour of these particulates that effectively governs the transport behaviour of tetrabromobisphenol-A itself. A study by de Wit and Muir (2004) and de Wit *et al.* (2006) reported that tetrabromobisphenol-A had been detected at a concentration of 70 pg/m³ in a single archived air filter sample from Dunai (Russian Arctic). Tetrabromobisphenol-A has also been found in samples of moss from Norway (SFT, 2002) and whilst this may provide an indication that atmospheric transport can occur, local sources cannot totally be ruled out.

4.3 Concentrations in the marine environment (and other waters/sediments)

There are no available measured levels of tetrabromobisphenol-A in marine waters, but there are measurements in estuarine sediments, as well as in freshwaters, freshwater sediments and waste waters. A summary of these data is included in **Table 3** to **Table 5**. Most of these data have been reviewed in detail in ECB (2008) and so the relevant details of the methodologies are not repeated here. However, details are provided for a number of further studies that have become available since that report was finalised. When considering these data it is relevant to note that most of the samples were collected before the Industry VECAP was in place (for example, the samples from the Bakke *et al.* (2008) study were collected in 2006/2007 and those from the Evenset *et al.* (2009) study were collected in either 2004 or 2008). Environmental concentrations are expected to have fallen significantly in response to local emission reduction at sites participating in the VECAP. However, there are no recent data from sites close to potential sources with which to compare the older data, so the extent to which the reported levels reflect the current levels of tetrabromobisphenol-A in the environment is unknown.

Table 3: Measured levels of tetrabromobisphenol-A in surface water

Location	Concentration	Reference
Creek, Finland	<0.2 µg/l	Peltola (2002)
Baden-Wurtenburg, Germany	0.81 – 20.4 ng/l (7 of 30 samples)	Kuch <i>et al.</i> (2001)

Table 4: Measured levels of tetrabromobisphenol-A in sediments

Location	Concentration	Reference
Rivers		
Elbe, Germany (2001)	0.5 – 4.6 µg/kg dwt (7 of 30 samples)	Heemken <i>et al.</i> (2001)
Various rivers, Germany	0.17 – 1.83 µg/kg dwt	Kuch <i>et al.</i> (2001)
River, UK (1998)	2.3 mg/kg wwt	CEFAS (2002)
River, Ireland	<2.4 – 3.7 µg/kg dwt (3 of 4 samples)	de Boer <i>et al.</i> (2002)
Tees, Tyne, Skerne (UK)	<2.4 – 9753 µg/kg dwt	de Boer <i>et al.</i> (2002)
Berlin area, Germany	0.16 – 19 µg/kg dwt	Kemmlin (2000)
Drammens River, Norway	0.2-10 µg/kg dwt (7 sites)	Fjeld <i>et al.</i> (2004)
Rivers in the Netherlands	0.4 – 4.2 µg/kg wwt (8 of 9 rivers)	de Boer <i>et al.</i> (2002)
Lakes		
Lake Ellasjøen, Bjørnøya	ND (<0.38 µg/kg dwt)	Evenset <i>et al.</i> (2009)
Lake Mjøsa and Lake Losna, Norway	0.04-0.13 µg/kg dwt (15 sites)	Fjeld <i>et al.</i> (2004)
Drammens Fjord, Norway	0.3-39 µg/kg dwt (4 sites)	Fjeld <i>et al.</i> (2004)
Estuarine		
Scheldt, Netherlands	<0.1 – 32 µg/kg wwt (13 of 19 samples)	de Boer <i>et al.</i> (2002)
Western Scheldt, Netherlands	<0.1 – 1.3 µg/kg wwt (14 of 19 samples)	de Boer <i>et al.</i> (2002)
Scheldt, Netherlands	ND (<0.1 µg/kg dwt) (samples from 3 locations)	Verslycke <i>et al.</i> (2005)
Dublin Bay, Ireland	ND (<2.4 µg/kg dwt)	de Boer <i>et al.</i> (2002)

Location	Concentration	Reference
	(8 samples)	
Humber, Mersey, Clyde (UK)	ND (<2.4 µg/kg dwt)	de Boer <i>et al.</i> (2002)
Coastal		
Finnish Gulf, Finland	ND (<0.2 µg/kg dwt) (3 samples)	Peltola (2002)
Eastern Sweden	ND (<5 µg/kg dwt) (14 coastal locations and 20 samples from the Stockholm municipality)	Sternbeck <i>et al.</i> (2003)
Norwegian coast	0.01-2.4 µg/kg dwt (6 locations)	Fjeld <i>et al.</i> (2004)
Remote marine		
Barents Sea	ND (<0.20 to <0.62 µg/kg dwt)	Bakke <i>et al.</i> (2008)
Norwegian Arctic (Kongsfjorden, Liefdefjorden, Smeerenburgfjorden, Hopen Bank and Hopen Trench)	ND (<0.17 to <0.62 µg/kg dwt)	Evenset <i>et al.</i> (2009)

Note: ND – not detected

Table 5: Measured levels of tetrabromobisphenol-A in waste waters

Country	Influent/effluent	Concentration	Dissolved/particulate	Reference
UK	Influent	2.6 – 85.2 ng/l (4 of 5 samples)	Dissolved	de Boer <i>et al.</i> (2002)
	Effluent	ND (<15 ng/l)	Dissolved	
		21.7 µg/kg dwt (1 of 5 samples)	Particulate	
	Effluent	ND (< 3.9 µg/kg dwt)	Particulate	
Netherlands	Influent	ND (< 1-3.8 µg/kg dwt)	Particulate	de Boer <i>et al.</i> (2002)
	Effluent	31 – 63 µg/kg dwt	Particulate	
Germany	Influent	0.81 – 17.4 ng/l (5 of 5 samples)	Dissolved	Kuch <i>et al.</i> (2001)
		ND (< 0.2 µg/kg dwt)	Particulate	

Note: ND – not detected

Bakke *et al.* (2008) investigated the levels of tetrabromobisphenol-A in sediments from the Barents Sea. The sediment samples (one sample from a depth of 0-1 cm or 0-3 cm from each of 11 locations) were collected in 2006/2007. The analytical method used was LC-HRMS (liquid chromatography with high resolution mass spectrometry detection) utilising ¹³C-labelled internal standards for quantification. Few other details of the quality assurance/quality control procedures used were given. Tetrabromobisphenol-A was not detectable in any of the samples analysed. The limit of detection of the method used was dependent upon the sample and varied between 0.20 µg/kg dry weight and 0.62 µg/kg dry weight.

Similarly Evenset *et al.* (2009) did not detect TBBPA in sediment samples from the Norwegian Arctic. The samples analysed included surface sediments (from a depth of 0-2 cm) from Kongsfjorden (two sampling stations; 78°57.60'N, 11°56.40'E and 78°57.30'N, 09°34.80'E), Liefdefjorden (79°37.10'N, 12°57.94'E), Smeerenburgfjorden (79°41.57'N, 11°07.58'E), Hopen Bank (75°55.12'N, 25°20.88'E) and Hopen Trench (75°03.40'N, 30°28.23'E collected between April and September 2008, along with a sediment sample

collected from Lake Ellasjøen (74°23.19'N, 19°01.54'E) on Bjørnøya (74°23.19'N, 19°01.54'E) collected in 2004. The analytical method used was UPLC-HRMS (ultra pressure liquid chromatography with high resolution mass spectrometry detection) utilising ¹³C-labelled internal standards for quantification. Few other details of the quality assurance/quality control procedures used were given. The limit of detection of the method used was between 0.17 and 0.62 µg/kg dry weight depending on the sample.

Most of the positive measurements cover a similar range of values. The more elevated levels (e.g. CEFAS, 2002, Fjeld *et al.*, 2004 and de Boer *et al.*, 2002), generally relate to sites close to potential sources of release, and relate to before the initiation of the Industry VECAP program. Of note are the recent studies from Evenset *et al.* (2009) and Bakke *et al.* (2008) which did not detect tetrabromobisphenol-A in marine sediment or sediments from remote areas using limits of detection up to about 0.6 µg/kg dry weight (some, but not all, of these samples were collected after the Industry VECAP program was instigated). Therefore although tetrabromobisphenol-A is detectable in sediments influenced by point sources, the available data suggest that the concentration of tetrabromobisphenol-A in more remote areas is very low (not detectable).

4.4 Concentrations in biota

The available data on the levels of tetrabromobisphenol-A in biota are summarised in **Table 6**. Most of these data have been reviewed in detail in ECB (2008) and so the relevant details of the methodologies used are not repeated here. However further data have become available since the European report was finalised and details of these studies are reported below. As before, when considering these data it is relevant to note that most of the samples were collected before the Industry VECAP was in place and so the levels reported may not reflect the current levels of tetrabromobisphenol-A in the environment. In addition, different detection limits make it difficult to make comparisons between studies.

Law *et al.* (2008) carried out a follow-up study to a survey carried out in 2006 (Law *et al.* (2006), reported in ECB (2008)) on the levels of tetrabromobisphenol-A in stranded or bycaught harbour porpoises (*Phocoena phocoena*). The Law *et al.* (2006) survey detected tetrabromobisphenol-A in a total of 18 out of 68 samples analysed from the period 1994-2003 at a concentration between 6-35 µg/kg wet weight (the detection limit of the method used was 5 µg/kg wet weight). The follow-up study by Law *et al.* (2008) analysed a further 138 samples collected between 2003 and 2006. The Law *et al.* (2006) survey detected tetrabromobisphenol-A in a total of 18 out of 68 samples analysed from the period 1994-2003 at a concentration between 6 and 35 µg/kg wet weight (the detection limit of the method used was 5 µg/kg wet weight). The follow-up study analysed a further 138 samples collected between 2003 and 2006. The Law *et al.* (2008) study used two methods for quantification. Using liquid chromatography-mass spectrometry, low concentrations of tetrabromobisphenol-A could be detected similar to those in the 2006 study (using the same analytical method). However when a newly developed liquid chromatography-mass spectrometry-mass spectrometry confirmatory method was used tetrabromobisphenol-A was not detectable in any of the samples (detection limit 5 µg/kg wet weight). Law *et al.* (2008) concluded that tetrabromobisphenol-A was not detectable in the samples from 2003-2006 and questioned the positive findings in the Law *et al.* (2006) study (although it was not possible to say that the reported concentrations were definitely overestimated in that study).

Evenset *et al.* (2009) screened fish samples from the Norwegian Arctic for the presence of tetrabromobisphenol-A. Sediment samples were also analysed as part of this study (see Section 4.3). The fish samples analysed included Atlantic cod (*Gadus morhua*) liver from Kongsfjorden (five samples), polar cod (*Boreogadus saida*) liver from Liefdefjorden (two samples), polar cod liver from Billefjorden (four samples), whole polar cod from Moffen (five samples) and Arctic char (*Salvelinus alpinus*) muscle from Lake Ellasjøen on Bjørnøya (five samples). The samples were collected in 2008 (Atlantic cod and polar cod) or 2004 (Arctic char). The analytical method used was UPLC-HRMS (ultra pressure liquid chromatography with high resolution mass spectrometry detection) utilising ¹³C-labelled internal standards for quantification. Few other details of the quality assurance/quality control procedures used were given. The limit of detection of the method used was between 0.25 and 3.1 µg/kg wet weight depending on the sample. Tetrabromobisphenol-A was not detectable in any of the samples.

In addition to the fish samples, Evenset *et al.* (2009) also screened samples of kittiwake (*Rissa tridactyla*) liver (five samples from Kongsfjorden and four samples from Leifdefjorden) and common eider (*Somateria mollissima*) liver (five samples from Kongsfjorden) collected in 2008. Again tetrabromobisphenol-A was not detectable in any of these samples. For the bird liver samples the limit of detection of the method used was in the range 0.15 to 0.41 µg/kg wet weight.

The levels of tetrabromobisphenol-A (and also the dimethyl-derivative) have been determined in marine biota from Greenland and the Faroe Islands (Frederiksen *et al.*, 2007). The samples included liver and adipose tissue from shorthorn sculpins (*Myoxocephalus scorpius*), long-finned pilot whales (*Globicephala melas*), ringed seals (*Phoca hispida*), minke whales (*Balaenoptera acutorostrata*), northern fulmars (*Fulmarus glacialis*), black guillemots (*Cephus grille*) and polar bears (*Ursus maritimus*), along with black guillemot eggs. The samples were pooled for analysis (generally pools of five samples) and between one and two pooled samples were analysed per species/sampling location or, in the case of the long-finned pilot whales and northern fulmars, one pooled sample from each sex/age group. In all a total of 36 pooled samples were analysed. The analytical methodology was developed specifically for the study to allow the determination of tetrabromobisphenol-A, along with dimethyl tetrabromobisphenol-A² and another brominated flame retardant (hexabromocyclododecane). It involved Soxhlet extraction, sample clean-up using gel-permeation chromatography, treatment with sulphuric acid, and finally a silica column and analysis by liquid chromatography tandem mass spectrometry (LC-MS-MS). The samples were analysed in batches of twelve with each batch also including a blank sample, one duplicate sample and two samples of a reference material (sand eel oil). ¹³C-labelled tetrabromobisphenol-A was used as the recovery standard (added to the sample prior to Soxhlet extraction). The average recovery for tetrabromobisphenol-A from spiked sand eel oil using the method was 28% (and 35% for the ¹³C-labelled tetrabromobisphenol-A). The limit of detection of the method (corrected for approximate recovery) for tetrabromobisphenol-A was 0.38 µg/kg wet weight for liver and 2.83 µg/kg wet weight for blubber. The limit of detection was determined based on a signal-to-noise ratio of 3 (the limit of quantification was set on a signal to noise ratio of 5). Neither tetrabromobisphenol-A nor dimethyl tetrabromobisphenol-A was detected in any of the samples. The same data are summarised in a review by de Wit *et al.* (2010). This review indicates that the samples were collected in 1998/1999-2002.

Another review by Muir and de Wit (2010) considered the trends in the occurrence of brominated flame retardants in Arctic biota. However this review does not contain any new information on tetrabromobisphenol-A. The review concluded that tetrabromobisphenol-A³ has been found at low levels in several animals and plants from the Arctic but that more data are needed in order to assess the potential of tetrabromobisphenol-A to undergo long-range transport.

Some of the available data are associated with industrial or urban sources of tetrabromobisphenol-A, but there is a limited amount of data from more remote regions (including the Arctic) that is relevant. For example, tetrabromobisphenol-A has been detected in each of eleven samples of moss from Norway (SFT, 2002): whilst this suggests that transport via the atmosphere is possible, local sources cannot totally be ruled out (the distance to the nearest village/town was at least 10 km for these samples). For the levels in biota, Herzke *et al.* (2003 and 2005) found that tetrabromobisphenol-A was present in eight samples of predatory birds eggs from Norway (including some sampled from within the Arctic circle). In contrast to this, tetrabromobisphenol-A was not detectable in thirty two samples of peregrine falcon eggs from South Greenland (Sørensen *et al.*, 2004 and Vorkamp *et al.*, 2005).

There is a more extensive set of monitoring data in aquatic organisms. Tetrabromobisphenol-A has been detected at low levels in a number of aquatic species, including some top predators such as harbour porpoise (up to a few µg/kg wet weight in most cases, although up to 376 µg/kg wet weight in harbour

² Dimethyl tetrabromobisphenol-A was extracted using a similar method. Analysis was by gas chromatography-mass spectrometry (GC-MS) utilising a polybrominated diphenyl ether (PBDE-77) as recovery standard and PBDE-71 as quantification standard (added after sample clean-up). The average recovery of the method from spiked sand eel oil was 68%. The limit of detection, corrected for approximate recovery, was 0.55 µg/kg wet weight for liver and 4.2 µg/kg wet weight for blubber.

³ The paper uses the name tetrabromobisphenol; it is presumed here that this is tetrabromobisphenol-A.

porpoise blubber). Most of these data were collected from sites that may be influenced by local or regional sources of emission, and pre-date the Industry VECAP program. The absence of concurrent exposure measurements make them difficult to interpret in terms of the bioaccumulative properties of the substance. In addition, it should be noted that tetrabromobisphenol-A was not detectable in a significant number of samples, including the two recent studies by Evenset *et al.* (2009) and Frederiksen *et al.* (2007). Overall the available biota monitoring data indicate that tetrabromobisphenol-A may be present at elevated levels in biota from more source-dominated areas but the levels in biota more remote from sources are lower, and frequently not detectable.

Table 6: Measured levels of tetrabromobisphenol-A in biota

Sample	Comment	Concentration	Reference
Arctic char muscle	Norwegian Arctic (Lake Ellasjøen). Not detected in 5 samples (detection limit 0.25-0.43 µg/kg wet weight).	Not detected	Evenset <i>et al.</i> , 2009
Baltic salmon	Blood sample from 1995.	Detected but not quantified	Asplund <i>et al.</i> , 1999
	Ten muscle samples from the River Kymijoki and River Simojoki, Finland, 1993-1999.	Detected in 2 samples at 2.0 and 5.0 µg/kg fresh weight	Peltola, 2002
Eel	Two samples from Berlin area, Germany from 1998/1999.	0.045 and 0.10 µg/kg fresh weight	Kemmlein, 2000
	Samples from Scheldt basin, 2000. Detected in 6 out of 18 samples (detection limit 0.1 µg/kg wet weight).	<0.1-2.6 µg/kg wet weight	de Boer <i>et al.</i> , 2002
	Samples from rivers in the Netherlands. Detected in 3 out of 11 samples (detection limit 0.1 µg/kg wet weight).	<0.1-0.2 µg/kg wet weight	de Boer <i>et al.</i> , 2002
Fish	Pooled samples from Lake Mjøsa, Norway. Detected in 6 out of 8 samples.	0.01-0.18 µg/kg wet weight	Fjeld <i>et al.</i> , 2004
	Pooled samples from River Vormå, Norway. Detected in 1 out of 2 samples.	0.01 µg/kg wet weight	Fjeld <i>et al.</i> , 2004
	Pooled samples from Lake Øyeren, Norway. Detected in 2 out of 2 samples.	0.03 µg/kg wet weight	Fjeld <i>et al.</i> , 2004
	Pooled samples from Drammensfjord, Norway. Detected in 1 out of 6 samples.	0.05 µg/kg wet weight	Fjeld <i>et al.</i> , 2004
Gudgeon	Western Scheldt, the Netherlands. Not detected in 1 sample. Detection limit 0.1 µg/kg wet weight.	Not detected	de Boer <i>et al.</i> , 2002
Perch	Sample from Berlin area, Germany from 1998/1999.	0.033 µg/kg fresh weight	Kemmlein, 2000
Pike	Sample from Berlin area, Germany from 1998/1999.	0.021 µg/kg fresh weight	Kemmlein, 2000
	Three muscle samples from Finland, 1997.	Not detected	Peltola, 2002

Sample	Comment	Concentration	Reference
Atlantic cod liver	Norwegian Arctic (Kongsfjorden). Not detected in 5 samples (detection limit 1.1-3.3 µg/kg wet weight).	Not detected	Evenset <i>et al.</i> , 2009
Cod liver	Samples from North Sea. Detected in 1 out of 2 samples. Detection limit 0.1 µg/kg wet weight.	<0.1-0.8 µg/kg wet weight	de Boer <i>et al.</i> , 2003
	Samples from around Norway. Detected in 5 out of 6 samples.	0.35-1.73 µg/kg wet weight	Fjeld <i>et al.</i> , 2004
	Samples from around Norway. Detected in 6 out of 6 samples.	0.08-0.16 µg/kg wet weight	SFT (2002)
Hake liver	Not detected in 1 sample. Detection limit 0.1 µg/kg wet weight.	Not detected	de Boer <i>et al.</i> , 2003
Polar cod liver	Norwegian Arctic (Levdifjorden and Billefjorden). Not detected in 6 samples (detection limit 0.34-1.9 µg/kg wet weight).	Not detected	Evenset <i>et al.</i> , 2009
Polar cod (whole fish)	Norwegian Arctic (Moffen). Not detected in 5 samples (detection limit 0.19-0.47 µg/kg wet weight).	Not detected	Evenset <i>et al.</i> , 2009
Shorthorn sculpin (liver)	Greenland (location not stated but presumably East Greenland). Not detected in two pooled samples (detection limit 0.38 µg/kg wet weight).	Not detected.	Frederiksen <i>et al.</i> , 2007
	West Greenland. Not detected in two pooled samples (detection limit 0.38 µg/kg wet weight).	Not detected.	Frederiksen <i>et al.</i> , 2007
Whiting (fillet)	North Sea, 1999. Detected in 2 out of 3 samples. Detection limit 97 µg/kg lipid.	<97-245 µg/kg lipid	de Boer <i>et al.</i> , 2002
Whiting muscle	UK sea estuaries. Detected in 1 out of 2 samples. Detection limit ~4.8 µg/kg wet weight.	<4.8-3.3 µg/kg wet weight	de Boer <i>et al.</i> , 2002
Blue mussel	Samples from around Norway. Detected in 6 out of 6 samples.	0.01-0.03 µg/kg wet weight	SFT (2002)
Mussel	Samples from four sites around Norway.	Not detected	Fjeld <i>et al.</i> , 2004
Hermit crab (abdomen)	North Sea, 1999. Detected in 5 out of 9 samples. Detection limit 1 µg/kg lipid.	<1-35 µg/kg lipid	de Boer <i>et al.</i> , 2002
Mysid shrimp	Western Scheldt, The Netherlands. Not detected in 1 sample. Detection limit 0.1 µg/kg wet weight.	Not detected	de Boer <i>et al.</i> , 2002

Sample	Comment	Concentration	Reference
	Scheldt estuary. Samples from three locations, detected in 2 samples.	<7.7, 0.8 and 0.9 µg/kg lipid	Verslycke <i>et al.</i> , 2005
Sea star (pyloric caeca)	North Sea, 1999. Detected in 2 out of 3 samples. Detection limit 1 µg/kg lipid.	<1-10 µg/kg lipid	de Boer <i>et al.</i> , 2002
Star fish	UK estuaries. Detected in 1 out of 1 sample.	4.5 µg/kg wet weight	de Boer <i>et al.</i> , 2002
Whelk (whole body)	North Sea, 1999. Detected in 3 out of 3 samples.	5-96 µg/kg lipid	de Boer <i>et al.</i> , 2002
Harbour porpoise (blubber)	North Sea. Not detected in 5 samples (detection limit 18 µg/kg lipid).	Not detected	de Boer <i>et al.</i> , 2002
	North Sea estuaries. Detected in 5 out of 5 samples. (CEFAS, 2002 reports the results as detected in 8 out of 25 samples; and Law <i>et al.</i> (2003 report the results as detected in 4 out of 25 samples).	0.05-376 µg/kg wet weight	de Boer <i>et al.</i> , 2002; CEFAS, 2002; Law <i>et al.</i> , 2003
	Stranded or bycaught in the United Kingdom. A total of 68 samples from the period 1994-2003 analysed. Detected in 18 samples (detection limit was around 5 µg/kg wet weight).	6-35 µg/kg wet weight	Law <i>et al.</i> (2006)
	Stranded or bycaught in the United Kingdom. A total of 138 samples from the period 2003-2006 analysed. Detection limit was 5 µg/kg wet weight.	Not detected	Law <i>et al.</i> (2008)
Harbour seal (blubber)	North Sea. Not detected in 5 samples (detection limit 14 µg/kg lipid).	Not detected	de Boer <i>et al.</i> , 2002
Harbour seal (liver)	North Sea. Not detected in 5 samples (detection limit 231 µg/kg lipid).	Not detected	de Boer <i>et al.</i> , 2002
Long-finned pilot whale (blubber)	Juveniles from Faroe Islands. Not detected in one pooled sample (detection limit 2.83 µg/kg wet weight).	Not detected	Frederiksen <i>et al.</i> , 2007
	Females from Faroe Islands. Not detected in one pooled sample (detection limit 2.83 µg/kg wet weight).	Not detected	Frederiksen <i>et al.</i> , 2007
	Males from Faroe Islands. Not detected in one pooled sample (detection limit 2.83 µg/kg wet weight).	Not detected	Frederiksen <i>et al.</i> , 2007

Sample	Comment	Concentration	Reference
Long-finned pilot whale (liver)	Juveniles from Faroe Islands. Not detected in one pooled sample (detection limit 0.38 µg/kg wet weight).	Not detected	Frederiksen <i>et al.</i> , 2007
	Females from Faroe Islands. Not detected in one pooled sample (detection limit 0.38 µg/kg wet weight).	Not detected	Frederiksen <i>et al.</i> , 2007
	Males from Faroe Islands. Not detected in one pooled sample (detection limit 0.38 µg/kg wet weight).	Not detected	Frederiksen <i>et al.</i> , 2007
Minke whale (blubber)	West Greenland. Not detected in one pooled sample (detection limit 2.83 µg/kg wet weight).	Not detected.	Frederiksen <i>et al.</i> , 2007
Minke whale (liver)	West Greenland. Not detected in one pooled sample (detection limit 0.38 µg/kg wet weight).	Not detected.	Frederiksen <i>et al.</i> , 2007
Ringed seal (blubber)	East Greenland. Not detected in two pooled samples (detection limit 2.83 µg/kg wet weight).	Not detected.	Frederiksen <i>et al.</i> , 2007
	West Greenland. Not detected in two pooled samples (detection limit 2.83 µg/kg wet weight).	Not detected.	Frederiksen <i>et al.</i> , 2007
Ringed seal (liver)	East Greenland. Not detected in two pooled samples (detection limit 0.38 µg/kg wet weight).	Not detected.	Frederiksen <i>et al.</i> , 2007
	West Greenland. Not detected in two pooled samples (detection limit 0.38 µg/kg wet weight).	Not detected.	Frederiksen <i>et al.</i> , 2007
Moss	Samples from Norway. Detected in 11 out of 11 samples.	0.019-0.089 µg/kg wet weight	SFT (2002)
Polar bear (adipose)	East Greenland. Not detected in two pooled samples (detection limit 2.83 µg/kg wet weight).	Not detected.	Frederiksen <i>et al.</i> , 2007
Polar bear (liver)	East Greenland. Not detected in two pooled samples (detection limit 0.38 µg/kg wet weight).	Not detected.	Frederiksen <i>et al.</i> , 2007
Black guillemot (liver)	East Greenland. Not detected in two pooled samples (detection limit 0.38 µg/kg wet weight).	Not detected	Frederiksen <i>et al.</i> , 2007
	West Greenland. Not detected in two pooled samples (detection limit 0.38 µg/kg wet weight).	Not detected	Frederiksen <i>et al.</i> , 2007

Sample	Comment	Concentration	Reference
Black guillemot (eggs)	East Greenland. Not detected in two pooled samples (detection limit for eggs not stated but presumably similar to that for liver (0.38 µg/kg wet weight) and blubber (2.83 µg/kg wet weight) used in the analysis of marine mammal samples in the study).	Not detected	Frederiksen <i>et al.</i> , 2007
	West Greenland. Not detected in two pooled samples (detection limit for eggs not stated by presumably similar to that for liver (0.38 µg/kg wet weight) and blubber (2.83 µg/kg wet weight) used in the analysis of marine mammal samples in the study).	Not detected	Frederiksen <i>et al.</i> , 2007
Common Tern eggs	Western Scheldt, The Netherlands. Not detected in 10 samples (detection limit <0.1-<0.3 µg/kg wet weight or 2.9 µg/kg lipid).	Not detected	de Boer <i>et al.</i> , 2002
Cormorant liver	Archived samples from around the United Kingdom. Detected in 7 out of 28 samples.	0.07-10.9 µg/kg fresh weight	CEFAS, 2002
	United Kingdom. Detected in 5 out of 5 samples.	0.07-0.28 µg/kg wet weight	de Boer <i>et al.</i> , 2002
Eider (liver)	Norwegian Arctic (Kongsfjorden). Not detected in 5 samples (detection limit 0.15-0.41 µg/kg wet weight).	Not detected	Evenset <i>et al.</i> , 2009
Fulmar (subcutaneous fat)	Females from Faroe Islands. Not detected in one pooled sample (detection limit 2.83 µg/kg wet weight).	Not detected	Frederiksen <i>et al.</i> , 2007
	Males from Faroe Islands. Not detected in one pooled sample (detection limit 0.38 µg/kg wet weight).	Not detected	Frederiksen <i>et al.</i> , 2007
Fulmar (liver)	Females from Faroe Islands. Not detected in one pooled sample (detection limit 0.38 µg/kg wet weight).	Not detected	Frederiksen <i>et al.</i> , 2007
	Males from Faroe Islands. Not detected in one pooled sample (detection limit 2.83 µg/kg wet weight).	Not detected	Frederiksen <i>et al.</i> , 2007
Kittiwake (liver)	Norwegian Arctic (Kongsfjorden and Liefdefjorden). Not detected in 9 samples (detection limit 0.15-0.21 µg/kg wet weight).	Not detected	Evenset <i>et al.</i> , 2009

Sample	Comment	Concentration	Reference
Peregrine falcon eggs	Samples from South Greenland from between 1986 and 2003 (total of 37 samples).	Not detected.	Sørensen <i>et al.</i> , 2004; Vorkamp <i>et al.</i> , 2005
Predatory birds' eggs	Samples from Norway including 2 White-tailed Eagle, 2 Peregrine Falcon, 2 Golden Eagle and 2 Osprey. The samples were collected between 1992 and 2002.	<0.004-0.013 µg/kg wet weight	Herzke <i>et al.</i> , 2003 and 2005; Berger <i>et al.</i> , 2004.

5. Assessment of the extent of the problem

5.1 Introduction

In order to assess the extent of the problem, a marine risk assessment based on the guidance developed by OSPAR and the EC in recent years was carried out in ECB (2008). The Marine Risk Assessment involved two steps. Firstly, the preparation of a PBT assessment to ascertain whether the substance is so hazardous that measures should be developed solely on the basis of the information available on sources and pathways to the marine environment. This was followed by a more traditional risk assessment approach where the predicted environmental concentrations were compared with the predicted no effect concentrations to give a PEC/PNEC ratio for various scenarios. The PEC/PNEC ratios give a numerical indication of the degree of risk. The details of the marine risk assessment are given in Annex 2 of this document. The marine risk assessment draws heavily on data and information in ECB (2008). It is clear that the marine risk assessment would be greatly improved with the provision of better quality information.

5.2 PBT Assessment

Criteria for persistency (P), bioaccumulation (B) and toxicity (T) are considered both within the OSPAR context and the ESR/REACH context. However the criteria are slightly different, as summarised below.

	OSPAR	ESR/REACH
Persistent (P)	Half-life ≥50 days	Half-life >60 days (marine water) >40 days (fresh/estuarine water) or >180 days (marine sediment) or >120 days (freshwater/estuarine sediment or soil)
Very Persistent (vP)	Not applicable	Half-life >60 days (fresh/estuarine/ marine water) or >180 days (freshwater/estuarine sediment or soil)
Bioaccumulative (B)	Log Kow ≥4 or BCF ≥500 l/kg	BCF >2,000 l/kg
Very Bioaccumulative (vB)	Not applicable	BCF >5,000 l/kg
Toxic (T)	Acute L(E)C ₅₀ ≤1 mg/l or long-term NOEC ≤0.1 mg/l or CMR ⁴ or chronic mammalian toxicity	Long-term NOEC <0.01 mg/l or CMR or chronic mammalian toxicity

⁴ Carcinogenic, mutagenic or toxic to reproduction

A full assessment of tetrabromobisphenol-A against the criteria used under ESR (according to the EC Technical Guidance Document; essentially the same criteria are now used under REACH) is available in ECB (2008). In summary:

Persistence: The available screening studies indicate that tetrabromobisphenol-A is unlikely to be considered as readily or inherently biodegradable. Primary biodegradation does occur in some situations. The half-life for primary degradation in freshwater aerobic sediments is estimated to be of the order of 50 to 70 days at 25°C, but no mineralization was observed over 56 days. A primary degradation half-life of around 25-30 days was measured at 30°C in a marine anaerobic sediment. Half-lives for primary degradation of 24-28 days at 20°C (for the whole waste/sediment system) and 28-42 days at 20°C (for the sediment phase alone) were also determined in freshwater anaerobic sediments. Recent studies with soil have indicated an aerobic mineralisation half-life of >6 months. It should be noted that most of the available biodegradation data have been obtained at temperatures of 20-30°C and so the degradation half-life could be longer at the generally lower temperatures found in the environment. It can therefore be concluded that tetrabromobisphenol-A is P or potentially vP under the criteria used.

Bioaccumulation: The highest measured BCF value for fish is 1,234 l/kg (based on total radiolabels and so including metabolites; the BCF from this study based on parent compound is around 160-177 l/kg), and there are several other determinations below this value. This value is below the cut-off value of 2,000 l/kg, and so tetrabromobisphenol-A does not meet the B criterion. Monitoring data indicate that the substance is bioavailable and can be taken up by aquatic organisms in the wild, but lack of exposure information means the data cannot be readily interpreted in terms of bioaccumulation potential.⁵

Toxicity: The lowest valid NOEC/EC₁₀ values available for tetrabromobisphenol-A are a 5-d EC₁₀ of 0.0127 mg/l for the marine copepod *Acartia tonsa* and a 70-d NOEC of 0.017 mg/l for marine mussels *Mytilus edulis*. In addition tetrabromobisphenol-A is thought to show relatively low toxicity to mammalian systems. Therefore it can be concluded that tetrabromobisphenol-A does not meet the T-criterion.

The possible effects of tetrabromobisphenol-A on the endocrine system have been studied in several aquatic and mammalian systems (ECB, 2008). The evidence available so far shows that although there are a number of tests showing little or no effects, there are indications of potential effects on the endocrine system in some *in vitro* tests with aquatic organisms, particularly thyroid hormone antagonist/agonist effects in amphibians. Although possible thyroid-mediated effects of tetrabromobisphenol-A are evident in *in vitro* assays, the results of a recent, well conducted, *in vivo* assay suggest that the effects seen *in vivo* may be the result of a toxic side effect rather than direct effects on thyroid function. The concentrations at which adverse effects on amphibian metamorphosis have been seen are generally around 100 µg/l and above (and so are above the criteria for T). Effects on various biomarkers have been seen at lower concentration (as low as around 5.4 µg/l) but the significance of these effects in terms of population survival is unclear.

One recent lifecycle study with zebrafish has found effects on some reproductive endpoints at relatively low concentrations (note: the effects seen were not necessarily related to disruption of the endocrine system). This study is discussed in detail in ECB (2008). A number of aspects of this study make the interpretation of the results difficult, in particular the decline in the exposure concentrations with time, and the variability and lack of dose response seen in some of the reproductive endpoints studied. The authors of the study concluded that effects on population-relevant parameters can result at tetrabromobisphenol-A body burdens of 5-7 mg/kg lipid. Based on the data reported in this study, it has been estimated in ECB (2008) that such body burdens would have resulted from exposure to around 3-6 µg/l. Based on this interpretation, it could be considered that tetrabromobisphenol-A may meet the T-

⁵ He *et al.* (2010a and 2010b) investigated tetrabromobisphenol-A concentrations in six bird species as well as dietary items (including fish) collected from South China. This study is important because it considers field evidence of bioaccumulation, and was not available when ECB (2008) was finalised. It indicates that uptake occurs in wild fish and birds, although the exposure pathways were not clarified. However, it is not possible to draw reliable conclusions about biomagnification or trophic magnification potential from this study due to the methodological problems that have been identified (see Annex 4 for full details).

criterion. However, the limitations of this study mean that it is not possible to derive a reliable NOEC for tetrabromobisphenol-A. Therefore it cannot be concluded that tetrabromobisphenol-A meets the T-criterion based on the results from this study, although it could be potentially T.

For mammalian systems, the human health assessment concludes that the weight of evidence from *in vitro* screening assays indicates that tetrabromobisphenol-A has no significant estrogenic potential in mammalian systems. In addition, although the potential for tetrabromobisphenol-A to compete with binding of thyroxine to transthyretin (TTR) has been demonstrated *in vitro*, no firm conclusions regarding the affinity of tetrabromobisphenol-A for TTR *in vivo* could be drawn from the limited data available. It should, however, be noted that the effects of tetrabromobisphenol-A on the endocrine system are currently subject to much current research and so this endpoint may need to be reconsidered once the full results of these studies are available.

In summary, tetrabromobisphenol-A meets only the persistence criteria for the PBT assessment (it is considered to be P or vP) based on the EC Technical Guidance Document/REACH criteria (ECB, 2008). Although the measured BCF value is around 60% of the threshold value, it was considered to be a maximum value as it may include a contribution from metabolites. The substance potentially meets the T criterion on the basis of a fish study that gave inconclusive results. Overall, tetrabromobisphenol-A is not considered to meet the REACH PBT criteria.

Nevertheless, based on the same data set, the following conclusions are drawn when comparing the properties of tetrabromobisphenol-A against the OSPAR PBT criteria:

Persistence: Tetrabromobisphenol-A is not considered to be readily or inherently biodegradable. The half-life for primary degradation in freshwater aerobic sediments is around 50-70 days at 25°C but no mineralisation was apparent after 56 days. Primary degradation half-lives are in the range of 24-42 days in marine and freshwater anaerobic sediments at 20°C or above. Recent studies with soil have indicated an aerobic mineralisation half-life of >6 months. It should be noted that most of the available biodegradation data have been obtained at temperatures of 20-30°C and so the degradation half-life could be longer at the generally lower temperatures found in the environment. On this basis, the substance meets the OSPAR criteria for P.

Bioaccumulation: The highest measured BCF value for fish is 1,234 l/kg, which is above the B criterion. However, it should be noted that this value is based on ¹⁴C-measurements and so may represent accumulation of metabolites as well as tetrabromobisphenol-A (the BCF from this study based on parent compound analysis is around 160-177 l/kg) and there are several other BCF values below this value. A BCF value of 780 l/kg has been determined for a marine mollusc (*Crassostrea virginica*), which is also above the B criterion but again is based on ¹⁴C-measurements. When the data based on analysis of tetrabromobisphenol-A itself are considered the BCF values are up to 485 l/kg for fish and 160-148 l/kg for the marine invertebrates. Therefore it can be concluded that tetrabromobisphenol-A does not strictly meet the OSPAR B criterion based on parent compound, but would clearly meet the criterion based on ¹⁴C-measurements. The identities of the metabolites present in these studies are unknown, and so they could possibly include substances that themselves are potentially toxic and accumulative. In addition it is also possible that the BCF value for tetrabromobisphenol-A may vary with pH value (see ECB, 2008). Therefore, given that the fish BCF based on parent compound is only just below 500 l/kg, it is concluded (as a borderline) that tetrabromobisphenol-A can be considered to meet the OSPAR B criterion. Detection at up to 376 µg/kg wet weight in harbour porpoise blubber might be used as supporting evidence for this conclusion (i.e. the substance is bioavailable and can accumulate in top predators, even though it is not known how the animal was exposed).

Toxicity: There are a number of experimental data demonstrating toxicity to aquatic organisms (including marine species) at concentrations below the OSPAR cut-off for T. The lowest acute L(E)C₅₀ for freshwater species are 0.54 mg/l for fish (*Pimephales promelas*), 0.96 mg/l for invertebrates (*Daphnia magna*) and >5.6 mg/l for algae (*Pseudocirrhineriella subcapitata*). For marine species an acute EC₅₀ of 0.09 mg/l was determined for algae (*Skeletonema costatum*) and a short-term EC₅₀ of 0.098 mg/l was

obtained for effects on shell regrowth in eastern oysters (*Crassostrea virginica*). Long-term data also demonstrate that the OSPAR T criterion is met. For example, a 5-day EC₁₀ of 0.0127 mg/l for the marine copepod *Acartia tonsa* and a 70-day NOEC of 0.017 mg/l for the marine mussel (*Mytilus edulis*) have been measured.

Tetrabromobisphenol-A therefore meets all three of the OSPAR criteria for the PBT assessment, although it should be acknowledged that the B decision is borderline.

5.3 PEC/PNEC ratios for the local marine risk assessment

The PEC/PNEC ratios for the local marine risk assessment are given in **Table 7** (for details of the derivation of the PECs and PNECs and the various assumptions which have been used, see Annex 2). There is a potential risk for aquatic organisms (including sediment) for the compounding of tetrabromobisphenol-A as an additive flame retardant for ABS. The PEC/PNEC ratios for secondary poisoning in the marine environment (not shown here) are all very much less than 1 (i.e. no risks). Further details of the marine risk assessment can be found in ECB (2008) and Annex 1. It should be noted that these PEC calculations do not take into account the recent reduction in emissions reported in the Industry VECAP and so the current PEC/PNEC ratios are likely to be reduced from those in **Table 7**. However, the PECs might still be relevant for companies that do not participate in the VECAP.

Table 7: Estimated PEC/PNEC ratios for tetrabromobisphenol-A for the local marine risk assessment

Scenario	Step	PEC/PNEC ratio water	PEC/PNEC ratio sediment
Reactive flame retardant use	Manufacture of epoxy and/or polycarbonate resins	0.092	0.067
	Processing of epoxy resins	1.4×10 ⁻³	1.0×10 ⁻³
	Processing of polycarbonate resins	1.4×10 ⁻³	1.0×10 ⁻³
Additive flame retardant use - ABS	Compounding	3.7	2.8
	Conversion	0.92	0.66

5.4 Conclusion of the Risk Assessment for the marine compartment

The risk assessment for the marine environment⁶ indicates a potential risk to water and sediment from the compounding step for the additive uses of tetrabromobisphenol-A in ABS. The manufacture and processing of epoxy and polycarbonate resins, and the conversion step for ABS, do not appear to present a risk. It would be possible to revise the PECs for the other endpoints by collection of further exposure information⁷. Industry has indicated that none of the major manufacturing sites in the EU using tetrabromobisphenol-A as a reactive flame retardant, or compounding sites using tetrabromobisphenol-A as an additive flame retardant, are situated close to coastal areas (ECB, 2008), and that the sole ABS plant in the EU where a risk was identified has since closed.

It would also be possible to revise the PNEC for water and sediment by carrying out further testing to a) determine the long-term NOEC for tetrabromobisphenol-A in additional marine species and b) investigate the toxicity of tetrabromobisphenol-A to marine sediment organisms.

⁶ This risk assessment methodology has been formally agreed by the EC in April 2003 and has been adopted by the OSPAR Commission in June 2003 as the common EU/OSPAR risk assessment methodology for the marine environment.

⁷ The PECs for manufacturing of resins are based on default emission factors but with more specific information on amounts used on sites. All other emissions are estimated using the Emission Scenario Document on Plastics, where the emission factors are based on those for other substances (largely diethylhexyl phthalate). Hence all areas could be refined with substance-specific information.

The conclusions of the marine risk assessment above are generally consistent with those for the freshwater environment in ECB (2008).

The risk from secondary poisoning appears to be low for all scenarios.

In terms of the PBT properties, tetrabromobisphenol-A is considered to meet all three of the OSPAR criteria for the PBT assessment, although it should be acknowledged that the B-criterion is borderline. However, tetrabromobisphenol-A does not meet the criteria for a PBT or a vPvB substance that are used under REACH/ESR (it would be considered P or vP only); it is not B or vB, but potentially meets the T criterion on the basis of a fish study that gave inconclusive results.

ECB (2008) also considers a study in estuarine sediments that has indicated that tetrabromobisphenol-A has the potential to degrade through debromination under anaerobic conditions to form bisphenol-A, which is relatively stable under anaerobic conditions. However, bisphenol-A does not adsorb as strongly onto sediment as tetrabromobisphenol-A and so re-partitioning from sediment to water is likely to occur, where bisphenol-A may be degraded (bisphenol-A is considered to be readily biodegradable under aerobic conditions). This is considered further in the ESR assessment of bisphenol-A (ECB, 2010). Potential adverse effects of bisphenol-A on aquatic molluscs at low concentrations remain uncertain despite extensive scientific investigations. However, the risk assessment concluded that risks arising from bisphenol-A formation in the marine compartment would be low.

Another potential metabolite/degradation product (tetrabromobisphenol-A bis(methyl ether)) may be formed by O-methylation of tetrabromobisphenol-A, and this substance can be considered to meet the ESR/REACH screening criteria for a vPvB substance (see ECB, 2008 and Annex 1). The presence of tetrabromobisphenol-A bis(methyl ether) has been investigated in some recent studies of anaerobic transformation in freshwater aquatic sediment and sewage sludge, and anaerobic and aerobic soil transformation (summarised in ECB, 2008). The results were inconclusive but did provide some indication that if tetrabromobisphenol-A bis(methyl ether) was formed it was generally only present in small amounts. Since then it has been detected in some organisms in the environment (see Section 4.4, although this is not necessarily an exhaustive review). ECB (2008) concluded that further investigation of this substance was not warranted because a need for risk reduction measures had already been identified for some uses of tetrabromobisphenol-A, which was expected to reduce the environmental burden. However, the resulting risk reduction strategy (Defra, 2007) did not propose any specific measures that would lead unequivocally to a reduction in emissions. Since then, the majority of point source emissions have declined further (see Section 4.1), although it is known that some sites are not included in the voluntary industry programme. Therefore the extent of the risk posed by tetrabromobisphenol-A bis(methyl ether) is unclear, but likely to be declining. Nevertheless, it remains a potential concern.

6. Achieving the desired reductions

6.1 OSPAR targets

The OSPAR Strategy with regard to Hazardous Substances sets out that the OSPAR objective with regard to hazardous substances 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.*"

The timeframe given in the Strategy states that "every endeavour will be made to move towards the target of cessation of discharges, emissions and losses of hazardous substances of concern by the year 2020."

At OSPAR 2002, OSPAR adopted guidance on the role of marine risk assessment, which gives, in particular, advice on the urgency of taking measures based on particular PEC/PNEC ratios (cf. Annex 6 of OSPAR

2002 Summary Record). The UK has attempted to apply this guidance and reached the following conclusions. However, these conclusions are considered to be provisional, and could change in the light of further information which is needed to get realistic estimations of a number of emissions.

The estimated local PEC/PNEC ratios for tetrabromobisphenol-A for marine water and sediment are greater than 1 for the processing in ABS as an additive flame retardant (compounding step). The use of tetrabromobisphenol-A as a reactive flame retardant, and the conversion step in the use of ABS as an additive flame retardant lead to a low risk to marine water and sediment (PEC/PNEC ratios <1). The assessment of secondary poisoning in the marine environment does not give rise to any PEC/PNEC ratios above one for any scenario.

The guidance recognises, however, that where the uncertainties are high in the estimation of risk, this should be taken into account by the Contracting Parties when considering the actions necessary to achieve OSPAR's objectives.

In this instance, default values have been used in the calculation of emissions from the various processes, and further exposure information is needed to refine the PEC assessments. There is also only a limited amount of long-term toxicity information on seawater species and further testing could potentially revise the PNEC for marine water and marine sediment. However, as no major manufacturing sites using tetrabromobisphenol-A appear to discharge directly into marine waters, these local PEC/PNEC ratios for the marine environment appear to be of limited relevance.

Industry has instigated a voluntary programme with the aim of reducing emissions to the environment from the main industrial users of tetrabromobisphenol-A (VECAP). This programme has shown that emissions to the environment in general are reducing, and provides a mechanism by which to monitor future reductions in emissions.

In addition, the available monitoring data show that tetrabromobisphenol-A is present in the marine environment albeit at very low concentrations. Most of the reported occurrences of tetrabromobisphenol-A relate to locations close to potential sources of release/populated areas. In this respect it is important to note that two recent studies in more remote marine locations did not find detectable levels of tetrabromobisphenol-A in marine sediment and biota from more remote locations (using limits of detection up to about 0.6 µg/kg dry weight).

Nevertheless, although tetrabromobisphenol-A itself does not meet the PBT criteria of the EC Technical Guidance Document, it does meet the OSPAR PBT criteria, and concerns remain about possible degradation products. It is therefore imperative from OSPAR's point of view that appropriate actions, commensurate with the estimated risks, and taking account of the uncertainties in their estimation, should be taken to achieve the OSPAR objectives on hazardous substances.

6.2 OSPAR's role in achieving the desired targets

In order to meet the targets specified in the OSPAR objective and timeframe, it will be necessary to:

- assess the need for further reductions from the various sources and the practicability of such reductions;
- review existing regulations and controls in the light of the need for further reductions;
- decide which organisation is responsible and/or best placed for carrying out detailed assessments and/or implementing controls;
- inform the relevant organisation (if OSPAR sees fit) of the OSPAR Ministerial commitments with regard to hazardous substances and the need for action to address OSPAR concerns;
- set up mechanisms for monitoring the compliance with measures adopted in the relevant forum;

- set up mechanisms to monitor inputs to the marine environment and concentrations in the marine environment and biota to check that levels are falling at a satisfactory rate.

For a number of the sources of tetrabromobisphenol-A, OSPAR may not be the most appropriate international body to instigate further controls or to assess whether the controls are practicable or necessary. Therefore, setting and achieving the desired reduction targets will need to be carried out through close co-operation with other international forums.

It will also be possible, through appropriate assessment and monitoring activities, to consolidate the values obtained in **Table 3**, **Table 4**, **Table 5** and **Table 6** to determine whether tetrabromobisphenol-A occurs in the marine environment at significant levels, and to assess whether the levels are falling due to the implementation of agreed actions (and also the VECAP), and whether values are approaching near to zero concentrations.

7. Identification of possible measures

7.1 Review of Existing OSPAR, EU and National Measures

7.1.1 Measures in OSPAR

No measures have been taken to date.

7.1.2 Ongoing activities within the European Union

Tetrabromobisphenol-A has undergone a risk assessment under the Existing Substances Regulation in the EU (Regulation 793/93). The UK led this work. The final agreed conclusions of the risk assessment are available (ECB, 2008).

Directive 2002/96/EC⁸ on Waste Electrical and Electronic Equipment (WEEE Directive) entered European law on the 13th February 2003 and should have been implemented by Member States by the 13th August 2004. The Directive contains the following elements:

- Member States shall set up separate collection schemes and ensure the proper treatment, recovery and disposal of WEEE;
- The treatment, recovery and disposal of WEEE shall be financed by producers to create economic incentives to adapt the design of electrical and electronic equipment to the prerequisites of sound waste management;
- Consumers shall have the possibility to return their equipment free of charge. They need to be informed about the possibilities of returning WEEE.

The Directive encourages producer responsibility for waste management, separate collection of WEEE, improved treatment and reuse/recycling, and improved dissemination to users. In implementing the Directive, producers are required to set up systems to treat WEEE which would include, amongst other things, separation of plastic containing brominated flame retardants from collected WEEE (RPA, 2001).

7.1.3 National initiatives within some Contracting Parties

In Denmark regulations are already in place on the management of waste from electrical and electronic products (Danish Environmental Protection Agency, 2001). According to the Ministry of Environment and Energy's Statutory Order No. 1067 of 22 December 1998, flame-retarded plastic has to be separated out from other waste from electrical and electronic equipment and this plastic has to be recycled, incinerated or deposited at approved facilities. In the case of recycling, the plastic has to be used for products for which

⁸ Directive 2002/96/EC of the European Parliament and of the Council of 27 January 2003 on waste electrical and electronic equipment (WEEE). Official Journal of the European Union, L37, 13/2/2003, pp24-38.

special requirements apply for fire safety reasons. There are around 25 companies that separate electronic waste in Denmark.

7.2 Alternatives

One of the guiding principles of the OSPAR Strategy on Hazardous Substances is the principle of substitution (the substitution of hazardous substances or preferably non-hazardous substances where such alternatives are available.)

Substitution has been discussed by various OSPAR subsidiary bodies in the 1999/2000 inter-sessional period. The substitution of hazardous substances used offshore has been addressed in OIC and is an essential element of the measures adopted at OSPAR 2000 with respect to the use and discharge of offshore chemicals.

The UK assessment has not yet revealed any definitive substitutes or alternatives which have been used for tetrabromobisphenol-A. It should be noted that tetrabromobisphenol-A is itself considered as an alternative to octabromodiphenyl ether as an additive flame retardant in ABS.

Substitution of tetrabromobisphenol-A by another substance requires consideration of the following:

- that the substitute is less harmful and poses a lower risk;
- the physical behaviour of the substance and thus the nature of the processes used to produce these substances;
- the price differential between these substances and tetrabromobisphenol-A, based on these processes and resulting performance of the product;
- the efficacy of substitutes and the volumes required.

8. Choice for action/measures

8.1 General considerations

When considered in the light of the guidance on the role of risk assessment, the initial results from the marine risk assessment indicate that there should be concern over some uses of tetrabromobisphenol-A as a flame retardant.

However, it should be noted that the majority of the PEC values are derived from default emission estimates and this should be taken into account in the consideration and timing of measures. The conclusion of the ESR risk assessment for the marine environment was that there is a potential risk, which could be refined with further information and/or testing (ECB, 2008). This included better exposure information to improve the estimates of exposure and also further long-term tests on marine organisms to reduce the uncertainties over the existing data.

However ECB (2008) also recommended that the need for further toxicity data on marine organisms should be evaluated once the implications of any risk reduction activities resulting from the assessment for freshwater and freshwater sediment were known. Industry have indicated that none of the major manufacturing sites in the EU using tetrabromobisphenol-A as a reactive flame retardant, or compounding sites using tetrabromobisphenol-A as an additive flame retardant, are situated close to coastal areas and so the relevance of the local marine risk assessment to these uses appears to be limited. The main producers/suppliers of tetrabromobisphenol-A in the EU have instigated a VECAP with the aim of reducing emissions to the environment through a better understanding and better management of chemical substances throughout the supply chain. Although no formal decision was made on whether to pursue further testing following the risk reduction strategy under the ESR, it would appear to be a low priority in the light of the latest information.

A proper evaluation of the appropriate choices for action can therefore only be made when all the relevant risk reduction scenarios have been developed. Assessment will be required of possible additional measures, examining options against key criteria such as effectiveness, practicability and economic impact. In particular, there needs to be a better understanding of the availability and risks posed by substitutes which are available to replace tetrabromobisphenol-A. However, the following actions are already thought to be justified.

8.2 Action in the EC

To support this process and to ensure that the information in this background document and the conclusions reached by OSPAR are generally taken into account in the approach of the European Community, OSPAR should communicate this background document to the European Commission.

8.3 Action within OSPAR

In recognition of the large uncertainties in the estimations of risk made, the relevant industries should be invited to work with Contracting Parties to improve the estimates of emissions, environmental levels and if necessary, the estimation of PNEC values and clarification of PBT properties of relevant degradation products, to ensure the most effective risk reduction measures can be adopted.

OSPAR should re-evaluate the risks posed by tetrabromobisphenol-A releases when further information has been collected. Any associated measures which might be justified in the light of new findings should be addressed through the background document review process.

OSPAR supports the substitution of hazardous substances with safer substitutes. However, the UK assessment has not yet revealed any definitive substances or alternatives which have been used for tetrabromobisphenol-A, and should therefore keep the situation under review.

8.4 Action in other forums

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 with 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 parties both 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.

9. References

- Arias P. A. (2001). Brominated flame retardants - an overview. Second International Workshop on Brominated Flame Retardants, May 14-16, Stockholm University, Sweden, pp17-19.
- Asplund L., Athanasiadou M., Sjödin A., Bergman Å and Börjeson H. (1999). Organohalogen substances in muscle, egg and blood from healthy Baltic Salmon (*Salmo salar*) and Baltic Salmon that produced offspring with the M74 Syndrome. *Ambio*, **28**, 67-76.
- Bakke T., Boitsov S., Brevik E. M., Gabrielsen G. W., Green N., Helgason L. B., Klungsøyr J., Lekens H., Miljeteig C., Måge A., Rolfsnes B. E., Savinova T., Schlabach M., Skaare B. B. and Valdersnes S., 2008. Mapping selected organic contaminants in the Barents Sea 2007. SPFO-Report 1021/2008, TA-2400/2008. Norwegian Pollution Control Authority.
- Berger U., Herzke D. and Sandanger T. M. (2004). Two trace analytical methods for determination of hydroxylated PCBs and other halogenated phenolic compounds in eggs from Norwegian birds of prey. *Anal. Chem.*, **15**, 441-452.

- BSEF (2007). VECAP. North America Progress Report 2007. The Voluntary Emissions Control Action Programme for Brominated Flame Retardants. Bromine Science and Environmental Forum, 2007.
- CEFAS (2002). Sampling for priority chemicals in the environment. CEFAS Contract Report C1337 for Department of Environment, Food and Rural Affairs (DEFRA).
- de Boer J., Allchin C., Zegers B., Boon J. P., Brandsma S. H., Morris S., Kruijt A. W., van der Veen I., van Hesseligen J. M. and Haftka J. J. H. (2002). HBCD and TBBP-A in sewage sludge, sediments and biota, including interlaboratory study. RIVO Report No. C033/02. September 2002.
- Defra (2007). Risk Reduction Strategy and Analysis of Advantages and Drawbacks for Tetrabromobisphenol-A: Stage 4 Report. Prepared by Entec UK Limited on behalf of the UK Department for the Environment, Food and Rural Affairs (Chemicals and Nanotechnologies Division), September 2007.
- de Wit C. A. and Muir D. C. G. (2004). Levels and trends of brominated flame retardants in the Arctic. Abstract from "Third International Workshop on Brominated Flame Retardants, BFR2004". University of Toronto, Canada, June 6-9, 2004.
- de Wit C. A., Alae M. and Muir D. C. G. (2006). Levels and trends of brominated flame retardants in the Arctic. *Chemosphere*, **64**, 209-233.
- de Wit C. A., Herzke D. and Vorkamp K. (2010). Brominated flame retardants in the Arctic environment – trends and new candidates. *Science of the Total Environment*, **408**, 2885-2918.
- EBFRIP (2006). VECAP. Annual Progress Report 2006. The Voluntary Emissions Control Action Programme from the Brominated Flame Retardant Deca-BDE. European Brominated Flame Retardants Industry Panel and Bromine Science and Environmental Forum, 2006.
- EBFRIP (2007). VECAP. Second Annual Progress Report 2007. The Voluntary Emissions Control Action Programme for Brominated Flame Retardants. European Brominated Flame Retardants Industry Panel and Bromine Science and Environmental Forum, June 2007.
- EBFRIP (2008). VECAP. Third Annual Progress Report 2008. The Voluntary Emissions Control Action Programme for Brominated Flame Retardants. European Brominated Flame Retardants Industry Panel, Textile Finishers' Association and Bromine Science and Environmental Forum, 2008.
- EBFRIP (2009). VECAP. Annual Progress Report 2009. The Voluntary Emissions Control Action Programme for Brominated Flame Retardants. European Brominated Flame Retardants Industry Panel, SECURE (Sustainable use of HBCD) and Bromine Science and Environmental Forum, 2009.
- ECB (2008). Risk Assessment of 2,2',6,6'-tetrabromo-4,4'-isopropylidene diphenol (tetrabromobisphenol-A). Final Environmental Draft for Publication, February 2008. European Chemicals Bureau.
- ECB (2010). Risk Assessment of 4,4'-isopropylidene diphenol (bisphenol-A). Final approved version awaiting publication, February 2010. European Chemicals Bureau.
- Evenset A., Leknes H., Christensen G. H., Warner N., Remberger M. and Gabrielsen G. W., 2009. Screening of new contaminants in samples from the Norwegian Arctic. Silver, platinum, sucralose, bisphenol A, tetrabromobisphenol A, siloxanes, phthalates (DEHP) and phosphororganic flame retardants. SPFO-Report 1049/2009, TA-2510/2009. Norwegian Pollution Control Authority.
- Fjeld E., Schlabach M. Berge J.A., Eggen T., Snilsberg P., Källberg G., Rognerud S., Enke E. K., Borgwn A. and Gundersen H. (2004). Screening of selected new organic contaminants – brominated flame retardants, chlorinated paraffins, bisphenol-A and triclosan. Norsk Institutt for vannforskning, 25th February 2004.

- Frederiksen M., Vorkamp K., Bossi R., Rigéts F., Dam M. and Svensmark B. (2007). Method development for simultaneous analysis of HBCD, TBBPA, and dimethyl-TBBPA in marine biota from Greenland and the Faroe Islands. *International Journal of Environmental and Analytical Chemistry*, **87**, 1096-1109.
- Hakk H. (2001). A survey of tetrabromobisphenol A. Second International Workshop on Brominated Flame Retardants, May 14-16, Stockholm University, Sweden, pp27-30.
- He M.-J., Luo X.-J., Yu L.-H., Juan L., Zhang X.-L., Chen S.-J., Da C. and Mai B.-X. (2010a). Tetrabromobisphenol-A and hexabromocyclododecane in birds from an e-waste region in South China: Influence of diet on diastereoisomer- and enantiomer-specific distribution and trophodynamics. *Environmental Science & Technology*, **44**(15), 5748-5754.
- He M.-J., Luo X.-J., Yu L.-H., Juan L., Zhang X.-L., Chen S.-J., Da C. and Mai B.-X. (2010b). Tetrabromobisphenol-A and hexabromocyclododecane in birds from an e-waste region in South China: Influence of diet on diastereoisomer- and enantiomer-specific distribution and trophodynamics. *Environmental Science & Technology*, **44**(15), 5748-5754. Correction published on web 13 October 2010.
- Heemken O. P., Kuballa J. and Stachel B. (2001). Flame retardants in sediments of the River Elbe. A first review and assessment. Poster presentation at Second International Workshop on Brominated Flame Retardants, May 14-16, Stockholm University, Sweden.
- Herzke D., Berger U., Nygård T. and Vetter W. (2003). Organochlorines, organobromines and their metabolites in eggs of Norwegian birds of prey. *Dioxin 2003, Organohalogen Compounds*, **60-65**, pages unknown.
- Herzke D., Berger U., Kallenborn R., Nygård T. and Vetter W. (2005). Brominated flame retardants and other organobromines in Norwegian predatory birds eggs. *Chemosphere*, **61**, 441-449.
- Industry Consortium (2002). Industry comments of August 16, 2002 on the European Union Risk Assessment - Environmental Draft Report 2,2', 6,6'-Tetrabromo-4,4'-isopropylidene diphenyl (tetrabromobisphenol-A), CAS No.: 79-94-7.
- Kemmlin S. (2000). Polybromierte Flammschutzmittel: Entwicklung eines Analyseverfahrens und Untersuchung und Bewertung der Belastungssituation ausgewählter Umweltkompartimente. Fachberiech 06. Vorgelegt von Diplom-Chemikerin, Berlin.
- Kuch B., Körner W. and Hagenmaier H. (2001). Monitoring von bromierten Flammschutzmitteln in Fließgewässern, Abwässern und Klärschlämmen in Baden-Württemberg. Abschlussbericht des BWPlus-Forschungsvorhabens BWBO 99-11.
- Law R. J., Allchin C. R., Morris S. and Jepson P. D. (2003). Persistent organohalogen compounds in marine mammals stranded or bycaught in the UK. *Dioxin 2003, Organohalogen Compounds*, **60-65**, pages unknown.
- Law R. J., Bersuder P., Allchin C. R. and Barry J. (2006). Levels of flame retardants hexabromocyclododecane and tetrabromobisphenol A in blubber of harbour porpoises (*Phocoena phocoena*) stranded or bycaught in the U.K., with evidence for an increase in HBCD concentrations in recent years. *Environmental Science and Technology*, **40**, 2177-2183.
- Law R. J., Bersuder P., Barry J., Wilford B. H., Allchin C. R. and Jepson P. D. (2008). A significant downturn in levels of hexabromocyclododecane in the blubber of harbour porpoises (*Phocoena phocoena*) stranded or bycaught in the UK: An update to 2006. *Environmental Science and Technology*, **40**, 9104-9109.
- Leisewitz A., Kruse H. and Schramm E. (2000). Substituting Environmentally Relevant Flame Retardants: Assessment Fundamentals. Volume 1: Results and Summary Overview. Research Report 297 44 542. German Federal Environmental Agency (Umweltbundesamt).

- Muir D. C. G. and de Wit C. A. (2010). Trends of legacy and new persistent organic pollutants in the circumpolar arctic: Overview, conclusions, and recommendations. *Science of the Total Environment*, **408**, 3044-3051.
- Peltola J. (2002). An environmental screening of four brominated flame retardants in Finland. To be published in *Chemosphere*.
- RPA (2001). Octabromodiphenyl ether: Risk Reduction Strategy and Analysis of Advantages and Drawbacks. Draft Stage 2 Report prepared for Department for Environment, Food and Rural Affairs. Risk and Policy Analysts Limited, November 2001.
- SFT (2002). Kartlegging av bromerte flammehemmere og klorerte parifiner. Rapport 866/02. Norwegian Pollution Control Authority.
- Sørensen P. B., Vorkamp K., Thomsen M., Falk K. and Møller S. (2004). Persistent organic pollutants (POPs) in the Greenland environment – Long-term temporal changes and effects on eggs of a bird of prey. NERI Technical Report No. 509, National Environmental Research Institute, Ministry of the Environment, Denmark.
- Sternbeck J., Brorström-Lundén E., Remberger M., Kaj L., Palm A., Junedahl E. and Cato I. (2003). WFD Priority substances in sediments from Stockholm and the Svealand coastal region. IVL Report B1538, September 2003. Swedish Environmental Research Institute.
- Verslycke T.A., Vethaak A.D., Arijs K. and Janssen C.R. (2005). Flame retardants, surfactants and organotins in sediment and mysid shrimp in the Scheldt estuary (the Netherlands). *Environmental Pollution*, **136**, 19-31.
- Vorkamp K., Thomsen M., Falk K., Leslie H., Møller S. and Sørensen P. B. (2005). Temporal development of brominated flame retardants in peregrine falcon (*Falco peregrinus*) eggs from South Greenland (1986-2003). *Environ. Sci. Technol.*, **39**, 8199-8206.
- Wu J.-P., Zhang Y., Luo X.-J., Wang J., Chen S.-J., Guan Y.-T. and Mai B.-X. (2010). Isomer-specific bioaccumulation and trophic transfer of Dechlorane Plus in the freshwater food web from a highly contaminated site, south China. *Environ. Sci. Technol.*, **44**, 606–611.

Annex 1: Marine risk assessment

1. Introduction

This Annex considers the risks to the marine environment from the production, use and disposal of tetrabromobisphenol-A. The methodology used is based on the marine risk assessment chapter of the Technical Guidance Document⁹ for EU Regulation 793/93. The marine risk assessment was carried out as part of the environmental risk assessment for tetrabromobisphenol-A carried out under the EU Existing Substances Regulation (ECB, 2008) and the main assumptions and findings of that risk assessment are reproduced here. The PBT assessment is discussed in the background document main text.

2. Marine exposure assessment

The methodology outlined in the marine risk assessment guidance essentially assumes that the adsorption/desorption, degradation and accumulation behaviour in the marine environment can, in the absence of specific information for the marine environment, be adequately described by the properties of the substance relevant for the freshwater environment. The relevant properties for tetrabromobisphenol-A are summarised in **Table A1.1**.

Table A1.1: Adsorption and accumulation properties for tetrabromobisphenol-A used in the marine assessment

Property	Value
n-Octanol-water partition coefficient (log Kow)	5.90
Water solubility	1.26-2.34 mg/l
Organic carbon - water partition coefficient (Koc)	49 726 l/kg
Solid-water partition coefficient in suspended matter (Kp _{susp})	7 299 l/kg
Suspended matter - water partition coefficient (K _{susp-water})	1 826 m ³ /m ³
Fish bioconcentration factor (BCF _{fish})	485 l/kg (tetrabromobisphenol-A alone) 1 234 l/kg (tetrabromobisphenol-A plus metabolites)
Biomagnification factor in fish (BMF ₁) ^a	1
Biomagnification factor in predators (BMF ₂) ^a	1

Note: a) Taken from the marine risk assessment guidance using the BCF_{fish} as the trigger value. Actual biomagnification factors for tetrabromobisphenol-A appear to be <1 based on feeding studies.

As the pH of seawater is around 8, tetrabromobisphenol-A is expected to be present in an ionised form in the marine environment. The effect of pH on the partition coefficients and water solubility of the substance is considered in Section 1 and Section 3.1.0 of the ECB (2010) and the values reported in **Table A1.1** are considered to be those most appropriate for the pH conditions likely to be found in the marine environment. The one possible exception to this is the log Kow, where the pH of the water used in the determination was not given. However, as suitable values for Koc and BCF_{fish} are available from elsewhere, the log Kow is not vital to the assessment.

⁹ Available from ECB web-site – <http://ecb.jrc.it/existing-chemicals>

The starting point for the local marine assessment is the concentration of tetrabromobisphenol-A in effluent from the site of discharge. This effluent from industrial sites is assumed to enter into the marine environment without further waste water treatment.

As all the emissions are estimated on a mass/day basis, in order to estimate these concentrations, knowledge of the total aqueous effluent volume discharge from generic sites is needed. These data are not available. In this situation the Technical Guidance indicates that it can be assumed that the amount emitted per day is diluted into a volume of 200 000 m³, with adsorption onto suspended matter also being taken into account.

The emissions used as the starting point for the marine risk assessment are shown in **Table A1.2**. **Table A1.2** also shows the resulting concentrations in seawater, marine sediment and marine biota. These have been estimated using the methods outlined in the Technical Guidance Document and the properties shown in **Table A1.1** for the adsorption and accumulation behaviour of tetrabromobisphenol-A (EUSES version 2.0.3 was used for the calculation).

It should be noted that neither the production of tetrabromobisphenol-A nor the use of tetrabromobisphenol-A as an intermediate currently occur in the EU. The calculations of the PEC values for these scenarios are based entirely on default values and are included for illustration only. They are not taken on to the risk characterisation.

For secondary poisoning, the concentrations in predators and top predators have been estimated using the following equations.

$$PEC_{oral, predator} = 0.5 \times (PEC_{local, seawater, ann} + PEC_{regional, seawater, ann}) \times BCF_{fish} \times BMF_1$$

$$PEC_{oral, top predator} = (0.1 \times PEC_{local, seawater, ann} + 0.9 \times PEC_{regional, seawater, ann}) \times BCF_{fish} \times BMF_1 \times BMF_2$$

The $PEC_{regional, seawater}$ is estimated as 1.3×10^{-4} µg/l and the $PEC_{regional, sediment}$ is estimated as 4.0×10^{-4} mg/kg wet weight.

For sites manufacturing epoxy and/or polycarbonate resins, and the major compounding sites for additive use of tetrabromobisphenol-A, information has been received from Industry indicating that none of the sites within the EU discharge directly into the marine environment. One site was identified around 50 km from the coast that discharged their effluent via a waste water treatment plant into a water course. The generic calculations in **Table A1.2** have therefore assumed that the effluent is treated in a waste water treatment plant.

Table A1.2: Estimated PECs for tetrabromobisphenol-A for the local marine risk assessment

Scenario	Comment	Daily emission to water (kg/day)	No. of days of release	$C_{local, seawater}$ ($\mu\text{g/l}$) ^c	$C_{local, seawater, ann}$ ($\mu\text{g/l}$)	$PEC_{local, seawater}$ ($\mu\text{g/l}$) ^d	$PEC_{local, seawater, ann}$ ($\mu\text{g/l}$) ^d	$PEC_{local, sed}$ (mg/kg wet wt.)	$PEC_{oral, predator}$ (mg/kg) ^d		$PEC_{oral, top predator}$ (mg/kg) ^d	
									a	b	a	b
Production of tetrabromobisphenol-A	Example calculation	13.6	300	61.3	50.4	61.3	50.4	97.3	31.1	12.2	6.2	2.4
Use as an intermediate in the production of derivatives	Example calculation	17.5	200	78.9	43.2	78.9	43.2	125	26.7	10.5	5.3	2.1
Reactive flame retardant use	Manufacture of epoxy and/or polycarbonate resins	0.027	300	0.023	0.019	0.023	0.019	0.036	0.012	4.6×10^{-3}	2.4×10^{-3}	9.6×10^{-4}
	Processing of epoxy resins	5.0×10^{-5}	32	2.3×10^{-4}	2.0×10^{-5}	3.6×10^{-4}	1.5×10^{-4}	5.6×10^{-4}	1.7×10^{-4}	6.8×10^{-5}	1.6×10^{-4}	6.4×10^{-5}
	Processing of polycarbonate resins	5.0×10^{-5}	28	2.3×10^{-4}	1.7×10^{-5}	3.6×10^{-4}	1.5×10^{-4}	5.6×10^{-4}	1.7×10^{-4}	6.7×10^{-5}	1.6×10^{-4}	6.4×10^{-5}
Additive flame retardant use - ABS	Compounding	1.1	171	0.92	0.43	0.92	0.43	1.5	0.27	0.10	0.053	0.021
	Conversion ^e	0.05	171	0.23	0.11	0.23	0.11	0.36	0.065	0.026	0.013	5.2×10^{-3}

Notes: a) Calculations assuming $BCF_{fish} = 1\ 234$ l/kg.

b) Calculations assuming $BCF_{fish} = 485$ l/kg.

c) Assumes the daily emission is diluted into $200\ 000\ \text{m}^3$ of water and the concentration of suspended matter in the seawater is 15 mg/l.

d) Calculations use a $PEC_{regional, seawater}$ of 1.3×10^{-4} $\mu\text{g/l}$ calculated with EUSES 2.0.3 and a Koc of 49 726 l/kg.

e) The calculations for these scenarios assume that the effluent is treated in a waste water treatment plant prior to discharge.

3. Predicted no effect concentration (PNEC) for the marine compartment

3.1 Water

The Technical Guidance recommends that the pooled data for both freshwater and marine organisms are considered in the PNEC derivation. As discussed in ECB (2008), the overall data set for tetrabromobisphenol-A consists of NOEC values for freshwater fish (0.16 mg/l), two species of freshwater invertebrates (lowest NOEC <0.066 mg/l), three species of marine invertebrate (lowest NOEC/EC₁₀ = 0.012 mg/l), and one freshwater algal species (NOEC ≥5.6 mg/l). In addition acute EC₅₀ values (but no NOEC values) are available for 1 freshwater algal species and 3 marine algae (lowest EC₅₀ is 0.09 mg/l). There is some evidence that the toxicity of tetrabromobisphenol-A to marine algae may increase with decreasing pH in the range pH 7.6 to 8.2, but, given that natural seawater is effectively buffered at around pH 8, such trends in toxicity are not likely to be important in reality.

From the Technical Guidance Document an assessment factor of 50 could be applied to the available data as there are NOECs from freshwater/marine species covering three trophic levels (algae, fish and crustaceans) with in addition a long-term NOEC from an additional marine taxonomic group (molluscs). As marine as well as fresh water species have been tested in two of the trophic levels (algae and crustaceans) it could be considered to reduce the assessment factor to a value of 10. However, there is some uncertainty over the actual NOECs for some of the species tested and no NOEC has been determined for marine algae.

Therefore it is proposed that an assessment factor of 50 will be used on the 5-day EC₁₀ value for *Acartia tonsa* of 0.0127 mg/l. This gives a PNEC for marine water of 0.25 µg/l.

3.2 Sediment

Reliable long-term toxicity tests have been carried out with the freshwater sediment oligochaete *Lumbriculus variegatus* for two sediment types. The NOEC values for the two sediments from this study, normalised to the Technical Guidance Document default organic carbon content of 5%, were 40 and 47 mg/kg wet weight. In addition, a 28-day study have been carried out with the freshwater midge *Chironomus riparius* and the freshwater amphipod *Hyalella azteca*. These gave NOECs of 27 mg/kg wet weight and 54 mg/kg wet weight respectively (ECB, 2008).

According to the Technical Guidance Document, for marine risk an assessment factor of 50 should be applied to the results of long term tests for three freshwater species. Therefore, applying an assessment factor of 50 to the NOEC value of 27 mg/kg wet weight gives a PNEC_{marine sediment} of 0.54 mg/kg wet weight (ECB, 2008).

4 Risk characterisation for the marine environment

The provisional risk characterisation ratios for water, sediment and predators/top-predators are shown in **Tables A1.3**, **A1.4** and **A1.5** respectively. The PNECs for marine water, sediment and predators/top-predators are respectively 0.25 µg/l, 0.54 mg/kg wet weight and >667 mg/kg food respectively.

Table A1.3: Risk characterisation ratios for marine water

Scenario	Step	PEC ($\mu\text{g/l}$)	Risk characterisation ratio
Reactive flame retardant use	Manufacture of epoxy and/or polycarbonate resins	0.023	0.092
	Processing of epoxy resins	3.6×10^{-4}	1.4×10^{-3}
	Processing of polycarbonate resins	3.6×10^{-4}	1.4×10^{-3}
Additive flame retardant use – ABS	Compounding ^a	0.92	3.7
	Conversion	0.23	0.92

Note a) The calculations for these scenarios assume that the effluent from the site is treated in a waste water treatment plant prior to discharge to the marine environment.

Table A1.4: Risk characterisation ratios for marine sediment

Scenario	Step	PEC (mg/kg wet weight)	Risk characterisation ratio
Reactive flame retardant use	Manufacture of epoxy and/or polycarbonate resins	0.036	0.067
	Processing of epoxy resins	5.6×10^{-4}	1.0×10^{-3}
	Processing of polycarbonate resins	5.6×10^{-4}	1.0×10^{-3}
Additive flame retardant use - ABS	Compounding ^a	1.5	2.8
	Conversion	0.36	0.66

Note a) The calculations for these scenarios assume that the effluent from the site is treated in a waste water treatment plant prior to discharge to the marine environment.

Table A1.5: Risk characterisation ratios for secondary poisoning in the marine environment

Scenario	Step	Risk characterisation ratio for predators		Risk characterisation ratio for top predators	
		a	b	a	b
Reactive flame retardant use	Manufacture of epoxy and/or polycarbonate resins	$<1.8 \times 10^{-5}$	$<6.9 \times 10^{-6}$	$<3.6 \times 10^{-6}$	$<1.4 \times 10^{-6}$
	Processing of epoxy resins	$<2.5 \times 10^{-7}$	$<1.0 \times 10^{-7}$	$<2.4 \times 10^{-7}$	$<9.6 \times 10^{-8}$
	Processing of polycarbonate resins	$<2.5 \times 10^{-7}$	$<1.0 \times 10^{-7}$	$<2.4 \times 10^{-7}$	$<9.6 \times 10^{-8}$
Additive flame retardant use – ABS	Compounding ^c	$<4.0 \times 10^{-4}$	$<1.5 \times 10^{-4}$	$<7.9 \times 10^{-4}$	$<3.1 \times 10^{-5}$
	Conversion	$<9.7 \times 10^{-5}$	$<3.9 \times 10^{-5}$	$<1.9 \times 10^{-5}$	$<7.8 \times 10^{-6}$

Notes: a) Based on $\text{BCF}_{\text{fish}} = 1\,234$ l/kg.

b) Based on $\text{BCF}_{\text{fish}} = 485$ l/kg.

c) The calculations for these scenarios assume that the effluent from the site is treated in a waste water treatment plant prior to discharge to the marine environment.

The risk assessment for the marine environment indicates a potential risk to water and sediment from compounding sites where tetrabromobisphenol-A is used as an additive flame retardant. Manufacture and processing of epoxy and polycarbonate resins, and conversion of ABS containing tetrabromobisphenol-A as an additive, do not appear to present a risk. It would be possible to revise the PECs for the other endpoints by collection of further exposure information. Industry has indicated that none of the major manufacturing

sites using tetrabromobisphenol-A as a reactive flame retardant, or compounding sites using tetrabromobisphenol-A as an additive flame retardant, are situated close to coastal areas, and so the relevance of a local marine risk assessment for these uses is questionable (ECB, 2008).

It would also be possible to revise the PNEC for water and sediment by carrying out further testing (ECB, 2008).

The risk from secondary poisoning appears to be low for all scenarios (ECB, 2008).

Other issues relevant to the risk assessment¹⁰

A study in Norway has detected tetrabromobisphenol-A in the eggs of a number of predatory bird species. No information is available about possible trends, and the route of exposure of these birds is unknown (it could be from sources other than food), and so the levels cannot be linked with any particular source at present (ECB, 2008).

The presence of a synthetic substance in the tissues of top predators is clearly undesirable, but does not by itself necessarily constitute a risk. However, tetrabromobisphenol-A is expected to be highly persistent in the environment, and a single study has been performed involving exposure of birds' eggs that demonstrates toxicity. The presence of tetrabromobisphenol-A in the eggs of top predators is therefore an important and serious finding that cannot be overlooked.

Since the normal PEC/PNEC comparison methods described in the Technical Guidance Document do not apply to this situation, it is proposed to derive an indicative estimate of the significance of these levels as follows:

- It is not possible to estimate a 90th percentile concentration in eggs. The maximum concentration was 0.013 µg/kg wet weight for Osprey.
- A dose of tetrabromobisphenol-A of 45 µg/g egg caused 80% mortality in quail and 96% mortality in chicken. These mortality rates were statistically significantly different from the mortalities seen in the control populations (13% in quail and 8% in chicken). No statistically significant mortalities occurred in the 15 µg/g egg treatment groups compared to control populations. No other significant effects were observed at this dose in either of two studies.
- When the lower of these two doses is compared to the highest concentration in Osprey eggs, the ratio obtained is $>10^6$.

Such a large 'margin of safety' suggests that the significance of the levels detected in predatory bird eggs is low. There is therefore currently no reason for concern, even in the absence of information on trends. It should be noted that no significant effects have been observed in mammals (including in studies that were designed to examine neurotoxic effects).

Transformation products

A number of degradation products (or metabolites) of tetrabromobisphenol-A have been postulated (and in some cases identified experimentally). These include the formation of bisphenol-A by the sequential debromination of tetrabromobisphenol-A under certain anaerobic conditions and the possible formation of the dimethylated derivative of tetrabromobisphenol-A (tetrabromobisphenol-A bis(methyl ether), a substance that has been found to occur in the environment) via O-methylation of tetrabromobisphenol-A (see ECB (2008) for further details).

With the exception of bisphenol-A (for which an EU risk assessment exists) very little is known about the bioaccumulation, persistence and toxicity of these potential degradation products and metabolites.

¹⁰ The analysis in this section has been provided by The Netherlands based on the data in the assessment. The analysis was subsequently included in ECB (2008).

In order to evaluate the possible PBT properties of the various possible degradation products and metabolites of tetrabromobisphenol-A, the USEPA EPI estimation program (version 3.12) has been used to estimate the key properties of the dimethylated derivative and tribromo-, dibromo- and bromobisphenol-A (possible intermediaries in the debromination to bisphenol-A). The results are discussed in detail in ECB (2008) and the following tentative conclusions were reached.

Substance	Tentative PBT assessment	
Tetrabromobisphenol-A bis(methyl ether)	P or vP	B or vB
Tribromobisphenol-A	P or vP	B or vB (but BCF would be expected to be lower than for tetrabromobisphenol-A)
Dibromobisphenol-A	P or vP	
Bromobisphenol-A	P?	

On this basis tetrabromobisphenol-A bis(methyl ether) potentially meets the screening vPvB criteria. It is worth noting that this substance has been found in 28 out of 32 samples of Peregrine falcon (*Falco peregrinus*) egg samples from South Greenland analysed by Sørensen *et al.* (2004). The levels found were in the range 0.1-940 µg/kg lipid. In addition, tetrabromobisphenol-A bis(methyl ether) has been detected in mussels and sediment samples although there are some uncertainties with the data (see ECB, 2008).

The lower brominated bisphenol-A derivatives would not be expected to meet the PBT criteria as they are expected to show lower bioaccumulation (based on lower log K_{ow} values) and lower toxicity than tetrabromobisphenol-A itself.

Annex 2: Fact Sheet from List of Substances of Possible Concern modified to include values from the risk assessment

	NAME	phenol, 4,4'-(1-methylethylidene)bis[2,6-dibromo-		VERSION: 2002-04-15
IDENTIFICATION				
1.1	CasNo	79044		
1.2	EMPCs/ELMPCs	201-230-3		
1.3	Synonyms	2,6-dibromophenol, 4,4'-(1-methylethylidene)bis[2,6-dibromophenol]		
1.4	Group/Function	Phenol, halogenated		
1.5	Initial selection	REI, POP, OSP, DANU		
1.6	Prioritised for action	Date: OSPAR 2000, Lead Country: United Kingdom, Background document: OSPAR 2003		
	Parameter	Value	Source/Reference	Remarks
PHYSICAL/CHEMICAL PROPERTIES				

2.1	<i>Molecular weight, g/mole</i>	543.9	EU - ECB, 2010	
2.2	<i>Water solubility, mg/l</i>	0.148 1.26 2.34	EU - ECB, 2010	Measured value at 25oC and pH 5 Measured value at 25oC and pH 7 Measured value at 25oC and pH 9
2.3	<i>Vapour pressure, Pa</i>	0.00000624	EU - ECB, 2010	Measured value at 25oC
ABIOTIC/BIOTIC DEGRADATION PROPERTIES				
3.1	<i>Abiotic OH-oxidation t½ d</i>	5.4	EU - ECB, 2010	Estimated value for half-life 130 hours. Based upon rate constant of 2.96e-12 cm ³ /molecule/s estimated using AOPWIN 1.88.
3.2	<i>Photolysis t½d</i>		EU - ECB, 2010	The available information suggests that tetrabromobisphenol-A is susceptible to direct photodegradation using UV radiation leading to a variety of products (significance for the environment not clear).
3.3	<i>Ready Biodegradability</i>	No	EU - ECB, 2010	
3.4	<i>Half-life</i>		EU - ECB, 2010	TBBPA can undergo primary biodegradation to form several products. Based upon the available data ultimate degradation occurs around 64 days.
3.5	<i>Inherent Biodegradability</i>	No	EU - ECB, 2010	
3.6	<i>Biodeg-QSAR</i>			
BIOACCUMULATION/BIOCENTRATION				
4.1	<i>logKow</i>	5.9	EU - ECB, 2010	Measured value.
4.2	<i>Bcf</i>	1234	EU - ECB, 2010	Representative value for fish based upon measured data.
AQUATIC TOXIC PROPERTIES				
5.1	<i>Acute toxicity algae IC50, mg/l</i>	>= 5.6	EU - ECB, 2010	In the experiment no effects observed at solubility limit.
5.2	<i>Acute toxicity daphnia EC50,</i>	0.96	EU - ECB, 2010	Measured 48hr LC50

	mg/l			
5.3	Acute toxicity fish LC50, mg/l	0.5	EU - ECB, 2010	Measured 96hr LC50 for Pimephales promelas
5.4	Chronic toxicity daphnia NOEC, mg/l	0.3	EU - ECB, 2010	Measured 21 day NOEC
5.5	Chronic toxicity fish NOEC, mg/l	0.16	EU - ECB, 2010	Measured 35 day NOEC (Larval survival) for Pimephales promelas
5.6	Aquatox-QSAR			
5.7	Aquatic toxicity - other species, mg/l	0.0127 0.017	EU - ECB, 2010	5 day EC10 for <i>Acartia tonsa</i> 70 day NOEC for <i>Mytilus edulis</i>
HUMAN TOXIC PROPERTIES				
6.1	Acute toxicity			
6.2	Carcinogenicity			
6.3	Chronic toxicity			
6.4	Mutagenicity			
6.5	Reprotoxicity			
EXPOSURE				
7.1	Production Volume	HPVC	EU - ECB, 2010	150000 (global production - not produced in Europe)
7.1	Production Volume	50000	Industry	
7.2	Use/Industry Category	The primary use of HPVC is as a resin in intermediate manufacture of plastic products, especially and predominantly in the form of pipes, tubes, rods, sheets, and other extruded or formed products. It may also be used as an		Source: EU - ECB, 2010

		additional information and in the manufacture of derivatives		
7.3	<i>Use in articles</i>			
7.4	<i>Environm.Occur. Measured</i>		Surface water: <0.001 – 0.02 ug/l	EU - ECB, 2010
7.4			Sediment: <0.2 -9752 ug/kg ww	EU - ECB, 2010
7.5	<i>Environm.Occur. Modelled</i>		Surface water: Local PEC 0.0015 – 9.2 ug/l	EU - ECB, 2010
7.5			Sediment: Local PEC 0.0027 - 18 mg/kg wet wt	EU - ECB, 2010
7.5			Agricultural soil: Local PEC 0.00026 – 17.9 mg/kg wet wt	EU - ECB, 2010
7.5			Air: Local PEC < 7.5x10 ⁻⁴ mg/m3.	EU - ECB, 2010
8	EU-LEGISLATION			
8.1	<i>Dir 67/548/EEC (Classification)</i>		:Annex1, Dir 67/548/EEC	
8.2	<i>Reg 793/93/EEC (Existing substances)</i>	4(UK)		
8.3	<i>Dir 2000/60/EEC (WFD)</i>			
8.4	<i>Dir 76/769/EEC (M&U)</i>			
8.5	<i>Dir 76/464/EEC (water)</i>			
8.6	<i>Dir 91/414/EEC (ppp)</i>			
8.7	<i>Dir 98/8/EEC (biocid)</i>			
9	ADDITIONAL INFORMATION			
9.1	<i>Hazard assessment-OECD</i>	YES		www.oecd.org/ehs/sidstable/
9.2	<i>Other risk assessments</i>			

Annex 3: Monitoring Strategy for Tetrabromobisphenol-A (TBBPA)

As part of the Joint Assessment and Monitoring Programme (*reference number 2003-22*), OSPAR 2005 adopted a revised Agreement on Monitoring Strategies for OSPAR Chemicals for Priority Action (*reference number 2004-14*) to implement the following monitoring for tracking progress towards the objectives of the OSPAR Hazardous Substances Strategy (*reference number 2003-21*) with regard to tetrabromobisphenol-A. The monitoring strategy for tetrabromobisphenol-A will be updated as and when necessary, and redirected in the light of subsequent experience.

The primary use of TBBPA is as a reactive intermediate in the manufacture of flame-retarded epoxy and polycarbonate resins. It may also be used as an additive flame retardant, for example in the manufacture of acrylonitrile-butadiene-styrene (ABS) resins and phenolic resins. It is also used in the manufacture of other flame retardant derivatives.

TBBPA is likely to reach the marine environment largely through industrial waste waters from land-based industrial activities. A smaller contribution to releases to water comes from particulate losses from products containing the substance over their lifetime. Emissions to air are smaller than those to water, and most such emissions are expected to be deposited close to the sources of emission. There are, however, some indications of possible transport over longer distance, possibly adsorbed to particulate matter, which could lead to a contribution to the marine environment through this route.

The Background Document reported that there were no available measured levels of tetrabromobisphenol-A in marine waters, but recorded a number of measurements of TBBPA in estuarine sediments, as well as in freshwaters, freshwater sediments and waste waters. It is therefore apparent that analytical methodologies are available, although these may need to be adapted to marine conditions.

TBBPA is undergoing risk assessment under the Existing Substances Regulation in the EU (Regulation 793/93). The UK is leading this work which is not likely to be finalised until the middle of 2005. Depending on the conclusions of the risk assessment, appropriate risk reduction measures, such as marketing and use restrictions, will be developed and agreed at EU level.

In the light of the factors listed above, and the fact that TBBPA is a flame retardant, and as such should have a similar approach to the monitoring strategy on flame retardants which has already been agreed (cf. appendix 1 to the Background Document on Brominated Flame Retardants, OSPAR publication number 135/2001), the two main components of the monitoring strategy for TBBPA are as follows:

- a. keeping a watching brief on the implementation of any measures on TBBPA, particularly in relevant EC legislation arising from the risk assessment which would enable sales and use of the chemical to be tracked;
- b. assessing the need for further monitoring to determine whether concentrations of TBBPA in marine sediments and biota are significant. In this respect, Contracting Parties are encouraged to extend their monitoring programmes to cover TBBPA and submit information to the UK who will assess whether concentrations in marine sediments and biota are significant, and whether there are gaps in knowledge which OSPAR should fill prior to the 2010 Quality Status Report. If sufficient information is not obtained in this way, a one-off exploratory survey will be considered, which might also monitor for the endocrine disruptor bisphenol-A in order to investigate whether there is a relationship between the two chemicals.

TETRABROMOBISPHENOL-A MONITORING STRATEGY	
Implementation of actions and measures	<ul style="list-style-type: none"> 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 (on-going by lead country as any EC measures develop).
Maritime area:	
Concentrations in sediments	<ul style="list-style-type: none"> Contracting Parties are encouraged to extend their monitoring programmes as soon as possible to cover TBBPA and to report results on a voluntary basis to the lead country and also through the data-handling mechanism operated by ICES for the CEMP. Before 2006 the lead country will collate information on concentrations of this substance in the marine environment in order to assess whether there is a gap in knowledge which OSPAR should fill prior to the 2010 QSR. If the information obtained through this mechanism is insufficient, the feasibility of carrying out a one-off survey should be considered¹¹. In the light of these steps, OSPAR will decide whether the CEMP should be expanded to include monitoring for tetrabromobisphenol-A. The review of the CEMP in 2005-2006 will review the availability of monitoring guidelines, quality assurance procedures and assessment tools in the marine environment. The need for EACs and BRCs will be considered in 2006-2007.
Concentrations in biota	<ul style="list-style-type: none"> Contracting Parties are encouraged to extend their monitoring programmes as soon as possible to cover TBBPA and to report results on a voluntary basis to the lead country and also through the data-handling mechanism operated by ICES for the CEMP. Before 2006 the lead country will collate information on concentrations of this substance in the marine environment in order to assess whether there is a gap in knowledge which OSPAR should fill prior to the 2010 QSR. If the information obtained through this mechanism is insufficient, the feasibility of carrying out a one-off survey should be considered¹¹. In the light of these steps, OSPAR will decide whether the CEMP should be expanded to include monitoring for tetrabromobisphenol-A. The review of the CEMP in 2005-2006 will review the availability of monitoring guidelines, quality assurance procedures and assessment tools in the marine environment. Any proposal for inclusion should take into account the possible need for monitoring in relation to any relevant EcoQOs adopted by OSPAR (organohalogen concentrations in seabird eggs).
Biological effects	<ul style="list-style-type: none"> Before 2006 the lead country will collate information available on any biological effects of this substance in order to assess whether this is a gap in knowledge which OSPAR should fill prior to the 2010 QSR.

¹¹ The UK believes that if possible, it would be sensible to include the parallel analysis of bisphenol-A in this survey to investigate the possible links between these substances.

Annex 4: New study on bioaccumulation

He *et al.* (2010a) investigated tetrabromobisphenol-A (TBBPA) concentrations in the muscles of six bird species (40 specimens in all, including aquatic and terrestrial birds with a range of food preferences) as well as dietary items collected from an electronic-waste recycling region (Qingyuan County) in South China. Bird specimens found dead or dying from various causes were collected between 2005 and 2008. Fish (Crucian carp: a Latin name is not provided) were collected from pools located in the same region using electric fishing devices; seven fish samples with a body weight less than 100 g were analysed to represent the diet of the piscivorous birds in this study. Grain samples were collected from five different rice fields in the study region, and they were mixed together to obtain three composite samples for analysis. Three composite leaf samples (*Eucalyptus* spp, the prevailing species of vegetation in the study area) were collected in two locations in the same region. Three water samples (from the fish pools) and four composite soil samples were also collected to represent the aquatic and terrestrial environmental matrix of the study area. The bird samples were immediately transferred to the laboratory. Muscle tissues were excised and stored at -20°C until chemical analysis. There is no information on the collection dates for the other samples, or their handling prior to analysis.

A labelled internal standard ($^{13}\text{C}_{12}$ -TBBPA) was added to the homogenized samples before solvent extraction. The lipid content was determined gravimetrically from one aliquot of the extract, whilst another aliquot of the extract was subjected to chromatography, and the eluate containing TBBPA collected and concentrated under a flow of nitrogen before instrumental analysis. Quantitative determination of TBBPA was performed using liquid chromatography and a triple quadrupole mass spectrometer with an electrospray interface working in negative ionization mode (LC-MS/MS). The procedural blank and spiking blank were analyzed for each batch of the samples. The mean recovery of TBBPA in the spiking blanks was 80%. The average recoveries of internal standards was 74.8% (8.9% for $^{13}\text{C}_{12}$ -TBBPA). The method detection limit was 0.27 ng/g (three times the standard deviation of the target value in blanks).

The reported levels of TBBPA are summarized in Table A4.1 (taken from He *et al.* (2010b): the originally reported values in He *et al.* (2010a) were a factor of ten higher due to a calculation error). TBBPA was detected in all bird muscle samples at median concentrations in the range 2.8 to 17.3 ng/g lipid weight. The highest levels on a lipid weight basis were found in white-breasted waterhen (up to 148 ng/g lipid weight). Actual wet weight concentrations for individual animals are not reported. TBBPA was also detected in the grain, plant leaf and soil samples (range 3.6 to 780 ng/g dry weight (dw)). (The authors cite another study that reported a comparable concentration range of 3.8-230 ng/g dw in riverine sediments from an electronics manufacturing site in the same region.)

Table A4.1: Concentration of TBBPA in birds, fish, water, grain, plant leaf and soil

Sample (and sample number, n)	Lipid content (%) ^a	$\delta^{15}\text{N}$ value ^c	$\delta^{13}\text{C}$ value ^c	TBBPA concentration ^a
Chinese pond heron <i>Ardeola bacchus</i> (pectoral muscle) (n = 5)	1.34 (1.01-10.1)	10 to 13 ‰	-23.5 to -19.7 ‰	17.3 (13.3-24.3) ng/g lipid weight
White-breasted waterhen <i>Amaurornis phoenicurus</i> (pectoral muscle) (n = 11)	1.58 (0.92-5.11)	8.5 to 11.2 ‰	-26.2 to -20.2 ‰	17.0 (2.81-148) ng/g lipid weight
Common snipe <i>Gallinago gallinago</i> (pectoral muscle) (n = 8)	5.5 (1.21-8.06)	6 to 9.5 ‰	-27 to -23 ‰	5.43 (1.06-14.9) ng/g lipid weight
Slaty-breasted rail <i>Gallirallus striatus</i> (pectoral muscle) (n = 4)	1.59 (1.21-6.52)	6.2 to 7.5 ‰	-26.5 to -21.5 ‰	10.3 (0.9-13.9) ng/g lipid weight
Spotted dove <i>Streptopelia chinensis</i> (pectoral muscle) (n = 9)	1.92 (1.22-3.95)	5 to 7 ‰	-25.4 to -23.9 ‰	9.01 (3.92-50.3) ng/g lipid weight
Chinese francolin <i>Francolinus pintadeanus</i> (pectoral muscle) (n = 3)	5.20 (3.88-5.62)	6.2 to 8.3 ‰	-27.5 to -26.4 ‰	2.82 (2.42-5.48) ng/g lipid weight
Fish (n = 7)	4.13 (1.30-6.85)	-	-	1.14 (0.23-1.74) ng/g lipid weight
Water (n = 3)	-	-	-	68 pg/l ^b
Grain (n = 3)	-	-	-	3.6 ng/g dry weight ^b
Plant leaf (n = 3)	-	-	-	8.9 ng/g dry weight ^b
Soil (n = 4)	-	-	-	295 (2.9-780) ng/g dry weight

Note: a - Data are reported as median values with the range in brackets.
b - Mean values reported due to the non-significant difference between the three samples.
c - Values read from a graph.

Stable isotope ratios ($\delta^{15}\text{N}$ and $\delta^{13}\text{C}$) were also analysed for the bird samples. The stable isotope ratio of nitrogen ($\delta^{15}\text{N}$) increases with trophic level so is used to estimate the position of organisms in the food web. The relative trophic status of the collected birds, defined by mean $\delta^{15}\text{N}$ value, increased in the following order: spotted dove (6.0‰) < slaty-breasted rail (6.9‰) and Chinese Francolin (7.0‰) < common snipe (7.8‰) < whitebreasted waterhen (9.5‰) < Chinese pond heron (11.1‰) (though there was a large degree of overlap for some species when all the data are considered). The stable isotope ratio of carbon ($\delta^{13}\text{C}$) is generally used to analyze the diet composition and carbon source of the organisms. The Chinese pond heron has a higher $\delta^{13}\text{C}$ value (mean of -22.4‰) than the spotted dove (-25‰) and Chinese francolin (-27‰), which is in line with its foraging behaviour (birds feeding on aquatic food have a higher $\delta^{13}\text{C}$ value than birds feeding on terrestrial food).

Trophic magnification was examined by simple linear regression of the log-normalized tissue concentrations against $\delta^{15}\text{N}$ values. A slight positive correlation was observed ($p = 0.057$, so this was not statistically significant ($p > 0.05$)), and the authors suggested that trophic magnification might have been occurring. A biomagnification factor (BMF) was also calculated for two possible food chains. The lipid-based BMF for the fish → piscivorous bird (Chinese-pond heron) food chain was 15. In contrast, the wet weight-based BMF for the grain → terrestrial phytophagous bird (spotted dove) food chain was less than one. The authors suggested that this large discrepancy between the two feeding relationships could be partly explained by the metabolism resulting in a low concentration of TBBPA in fish.

There are a number of problems in interpreting this study:

- Bird samples were collected over a very long time (three years); there is no information on collection dates for the other samples, and the spatial distribution of sample locations is not explained. Sample numbers were also very low (e.g. five Chinese Pond Herons, seven fish and three water samples), and the birds were all dead when found. It is therefore unclear whether the samples represent any sort of steady state situation, or whether they are truly representative for the particular species/media that were collected.

- b) The low concentrations detected (parts per billion for most samples but parts per trillion for water) mean that measurement errors may be significant for some samples. Full details of the analytical variation are lacking and so the precision cannot be assessed. The lipid content varied over a fairly wide range in some cases (e.g. 1-10% for Chinese pond heron), presumably reflecting the health of the birds when they were collected. This introduces further uncertainty given the small sample size, since the mean TBBPA concentration expressed on a lipid normalised basis might not necessarily reflect typical levels.
- c) The reported levels for birds relate to pectoral muscle only and whole body values are not available. The distribution of TBBPA over different tissues is unknown, and whilst lipid-normalised levels might be consistent, this is not certain. No information is provided for fish, but it might be assumed that whole fish were used. It might therefore be misleading to derive BMF or TMF data from these results.
- d) It is possible that the samples were collected in a similar way to those reported in another publication by the same research group (Wu *et al.*, 2010), although this is not certain. It is therefore likely that the fish species is *Carassius auratus* (the common name used in the article is also sometimes used for *Carassius carassius* (www.Fishbase.org)), and that samples of fish and water were collected at the same time. On this basis, it is possible to estimate a field bioaccumulation factor (BAF) from the ratio of the chemical concentrations in fish and water. The resulting BAF is 16,800 L/kg (on a lipid normalised basis). Converting this to a fish with 5% lipid content (typical of small fish) gives a BAF of 840 L/kg (this value is based on the mean measured fish concentration; if the reported range is used the BAF falls in the region of 170 – 1,300 L/kg). It should be noted that the fish concentration will also be influenced by dietary exposure, and since this was not measured, its overall contribution is unknown. It might therefore be misleading to compare the BAF directly with the OSPAR or REACH B criteria based on BCF (indeed, it is often the case that BAFs are somewhat higher than BCFs for the same substance). In addition, there is no information about how water levels might have changed with time so it is unclear whether the measured concentration in fish is directly related to the reported concentration in water. For these reasons, and given the very small number of samples involved, this BAF value is of limited reliability in terms of bioaccumulation assessment.
- e) The trophic magnification factor (TMF) can be estimated from the antilog of the slope of the plot of the logarithm of the measured (lipid-normalised) tissue concentration against trophic level. There is no agreed regulatory guidance available to explain how this should be done consistently. Figure 4 of the paper shows that data were plotted individually without error bars (i.e. they are not grouped by species mean or trophic guilds in any way), with the trophic level indicated by $\delta^{15}\text{N}$ value. A TMF was not derived and only 36 data points appear (no explanation is provided for the apparently four missing data points). The paper does not give the individual concentrations for each data point (rather they are shown graphically), so a plot has therefore been recreated for the purposes of this document on the basis of the mean measured values (as reported by He *et al.*, 2010b) to illustrate the findings (see Figure A4.1).

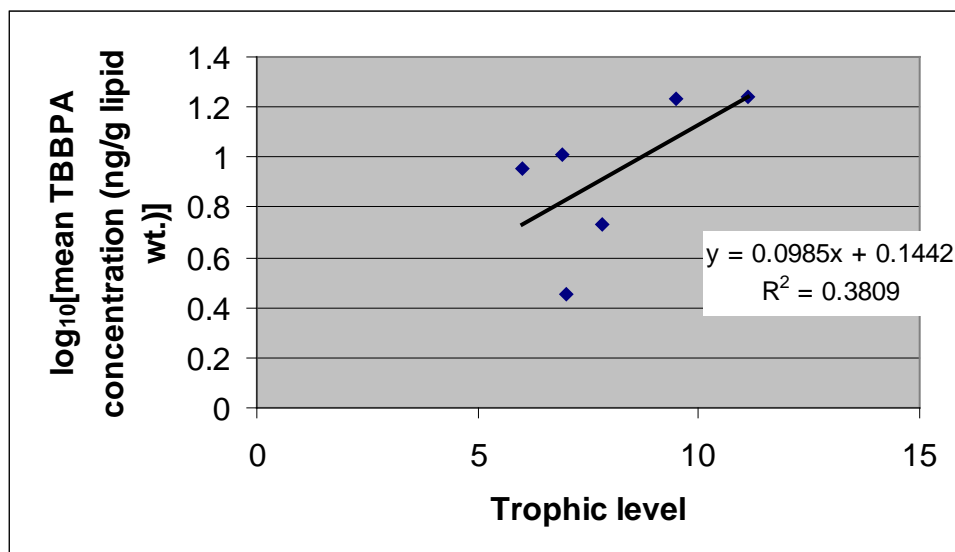


Figure A4.1. Plot of \log_{10} [mean TBBPA concentration] (on a lipid weight basis) against trophic level (mean $\delta^{15}\text{N}$ values) for Chinese bird samples

- f) It should be noted that the way that trophic position is expressed can influence the slope of this plot and therefore the TMF. The $\delta^{15}\text{N}$ signal at the base of the food web may vary significantly and affect the signals of top consumers. It is therefore more appropriate to report trophic position in terms of the absolute difference between $\delta^{15}\text{N}$ of primary producers (or a primary consumer with inherently less variability in its $\delta^{15}\text{N}$ due to its longer lifespan) and the $\delta^{15}\text{N}$ of a predator. For example, the trophic level of a consumer organism (TL_{consumer}) relative to the position of a known food item can be defined as follows, assuming the trophic level of the food item is x and that the average difference in $\delta^{15}\text{N}$ between two trophic levels is 3.4:

$$TL_{\text{consumer}} = x + \frac{(\delta^{15}\text{N}_{\text{consumer}} - \delta^{15}\text{N}_{\text{fooditem}})}{3.4}$$

This approach has been used to examine trophic levels in aquatic food webs, where the data refer to fish and their food. A TMF of 2.16 can be derived from the data using this equation¹². However, the bird species belong to different though partially overlapping food webs, and there are no predator-prey relationships between the birds. It is probably inappropriate, therefore, to attempt to estimate a TMF this way.

- g) A TMF based on each individual data point might be preferred over a TMF derived from the mean concentration for each species as it minimises errors associated with unbalanced sampling (for example different numbers of organisms were collected for each species). As noted above, the slope of such a plot is not statistically significant in this case (although only marginally so). On the other hand, the plot in the paper shows a large scatter. A 'leave one out' analysis has not been performed, so the influence of any individual data point (i.e. individual species' trophic position or measured concentration) on the analysis is unknown. The placing of different species at particular trophic levels depends on the reliability of the $\delta^{15}\text{N}$ approach in determining trophic level, which might not always reflect actual ecological relationships, especially if diets differ slightly in different locations (as seems to be suggested by the broad spread of $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ values).

¹² The slope of the plot was 0.335. The correlation coefficient for the plot of \log_{10} [concentration] against trophic level is low ($r^2 = 0.38$). It is good practice to report the statistical significance of the slope along with its standard error and lower and upper 95th percentile values (to give a TMF range). However, this has not been done here because of the limitations in the data set. The slope and therefore TMF would also be different if another value for the denominator were chosen.

- h) The estimation of trophic level from $\delta^{15}\text{N}$ values integrates all potential feeding relationships in the food web. However, BMFs were estimated by assuming that a species consumes one specific type of food item only. This is unlikely to be the case in reality, and so the BMFs must be treated with caution (ignoring the low sample sizes). It is also possible that the organisms were exposed to other sources that were not examined in this study (there was no direct measurement of sediment concentrations for example).

In summary, this study indicates that uptake of TBBPA occurs in wild fish and birds, although the exposure pathways are unclear. Whilst there is a suggestion that trophic magnification might be occurring, it is not possible to draw reliable conclusions about bioaccumulation potential from this study due to the methodological problems that have been identified.



New Court
48 Carey Street
London WC2A 2JQ
United Kingdom

t: +44 (0)20 7430 5200
f: +44 (0)20 7430 5225
e: secretariat@ospar.org
www.ospar.org

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